# KRAFT PULP MILL MODELLING WITH ASPEN PLUS

Lappeenranta–Lahti University of Technology LUT

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ABSTRACT

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**Kraft pulp mill modelling with Aspen Plus**

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85 pages, 11 figures, 19 tables and 1 appendix

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Modelling in pulp and paper industry has primarily been done with software which are developed for pulp mill modelling. These modelling tools often have limited usability modelling processes that are not part of the traditional pulp mill processes. The industry has seen increase in novel processes with the increasing interest in development of biorefinery concepts built around the kraft process.

Aspen Plus is general purpose process simulation tool which is already widely used for research in pulp and paper industry. The existing Aspen Plus models are primarily focused on single sections of a pulp mill or only on new processes. In the available research Aspen Plus has not been used for modelling pulp mill digesters or larger sections from pulp mills.

Simplified kraft mill was built on Aspen Plus with objective of modeling mass balance and sodium and sulfur balances in the mill. The model is calibrated with data from UPM Kymi pulp mill and literature. The development and the result of the model are gone through in the methods section.

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**Sulfaattisellutehtaan mallintaminen Aspen Plus:alla**

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Sellu- ja paperiteollisuusprosessien mallintaminen on tehty pääasiassa kyseiseen teollisuuteen tarkoitetuilla mallinnusohjelmilla. Nämä mallinnusohjelmat eivät kuitenkaan sovellu yhtä hyvin yleiseen prosessimallintamiseen. Kasvava kiinnostus sulfaattimenetelmän ympärille rakennettuihin biojalostamoihin on lisännyt uusien perinteisestä selluteollisuusprosesseista poikkeavien osaprosessien määrää.

Aspen Plus mallinnustyökalu on suunniteltu yleiseen prosessimallintamiseen, mutta on myös käytössä sellu- ja paperiteollisuuden tutkimuksissa. Jo olemassa olevat mallit ovat pääasiassa keskittyneet sellutehtaiden osaprosessien ja uusien prosessien mallintamiseen. Saatavilla olevissa tutkimuksissa Aspen Plus:ssaa ei ole käytetty sellutehtaiden keittokattiloiden tai suurempien kokonaisuuksien mallintamiseen.

Yksinkertaistettu sulfaattisellutehdas onnistuttiin mallintamaan Aspen Plus ohjelmalla. Aspen Plus malli keskittyy esittämään sellutehtaan massatasapainoa sekä natrium- ja rikkitasapainoja. Malli on kalibroitu UPM Kymi sellutehtaan sekä kirjallisuuden pohjalta. Työssä tehdyn Aspen Plus mallin kehitys ja tuloksia käsitellään metodit osiossa.

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This thesis could not have been possible without my wonderful partner. Their support helped me through the entire endeavor. Thank you for reminding that life is more than a thesis.

# SYMBOLS AND ABBREVIATIONS

## Abbreviations

| | |
|---|---|
| AA | Active Alkaline |
| ADt | Air Dry ton |
| BDt | Bone Dry ton |
| D | Chlorine dioxide bleaching |
| E | Extraction bleaching |
| EA | Effective Alkaline |
| ECF | Elemental Chlorine Free |
| NCG | Non-Condensable Gas |
| NPE | Non-Process Element |
| S | Sulfidity |
| TCF | Total Chlorine Free |

**Table of contents**

Abstract

Acknowledgements

Symbols and abbreviations

Declarations

1 Introduction ..... 10
1.1 Background and objectives ..... 11
1.2 Definitions ..... 11
Literature review ..... 14
2 Wood composition ..... 14
2.1 Main polysaccharides in wood ..... 14
2.2 Lignin in wood ..... 16
2.3 Extractives and inorganics in wood ..... 17
3 Kraft mill ..... 19
3.1 Kraft pulping ..... 19
3.2 Wood debarker and chipper ..... 20
3.3 Digester ..... 21
3.4 Screening ..... 22
3.5 Washers ..... 23
3.6 Oxygen delignification stage ..... 23
3.7 Bleaching stages ..... 24
3.7.1 Chlorine dioxide ..... 25
3.7.2 Extraction ..... 25
3.7.3 Hydrogen peroxide ..... 26
3.8 Chemical recovery ..... 26
3.8.1 Black liquor evaporation ..... 26
3.8.2 Recovery boiler ..... 27
3.8.3 Causticization ..... 29

3.8.4 White liquor oxidation ..... 29
3.8.5 Lime cycle ..... 30
3.9 Recovery of other components ..... 31
3.9.1 Methanol ..... 31
3.9.2 Wood extractives ..... 31
3.9.3 Non-condensable gases ..... 32
4 Pulp mill modelling ..... 33
4.1 Modelling software ..... 33
4.2 Modelling approaches ..... 35
4.2.1 Digester modelling ..... 35
4.2.2 Modelling of the process chemicals ..... 36
4.3 Previous Aspen Plus models ..... 36
4.4 Previous kraft pulping models ..... 37
Experimental section ..... 38
5 Methods ..... 38
5.1 Data for the model ..... 38
5.1.1 UPM Kymi pulp mill ..... 38
5.2 Modelling approach ..... 39
5.1 Energy ..... 40
5.2 Wood modelling ..... 40
5.3 Components ..... 41
5.3.1 Component types ..... 41
5.3.2 Organic components ..... 42
5.3.3 Inorganic components ..... 44
6 Aspen Plus model ..... 46
6.1 Fiberline ..... 46
6.1.1 Debarking and chipping ..... 46
6.1.2 Pulping ..... 47
6.1.3 Brownstock washing and screening ..... 48
6.1.1 Bleaching and delignification ..... 49
6.2 Chemical recovery ..... 52
6.2.1 Black liquor evaporation and tall oil recovery ..... 52
6.2.2 NCG capture and methanol recovery ..... 55

6.2.3 Recovery boiler and heat recovery ..... 56
6.2.4 Causticization ..... 58
6.2.5 Lime cycle ..... 59
6.2.1 White liquor oxidation ..... 60
7 Results ..... 62
7.1 Fiberline organic balance ..... 62
7.2 Liquor composition ..... 63
7.3 Sodium and sulfur balance ..... 67
7.4 Atomic balance ..... 68
8 Discussion ..... 71
8.1 Main findings ..... 71
8.2 Limitations ..... 72
8.3 Comparison to WinGEMS ..... 73
9 Conclusions ..... 74
9.1 Future work ..... 74
References ..... 78

Appendices

Appendix 1. Evaporator parameters

DECLARATIONS

## Turnitin

The originality of this thesis has been reviewed with the Turnitin similarity checking service.

## AI usage

The author of the thesis, Elmeri Pöllänen, used the following AI-tools during the preparation of the thesis:

1. LUT Primo AI Search
    a. Tool was used for finding sources from LUT Primo.
    b. The AI tool was fed prompts such as “kraft pulp modelling” and “Aspen Plus kraft pulp” for finding possible publications used by the AI tool for short summary on the topic.

## Responsibility

The author, Elmeri Pöllänen, takes full responsibility for the content of this thesis and has reviewed and edited the content generated by the possible use of AI tools.

# 1 Introduction

With increasing interest in bio-based products and fuels pulp and paper industry has an opportunity to pivot towards more versatile product portfolio. In pulp and paper industry, kraft process is the prominent pulping method globally due to its high-quality pulp and efficient chemical recovery (Mboowa 2024). Due to the nature of the raw material only around 50% of wood is turned into pulp during the process while most of the left-over organic material gets used in the mill for energy generation. This means that large fraction of the raw material in the kraft mill is not fully utilized, making them prime candidates for biorefinery concepts. Kraft mills have been used as the basis for biorefinery models for example by Huang, Lin, Ramaswamy & Tschirner (2009) and Bijok (2024).

The basic kraft mills also face changes with constant process improvements. With increasing legislative and economic pressure kraft mills have for example reduced amount of wastewater and increased the amount of recirculation within the mill. This continuous improvement of pulp mills creates both new processes and variables that need to be considered in the mill. In modern kraft mills pulp production, chemical recovery and energy generation are highly interconnected as the mills are operated almost as closed systems. Because of this, changes in one process often influence other operations which makes predicting the effects of operational changes essential part for mill operations and for evaluation of new technologies. Process simulation allows these predictions to be made without changes into production lines or physical experiments.

Process simulation has become valuable tool for assessing new processes, finding issues in process lines and feasibility studies. Simulations for research in pulp industry have traditionally been made with software specifically developed for pulp and paper industry. More general-purpose process simulators such as Aspen Plus have often been avoided due to the lack of calculation blocks for some unit operations in pulp and paper industry (Huang et al. 2009).

## 1.1 Background and objectives

Aspen Plus is widely used especially outside of pulp and paper industry. It offers existing libraries of chemicals and components, unit operations, thermodynamic models and calculation tools that provide flexibility to model processes outside of its primary functions. Aspen Plus is already being used for modelling parts of the kraft mill operations (Caldeira Silva Rodrigues & Zanuncio 2023, Damasceno 2020), new processes (Parkhi et al. 2023) and biorefinery concepts (Ellapan, Handani, & Abu 2025; Hruška, Variny, Haydary, & Janošovský 2020). Kraft pulp mill model in Aspen Plus could allow evaluation of the effect of process modifications on mass and energy balances in entire pulp mill with single simulation tools.

The objective of this thesis is to develop a steady-state model of kraft pulp mill with Aspen Plus and to evaluate applicability of Aspen Plus for pulp mill modelling. The model focuses on sodium and sulfur mass balances in fiberline and chemical recovery cycles. The model is built using existing calculation blocks and components which will be modified to achieve functional model. Process layout and data for the model are from UPM Kymi pulp with literature sources used for information that is not typically tracked in kraft mill such as wood composition. The model is evaluated by comparing liquor composition, pulp yield and key process flows in the model.

## 1.2 Definitions

**Key parameters of liquor composition**

The amount of sodium compounds in kraft mills is often presented with effective alkaline (*EA*), active alkaline (*AA*) and sulfidity (*S*). *AA* and *EA* are typically expressed as g/l NaOH or $Na_2O$ equivalents in liquor. In some instances, they can be presented as a percentage compared to amount of wood. In this thesis they are calculated as NaOH equivalents.

Active alkaline tells the amount of NaOH and $Na_2S$ in the solution. These are the main alkaline components forming hydroxide ions ($OH^-$) in liquors. AA is calculated:

$$AA = NaOH + Na_2S \quad (1)$$

where *AA* is active alkaline (g/l), *NaOH* is concentration of natrium hydroxide (g/l) and $Na_2S$ is concentration of natrium sulfide (g/l).

Where active alkaline shows the concentration of alkaline components, the effective alkaline tells more accurately how much alkalinity is in the solution. As $Na_2S$ reacts with water it produces NaOH and sodium hydrosulfide (NaSH). The mass of produced NaOH accounts for around half of the reacted $Na_2S$ mass. *EA* is calculated:

$$EA = NaOH + 0.5 \cdot Na_2S \quad (2)$$

where *EA* is effective alkaline (g/l).

Sulfidity tells the concentration of $Na_2S$ compared to the active alkaline. It is calculated:

$$S = \frac{Na_2S}{NaOH+Na_2S} \quad (3)$$

where *S* is sulfidity (%).

Reduction and causticity are also used for presenting liquor compositions. They are similar to sulfidity and show a ratio between two chemicals in liquor. Reduction shows the amount of sodium sulfide compared to sodium sulfate concentration and is calculated:

$$R = \frac{Na_2S}{Na_2S+Na_2SO_4} \quad (4)$$

where *R* is reduction (%) and $Na_2SO_4$ is concentration of sodium sulfate in liquor (g/l).

Causticity tells the concentration of sodium hydroxide compared to sodium carbonate and is calculated:

$$C = \frac{NaOH}{NaOH+Na_2CO_3} \quad (5)$$

where *C* is causticity (%) and $Na_2CO_3$ is concentration sodium carbonate (g/l).

**Dilution factor**

The amount of liquid used for washing is often defined as a dilution factor. It tells how much liquids is fed into the washer in relation to how much liquids leave with the solids.

$$\mathrm{DF} = \frac{m_1 - m_2}{m_P} \quad (6)$$

where DF is dilution factor, $m_1$ is washing liquid going in (kg), $m_2$ is the amount of liquid leaving with the pulp (kg) and $m_P$ is the amount of washed pulp (kg).

**Liquor-to-wood ratio**

Liquor-to-wood ratio tells how much liquor goes into the digester relative to the amount of wood. Despite the name, in this context liquor refers to all the water going into the digester rather than just to the amount of white and black liquor. For example, this also includes steam and moisture in the wood. Wood part refers to the amount of bone-dry or oven-dry wood entering the digester. It is calculated:

$$\mathrm{LtoW} = \frac{\sum m_i}{m_w} \tag{7}$$

where LtoW is liquor-to-wood ratio, $\Sigma m_i$ is sum of all the liquid mass entering the digester (kg) and $m_w$ is oven-dry mass of wood entering the digester (kg).

**Kappa number**

Kappa number indicates the amount of remaining lignin in pulp. It is defined by how many milliliters of 0.1 M $KMnO_4$ is consumed in 10 minutes during oxidation of 1 gram of pulp in an acidic condition. It doesn't directly correlate with the lignin content, as there can be other oxidation reactions and variation in the lignin composition. Although it is still widely used for determining the extent of cooking, delignification and bleaching processes. Equation 5 represent relationship between kappa number and lignin concentration. For softwoods the coefficient is typically around 0.15. (Bajpai 2018, 469–470.)

$$c_{lignin} = \mathrm{n} \cdot \mathrm{K} \tag{8}$$

where $c_{lignin}$ is concentration of lignin (%), n is coefficient that depends on the wood type and K is kappa number.

# Literature review

# 2 Wood composition

Wood and other bio raw materials are often referred to as lignocellulose materials as the three dominant components are lignin, celluloses and hemicellulose. Woody biomass also includes extractives and inorganic compounds which contribute to biomass behavior but also can be source of valuable products such as tall oil. Composition of some of the most common woods in pulping industry are presented in table 1 with range of composition of typical hardwoods and softwoods.

*Table 1. Composition of hardwoods, softwoods and typical woods used for pulping. Adapted from Sixta (2008, 23–24) and Henriksson, Brännvall, & Lennholm (2009, 24).*

| | **Cellulose, [%]** | **Hemicellulose, [%]** | **Lignin, [%]** | **Extractives, [%]** |
|---|---|---|---|---|
| **Hardwoods** | **43–47** | **25–35** | **16–24** | **2–8** |
| Silver birch, *Betula verrucosa* | 41.0 | 29.8 | 22.0 | 3.2 |
| Blue gum, *Eucalyptus globulus* | 51.3 | 21.3 | 21.9 | 4.6 |
| **Softwoods** | **40–44** | **25–29** | **25–31** | **1–5** |
| Scots pine, *Pinus sylvestris* | 40.0 | 24.9 | 27.7 | 3.5 |
| Norway spruce, *Picea abies* | 41.7 | 24.9 | 27.4 | 1.7 |

## 2.1 Main polysaccharides in wood

Polysaccharides are the main components in wood and are often divided into cellulose and hemicellulose. Hemicellulose is more heterogenous of these two and has multiple polysaccharides composing of different monosaccharides. (Scheller & Ulvskov 2010)

Cellulose is the most abundant compound in wood, often accounting for around 40–45% of dry weight depending on the species (Sjöström 1993, 54). It is composed βglucose monosaccharides connected by β-1,4-glycosidic bonds and are arranged in linear polymers (Figure 1). The level of polymerization differs between wood species; with woods used for pulping it varies in the range from 2000 to 4000 (Sjöström & Westermark 1999, 15–16). Cellulose polymers also tend to form strong intra- and interpolymer hydrogen bonds which stabilize and stiffen the structure and form larger sheets (Henriksson & Lennholm 2009, 89).

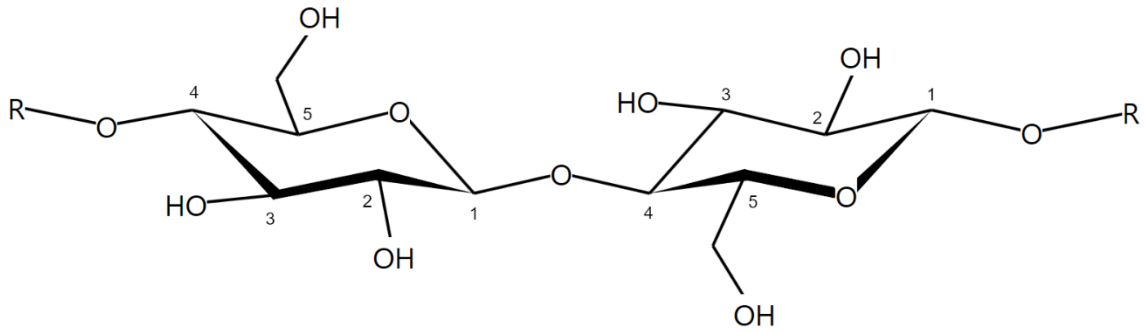


*Figure 1. Chemical structure of cellulose polymer.*

Hemicellulose includes often around 20–35% of wood dry mass and has a low degree of polymerization, usually around 100–200. Cellulose hemicelluloses are composed of multiple types of monosaccharides such as glucose, mannose, galactose, xylose and arabinose. In addition, some of the hemicelluloses have acetyl group branches. (Teleman 2009, 102.) This makes the hemicelluloses a heterogenous group of polysaccharides with varying structures and properties. Only property that is common among most of them is solubility in alkaline solutions. (Scheller & Ulvskov 2010.)

Most common hemicelluloses in wood are xylans and glucomannans, which have distinct structures in different wood types. Xylans have β-(1-4)-linked d-xylose chains, with glucuronoxylan typically found in hardwoods and arabinoglucuronoxylan in softwoods. Hardwood xylans have branching d-glucuronic acids and acetyl groups while softwood acetyl group is replaced by l-arabinose. Glucomannans' backbones have irregular pattern of β-(1-4)-linked d-mannose and d-glucose monosaccharides with ratios varying from 1:1 to

4:1. In hardwood glucomannan is a linear polymer with no branching. Softwoods have galactoglucomannan and glucomannan which have acetyl groups and d-galactose branches. (Sjöström 1993, 63–68.)

## 2.2 Lignin in wood

Lignin is a complex biomolecule which binds together cellulose fibrils and hemicellulose. It typically accounts for 15–35% wood dry mass but varies depending on the species (Table 2). In general, hardwoods have a lower lignin content compared to softwoods. Lignin has three-dimensional heterogenous structure composed of monolignols. (Henriksson 2009, 121–123.)

*Table 2. Lignin content of different softwoods adapted from Sharma et al. (2020, 3).*

| Plant | Lignin content, [%] |
|---|---|
| Norway spruce, *Picea abies* | 20–40 |
| Maritime pine, *Pinus pinaster* | 25–35 |
| Loblolly pine, *Pinus taeda* | 28–45 |
| Monterey pine, *Pinus radiata* | 25–30 |
| Black wattle, *Acasia mollissima* | 20–25 |

Lignin is composed of aromatic monolignol precursors which have different relative amounts depending on wood type and species. The most common monolignols in wood are *p*-coumaryl alcohol (H unit), coniferyl alcohol (G unit) and sinapyl alcohol (S unit) (Figure 2). Softwood lignin is mainly composed of coniferyl alcohol which accounts for over 95% of monolignols while the rest is made of *p*-coumaryl alcohol. In hardwoods there is higher variety in lignin composition than softwoods. Sinapyl and coniferyl alcohols make up the bulk of monolignols with amounts varying from 45–75% and 25–50% while *p*-coumaryl alcohol accounts for less than 10%. (Lu, Lu & Fan 2020, 20.)

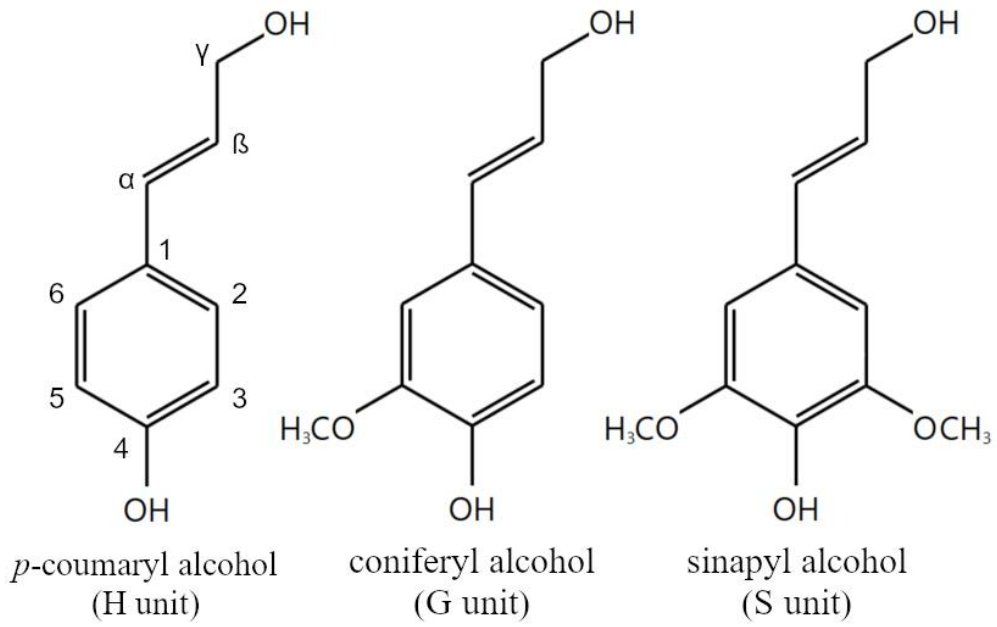


*Figure 2. The main monolignols of lignin: p-coumaryl alcohol (H unit), coniferyl alcohol (G unit) and sinapyl alcohol (S unit).*

## 2.3 Extractives and inorganics in wood

Extractives make up only a small percent of wood weight but account for highest variety of components. The term extractives can be used to describe the hydrophobic compounds which are extractable with neutral solvents. It may also include the hydrophilic fraction in which case the term refers to everything else except cellulose, hemicellulose and lignin. (Holmbom 1999, 125.) Extractives are often divided by their composition into fats, waxes, phenolic compounds, terpenes and inorganic salts or by solubility into resins and water soluble (Jansson & Nilvebrant 2009, 148; Sixta 2006, 33). In this thesis extractives will only refer to hydrophobic fraction with the inorganic salts referred as inorganic.

Softwoods contain high amounts of resins compounds for example terpenes, which can be extracted as turpentine and tall oil. Hardwoods, on the other hand, have less terpenes but contain phenolic compounds like tannins and flavonoids which are generally not present in softwoods. Extractive composition and relative amounts vary among different sections of

wood, wood types, geography and seasons. In temperate climate extractives make around 2–5% of wood dry mass while it can reach even high as 20% in tropical regions. Even though the extractives only make up a small amount of overall wood biomass, they can have negative effects on pulping. (Sixta 2006, 33–35.)

Inorganic compounds are sometimes grouped with the extractives or treated as a separate thing depending on the definitions used. In most of the wood species the most common are in descending order calcium, potassium, magnesium, iron and sodium. (Sixta 2006, 39–40.) Chlorine and sulfur also make a significant portion of wood inorganics and are important especially for pulp mill chemical composition (Paleologou et al. 1999). The metals are often formed into organic salts with compounds such as oxalates, carbonates and glucuronates (Sixta 2006, 39–40). For kraft pulping inorganics from wood plays a significant role as they make up most of the non-process elements (NPEs) in the pulp mill. (Paleologou et al. 1999).

# 3 Kraft mill

The aim of pulping processes is to separate individual fibers from the biomasses' matrix. In kraft pulping this is achieved with a combination of alkaline solution and thermal energy. (Bajpai 2018, 295; Mboowa 2024.)

## 3.1 Kraft pulping

Sulphate pulping, which is often referred to as kraft pulping, gets its name from usage of sodium sulphate ($Na_2S$) as a reactive chemical. Another major reactive chemical used in the pulping process is sodium hydroxide (NaOH). These chemicals are suspended in water-based mixture which is referred to as white liquor. In a pulp mill white liquor also contains other components which accumulate as the liquor gets used and recycled. Typically recycled white liquor includes components of reacted white liquor chemicals such as sodium carbonate ($Na_2CO_3$) and sodium sulphate ($Na_sSO_4$). Often there also are chemicals from wood or other parts of the mill like potassium salts or chlorine compounds.

The most common lignin bond in both soft and hard woods is ether linkages which typically account for over half of the bonds between monolignols. The most abundant of these bonds is β-O-4 linkage. (Lu, Lu, & Fan 2020, 24–27.) These bonds can be broken by hydroxide ions in sulfur dependent and sulfur independent reactions. The sulfur dependent is more efficient and faster which leads to reduced cellulose degradation and therefore improved yields. Some of the lignin fragments repolymerize with each other or undegraded lignin. In these reactions the new linkages have carbon - carbon bonds which can't be broken by $OH^-$ or $S^{2-}$. This is partially responsible for the slowdown in lignin removal during residual delignification. (Smook 2016, 80–84.)

Saccharides are also degraded during kraft pulping, but – compared to cellulose – hemicellulose is affected more. Most common form of polysaccharide degradation is monosaccharide peeling which affects the ends of polymers. (Fearon et al. 2020.) This process only affects around 70 monomers before stabilizing and effectively stopping. Cellulose is less affected by peeling as it typically has much higher polymer length compared to hemicellulose. Cellulose also possesses more crystalline regions which are more resilient

for this type of degradation. Hemicellulose have branching in polymers which also make them more vulnerable to degradation. This means only 5–10% of cellulose gets dissolved compared to 80–90% of hemicellulose. (Fearon et al. 2020; Henriksson, Germgård, & Lindström 2024; Smook 2016, 80–82.)

Pulping also produces noticeable amount of side products. When wood is broken, new degradation products are formed. Most numerous of these are the different extractives that are dissolved into liquor. These include inorganics that form salts and organics components like fatty acids. During pulping degradation products from wood and white liquor also form components such as methanol and water (Fearon et al. 2020). At higher concentrations the side products can cause issues for kraft mill operations. The inorganics from wood can build up due to chemical recovery and cause scale formation, for example in evaporation. During evaporation fats and waxes can cause bubbling in evaporators, reducing heat transfer and increasing scaling. Removing the side products can improve kraft mill operations and be source of income as methanol, turpentine and tall oil are valuable commodities.

Chemicals containing sodium and sulfur are often recovered as they can be recycled to be used for white liquor. Most of the sodium in black liquor has formed organic salts with the decomposition products from wood. The sodium in inorganic salts is mostly $Na_2CO_3$ and $Na_2SO_4$ with small amount of undegraded NaOH and $Na_2S$. (Magdeldin & Järvinen 2020; Niemelä & Alén 1999, 196; DeMartini & Hart 2022, 12.) These chemicals are not volatile and can be therefore recovered by washing brownstock and burning them in recovery boiler. On the other hand, the sulfur compounds that are not salt are more volatile and often referred as non-condensable gases (NCGs). These include hydrogen sulfide ($H_2S$), methyl mercaptan ($CH_3SH$), dimethyl sulfide ($[CH_3]_2S$) and dimethyl disulfide ($[CH_3]_2S_2$). They are formed by sulfide and hydrogen sulfide ions reacting with free protons and lignin fragments. NCGs are often attributed to odorous emissions from kraft mills. (Hovikorpi 2025, 38–42.)

## 3.2 Wood debarker and chipper

Before debarking logs are washed with water to remove sand and other surface debris and transferred from log yard to pulp mill. During colder seasons washing is also used for defrosting the wood before processing. There are multiple methods of debarking, with most common one being drumdebarker. In drumdebarker logs rub against each other and the

agitators in the drum shell. Bark removal can result in wood losses up to 4–5% but can be as low as 1–2%, depending heavily on amount level of bark removal, wood species and debarking method. (Bajpai 2018, 279–285; Smook 2016, 27–29.)

Chipping is done to increase the reaction surface area and make the wood handling more manageable. Chips are typically cut at 35° to 40° angle compared to width of the log and aimed to have length of 20 mm and thickness of 4–5 mm. Commonly accepted chips are 10–30 mm long and 3–6 mm thick, as larger deviations will affect quality of the pulp due to uneven cooking and shorter fibers. (Smook 2016, 27–29.)

## 3.3 Digester

Sulfate pulping process, more commonly referred as kraft pulping, is a chemical pulping method which utilizes alkaline solution of sodium hydroxide (NaOH) and sodium sulfide ($Na_2S$) called white liquor to remove lignin and extractives. Carbohydrates, especially hemicellulose, are also degraded during the process due to the reaction's low selectivity. This is more prevalent with longer cooking times and higher temperatures. Sodium sulfide is utilized to reduce the required cooking time and hence reduces cellulose degradation. (Bajpai 2018, 299; Smook 2016, 76–77.)

As kraft pulping relies on NaOH and $Na_2S$ the amount of these chemicals is often described with effective alkali (EA), active alkaline (AA) and sulfidity (S). In a digester EA for typically kraft pulp mill is around 110 g/l and AA of 130 g/l (Sixta 2005, 113). Sulfidity is typically around 30% but is more dependent on the wood species than AA and EA (Bajpai 2018, 333–334; Sixta 2005, 113).

Chemical pulping can be done as batch or continuous processes. In batch process the digester is filled with wood chips, which are covered with white liquor and black liquor. After the digester is sealed, it is heated up and pressurized by circulating liquor through heat exchanger. The required cooking temperature is around 170°C, which is typically achieved in 90 minutes. This gives sufficient time for cooking liquor to impregnate the chips. During the heating non-condensable gases (NCGs) are vented out of the digester. Cooking temperature is maintained for 20–45 min or even up 2 h. After the cooking brownstock mass is emptied into blow tank where fibers are separated from each other. Heat from the released

vapors is captured and used for heating water for the washing stage. (Bajpai 2018, 314–316; Smook 2016, 78.)

In continuous cooking wood chips and liquor mixture are heated up in a steaming vessel where NCGs are removed. Special feeders, such as screw feeder or rotary valves, are required to keep the continuous digester pressurized. In continuous digesters pressurized feeder input chips and liquor from the top which allows the heavier saturated chips to be gravity fed through the digester. (Smook 2016, 95.) Inside the digester the mass moves through intermediate zone, around 115–120°C, where liquor penetrates into the chips. In the next stage the mass is gradually brought up to cooking temperature by circulating liquor through heat exchangers or with steam injection. The cooking stage last for 1–1,5 hours. After cooking black liquor and pulp are partially separated, and the temperature of pulp is cooled down. (Bajpai 2018, 314–316; Smook 2016, 78.)

## 3.4 Screening

Due to inconsistency in kraft cooking, parts of the wood chip remain intact while some fibers are too fine for the product. Pulp can also contain some impurities which were not removed during debarking such as sand and stones. The knots and impurities can intervene with the downstream processes because of the large size and high residual lignin content. These are separated during deknotting and screening. (Smook 2016, 105–106; 115.)

Deknotting removes the largest fraction from pulp which is often referred to as knots. These mainly consist of uncooked wood chips and dense parts of wood such as knots. Deknotting is typically done before washing as the knots are often re-pulped. (Bajpai 2018, 408; Smook 2016, 105–106.) Knots can be re-pulped in regular digester, but some mills include dedicated knot digester for re-pulping the larger rejects. (Smook 2016, 105–106).

Screening is typically for removing finer particles from the pulp. It is mainly used for removing shives which are described by Bajpai (2018, 408) as “small fiber bundles that have not been separated by chemical pulping or mechanical action”. These are typically combusted for heat production or sent to oxygen delignification for the fibers to separate. Screening is also increasingly used for fractioning the fibers by size as quality control measure. (Bajpai 2018, 408–409.)

## 3.5 Washers

During cooking, extractives and other wood compounds are dissolved into black liquor which also contains the used pulping chemicals. The degraded wood fractions from cooking can increase the chemical demand in delignification and bleaching stages making them less efficient. In some mills washing liquids from oxygen delignification stage are used for brownstock washing as they share similar chemical composition. Black liquor also contains valuable pulping chemicals which need to be recycled for the processes to be profitable. To improve the pulp mill efficiency and the final pulp quality, black liquor needs to be separated from the pulp. Purpose of washing is to recover as much of black liquor while using as little water as possible as lower water content allows lower energy usage during evaporation.

There are multiple washing methods aiming for lower water consumption. In dilution/extraction washing pulp is diluted with cleaner water and is then removed resulting in some of the black liquor being washed off. The extraction stage can include vacuum filtering or mechanical pressing which force dirty water off the pulp. Displacement washing is the most prominent washing method due to lower black liquor dilution. In displacement washing pulp is washed with water while being vacuum filtered to remove black liquor. This allows the cleaner water to displace the black liquor resulting in relatively low dilution. (Bajpai 2018, 390–393; Santos & Hart 2014.)

Washing efficiency is further increased with multiple stages which enable counter flow washing. In counter flow washing used wash water is utilized in upstream washing stages where the dirtier pulp contains more residual black liquor. This allows higher solid concentrate and lower water consumption. With modern displacement washer resulting in weak black liquor can have a solid concentration of 18%. (Bajpai 2018, 390–393; Santos & Hart 2014.)

## 3.6 Oxygen delignification stage

Oxygen delignification is commonly used process in kraft pulp mills before bleaching. It is sometimes considered as the first bleaching stage and therefore often called oxygen bleaching. Compared to bleaching methods, oxygen delignification has low cost but also low specificity for lignin degradation which can cause polysaccharide losses. In oxygen

delignification oxidized white liquor is as the alkali source which makes the process comparable to kraft pulping due to similar chemical compositions. Despite this similarity oxygen delignification has less saccharide degradation as it has typically lower temperatures around 90–130 °C and retention times from 20–60 min. Polysaccharide degradation is further prevented with magnesium ions which has made it common addition to kraft mills. (Bajpai 2018, 479–480).

The main reactive chemicals are oxygen gas and NaOH with most pulp mills using oxidized white liquor. Due to the similar chemical composition, pulping washing liquids from oxygen delignification can be combined with black liquor streams and even used for brownstock washing. This allows better control over chemical balance in a pulp mill with a small increase in recovery boiler load. (Bajpai 2018, 479–480; Smook 2016, 176)

## 3.7 Bleaching stages

After pulping, oxygen delignification and washing pulp still contains lignin and its' derivatives. These impurities give the pulp darker color that can increase intensity over time. Bleaching stages are designed to remove the remaining impurities. Historically chlorine gas has been the most prevalent bleaching chemical but has been phased out due to environmental regulations limiting adsorbable organic halogens (AOX) discharges. It has been replaced with elemental chlorine-free (EFC) and total chlorine-free (TFC) sequences. Currently EFC is the most prevalent bleaching method for economic factors and often means that the pulp mill has chlorine dioxide bleaching and delignification stages. The bleaching stages which are presented in this section are typical for bleached softwood. There are also numerous other bleaching methods with some being phased out while others are growing in interest.

Unlike cooking, bleaching is performed in multiple stages with varying bleaching agents to reduce the degradation of carbohydrates and to achieve better chemical efficiency. These stages also have typically lower concentration of reactants at milder conditions than pulping. Chemical concentrations range from 2% to 15% with temperatures in 35–95 °C range. These are heavily affected by specific reactants but also by wood type and desired kappa number or brightness. The specific bleaching reactant determines the reaction conditions but in

general less specific reactants require higher temperatures and concentrations. These are also often the initial bleaching stages before more specific ones. (Bajpai 2018, 477.)

### 3.7.1 Chlorine dioxide

Chlorine dioxide is the most prominent bleaching stage as its versatile but highly selective against lignin. It replaced chlorine bleaching as it produces fewer adsorbable organic halogens (AOX) while offering better selectivity. Chlorine dioxide gas ($ClO_2$) dissolves lignin and bleaches lignin chromophores while hardly reacting with the polysaccharides. This allows it to function in an early delignification and later bleaching stages. (Bajpai 2018, 476–478; Smook 2016, 177)

Chlorine dioxide is highly reactive which makes it a potent bleaching agent but also toxic and explosive so it must be manufactured on site. One of the most common methods for chlorine dioxide manufacturing is by reducing sodium chlorate ($NaClO_2$) in acidic conditions. Often sulfuric acid is used as it is often needed for tall oil recovery. The neutralization reaction can be controlled with reducing agents which have significant impact on resulting byproducts. During bleaching chlorine dioxide, hypochlorite and chlorine gas degrade lignin while side products chlorate ($ClO_3^-$) and chlorite ($ClO_2^-$) don't contribute (Suess 2010, 74; Svenson et al. 2006).

### 3.7.2 Extraction

Extraction stage is meant to dissolve degraded lignin that is left over after pulp washing, lowering the chemical demand in downstream bleaching stages. During chlorine dioxide bleaching part of the degraded lignin remains in pulp due to low pH level at the stage. In extraction alkali, such as NaOH, is used for increasing the pH level which allows the lignin fragments to be dissolved. In a pulp mill oxidized white liquor is often used as the source of NaOH. (Suess 2010, 111.) The extraction stage can be altered with addition of oxygen and/or hydrogen peroxide for improved lignin removal (Bajpai 2018, 478).

### 3.7.3 Hydrogen peroxide

Hydrogen peroxide ($H_2O_2$) is one of the more expensive bleaching chemicals but is also highly selective and therefore is commonly used as the last stage in bleaching. It's not just selective towards lignin but only towards certain functional groups. This allows the removal of last pigment, giving lignin compounds without sacrificing too much of the pulp strength. (Bajpai 2018, 479.)

## 3.8 Chemical recovery

Chemicals from white liquor break down wood components and, in the process, generate by products such as sodium carbonate and organic sodium salts. Due to the high price of the pulping chemicals and environmental regulation the kraft pulping relies on efficient recycling of sodium and sulfur compounds.

### 3.8.1 Black liquor evaporation

During pulping and washing black liquor gets diluted with water which needs to be removed for more economical firing. The weak black liquor from brownstock washers has low solid content of 14–18% which is not suitable for recovery boiler. (Hart 2022A, 31). To get most out of the potential thermal energy in the recovery boiler the mixture needs to be concentrated by removing the excess water. This is often done with multiple-effect evaporators (MEE) where four to eight effects are connected in series with each effect consisting of one or more evaporators. There are numerous evaporator options with falling film evaporators as one the most popular in the industry. The strong black liquor from the last effect has a solid content typically from 70% to all to way up to 85%. At higher solid concentrations black liquor viscosity increases significantly. This can result in black liquor that is too viscous to be pumped even at high temperatures. (Bajpai 2018, 425–428; Smook 2016, 137.)

Efficient evaporators and washers are highly important in pulp mills as black liquor evaporation is typically the highest consumer of steam in pulp mills. One of the most important methods of improving evaporation efficiency is recovering heat from the produced

vapor. In evaporation steam is commonly used in counterflow configuration compared to liquor stream. In such instances steam flows to the last evaporator from where the evaporate is utilized as steam for upstream effects. As black liquor contains volatile compounds such as methanol, the vapors are also contaminated and therefore kept separate from primary steam flows. (Hart 2022A, 31–47).

### 3.8.2 Recovery boiler

The strong black liquor is burned in recovery boiler to recover inorganic chemicals as smelt, mostly a mixture of sodium carbonate ($Na_2CO_3$) and sodium sulfide ($Na_2S$) and recover thermal energy from the organic chemicals. (Bajpai 2018, 432–433). The generated heat is used for steam and power generation. Temperature in recovery boiler is dependent on the solid black liquor concentration with higher concentration accounting for higher temperatures. With 65% concentration recovery boilers typically reach 1100–1300°C and have heat recovery around 60%. Higher black liquor concentration is desirable as these can reach higher combustion temperatures. (Bajpai 2018, 436–437; Smook 2016, 150–151.)

Heat from the recovery boiler is captured into steam which can be used to transfer heat into different processes and electricity production. Water fed into the is heated up gradually by multiple heat exchangers capturing the thermal energy from the furnace's walls and flue gases. (Smook 2016, 148–149.) The produced steam can be superheated all way up to 500 °C and may reach pressures of 100 bars (Sixta 2006, 982; Smook 2016, 148–149; Vakkilainen 2005, 90). As the high-pressure steam circulates in the pulp mill it loses some of its energy and gets downgraded to medium-pressure steam and ultimately low-pressure steam. These will be used for processes with lower energy demand and temperatures until recycled back to recovery boiler for superheating.

In the highest point of furnaces reaction zones, additional air is fed into allowing oxidization of unburnt gases and sulfur compounds. In this region hydrogen sulfide is oxidized, producing sulfur dioxide and trioxide. These further react with sodium carbonate binding the sulfur in sodium sulfite and sodium sulfate. (Smook 2016, 149.)

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O \quad (1)$$

$$SO_2 + 1/2\ O_2 \rightarrow SO_3 \quad (2)$$

$$Na_2CO_3 + SO_3 \rightarrow Na_2SO_4 + CO_2 \quad (3)$$

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \quad (4)$$

In the oxidization zone sodium sulfide and sodium sulfite are also oxidized into sodium sulfate. Sodium sulfide can also react with carbon dioxide resulting in sodium carbonate and sulfur dioxide. (Smook 2016, 149.)

$$Na_2S + 2\ O_2 \rightarrow Na_2SO_4 \quad (5)$$

$$Na_2SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4 \quad (6)$$

$$Na_2S + 3/2\ O_2 + CO_2 \rightarrow Na_2CO_3 + SO_2 \quad (7)$$

In the drying zone black liquor is fed into the furnace. Sodium sulfide and sodium oxide form sodium carbonate and sodium hydroxide as they react with carbon dioxide and water. Sodium sulfide reaction also results in the formation of hydrogen sulfide. These reactions are shown by reactions 8, 9 and 10. (Smook 2016, 149.)

$$Na_2S + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2S \quad (8)$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \quad (9)$$

$$Na_2O + H_2O \rightarrow 2\ NaOH \quad (10)$$

At the lowest point of the recovery boiler is the reducing zone where primary air is fed into the furnace and smelt is removed. Sodium sulfate is reduced in reactions with carbon as presented in reactions 11, 12 and 13. These result in formation of sodium sulfide or sodium oxide with carbon and sulfur oxides. Sodium sulfide can be reacted with water producing sodium oxide and hydrogen sulfide as presented in reaction 14. (Smook 2016, 149.)

$$Na_2SO_4 + 2\ C \rightarrow Na_2S + 2\ CO_2 \quad (11)$$

$$Na_2SO_4 + 4\ C \rightarrow Na_2S + 4\ CO \quad (12)$$

$$Na_2SO_4 + C \rightarrow Na_2O + CO + SO_2 \quad (13)$$

$$Na_2S + H_2O \rightarrow Na_2O + H_2S \quad (14)$$

The molten smelt from recovery boiler is dissolved in weak white liquor from dreg and lime mud washing forming green liquor. The smelt includes materials which do not get dissolved. These dregs mainly consist of carbon and non-process elements (NPEs) such as magnesium,

iron and other metal compounds. The separated dregs are washed to recover any soluble natrium and sulfur compounds and the washing water is used for dissolving smelt. This process reduces the build-up of the NPEs in the system.

### 3.8.3 Causticization

Green liquor is causticized into white liquor with the use of lime. Lime is used for regenerating sodium carbonate into sodium hydroxide allowing chemical recycling within pulp mill. The used lime is captured, regenerated in a limekiln and reused for causticization. Burnt lime (CaO) from the limekiln is transformed into slaked lime ($Ca(OH)_2$) when it comes in contact with the water in green liquor as shown on the reaction 15. Temperature control of the reaction is important as slaking is exothermic reaction causing the green liquor temperature to rice. Therefore, the temperature needs to be kept under 100 °C. (Bajpai 2018, 438–443; Smook 2016, 151–156.)

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (15)$$

The slaked lime reacts with sodium carbonate ($Na_2CO_3$) during slaking but most of the reaction happens in causticizer. This reaction results in the formation of sodium hydroxide (NaOH) and calcium carbonate ($CaCO_3$) as presented by reaction 16. The $CaCO_3$ is recovered from white liquor with clarification and burned at limekiln for reuse. Most of the white liquor clarification in the industry is done by filtration. (Bajpai 2018, 438–443; Smook 2016, 151–156.)

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaOH \quad (16)$$

### 3.8.4 White liquor oxidation

In a kraft mill sodium sulfide is an important component of white liquor, but in high concentrations it will negatively affect the pulp brightness and viscosity. Oxidation of white liquor converts active sodium sulfide into less active sodium sulfate and sodium thiosulfate. This allows the usage of white liquor for oxygen delignification without reducing pulp quality and it will reduce sodium accumulation in the mill. (Karlsson 2010, 156-157.)

The main oxidation reactions during the white liquor oxidation are formation of sodium thiosulfate, sodium sulfite and sodium sulfate. These are shown by reactions 17, 18 and 19. The main reaction products are sodium thiosulfate and sodium sulfate although the composition depends on the residual time in the reactor.

$$2\ Na_2S + 2\ O_2 + H_2O \rightarrow Na_2S_2O_3 + 2\ NaOH \quad (17)$$

$$Na_2S_2O_3 + 2\ NaOH + O_2 \rightarrow 2\ Na_2SO_3 + H_2O \quad (18)$$

$$2\ Na_2SO_3 + O_2 \rightarrow Na_2SO_4 \quad (19)$$

White liquor oxidation is typically carried out with air or pure oxygen at elevated temperatures for faster conversion. Using air for oxidation has a benefit of lower material cost but contains low concentration of oxygen. The unreactive gases in air reduce conversion and their removal is a major contributor to heat loss. Oxidation with pure oxygen on the other hand increases material costs but allows more effective oxidation. (Karlsson 2010, 156.)

### 3.8.5 Lime cycle

The lime mud from white liquor clarification is washed to recover any remaining pulping chemical and to remove impurities before firing. After washing the excess water is removed by filtration to around 80% solid concentration before drying (Smook 2016, 157). Separate dryers are typically used as feeding the wet lime into the limekiln reduces the capacity. The dryers are heated with waste heat from limekiln improving the overall economics. (Bajpai 2018, 442–445; Smook 2016, 157–158.)

In the lime kiln lime burning is the main reaction beside burning of the fuel. When $CaCO_3$ is heated resulting rection forms CaO by releasing carbon dioxide ($CO_2$) as presented by reaction 20. (Smook 2016, 157.) Typically, oil or gas are used for fuel sources for the kiln although pulping byproducts such as lignin can be used as alternative fuel sources. However, this can result in increased amount impurities in the lime cycle. (Bajpai 2018, 444; Hart 2022B, 149.)

$$CaCO_3 \rightarrow CaO + CO_2 \quad (20)$$

## 3.9 Recovery of other components

In kraft mill other components are formed beside pulp and degraded white liquor chemicals. Some of these are captured in kraft mills for reducing emissions, improving operational efficiency, monetary value or multiple these reasons.

### 3.9.1 Methanol

Methanol is produced during pulping as a byproduct of wood polymer degradation. Due to its volatility, it is easily evaporated during digester blow out and evaporation. Methanol in foul condensate from evaporator or digester is concentrated by steam stripping. Methanol is recovered from the strippers' vapors and can be further refined with distillation. The purified methanol can be sold, fired at furnace, or used at mills $ClO_2$ plant. (Hart et al. 2022, 175.)

### 3.9.2 Wood extractives

Pulping of coniferous trees, such as pines and spruces, produces tall oil soap which can cause issues in evaporation. Tall oil soap is produced from resin and fatty acids in alkaline conditions of kraft pulping (Bajpai 2018, 242). It separates from black liquor especially in higher solid concentrations which can result in bubbling during evaporation. This reduces the heat transfer efficiency and can cause scaling, and therefore in pulp mills the tall oil soap is typically separated from black liquor before evaporation. Separation is typically done in black liquor storage tanks where tall oil soap forms a layer on top of the black liquor. The tall oil soap can be recovered by overflowing the tank. This allows separation of most of the tall oil soap which can turned into tall oil by reversing the saponification in acidic conditions. (Foran 2022, 68.)

Turpentine from kraft mill is sometimes called crude sulfate turpentine is another important component form wood extractives and is often used for tall oil production. Turpentine is composed of terpenes of which the most common ones are alfa pinene and beta pinene. These are more volatile than the tall oil soaps, so they often concentrate at foul condensates from digester blow out or evaporation. (Bajpai 2018, 242–243). These compounds are often

concentrated similarly to methanol with strippers while the recovery happens with using decanters.

### 3.9.3 Non-condensable gases

Non-condensable gases (NCGs) as their name suggest remains gaseous at kraft mill operational parameters. This means that NCG emissions are released throughout the mill if not properly accommodated for. Most potent of these gases are from digester, evaporation, methanol plant and turpentine capture. (Hovikorpi 2025, 111; 113–118.) With the aim of reducing these emissions NCGs are captured and burned at recovery boiler, bark boiler, lime kiln, NCG boiler or flare. The NCG boiler is often used for capturing sulfur and producing sulfuric acid and/or sodium bisulfite. (Hovikorpi 2025, 124.)

# 4 Pulp mill modelling

Pulp mills have been modelled since 1950s for predicting pulping outcomes and process optimization (Fearon 2021, 13). Computerization of the operation has allowed inexpensive and faster way of evaluation on different process designs. As the amount of real time data gathered from industrial processes and research on the process chemistry has increased these models can be more accurate. Still one of the largest uncertainties for process modelling is still data scarcity as most mills don't monitor every variable especially in real time (Brucel, Thibault, Patience & Stuart 2024). Also, the alkaline pulping chemistry is still not fully understood due to its complexity and heterogeneousness of the materials. Therefore, the models are often only valid for narrow range of operational parameters and use cases.

In addition to process optimization (Ahmetović et al. 2021; Gonzalez-Vogel et al. 2021; Li et al. 2014) and new pulp mill concepts (Kangas, Kaijaluoto & Määttänen 2014) one of the important use cases of simulations in pulp industry is integrated biorefinery concept. Inclusion of additional processes to existing kraft mills such as ethanol production (Kautto et al. 2010) and lignin recovery (Culbertson et al. 2016; Kihlman 2016; Tiller et al. 2025).

## 4.1 Modelling software

Many of the pulp mill models in literature are made using simulation software with design emphasis for pulp and paper industry. Most common of these are WinGEMS, VTT BALAS and CADSIM Plus. Aspen Plus is also used for modelling for biorefineries but is not designed for pulp and paper industry and therefore does not contain modules for this. All these simulation tools have graphical user interface where calculation blocks are linked together streams and utilize steady state calculations for simulations.

- WinGEMS or Windows General Energy and Material balance System is based developed by University of Idaho Chemical Engineering department in the 1960s (Andersson 2014). Currently the license is owned and managed by Valmet and is the most prominent modelling software in the cited sources. It is purpose build for modelling pulp and paper mills mass and energy balances making it an efficient and reliable option for this purpose. Despite this it comes with its' own set of drawbacks,

as it lacks flexibility to model unit operations outside of a traditional pulping process. Chemical reactions must be defined manually in WinGEMS, and it does not contain chemistry equilibrium data (Kihlman 2016).

- CADSIM Plus is owned by Aurel Systems Inc. and it has dedicated section for pulp modelling in addition to wider use cases in chemical processes. It also includes engineering drawings and allows them to be exported or used for simulations and supports logic operations. The software includes modules, for example fiber production but also power production and mineral processing. (Aurel Systems n.d.; Brucel et al. 2024)

- VTT BALAS is a steady state simulation software developed in 80s by VTT for pulp and paper production simulations. It has ready-made unit operations such as for TMP production and bioethanol production. It uses Microsoft Vision and Excel as tools while conducting simulation on different applications. (VTT. n.d.)

- Aspen Plus is simulation software developed by AspenTech. It has extensive libraries with different types of compounds with their properties. These include more conventional chemicals such as methane but also less conventional compounds like almond shells. It allows addition of user defined components such as polymers, non-conventional and biocomponents. All the missing or default component properties can also be user defined.

In some research multiple simulation software has been used. For example, Huang et al. (2009) modelled ethanol recovery in integrated forest biorefinery with WinGEMS and Aspen Plus. In the simulation WinGEMS was used for the pulping and chemical recovery processes while the ethanol, chemical and energy production were modelled using Aspen Plus. As these software's have no direct way of communication between them Excel was used as "translation layer". This adds restrictions as data transfer can be difficult without careful design considerations. Multiple simulations software have also been used for validation of the system. For example, Kangas, Kaijaluoto & Määttänen (2014) used VTT BALAS for validations of the main model made with WinGEMS.

## 4.2 Modelling approaches

Through the years numerous modelling methods have been developed for different purposes. With desire for more accurate models, increases in understanding, available data and computational power, more variables have been added to the models to account for all the relevant mechanisms. Yet the simpler models are still useful in situations where some of the variables are unknown, not well understood or the added complexity sacrifices model usability. This has made process modelling landscape varied and filled with different approaches and possibilities.

### 4.2.1 Digester modelling

The simplest way of modelling pulp digesters is using known inputs and outputs to define chemical conversions. This method makes the model accurate for set parameters but unable to adapt to any changes in conditions. Predictive modelling of the complex reactions inside of a pulp digester have started by Vroom. He combined pulping temperature and time into single variable H-factor which could be used for estimating pulping outcomes. (Fearon 2021, 13.) This model leaves out crucial factors like chemical concentrations which include future iterations by Kerr. Although the model only considered effective alkaline leaving out actual hydroxide and sulfide concentrations. Neither of the models tried to predict conversions of white liquor chemicals. (Rahman, Avelin, & Kyprianidis 2020.)

Better understanding of the pulping chemistry and increased computational power has facilitated models based on chemistry during alkaline pulping. This approach could allow models to be applicable to wider range of pulping conditions. Fearon (2021) has developed models where the chemical reactions between lignin, carbohydrates and white liquor were predicted based on practical data. These models consider time, temperature and hydroxide and hydrosulfide concentrations while predicting raw material degradation and product formation.

### 4.2.2 Modelling of the process chemicals

Kraft pulp mills include streams with multiple components with varying chemical compositions. Wood alone has multiple types of hemicellulose, lignin, extractives and inorganic compounds. Pulp mills also contain sodium compounds used for pulping, bleaching chemicals and non-process elements (NPEs). The variety often means that not every component can be or needs to be modelled accurately or at all depending on the purpose of the model.

Most pulp mill models represent wood with simplified component fractions. Huang et al. (2009) only used cellulose, hemicellulose and lignin for kraft mill with integrated ethanol production. Kangas et al. (2014) modelled wood components with more detail by including extractives in addition to the previous mentioned. On the other hand, Culbertson et al. (2016) simplified the biomass model even more by having only carbohydrates and lignin as only components. Their model did account for extractives by removing part of the wood from stream to simulate tall oil recovery. Some models have gone even further by having organics as a single component such as Rogerson (2022) which focused more on the inorganic chemicals in kraft pulp mill.

The inorganic fraction of kraft mill models is often presented by limited number of key elements. Most models with inorganics include sodium and sulfur as these are essential in kraft pulping. Andersson's (2014) model for sodium-sulfur balances in the chemical cycle included magnesium with sodium and sulfur. Kangas et al. (2014) had sodium, sulfur, magnesium, chlorine and potassium as main inorganics in the model.

## 4.3 Previous Aspen Plus models

One of the strengths of Aspen Plus is its extensive directories of chemicals and other components with their properties. Aspen Plus versions 14 onwards even include biocomponents with access to predetermined components like lignin, extractives and wood bark. Even still it does not include calculation/modelling blocks needed for modelling pulping operations such as debarking, chipping and pulping. Therefore, Aspen Plus has been used more for processes which can benefit from the extensive chemical libraries and the listed properties.

Even though Aspen Plus is not specifically designed for pulp and paper industry it is still widely used for modelling biorefinery concepts. These models include biorefinery processes such as biogas production from rejected biomass in thermomechanical pulp (TMP) mill (Zhang et al. 2015), sulfur recovery in pulp mill with integrated black liquor gasification (Hruška et al. 2020), economic feasibility of nanocellulose production (Ellapan et al. 2025) and lignin gasification (Ribeiro Domingos et al. 2023). There have also been models for more traditional pulp mill processes such as recovery boiler optimization (Damasceno 2020), bleaching process in TMP mill (Caldeira Silva Rodrigues & Zanuncio 2023) and carbon dioxide capture from limekiln (Parkhi et al. 2023).

In the previously mentioned Aspen Plus models pulp mill fibers lines are completely left out or in some cases only small part of the mills are included in the models. Huang et al. (2009) even opted for using WinGEMS for the fiber line instead of utilizing Aspen Plus for the whole process.

## 4.4 Previous kraft pulping models

There are numerous models made of pulp and paper mills from plant specific to generic models with literature or experimental data. Most of the models found in literature are made with WinGEMS.

In numerous sources the purpose of the model has been process optimization or improvement. Culbertson et al. (2016), Huang et al. (2009), Kihlman (2016) and Partanen (2015) modelled pulp mills with additional processes. Huang et al. (2009) studied integration of ethanol production into model kraft mill while the other models were set for researching effects of lignin recovery. Andersson's (2014) model focused on studying and predicting sodium and sulfur balances within existing pulp mill. On the other hand, pulp mill models by Kangas et al. (2014) and Rogerson et al. (2024) were made as reference models showcasing typical pulp mills within Nordics and Canada.

# Experimental section

# 5 Methods

The purpose of the research is to evaluate the suitability of Aspen Plus modelling software for kraft mill modelling. Earlier models in the field have generally been developed using software specifically designed for pulp mill modelling and have often avoided using Aspen Plus because of its complexity (Huang et al. 2009). In this study the aim is to utilize predefined materials and calculation blocks in Aspen Plus to model essential parts of kraft mill. The suitability and accuracy of the model are validated by calibrating it against mill and literature data and comparing key mass balance parameters with values reported in previous studies.

## 5.1 Data for the model

The model is mostly based on single softwood fiberline and the shared chemical recovery processes at UPM Kymi pulp mill. The values used in the model are a mixture of data from literature and UPM Kymi factory. As operational values can differ between mills and literature sources the mill data is prioritized. However, some of the required values are not tracked during normal operations and will have to rely on literature data for estimation.

### 5.1.1 UPM Kymi pulp mill

The UPM Kymi pulp mill consists of two fiberlines, one producing mainly soft wood and switch line alternating between soft and hard wood. This model is based on the switch line and the shared chemical recovery cycles.

The fiberline begins with wood handling, where the wood is debarked and chipped before being fed into continuous digester. After the digester larger fractions of uncooked wood are separated from the pulp and cooked in a knot digester. The pulp is washed with two stage drum displacement (DD) washer followed by oxygen delignification after which the pulp is

washed by two parallel DD washers. The bleaching is conducted parallel in two lines and in three stages, two chlorine dioxide stages and extraction stage with oxygen and hydrogen peroxide.

Black liquor from the washers is directed into black liquor storage tanks which balance the recovery boiler operations but are also used to separate tall oil soap from the liquor. The evaporation is conducted with seven effect evaporation system with eleven evaporators. The strong black liquor is mixed with fly ash before being burned in the recovery boiler where the inorganic chemicals are recovered as smelt and regenerated with causticization. Part of the regenerated white liquor is oxidized for use in oxygen delignification.

The mill also contains recovery systems for volatile compounds such as NCGs, terpenes and methanol which are mainly captured from digester blow out and foul condensate. NCGs are burned either recovery, bark or dedicated NCG boiler where the sulfur is captured into sodium bisulfide depending on the mill operations. These products can be sold or utilized in the mill.

## 5.2 Modelling approach

As the objective of this work is to evaluate the usability of Aspen Plus for kraft mill modelling, the model is constructed using standard Aspen Plus unit operations whenever possible. Processes with greatest impact on the mill mass balance in kraft mill were prioritized over, for example, accurate energy modelling. Basics of the kraft mill such as digester, washing, evaporation and recovery boiler were initially prioritized in the modelling process. These processes were complemented by the addition of delignification, bleaching, tall oil recovery, NCG capture and methanol separation as they were deemed important for mass balance. On the other hand, water treatment was excluded from the model because they have limited influence on the primary chemical recovery cycle in kraft mill.

The model includes several calculator blocks that are used for operation conditions and when exact reaction parameters are unknown. Digester, delignification and bleaching reactors are modelled with yield reactors as these offer more flexibility. This allows the modelling efforts to focus on representing reactor mass balances rather than determining atomic composition of biocomponents. These reactors are used with included Fortran-based calculator which

allows greater control over the reactor and the modelled reactions. This enables the model to achieve better reaction elemental balances despite using yield reactors. Reactors used for boilers, causticization, lime cycle and white liquor oxidation are modelled instead with stoichiometric reactors. For these reactors, reaction stoichiometry is more important, and biocomponents are not present or play a minor role.

Methods in Aspen Plus models are used for defining the equations used for calculating the models' properties. Aspen Plus offers multiple types of methods, each best suited for different purposes. For this model, the NRTL (Non-Random Two-Liquids) method is used as the primary property method. As it can be used for mixtures with different types of compounds if they are not close to the critical temperature. However, this method does not function for all the processes as the Aspen Plus databank does not include all the components used. In these instances, PENG-ROB (Peng-Robinson) or WILSON methods are used for singular calculation blocks depending on the component separation.

## 5.1 Energy

Energy recovery and energy utilization is done using Aspen Plus utilities. This allows easier implementation of energy flows between different parts of the model. The utilities include predefined options such as electricity and steam utilities which are used as templates for factory parameters from UPM Kymi.

The steam utilities are defined based on their inlet and outlet temperatures and vapor fractions. Low pressure steam has an inlet temperature of 148 °C and outlet temperature of 147 °C while medium pressure steam has 183 °C and 182 °C. Both steam utilities have inlet vapor fractions of 1 and an outlet vapor fraction of 0. The minimum approach temperatures are set to 1 °C.

## 5.2 Wood modelling

For the model equal mixture of spruce and pine was chosen as the raw material with the compositions based on literature on sources. The components chosen to represent stem wood were cellulose, hemicellulose, lignin, extractives, calcium, potassium, magnesium and

chlorine (Table 3). These were selected based on their relevance to the kraft pulping process and abundance in wood. Wood also contains other metals such as aluminum, iron and manganese but in relatively low concertation and has limited influence on the mass balance.

*Table 3. Composition of Scots pine and Norway spruce stem wood (Alakangas, Hurskainen, Laatikainen-Luntama, & Korhonen 2016, 56; Sixta 2006, 23 & 40).*

| | Scots pine *(Pinus sylvestris)* | Norway spruce *(Picea abies)* |
|---|---|---|
| Organics | | |
| Cellulose, [%] | 40.0 | 41.7 |
| Hemicellulose, [%] | 28.5 | 28.3 |
| Lignin, [%] | 27.7 | 27.4 |
| Extractives, [%] | 3.5 | 1.7 |
| Inorganics | | |
| Ca, [ppm] | 760 | 1800 |
| Cl, [ppm] | 85 | 51 |
| K, [ppm] | 40 | 250 |
| Mg, [ppm] | 110 | 160 |

## 5.3 Components

In Aspen Plus each component can either be defined by the user or selected from the component library. For the model all the components were selected from the Aspen Plus components library and most of them were defined as conventional with addition of biocomponents and solids. In order to maintain the model's core purpose and limited option in the component library some chemical groups are presented with just one or two components.

### 5.3.1 Component types

Conventional component type allows Aspen Plus to determine the state of matter for these components to be in liquid or gaseous phases depending on the conditions. For solid phase components can be defined as conventional solid, often called solid in Aspen Plus, allowing

the use of solid unit operations. This allows the separation of solids from other components with the use of washers, filters and driers.

Aspen Plus 14 and newer versions also include biocomponents with some pre-determined ones such as wood bark, wood chips, cellulose, different types of lignin and extractives. The composition of biocomponents is defined by their carbon, hydrogen, oxygen, nitrogen and ash contents. For this model the ash content of the biocomponents is set to zero as Aspen Plus has option for automatically generated combustion reactions which only consider fully organic compounds. They must also be defined as liquids or solids and therefore can't be in gaseous form. In addition, more complex biocomponents such as wood chips and bark have a predefined composition of cellulose, hemicellulose, lignin and extractives. However, these compositions are not used for the model.

### 5.3.2 Organic components

Due to the heterogenous nature of organic components, they are simplified for the model. Most of them have a heterogenous structure such as wood, lignin and hemicellulose and are therefore modelled as biocomponents. On the other hand, organic chemicals which have a well-defined chemical structure that could be found in Aspen Plus databanks were defined as conventional components. This allows Aspen Plus to calculate thermodynamic properties using the existing databank parameters.

The included component databanks have multiple types of models for different components. For example, lignin has carbon, oxygen and hydrogen rich variants which could be as a mixture for closer representation of different lignin compositions. For the model each biocomponent was modelled using only one model from the databank which was used for both undissolved and dissolved components. The dissolved biocomponents were defined as liquids while undissolved were solids making the washing and separation of these fractions easier in Aspen Plus. All the biocomponents used for the model are presented in Table 4. The table shows the components name and alias used by Aspen Plus as well as the phase in which it is modelled.

*Table 4. Biocomponents in Aspen Plus model.*

| Component name | Phase | Alias |
|---|---|---|
| Pine-1 | Solid | SWOOD-036 |
| Pine-chips-1 | Solid | SWOOD-040 |
| Pine-bark-2 | Solid | SWOOD-039 |
| Spruce-1 | Solid | SWOOD-060 |
| Spruce-chips-1 | Solid | SWOOD-070 |
| Spruce-bark-2 | Solid | SWOOD-065 |
| Biomass-cellulose | Solid | C6H10O5-B1 |
| Biomass-glucomannan | Solid | C5H8O4-B1 |
| C-rich-lignin | Solid | C15H14O4-B1 |
| Biomass-cellulose | Liquid | C6H10O5-B1 |
| Biomass-glucomannan | Liquid | C5H8O4-B1 |
| C-rich-lignin | Liquid | C15H14O4-B1 |
| Water-soluble-extractives | Liquid | C15H12O7-B1 |

Organic chemicals that can be found in Aspen Plus are used for modelling multiple components. For example, formic and acetic acids are used to model the variety of organic acids produced during kraft pulping. This approach does not represent all the organic acids perfectly but allows Aspen Plus to use existing parameters to easily simulate their behavior in the model. Similarly, simplifications are made with sodium acetate and sodium formate for representing organic sodium salts. Alfa-pinene and beta-pinene are used to represent terpene compounds. All the conventional organic components are shown in Table 5.

*Table 5. Conventional organic components in Aspen Plus model.*

| Alias | Type | Component name | CAS-number |
|---|---|---|---|
| C2H3NAO2 | Conventional | Sodium-Acetate | 127-09-3 |
| NACHO2 | Conventional | Sodium-Formate | 141-53-7 |
| CH2O2 | Conventional | Formic-Acid | 64-18-6 |
| C2H4O2-1 | Conventional | Acetic-Acid | 64-19-7 |
| C10H16-D2 | Conventional | Alpha-Pinene | 80-56-8 |
| C10H16-D3 | Conventional | Beta-Pinene | 127-91-3 |
| CH4O | Conventional | Methanol | 67-56-1 |

All the components have their Aspen Plus defined structures except Pine-1, Spruce-1 and C-rich-lignin which were modified to improve the carbon, oxygen and hydrogen balances. These components were chosen for the modification as the exact elemental balances varies and are not well defined. Pine-1 and Spruce-1 have same compositions as Pine-chips-1 and Spruce-chips-1 (Table 6). The composition of C-rich-lignin is instead calibrated to improve the elemental balance in digester.

*Table 6. Composition of the changed biocomponents in the Aspen Plus model.*

| Component | Carbon | Hydrogen | Oxygen |
|---|---|---|---|
| Pine-1 | 1.00 | 1.53 | 0.64 |
| Spruce-1 | 1.00 | 1.53 | 0.63 |
| C-rich-lignin | 1.00 | 1.50 | 0.16 |

### 5.3.3 Inorganic components

Most of the inorganic compounds are defined as conventional components, allowing Aspen Plus to determine their phase. Components used for modelling lime and dregs were instead defined as conventional solids which allow them to be separated from the conventional components with solid separators.

The most important inorganic chemicals for kraft pulping are sodium and sulfur compounds with these salts shown in Table 7. Sodium hydroxide and sodium sulfide are the main reactive chemicals for kraft pulping and during pulping they form new salts which are recovered. For the model sulfates, carbonates, sulfites and thiosulfates were chosen as the main inorganic sodium compounds based on their relevance in literature. Sodium chloride is also included and considered in all the mass balances but is primarily used to represent inorganic chlorine released during pulping. Sodium also forms salts with organic ions produced from degraded wood components.

*Table 7. Inorganic sodium salts in Aspen Plus model.*

| Alias | Type | Component name | CAS-number |
|---|---|---|---|
| NaOH | Conventional | Sodium-Hydroxide | 1310-73-2 |
| $Na_2S$ | Conventional | Sodium-Sulfide | 1313-82-2 |
| $Na_2CO_3$ | Conventional | Sodium-Carbonate | 497-19-8 |
| $Na_2SO_3$ | Conventional | Sodium-Sulfite | |
| $Na_2SO_4$ | Conventional | Sodium-Sulfate | 7772-98-7 |
| $Na_2S_2O_3$ | Conventional | Sodium-Thiosulfate | 7757-82-6 |
| NaCl | Conventional | Sodium-Chloride | 7647-14-5 |

Inorganic components in wood are often formed into salts with organic compounds like oxalates, carbonates and glucuronates or connected to hemicellulose. The specific salts formed by inorganic ions from wood form in black liquor are not well documented. For this model metal ions from wood form carbonates, sulfates and hydroxides (Table 8) while chlorine is fully bonded to sodium chloride. Aspen Plus does not contain adequate data for magnesium hydroxide modelling, and it could not be found from other databanks or literature. Therefore, it was excluded from the model. The carbonates were chosen to be modelled as solids which allows them to be separated as dregs with solid processes.

*Table 8. Inorganics from wood composition in the Aspen Plus model.*

| Alias | Type | Component name | CAS-number |
|---|---|---|---|
| CACO3 | Solid | Calcium-Carbonate-Calcite | 471-34-1 |
| CA(OH)2 | Solid | Calcium-Hydroxide | 1305-62-0 |
| CASO4 | Conventional | Calcium-Sulfate | 7778-18-9 |
| MGCO3 | Solid | Magnesium-Carbonate | 546-93-0 |
| MGSO4 | Conventional | Magnesium-Sulfate | 7487-88-9 |
| K2CO3 | Solid | Potassium-Carbonate | 584-08-7 |
| KOH | Conventional | Potassium-Hydroxide | 1310-58-3 |
| K2SO4 | Conventional | Potassium-Sulfate | |
| NACl | Conventional | Sodium-Chloride | 7647-14-5 |

# 6 Aspen Plus model

This section describes the design and modelling choices made for the Aspen Plus model of sulfate pulp mill. The assumptions and design restrictions are presented first followed by discussion on the components used in the model. The design of the pulp model is presented in separate sections while shortcomings and challenges discussed afterwards.

## 6.1 Fiberline

The fiberline model represents the conversion of incoming wood into bleached pulp. It consists of debarking, chipping, digester, washers, screening, oxygen delignification and bleaching stages. The focus of the modelled fiberline is to represent materials flows, pulp yield and maintain chemical balances.

### 6.1.1 Debarking and chipping

The objective of the wood handling section is to produce chip feed for pulping and account for losses in debarking and chipping. Wood feed entering the model is composed of mixture of bark and softwood which are separated during debarking bark. This is accomplished with component separator module as Aspen Plus lacks readymade modules for this process. Wood losses during debarking are simulated by removing a fraction of the wood stream into the bark stream. Wood losses during debarking were set at 4%, corresponding to typical industrial values. Chipping is modelled using a yield reactor where 97% of the wood is turned into wood chips while the remaining wood represents larger chips and knots which are removed in screening. The chips and rejects are separated with component separator.

The generated waste streams from the wood handling are directed into bark boiler where the burning reaction automatically in a stoichiometric reactor. Boiler pressure and heat duty are set to zero to allow the model to calculate the adiabatic combustion temperature. Flue gases from the boiler are directed into a heat exchanger for medium pressure utility steam generation. The boiler lacks an ash stream which exists in real boilers.

### 6.1.2 Pulping

The digester is modelled as a single yield reactor as the focus of pulping reactions are mass balances instead of reaction kinetics or stoichiometries. The yield reactions are defined and calculated using Aspen Plus Fortran-based calculator connected to the yield reactor. This allows greater control over the reaction chemicals such as enabling chemical accumulation in a closed-loop system and allows adaptation to different feed compositions. This level of flexibility would not be possible with stand-alone Aspen Plus yield reactor.

The purpose of the pulping calculations is to maintain metal, sulfur and overall mass balances and is based on mixture of factory and literature data. The backbone of the yield reactions is liquor, wood and pulp composition values from UPM Kymi pulp mill, Magdeldin & Järvinen (2020) and DeMartini & Hart (2022, 12). Values from UPM Kymi are used as the main source with literature being as representative and filling knowledge gaps. Due to lack of experimental data for interaction between wood composition and liquor chemistry, the wood degradation and liquor reactions were calculated independently.

Wood chips, steam and white liquor streams are combined before being fed into the digester with liquor to wood ratio of 3.8. The steam is modelled as component stream instead of using utilities as it affects liquor-to-wood ratio and therefore the reactor mass balance. In the digester spruce and pine chips are broken down into their basic components based on tree trunk composition found in literature and presented in Table 9 and Table 10. Extractives and inorganics from the chips are fully dissolved into the liquor while parts of lignin and carbohydrates remain undissolved. The selected reaction results in a pulp yield of approximately 46% with 95% cellulose retention, 82% hemicellulose and 92.4% lignin removal. The resulting pulp has a lignin content of 4.6% (kappa number 30).

*Table 9. Pine composition in the Aspen Plus model.*

| Component | Total, [%] | Solid, [%] | Liquid, [%] |
|---|---|---|---|
| Biomass-cellulose | 40 | 38 | 2 |
| Biomass-glucomannan | 28.5 | 5.1 | 23.4 |
| C-rich-lignin | 27.7 | 2.1 | 25.6 |
| Water-soluble-extractives | 3.5 | 0 | 3.5 |

*Table 10. Spruce composition in the Aspen Plus model.*

| Component | Total, [%] | Solid, [%] | Liquid, [%] |
|---|---|---|---|
| Biomass-cellulose | 41.7 | 39.6 | 2.1 |
| Biomass-glucomannan | 28.3 | 5.1 | 23.2 |
| C-rich-lignin | 27.4 | 2.1 | 25.3 |
| Water-soluble-extractives | 1.7 | 0.0 | 3.5 |

The inorganic chemistry of the digester is simplified to maintain the sodium and sulfur balances. The incoming sodium hydroxide, sodium sulfide and sodium carbonate flows are combined to determine the amount of active sodium in the feed. During pulping, most of the active sodium reacts to form organic sodium salts which are presented with sodium formate and sodium acetate. Rest of it reacts to form sodium sulfite, sodium thiosulfate, sodium sulfate and a small amount of sodium chloride. The extent of these reactions is calibrated to match literature liquor composition while maintaining sodium and sulfur balances.

### 6.1.3 Brownstock washing and screening

Two phase drum displacement (DD) washers are presented with six solid stage washers in countercurrent configuration (Figure 3). Three of the washers receive water which is then used by three washers upstream simulating the two phases. Wash water is recycled secondary condensate from the evaporators and is used for both oxygen delignification and brownstock washers. With the water from the oxygen delignification reused in brownstock washing. The brownstock washers based on the factory values have a dilution factor of 2.5.

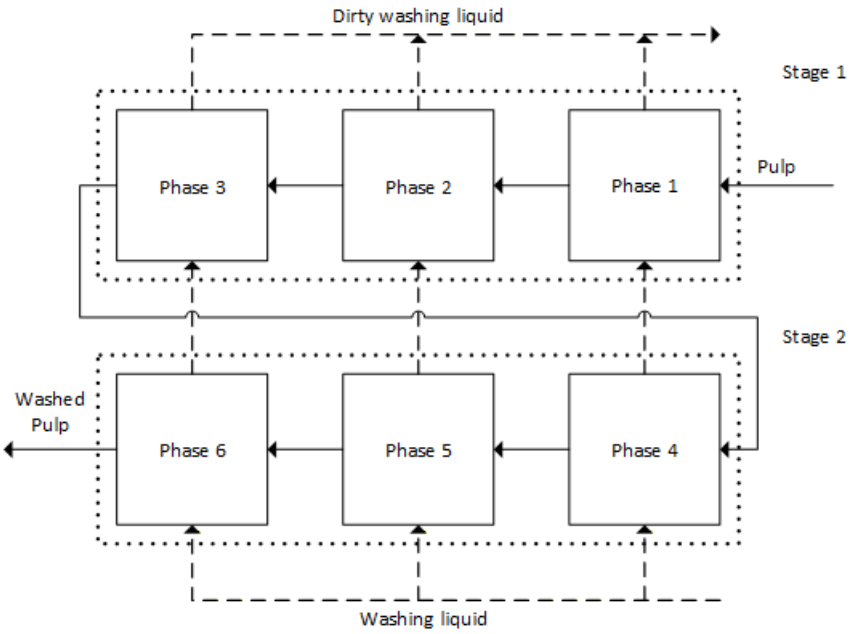


*Figure 3. Flow diagram of DD washer setup in the Aspen Plus model.*

Washed pulp from the brownstock washer is directed into screen and from there to oxygen delignification. The separation is modelled with a screen meant for solid-solid separation where the largest solid fraction is removed. The screened pulp is fed into oxygen delignification while the larger fraction is discarded.

Output from the delignification is fed into a flash separator to remove any vapor fraction before washing as high enough vapor fraction will cause error messages in the solid washers. Pulp from oxygen delignification is washed similarly to brownstock with six washers forming a two-stage DD washer. There are two washers in parallel which are configured to be identical in terms of pulp and water flows. Condensate from the black liquor evaporators is used as a washing liquid and the used water is used for brownstock washing. Washed pulp from the DD washers is combined into a single stream and fed into the first bleaching stage.

### 6.1.1 Bleaching and delignification

After cooking the pulp has residual lignin concentration of approximately 4.6%. Most of the remaining lignin removed in oxygen delignification before bleaching. The bleaching sequence is chlorine dioxide delignification, extraction and chlorine dioxide bleaching or

$D_0$-$E_{OP}$-$D_1$ with washing conducted between each stage (Figure 4). The delignification and bleaching stages are represented with yield reactors coupled with the Fortran-based calculator similarly to digester. Wash water recycling is represented similarly to a real plant with by recycling filtrates from downstream washers upstream. Water for oxygen delignification washer is recovered from black liquor evaporation and reused for brown stock washing. In the bleaching stages fresh water is used in $D_1$ and partially for $E_{OP}$ stage washer and reused in upstream washers and discarded after $D_0$ stage washer.

Oxygen delignification utilizes oxidized white liquor as the source of alkali and additional oxygen to reach desired oxygen levels. The reactor is fed with pure oxygen and oxidized white liquor from white liquor oxidizer which are combined into one feed stream. The lignin removal is set to 66% to achieve a lignin concentration of 1.5% (kappa number 10) similarly to Kymi mill. Carbohydrate degradation is not modelled as it is assumed to be minimal. Before washing the output from the reactor is fed into flash separator to separate vapor fraction, as Aspen Plus solid washers are not meant for stream containing significant vapor fractions. Washing is conducted using two parallel two-stage DD washers.

The $D_0$ stage receives delignified pulp from oxygen delignification and pure chlorine dioxide. Pulp from oxygen delignification (stream S110) and chlorine dioxide (stream D0CHEM) are combined and fed into the D0 reactor (Figure 4). Undissolved lignin removal of 50% with the resulting pulp has lignin content of 0.8% (kappa number 5). In the reactor the chlorine dioxide is turned into chlorate ($ClO_3^-$) and chlorous acid ($HClO_2$). Output from the $D_0$ is washed with six solid washers forming a two-stage DD washer similarly to brown stock washing.

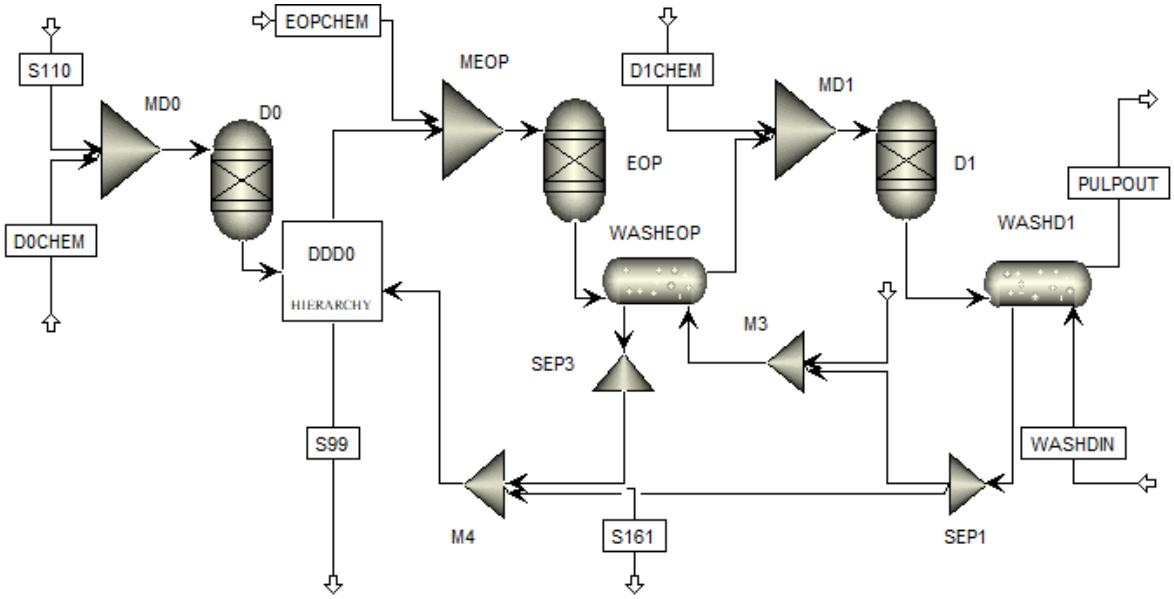


*Figure 4. Bleaching stages $D_0$, $E_{OP}$ and $D_1$ and their washers in the Aspen Plus model.*

In extraction stage sodium bisulfite is used as an alkaline source with hydrogen peroxide ($H_2O_2$) and oxygen ($O_2$) added for better lignin removal. The bleaching chemical stream (EOPCHEM) and pulp from the $D_0$ stage washer (DDD0) are combined before the reactor (Figure 5) Similarly to the $D_0$ stage 50% of the lignin is dissolved resulting in a lignin concentration of 0.4% (kappa number 2.5). Pulp from $E_{OP}$ is washed with single solid washer.

The second chlorine dioxide stage is set up similarly to $D_0$ with chlorate and chlorous acid degradation products. The chlorine dioxide stream (D1CHEM) and washed pulp from the $E_{OP}$ stage are fed into $D_1$ bleaching stage. In the $D_1$ stage 50% of the lignin is dissolved resulting in 0.2% lignin content (kappa number 1.3). Washer is modelled with single solid stage washer with a clean water input.

The washing in bleaching is conducted by recycling used water from downstream washers upstream. Pure water stream (WASHD1IN) with a flow rate of 14 $m^3$/ BDt is fed into stage $D_1$ washer (WASHD1). The dirty water from the washer is split with separator between $D_0$ washer (DDD0) and $E_{OP}$ stage washers (WASHEOP). Clean water is added to the dirty water used for $E_{OP}$ stage washer to maintain 14 $m^3$/BDt water flow. Part of the used water from the $E_{OP}$ washers is reused for $D_0$ stage washer and the rest is discarded with stream S161. Stream S99 contains the dirty water from $D_1$ stage washer which is removed from the process.

## 6.2 Chemical recovery

The recovery and regeneration of the pulping chemicals from black liquor is represented in this section. The model contains black liquor evaporation, tall oil recovery, recovery boiler, causticization, lime cycle and white liquor oxidation. The main objective of the chemical recovery is to maintain sodium and sulfur circulation through the mill.

### 6.2.1 Black liquor evaporation and tall oil recovery

The black liquor evaporation is modelled by series of flash separators coupled with heat exchangers. This approach allows progressive concentration of black liquor and enables modelling of heat recovery from the vapor streams. After heat recovery the produced vapors are fully condensed and stripped for recovering any volatile compounds.

The evaporation system consists of seven effects with total of eleven evaporators corresponding to the configuration at UPM Kymi. The first effect contains four evaporators in series (1A-1D) while the second effect contains two evaporators (2 and 2B). The remaining effects contain one evaporator each. Evaporators are numbered according to their position in the system with lower numbers located closer to the recovery boiler.

Each evaporator is defined by two operational conditions which are the flash separator temperature and the condensation level in the connected heat exchanger. Operational temperatures are specified for every evaporator, while the heat exchangers have condensation fraction of 80%. Evaporators 1A-1C require both temperature and pressure to be specified as they receive external steam inputs. The operational temperatures are from UPM Kymi while the pressures are defined to produce desired solid concentrations. These values are shown in appendix 2. Effect 1A is connected to the medium-pressure steam due to the higher operating temperature while evaporators 1B-1D are connected to the low-pressure steam. Heat recovered from the first effect is utilized in the second effect and upstream until the seventh effect.

Weak black liquor from the brownstock washer with solid concentration approximately at 17% enters the enters evaporation after tall oil soap extraction (Figure 5). A separator removes 90% of the extractives and 10% of the black liquor. The recovered extractives are

acidulated with sulfuric acid ($H_2SO_4$) in a stoichiometric reactor to simulate tall oil production. The acid also neutralized alkali compounds and organic salts in the black liquor. Part of the organic sodium salts are converted into formic and acetic acids while sodium hydroxide and sodium carbonate are converted into sodium sulfate. The acidified black liquor is separated from the extracts and is returned into the evaporation system. The evaporation concentrates the black liquor dry solid concentration from 17% to 78% before firing at recovery boiler.

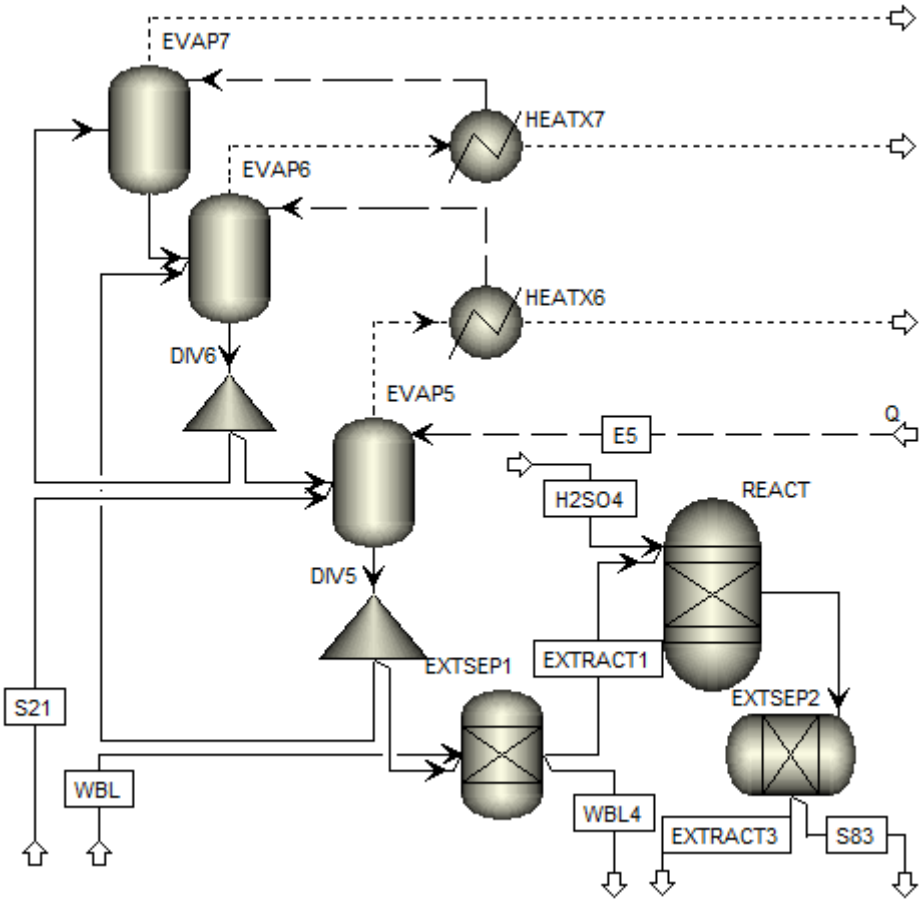


*Figure 5. Effects 5, 6 and 7 with tall oil and heat recoveries in the Aspen Plus model.*

The concentrated black liquor stream from evaporator four is split between evaporators 5 and 3 with stream S21 being directed to evaporator five (Figure 6). Part of the black liquor is similarly partially flown upstream from evaporator 5 to 6 and then from 6 to 7 (Figure 5). Captured heat from vapor of evaporator 4, shown with heat stream E5, is used for evaporator 5. For the second effect there are two evaporators instead of one (Figure 6). Captured heat

from the first (stream E21) is split evenly between evaporators 2 and 2B. Vapors from these evaporators is used for heating evaporator 3. Output from evaporator 2 goes into the first effect.

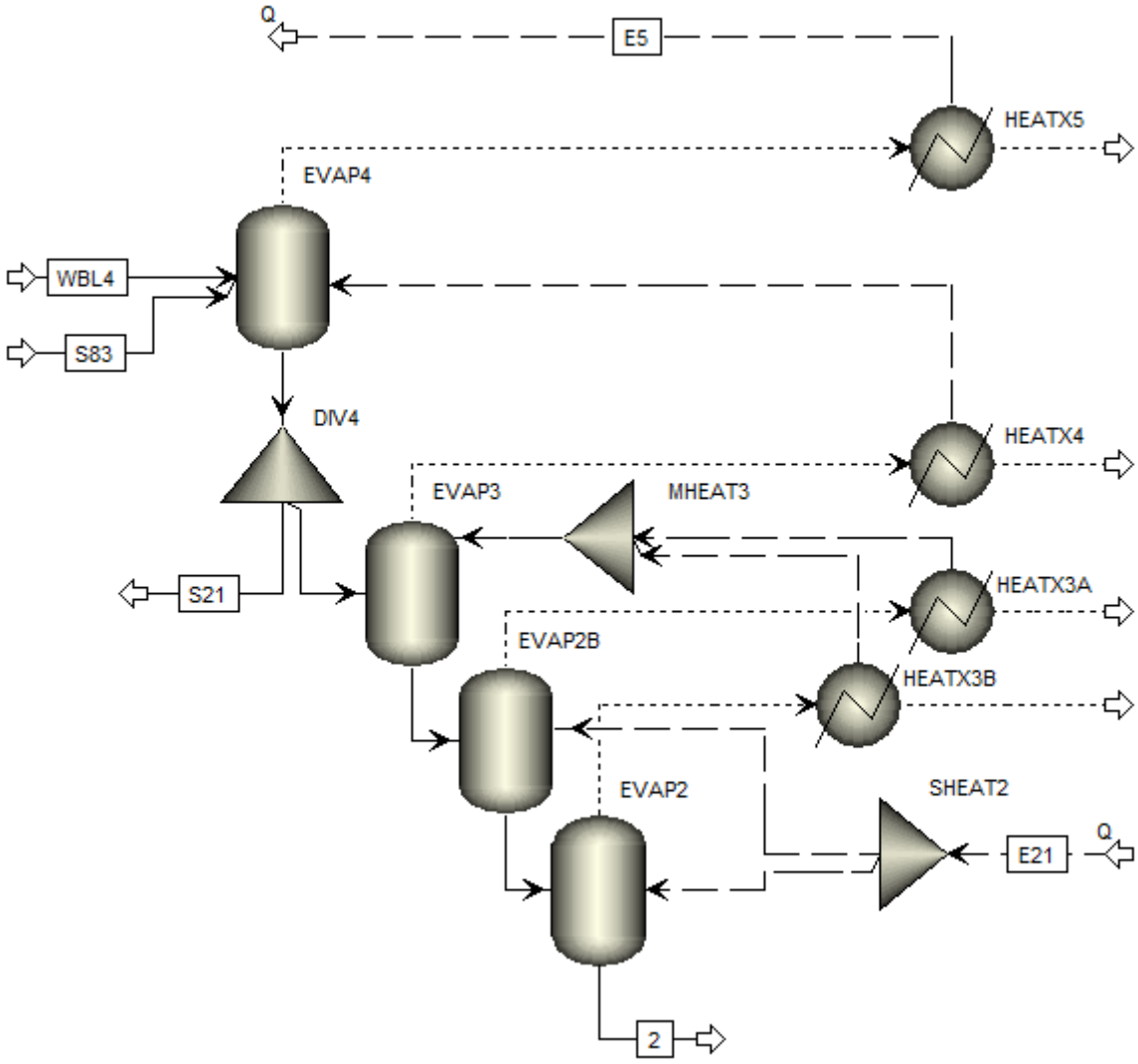


*Figure 6. Evaporators 2, 2B, 3 and 4 and heat recoveries from effects 2, 3 and 4 in the Aspen Plus model.*

The evaporators in first effect are connected to modified Aspen Plus steam utilities, but these connections are not shown (Figure 7). Evaporator 1A is connected to the medium pressure steam utility due to higher operational temperature which can't be achieved with low pressure steam. Evaporators 1B, 1C and 1D are connected to low pressure steam utility with 1D also receiving thermal energy from evaporate of 1A. Heat from the evaporators 1B, 1C and 1D vapors are recovered and used for heating up the evaporators 2 and 2B.

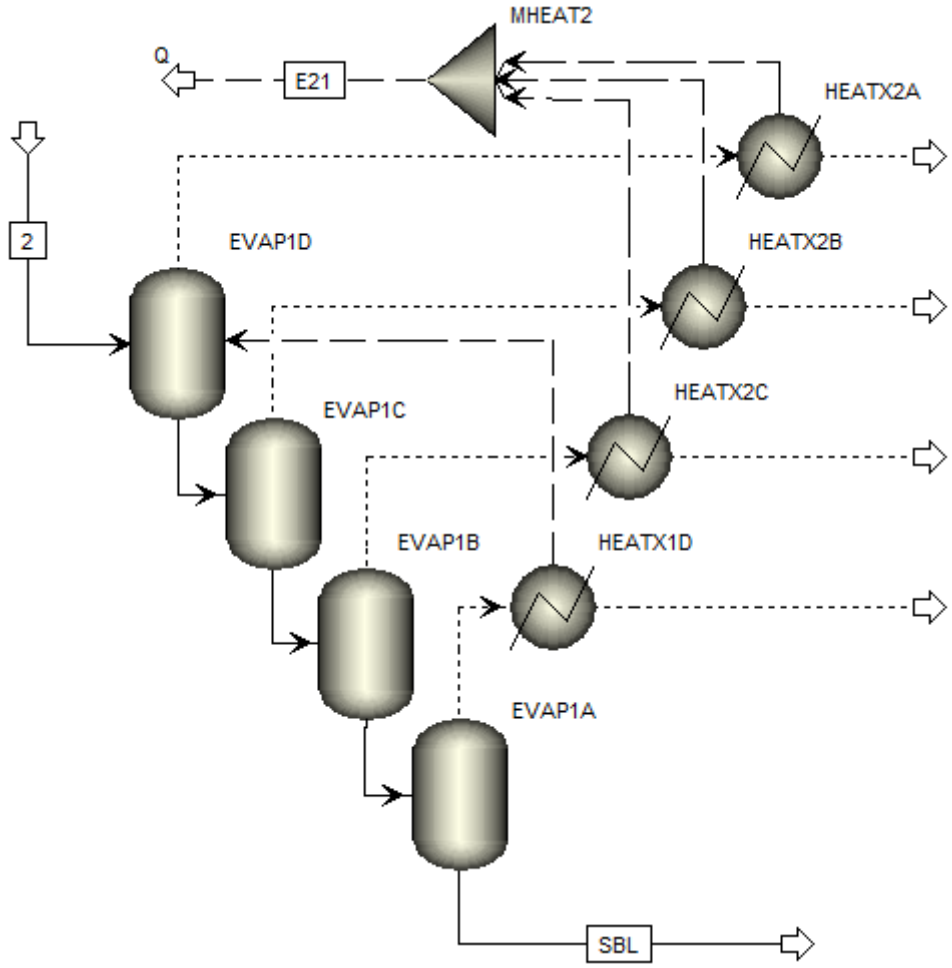


*Figure 7. Evaporators 1A, 1B, 1C and 1D and heat recoveries from effect 1 in the Aspen Plus model.*

### 6.2.2 NCG capture and methanol recovery

The separation of volatile compounds is simplified compared to an industrial system. Methanol, terpenes and non-condensable gases (NCGs) are recovered from condensates and gasses. In the model gases generated during digester blow out are separated from the brownstock and partially condensed to remove excess water condensable factions from NCGs and terpenes. The resulting dirty condensate is combined with condensate from black liquor evaporation and treated in two-stage stripping system.

The stripping system consists of two stripper columns with separately modelled evaporate condensers. The separated condenser allows better control over condensation and vapor

fraction than the ones integrated into the columns. Low pressure steam is used as heat source for stripping.

In the first stripper excess water is separated from the volatile compounds. Part of the condensate from the stripper is reused for brownstock, lime mud and dreg washing while the remaining fraction is removed from the process. The vapors from the first stripper are cooled down and fed into to the second stripper column where methanol and NCGs are separated from water and terpenes. The condensate from the second stripper contains mostly water and terpenes which are separated using a decanter. The vapor fraction from the stripper contains NCGs and methanol which are partially separated.

The recovered NCGs and terpenes are combusted in a dedicated burner to capture the potential sulfur emissions. The burner is modelled similarly to the recovery and bark boilers with stoichiometric reactors. During combustion sulfur containing compounds form sulfur dioxide ($SO_2$). The resulting sulfur dioxide is captured with sodium hydroxide which results in the formation of sodium bisulfite ($NaHSO_3$).

### 6.2.3 Recovery boiler and heat recovery

The strong black liquor from evaporation is mixed with recovery boiler fly ash which increases the solid concentration from 78% to 82% before feeding it to recovery boiler. The recovery boiler is modelled with stoichiometric reactor similarly to bark fuel boiler. In addition to the automatically generated combustion reactions for organic materials there are manually defined reactions for inorganic components. These reactions are based on Bajpai (2018, 146–149) and Paleologou et al. (1999). The extent of these reactions is controlled to reproduce the correct green liquor and causticized white liquor compositions.

Strong black liquor stream SBL from evaporation and fly ash from heat exchanger AIRHEAT are pressurized to 5 bars by pump (Figure 8). The black liquor from the pump and preheated air stream AIRB1 are directed into the recovery boiler. The output from the recovery boiler is divided into gaseous and non-gaseous components. As the focus of the model is not on the kraft mill energy balance, the flue gas stream from the recovery boiler is simply cooled down to reduce the heat accumulation.

The non-gaseous stream is directed into component separator to remove the fly ash stream from the smelt. The separator removes 95% of sodium sulfate and 11% sodium carbonate which gives the fly ash sodium sulfate and sodium carbonate composition of 88:12. Most of the fly ash is directed into the flue gas stream to be reintroduced into the strong black liquor feed. Around 5 kg/ADt of ash is removed from the mill. Remaining smelt from the separator is directed to smelt dissolving by stream SMELT.

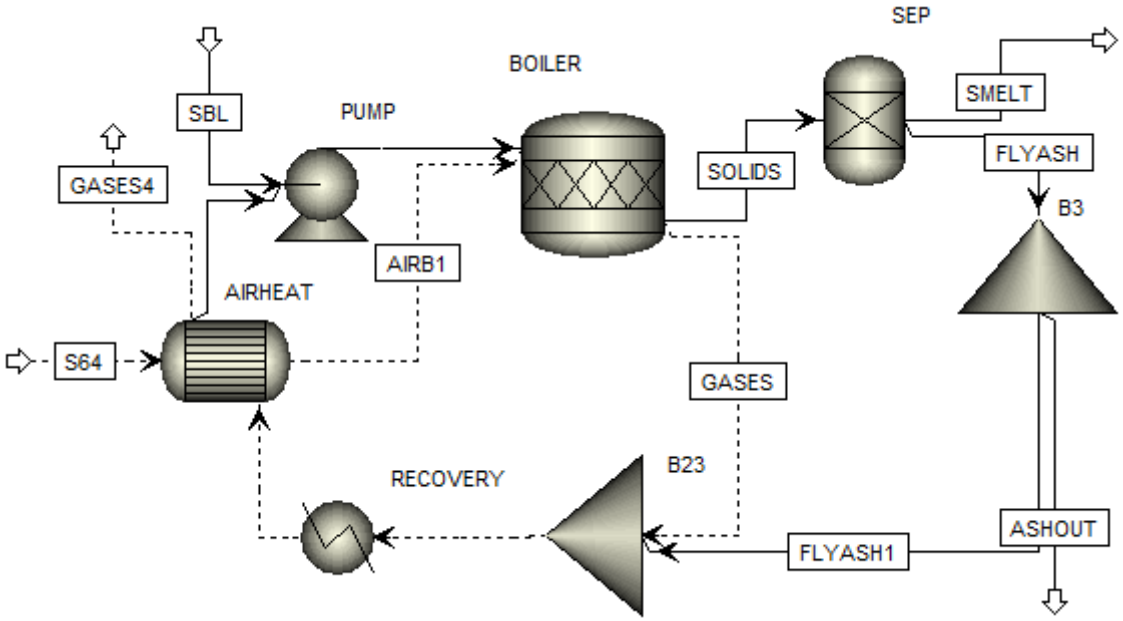


*Figure 8. Recovery boiler system in the Aspen Plus model.*

Smelt from the recovery boiler is dissolved into water used for dreg and lime mud washing (Figure 9). Undissolved solids are removed using Aspen Plus solid filter and the retentate is washed to recover remaining pulping chemical with solid washer. The water for the washer is recycled condensate from black liquor evaporation which is reused in smelt dissolving.

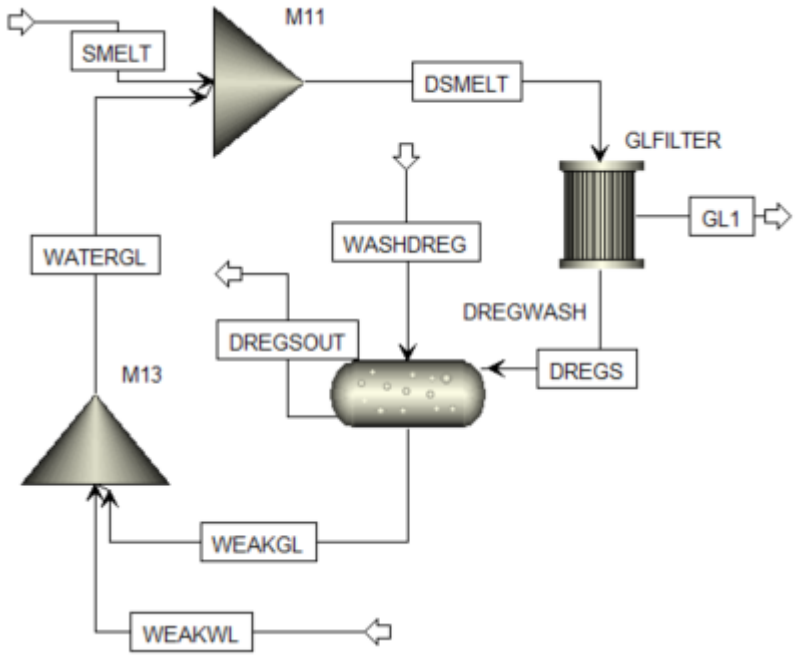


*Figure 9. Smelt dissolving, green liquor clarification and dreg washing in the Aspen Plus model.*

### 6.2.4 Causticization

Green liquor from the clarification stage (stream GL1) is combined with calcium oxide from lime cycle in the slaker (Figure 10). The slaker has two calcium oxide streams, LIMEIN1 represents regenerated calcium oxide from the lime kiln while LIMEIN represents fresh calcium oxide added to compensate for the losses in the lime cycle. In the slaker calcium oxide reacts with water to form calcium hydroxide ($Ca(OH)_2$).

The output from the slaker is fed into causticizer where sodium carbonate ($Na_2CO_3$) reacts with the calcium hydroxide to form sodium hydroxide. The causticization reaction is limited to 85% conversion of sodium carbonate. The conversion is calibrated to achieve same sodium carbonate concentration in white liquor as in the mill.

The resulting mixture of white liquor and lime mud is clarified using an Aspen Plus solid filter. The separation efficiency is set to 99% with lime mud represented as the solid retentate and white liquor as the liquid permeate. The lime mud stream (LIMEMUD) is directed to the lime mud washing and regeneration while the white liquor stream (S39) is sent for digester and white liquor oxidation.

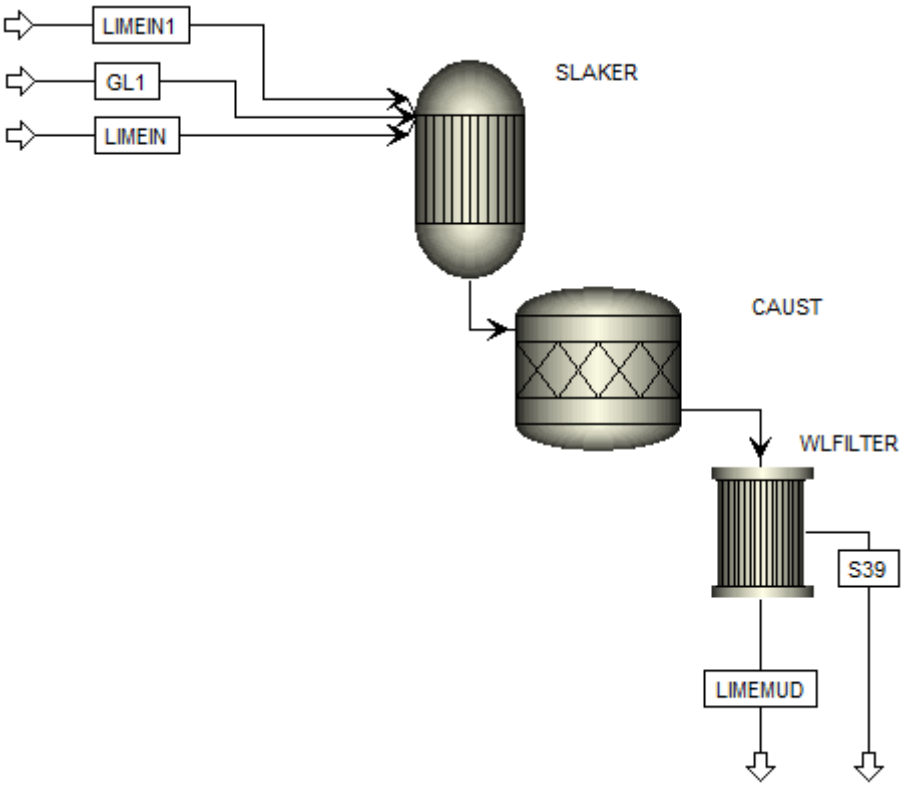


*Figure 10. Slaker, causticizer and filter for white liquor regeneration in the Aspen Plus model.*

### 6.2.5 Lime cycle

After causticization the lime mud is washed, dried and regenerated in the lime kiln (Figure 11). Lime mud washing is represented with a single solid washer which is also used for pulp washing stages. The lime mud stream (LIMEMUD) from the white liquor clarification is washed with condensate from the foul condensate stripper (COND). Excess water from the lime mud is removed with solid filter (LMFILTER). The moisture content of the washed lime mud is set to 75% which is reduced to 20% after filtration. Liquid streams from the washer and filter (WL1 and WL2) are recycled into smelt dissolving stage.

The filtered lime mud is dried in a flash separator (LMDRYER) before entering the lime kiln. The dryer uses heat recovered from the lime kiln flue gases as its heat source. This is represented by heat stream S28.

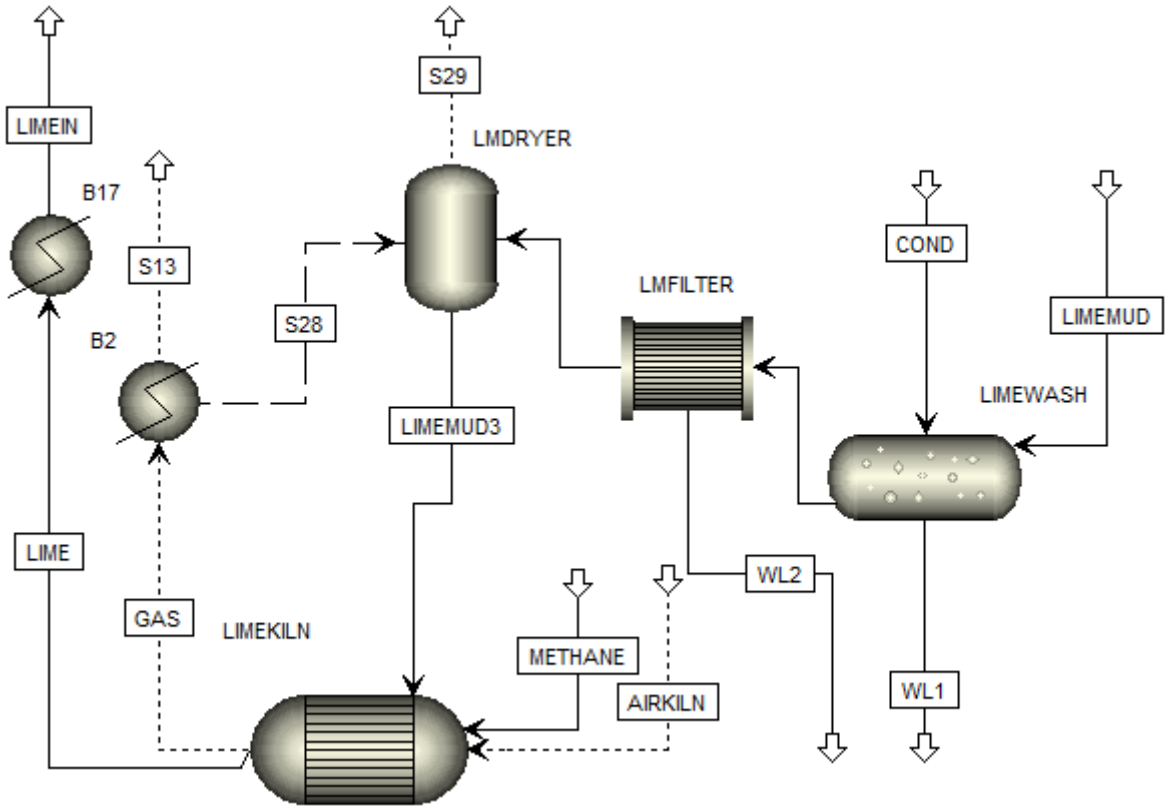


*Figure 11. Lime mud washing, drying and firing in the Aspen Plus model.*

Dried lime mud from the dryer is fed into the lime kiln where calcium carbonate is converted into calcium oxide. Methane is used as fuel for the kiln with combustion reactions automatically performed by Aspen Plus. The calcination reaction is modelled with full conversion of calcium carbonate into calcium oxide. The kiln outlet is divided into solid and gas streams with heat recovered from both streams using heat exchangers.

### 6.2.1 White liquor oxidation

Part of the regenerated white liquor is oxidized and used as an alkali source for oxygen delignification. Pure oxygen is used for the oxidation of the reactive sulfur compounds in white liquor into less reactive sodium sulfate. In the model sodium sulfide is oxidized into sodium sulfate through two sequential reactions.

The first oxidation reaction produces sodium thiosulfate and sodium hydroxide. The reaction is limited to 90% sodium sulfide conversion. The second reaction converts the sodium thiosulfate into sodium sulfate with 95% conversion. The conversion rates represent the extent of the oxidation reactions observed at the mill.

# 7 Results

This section summarizes the outcomes from kraft mill Aspen Plus model. The main parameters from the model will be compared to factory and literature values.

## 7.1 Fiberline organic balance

The conversion of raw wood into pulp is at the core of every pulp mill. Typically, in a mill yield from the digester feed is relatively well known whereas yield from raw wood is not tracked with same precision. Therefore, yield comparison in this section will have to rely on literature on both factory and literature values. The organics tracked through the model fiberline are wood, bark, chips and undissolved cellulose, hemicellulose and lignin.

Target yields for the model based on digester chip feed are 46% after cooking and 44% after bleaching. In the model screened pulp yield is achieved at 45.6% and bleached 43.6%, presented in Table 11, which are close to the target values suggesting that cooking and bleaching reactions are reasonably calibrated. Majority of organic losses occur during pulping where most of the lignin and hemicellulose get dissolved. Subsequent bleaching stages remove mostly residual lignin and therefore have relatively small effect on the pulp mass.

*Table 11. Fiberline organic yield from raw wood and digester feed in the Aspen Plus simulation.*

| | Organics, [BDt/h] | Yield from gate, [%] | Yield from chips, [%] |
|---|---|---|---|
| Input | 71.8 | 100 | 126 |
| Debarked | 58.6 | 82 | 103 |
| Screened chips | 56.8 | 79 | 100 |
| Washed brownstock | 26.2 | 36.5 | 46.1 |
| Screened pulp | 25.9 | 36.1 | 45.6 |
| After O | 25.1 | 35.0 | 44.2 |
| After D0 | 24.9 | 34.7 | 43.8 |
| After EOP | 24.8 | 34.5 | 43.6 |
| After D1 | 24.8 | 34.5 | 43.6 |

The pulp composition changes significantly throughout the fiberline, especially oxygen delignification as shown in Table 12. Cellulose content essentially remains constant at 21.84 BDt/h as the cellulose degradation is assumed to be negligible. Same is true for hemicellulose at 2.88 BDt/h. In contrast lignin content decreases throughout the fiberline from 1.19 BDt/h to only 0.02 BDt/h in the final pulp. As the lignin content decreases from 4.6% to 0.1% the cellulose content increases from 84.3% to 88.3%. Hemicellulose content remains relatively constant between 11–12% through the fiberline.

*Table 12. Pulp composition throughout the fiberline in the Aspen Plus simulation.*

| | Washed brownstock | Screened pulp | After O | After D0 | After EOP | After D1 |
|---|---|---|---|---|---|---|
| Stream | WASHPULP | DEKNOT | PREBLEAC | S8 | S15 | FINALOUT |
| Cellulose, [BDt/h] | 22.06 | 21.84 | 21.84 | 21.84 | 21.84 | 21.84 |
| Hemicellulose, [BDt/h] | 2.91 | 2.88 | 2.88 | 2.88 | 2.88 | 2.88 |
| Lignin, [BDt/h] | 1.21 | 1.19 | 0.39 | 0.19 | 0.05 | 0.02 |
| Cellulose | 84.3% | 84.3% | 87.0% | 87.7% | 88.2% | 88.3% |
| Hemicellulose | 11.1% | 11.1% | 11.5% | 11.5% | 11.6% | 11.6% |
| Lignin | 4.6% | 4.6% | 1.5% | 0.8% | 0.2% | 0.1% |

## 7.2 Liquor composition

As the model includes liquor causticization and recycling the liquor composition reflects how the model is calibrated. Concentrations of sodium hydroxide, sodium sulfide and sodium carbonate are known in parts of the liquor cycle and are used to determine amount of other sodium and sulfur compounds. The largest changes in sodium and sulfur compositions occur in the digester, recovery boiler and causticization stages.

White liquor feed to the digester has active alkali concentration of 125 g/l and sulfidity is at 42% (Table 13). In digester sodium hydroxide and sodium sulfide are converted into other chemicals, reducing active alkali to 4 g/l. The amount of sodium sulfide is reduced less resulting in 80% sulfidity. One of the pulping by-products is sodium sulfate which results in lowering of reduction from 93% at white liquor to 34% in black liquor. The reduction is further lowered to 30% when sulfur is added to the process during tall oil recovery from black liquor.

In the recovery, boiler sodium and sulfur compounds primarily are reduced into sodium sulfide and sodium carbonate. The resulting green liquor has low causticity of just 6% but the sulfidity and reduction are each over 90%. Causticity increases to 85% when bulk of the sodium carbonate is causticized into sodium hydroxide.

*Table 13. Liquor values in the Aspen Plus simulation.*

| | White liquor | Weak black liquor | Strong black liquor | Green liquor | Causticized white liquor |
|---|---|---|---|---|---|
| Stream name | WL | WBL | SBL | GL | REWL |
| EA, [g/l] | 99.2 | 2.5 | 48.3 | 27.7 | 86.5 |
| AA, [g/l] | 125.4 | 4.1 | 80.5 | 50.9 | 110.0 |
| S | 42% | 80% | 80% | 91% | 43% |
| Reduction | 93% | 34% | 31% | 93% | 93% |
| Causticity | 85% | 13% | 13% | 6% | 85% |

Composition of black liquor typically varies between mills and different raw materials. The relative amount of different organic components from wood and chemical load affects the black liquor composition. Black liquor composition from the model is compared to black liquor component and elemental compositions from literature. Component compositions tell how well the wood composition is modelled after digester as well as the inorganic composition. Elemental analysis on the other hand gives a better understanding of how well the atom balance of bio chemicals is modelled and better comparison for sodium, sulfur and NPE concentrations. Black liquor composition from the Aspen Plus model is compared to black liquors compositions from Niemelä & Alén (1999, 196; 222) and (Sixta 2006, 969).

The organic components considered for comparison are grouped into lignin, organic acids, extractives and other organics (Table 14). The amount of organic acids is determined from the organic sodium salts while the other organics category includes dissolved saccharides. Organic fraction in the modelled black liquor is within 0.2% of the comparison data which shows that the organic to inorganic ratio is well presented in the model. The largest difference between the model and literature is with organic acids and other organic components. The organic acid fraction in model is 2.5% lower compared to data from Niemelä & Alén (1999, 196) while other organics fraction is 1.6% higher. This is likely caused by the simplified presentation of dissolved organic fractions as multiple organic acids are presented by formic and acetic acids. There is also noticeable difference with lignin

concentration which is 1.6% higher in the model which could be due to varying lignin concentration in wood, model calibration or improved lignin removal before bleaching.

The inorganics are only separated into organically bound sodium and inorganics. The total inorganics fraction in the black liquor is only 0.2% lower than in the comparison data. However, the composition of the total inorganics fraction varies between them. The organically bound sodium concentration is 1.1% higher in the model even though the organic acids fraction and therefore the organic salts fraction is lower. This is likely caused by the simplification made to organic salts representation in the model as the chosen organic salts have relatively low molar masses. The inorganic fraction is 1.3% lower likely due to higher amount of organically bound sodium.

*Table 14. Black liquor dry solids composition in the Aspen Plus simulation and Niemelä & Alén (1999, 196).*

| | Weak black liquor dry solids in Aspen Plus simulation | Pine black liquor (Niemelä & Alén 1999, 196) | Difference |
|---|---|---|---|
| **Organics**, [%] | **67.2** | **67** | **0.2** |
| Lignin, [%] | 32.6 | 31 | 1.6 |
| Organic acids, [%] | 26.5 | 29 | -2.5 |
| Extractives, [%] | 3.7 | 4 | -0.3 |
| Other organics, [%] | 4.6 | 3 | 1.6 |
| **Total inorganics**, [%] | **32.8** | **33** | **-0.2** |
| Inorganics, [%] | 20.7 | 22 | -1.3 |
| Organically bound Na, [%] | 12.1 | 11 | 1.1 |

The elemental composition of the black liquor shows how well the organic compounds are represented in Aspen Plus but also how well elements such as sodium and sulfur are balanced. Carbon, hydrogen and oxygen balances in the modelled black liquor are close to the ranges found in literature varying less than 0.3% (Table 15). Ther model has a carbon concentration of 38.1% which is close to the high end in Sixta (2006, 969) and Niemelä & Alén (1999, 222) at 38%. The hydrogen concentration is higher in the model at 4.5% while in the literature references the highest concentration is 4.2%. The oxygen concentration is on the low end at 33.0% while the comparison data ranges from 33.1% to 33.6%. This suggests that the elemental composition of the chosen organic components in Aspen Plus matches well with current understanding.

*Table 15. Black liquor dry solids elemental composition in the Aspen Plus simulation, Sixta (2006, 969) and Niemelä & Alén (1999, 222).*

| | Weak black liquor in Aspen Plus simulation | Strong black liquor in Aspen Plus simulation | Softwood black liquor composition (Sixta 2006, 969) | Pine black liquor composition (Niemelä & Alén 1999, 222) |
|---|---|---|---|---|
| C, [%] | 38.1 | 36.8 | 35.8–38.0 | 38 |
| H, [%] | 4.5 | 4.4 | 3.5–4.2 | 3.6 |
| O, [%] | 33.0 | 32.7 | 33.6 | 33.1 |
| Na, [%] | 19.4 | 20.1 | 17.9–19.9 | 19.1 |
| S, [%] | 5.4 | 5.8 | 3.7–4.8 | 4.8 |
| K, [%] | 0.03 | 0.03 | 0.6–1.8 | 0.9 |
| Cl, [%] | 0.1 | 0.1 | 0.2–2.9 | 0.2 |

The elemental analysis also gives better understanding of the inorganic composition in black liquor. The sodium content in the model is 19.4% which is in the range of 17.9–20.1% found in the literature. Sulfur on the other hand has higher concentrations in the model at 5.4% compared to the highest concentration in literature at 4.8%. Potassium and chlorine concentration are much lower in the model than in the literature sources. The chlorine content of 0.1% in the model is just half of the lowest concentration 0.2% found in the reference data. The potassium concentration in the model is only 0.03% while the concentration in the literature is over 0.6%.

The black liquor composition in the model is comparable to the literature values. The compared component fractions differ less than 3%pt from the literature data indicating that pulping and liquor chemistry are well presented. In the elemental analysis only sulfur, chlorine and potassium had large deviations in concentration. The increased sulfur content could be explained by higher sulfidity or higher concentration of sodium sulfite or sodium thiosulfate. The low chlorine and potassium concentrations indicate that their input streams are underestimated or that the losses through dreg removal are over-estimated. These discrepancies can also be partially explained by the age of the reference data as mills and their operational parameters have changed in the last twenty years.

## 7.3 Sodium and sulfur balance

Sodium and sulfur make up the pulping chemicals in the white liquor and recycled in the mill. This makes identifying the input and output flows essential for maintaining desired chemical balance. The input and output flows of sodium and sulfur from the Aspen Plus model are compared to reference values from UPM.

In the model sodium and sulfur are lost with dregs, flyash, bisulfite and as wash losses. The largest sodium and sulfur losses occur through fly ash removal, bisulfite streams and wash losses (Table 16). The same is true with the UPM reference values but the amounts are slightly different. In the model, fly ash removal is fixed to match the reference values so in both 1.1 kg/ADt of sulfur and 1.8 kg/ADt of sodium is removed. Washing losses are determined by the Aspen Plus from the given parameters and results in higher sulfur losses at 0.9 kg/ADt but identical sodium losses of 3.2 kg/ADt. This discrepancy could be caused by lack of organically bound sulfur in the model as the sulfur concentration is higher in the black liquor values (Table 15). In the bisulfite flows both sodium and sulfur flows are smaller compared to the reference data suggesting that the sulfite emissions are modelled conservatively or are not captured effectively. The model has bisulfite sulfur and sodium flows of 1.5 kg/ADt and 1.0 AD/t when they should be closer to 2.5 kg/ADt and 1.8 kg/ADt.

Sulfur and sodium are also lost in smaller quantities with dregs and tall oil recovery. In the model dregs contain more sulfur and sodium than the reference. The sodium content is around ten times as high as at 0.8 kg/ADt while the sulfur content is over two times as high at 0.2 kg/ADt. Currently the model does not include any sulfur or sodium losses with tall oil production while in the mill they are around 0.2 kg/ADt and 0.0006 kg/ADt.

*Table 16. Sodium and sulfur outputs by type from mill.*

| Output | Dregs | Tall oil | Flyash removed | Bisulphite | Wash losses |
|---|---|---|---|---|---|
| UPM | | | | | |
| S, [kg/Adt] | 0.08 | 0.2 | 1.1 | 2.5 | 0.7 |
| Na, [kg/Adt] | 0.07 | 0.0006 | 1.8 | 1.8 | 3.2 |
| Aspen Plus simulation | | | | | |
| S, [kg/Adt] | 0.2 | 0.0 | 1.1 | 1.5 | 0.9 |
| Na, [kg/Adt] | 0.8 | 0.0 | 1.8 | 1.0 | 3.2 |

In the Aspen Plus model there are only three input streams for sodium and sulfur compounds. These are flue gas scrubbers of NCG burner, tall oil production and make-up chemicals for white liquor (Table 17). In a real kraft mill there are more input of pulping chemicals which are not included in the model which partially explains the higher inputs. The only sulfur input in the model is tall oil production and has a sulfur feed of 3.7 kg/ADt while value from UPM is only 2.9 kg/ADt but when accounting for rest of the sulfur feeds UPM sulfur input is closer to the model at 3.6 kg/ADt. Sodium is added to the model to the NCG burner flue gas scrubber and as make-up chemical. Only 1.0 kg/ADt of sodium is added to the flue gas scrubber in the model compared to 1.8 kg/ADt as the NCG emissions are much lower in the model. Make-up flow on the other hand is much higher at 6.4 kg/ADt while in the comparison data only 0.1 kg/ADt of sodium is added.

*Table 17. Sodium and sulfur inputs by type from mill.*

| Input | NCG scrubber | Tall oil | Make-up | Other |
|---|---|---|---|---|
| UPM | | | | |
| S, [kg/Adt] | 0.0 | 2.9 | 0.0 | 0.7 |
| Na, [kg/Adt] | 1.8 | 0.0 | 0.1 | 2.8 |
| Aspen Plus simulation | | | | |
| S, [kg/Adt] | 0.0 | 3.7 | 0.0 | 0.0 |
| Na, [kg/Adt] | 1.0 | 0.0 | 6.4 | 0.0 |

## 7.4 Atomic balance

As the model contains multiple yield reactors which are not in perfect atomic balance, one of the tracked parameters is models' overall atom balance. All the atoms in the model except argon and nitrogen which do not take part in any reactions are tracked. Total input and output flows from the entire model are shown by their elemental composition (Table 18).

From the table 18 we can see that carbon, hydrogen and oxygen have the largest changes between inputs and outputs. Carbon and hydrogen are lost at rates of 22 and 23 kg/ADt while 46 kg/ADt of oxygen is produced in the model with the relative differences under 2%. These

elements also have the largest flows in the model as they are present in both organic and inorganic compounds. Oxygen has especially high flow rate as it is the primary element in water.

The metals, sulfur and chlorine in the model have much lower flows and therefore smaller difference between input and output. From these magnesium and potassium are the only ones with no input flows in the model as these are only modelled as wood products and produced in the digester. Calcium and chlorine are also modelled similarly but also have input streams due to them being used for causticization and bleaching stages. Especially chlorine has high losses at 1.5 kg/ADt or 11.5% due to bleaching stages. Calcium has difference of 0.04 kg/ADt or 0.6% between input and output as most of the calcium reactions are modelled with stoichiometric reactors which maintain atom balances. Sodium balance is slightly positive with 0.06 kg/ADt more output which accounts for only 0.8% difference. Sulfur has similarly small difference with 0.03 kg/ADt lost or 0.8%.

*Table 18. Atomic mass balance of the Aspen Plus simulation.*

| | C | H | O | Na | S | Mg | Ca | K | Cl |
|---|---|---|---|---|---|---|---|---|---|
| Input, [kg/Adt] | 1363 | 3273 | 28729 | 6.76 | 3.71 | 0.00 | 7.79 | 0.00 | 13.13 |
| Output, [kg/Adt] | 1341 | 3250 | 28776 | 6.82 | 3.68 | 0.54 | 7.83 | 0.44 | 11.61 |
| Diff, [kg/Adt] | -22.09 | -23.34 | 46.09 | 0.06 | -0.03 | 0.54 | 0.04 | 0.44 | -1.51 |
| Diff, [%] | -1.6 | -0.7 | 0.2 | 0.8 | -0.8 | - | 0.6 | - | -11.5 |

In the digester elemental balance is much closer to ideal than comparing to entire model but has some differences (Table 19). If the outliers from magnesium and potassium flows are discarded most atom balances are within 1% between input and output. Other noticeable differences are with carbon and chlorine which are generated in digester while their balance on the model level is negative. Oxygen is also lost in digester while it is being produced when looking at the entire model.

*Table 19. Digester atom mass balance from the Aspen Plus simulation.*

| | C | H | O | Na | S | Mg | Ca | K | Cl |
|---|---|---|---|---|---|---|---|---|---|
| Input, [kg/Adt] | 1056 | 922 | 7240 | 326 | 92 | 0.03 | 4.08 | 0.05 | 1.42 |
| Output, [kg/Adt] | 1063 | 920 | 7235 | 326 | 92 | 0.28 | 4.12 | 0.55 | 1.44 |
| Diff, [kg/Adt] | 7.07 | -2.24 | -5.32 | 0.01 | -0.31 | 0.25 | 0.04 | 0.50 | 0.02 |
| Diff, [%] | 0.67 | -0.24 | -0.07 | 0.00 | -0.34 | 824.38 | 1.07 | 983.64 | 1.25 |

The overall elemental balance of the model is close to ideal despite the use of yield reactors. Relative differences are under 2% except for magnesium, potassium and chlorine. Out of these magnesium and potassium are not modelled in input flows but produced during pulping. Chlorine, on the other hand, has input flows in bleaching but has relatively high losses due to yield reactors.

# 8 Discussion

The results from the model show similar results with reference data from literature and UPM. Fiberline yields, black liquor composition and elemental balances are generally within acceptable ranges. Although some deviations remain especially for chlorine, potassium and sodium make-up requirements, the overall results provide realistic representation of kraft mill operations.

## 8.1 Main findings

The pulp yield of the model matches with targeted values. Digester yield in the model is 45.6% with a target of 46% proving that the assumptions and data used for the wood composition and pulping reactions give desired results. The bleached pulp yield target was 44% or 2%pt decrease from the digester. The delignification and bleaching reaction were calculated based on reduction in lignin concentration and assumed minimal saccharide degradation. This resulted in yield reduction of 2%pt to 43.6% in the model. These results indicate that assumptions and methods used in the fiberline model produce realistic results.

The model and the literature sources have similar black liquor compositions. The ratio of inorganic and organic dry solids in black liquor is within 0.2%pt of the literature values. The organics components have larger deviations with literature data but remain under 3%pt. This suggests that the pulping calculations are not as well calibrated for all the organic component types. Inorganic compounds also have deviations from reference data with around 1%pt higher organically bound sodium concentration. However, the elemental analysis of the black liquor reveals that the model has similar carbon, hydrogen, oxygen and sodium composition with existing data. The sulfur concentration is higher in the model at 5.4% when in literature the highest is 4.5% which could explain the imbalance in inorganics. The model also contains less potassium and chlorine, likely due to higher dreg removal and lack of impurities in the feed water.

The sodium and sulfur balances show reasonable similarity to the reference data. The model has higher concentration of sodium and sulfur flows but with fewer streams. Most noticeably

the model lacks flue gas scrubbers which results in much higher make-up chemical demand. Despite this the overall sodium and sulfur balances are much closer to the reference data.

Elemental mass balance of the model shows small deviations in input and output flows. Most of the differences are within 1% but carbon and chlorine flows have larger deviations. In the model 1.6% of carbon is lost while for chlorine is lost at a rate of 11.5%.

## 8.2 Limitations

The comparison of results with data from literature and UPM indicates that the model represents the major processes in a kraft mill. Fiberline yield, liquor composition and sodium and sulfur balances are close to the reference values despite some deviations. This demonstrates that the model provides a suitable platform for pulp mill modelling and possibly even for evaluating process modifications. However, there are still some larger deviations with chlorine balance, sodium and sulfur inputs and NPEs concentrations.

The fiberline yields indicate that the model is close to the factory values but remains simplified compared to industrial mills. The model does not include all the processes that influence the pulp yield such as detailed screening system and reject recycling. Screening is currently conducted in a single stage whereas industrial mills have multiple screening stages. Industrial mills also have pulping systems for the large rejects which can increase the overall pulp yield. Therefore, the model may not fully capture pulp yield and fiber losses.

Representation of sodium and sulfur circulation is also simplified. Compared to industrial mills, the current model has fewer sodium and sulfur inputs requiring a higher concentration input concentration to maintain the chemical balance. This can affect the accuracy of the sodium and sulfur balances and may also lead to small inaccuracies in liquor compositions because the chemical inputs are concentrated in fewer locations within the model.

Another limitation of the model is the non-process elements. Concentrations of chlorine and potassium are significantly lower in the model than compared to ones reported in literature. This indicates that the input and output flows of these chemicals are not fully represented in the model. Currently the model does not contain impurities in the input water and has simplified dreg removal which can account for the inaccuracies.

The model also has small elemental imbalances due to the use of yield reactors in the fiberline. Pulping, oxygen delignification and bleaching stage reactions have complex reactions between inorganic and organic compounds which are difficult to represent with complete stoichiometries. Therefore, yield reactors are used for these stages. With proper calibration the elemental difference can be minimized as seen in digester atom balance. However, the use of yield reactors inherently limits the accuracy of elemental balance.

As the model relies on yield reactors it also uses Fortran based calculators. These improve the model's flexibility and allow for more complex unit operations which would be difficult to implement without them. At the same time, they are also not as transparent or documented compared to conventional approaches. This may increase complexity of the model and make it less flexible for modification.

## 8.3 Comparison to WinGEMS

The information about WinGEMS in this comparison is based on WinGEMS user manual. This comparison aims to highlight differences in these modelling tools but should not be considered definitive as WinGEMS was not available for this thesis nor do I have prior experience with the software.

WinGEMS is a modelling tool dedicated to the pulp and paper industry. It includes dedicated blocks designed for modelling digesters, black liquor evaporation and other processes commonly used in pulp and paper mills. This differs from Aspen Plus where the blocks are more general purpose. The difference is especially apparent with digester modelling. In WinGEMS digester calculates kappa, yield, chemical usage, and H-factor from initial parameters while in Aspen Plus the pulping reactions need to be defined manually. In case of this thesis the pulping reactions were determined in mass yield base calculations with yield reactor and included calculator. Similar differences can be found with modelling of evaporation and bleaching stages significantly increasing the development effort on Aspen Plus.

Aspen Plus also noticeably lacks parameters which are usually used in pulp and paper industry such as kappa, H-factor, pulp viscosity and brightness which can be found in

WinGEMS. Calculating or estimating these values from the results adds a level of complexity to the model.

WinGEMS provides much more focused modelling options compared to Aspen Plus. Based on this thesis the WinGEMS is better suited for conventional pulp mill mass and energy models which can be built relatively fast. Aspen Plus on the other hand provides more flexibility when the model requires processes outside of conventional pulp mill applications.

## 8.4 Future work

To improve sodium, sulfur and non-processes element (NPE) balances in the model any missing input and output streams should be added and calibrated. In the current model incoming water flows do not include salt impurities which are typically found in industrial process waters. The model also does not consider sodium and sulfur with incoming wood and has missing chemical streams such as flue gas scrubbers. Without these the model can maintain correct sodium and sulfur balances but some of the flows have higher chemical contents. On the other hand, current modelling of NPEs is currently based on limited literature. This means that the model severely lacks accuracy of NPE chemical compositions and amounts. Improving the accuracy of these inorganic components could allow better understanding of their accumulation in current pulp mills and in alternative configurations.

The fiberline is currently comparable to the reference values but lacks detail for bleaching reactions and screening reject handling. The existing bleaching reactions are not balanced stoichiometrically and are limited by the variety of degradation products. Especially chlorine dioxide degradation products are simplified to just chlorate and chlorous acid. Additional reaction products and more detailed bleaching chemistry could improve the elemental balances. Furthermore, the inclusion of knot pulping, multi-stage screening and reject recycling could allow for more accurate representation of fiber losses and pulp yield throughout the fiberline.

At this stage the model also lacks detailed representation of steam, electricity and heat production and usage. Extending the model to include energy generation and consumption would allow the model to be used for simultaneous mass and energy balances. This would be especially beneficial for process integration and optimization.

The current state of the model provides a solid foundation for further development which should focus on enhancing the chemical balances and fiberline operations. The model could also be improved with comprehensive energy systems adding more depth and potential use cases for the model.

# 9 Conclusions

The goal of the thesis was to study how well Aspen Plus can be utilized for modelling kraft pulping. Aspen Plus is general-purpose process modelling tool which is widely used in different fields and even for partial pulp mills and related processes. Despite this it has not been used for modelling pulp mill fiberlines or even digesters. Compared to modelling tools traditionally used for pulp and paper industry, Aspen Plus offers more flexibility and tools to model outside of the typical kraft mill processes.

The initial scope of the model was to model pulp mill mass balances within simplified kraft mill fiberline and chemical recovery. The modelled fiberline is composed of debarking, chipping, digester, washers, oxygen delignification and bleaching stages. The chemical recovery includes black liquor evaporation, recovery boiler, causticization, lime cycle, white liquor oxidation, tall oil recovery and methanol capture.

Despite the lack of modules for pulp mill modelling within the Aspen Plus the basic mass flow was able to be achieved with the simple modules. Fortran calculator had to be used to complement some of the processes as the stock Aspen Plus modules were not suitable for these tasks. Overall mass balance in the model matches closely with the reference data and the sodium and sulfur balances are close to the factory values. Some elements such as chlorine and NPEs like potassium have much larger deviations within the liquor when compared to the reference values. In short, the model accomplished modelling of the basic mass flow of the most important elements within fiberline and recycling of the pulping chemicals.

Despite the possibility of using Aspen Plus for pulp mill modelling in the current stage, it is more effective to use traditional pulp and paper industry modelling software. Currently Aspen Plus offers all the tools for pulp mill modelling but doesn’t include safety nets or guides for the user. This means that pulp mill modelling with Aspen Plus requires more time and effort compared to alternative tools.

The model still lacks information and detail in some areas. Including better energy recovery and usage could be implemented within the model to broaden the possible use cases and available information. Some of the mass balances in the mill could be improved, especially

the NPEs. The current salt composition of the NPEs is simplified and could be expanded as Aspen Plus includes modelling of ionic compounds.

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Appendix 1. Evaporator parameters

| Evaporator | Temperature, °C | Pressure, bar |
|---|---|---|
| 1A | 174 | 3,8 |
| 1B | 146 | 2,2 |
| 1C | 145 | 2 |
| 1D | 143 | - |
| 2 | 129 | - |
| 2B | 120 | - |
| 3 | 105 | - |
| 4 | 92 | - |
| 5 | 79 | - |
| 6 | 69 | - |
| 7 | 59 | - |