MODELLING OF BIOMASS COMBUSTION CHEMISTRY TO INVESTIGATE GAS PHASE ALKALI SULFATE FORMATION.
ABSTRACT

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Master’s Degree Program in Environmental Technology

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MODELLING OF BIOMASS COMBUSTION CHEMISTRY TO INVESTIGATE GAS PHASE ALKALI SULFATE FORMATION.

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Alkali, alkali chlorides, plug flow reactor, chemical kinetics, kinetic modelling, reactive flow.

This study is about the chemistry of biomass combustion, and modelling of combustion inside a boiler. Also, some implication are done as to detailed chemistry of the combustion. It explains the necessity of biomass combustion and states the problems in the regards of aerosol formation and corrosion inside the boiler walls. The alkali chlorides in the flue-gas will convert to alkali sulfates which are the main species of corrosion. The Previous studies have been mentioned and the advancements are explained. Moreover, homogeneous and heterogeneous mechanisms are explained and gas mechanisms resulting in alkali sulfates mentioned in the literature is summarized and simply visualized. The solver used for modeling is Cantera implemented in Python. The details of equilibrium and kinetics calculation are explained, and finally the results of the simulations are presented.
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## LIST OF SYMBOLS AND ABBREVIATIONS

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<th>Description</th>
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<tr>
<td>$\hat{R}_i$</td>
<td>Molar rate of creation/destruction</td>
</tr>
<tr>
<td>A</td>
<td>Helmholz function, area of reactor</td>
</tr>
<tr>
<td>C</td>
<td>Molar concentration</td>
</tr>
<tr>
<td>CSR</td>
<td>Continuously-stirred reactor</td>
</tr>
<tr>
<td>CSTR</td>
<td>Continuously-stirred tank reactor</td>
</tr>
<tr>
<td>f</td>
<td>Fugacity</td>
</tr>
<tr>
<td>G</td>
<td>Gibbs free energy</td>
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<tr>
<td>H</td>
<td>Enthalpy</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental panel for climate change</td>
</tr>
<tr>
<td>k</td>
<td>Rate constant of reaction</td>
</tr>
<tr>
<td>LEF</td>
<td>Laminar entrained flow reactor</td>
</tr>
<tr>
<td>M</td>
<td>Number of elements, molecular weight</td>
</tr>
<tr>
<td>m</td>
<td>Mass</td>
</tr>
<tr>
<td>N</td>
<td>Number of species</td>
</tr>
<tr>
<td>n</td>
<td>Number of moles</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
</tr>
<tr>
<td>PFR</td>
<td>Plug flow reactor</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate matter</td>
</tr>
<tr>
<td>PSR</td>
<td>Perfectly-stirred reactor</td>
</tr>
<tr>
<td>R</td>
<td>Reaction source term</td>
</tr>
<tr>
<td>S</td>
<td>Entropy</td>
</tr>
<tr>
<td>U</td>
<td>Internal energy</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>v</td>
<td>Stoichiometric coefficient</td>
</tr>
<tr>
<td>X</td>
<td>Mole fraction</td>
</tr>
<tr>
<td>Y</td>
<td>Mass fraction</td>
</tr>
<tr>
<td>z</td>
<td>Length of reactor</td>
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Greek Symbols

\[ \mu \] Chemical potential
\[ \lambda \] Lagrange multiplier
\[ \mathcal{L} \] Lagrangian function
\[ \omega \] Production rate
\[ \rho \] Density
\[ \eta \] Rate exponent of species
\[ \Gamma \] Net effect of third body
\[ \gamma \] Third body efficiency
\[ A_r \] Pre-exponential factor
\[ E \] Activation energy
\[ K \] Equilibrium constant
\[ u_0 \] Input velocity

Subscripts and superscripts

\[ 0 \] Standard state
\[ \text{ad} \] Adiabatic system
\[ \text{res} \] Residence time
\[ i \] Arbitrary variable
\[ ' \] Forward reaction
\[ " \] Backward reaction
\[ * \] Specific property
1. INTRODUCTION

Bioenergy has been increasingly paid attention to as a sustainable energy generation method in the past decades. It is the largest source of renewable energy today, covering a significant share of energy production in the world as it provides 35% of energy needs of three quarters of the population of the world as well as 10% of global energy supply (WorldEnergyResources, 2016) (Frank Rosillo-Calle, 2007). This mainly composes of developing countries, however, in industrial and developed countries bioenergy has a large share of energy, and for instance in Finland 20% of the primary energy comes from bioenergy. Developing countries use biomass mainly for the purposes of cooking, heat generation and industrial applications while developed countries, which accounted for a fifth of biomass consumption in 2010, use biomass primarily for heat and electricity production using efficient equipments and combined heat and power generation. The combustion of biomass has been encouraged by different governments as a tool for mitigating the CO2 and other greenhouse gases’ emissions (Kurt A. Christensen, 1996). There is a growth of 10% per year for electricity generation from biomass, also with district heating (Shunichi Nakada, 2014). This growth in electricity generation rises the importance of making the processes of electricity generation as efficient and as clean as possible, i.e. emission of less harmful particles into the atmosphere along with producing less corrosive species in order to keep the energy costs as low as possible along with keeping bioenergy in the class of clean energies.

Biomass combustion process is a combination of endothermic and exothermic reactions which takes place as a series of separate stages. Figure 1 illustrates these main stages and some of the species involved (Palmer, 2014). These stages do not take place explicitly as shown in Figure 1 and there are overlaps between these phenomena. The temperature reached at each stage also the time of each of these stages vary for different circumstances and the type, quality and size of the fuel in use (Nussbaumer, 2010).
Figure 1. Stages of biomass combustion (Palmer, 2014).

Figure 2 shows the time for each of the stages in one example. Some overlapping is remarkable in the progression of the combustion process. The main purpose of this work is intended at the devolatilization and char burning stages as we focus on the combustion process after the secondary air inject inside the biomass boiler.

Figure 2. Duration of individual combustion processes (Jun Li, 2015).
1.1. Problem Definition and Objectives

Bioenergy and combustion of biomass for power and heat generation have been increasing for the past decades (Kurt A. Christensen, 1998). However, there are still modifications necessary to the processes and technologies in this sector. Among the concerns are the problems with aerosol formation, deposits, corrosion, and gaseous emissions have been investigated by scientists and engineers to a great deal and yet need improvements.

Biomass is often identified as “carbon neutral” or “zero carbon” fuel, since the CO₂ emissions from biomass are offset by the CO₂, which had been captures and stored during the original growth of the biomass and as well by the replacement planting of trees and crops. However, this does not mean that emissions from biomass are restricted to CO₂ nor the emissions are to be ignored. The main emissions from biomass are:

- Particulate Matter
  - Soot
  - Volatile organic matter
  - Intermediate products e.g. polycyclic aromatic hydrocarbons (PAH)
- Nitrogen oxides (NOx)
  - Nitrogen dioxide (NO₂)
  - Nitrous oxide (N₂O)
  - Nitric oxide (NO)
- Carbon oxides (COx)
  - Carbon dioxide (CO₂)
  - Carbon oxide (CO)
- Sulfur oxides (SOx)
  - Sulfur dioxide (SO₂)
  - Sulfur trioxide (SO₃)
- Dioxins/Furans

It has been found that PM and NOx are the most relevant emissions when discussing about the biomass combustion emissions (Irbea, 2016). Perrino et al. have introduced the chemical composition of particulate matter and Na and K are amongst those (C. Perrino, 2014).

It is essential to know the combustion residuals and gaseous emissions in order to devise measures to reduce the emissions from the combustion of biomass. Although experiments
have been done on this, to reduce the time and costs of a complete investigation, a complete simulation of biomass combustion and combustion residual species is of significance. The validated simulation results will contribute greatly to finding solutions to reduce the emission and to reduce the boiler and parts’ corrosion problems, resulting in a more efficient combustion with less maintenance and performing costs.

In a recent IPCC report, it is mentioned that Stern et. al have calculated the contribution of emissions from biomass combustion to be globally 1.08 TgS/a over the period 1980 to 2000 (Anon., 2007). Although this is much smaller than the share of emissions from fossil fuels, considering the fact that biomass have become one of the replacements for fossil fuels, this amount is to be reduced as well.

In this work, some background in gas mechanism and alkali sulfate formation is presented, and it goes on to validate a gas mechanism model by reproducing the results of experiments previously performed and also more modeling work is done and will be presented in later chapters.

High-temperature gas-phase chemistry of alkali metals has been paid attention to due to a variety of reasons such as combustion of solid fuels, coal, black liquor, corrosion and deposition in naval engines, as well as aerosol formation in biomass combustion (Peter Glarborg, 2005)(Kurt A. Christensen, 1996). Therefore, in the last two decades there has been significant growth in knowledge of alkali metals and their reaction chemistry at high temperatures (Peter Glarborg, 2005). Many studies have been done based on experiments to further understand the behavior of alkali metals and other species in high temperatures (Kurt A. Christensen, 1996) (Kurt A. Christensen, 1998) (K. Iisa, 1999) (S. Jiménez, 2005) (Hindiyarti, 2007).

The main focus in this work is on the alkali metals since their existence along with chlorine in many biomass types are the main concerns due to their corrosive behavior (H.P. Nielsen, 2000). Depositions of such salts as alkali chlorides and sulfates are among the reasons for drastic corrosion inside the boiler well below their melting point, which takes place as the flue-gas is cooled down inside the boiler (H.P. Nielsen, 2000)(Jacob N. Knudsen, 2004).

In this work, the chemistry of the flue-gas inside the boiler will be investigated with a special attention to the corrosive (and corrosive-resulting) species and the effects of each of the reaction routes also presence of certain species in the flue-gas will be looked into with more
detail. To serve this purpose, equilibrium and kinetics calculations are done and plug flow reactor models are developed. Sensitivity analyses for some properties will be presented in chapter 7. There is still plenty left to do in this regard as the efficient combustion of biomass is yet to be achieved, one reason is the complexity of alkali metals and their species in both theoretical and experimental aspects (Peter Glarborg, 2005).

1.2. Outline of the Study
This study comprises of different chapters which give a step by step approach to the problem and the calculations done onto it. Second chapter introduces the foremost studies which have been previously performed related to our problem definition and the advancements will be introduced. Later, the gas mechanism utilized is introduced in detail and all the related terminology will be presented. The software package used in this study will be presented in chapter 3 and points of advantage and points of weaknes of it will be introduced. Next will be the equilibrium calculation procedure of the flue-gas inside the boiler is introduced. Kinetics calculations as well as PFR modeling procedures are explained in chapter 5. In chapter 6 kinetic calculations for some experiments are performed using plug flow reactors of different specifications (number of perfectly stirred reactors, input, length and velocity and so on) and the results are shown and discussed. Sensitivity analysis of the different species and reactions routes are done in 7 and results are discussed. In chapter 8, the outcome of this thesis work will be stated and some suggestions for the further work as to a thorough and accurate simulation of biomass combustion with a correct gas mechanism will be presented. Chapter 9 provides a summary of the work.
2. FORMATION OF ALKALI SULPHATES

The formation of submicron aerosols and alkali sulfates have been points of attention in the biomass combustion for the past decades (Kurt A. Christensen, 1998) (Peter Glarborg, 2005), moreover, the recognition of the risk to human health of the submicron particle has been an important step in the emphasizing on this problem (Friedlander, 1994). Also, the combustion of biomass was proven to emit large amounts of submicron particles (Kurt A. Christensen, 1998). These reasons were the driving force behind extensive studies to investigate the mechanisms of aerosols and submicron particles formations as well as corrosion of boiler walls in the past two decades. This study serves this purpose as it updates some of the knowledge concerning the chemistry of combustion in terms of specific species.

2.1. Sulfur Emissions

Along with other species emitted to the environment, SO\textsubscript{2} and SO\textsubscript{3} are as well in the list of biomass emissions which harm both the environment and human health. They cause and aggregate the respiratory diseases, weaken lung function and irritate eyes and throat. It also brings about indirect human health problems such as facilitating the production of PM in the atmosphere (PFIP, 2011). From the harms to the environment, one can enumerate the formation of acid rain and regional haze, both affecting the ecosystems drastically.

The sulfur content of the biomass is converted to H\textsubscript{2}S in the gas phase, such compounds are later oxidized to sulfur oxides to make SO\textsubscript{2}, and during combustion, a part of that is oxidized into SO\textsubscript{3} (Kurt A. Christensen, 1998). Parts of this sulfur react with the alkali metal and form sulfates, which is known to be the cause of aerosol formation, corrosion and deposit formation (Hindiyarti, 2007). Figure 3 depicts formation of some of the possible species along the boiler. Note the appearance of K\textsubscript{2}SO\textsubscript{4} in the figure.
Boman et al. have experimentally determined the elemental and inorganic phase distribution and mass size of PM emissions of pelletized biomass fuels. They have found that the *dominant inorganic emission elements* of fine particle samples were K, Cl, and S. Figure 4 depicts the elemental composition of the fine PM from burner with 5 different low pressure impactor stages. It was also found that the main alkali found was KCl, K$_3$Na(SO$_4$)$_2$ and K$_2$SO$_4$(Boman C., 2004).
2.2. Alkali Sulfates

It was known that the flue-gas of biomass, particularly straw contain submicron aerosol particles such as SO$_2$ and HCl (Kurt A. Christensen, 1998), also earlier it was suggested that these particles are almost purely potassium chloride and sulfate (Kurt A. Christensen, 1998).

Iisa et al. performed some experiments to observe the sulfation rate of KCl in a laminar entrained-flow reactor (LEFR) (K. Iisa, 1999). Oxygen, water vapor, and solid particles of KCl and SO$_2$ were fed into the reactor. KCl particles’ (continuously fed into the reactor) evolution from molten to gas phase and reacting with different species were investigated. It was proposed that KCl in the molten phase will react with SO$_2$, O$_2$, and H$_2$O to form K$_2$SO$_4$ through the reaction R(2-1). KCl is studied since it is one of the main species above the bed at temperatures between 1100 and 1300 K.

$$2KCl + SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow K_2SO_4 + 2HCl$$ \hspace{1cm} R(2-1)

Iisa et al. suggested that the sulfation rate of potassium is limited by the availability of SO$_3$ (K. Iisa, 1999). This fact is proven in further work and it has been concluded that conversion of SO$_2$ to SO$_3$ is the rate-limiting step for the sulfation of the potassium in the boiler (Peter Glarborg, 2005). Iisa et al. did not have access to the rate data for KCl sulfation and instead they have compared this to the sulfation of NaCl for which there had been data.
available. They have stated that sulfation of KCl in the molten phase is some orders of magnitude faster than that of NaCl in the condensed phase, and this has been concluded considering the experiments they had performed. This results in the fact that most of the KCl is sulfated in the gas phase, and the sulfation in the condensed phase is drastically slower (K. Iisa, 1999). This had already been mentioned in other previous works such as the work by Christansen et al. (Kurt A. Christensen, 1998). That is the reason for further studies using the gas phase mechanisms of biomass combustion to investigate corrosion and aerosol formations.

It has also been suggested that the gas phase K$_2$SO$_4$ partly condenses and sticks to the walls due to its low vapor pressure (K. Iisa, 1999), and this is the basis for the homogeneous and heterogeneous nucleation concepts which are suggested and worked on in the later studies (Kurt A. Christensen, 1998) (Peter Glarborg, 2005) (Hindiyarti, 2007) (Lusi Hindiyarti, 2008).

### 2.3. Reaction Route for Formation of Alkali Sulfates

There is a consensus on the fact that aerosol in biomass combustion are the results of nucleation/condensation of volatilized mineral matter (Kurt A. Christensen, 1996) (Kurt A. Christensen, 1998). When the flue-gas is being cooled down, alkali chlorides might deposit and react with sulfur oxides to form K$_2$SO$_4$ (Livbjerg, 2001). This is done in either of the two main reaction routes which have been suggested in various literatures (Lusi Hindiyarti, 2008) (Peter Glarborg, 2005) (Hindiyarti, 2007). The homogeneous mechanism suggests that alkali sulfates are formed in the gas phase and then they are condensed on boiler walls to form aerosols, while heterogeneous mechanism is based on the hypothesis that KCl and other similar species involving alkali are first deposited and then sulfated in the condensed phase (Peter Glarborg, 2005). Some studies have stated that the conversion of alkali metals to A$_2$SO$_4$ takes place through a homogeneous nucleation (Kurt A. Christensen, 1998) and experiment of Iisa et al. supports this hypothesis that alkali sulfates are formed in the vapor phase rather than molten or solid phase (K. Iisa, 1999). This is also the basis of later simulation in this study.

Glarborg et al. suggested a complete reaction mechanism for gaseous alkali formation. It is a three-step mechanism which consists of stable species in each step. The first step is the conversion of SO$_2$ to SO$_3$, previously mentioned as the rate-limiting step (Kurt A.
Christensen, 1998). Subsequently, in the next steps are association reactions which involve alkali hydroxides and chlorides; these are the most abundant species of alkali in the gases of combustion (Peter Glarborg, 2005).

\[
AOH + SO_3(+M) = AHSO_4(+M) \quad \text{R(2-2)}
\]

\[
ACl + SO_3(+M) = ASO_3Cl(+M) \quad \text{R(2-3)}
\]

AHSO₄ and ASO₃Cl are the main precursors of alkali sulfates and are rather stable at high temperatures (Peter Glarborg, 2005). These precursors take part in a series of shuffle reactions which conclude in the formation of alkali sulfates as mentioned below:

\[
ASO_3Cl + H_2O = AHSO_4 + HCl \quad \text{R(2-4)}
\]

\[
ASO_3Cl + AOH = A_2SO_4 + HCl \quad \text{R(2-5)}
\]

\[
AHSO_4 + AOH = A_2SO_4 + H_2O \quad \text{R(2-6)}
\]

\[
AHSO_4 + ACl = A_2SO_4 + HCl \quad \text{R(2-7)}
\]

There are other paths for the conversion of species towards alkali sulfates, which are suggested in the literature, however this seems to be the most probable route to formation of alkali sulfates. Figure 5 shows the summary of different pathways made by the author with the indication of the major reaction routes and the reaction rates. Figure 6 is also a schematic pathway diagram for potassium transformation proposed by Glarborg et al. (Peter Glarborg, 2005).
KCl is the dominant K species in gaseous form, at 1373K, 2% SO₂, 5% O₂, 10% H₂O. Two main sequences:

**Figure 5.** The mechanism of potassium sulfation.

**Figure 6.** Pathway diagram of K sulfation (Peter Glarborg, 2005).

The shuffle reactions are expected to be fast by analogy, which makes the proposed mechanism a rather fast one (Peter Glarborg, 2005). The plausibility of this mechanism relies on the stability of AHSO₄ and ASO₃Cl, and this is in agreement with previously performed experiments (Peter Glarborg, 2005). The gas mechanism utilized in the simulations works
kinetically on the basis of these shuffle reactions and the main routes of alkali formation mentioned in Figure 5.

2.4. Gas Mechanism

Gas mechanism utilized to validate the experiments that will be presented in the later chapters are proposed by Glarborg et al. which is also used in their publication to validate Iisa et al. experiments (Peter Glarborg, 2005). The mechanism is a developing work proposed by the same team of scientists earlier as well, and some other work has also used this mechanism in their studies with some modification (Hindiyarti, 2007) (S. Jiménez, 2005) (Santiago Jimenez, 2007). The modified Glarborg mechanism is the one used in the simulations.

Due to the fact that KCl in Iisa’s work is introduced to the system in the form of solid particles (K. Iisa, 1999), KCl (s) to KCl (g) conversion is a matter of importance, since in the early version of the mechanism subsumes only the gas phase. The method Glarborg et al. have used is that, in the modeling, they have considered the conversion of KCl solid particles to gas phase as a series of three pseudo-first-order reactions. The rate constants are obtained from fitting with the experimental data (K. Iisa, 1999) and are obtained to be \( k'=k''=k''' = 2.4 \text{ s}^{-1} \). This number has given the best match with the experimental data.

The mechanisms have between 47 to 51 species with elements: O, H, (C), N, Ar, S, Cl, K. The variation in the number of the species comes from the fact that in the Jimenez experiments, the KCl is only in the gas phase therefore, there is no need for phase change. It is noteworthy that the mechanism contains only potassium as alkali metals and not sodium. The reason is that they both behave similarly, and this assumption is to serve simplification of the mechanism as this reduces the number of reactions, and eventually calculation time significantly.
3. MODELLING TOOLS

There are different software tools for modeling of kinetic reactions, equilibrium state and reacting flows such as the flue-gas in the boiler. Some of which are CHEMKIN software package, FactSage and Cantera. CHEMKIN is a popular software for modeling of gas-phase and surface chemistry and it is used a large variety of applications from combustion systems to boilers and process equipments (ReactionDesign, 2015). It is one of the most quoted kinetics interpreters in the literatures. Moreover, the previous simulations by Glarborg et al. and Hindiyarti et al. and Jimenez et al. have been performed using this kinetics software (Hindiyarti, 2007) (Peter Glarborg, 2005) (S. Jiménez, 2005).

Fact sage is a computer program capable of chemical manipulations through different modules for a variety of calculations such as equilibrium calculations, reaction, and phase diagrams. It enables user to perform different calculations and generate figures and tables for a variety of applications (C.W.Bale, 2016). However, since the objective of this work is looking into the kinetics of the reacting flow in the boiler, this software is not used since chemical kinetics is out of the scope of this software.

Cantera is an object-oriented toolkit written in C++ programming language which has been developed to for problems in thermodynamics, reacting flows, transport processes and chemical kinetics (Felden, 2015). It is a suitable tool for the different calculation purposes, such as reactor networks, 1D-flames, reaction path diagrams, heterogeneous chemistry and so on. There are multiple interfaces to the language which are C, Python, Fortran90 and Matlab. The interfaces are interactive scripting environments which make Cantera work as a normal coding environment. In C++, it is in the form of a class library, in Fortran90 it is a module, in Python a package and in Matlab, it is installed in the form of a toolbox (Goodwin, 2001).

Cantera is constantly being developed and modified. The C++ interface seems to be the most complete one, and Matlab interface is still rather young in development process, since there are quite a few functions and possibilities yet to be available in Matlab interface. There is a Cantera user group on the internet in which users constantly ask question and users’ community and specifically developers answer those question and problems.
3.1. Comparison of Cantera with other Softwares

The comparison is made between CHEMINK and Cantera. Since these two choices are more suitable for the application of this work. Table 1 presents some of the cons and pros of each of these two packages.

<table>
<thead>
<tr>
<th></th>
<th>CHEMKIN</th>
<th>Cantera</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pros</strong></td>
<td>Licensed software</td>
<td>Free open source software</td>
</tr>
<tr>
<td><strong>cons</strong></td>
<td>Lack of complete and proper documentation</td>
<td>Suits the computational resources and the latest scientific demand</td>
</tr>
<tr>
<td>Well/established software</td>
<td>Not possible to link to programing language and write own models</td>
<td>Still not a refined software</td>
</tr>
<tr>
<td>Several built-in reactor models</td>
<td>Difficult to extract basic and detailed chemistry</td>
<td>Possible to link with programming languages</td>
</tr>
<tr>
<td>standardized mechanism formats</td>
<td>Writing new and own models are possible</td>
<td>Not as user friendly</td>
</tr>
</tbody>
</table>

**Table 1.** Points of strength and points of weakness of the two kinetic interpreters.

Furthermore, Nogare has used the same mechanism and done a calculation with CHEMINKIN and Cantera to compare the results using the same settings. Both CHEMINKIN and Cantera use the same database format, however the databases are written in different ways which could be converted to each other (this will be elaborated in section 3.2). Nogare has used Deutschmann – Pt mechanism and calculated the mole fractions of some species using both softwares and has demonstrated the results.

Figure 7 shows the calculation results from CHEMINKIN and Cantera and it is apparent that they are in very close compliance. Figure 8 also shows the numerical errors from the two interpreters’ results. Looking at these figures, it is noticed that the results are the same for both softwares. Nogare has mentioned that calculating with consideration of sticking coefficients; results from the two softwares differ up to several percent points. Also, in surface chemistry some results are different but they are negligible. However, since the governing equations are the same, they can perform the same simulations, and they give approximately identical outcomes.

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Furthermore, the author has compared the equilibrium calculations of FactSage and Cantera and has concluded that the results are also the same.

It is concluded that considering the figures shown here the two softwares, although working in different formats, yield the same results. The author has chosen to use Cantera as it is more appropriate for the purpose of this study.

Figure 9 shows the same command in Cantera for the different programming languages.
3.2. Cantera Data File

The mechanisms which are in CHEMKIN format should be input to Cantera. For this reason, the data files need to be merged into one single file. The data files usually consist of two or three different files: Thermodynamic file contains the thermodynamics data such as specific heat polynomial coefficients. Kinetics file contains declaration of elements, species, reactions, reaction rates, and activation energies, and third body efficiencies (if available). Transport file in which some properties such as viscosity are mentioned.

These kinds of thermo file (.dat) and kinetics file (.inp) are suitable input files to be used with CHEMKIN. However, there is a way to convert those CHEMKIN format files to Cantera format. The code line to do this is shown below. It shows the line to convert CHEMKIN format files to Cantera formats specific to the python interface.

```
ck2cti --input=kinetics_filename.inp -- thermo=thermos_filename.dat --transport=transport_filename.dat
```

This line of code makes one file which contains thermodynamics, kinetics and transport data in an order readable by Cantera with the extension .cti. However, this file contains only gas
phase species. In the case there are some species in other phases, the user should make the changes manually to the .cti file (Ray Speth, 2016). This was asked on the Cantera users’ group and done by the author of this work.
4. CALCULATION OF THE FLUE-GAS EQUILIBRIUM INSIDE THE BOILER

Equilibrium calculation is a fundamental tool for kinetics and transport modeling, applications of kinetics and transport modeling may contain thousands of equilibrium calculations in a single simulation, therefore they have proven efficient (Leal A, 2014).

To help the interpretation of experimental findings, chemical equilibrium calculations have been carried out. Although the gases in the biomass boilers are not in the state of equilibrium, equilibrium calculations could give a useful glance at how it would look like and these calculations give an estimation of the presence and abundance of each (group of) gases at each section of the boiler. Kinetic calculations are compared with equilibrium calculations and it could be seen how much flue-gases are away from equilibrium state. Knowing the composition at chemical equilibrium of a system helps to calculate theoretical properties of the system which is used in the design and optimization of equipments (Sanford Gordon, 1994). Equilibrium calculations also predict the presence of alkali sulfates in the emissions (Santiago Jimenez, 2007).

The coming section delivers the procedure of the equilibrium calculations performed in Cantera. It is necessary to understand the background procedure in Cantera before modeling the equilibrium conditions in the software.

4.1. Equilibrium Calculations

There are several potential functions, which are the results of the second law of thermodynamics utilized in different situations. That which one of the functions would be used is dictated by the choice of thermodynamics variables taken as independent. These functions are known as the state functions. Some of the more important ones are Gibbs and Helmholtz functions. The second law states the criterion for a natural process to take place as well as for equilibrium state. The criteria for entropy function $S$, Gibbs function $G$, and Helmholtz function $A$ are as follows.

\[
dS_{ad} \geq 0 \tag{4-1}
\]

\[
dA_{TV} \geq 0 \tag{4-2}
\]
The subscript for entropy refers to adiabatic system. In the above equations, the inequality sign refers to spontaneous reaction and the equal sign stands for the equilibrium state. At equilibrium state entropy is at local maximum, while Helmholtz and Gibbs functions are at minimum. The Gibbs function is sometimes called free energy function as well.

A chemical system could be thermodynamically described in the one of the following forms:

\[
U = U(S, V, n) \quad (4-4)
\]

\[
H = H(S, P, n) \quad (4-5)
\]

\[
A = A(T, V, n) \quad (4-6)
\]

\[
G = G(T, P, n) \quad (4-7)
\]

Each of these equations has a differential form which looks like:

\[
dU = TdS - PdV + \sum_{i=1}^{N} \mu_i dn_i \quad (4-8)
\]

\[
dH = TdS + VdP + \sum_{i=1}^{N} \mu_i dn_i \quad (4-9)
\]

\[
dA = -SdT - PdV + \sum_{i=1}^{N} \mu_i dn_i \quad (4-10)
\]

\[
dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i \quad (4-11)
\]

Chemical potential is defined by the equation (4-12).

\[
\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_j \neq 1} = \left( \frac{\partial H}{\partial n_i} \right)_{S,P,n_j \neq 1} = \left( \frac{\partial A}{\partial n_i} \right)_{T,V,n_j \neq 1} = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq 1} \quad (4-12)
\]

Chemical potential depends only on the intensive states of the system and its compositions.

Total Gibbs function of the system is obtained by the integration of (4-11).

\[
G(T,P,n) = \sum_{i=1}^{N} \mu_i n_i \quad (4-13)
\]

From the differentiation of the (4-13) and(4-11), the Gibbs-Duhem equation is derived:
\[ SdT - VdP + \sum_{i=1}^{N} n_i d\mu_i = 0 \]  \hspace{1cm} (4-14)

For a system to be at equilibrium state, whether single-phase or multi-phase, \( G \) has to be at global minimum and non-negativity constraints should apply at a given \( T \) and \( P \). Considering the non-negativity constraint, it yields that at equilibrium the equation \( dG_{T,P} = 0 \) has to be satisfied.

This is a necessary but not a sufficient condition for a system to be in equilibrium. The task is to express \( G \) in terms of \( n \), to find the molar values which give the minimum of Gibbs energy. There are two formulations for the minimization of \( G \).

1. Stoichiometric formulation; in which the closed-system is treated with stoichiometric equations.
2. Non-stoichiometric formulation; in which the closed-system is treated with Lagrange multipliers.

### 4.2. Choice of Formulation

If we consider the number of elements to be \( M \) and the number of species to be \( N \), the comparison between \( M \) and \( (M-N) \) is a useful condition as to choosing which formulation to go with for the case of relatively small systems.

- \( (N - M) < M \rightarrow \) Stoichiometric formulations;
- \( (N - M) > M \rightarrow \) Non-stoichiometric formulations.

The system under this study (Glarborg’s mechanism) and others consists of 47 to 51 species and 8 elements (Peter Glarborg, 2005). Therefore, and this is the case most of the times, the chosen formulation to perform the equilibrium calculations is the non-stoichiometric formulation.

### 4.3. Non-stoichiometric Formulation

Lagrange multiplier is used to remove the constraints that exist in the calculation of equilibrium in the non-stoichiometric method. One should consider the Lagrangian at first.
\[ L(n, \lambda) = \sum_{j=1}^{N} \mu_i n_i + \sum_{k=1}^{M} \lambda_k \left( b_k - \sum_{i=1}^{N} a_{ki} n_i \right) \]  

(4-15)

While \( \lambda \) is a vector of \( M \) unknown Lagrange multipliers, \( n \) is the mole of species and \( \mu \) is the chemical potential. The first term on the right-hand side is the term to be optimized and the terms in brackets are the constraint functions. Certain conditions provide the set of \((N+M)\) equations and the unknowns to solve the conditions.

\[
\frac{\partial L}{\partial n_i} = \mu_i - \sum_{k=1}^{M} a_{ki} \lambda_k = 0 \quad (n_i > 0) 
\]  

(4-16)

\[
\frac{\partial L}{\partial \lambda_k} = b_k - \sum_{i=1}^{N} a_{ki} n_i = 0 
\]  

(4-17)

To solve the equation (4-15), it is necessary to introduce appropriate expression for chemical potential.

**4.3.1. Expression of chemical potential**

Chemical potential depends on temperature and pressure of the system and not on the species composition. Expressions of chemical potential have to be derived in order to satisfy the Gibbs-Duhem equation (4-14). The expressions for chemical potential for some important cases are introduced. The description and complete derivation procedure could be found in the literature.

**4.3.1.1. Pure species**

Using the equation (4-11) and the derivative of chemical potential, it is yielded:

\[
\left( \frac{\partial \mu}{\partial P} \right)_T = \nu 
\]  

(4-18)

If one integrates this equation for a fixed temperature in the range of a reference pressure and \( P \):

\[
\mu(T, P) - \mu(T, P^o) = \int_{P^o}^{P} \nu dP
\]  

(4-19)

This equation for three particular cases will look like:

- Ideal gases:

\[
\mu(T, P) = \mu^o(T) + RT \ln P
\]  

(4-20)

Where \( \mu^o \) is the standard chemical potential and is only a function of temperature.
• Non-ideal gases:

\[ \mu(T, P) = \mu^o(T) + RT\ln P + \int_0^P \left( v - \frac{RT}{P} \right) dP \]  
(4-21)

• Liquid or solid:

\[ \mu(T, P) \equiv \mu^o(T) + RT\ln p^* \]  
(4-22)

Where \( p^* \) is the vapor pressure of the liquid or solid.

4.3.1.2. Species in solution

Equation (4-20) for the liquid and solid is changed only in a way that \( P \) is replaced by \( p_i \).

\[ \mu(T, P, x_i) = \mu^o(T) + RT\ln p_i \]  
(4-23)

\( p_i \) is the partial pressure of the species in the solution and is defined as:

\[ p_i = \left( \frac{n_i}{n_t} \right) P \equiv x_i P \]  
(4-24)

In which \( x_i \) is the mole fraction of species \( i \), \( n_t \) is the total number of moles in the solution. The general chemical potential for species in solutions will look like:

\[ \mu_i(T, P, x_i) = \mu^o(T) + RT\ln P + RT\ln x_i \]  
(4-25)

• Ideal solution:

\[ \mu_i(T, P, x_i) = \mu^*(T, P) + RT\ln x_i \]  
(4-26)

Where \( \mu^* \) is the standard chemical potential of species \( i \).

• Non-ideal solution:

\[ \mu_i(T, P, x) = \mu^o(T) + RT\ln f_i \]  
(4-27)

Where \( f_i \) is the fugacity of the species \( i \).

4.4. Final Form of Equilibrium Mole Fractions

4.4.1. The general case

For a system of \( N \) species and \( M \) elements, there are the conditions for Lagrangian equations already stated which are:
\[\mu_i = i\lambda; i = 1,2,\ldots,n\]  \hspace{2cm} (4-28)

\[\sum_{i=1}^{N} in_i = b\]  \hspace{2cm} (4-29)

Using the equations presented for the chemical equilibrium, and substituting it into (4-28), one obtains:

\[n_i = n_t \exp\left(\frac{i\lambda - \mu_i^*}{RT}\right); i = 1,2,\ldots,n\]  \hspace{2cm} (4-30)

And also substituting this equation into (4-29) would yield:

\[n_t \sum_{i=1}^{N} i \exp\left(\frac{i\lambda - \mu_i^*}{RT}\right) = b\]  \hspace{2cm} (4-31)

\[\sum_{i=1}^{N} i \exp\left(\frac{i\lambda - \mu_i^*}{RT}\right) = 1\]  \hspace{2cm} (4-32)

The system of equation above gives \(n_t\), and equation (4-30) gives the \(n_i\) which is the mole fraction of species \(i\) in the state of equilibrium.

4.5. Choice of Fixed Properties in Equilibrium Cantera

In Cantera, the choice of equilibrium calculations is dependent on which properties to keep fixed:

- ‘TP’ \(\rightarrow\) fixed temperature and pressure;
- ‘TV’ \(\rightarrow\) fixed temperature and volume;
- ‘UV’ \(\rightarrow\) fixed specific internal energy and specific volume;
- ‘SV’ \(\rightarrow\) fixed specific entropy and specific volume;
- ‘SP’ \(\rightarrow\) fixed specific entropy and pressure;
- ‘HP’ \(\rightarrow\) fixed enthalpy and pressure;
- ‘UP’ \(\rightarrow\) fixed specific internal energy and pressure.

The one chosen for the equilibrium calculations performed in this study based on the description of the problem is the TP equilibrium, since the temperature and pressure of the gas mixture is supposed to remain approximately constant inside the boiler.
5. FLUE-GAS KINETIC CALCULATIONS PROCEDURE AND PLUG FLOW REACTOR MODELLING

The problem we are dealing with is a problem of chemically reacting flow. The chemical process involved initiates with a group of elementary reactions rather than a single reaction. A reaction mechanism is the collection of these series of reactions taking place. The priority of a reaction taking place over others and speed of each reaction is dominated by the reaction rate constant (and reaction activation energy) as well as reactants and their presence and amount available at every moment during the reactor progression with time. Once the rate constants are assigned to their corresponding reactions, a chemical kinetics model can be developed. It provides a thorough description of chemistry in the reacting flow, and obviously it requires a significant computational effort.

To study chemical kinetics and even equilibrium, laboratory experiments need to be modeled and mathematically approximated. This is done with the help of ideal reactor models. Some examples of the most common ideal reactors are batch reactors, plug flow reactors (PFR) and perfectly-stirred reactors (PSR), also known as continuously-stirred reactors (CSR). These reactors are idealizations which help in modeling of complex chemical reactions in real systems. Even in systems with high complex fluid dynamics, in which an ideal reactor is not adequate to treat the modeling, a network of such reactors can give acceptable approximations of the real phenomena taking place in the system. Such networks of simple ideal reactors have been used in a variety of important applications to model the complex reacting flows, such as gas turbine, rocket propulsion, and NOx control techniques (Robert J. Kee, 2003).

A plug flow reactor is a representation of a reactor with the assumption that there are no radial variations across the channel and transport of axial diffusivity can be ignored. Plug flow reactor (zero-dimensional reactor) is a kind of simplification to facilitate the process of channel flow modeling. Other simplifications include boundary-layer behavior, and one-dimensional axial flow (Robert J. Kee, 2003).

5.1. Plug Flow Reactor

Also known as slug flow, piston flow, ideal tubular reactions, plug flow reactor is a one-dimensional model as there is one spatial dimension. Plug flow model assumes infinite radial
diffusion and zero axial diffusion, and convection of species and heat equals the production or consumption of those properties. The steady flow inside the reactor and the axial concentration are constant. Since the composition of the fluid inside the reactor differs from point to point, the material balance of the reaction component must be made along the length of the reactor (Levenspiel, 1999). There are temperature and composition variations along the reactor but not across it, neither is there any diffusive transport along the channel.

![Figure 10. Schematic of a plug flow reactor (Gurmen, 2008).](image)

The goal is to find the species conservation equation. Conservation law for flowing systems is:

\[
\frac{dn_k}{dt}_{sys} = \int_{CV} \dot{\omega}_k W_k dV
\]

(5-1)

\(\dot{\omega}_k\) represents the production rate of homogeneous chemical reaction within the system. The assumption is that there is one spatial dimension but since this takes the place of time, a system of ordinary differential equations has to be solved. Using the Reynolds transport theorem, one can relate the flow system to control volume:

\[
\int_{CV} \frac{\partial \rho Y_k}{\partial t} dV + \int_{CS} \rho Y_k V_{,n} dA = \int_{CV} \dot{\omega}_k M_k dV
\]

(5-2)

In which \(Y_k\) is the species mass fraction. Because the reactor is assumed to work under steady flow, the first term in(5-2) drops out. On the other hand, Gauss divergence theorem states that:

\[
\int_s (\varphi . n) ds = \int_V (\nabla \cdot \varphi) dV
\]

(5-3)
Thus using (5-3) to change the surface integration to volume integration in (5-2) yields:

\[ \int_{CV} \nabla \cdot \rho Y_k V dV = \int_{CV} \dot{\omega}_k M_k dV \]  

(5-4)

The integrands are taken to be constant since the differential control volume is differential in the flow direction. Thus:

\[ \nabla \cdot \rho Y_k V = \dot{\omega}_k M_k \]  

(5-5)

Because there is no variation across the channel, the divergence operator contributes only to an axial derivative:

\[ \frac{d \rho u Y_k}{dz} = \dot{\omega}_k M_k \]  

(5-6)

The term on the left-hand side is the convection term and the one on the right-hand side is the production term, while the omitted term of \( \frac{d \rho Y_k}{dt} \) is the accumulation term. \( u \) is the axial flow velocity. \( z \) derivative can be simplified, using the overall mass continuity equation:

\[ \frac{dm}{dt} = \int_{CV} \frac{\partial \rho}{\partial t} dV + \int_{CS} \rho V.nA = 0 \]  

(5-7)

This results in:

\[ \frac{d \rho u}{dz} = 0 \]  

(5-8)

Finally, the species continuity equation for steady, constant cross-sectional plug flow:

\[ \rho u \frac{d Y_k}{dz} = \dot{\omega}_k M_k \]  

(5-9)

For the plug flow energy equation, with the assumption of neglecting the gravitational and kinetic energy, the energy balance of the system is:

\[ \frac{dE}{dt} = \frac{dQ}{dt} + \frac{dW}{dt} \]  

(5-10)

\[ \int_{CS} \rho e V.nA = d\dot{Q} - \int_{CS} p V.nA \]  

(5-11)

\[ \int_{CS} (e + \frac{p}{\rho}) \rho V.nA = d\dot{Q} \]  

(5-12)

Using the Gauss divergence again and the definition of enthalpy \( h = e + p/\rho \), we will have:
\[
\int_{CS} \nabla \cdot \rho h \mathbf{v} dV = d\dot{Q} 
\]  \hspace{1cm} (5-13)

With the assumption of uniformity in the radial direction, and a differential control volume in the flow direction, it yields:

\[
\frac{d(\rho uh)}{dz} = \frac{d\dot{Q}}{\delta V} 
\]  \hspace{1cm} (5-14)

Where \( \delta V \) is the differential volume through which heat is convected and is equal will \( Adz \). Taking into consideration the (5-8), we have:

\[
\rho u \frac{dh}{dz} = \frac{d\dot{Q}}{\delta V} = \frac{h_p}{A_c} (T_w - T) 
\]  \hspace{1cm} (5-15)

For a perfect gas, the mass-averaged mean properties of enthalpy and heat capacity could be written as:

\[
h = \sum_{k=1}^{K} Y_k h_k 
\]  \hspace{1cm} (5-16)

\[
C_p = \sum_{k=1}^{K} Y_k C_{p,k} 
\]  \hspace{1cm} (5-17)

Using these 2 equations into (5-15) gives the **plug flow energy equation** (Robert J. Kee, 2003):

\[
\rho u C_p \frac{dT}{dz} = \frac{h_p}{A_c} (T_w - T) - \sum_{k=1}^{K} h_k (\omega_k M_k) 
\]  \hspace{1cm} (5-18)

Not always the plug-flow reactors are considered to have the same area, but in our case of experiments to model, the constant area plug-flow reactor gives the right model.

### 5.2. Perfectly Stirred Reactors

Perfectly stirred reactor (PSR) also known as continuously stirred tank reactor (CSTR) is another idealization which has proved to be of great use in modeling of the real phenomena.
Figure 11 illustrates the PSR and shows that a mixture enters the reactor with a flow rate, composition and temperature. Once the mixture enters, it is stirred and mixed perfectly with the mixture that is already inside at the instant it enters the reactor, resulting in a uniform density, temperature and composition in the entire reactor. Therefore, it is considered that the reactions take place homogeneously inside the PSR (Levenspiel, 1999). The condition of the mixture inside the reactor is controlled by the composition of the mixture which enters to it, its temperature and residence time (the time during which PSR hosts the mixture/mixtures). If the temperature of the reaction is constant, the energy equation could be ignored. In reality, the mixing cannot be considered to take place instantaneously as they enter the reactor. The PSR in the laboratory is designed to take high-intensity turbulence which contributes to the efficiency of mixing of the mixtures (Robert J. Kee, 2003).

This is a zero-dimensional system, therefore the mass conservation equation can be easily taken from the Reynolds transport theorem, to directly relate system and control volume. We start with the species conservation equation:

\[
\left( \frac{dm_k}{dt} \right)_{sys} = \int_{CV} \omega_k W_k dV \tag{5-19}
\]

The right-hand side shows the species production/destruction by homogeneous chemical reactions. The integral is over the control volume which coincides with the system at an instant in time. Using the Reynolds transport theorem will help to represent the system at the
right-hand side which gives (5-2). By assuming a fixed volume, inside which every property is taken to be uniform, the volume integrals are evaluated and will give:

$$\frac{\partial (\rho Y_k)}{\partial t} V + \int_{CS} \rho Y_k V n dA = \dot{\omega}_k M_k dV$$

(5-20)

The integral which represents the convective transport through the control surface is easily calculated by the inlet and outlet flows:

$$\frac{\partial (\rho Y_k)}{\partial t} V + \dot{m}(Y_k - Y_k^*) = \dot{\omega}_k M_k dV$$

(5-21)

Due to no continuously differentiable relationship between the inlet and outlet, the divergence theorem is not a valid operation. Therefore, the mass-continuity equation for PSR will be:

$$\frac{dY_k}{dt} = \frac{\dot{m}}{\rho V} (Y_k^* - Y_k) + \frac{\dot{\omega}_k M_k}{\rho}$$

(5-22)

With $Y_k^*$ being the mass fraction of the species $k$ at the inlet of the reactor.

The energy equation for the PSR is derived as:

$$C_p \frac{dT}{dt} = \frac{\dot{m}}{\rho V} \sum_{k=1}^{K} Y_k^* (h_k^* - h_k) - \sum_{k=1}^{K} h_k \dot{\omega}_k M_k \rho - \frac{\dot{Q}}{\rho V}$$

(5-23)

With $h_k^*$ being the specific enthalpy of the species $k$ at the inlet.

The nominal residence time that the species remain at the reactor is:

$$t_{res} = \frac{\rho V}{\dot{m}}$$

(5-24)

5.3. Plug Flow Model in Cantera

One way to model plug flow reactor in Cantera is to consider a reactor network consisting of a series of $n$ perfectly stirred reactors. In Cantera, to model each of these reactors and the connection of them to those before and after them, each reactor is assigned to be attached to an upstream and a downstream reservoir. The way to attach the upstream and downstream reservoirs to the main reactor is through a mass flow controller for the up-stream reactor and a pressure controller for the downstream reactor in the Python interface and a valve for the Matlab interface. Figure 12 illustrates the way to model a reactor in the reactor network in Cantera for both Python and Matlab interfaces.
5.3.1. Mass flow controller in Cantera
If two or more reactors are supplied as argument, a mass flow controller is installed between the two. It maintains a specific mass flow rate independent of upstream and downstream. The codes to model this in Python and Matlab are different (Cantera, 2016):

- In Python →
  - \( m = ct.MassFlowController(upstream,r,mdot=mass\_flow\_rate) \)

- In Matlab →
  - \( mfc = MassFlowController; \)
  - \( install(mfc, upstream, r); \)
  - \( setMassFlowRate(mfc, mass\_flow\_rate); \)

5.3.2. Pressure controller in Cantera
Between the reactor and the downstream reservoir, there needs to be a pressure controller. A pressure controller works in conjunction with another “master” flow controller. It is typically a mass flow controller. The pressure controller gets the permission from a master. Mass flow
rate of a pressure controller equals the one of master plus a small correction amount, which depends on the $\Delta P$.

$$\dot{m}_{p,c} = \dot{m}_m + K_v(P_1 - P_2) \tag{5-25}$$

### 5.3.3. Valve

In Matlab interface, the pressure controller has not been introduced. Therefore, to replace the function of pressure controller, one requires to define a valve at the outlet of the reactor.

- **valve (upstream, downstream)** → A valve which produces a flow rate proportional to $\Delta P$ of upstream and downstream reactors.

$$\dot{m}_v = K(P_1 - P_2) \tag{5-26}$$

Mass flow rate of valve is a positive quantity, if it is negative, zero is returned, therefore, the valve works as a check valve (Speth R., 2017).

$$\dot{m} = K(P_{up} - P_{down}) \tag{5-27}$$

### 5.3.4. Molar rate of creation/destruction of species $i$

The $i$-th species transport equation is:

$$\frac{\partial}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j Y_i) = \frac{\partial}{\partial x_j} \left( \rho D_i \frac{\partial Y_i}{\partial x_j} \right) + R_i + S_i \tag{5-28}$$

In which $R_i$ is the reaction source term. Chemical reactions are modelled as source terms in the species transport equation.

$$R_i = M_i \sum_{r=1}^{N_R} \dot{\omega}_{i,r} \tag{5-29}$$

$\dot{\omega}_{i,r}$ also known as $\dot{R}_i$ is the molar rate of creation/destruction of species $i$ in reaction $r$. In Cantera:

- $\text{omega} = \text{creationRates(gas)} - \text{destructionRates(gas)}$;
- $\text{omega} = \text{netProdRates(gas)}$;

Molar rate of creation/destruction in detail is shown in the equation below:
\[
\dot{\omega}_{i,r} = \Gamma(\nu'_{i,r} - \nu''_{i,r}) \left( k_{f,r} \prod_{j=1}^{N} (G_{j,r})^{\eta'} - k_{b,r} \prod_{j=1}^{N} (G_{j,r})^{\eta''} \right) 
\] (5-30)

- \( C_{j,r} \rightarrow \) Molar concentration of species \( j \) in reaction \( r \).
- \( \eta' \rightarrow \) Forward rate exponent of species \( j \) in reaction \( r \).
- \( \eta'' \rightarrow \) Backward rate exponent of species \( j \) in reaction \( r \).
- \( k_{f,r} \rightarrow \) Forward rate constant for reaction \( r \).
- \( k_{b,r} \rightarrow \) Backward rate constant for reaction \( r \).
- \( \nu'_{i,r} \rightarrow \) Stoichiometric coefficient for reactant \( i \) in reaction \( r \).
- \( \nu''_{i,r} \rightarrow \) Stoichiometric coefficient for product \( i \) in reaction \( r \).
- \( \Gamma \rightarrow \) Net effect of third bodies on the reaction rate.

Net effect of third bodies:

\[
\Gamma = \sum_{j}^{N_r} \gamma_{j,r} G_j 
\] (5-31)

- \( \gamma_{j,r} \rightarrow \) Third body efficiency of species \( j \) in reaction \( r \).
- \( \Gamma \rightarrow \) Could be arbitrarily included if one has the data for it.

Forward rate constant:

\[
k_{f,r} = A_r T^a \exp \left( - \frac{E}{RT} \right) 
\] (5-32)

- \( A_r \rightarrow \) Pre-exponential factor.
- \( T^a \rightarrow \) Temperature exponent.
- \( E \rightarrow \) Activation energy of reaction.

Backward rate constant:

\[
k_{b,r} = \frac{k_{f,r}}{K_r} 
\] (5-33)

- \( K_r \rightarrow \) Equilibrium constant for reaction \( r \).

\[
K_r = \exp \left( \frac{\Delta S^0_r}{R} - \frac{\Delta H^0_r}{RT} \right) \left( \frac{P_{atm}}{RT} \right)^{\Sigma_{i=1}^{N_r} (\nu''_{i,r} - \nu'_{i,r})} 
\] (5-34)

- \( \Delta S^0_r \rightarrow \) Standard state entropy.
- \( \Delta H^0_r \rightarrow \) Standard state enthalpy (heat of formation).
6. DIFFERENT EXPERIMENTS AND THEIR MODELLING AND SIMULATION

6.1. KCl Vaporization and K2SO4 Formation Experiment

Iisa et al. experimented the sulfation of KCl in a laminar entrained-flow reactor (LEFR) at temperatures between 900 to 1100 °C. In their work, they investigated the state of KCl sulfation in the molten and vapor phases, also the effects of temperature and gas composition on the sulfation phenomenon. SO2, Oxygen, water vapor and nitrogen were fed into the reactor, as well as solid particles of KCl. KCl particles melted and partially vaporized. Both the molten and vaporized KCl might react with SO2 and become sulfated, having reacted with SO2, O2 and H2O. Figure 13 shows the LEFR reactor used in the experiments of Iisa et al.

The gases and solid particles are heated by radiation and convection with a rate of 300 – 400 °C/s. The hot gases and particles flow down the reactor in the laminar pattern. At the bottom of the reactor, they are cooled down rapidly and head into collectors and cyclone. The solid particles of KCl are continuously fed into the reactor and collected by the collectors.

Table 2 is a summary of experimental conditions. Glarborg et al. introduced a gas mechanism
for biomass combustion and alkali sulfate formations. They simulated numerically the experiments of Iisa et al. and verified the results of the experiment using CHEMKIN package in their published work.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Residence time</td>
</tr>
<tr>
<td>KCL particle size</td>
</tr>
<tr>
<td>SO₂ concentration</td>
</tr>
<tr>
<td>H₂O concentration</td>
</tr>
<tr>
<td>O₂ concentration</td>
</tr>
<tr>
<td>Gas flow rate</td>
</tr>
<tr>
<td>KCl feed rate</td>
</tr>
</tbody>
</table>

Table 2. Summary of experimental condition (K. Iisa, 1999).

Degree of KCl solid particles’ vaporization is depicted in Figure 14 and Figure 15 illustrates the conversion of solid KCl particles to K₂SO₄ both as a function of residence time. They are simulated by Glarborg et al. and in this work as well. The amount of sulfated KCl is measured from the composition of the submicron particles in the filter at the downstream of the reactor also from the coarse particles in the cyclone. The former is to determine the gas phase sulfated particles and the latter belongs to the molten phase conversion. The vaporization and sulfation calculation is described in 6.1.3.

![Figure 14. Potassium vaporization at temperatures 900, 100, 1100 °C (K. Iisa, 1999).](image-url)
6.1.1. KCl mechanism equilibrium

The first case we will look at is the case of KCl mechanism, which is a mechanism consisting of KCl equilibrium with decreasing temperature. It is a case similar to the one of Iisa et al. in which they have fed solid particles of KCl with SO₂, oxygen, water vapor, and nitrogen into a laminar-entrained flow reactor (K. Iisa, 1999). The mechanism for this case consists of KCl in solid, liquid and gas phase and Nitrogen. The objective of this equilibrium modeling is to test the sophistication of the model as to accurately predicting the phase changes of KCl.

Figure 15. K₂SO₄ formation in filter catch for 10 L/min total gas flow, for 2% SO₂, 5% O₂, 10% H₂O, and KCl feed rate 2.24 g/min (K. Iisa, 1999).
The graph correctly illustrates the melting point and boiling point of KCl solid and liquid KCl respectively to be 1043.15 and 1693.15 K. At 1693, some $K_2Cl_2$ is also produced which is then immediately decreasing giving its place to gas phase KCl. This proves that Cantera works correctly with the mechanism to predict the equilibrium state.

6.1.2. Full Mechanism Equilibrium

Equilibrium calculations are usually done to understand the behavior of different species at different temperatures, and interpret the chemical processes to find the final products of a mechanism. Utilization of chemical equilibrium models have increased since the 1960s in high temperature processes (Nordin A., 1993). As discussed in the 4, the chemical equilibrium calculation procedure, similar to other databases such as FactSage, is on the basis of Gibbs free energy minimization.
Figure 17 illustrates state of chemical equilibrium while holding temperature and pressure as fixed properties. This setting for the equilibrium calculations (fixing temperature and pressure) is the closest to the boiler conditions, as discussed in 4.5. It is apparent that the main species available at a significant amount are SO$_2$, SO$_3$, HCl and KCl. The formation of alkali sulfates are not much accounted for in the equilibrium calculations, since in lower temperatures, SO$_2$, SO$_3$ are more stable than K$_2$SO$_4$ and KSO$_3$Cl. However, KHSO$_4$ is available with a much higher amount than K$_2$SO$_4$ and KSO$_3$Cl in equilibrium state and that is also due to its stability in that temperature. The behavior of SO$_2$, SO$_3$ are worth looking into because in the absence of alkali sulfates, SO$_3$ is the agent to which SO$_2$ is mostly converted and later emitted to the environment.
Figure 18 depicts that in lower temperatures (downstream of the boiler) SO$_3$ is in much higher amounts than SO$_2$ due to the fact that SO$_3$ is more stable in lower temperatures in the equilibrium state.

### 6.1.3. Plug flow/kinetic calculations

The experiment is already explained in 6.1, and it has been designed and performed by Iisa et al. to study the sulfate formation of KCl in the gas and molten phase in a laminar entrained reactor (Iisa, 1999). Table 2 explained the conditions of the experiment and Table 3 shows the input of the model as well as some of the modeling conditions.

<table>
<thead>
<tr>
<th>Input</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>0.045002</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.056194</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.063274</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.816637</td>
</tr>
</tbody>
</table>
The vaporization of KCl and its sulfation have been measured and the results have been depicted in the publication and in this work. The degree of vaporization is calculated using below equations.

\[ X_{vap} = \frac{100 \times (X_{KCl(g)} + X_{other \ K \ species})}{0.007164} \]  

(6-1)

\[ X_{vap} = \frac{100 \times (1 - X_{KCl(s)} + X_{KCl(s)^{**}} + X_{KCl(s)^{***}})}{0.007164} \]  

(6-2)

Moreover, the sulfation of KCl has been calculated based on:

\[ X_{sul} = \frac{100 \times 2 \times X_{K_2SO_4}}{0.007164} \]  

(6-3)

\[ X_{sul} = \frac{100 \times X_{K_2SO_4}}{2 \times 0.007164} \]  

(6-4)

Equation (6-3) is the sulfation calculation method by the author of this work and (6-4) is suggested by Iisa et al.

As the potassium chloride which is fed to the reactor is in solid particle forms, the vaporization of KCl is modelled in the form of three pseudo-first-order reactions in series (Peter Glarborg, 2005). The rate constants, \( k', k'', k''' \) are fitted to match the experimental data for vaporization (K. Iisa, 1999). The rate constant for the three equations shown below is found to be 2.4 to best match the experimental data.
\[ KCL(S) \overset{\rightleftharpoons}{R(6-5)} KCL(S)^{**} \]

\[ KCL(S)^{**} \overset{\rightleftharpoons}{R(6-6)} KCL(S)^{*} \]

\[ KCL(S)^{*} \overset{\rightleftharpoons}{R(6-7)} KCL(G) \]

The trend of the vaporization is shown in Figure 19 and it is compared with different degrees of magnitude for the rate constant of the KCl phase change reactions.

![Figure 19](image)

**Figure 19.** The trend of KCl vaporization in comparison with one degree of magnitude larger and smaller.

The amount of rate constants fitted to be \(k' = k'' = k''' = 2.4\) is the best fit which was obtained at 1373 K, also can be seen from the figure above that the trend is similar to the vaporization of KCl presented in Figure 14.

However, the simulation with this mechanism and plug flow reactor model does not give satisfying results. The figures below illustrate the KCl vaporization, KCl sulfation, and mole fractions of KCl(s)**, KCl(s)*, KCl(s), KCl(g), and K\(_2\)SO\(_4\).
Figure 20. Degree of KCl vaporization.

Figure 21. Degree of KCl sulfation
The reason for this inconsistency of the results was investigated for some time and for different selections of criteria. Finally, the main Cantera developer was asked about it and he replied: “Cantera’s reactor network model is only suitable for modeling homogeneous phases within a single reactor.”. This concludes the modeling of Iisa et al. experiment using Cantera since they had different phases of KCl involved in the experiment which is not into capability scope of Cantera for the reactor network module. Therefore, an experiment done in gas phase should be modeled in order to validate the PFR model.

**Figure 22.** Mole fractions of KCl in gas and solid phases and K₂SO₄.
6.2. SO\textsubscript{2} – SO\textsubscript{3} Conversion Experiment Modeling and Simulation

Yilmaz performed some experiments to investigate and minimize the uncertainties on the sulfur chemistry (Ayten Yilmaz, 2006). Even though there is enough information on the formation of SO\textsubscript{3}, there is still information lacking on the kinetics of the process and these experiments were performed to clarify the kinetic data to establish a viable mechanism. The experiment investigates the SO\textsubscript{2}/SO\textsubscript{3} ratio under combustion conditions. A number of reactions are involved in the SO\textsubscript{2} - SO\textsubscript{3} conversion. Some of which are presented below:

\begin{align*}
SO\textsubscript{2} + O(\text{+M}) & \rightleftharpoons SO\textsubscript{3}(\text{+M}) & \text{R(6-8)} \\
SO\textsubscript{2} + OH & \rightleftharpoons SO\textsubscript{3} + H & \text{R(6-9)} \\
SO\textsubscript{2} + O_2 & \rightleftharpoons SO\textsubscript{3} + O & \text{R(6-10)} \\
SO\textsubscript{2} + HO\textsubscript{2} & \rightleftharpoons SO\textsubscript{3} + OH & \text{R(6-11)}
\end{align*}

HOSO\textsubscript{2} might as well be an intermediate:

\begin{align*}
SO\textsubscript{2} + OH(\text{+M}) & \rightleftharpoons HOSO\textsubscript{2}(\text{+M}) & \text{R(6-12)} \\
HOSO\textsubscript{2}(\text{+M}) & \rightleftharpoons SO\textsubscript{3} + H(\text{+M}) & \text{R(6-13)} \\
HOSO\textsubscript{2} + H & \rightleftharpoons SO\textsubscript{2} + H_2O & \text{R(6-14)} \\
HOSO\textsubscript{2} + O & \rightleftharpoons SO\textsubscript{3} + OH & \text{R(6-15)} \\
HOSO\textsubscript{2} + OH & \rightleftharpoons SO\textsubscript{3} + H_2O & \text{R(6-16)} \\
HOSO\textsubscript{2} + O_2 & \rightleftharpoons HO\textsubscript{2} + SO\textsubscript{3} & \text{R(6-17)}
\end{align*}

And the destruction of SO\textsubscript{3} may involve reactions such as:

\begin{align*}
SO\textsubscript{3} + H & \rightleftharpoons SO\textsubscript{2} + OH & \text{R(6-18)} \\
SO\textsubscript{3} + H & \rightleftharpoons HOSO + O & \text{R(6-19)} \\
SO\textsubscript{3} + O & \rightleftharpoons SO\textsubscript{2} + O_2 & \text{R(6-20)} \\
SO\textsubscript{3} + OH & \rightleftharpoons SO\textsubscript{2} + HO\textsubscript{2} & \text{R(6-21)}
\end{align*}

However, the main understanding is that the SO\textsubscript{2} - SO\textsubscript{3} concentration in the gas phase is mainly controlled by the reactions R(6-8) and R(6-20). Hindiyarti has noted that reaction R(6-8) has no measured rate constant under the combustion conditions. This reaction’s rate
constant is reported differently in several publications and most of them are reported to be rather high (Hindiyarti, 2007).

The experiment consists of two quartz reactors in separate ovens. In the first reactor, SO$_2$ was oxidized to SO$_3$ with the presence of catalyst operating at 673 K. The product gas from the first reactor was fed into the second reactor. The input gas consists of SO$_2$, O$_2$, and N$_2$, and is sent to catalytic reactor and then the output of this reactor was sent to a second reactor which was a homogeneous reactor. The second reactor consisted of a quartz tube which was located in an electrically heated oven. The tubes used for the second reactor were designed to resemble plug flow in laminar flow regime. Characteristic temperature profiles of the homogeneous reactor are shown in the figure below.

![Figure 23. The temperature profile of the homogeneous reactor (Hindiyarti, 2007).](image)

The isothermal region characterized by the flat temperature profile was obtained in most of the temperature range, and is around 40 cm.

The experiments were done in the atmospheric pressure with temperature in the homogeneous reactor (second reactor) in the range of 973 to 1373 K. Typically, the input of this reactor which is the output of the first reactor contained approximately SO$_2$ and SO$_3$ of about 200 to 500 ppm, 2.5-5% O$_2$, in nitrogen as well as trace amounts of water vapor.
estimated in the range of 30 -150 ppm. Figure 24 illustrates some of the experimental results obtained for the decomposition of SO$_3$ (Hindiyarti, 2007).

![Graph showing SO$_2$ concentration vs. temperature](image)

**Figure 24.** Experimental results from the homogeneous reactor (Hindiyarti, 2007).

Each set of experiment includes different shares of each gas which are presented in the table below:

<table>
<thead>
<tr>
<th></th>
<th>Set 1 (%)</th>
<th>Set 2 (%)</th>
<th>Set 3 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_3$</td>
<td>0.0342</td>
<td>0.0420</td>
<td>0.0406</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>0.0238</td>
<td>0.0500</td>
<td>0.0540</td>
</tr>
<tr>
<td>O$_2$</td>
<td>4.7</td>
<td>2.6</td>
<td>4.7</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.0100</td>
<td>0.0100</td>
<td>0.0100</td>
</tr>
<tr>
<td>N$_2$</td>
<td>95.232</td>
<td>97.298</td>
<td>95.1954</td>
</tr>
<tr>
<td>Residence time</td>
<td>2320/T</td>
<td>2550/T</td>
<td>2901/T</td>
</tr>
</tbody>
</table>

**Table 4.** Input of the second reactor.
As can be seen from Table 4, the residence time for each of the experiments varies with the reactor temperature (constant mass flow).

A plug flow reactor model has been constructed to model the experiments in the constant temperature to simulate the conversion using the gas mechanism suggested by Glarborg et al. The results of the simulations are compared to the experimental data and are demonstrated in Figure 25, Figure 26 and Figure 27 respectively for the three sets of experiments, the points represent the experimental data and the lines are the results of simulations.

**Figure 25.** Simulation results and experimental data for Set 1.
Figure 26. Simulation results and experimental data for Set 2.

Figure 27. Simulation results and experimental data for Set 3.
As can be seen from the figures above, the modeling predictions are accurately showing the behavior of the gases inside the reactor in the temperature range of the experiment. For set 1 the SO$_2$-SO$_3$ conversion has been modelled and it has very good agreement with the experimental data as shown by Figure 25. Set 2 and set 3 both show the dissociation of SO$_2$ by decrease of temperature. The model simulates the experiment well for set 2 (Figure 26), but as illustrated by Figure 27, set 3 results are a little less accurate especially for the higher temperatures. However, the main focus of the simulation is the lower temperature region since the species of attention start to matter in that region. The overall agreement of the model with the experimental data is well and this tells us two things:

1. The thermodynamic properties, reactor rates and activation energy quantities are with good approximation in the gas mechanism, verifying the accuracy and correctness of the gas mechanism.
2. It seems that the plug flow reactor model is well-constructed and simulates the reactor rather correctly.

This model can be used to predict the experiments of Jimenez et al. and for any kind of study of biomass combustion which has been designed for the gas phase which is in the modeling capacity of the solver Cantera.
6.3. Modeling and Simulation of Formation of Alkali Sulfate Aerosols

Jimenez et al. performed a series of experiments using a down-fired entrained flow reactor (EFR). The EFR is heated externally by three levels of four electrical resistances in order to obtain a uniform distribution of temperature. There is a gas stream flow which is the product of natural gas combustion and is to simulate the particle burning atmosphere inside the boiler in terms of gas composition and temperature (Santiago Jimenez, 2005).

Using a similar set-up, they performed a new set of experiments inside an EFR, with a natural gas burner upstream of the heated tube, along with streams of some different gas lines to adjust different input gases (SO₂, N₂, etc.) inside the EFR. The quantities of the species are changed for each case to provide different gas compositions for the experiment. There is a refractory along the heating tube to provide the cooling of the gas similar to the ones in the real systems (up to 750 K/s for the temperatures of up to 1450 °C). They used an 11-stage burner for this experiment. Orujillo was used as the fuel in this experiment and fuel sizes are in the range of microns to millimeters. The initial reactor temperatures are 1100, 1300, 1450 °C, and the cooling rates are different as depicted in Figure 28 (S. Jiménez, 2005). Jimenez et al. have done another study based on this experiment in which they have considered the initial reactor temperature to be 1300 °C, and they have looked into SO₂ - SO₃ conversion (Santiago Jimenez, 2007).

![Figure 28. Cooling rate inside the EFR (S. Jiménez, 2005).](image-url)
The figure above illustrates the conversion of SO₂ and SO₃. As already noticed in Figure 18 and Figure 25, in lower temperatures SO₂ converts more and more to SO₃. This conversion has been shown to be the rate-limiting step in sulfate formation inside the boiler.

6.3.1. Equilibrium calculations

The equilibrium calculations once more for this experiment have been done. The equilibrium model for Jimenez et al. experiment is set up in Matlab using Cantera toolbox. The equilibrium is done for the range of temperatures between 1500 and 600 K. The state of equilibrium is calculated for the constant temperature and pressure for this is the closest set up to the boiler. The input of the plug flow reactor is shown in the table below:

<table>
<thead>
<tr>
<th>Input</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>1E-5</td>
</tr>
<tr>
<td>O₂</td>
<td>0.05</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.2</td>
</tr>
<tr>
<td>KOH</td>
<td>1.3E-5</td>
</tr>
<tr>
<td>HCl</td>
<td>3.4E-5</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table 5. The input for the kinetic calculations.
Some species of importance are shown in Figure 30. The changes in the amounts of KOH and KCl are of importance. The input contains KOH and HCl, and as the temperature lowers, the amounts of KCl and KOH both decrease giving rise to the K₂SO₄. The prediction of equilibrium simulation is of use in this case when it comes to the investigation of the presence of each species. In reality and not in the equilibrium state, the trend of decrease of KCl and KOH is different than this. However, the prediction of equilibrium state can be compared to the one of kinetics calculations to understand how far from equilibrium the flue-gas inside the boiler is.

6.3.2. Kinetic calculations and simulation results

Kinetic calculations are made possible using a plug flow reactor model, which consists of a network of $n$ PSR reactors. The plug flow for Jimenez experiment is modelled following the temperature profile shown in Figure 28. Therefore, this case is very similar to reality as the
flue-gas undergoes a temperature decrease inside a boiler. The modeling of the reactor temperature profile is shown in Figure 31. As illustrated, the temperature profile along the PFR (consisting of the 23 PSRs) is modelled with a rather good accuracy, since the model is simulating the temperature of each of the reactor steps accurately.

![Figure 31. The temperature profile of the gas mixture along the reactor.](image)

The temperature starts from 1500 K and decreases to 506 K and the gas input velocity remains constant throughout the reactor. The characteristics of the model is shown in the table below:

<table>
<thead>
<tr>
<th>Input velocity</th>
<th>unit</th>
<th>quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor length</td>
<td>[m]</td>
<td>1</td>
</tr>
<tr>
<td>PSR length</td>
<td>[m]</td>
<td>0.043</td>
</tr>
<tr>
<td>Input velocity</td>
<td>[m/s]</td>
<td>0.305</td>
</tr>
<tr>
<td>Reactor area</td>
<td>[m²]</td>
<td>0.005</td>
</tr>
<tr>
<td>Mass flow rate</td>
<td>[kg/s]</td>
<td>0.00032</td>
</tr>
</tbody>
</table>
The SO$_2$-SO$_3$ conversion is shown in the figure below.

![Graph](image)

**Figure 32.** The SO$_2$-SO$_3$ conversion comparison.

Figure 32 shows acceptable accordance to the Figure 29, therefore the model has proven suitable and accurate to look into the evolution of alkali sulfates along the reactor with the 23 steps of temperature change. The mole fraction percentage of species of importance along the reactor is illustrated in Figure 33.
In Figure 33, the x-axis is the reactor length. The evolution of the species throughout the plug flow reactor is illustrated. Both sequences of reactions shown in Figure 5 can be traced in this figure. KOH decreases with a steep slope from halfway in the boiler to exist only with a scarce amount at the end. The amount of KCl also drops but with a less steep slope and at the end there is some KCl left. KHSO₄ and KSO₃Cl agents both increase and at the same time give rise to K₂SO₄. In the experiments of Yilmaz there was no Alkali agent therefore SO₂ converted to SO₃ and in lower temperatures SO₃ amount rose. However, here with the presence of alkali metal, the SO₂ first converts to SO₃ as the rate-limiting step and then SO₃ starts to convert through the chain reactions to K₂SO₄.

For the sake of clearer observation of the species change with the temperature in specific, the same figure is plotted with the x-axis as temperature as well. Formation of K₂SO₄ is seen in the end of the reactor with an amount of approximately 9.2e-6 mole fraction.
Along the boiler, the potassium content shifts from KCl and KOH to potassium sulfate agents such as KSO₃Cl, KHSO₄ and K₂SO₄ as the gas moves towards the downstream of the boiler. KHSO₄ and KSO₃Cl are agents present in the chain reaction to produce potassium sulfate. It is observed that most of the sulfur which turns into alkali sulfates and sulfation agents are coming from SO₃ of the flue-gas rather than SO₂, since the amount of SO₂ does not decrease significantly.

One can easily notice the increase in the alkali sulfate species K₂SO₄ as the condensing corrosive agent inside the boiler. This increase takes place as the gas mixture is cooled along the boiler. The plot illustrates the fact that by cooling the gas mixture, concentration of K₂SO₄ which is in the vapor phase increases beyond saturation level, as proved also by Glarborg et al (Peter Glarborg, 2005). This causes the K₂SO₄ particle formation by homogeneous nucleation of sulfate particles. These particles act as condensation nuclei for the sequential condensation of chloride vapors. All the potassium in this process converts...
finally to particle phase. It seems that the composition of the gas is determined by equilibrium composition at 820 °C (Livbjerg, 2001).

The other sulfur species of importance in terms of emissions to the atmosphere are shown in the figure below:

![Figure 35. Hydrogen and sulfur species mole fractions.](image)

The figure shows the amount of H$_2$S exiting the boiler in the gas phase which is in the order of $10^{-24}$. This is in accordance with the literature about the H$_2$S emissions of biomass combustion. The decrease in the concentration of the H$_2$S is due to the fact that at higher temperature H$_2$S is oxidized to SO$_2$ through a chain of reactions.
7. SENSITIVITY ANALYSIS

7.1. Length of the Reactor

The first property to check the sensitivity of the model to is the length of the reactor. The final amounts of SO$_2$ and K$_2$SO$_4$ are compared in each case. The objective is to investigate if the length of the reactor influences the composition of the flue-gas.

<table>
<thead>
<tr>
<th>Length (m)</th>
<th>SO$_2$</th>
<th>K$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>9.294e-6</td>
<td>5.629e-7</td>
</tr>
<tr>
<td>0.25</td>
<td>9.290e-6</td>
<td>5.626e-7</td>
</tr>
<tr>
<td>0.5</td>
<td>9.289e-6</td>
<td>5.612e-7</td>
</tr>
<tr>
<td>1</td>
<td><strong>9.288e-06</strong></td>
<td><strong>5.595e-07</strong></td>
</tr>
<tr>
<td>2</td>
<td>9.288e-6</td>
<td>5.581e-7</td>
</tr>
<tr>
<td>5</td>
<td>9.288e-6</td>
<td>5.577e-7</td>
</tr>
<tr>
<td>10</td>
<td>9.288e-6</td>
<td>5.576e-7</td>
</tr>
</tbody>
</table>

As can be seen from Table 7, change in the length of the reactor does not affect the quantities of the species inside the reactor much. This is because the input and output temperatures are the same in reactors of any length.

7.2. Residence Time

Residence time is related to the input velocity of the gas mixture. The higher the velocity of the gas mixture, the lower the residence time. The relations between the total residence time, velocity, length of PSR, and residence time inside each PSR is given as:

\[
\frac{dz}{n_{steps}} = \frac{\text{length}}{n_{steps}} \quad (7-1)
\]

\[
V_{psr} = \text{area} * dz \quad (7-2)
\]

\[
t_{res} = \frac{\text{length}}{u_0} \quad (7-3)
\]

\[
dt = \frac{t_{res}}{n_{steps}} \quad (7-4)
\]
While $dt$ is the residence time in each of the steps, $dz$ is the length of each of the steps i.e. length of each PSR, $u_0$ is the input velocity of the gas mixture. Table below includes the final amount of SO$_2$ and K$_2$SO$_4$ for different residence times.

### Table 8. The amount of certain species in relation with changes of residence time.

<table>
<thead>
<tr>
<th>Case</th>
<th>$u_0$ (m/s)</th>
<th>$t_{res}$ (s)</th>
<th>$t_{step}$ (s)</th>
<th>SO$_2$</th>
<th>K$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.025</td>
<td>40</td>
<td>1.69</td>
<td>8.762e-6</td>
<td>1.221e-6</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>20.02</td>
<td>0.84</td>
<td>9.022e-6</td>
<td>9.491e-7</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>10.1</td>
<td>0.44</td>
<td>9.174e-6</td>
<td>7.705e-7</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>4.017</td>
<td>0.16</td>
<td>9.277e-6</td>
<td>5.948e-7</td>
</tr>
<tr>
<td>5</td>
<td>0.305</td>
<td>3.293</td>
<td>0.14</td>
<td>9.288e-6</td>
<td>5.595e-7</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>1</td>
<td>0.042</td>
<td>9.279e-6</td>
<td>3.412e-7</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>0.50</td>
<td>0.21</td>
<td>9.242e-6</td>
<td>2.132e-7</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>0.20</td>
<td>0.0084</td>
<td>9.237e-6</td>
<td>8.525e-8</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>0.1</td>
<td>0.0044</td>
<td>9.274e-6</td>
<td>3.904e-8</td>
</tr>
</tbody>
</table>

The changes in the K$_2$SO$_4$ with respect to residence time is shown in the figure below.
Figure 36. $K_2SO_4$ change related to residence time change.

The plot demonstrates that the amount of alkali sulfate changes with the residence time. As the residence time of the gas mixture in the reactor increases, the alkali sulfate amount increases. This is in favor of shorter residence times. However, the input velocity cannot be faster than a certain amount either. Also, HCl has been investigated and it is noticed that it decreases with the decrease of residence time, however, its decrease is less than potassium sulfate, from $2.22e^{-5}$ for case 1 to $2.06e^{-5}$ for case 9.

7.3. Oxygen Amount and Oxyfuel

The amount of oxygen in the combustion plays an important role. Different amounts of oxygen percentage have been simulated up to the case of oxy-combustion.
Table 9. The cases with different amount of oxygen.

<table>
<thead>
<tr>
<th>Case</th>
<th>O₂</th>
<th>SO₂</th>
<th>K₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>9.689e-6</td>
<td>1.690e-7</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>9.288e-06</td>
<td>5.595e-07</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>8.960e-6</td>
<td>8.878e-7</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>8.266e-6</td>
<td>1.574e-6</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>7.465e-6</td>
<td>2.353e-6</td>
</tr>
<tr>
<td>6</td>
<td>0.719959</td>
<td>6.934e-6</td>
<td>2.861e-6</td>
</tr>
</tbody>
</table>

Figure 37. Different cases with differences in oxygen amount for K₂SO₄.

As can be observed in Figure 37, the amount of K₂SO₄ formation increases with amount of oxygen. This is because the more oxygen is available inside the reactor, the more reactions take place closer to complete combustion and therefore, K₂SO₄ as one of the products of combustion also increases. Case 6 is the case of oxyfuel and it is evidently producing the highest amount of potassium sulfate and this is the highest possible with this set up of input potassium and sulfur.
HCl is less affected by the oxygen available in the reactor, still there is some change in a lower order compared to K₂SO₄ with oxygen changes. The figure below depicts the HCl fluctuation with the input O₂ changes in the reactor.

![Figure 38. HCl change with the input oxygen.](image)

### 7.4. Reaction Route Reduction

Computation of reactive flows, such as the case for this study, requires accurate predictions of chemical properties such as reaction rate constants and so on. Such gas mechanisms are computed/measured accurately and are capable of correctly modeling different phenomena such as combustion. On the other hand, these gas mechanisms could include hundreds and thousands of reactions and species. Our case of gas mechanism includes 184 reactions and 47 species. One measure that scientists and engineers take in order to reduce the computation time is called mechanism reduction. Mechanism reduction is done in order to find the smallest possible mechanism which can still yield the same and as accurate prediction of the chosen targets.
In our case, one of the main targets of the gas mechanism is to predict the concentration of alkali sulfates, therefore, reduction of mechanism in terms of reaction reductions seems to be an obsolete job because different pathways of reactions serve directly or indirectly to produce alkali sulfates. Thus, mechanism reduction in this case requires a larger and more specific investigation on the mechanism which is out of the scope of this work. However, if the target is changed to, for instance, prediction of concentration of SO\(_2\) which is remained/found at the end of the process, one can look into the mechanism reduction in order to serve this purpose.

The different cases of reactions reduction are shown in the table below:

<table>
<thead>
<tr>
<th>case</th>
<th>Reduced reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>none</td>
</tr>
<tr>
<td>1</td>
<td>(\text{K}_2\text{SO}_4 + \text{K}_2\text{SO}_4 \rightleftharpoons 2 \text{K}_2\text{SO}_4) (B)</td>
</tr>
<tr>
<td>2</td>
<td>(\text{KHSO}_4 + \text{KCl} \rightleftharpoons \text{K}_2\text{SO}_4 + \text{HCl})</td>
</tr>
<tr>
<td>3</td>
<td>(\text{KHSO}_4 + \text{KOH} \rightleftharpoons \text{K}_2\text{SO}_4 + \text{H}_2\text{O})</td>
</tr>
<tr>
<td>4</td>
<td>(\text{KSO}_3\text{Cl} + \text{KOH} \rightleftharpoons \text{K}_2\text{SO}_4 + \text{HCl})</td>
</tr>
<tr>
<td>5</td>
<td>(\text{KOH} + \text{SO}_3 (+ M) \rightleftharpoons \text{KHSO}_4 (+ M))</td>
</tr>
<tr>
<td>6</td>
<td>(\text{KSO}_3\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{KHSO}_4 + \text{HCl})</td>
</tr>
<tr>
<td>7</td>
<td>(\text{KCl} + \text{SO}_3 (+ M) \rightleftharpoons \text{KSO}_3\text{Cl} (+ M))</td>
</tr>
<tr>
<td>8</td>
<td>(\text{HOSO}_2 + \text{O} \rightleftharpoons \text{SO}_3 + \text{OH})</td>
</tr>
<tr>
<td>9</td>
<td>(\text{SO}_2 + \text{OH} (+ M) \rightleftharpoons \text{HOSO}_2 (+ M))</td>
</tr>
</tbody>
</table>

The results of the mechanism reduction is shown in the figure below and as illustrated, there is not much difference in the concentrations of SO\(_2\) in different cases from 1 to 8. Therefore, the gas mechanism in the case 8 is the reduced gas mechanism which could only be used for the target of SO\(_2\) prediction. On the contrary, the reduced mechanism of case 9 is an example of the gas mechanism wrongly reduced for the target of SO\(_2\) concentration modeling. It is showing an incorrect amount for SO\(_2\) which tells that some reactions have been reduced which contributed to SO\(_2\) greatly, thus they cannot be reduced from the mechanism.
Finally, some brief CFD model in COMSOL Multiphysics has been made. Using the dimension of Gruber et al. (Gruber T, 2014) the geometry was drawn and the boundary conditions were given to the model in accordance with the model. The velocity and temperature contours are presented below. It is noticed that the temperature range is from 1573 to around 673 with the cooling trend shown in the figure. Moreover, the velocity propagation is also noteworthy and how the velocity of the gas mixture is affected by the geometry. The further work could be a complete CFD model which can predict the amount of each of the species at every point inside the boiler considering the different phases. The content of Table 8 and Figure 40 can help predict the possible location of $\text{K}_2\text{SO}_4$ deposition inside the boiler as well.

**Figure 39.** The reduced reductions to model $\text{SO}_2$ concentrations.

### 7.5. CFD simulation

Finally, some brief CFD model in COMSOL Multiphysics has been made. Using the dimension of Gruber et al. (Gruber T, 2014) the geometry was drawn and the boundary conditions were given to the model in accordance with the model. The velocity and temperature contours are presented below. It is noticed that the temperature range is from 1573 to around 673 with the cooling trend shown in the figure. Moreover, the velocity propagation is also noteworthy and how the velocity of the gas mixture is affected by the geometry. The further work could be a complete CFD model which can predict the amount of each of the species at every point inside the boiler considering the different phases. The content of Table 8 and Figure 40 can help predict the possible location of $\text{K}_2\text{SO}_4$ deposition inside the boiler as well.
Figure 40. The velocity contour of the gas mixture inside the boiler.

Figure 41. Flue-gas temperature in the symmetry plan of the boiler.
8. CONCLUSION

This work investigates the alkali sulfate formation and combustion chemistry inside the boiler during biomass combustion. Alkali sulfates, as the corrosive and submicron aerosols agents, are important species formed inside the biomass boilers. A plug flow reactor model is considered which is implemented in Cantera. The model is used to validate the experiments performed previously. It can predict the behavior of alkali sulfates along with other important species such as SO$_2$ and SO$_3$, reasonably well throughout the boiler starting from the secondary air input. Thus, the mole fraction of the gas mixture at every stage and temperature of the boiler is known.

Sulfur chemistry important for the SO$_2$/SO$_3$ ratio, alkali sulfate concentrations and the intermediate species concentrations have been updated. The modeling predictions using the updated gas mechanism and reactor model are in good agreement with the experimental data, which verifies the model. This allows the trust on the model to reasonably predict the species throughout the reactor length at each intended temperature or distance. Sensitivity analysis have been performed to investigate the influences of the different lengths, residence times, and input oxygen amounts. The results are rather comprehensible and in accordance with the understanding of the gas mechanism and process of combustion.

All in all, this work contributes to solving the current problems in terms of sulfate formation, corrosion accumulation, and harmful emissions from the biomass boilers. Such chemistry insights are used in overcoming the current obstacles in emission reductions as well as enhanced boiler design. Better design of boiler with the help of accurate combustion chemistry can reduce the design costs and risks of leakage of poisonous species in the plant by reducing the corrosion possibilities. Knowing the amount of the emissions at the output of the boiler can also contribute to a better understanding of the emissions and consequently controlling them and their environmental impacts, which are significant due to the tightening of the emission policies.

A further step can be implementing the kinetic mechanism and reactive model of this work into a CFD solver such as ANSYS Fluent or Comsol Multiphysics in order to combine the predictions with more details, for instance geometry of the boiler. This will make the user able to observe concentrations of different species, their phases, accumulations and condensations at every single point and time in the boiler.
9. SUMMARY

A model for the chemistry of flue-gas after the secondary air injection is developed. The model works on the basis of a detailed chemical kinetics data for the high temperature gas-phase interactions between different species available after the secondary air inlet inside a biomass burning boiler. The main species of attention is the alkali sulfate as it is known to be the agent responsible for depositions inside the boiler causing corrosion, as well as aerosol formation. Moreover, the behavior of SO₂, SO₃, KCl, KOH along with alkali sulfate intermediate agents such as KHSO₄ and KSO₃Cl have been studied. The evolution towards alkali sulfate starts with SO₂ and a potassium agent in the flue-gas such as KOH. These species undergo different reaction routes and chains along the model which represents biomass burning boiler. KHSO₄ and KSO₃Cl are produced and these species have been shown be to sufficiently stable in the gas phase and act as precursors of A₂SO₄ species. Furthermore, alkali sulfates are formed and increase as the flue-gas is cooled down along the boiler. Model is validated as the results from the simulations are in reasonable accordance with the results from the experiments done by Yilmaz et al. (Ayten Yilmaz, 2006) for the thermal dissociation of SO₃ and formation of subsequent species, which was performed for the first time in the 1000-1400 K range. The model is made in Cantera library of Python. Cantera is an object-oriented open-source tool suite for chemical kinetics, reacting flows and thermodynamics. Using the model, the molar fraction of each of the species inside the boiler at every temperature and length of the boiler can be estimated. Finally some sensitivity analyses have been done in order to investigate the role of amount of oxygen, reactor length, and residence time.
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