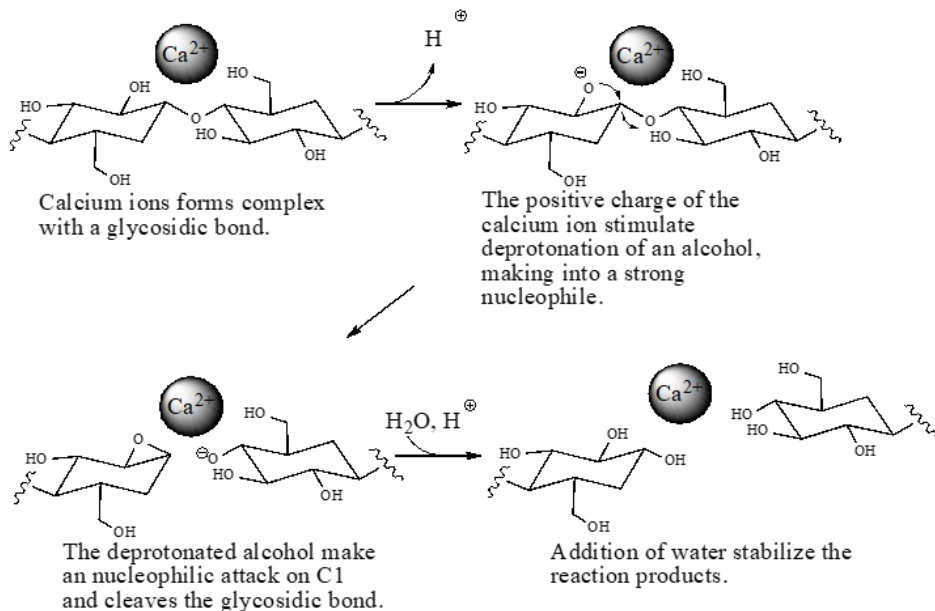


Licentiate Thesis in Fibre and Polymer Science

# On calcium-related problems in kraft pulping of *Eucalyptus dunnii*

VIJAYA LAKSHMI VEGUNTA



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Academic Dissertation which, with due permission of the KTH Royal Institute of Technology, is submitted for public defence for the Degree of Licentiate of Engineering on Friday the 17th February 2023, at 14:00 ECT in Tresearch conference room, Lindstedtsvägen 36, Stockholm.

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The quieter you become the more you hear.

*Buddha*



## Abstract

Kraft pulping is the most widely used pulping process for producing chemical pulp today. It has been in use for more than 130 years. During the pulping process most of the lignin and part of the hemicellulose are removed from the wood, resulting in an unbleached chemical pulp which is mainly composed of cellulose, some hemicellulose with smaller amounts of modified lignin. Several studies have been conducted to ensure effective delignification during the kraft cooking process. Nonetheless, due to the highly complex chemistry and anatomy of wood, there is a need to understand pulping chemistry in more detail.

The principal inorganic component in wood is calcium. A considerable share of the calcium in wood is released during the chemical pulping process. The calcium released initially during kraft pulping is mainly soluble in cooking liquor which passes through a thermodynamically stable limit before reacting with carbonate to form calcium carbonate. The calcium in the pulping process causes precipitation and scaling problems in the pulping process lines, especially in the black liquor evaporation sections.

The focus of this work is to increase the knowledge of kraft cooking of *Eucalyptus dunnii* which has high calcium content and cooking chemicals reactions during delignification. In addition, the aim was to investigate the influence of different calcium levels in *E. dunnii* wood chips on the kraft pulping process. Chips with different calcium levels were pulped in lab-scale digesters.

The results obtained in this work showed that the rate of delignification decreased and polysaccharide degradation increased during kraft pulping of *E. dunnii* when the calcium content was high. *E. dunnii* with low calcium content showed no adverse effect on the delignification rate and polysaccharide degradation during kraft pulping.

The uronic acid content in wood and the hexuronic acid content in pulp after kraft cooking showed no significant impact on the delignification rate. The detrimental effect of calcium during kraft pulping was studied using green liquor introduction in kraft pulping. Using green liquor during the kraft pulping of high calcium *E. dunnii* wood chips and extending the impregnation time resulted in good delignification and no degradation of polysaccharides. Unbleached pulps produced from high calcium content wood could be bleached with good results, i.e., equal brightness and increased strength properties. The drainage resistance of bleached pulp was slightly increased. The calcium present in the wood chips follows the fibre line with the pulp after kraft cooking and is less soluble in kraft black liquor. These phenomena are probably related to the carbonate present in green liquor "inactivating" the adverse effects of calcium ions. Possible scientific mechanisms and hypotheses are discussed in this work. Preliminary studies using industrial green liquor compared to synthetic green liquor on a lab scale are also discussed in this work.

**Keywords:** kraft pulping, delignification, polysaccharide degradation, viscosity, H-factor, kappa number, calcium content

## Sammanfattning:

Sulfatprocessen är idag den mest använda metoden för framställning av kemisk massa, och har varit i användning i mer än 130 år. Under denna process avlägsnas det mesta av ligninet och en del av hemicellulosa från veden, vilket producerar en oblekt kemisk massa främst bestående av cellulosa och en del hemicellulosa med mindre mängder modifierat lignin. Flera studier har fokuserat på effektiv delignifiering under sulfatkoket, men trots detta finns det ännu brister i förståelsen av processen beroende på den komplexa kemin och morfologin hos trä.

Den viktigaste oorganiska komponenten i ved är kalcium. En stor del av detta frigörs under sulfatprocessen. Det som frigörs tidigt under koket är huvudsakligen löst i kokvätskan innan det kan reagera med karbonat och bilda calciumkarbonat. Kalcium i massakokningsprocesser orsakar problem med utfällningar på utrustningen, särskilt i indunstningssystemet.

Fokuset för detta arbete är att öka kunskapen om sulfatkok av ved från *Eucalyptus dunnii* med hög kalciumhalt, och kemiska reaktioner under massatillverkningen. Ett vidare mål är att undersöka betydelsen av varierande kalciumhalter i ved från *E. dunnii*. Flis med olika halt av kalcium kokades i labbskala.

Resultaten i detta arbete visade att delignifieringshastigheten avtog och polysackaridnedbrytningen tilltog vid högre kalciumhalter i veden. Det var däremot ingen påverkan på hexenuronsyrabildningen. Dessa negativa effekter av hög kalciumhalt kunde minimeras genom närvaro av grönlut. Användes grönlut vid massatillverkning av *E. dunnii* ved med hög kalciumhalt. Kunde massatillverkning utföras med tillfredställande delignifiering och låg kolhydratnedbrytning. Massor framställda på detta sätt kunde blekas med gott resultat, d.v.s. hög ljushet och goda styrkeegenskaper. Avvattningsmotståndet var dock något högre. Vid användning av grönlut följer calciumet med massan snarare än hamnar i svartluten. De positiva effekterna av grönlutsanvändning beror troligen på att kalciumjonerna inaktiveras och därmed undviker negativa effekter av lösligjorda kalciumjoner. Förslag till möjliga mekanismer som förklarar dessa effekter diskuteras i avhandlingen. En jämförelse mellan syntetiska grönlutar och industriella grönlutar presenteras också.

**Nyckelord:** Sulfatmassaprocessen, delignifiering, polysackaridnedbrytning, viskositet, H-faktor kappatal, kalciumhalt

## List of papers and author's contributions

This thesis is a summary based on the following papers.

- I. Vegunta, V., Senthilkumar, E. R., Lindén, P., Sevastyanova, O., Vilaplana, F., Garcia, A., Björk, M., Jansson, U., Henriksson, G., and Lindström, M. E., (2022) **High calcium content of *Eucalyptus dunnii* wood affects delignification and polysaccharide degradation in kraft pulping.** *Nordic Pulp Paper Res J*, 37(2), 338 – 348
- II. Vegunta, V., Deshpande, R., Lindén, P., Sevastyanova, O., Garcia, A., Björk, M., Jansson, U., Henriksson, G., and Lindström, M., **Green and black liquor impregnation: possible solutions for problems with kraft pulping caused by calcium content.** *Manuscript*
- III. Andersson, A., Vijaya Vegunta, V., Lindström, M., Olena Sevastyanova, O., Jansson, U., and Henriksson, G., **Presence of Calcium Cations Stimulate Alkaline Hydrolysis of Cellulose During Kraft Pulping Conditions:** *Manuscript*

Other Papers not included in this thesis:

- IV. Karlsson, M., Vegunta, L.V., Deshpande, R., Lawoko, Martin (2022) Corrections: **Protected lignin biorefining through cyclic extraction: gaining fundamental insights into the tuneable properties of lignin by chemometrics.** *Green chemistry*. 24(6), 2636-2637.

## **Authors contribution**

### **Paper I**

Performed experimental work on pulp characterization. Analyzed results, participated in discussions, drafted, and revised the manuscript. This paper includes some results from the master thesis project work by Eashwara Raju Senthilkumar (KTH, 2019)

### **Paper II**

Planned and executed experiments, including kraft cooking, pulp characterization, and liquors characterization. Bleaching experiments and part of analysis on bleached pulps were done by Stora Enso (Imatra). Analyzed results, participated in discussions, and drafted the manuscript.

### **Paper III**

Contributed to the planning of the experimental work and performed an analysis of pulps for Calcium metal content. Participated in the discussions and drafted the manuscript.

### **Paper IV**

Contributed to part of the experimental work.

## **Contribution to conferences**

**Treeseach progress conference 2022**, 11<sup>th</sup> to 12<sup>th</sup> May, Norrköping, Sweden.

Role of Calcium in kraft pulping.

Oral presentation

**CIADICYP 2022-Iberoamerican Congress on pulp and Paper Research**, 28<sup>th</sup> June to 1<sup>st</sup> July, Girona, Spain.

The high Calcium Content of Eucalyptus dunnii Wood Affects Delignification and Polysaccharide Degradation in Kraft Pulping.

Oral presentation

## Abbreviations

<i>E. dunnii</i>	<i>Eucalyptus dunnii</i>
O.D	Oven-dry
Kappa number	Residual lignin in pulp
P	PFI refiner
HexA	Hexeneuronic acid
Corrected kappa number	Kappa number minus Hexeneuronic acid content in pulp
NPE	Non-process elements
EA	Effective alkali
ICP-OES	Inductively coupled plasma optical emission spectroscopy
DEDED	Bleaching sequence (D=Chlorine dioxide stage, E=Alkali extraction stage)
L:W	Liquor to Wood ratio

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# 1. Introduction

An aqueous solution containing the primary pulping ions hydroxide ion and hydrogen sulfide ion is used in kraft pulping to delignify the wood and free the fibers for pulp production. Soda pulping liquor is distinguished from kraft pulping liquor by hydroxide but not sulfide. The most used raw material for kraft pulping globally is different species of eucalypt (Pereira et al., 2011; Potts et al., 2004). The eucalypt trees grow quickly and adapt well to different climates and soils (Sembiring et al., 2021). They are very effective nutrient and water users. *Eucalyptus dunnii* is just a diploid species in the Myrtaceae family that originated in small numbers in Queensland, Australia (Rassaeifar et al., 2013). It tends to grow well in temperate climates and is frost tolerant. Eucalypt plantations are one of the most important sectors in Uruguay, Owing primarily to cellulose pulp production and, to a smaller extent, solid hardwood production for furniture, as well as panel chip manufacturing (del Los Santos, 2016). *E. globulus*, *E. grandis*, and *E. dunnii* are the most cultivated species. In South America, these species are often cultivated in plantations and used for kraft pulping in extensive chemical pulp mills. An interesting phenomenon is that *E. dunnii* cultivated in different areas in Uruguay could have very different kinetics in pulping (del Los Santos, 2016). In the most severe cases, successful kraft pulping was rather tricky. Preliminary data suggested that the calcium oxalate content in the lumen varied, and the highest calcium content gave the worst pulping properties (Vegunta et al., 2022).

The main issue with calcium in the pulping and paper-making processes is the complex scale, which causes significant operational and quality problems. However, this is certainly not the case with mills in Uruguay. One type of inorganic matter is vital for odd kraft pulping and lowering the rate of delignification. Until now, the problems associated with the pulping process are being focused on the calcium content of the wood. In our studies, we conducted in-depth fundamental research on the role of calcium in kraft pulping and the decrease in the delignification rate (Vegunta et al., 2022).

In this work, we highlight the problems associated with calcium caused during pulping on a lab scale and provide a possible scientific explanation. Initiated with wood's chemical composition, continued monitoring calcium content and other cooking chemicals at the impregnation stage, kraft pulping, and bleaching steps. This work also provides a possible solution for reducing the detrimental effects of calcium during pulping while using high calcium-containing wood chips. Laboratory scale tests were performed under mill conditions.

## 2. Background

### 2.1. Wood structure and chemistry

Wood which is called secondary xylem, is produced by many seed-bearing plants (Spermatophyte) (Saka, 1993). It has a complex structure responsible for determining its products' mechanical and physical properties, including pulp and saw wood (Parham & Gray, 1984). As outlined below, these wood properties are governed by wood structure, such as anatomical organization and cell wall ultrastructure. Softwood (i.e., coniferous) and hardwood (i.e., Eudicotyledons angiosperms) are two types of wood. Softwood is a build-up of long and slim tracheid's and some much smaller ray cells (Siau, 1984).

In contrast, hardwoods have a more complex composition, consisting of libriform fibers, narrow but shorter than softwood tracheids, thick, thin-walled vessel cells, small parenchyma cells, and some other minor cell types (Rowell et al., 2012). Chemically, wood consists of cell walls comprised of polysaccharides, lignin, extractives, and some minerals (Henriksson et al., 2009). The chemical

composition of these components, especially the polysaccharides, not only dramatically varies between softwood and hardwood but also within the same genus (Pansgin A.J. et al., 1980; Sjöström, 1981).

### 2.1.1. Cellulose

The polysaccharide cellulose, which accounts for approximately 30 - 50% of the total organic mass of the wood cell, is the most critical contributor to its characteristics (Klemm et al., 2012). Wood cellulose is a linear polymer with a degree of polymerization of up to 10,000 monomer glucose units, or even more, linked by beta (1-4) glycosidic bonds (Goring et al., 1962; Figini et al., 1960; Simson, 1978 b) as illustrated in the diagram below (see figure 1).

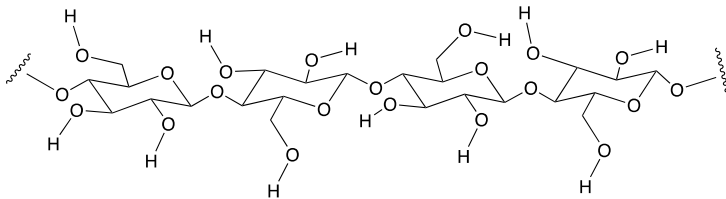


Figure 1: Structure of cellulose in wood

Hydrogen bonds between hydroxyl groups on the cellulose backbone connect the cellulose polymers to form microfibrils with crystalline structures (Kerr et al., 1975).

### 2.1.2. Hemicelluloses

Cell wall polysaccharides with DP much lower than cellulose, a DP around 200 and organized in the less structured amorphous structure of branched polymers, are often referred to as hemicelluloses (Lawoko et al., 2005). The superstructure of these carbohydrates is composed of various sugar monomers with different monomeric substituents on the sides (Timell et al., 1964, 1965; Bauer et al., 1973).

Softwood hemicelluloses usually account for 25-30% of the total solids. O-acetyl galactoglucmannan, also known as glucomannan, and arabino (4-O-methyl-glucurono) xylan, also known as xylan, are the two most essential hemicelluloses (Paananen et al., 2013). The most common hemicellulose in softwood is glucomannan (Simson and Timell, 1978 a; Simson et al., 1968). The most common hemicellulose found in softwood is glucomannan, which has a structure of glucose and mannose with galactose substituents (Burgert et al., 2013). Backbone monomers are joined via beta (1-4) glycosidic bonds and are partially O-acetylated on C-2 and C-3 (Figure 2 below). The monomer ratios separate glucomannan into two fractions. The ratio of galactose monomers in one fraction is low, whereas the galactose units in the other are high (Sjöström, 1993).

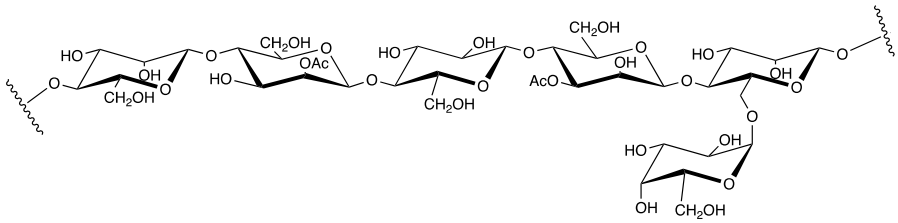


Figure 2: Structure of softwood galacto-glucomannan.

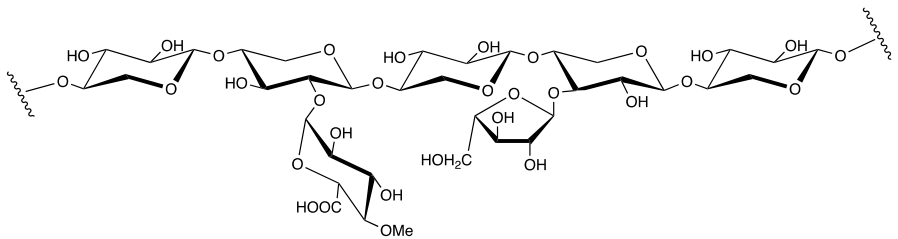


Figure 3: Structure of Arabino glucuronoxylan softwood.

Xylan comprises of (1-4) linked xylose monomers. The xylose is often partially substituted at C-2 by 4-O-methyl glucuronic acid, which reacts, forming hexeneuronic acid under alkaline conditions such as in a kraft cook. The xylose backbone comprises of arabinose monomers connected to C3 (Timell, 1964).

Hardwood consists of two significant hemicelluloses. In common with softwood, these are also referred to as glucomannan and xylan, even though they differ in structure and the proportions in which they are present in the original wood (Liang et al., 1960; Page et al., 1976). The total hemicellulose content of hardwood present varies between 15 and 30%, and xylan is the dominant hemicellulose; glucomannan occurs only in smaller amounts (Johansson & Samuelson, 1977).

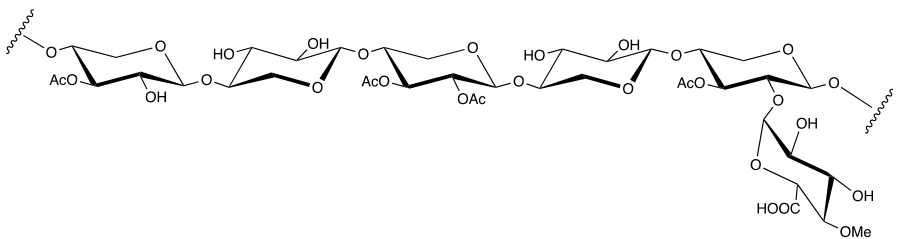


Figure 4: Structure of hardwood hemicellulose xylan.

The most common hemicellulose in hardwood is xylan or O-acetyl (O-methyl glucuronic) xylan. Xylan has a backbone of (1-4) linked xylose residues partially substituted with the O-acetyl group near C-2 and C-3 along with 4-O-methyl glucuronic acid (Bauer et al., 1973; Liang et al., 1960; Page et al., 1976).

### 2.1.3. Lignin

In contrast to the carbohydrate's simple straight polymer structure, the wood lignin polymer is complex and has a 3D Matric-like arrangement. The polymer is composed of phenylpropane units connected with several types of inter-monomer bonds, of which the  $\beta$ -O-4 ether is the most common. Lignin also has multiple covalent bonds to hemicelluloses and is the substance that holds the fibers of wood together (Sarkanen, 1975; Stelte et al., 2011 b; Sakakibara, 1991). It has a complex structure and is an amorphous, heterogeneous, polyphenolic, and crosslinked polymer. Lignin is produced by radical polymerization of the monolignols *p*-coumaryl-, coniferyl-, and sinapyl alcohol (Lawoko et al., 2005). Different wood species have different compositions of monolignols. The lignin concentration in the tree is highest in the middle lamella between the fibers. However, most of the lignin is in the S<sub>2</sub>-layer of the fiber wall. Coniferyl and sinapyl alcohol are both present in hardwood lignin, whereas coniferyl alcohol is almost entirely present in softwood lignin (Sakakibara, 1991; Zandersson et al., 2004; Rowell et al., 2005). Where there are different lignin components, the middle lamella has a higher amount of coniferyl, whereas the S<sub>2</sub> has a lignin composition with higher proportion of sinapyl and coniferyl alcohol (Fergus et al. 1970 and Sjöström et al. 1983). The most likely explanation is that hardwood lignin in the S<sub>2</sub> layer dissolves faster than lignin in the middle lamella. This influences the defibration point when the fibers can be easily separated from each other (with only a tiny number of shives) and appears at a lower kappa number in hardwoods than in softwoods (Hatler, 1959; Söderqvist et al., 1992).

### 2.1.4. Extractives and minerals

Wood structure has been described as an interpenetrating polymer system composed of holocellulose and lignin (Browning, 1963). Additionally, wood contains non-structural organic and inorganic substances that are classified, as extractives and mineral compounds (Pereira, 2003). These extractives influence wood resistance to fungal and insect attack, coloration, odor permeability, density, and hardness. Extractives can account for 4% and 10% of the dry mass of temperate hardwood species and up to 20 % of the dry group of tropical hardwood species (Pettersen, 1984). Terpenes, resin acids (which contain isoprene units), and polyphenols are essential extractives (Pettersen, 1984). In addition, flavanols, anthocyanins, quinones, lignan, and tannins. The distribution of extractives in a tree's wood varies greatly: sugars and other soluble sap constituents, as well as food reserves (starch and fats), are found in the sapwood, whereas phenolic substances are typically found in the heartwood (Pereira, 2003). Heartwood has a higher concentration of benzene alcohol extractives, whereas sapwood has a higher acidic/pH value (Li, 2019). Although extractives make up a small percentage of wood composition, their solubility in wood is essential for its properties and, thus, in industrial applications (Shebani, 2008). For example, extractives significantly negatively impact cellulosic pulp's pulping and bleaching processes (He et al., 2013). Moreover, their oxidation tends to raise the acidity of the wood, promoting its degradation (Shebani, 2008). Removing some extractives reduces fixed carbon content, lowering charcoal yield and changing the thermogravimetric curve to an elevated temperature (Varhegyi, 2004). However, extracts from forest wood species may have nutraceutical applications (Santos, 2017) as antioxidants (Cetera et al., 2019). And as antifungal/antimicrobial agents (Lovaglio, 2017). As a result, the role of wood extractives is therefore necessary for several industrial applications.

The mineral substance content of wood and bark varies depending on the species, age, and habitat of a tree, as well as the sampling position in the cross and longitudinal sections of the stem (Rademacher et al., 1986; Krutul, 1996; Krutul et al., 2006; Okada et al., 1993; Watmough et al., 1999). A notable change in mineral substance content was observed between the top and butt-end sections, which contain more mineral substances than wood from the bottom section. This significance is often greater in bark than wood but even higher in butt-end bark (Krutul, 1996; 1998). Mineral substance content of wood of the same species varies greatly, according to Fengel and Wegner (1984), Loto and Fakunkun (1989), and Rademacher et al., (1986). Regardless of species, the content and distribution of mineral substances on the cross and longitudinal sections of the stem differ and are influenced by factors that cause environmental pollution (Krutul et al., 2006, 2010; Watmough et al., 1998; Watmough and Hutchinson, 1999). Roots are required for mineral uptake to meet the high demand imposed by the rapid growth rate. Along with this phenomenon, leaves (photosynthetic display) and a transport system (xylem and phloem) develop to produce needed metabolites and ensure the proper delivery of water and nutrients to plant tissues. Some of the minerals present in the wood are Calcium (Ca), Potassium (K), Magnesium (Mg), Manganese (Mn), Iron (Fe), Sodium (Na), Zinc (Zn), aluminum (Al), lead (Pb) and Strontium (Sr).

## 2.2. Kraft pulping

The sulfate process, also known as the kraft process because of the high physical and mechanical resistance the pulp generates (kraft means strength in German), is the most prominent method in the world (80% of total chemical pulp production). Globally, approximately 130 million tons of kraft pulp are produced per year (Bajpai, 2016). Representing two-thirds of the world's pulp production and more than 90% of chemical pulp production. The adaptability to different wood species, regardless of physiochemical properties, numerous pulp applications, ions, and efficient use of cooking chemicals offset the high capital costs, making it economically viable and competitive (Goring, 1970, 1980; Hardel et al., 1980 a,b; Goring, 1988).

Sodium hydroxide (NaOH) and sodium hydrogen sulfide (NaSH) are the primary active chemicals used in the kraft process. A solution of these active chemicals is also known as white liquor. The sulfate process derives its name from adding sodium sulfate to replace lost chemical reagents (Bajpai, 2016). This mixture causes lignin fragmentation and dissolution as well as the release of cellulose fibers. The cooking chemicals are not entirely selective for lignin and unwanted reactions of polysaccharides, principally hemicelluloses, have more vulnerability to the chemicals due to their chemical structure (Bajpai, 2012). Based on the delignification rates, the kraft cook can be divided into three phases: initial, bulk, and residual (Wilder & Deleski, 1965; Kleinert, 1966; Lemon et al., 1973). The secondary wall of fibers delignifies faster than the middle lamella region (Whiting et al., 1981; Fergus et al., 1969). The rate of delignification is determined by the chemical structure of the lignin in each area rather than its accessibility (Goring, 1980; Hardelet et al., 1980 a; Meshitsuka et al., 1985). Based on studies on compounds with guaiacol units (Gierer, 1980), potential chemical reactions have been directly linked to the varying delignification phases. The rapid initial delignification phase is diffusion controlled and involves cleavage of a and b aryl ether bonds in phenolic lignin units (Olm & Tistad, 1979). During the bulk delignification phase, once a significant portion of the lignin is eliminated, non-phenolic a and b aryl ether bonds are also cleaved (Lundgren, 1980). The residual phase's lower delignification rate is attributed to carbon bond cleavage. During the cook, condensation reactions among lignin fragments and lignin and carbohydrate moieties may also occur. Due to the lower concentration of hydroxide ions which would otherwise inhibit the formation of condensed structures, such reactions retard lignin dissolution and become more critical near the end of the cook (Gierer, 1980).

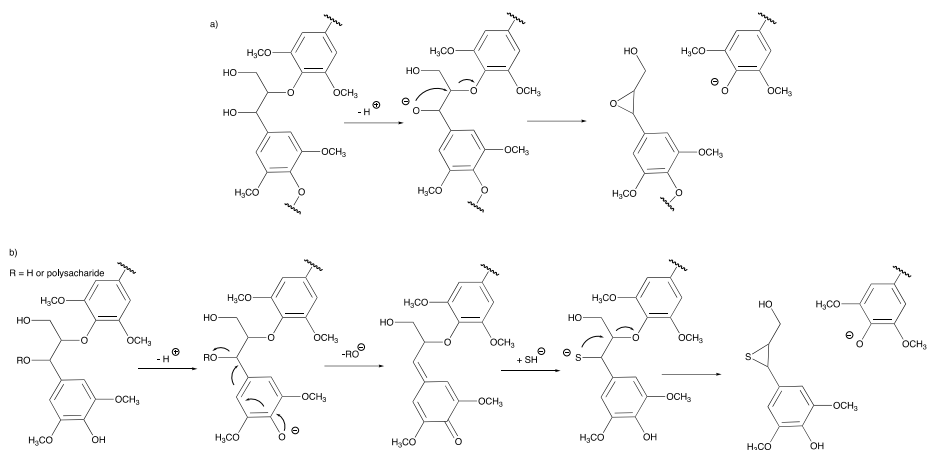


Figure 5: Central delignifying reactions in kraft pulping. a) Cleavage of the non-phenolic beta-O-4 bond. b) Cleavage of the phenolic beta-O-4 bond.

During pulping, the composition and amount of carbohydrate polymers change continuously. The extent to which these transformations occur influences the yield and characteristics of the final pulp. Deacetylation and end-wise degradation (peeling) are the most critical carbohydrate reactions. During the initial delignification phase, hemicelluloses are deacetylated, and the number of uronic acid groups is reduced (Sjöström, 1993; Sjöholm E, 1999). The peeling reaction and immediate dissolution of hemicelluloses are responsible for yield reduction during the initial delignification phase. The peeling reaction begins at approximately 100 °C (Gierer, 1980) and continues at the reducing end till the competitive stopping reaction has formed a solid acid end group (Johansson & Samuelson, 1975). Glucmannan is easily peeled, whereas xylan is mainly dissolved in black liquor and is not extensively degraded. A portion of the dissolved xylan is afterward reabsorbed onto the fiber's surface. Deacetylation and a decrease in uronic acid groups in xylan, as well as a reduction of alkaline hydrolysis, become noticeable, i.e., during the bulk delignification phase. Due to its high DP, cellulose undergoes most of this degradation. Alkaline hydrolysis also generates new reducing end groups confined to peeling reactions, lowering the yield even further and, maybe most importantly, lowering the degree of polymerization of cellulose and, thereby, the strength of the pulp fibers (Gierer, 1980).

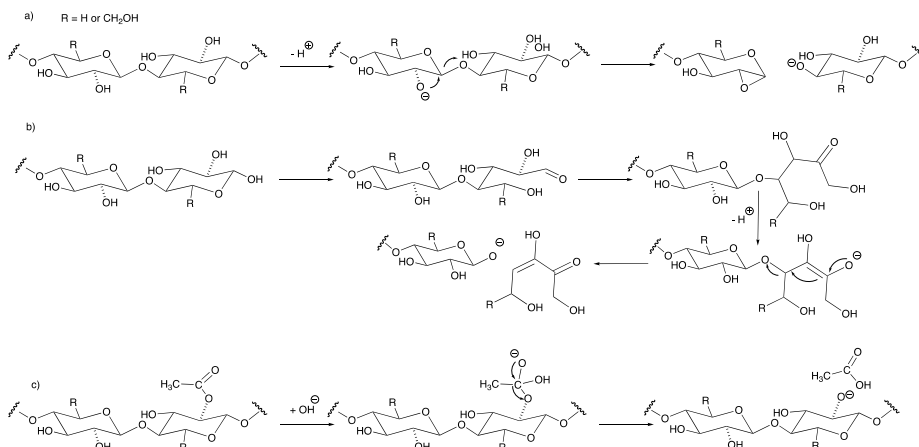


Figure 6: Central polysaccharide degrading reactions during kraft pulping. a) Alkaline hydrolysis, b) "Peeling" reaction and c) Alkaline deacetylation.

The operation is divided into four stages: raw material management, chemical delignification of wood with an effective chemical and energy recovery system, bleaching with high water demand, and wastewater treatment. During the kraft process, half of the wood is dissolved and, along with the spent pulping chemicals, forms a liquid stream known as weak black liquor (Bajpai, 2008). Washing separates the weak black liquor from pulp, which is then sent to the recovery system, where the inorganic pulping chemicals are recovered for reuse, and the dissolved organics are used as a fuel to generate steam and power (Kulkarni et al., 2005).

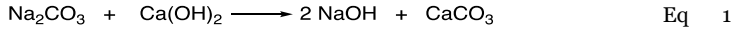
The recovery process serves three primary purposes:

1. Reducing the environmental impact of pulping waste material (such as black liquor)
2. Generate pulping chemicals, i.e., NaOH and Na<sub>2</sub>S, from recycled pulping chemicals
3. Cogeneration of steam and electricity

*Recovery of pulping chemicals, NaOH and Na<sub>2</sub>S:*

Weak black liquor, i.e., the liquor directly from the washing of the pulp, brown stock washing, is exposed to several evaporators and condensers to a stage that it can be successfully burned in a recovery boiler, typically at 65% solids or higher (Ibrahim, 1988). Highly concentrated black liquor is dosed in a recovery boiler, which burns in an oxygen-deficient environment, resulting in the formation of Na<sub>2</sub>S (Mishra, 1982). The reduction efficiency, typically greater than 90%, shows the amount of sulfide forming. Other sodium ends as Na<sub>2</sub>CO<sub>3</sub> in the recovery boiler (Grace, 1987 a,b). Many factors influence black liquor's chemical, physical, and combustion characteristics, including mill location (land or coastal), digester environments, pulp yield, wood, white liquor characteristics, chemicals-to-wood ratio, and brown stock washing efficiency. Hardwood pulping requires fewer chemicals, produces more pulp, and thus produces less black liquor (Mandavgane et al., 2007). Hardwood black liquor generally contains fewer organics, tall oil, and soap and exhibits a lower value for heating than softwood black liquor (Tikka, 2008).

According to Eq 1 the main purpose of the sodium cycle (or causticizing process) will be to transform the major elements of green liquor, particularly the non-active sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), into sodium hydroxide (NaOH), which serves as a crucial cooking compound in white liquor (Grace, 1987).



The green liquor is clarified and morphed into white liquor during the causticizing process by expelling inorganic compounds (green liquor dregs-GLD), then drained and calcined at elevated temp into CaO, as per Eq 2 in the calcium cycle:



Eq 2 is an endothermic reaction that emits  $\text{CO}_2$  into the atmosphere. CaO interacts with water (see Eq 3) to produce hydrated lime, which is then employed as a reactant (see Eq 1):



Slaker grits are the non-soluble portion produced during the slaking process. A crucial point in chemical recovery is a third cycle affiliated with a recovery boiler generally fitted with an electrostatic precipitator to acquire dust from the flue gas. Finally, the particles, primarily  $\text{Na}_2\text{SO}_4$ , are brought back to a furnace by blending those well with black liquor (Seppa & Venter, 1988).

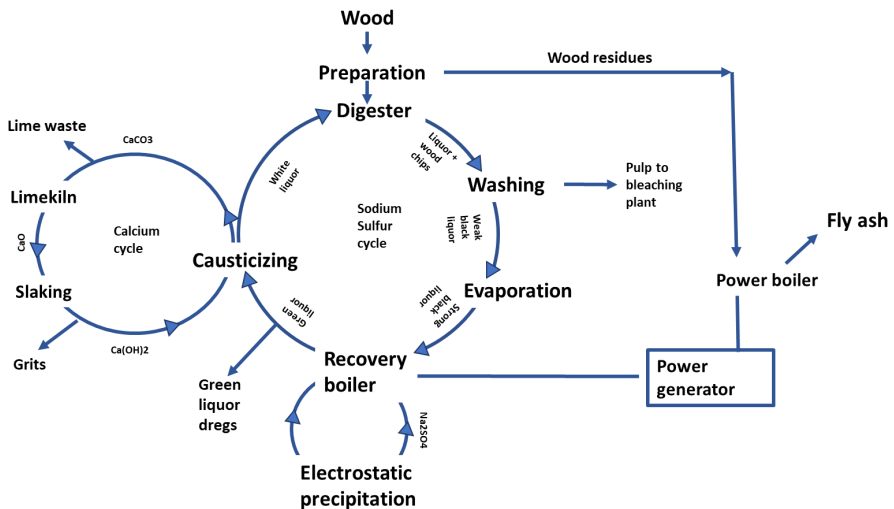


Figure 7: Outline of the typical kraft mill process.

Figure 7 depicts the generation points of the four major inorganic wastes generated in large amounts in the kraft pulp mill: green liquor dregs (GLD), slaker grits (SG), lime mud (LM), and boiler fly ash (BFA). These waste products are of significant concern because, despite several laboratory-scale tests,

little has made it to the industrial plant, and thus landfill is the primary management method. GLD has been produced during the clarification of green liquor and contains insoluble inorganic flux from the recovery boiler (smelt) (Jia et al., 2019; Monte et al., 2008; Quina et al., 2020; Wang et al., 2003).

The GLD is highly alkaline. Lime mud (LM) results from the chaotizing reaction isolated from white liquor, washed, and calcinated in a lime kiln, whereas a portion might be expelled as waste and replaced by fresh  $\text{CaCO}_3$ . Greater LM formation occurs when there is a variation between white liquor production and lime kiln manufacturing capability (Martin et al., 2010). The pH of LM varies and is frequently highly alkaline. Slaker grits (SG) have been the primary substance deleted from lime slaker discharge to prevent causticizer build-up, and mechanical was in the filtration system. SG typically has a solid content of 75% and a pH greater than 12.5 (Mandolo, 2009). In a biomass boiler, boiler ash is produced as a by-product of the burning of wood and its residues for energy recovery (Pöykö et al., 2014). The particles travel upwards with the flue gas. As the flue gas cools, the fused particles crystallize to produce fly ash, collected by cyclones, fabric filters, and electrostatic precipitators (ESP), of greater than 99 % cleaning quality. Fly ash comprises dust and precipitated volatiles with a large surface area (Sanchez et al., 2005).

Closing the cycles in kraft mills does have environmental benefits. However, it accumulates non-process elements (NPE) in the liquor cycle, which can impede the pulping, bleaching, or chemical recovery process. NPE joins the pulping process via the principal materials, such as wood, make-up chemicals, and water, or it may be caused by equipment corrosion (Roberts, 1982). Furthermore, the closing of the water cycle aggregates NPE, which includes Ca and K in the recovery cycle. Their accumulation may cause filtration issues and precipitate formation. Therefore, the procedure purges associated with GLD, SG, and LM are critical for NPE elimination (Golmaei et al., 2018).

The significance of the recovery process should be more frequently considered. Over 1.3 billion tons of weak black liquor is processed globally; approximately 200 million tons of black liquor dry solids are burned in recovery boilers yearly to recover 50 million tons of cooking chemicals such as  $\text{Na}_2\text{O}$  and produce 700 million tons of high-pressure steam (Svensson, 2012). This scenario makes black liquor the world's fifth most crucial fuel, after coal, oil, natural gas, and gasoline (Reeve, 2002). Because it is derived from wood, black liquor is the most significant and abundant renewable biofuel, particularly in Sweden and Finland (Magnus et al., 1979). Many factors influence black liquor's chemical, physical, and combustion properties, such as mill location (inland or coastal), digester conditions, pulp yield, wood species, white liquor properties, chemicals-to-wood ratio, and brown stock washing efficiency (Martell, 1964;1971). Hardwood pulping generally uses fewer chemicals, produces more pulp, and produces minimal black liquor solids than softwood pulping. Hardwood black liquor contains less organic, tall oil and soap than softwood black liquor and has a reduced heating value (about 5% lower). Eucalyptus is the most common wood species used throughout kraft pulping in Brazil, Chile, and other tropical countries (Bialik et al., 2014). Because eucalyptus black liquor's qualities are comparable to those of other hardwood black liquor, the chemical recovery process in eucalyptus kraft mills is the same as in others (Tran et al., 2016).

### 2.2.1. Impregnation

The purpose of impregnation is to ensure that effective cooking chemicals penetrate the wood chips (Zanuttini & Marzocchi, 2000). A homogenous dispersion of hydrogen sulfide and hydroxide ions from the wall to the core of the wood chips is essential for ensuring homogeneous delignification throughout cooking and, as a result, a lower reject content in all the chips, allowing the delignification reactions to occur (Zanuttini et al., 2005). This indicates that any alkali shortage in the wood chips cores should not adversely affect the alkali profile throughout the cooking process (Jacobson et al., 2006). Wood-chip quality and size, steaming pressure, impregnation temperature, liquor-to-wood ratio, and impregnation time are all essential factors in impregnation (Karlström, 2009; Wedin et al., 2010). The thickness of the wood chips has a significant impact on all crucial processes. Therefore, the wood chip's thickness substantially affects the impregnation time; logically, thicker chips take longer to be impregnated (Hartler & Onisko, 1962; Gullichsen et al., 1992). High steaming pressure

is also necessary for the rapid removal of air inside the chips and the faster penetration of the liquor (Malkov et al., 2003; Määttänen & Tikka, 2008). Extended impregnation focuses on the latter three, the impregnation temperature, the liquor-to-wood ratio, and the impregnation time. During impregnation, both penetration and diffusion occur.

Compared to diffusion, penetration is faster, and in hardwood, penetration occurs primarily via the vessel system, whereas diffusion moves ions into the fiber walls (Gullichsen et al., 1992; Egas et al., 2002). When the wood components meet the active ions, chemical reactions and physical dissolution begin. Alkali is consumed by all the wood matrix components, including lignin, extractive, pectin, hemicellulose, and cellulose (Hartler & Onisko, 1962). Deacetylation and neutralization are important alkali-consuming reactions in hemicellulose during impregnation. Peeling reactions occur during impregnation and at higher temperatures, and the rate of alkali-consuming reactions increases. This is also true for diffusion rate but to a much smaller extent, as for alkali-consuming reactions (Hartler & Onisko, 1962). In other words, lowering the impregnation temperature promotes diffusion over alkali consumption and enhances the number of hydroxide ions accessible to diffuse into the chip core (Bränvall et al., 2016). Because fewer carbohydrates are dissolved and degraded as the reaction rate slows, the carbohydrate yield suffers (Hartler & Onisko, 1962). Alternatively, the diffusion rate can be improved by using a higher liquor-to-wood ratio. A higher liquor-to-wood ratio increases the number of active ions at the same hydroxide ion concentration (Jimenez et al., 1990; Egas et al., 2002) since a longer impregnation time improves impregnation (Jimenez et al., 1990).

Considering all the factors above, we have used increased impregnation time since impregnation increases with an increase in impregnation time (Jimenez et al., 1990). In addition, calcium content was monitored during impregnation and continued kraft pulping. During the impregnation stage, we considered three different cooking liquors: white liquor (reference), black + white liquor, and green liquor (synthetic).

## 2.2.2. Green liquor in kraft pulping

Extended kraft pulping via customized cooking chemical reactions has been the subject of numerous studies in the past and present. Global competition for improved pulp quality, energy-saving demands, and increasingly strict environmental standards have obligated the pulp and paper sector to seek customized pulping and bleaching innovations over the last several decades (Johakim et al 2018). As a result, extended delignification pulping innovations have emerged as a viable option for enhancing the overall market efficiency of the kraft process in modern operations. Green liquor is the solubilized smelt encountered in the recovery boiler during the kraft process used in the paper industry. This comprises sodium carbonate, sodium sulfide, and many other ingredients (Cornell et al., 1985). It gets its name from the green color due to the low amount of iron hydroxide in the liquid. A modern displacement batch cooking pilot digester used green liquor for impregnation and the initial phase of cook showed positive results. The most significant outcomes are increased bleachability and pulp strength. Green liquor pretreatment also speeds up pulping by increasing the lignin removal at the start of the bulk delignification stage (Fišerová et al., 2012).

Furthermore, green liquor pretreatment enhances the effectiveness of green liquor's chemical reactions during the pulping process. In a modified pulping process, a direct fit between chemical performance and lignin removal was established (Lucia, 2005). It was discovered that after pretreatment at 0.7 M and 4 M liquor-to-wood ratio of green liquor, the delignification rate increased by 12 and 5%, respectively, in the initial stage and 10% to 6% in the bulk phase. The selectivity of delignification was more significant when the liquor-to-wood ratio was low during the impregnation stage (Bykova, 1997). An increased green liquor concentration can boost both reabsorption and degradation. A striking discovery in their work is that hydrogen sulfide did appear to interact with wood composites during the pretreatment phase to create a very tight chemical bond. Sulfur seems scary to have a chemical bonding behavior in wood that correlates with carbohydrate preservation; a greater level of bonded sulfur leads to better carbohydrate preservation. As it is known, green liquor is rich in high sulfur content (Bykova, 1997). Finally, various additives used during green liquor

pretreatment were discovered to impact sugar preservation (Ban, 2004) significantly. In these earlier studies, it is observed that the effects of the increase in yield and polysaccharide protection are related to sulfur and concentration of green liquor, i.e., green liquor addition is mainly a way to increase the hydrogen sulfide content. Nevertheless, in our work, we are investigating the reduction of the detrimental effects served with calcium content in wood by using green liquor. Our hypothesis for using green liquor is the idea of carbonate that is present in green liquor binding with calcium by forming stable complexes and improving the pulping properties.

### 2.2.3. Non-process elements (NPE's)

Non-process elements (NPEs) are compounds that do not participate in the kraft pulping process (Salmenoja et al., 2009), at least not in a positive way. To put it in other words, not all NPEs are harmful. However, if allowed to accumulate, a few NPEs may turn detrimental and pose a risk or unnecessary dead load. NPEs are introduced into the pulping process primarily through raw material (wood), lime, makeup chemicals, and process water (Taylor et al., 2007). Because bark contains more NPEs than stem wood, it is critical to have a well-functioning barking procedure to decrease NPE intake as much as possible. Wood's NPE content varies depending on location, species, and maturity level (Tylor & Bussons, 2006). NPE intensities are approximately tenfold higher in the green areas of the tree, i.e., bark, branches, and twigs, compared to stem wood (Jonsson et al., 1990). Phosphorus (P), silicon (Si), aluminum (Al), magnesium (Mg), iron (Fe), calcium (Ca), chlorine (Cl), potassium (K), and manganese (Mn) are the most dangerous NPEs. Calcium is considered an NPE despite its active role in the lime cycle since it is not an active compound elsewhere in the procedure (Jemaa et al., 1999). NPEs can cause operational issues such as fouling, scaling, plugging, corrosion, inadequate efficiency, low solid content in lime mud settling, gaseous and particulate emissions, emissions of gases and particles imbalance of sodium and sulfur in the recovery cycle (Ulmgren, 1999; Svensson, 2012). Certain NPE (transition metal ions) can also disturb the bleaching of pulps. This work is mainly focused on Calcium (Ca) related problems.

Calcium (Ca) is a problematic element in digester and evaporation plants. In acidic solutions, Ca dissolves. It is primarily found in green and white liquor as calcium hydroxide, calcium sulfates, and calcinate (Björk et al., 2002). Except in the evaporator plants, there is no evident enrichment of Ca in the recovery cycle. Instead, it will enhance with brown stock and bleaching plant (Ulmgren & Rådesström, 1997). Wood and makeup lime are the primary sources of Ca. Ca is also introduced to the process with bark traces if the debarking is efficient. Ca mainly precipitates as calcium carbonate in green liquor (Hyvönrnr, 2009). Temperature is a factor that influences the precipitation of calcium carbonate. Precipitation increases as the temperature decreases (Hyvönrnr, 2009). Ca is typically removed from green liquor dregs in calcium carbonate (Milanez, 2007). Brown stock usually contains traces of calcium ions that can potentially cause scalability of calcium carbonate as washing, knitting, and screening equipment, resulting in gradual damage. Acidified effluents can be used to remove Ca. Because acid disperses almost all Ca compounds. They are terminated as acidic effluents (Doldan et al., 2011).

### 2.2.4. Calcium-related problems in kraft pulping

Calcium in black liquor and the pulping line comes from three primary sources: wood, water, and cooking chemicals from the recaustizing phase. Wood and pulping liquor calcium content varies based on variables such as wood age, water hardness, growing location, pretreatment, and pulping chemical quality (Salmenoja et al., 2009). In pulping and bleaching processes, stem wood contains more soluble calcium (low miscibility at high temperatures) (Holamo, 2000). According to recent research, the quantity of soluble calcium in a mill's black liquor differs significantly between kraft mills. Calcium is a non-process element in the pulping and bleaching processes (Li et al., 2014). Hard-scale deposits on pulping digester heating surfaces and screens, bleaching tanks, and evaporators are

caused by it (Ulmgren, 1997). Due to scaling and plugging, scalability prevents heat transfer and creates unplanned downtime throughout the operation (Li et al., 2014). High calcium levels damage the machinery and minimize the evaporation plant's efficiency.

Furthermore, calcium is considered detrimental to wood digestion by slowing delignification reactions. A detailed analysis of the occurrence of soluble calcium through the delignification process is to select liquor management approaches to avoid calcium scale problems (Li et al., 2014). The main disadvantage of calcium in wood is that it requires more cooking time and raises the likelihood of lignin condensation at extremely high temperatures (Li et al., 2014). Given all these drawbacks, this component must be carefully monitored.

Previous research found that adding carbonate to synthetic white liquor remarkably accelerated the rate of delignification (Lundqvist et al., 2006). Calcium carbonate precipitates during digestion, reducing the amount of free calcium in black liquor solutions and, as a result, interfering with it. Rise's study (Lundqvist et al., 2006) concluded that removing calcium or adding DTPA to white liquor has no significant impact on the delignification rate of eucalyptus (Saltberg et al., 2009). The preparatory explanation is that substances formed during cooking from eucalypt form complexes with calcium ions, preventing the calcium impact on pulping yield, which varies depending on the species (Saltberg et al., 2009). The one drawback of this species is that this alkaline earth metal most likely interferes with delignification reactions. One such effect has been detected through the H-factor to attain kappa number 18 for samples containing a significant calcium content, even though it occurs in all samples containing a high calcium content and may have drawbacks in terms of processability and pulp quality (Saltberg et al., 2009).

### 2.2.5. Chemistry of calcium, wood components, and cooking chemicals

Cellulose, hemicellulose, and lignin are the main wood components that undergo important chemical reactions during kraft pulping. Generally, kraft pulping is done under highly alkaline conditions. Several studies were conducted in the early 1980s to understand better the binding efficiency of calcium to these wood components (Camire & Clydesdale, 1987; Deiana et al., 1989; Kohn, 1987; Kohn & Hirsch, 1986; Kohmetal, 1968; Lazlo, 1987; Leight & Miller 1983; Mc Burney et al., 1986; Malovikova & Kohn, 1983; South gate, 1987; Torea, 1991; Rendleman, 1982; Selvendran, 1984; Van Soest & Joes, 1988; Weiber et al., 1988). An earlier study by De Lanson (2003) demonstrated that metal uptake occurs via the ion exchange of aqueous metal ions and proton displacement at anion sites associated with metals like Ca. These interactions can be defined by using reciprocal plots, such as scratched plots to determine binding affinity and the type of binding sites (Scatchard, 1949). An essential finding of this work is that lignin has two specific binding sites for calcium, while cellulose only has non-specific binding sites for metals (Platt & Clydesdale, 1987; Scatchard, 1949).

When the pH exceeds 10, the presence of sodium hydroxide creates accessible areas for calcium absorption. Calcium binding to cellulose significantly increases under these conditions. The sodium hydroxide used to raise the pH to 10 may have loosened the cellulose structure, giving rise to accessible areas for entrapping and adsorbing calcium (Zhou et al., 2015). Rendleman (1973) discovered that the ionization of polyhydroxy compounds in the presence of a base promotes the formation of metal alcoholate complexes. The ionization of Poly-hydroxy compounds in the presence of a base aids in forming a metal alcoholate complex (Chiang et al., 1994). Calcium binding to cellulose increases as the pH rises to ten. Calcium is entrapped and bound to the accessible areas created by sodium hydroxide as the pH is raised (Zhou et al., 2013). However, in Torre's studies, fewer or no binding sites were observed under these conditions. Calcium could be retained by adsorption to the surface of this glucose polymer (Torre, 1991), explaining the cation's weak binding to cellulose. Furthermore, it was demonstrated that the cellulose-binding ability was unrelated to its polymeric chains and the hydroxyl functional groups (Rendleman, 1982; Camira & Clydesdale, 1981).

The solubility of lignin is assumed to be lower in the presence of calcium. Because this species hinders the smooth ionizable functional groups in lignin, including carboxylic groups, methoxy groups, and

hydroxyl groups, in the presence of calcium ions (Ishaigire et al., 2015). Torre's research revealed that lignin's potential binding capacity at higher pH levels was moderately higher. It is likely due to the increased ionization of this polymer's functional groups with increasing pH. (Leight & Miller, 1983; McBurney et al., 1986; Wieber et al., 1988). The release of protons from lignin's effortlessly ionizable functional groups under less acidic calcium solution conditions led to a slight but reproducible decrease in pH.

Previous research shows calcium strongly bonds with pectin during cell wall maturation (Catesson, 1994). Therefore, it has been proposed that reducing esterified pectin loss influences growth and cell wall rigidity via calcium and D-galacturonic acid, pectin's primary monomeric unit. (Rendleman, 1982; Laszlo, 1987; Deina et al., 1989). Likewise, studies on the interactions of D-galacturonic acid and other monouronates with Ca +2 ions were conducted (Kohn et al., 1968; Malovikove & Kohn, 1983; Kohn & Hirsch, 1986).

Based on previous studies, it appears that the predominant mechanism of interaction in the calcium-binding by pectin was a different complex formation because the carboxyl group of the D-galacturonic monomeric unit of this polysaccharide did not bind calcium ions (Whistler & Bemiller, 1958). So, calcium adsorption to the surface of the pectin should explain the minimum binding to calcium. The primary binding mechanism appears to be complex formation via the polymer's easily ionizable functional groups. Cellulose and low methoxylated pectin are less active quantitatively than lignin. Calcium adsorption to the surface of cellulose and pectin may explain why these fiber's constituents bind so little (Torre et al., 1992).

Based on previous research, this review concludes that metal ions have a much higher affinity for lignin than carbohydrates (Cardona-Basro et al., 2001; Perat et al., 2001; Carrot et al., 2001). The most apparent metal binding groups in kraft pulping are phenol and carboxyl (Sjöström, 1989). The phenolic groups are formed by residual lignin. Most carboxyl groups in kraft pulp are in hexeneuronic acids formed during the kraft cooking process. They have been shown to strongly bind transition metals (Teleman et al., 1995; Buchert et al., 1995; Denevind & Chaveheid, 1997).

### **2.2.6. Role of calcium oxalates in pulp mill**

Calcium oxalate crystals are found in photosynthetic organisms of all levels, from tiny algae to angiosperms and huge gymnosperms. These organisms can accumulate a significant number of crystals. Plants use calcium oxalate crystals for various purposes, including high-capacity calcium resolution, herbivory protection, detoxification, ion balance, tissue support, and even light gathering (Levy-Lior et al., 2003). Because crystals can have a complex morphology, calcium carbonate crystals' main components seem simple. Plants form crystals from biochemically synthesized oxalic acid and calcium from the environment. Oxalic acid can form complexes with calcium to form calcium oxalate crystals, which are highly insoluble (Kavanagh, 1995).

Calcium oxalate scaling is a significant particle issue in a paper mill, particularly in the evaporator coils, pulp digesters, and bleach room (Ulmgren, 1997). Calcium oxalate deposits form in supersaturated calcium and oxalate solutions. Oxalic acid is a dicarboxylic acid found naturally in the wood. The source of oxalic acid within an unbleached pulp mill is wood (Härä et al., 2011). It is also formed during bleaching reactions with wood as an oxidation product of lignin (primarily) and hemicellulose (xylan/uronic acids).

Additionally, a large amount of oxalic acid was produced during the bleaching sequence (oxygen delignification and ozone bleaching stages). The quantity of oxalic acid formed was determined by the pulp's available lignin content (kappa number) rather than the oxidant concentration or heating rate. The formation of oxalic acid is proportional to the kappa number reduction (Elsander et al., 2000). Like the dissolved wood organics, oxalates act as weak chelating agents for most metal ions. The oxalate formed during the pulping process is washed from the pulp and joins the recovery cycle with black liquor (a dilute solution of spent pulping chemical compounds and dissolved organics) (Bryant,

1996). The oxalates may cause sodium oxalate scaling, as evaporators often concentrate the black liquor and calcium carbonate scaling within digesters and evaporators.

Furthermore, calcium oxalate increases calcium carbonate scalability in black liquor. A fundamental cause of scaling in digesters and evaporators acknowledging calcium carbonate scaling requires trying to quantify oxalates release and establishment during pulping (Li et al., 2012). The two main paths of oxalate formation recognized in the bleaching process are lignin oxidation and hexenuronic acid. In this work, oxalic acid in black liquor is investigated based on a hypothesis of oxalic acid regulating alkaline hydrolysis during pulping (Testova et al., 2014) and monitoring the release of oxalic acid throughout the pulping process.

### 2.2.7. Eucalyptus as a raw material for the pulp and paper industry

Because of its rapid growth, short rotation time, environmental adaptability, and suitability for pulp and paper production, eucalypt species are planted in tropical, subtropical, and temperate locations (Baldin et al., 2017; Gomes et al., 2015). Given its rapid advancement, *Eucalyptus dunnii* has attracted attention. This species is indigenous to southern Queensland and New South Wales around Coffs Harbour. High volumetric growth, high pulp yield of about 44 to 57 %, relatively high wood density of 455-618 kgm<sup>-3</sup>, and low lignin content are the beneficial conditions that brought attention to *E. dunnii* (Grattapaglia et al., 2012). *Eucalyptus* species growth and wood qualities are of utmost importance for high output and quality of cellulose, respectively, and make up most of the world's production of short-fiber pulp (Laclau et al., 2010; Versini et al., 2014).

The main demands on eucalypt breeding projects have been boosting forestry productivity, associated with wood enhancement as an industrial raw source, particularly for pulp and paper sectors. The industrial goals focus on operating cost reduction, wood performance improvements in industrial processes, and appropriateness for producing high-quality goods for various market niches. The significant requirements on eucalypt breeders for industrial applications, especially for the pulp and paper industries, have been centered on increasing forestry productivity, which is linked to wood advancement as an essential commodity. Industrial priorities primarily focus on operational cost reduction, improving wood efficiency in industrial processes, and suitability for increasing production of products for various market segments (Thomas et al., 2007).

The demand for eucalypts, therefore, grows as industries expand. However, plantation companies must precisely evaluate eucalypt market-associated consequences in eucalypt plantations and how these influence the surrounding environment and significantly impact the eucalypt distribution chain. These uncertainties must be counterbalanced. Two of the most popular trade species are, e.g., *Eucalyptus grandis* and *Eucalyptus globulus* (Leite, 2010). For production purposes, many of these industries have developed their eucalypt plantation. That means the demand for these woods will increase as a result of the number of pulp and paper mills (de los Santos, 2016).

### **3. Aim and Objectives of the study**

The study aims to understand better the mechanism behind the detrimental effects of calcium in wood during kraft pulping. The scientific objective includes assessing the physical and chemical state of the original calcium in wood and the reactions of calcium with lignin, and carbohydrates during kraft cooking. Depending on the reaction, there are various methods to facilitate delignification and improve yield. Thus, increased pulp production and a decreased need for cooking chemicals can be evaluated. The technical objective was to investigate different pre-treatment methods like impregnation and cooking phases (using black and green liquor). The goals are summarized in the following points:

- To investigate if the pulping problems are related to calcium content in the wood or if it could also be other differences between the pulps explaining these effects.
- To formulate scientific theories behind the detrimental effects of calcium and cooking liquors during kraft pulping.
- To find a solution, i.e., to allow easy pulping of the highest calcium-containing woods.

### 3.1. Sustainability goals:

Sustainability is a natural part of the kraft pulping process as the recovery area aims to reuse the process chemicals as much as possible and focus on improved energy efficiency and minimizing chemicals. Our challenge for the kraft pulp mills of today is to improve an existing efficient process further. This study addresses process monitoring and optimization of the kraft pulp process that comes with problems related to non-process elements, namely calcium. The study mainly focused on mapping calcium in the process stream to minimize kraft pulping problems using high calcium-containing *E. dunnii* wood chips cultivated in some parts of Uruguay. The problems observed by these species from our research work namely a decrease in pulp yield, rate of delignification, and increased polysaccharide degradation. Although we can increase the rate of delignification of these high calcium *E. dunnii* wood chips, we must use harsh conditions, for example, an increase in H-factor (consumes more energy) and cooking liquors concentrations (more consumption of cooking chemicals). Introducing green liquor in kraft pulping of high calcium-containing *E. dunnii* wood chips solves the above problems in one go.

The study aimed to critically evaluate and optimize the use of green liquor on the laboratory scale, which is easily accessible in kraft pulping mills. The results are exceptionally positive compared to black + white liquor and white liquor (control) in the lab scale. For high calcium-containing *E. dunnii* wood chips, green liquor-induced kraft pulping increases the pulp yield, saves energy, and offloads the lime kiln.

Moreover, green liquor increases fiber strength and produces a low kappa number at a lower h-factor. It also acts as a chelating or additive for the calcium-related problems in pulp mills, namely scaling and irregular pulping by following the calcium with fiber line instead of following black liquor and homogeneous kraft cook by producing low kappa pulp under lower H-factor, respectively. Also, observed improvements in brightness and strength properties can save the pulp amount without increasing wood inputs in the pulping process. From a sustainable point of view, a reduction in steam consumption leading to the usage of less coal or furnace oil in power boilers implies lower green gas emissions. From an economic point of view, using green liquor already available in pulp mills reduces investment and energy costs.

In summary according to UN sustainability development goals, this work reaches the following goals:

Goal 7: Affordable and clean energy

Goal 8: Decent work and economic growth

Goal 9: Industry innovation and infrastructure

Goal 12: Responsible consumption and production

## 4. Materials and methods

### 4.1. Materials

Wood chips were provided by from Stora Enso (Table 1).

Table 1: Details of wood chips used in this study

Sample name	Species	Farm	District	Age	Ca content (mg/kg)
<b>E.d. 705</b>	<i>E. dunnii</i>	Blanquillo	Lomas de Blanquillo	15	705
<b>E.d. 870</b>	<i>E. dunnii</i>	Rivermol S. A	Young	10	870
<b>E.d. 966</b>	<i>E. dunnii</i>	Palmar	LaFavorita de Garcia Notari	14	966
<b>E.d. 1500</b>	<i>E. dunnii</i>	Rivermol S. A	Young	11	1500
<b>E.d. 3366</b>	<i>E. dunnii</i>	Soriano	Bequelo	13	3366
<b>E.d.3756</b>	<i>E. dunnii</i>	Soriano	Bequelo	20	3756
<b>E.d. 4668</b>	<i>E. dunnii</i>	Grecco	Los Cercos	13	4668
<b>E. g.</b>	<i>E. globulus</i>	Not known	Spain	Not known	Not Known

For comparing industrial green liquor to synthetic green liquor, 900 trees were sampled with the non-destructive method from the same farm in Montevideo, Uruguay.

Composition of industrial green liquor ( $[\text{OH}^-] = 0.6 \text{ mol/l}$ ,  $[\text{HS}^-] 0.66 \text{ mol/l}$ )

### 4.2. Methods and analysis

#### 4.2.1. Impregnation

Dried hardwood chips (*Eucalyptus dunnii*, calcium content-3366 mg/kg) of 100 g of dry weight were taken and the moisture content of the chips were 92%. Stock solutions of  $\text{Na}_2\text{S}$  were prepared by dissolving technical grade flakes of  $\text{Na}_2\text{S}$ . Impregnation was performed in steel autoclaves with volume 1000 ml. First, the wood chips are deaerated under a vacuum for 30 minutes. Then, the liquor was sucked into the autoclaves and placed in a steam-heated glycol bath at 110 °C. The heating time to reach the required temperature was 10 minutes. After finishing the impregnation, the autoclaves were cooled in the water bath. The experimental design consists of time (minutes): 0, 20, 40, 60, and 90 minutes [Note: 10 minutes for heating to the required temperature]. The impregnation conditions: temperature (110 °C), sulfidity (35 %), liquid-to-wood ratio (4:1), and EA (18%). The black liquor production was carried out in the lab for the impregnation experiments, produced using *Eucalyptus dunnii* wood chips containing calcium 3366 mg/kg. The liquor at each point was collected and stored in the fridge. The wood chips were washed with deionized water after each end.

#### **4.2.2. Kraft cooking (Paper 1)**

Before the pulping process, chips were screened to confirm a uniform thickness and sorted by hand. Next, 100 o.d. g of wood chips is put in stainless rotative autoclaves with a total capacity of 2 liters in a steam-heated polyethylene glycol bath. After vacuuming the chips for 30 minutes, cooking chemicals were introduced through a valve without trying to break the vacuum. A liquor-to-wood ratio of 4:1, an effective alkali of 18%, and a sulfidity of 35% were used. The temperature was ramped to 110°C and maintained for 1 hour of impregnation, after which it was directly ramped (it took 10 minutes to reach the temperature) to 145 °C. The wood chips cooked for various lengths of time in the order: 2.75 hours, 3 hours, 3.25 hours, and 3.5 hours. Lastly, the cooking process was completed by trying to cool the autoclaves in a water bath before opening the autoclaves to collect the product.

#### **4.2.3. Stage 2 Kraft Cooking for pulps produced for bleaching experimental study (Paper 2)**

Dried hardwood chips (*Eucalyptus dunnii*, calcium content 3756 mg/kg) of 100 gm of dry weight are taken, and moisture content (is 92%). Stock solutions of Na<sub>2</sub>S were prepared by dissolving technical grade flakes of Na<sub>2</sub>S. Impregnation was performed in steel autoclaves with volume. The wood chips are deaerated under a vacuum for 30 minutes. Then, the liquor was sucked into the autoclaves and placed in a steam-heated glycol bath. The heating time to reach the required temperature was 10 minutes. [Note: 10 minutes for heating to temperature]. The Impregnation conditions: temperature (110 °C, 90 minutes), sulfidity (35 %), liquid-to-wood ratio (4:1), EA (18%). The kraft cook was performed for 3 hours 35 minutes with a change in temperature while using different impregnation (aimed for similar kappa numbers). While using white and black liquor + white liquor, we used 170 °C. The green liquor impregnation kraft cook was performed at 145 °C. All cooks are performed in duplicate.

#### **4.2.4. Preparation of green liquor (synthetic) for kraft pulping**

The green liquor was prepared by adding sodium carbonate with a concentration of 0.66M based on the water added after adjusting the EA (18%) and sulfide (35%) liquor to the wood ratio (4:1) with white liquor. The white liquor is made from sodium hydroxide and sulfide stock solutions. The kraft pulping is carried similarly as described in the section. For 50% green liquor, the concentration of sodium carbonate in water is adjusted to 0.33 M.

#### **4.2.5. Black liquor production for kraft pulping**

Black liquor production was carried out in the lab for the impregnation experiments, produced using *Eucalyptus dunnii* wood chips containing calcium same as the wood chips that are used for experimental study (example: kraft cook was performed on wood chips batch with calcium content 3366 mg/kg then the black liquor is produced using same wood chips). The kraft cooking conditions for black liquor production are impregnation temperature (110 °C, 90 minutes), sulfide (35 %), liquid-to-wood ratio (4:1), EA (18%), and kraft cooking at 145 °C for 1 hour. Therefore, the black liquor produced in the lab with hydroxyl and sulfide ions is like industrial black liquor.

### **4.3. Analysis**

#### **4.3.1. Determination of oxalic acid using HPLC**

Approximately 100 mg of dried black liquor samples are diluted with a dilution factor of 1000 with MQ water. The diluted samples were taken and filtered (0.25  $\mu\text{m}$ ) and then transferred to HPLC vials. The oxalic acid was determined by high-performance liquid chromatography (HPLC). The system (Thermo Fischer Scientific, USA) was equipped with a ROA-organic acid column (Thermo Fischer Scientific USA) and a refractive index detector. The mobile phase was a solution of sulphuric acid 0.45 (2<pH<8) at a flow rate of 0.5ml/min. The temperature of the oven was 50 °C.

#### **4.3.2. Dry solid content and ash content**

The method consists of placing a sample (approximately 5ml) in the ceramic crucible and placing it in an oven at a temperature of 105 °C until a steady mass is obtained (about 12 to 15 hours). Next, the residue from the 105 °C drying process is heated to 600 °C for 12 hours in the oven.

#### **4.3.3. Lignin isolation**

Concentrated sulphuric acid (97 to 98%  $\text{H}_2\text{SO}_4$ ) was added to 20 ml of impregnation liquor until the pH of the solution was reached (2-3) and centrifuged at 4800 rpm for ten minutes with 5 minutes intervals. The answer was separated from the precipitate and washed twice with a sulphuric acid solution of (pH=2) and centrifuged. Separated the filtrate, dry in the oven overnight (80°C,) and weighed the dried precipitate. The precipitation was quantified in duplicates.

#### **4.3.4. Viscosity and kappa number determination of pulps**

The viscosity of pulp samples was determined according to the (ISO 5351:2010) standard. Kappa's number of pulp samples was determined according to the ISO 302:2004 standard.

#### **4.3.5. Klason lignin and sugar composition analysis**

All pulp samples were Wiley milled using 40 mesh and then subjected to acid hydrolysis to determine lignin and sugar content. First, 3 ml of 72%  $\text{H}_2\text{SO}_4$  was added to each sample, then placed in a vacuum desiccator for 1 hour and 20 minutes and stirred occasionally. After that, the mixtures were diluted with 84 ml of MilliQ water and placed in an autoclave at 125°C for 1 hour. Next, the samples were filtered through a glass fiber filter using a 3-piece filter. The filtrates were then diluted at 1:10 for sugar analysis and acid-soluble lignin. The insoluble (Klason lignin) part was dried in an oven at 105°C and weighed. Acid-soluble lignin was measured using a Shimadzu UV-2550 UV-VIS-spectrophotometer at an absorbance of 205 nm. Carbohydrate content was determined using an (HPAEC-PAD) Dionex ICS3000 with a pulsed amperometric detector, using a CarboPac PA1 column (Thermo Scientific, USA) with an injection volume of 25 $\mu\text{l}$  and a flow rate of 1 ml/ min. External sugar standards based on the sample were used for calibration. The results were determined as anhydrous sugars and duplicates.

#### **4.3.6. Sample preparation for ICP-OES**

The total metal ion concentration amount has been measured using ICP-OES (Thermo Scientific iCAP 7000 series). Before ICP-OES measurements, approximately 100 mg of sample was taken for each analysis. Add 7 ml of aqua regia solution (2 ml H<sub>2</sub>O<sub>2</sub> + 5 ml HNO<sub>3</sub>) and seal it ultrasonic for several minutes. Then leave the beaker overnight for acid digestion. The sample was then filtered using filter paper and diluted to 50 ml using MQ water. It was further diluted to 1:50 ml using 5% HNO<sub>3</sub>. The final 10 ml of sample dilution is subjected to metal analysis using ICP-OES. (Initial calcium in the stock solution and water 800 is mg/kg)

#### **4.3.7. Residual alkali and sulfide determination**

The residual alkali of black liquor samples was determined according to the SCAN-N 33:94 standard. The Sulphidity of black liquor samples was determined according to the SCAN-N 31:94 standard.

#### **4.3.8. Bleaching and pulp characterization**

The bleaching process was carried out using the DEDED sequence. The pulps of unbleached and bleached pulps are characterized in terms of dry matter content (ISO 638), Drainability (ISO 5267-1), WRV 100 mesh (ISO 23714), Tensile index (ISO 1924-2), Tensile stiffness (ISO 1924-2) and tear index (ISO 1974).

#### **4.3.9. Storage of the samples**

The samples were stored in the refrigerator, left on the table to reach room temperature, and mixed before the respective analysis.

## 5. Results and discussion

### 5.1. Chemical characterization of *E. dunnii* wood samples with different calcium content

The presence of calcium oxalate in the lumen has been reported in numerous studies. Calcium oxalate crystals differ significantly in number and shape. An investigation using scanning electron microscopy reveals the existence of crystals in the lumen of *E. dunnii* samples (Figure 8).

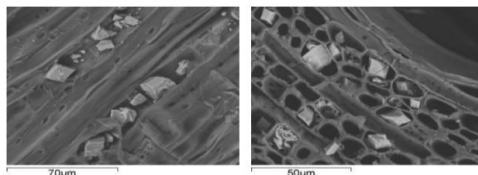


Figure 8: SEM analysis of calcium oxalate crystals within the lumen of *E. dunnii* wood cells with a high calcium content (Vegunta et al., 2022).

For the chemical characterization of *E. dunnii* wood samples, samples mainly grown at various plantations in Uruguay with four distinct calcium contents were chosen (Table 2). The samples were exposed to a wood chemical analysis for lignin content and carbohydrate composition, along with a reference sample of *Eucalyptus globulus*, to see if there were any other significant differences between the models besides the calcium content. All the pieces had a lignin content of 22-25%, cellulose content of 38-43%, xylan content of 10-13%, O-methyl glucuronic acid content of around 5%, a glucomannan content of 2-3%, and pectin content of 2-3%, where polygalacturonic acid dominates over rhamnoglactourans. There is no general tendency for the chemical wood composition to vary with calcium content; however, the sample with the most considerable calcium content, 4668 mg/kg is the exception; both xylan and pectin content seem to be increased by approximately 25% (Table 2). These two polysaccharides contain uronic acids and can thus bind to calcium ions. Fucose and glucuronic acid traces were also found (Lindberg et al., 1973). The anhydrosugar's molecular weight was used to calculate the molar content. The only clear trend among the *E. dunnii* samples with varying calcium content was that the sample with the most significant calcium content (*E. dunnii* 4668 mg/kg) contained more xylose, arabinose, galacturonic acid, and 4-O-methyl glucuronic acid and less glucose. Therefore, it is plausible that the difference between *E. dunnii* 4668 mg/kg and the remaining *E. dunnii* samples would be that the former contains the most xylan and polygalacturonic acid and less cellulose.

Table 2: Characterization *E. dunnii* wood species with different levels of calcium content in wood.

Wood	Calcium content	Lignin, Mass% on wood	Sugar composition (ass% on wood, mmol/kg wood)								sum
	mg/kg		Glucose	Xylose	Galactose	Mannose	Arabinose	Rhamnose	Galacturonic acid	4-O-methyl Glucuronic acid	
<i>E. dunnii</i> E.d 705	705	24.4±0.1	40.9± 2.2 2522	8.8±0.3 666	1.2±0.1 74	0.6±0.1 37	0.3±0.0 23	0.3±0.0 21	1.9±0.4 108	0.9±0.1 47	77.4
<i>E. dunnii</i> E.d 966	966	24.0±0.8	43.4±0.9 2677	10.9±0.0 825	0.9±0.0 56	1.5±0.2 93	0.3±0.0 23	0.3±0.0 21	1.8±0.4 102	1.1±0.1 58	82.2
<i>E. dunnii</i> E.d 1500	1500	25.6±0.6	42.8±1.5 2640	10.2±1.2 772	0.9±0.0 56	1.1±0.2 68	0.3±0.0 23	0.3±0.1 21	1.8±0.2 102	0.9±0.1 47	81.9
<i>E. dunnii</i> E.d 3668	3366	22.7±0.1	42.9±0.7 2646	9.4±0.2 712	1.4±0.1 86	0.9±0.4 56	0.3±0.0 23	0.4±0.1 27	1.4±0.0 79	0.8±0.1 42	78.3
<i>E. dunnii</i> E.d 4668	4668	24.2±0.1	38.1±2.6 2350	11.5±1.0 870	0.7±0.1 43	1.1±0.1 68	0.4±0.0 30	0.4±0.1 27	2.2±0.2 125	1.3±0.2 68	78.1
<i>E. globulus</i>	NA	22.7±1.2	42.5±1.5 2621	11.6±1.1 878	1.0±0.1 62	1.4±0.4 86	0.3±0.0 23	0.4±0.1 27	1.4±0.1 79	1.3±0.1 68	80.8

With different calcium content within the wood, no considerable difference in wood density was observed (see Table 3).

Table 3: Density of *E. dunnii* wood species with different calcium content.

Sample name	Species	Calcium content (mg/kg)	Density (g/cm <sup>3</sup> )
<b>E.d. 705</b>	<i>E. dunnii</i>	705	0.563
<b>E.d. 870</b>	<i>E. dunnii</i>	870	0.546
<b>E.d. 1500</b>	<i>E. dunnii</i>	1500	0.515
<b>E.d. 4668</b>	<i>E. dunnii</i>	4668	0.580

## 5.1. Understanding the impact of the act of calcium on the rate of delignification (Paper 1)

The corresponding wood samples were subjected to lab-scale kraft pulping at an L: W ratio of 1:4, EA 18%, and sulfidity of 35% with impregnation temperatures of 110 °C and cooking temperature of 145 °C. Samples with a calcium content of 1500 mg/kg defibrated well under these conditions, with reject contents of 1.5 %. In contrast, samples with a calcium content of 3366 mg/kg (Table 1) needed an elevated cooking time of 165 °C to attain comparable defibration. Even at high cooking temperatures, the sample with the most significant calcium content (*E. dunnii* 4668 mg/kg) could not be defibrated with acceptable levels of rejects. The wood qualities were selected to conduct a more detailed characterization of pulping properties, with calcium content of (705, 870, and 1500 mg/kg), and pulped at various H-factors and characterized for kappa number, yield, and viscosity. Figure 9 shows that the delignification is significantly and noticeably slower with higher calcium content. This observation corresponds to the findings of Saltberg et al. (2009) on various hardwoods with varying calcium contents.

However, as illustrated in the figure, the lines are nearly parallel (Figure 9). Because there is no notable change in original lignin content among these samples (Table 2), the significant gaps in the delignification rate between the samples occur early in the kraft cook, indicating that the adverse effects of calcium peak early in the process and decline after that. The hexeneuronic acid content of the pulp was also determined. However, there was no notable change between the wood samples with various calcium content (Figure 10), implying that calcium does not affect hexeneuronic acid formation. The reject content was also prominent in the pulping experiments with higher calcium content wood than in the lower calcium content wood (Figure 11), which corresponds to a relatively low delignification rate (Figure 11). Higher calcium content, however, has noticeable yield effects (Figure 9). With more significant yield losses while the calcium content is relatively high. Furthermore, the lines in the graph are nearly parallel, indicating that the detrimental consequences for yield are present primarily during the initial stage of pulping. These two effects, slow delignification rate (Figure 9) and increased yield losses (Figure 12), significantly affect kraft pulping selectivity by calcium content as shown in Figures 7 to 10.

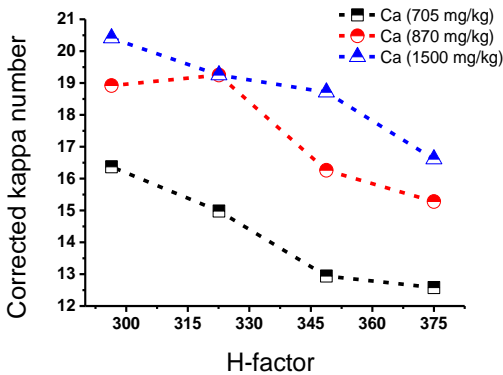


Figure 9: Corrected kappa number as a function of H-factor; corrected kappa number means that influence from hexeneuronic acid has been removed.

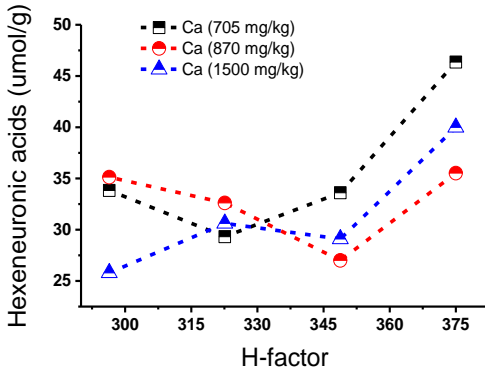


Figure 10: Hexeneuronic acid ( $\mu\text{mol/g}$ ) of unbleached kraft pulp produced with white liquor using different calcium-containing *E. dunnii* wood chips as a function of H-factor.

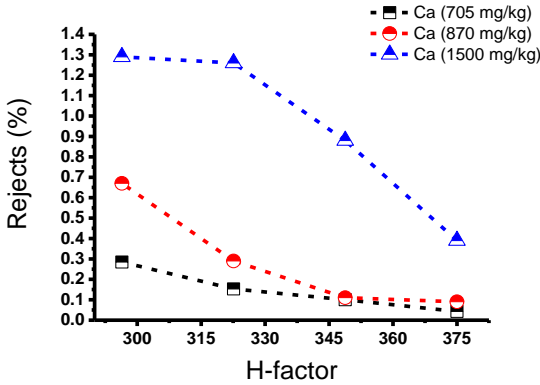


Figure 11: Rejects (%) of kraft pulp produced with white liquor using different calcium-containing *E. dunnii* wood chips as a function of H-factor.

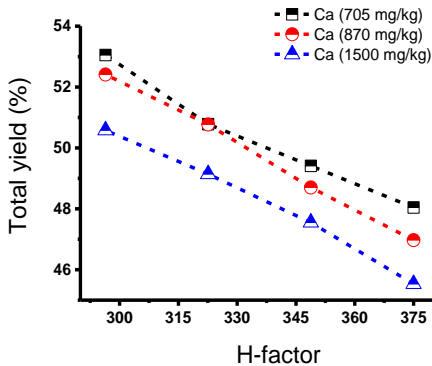


Figure 12: Total yield (%) of kraft pulp produced with white liquor using different calcium-containing *E. dunnii* wood chips as a function of H-factor.

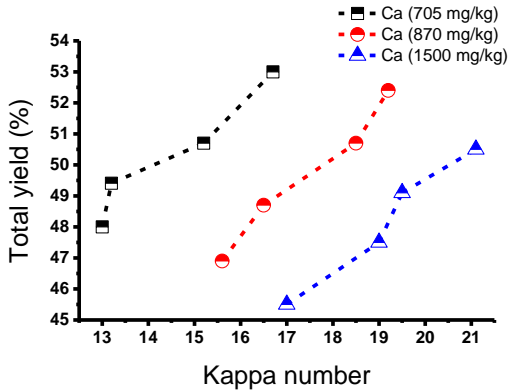


Figure 13: Total yield (%) of pulps produced with white liquor using different calcium-containing *E. dunnii* wood chips as a function of kappa number.

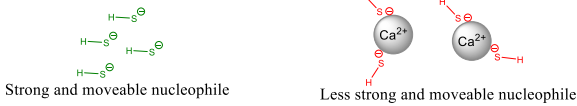
### 5.1.1. Suggestion for a possible mechanism for calcium on the rate of delignification (Paper 1)

The rate of delignification is affected by calcium; we can see at least four possible outcomes can be observed in the figure and below explained in detail:

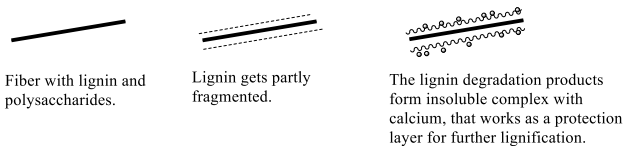
1. Delignification reactions, or lignin-degrading interactions induced by a strong nucleophile HS, slow down. The  $\text{Ca}^{2+}$  ion may form strong complexes with hydrogen sulfide ions, reducing the effect of solid nucleophiles (Figure 14).
2. The accessibility of nucleophiles to lignin can be reduced by precipitating soluble lignin fragments with calcium ions and creating a layer that protects the lignin in the fiber from nucleophilic degradation (Figure 14).
3. Calcium ions in the cell wall specifically bind with carboxylic acids, making it more compact and thus less accessible to delignifying chemicals.
4. Reactions that counteract delignification are accelerated. This is possible because lignin fragments form novel and stable chemical bonds during kraft pulping conditions. Sometimes when calcium ions aggregate lignin degradation products, this may speed up the formation of new bonds, lowering the rate of delignification (Figure 14).

It has previously been proposed that calcium-mediated lignin precipitation harms kraft pulping (Bogren et al., 2009; Flemming, 1983; Saltberg et al., 2009). The below picture is adapted from paper 1 (Vegunta et al., 2021).

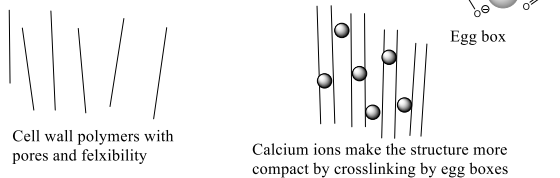
### a) Inactivation of hydrogen sulphides



### b) Creation of protecting layer



### c) Making the cell wall more compact



### d) Formation of novel stable bonds

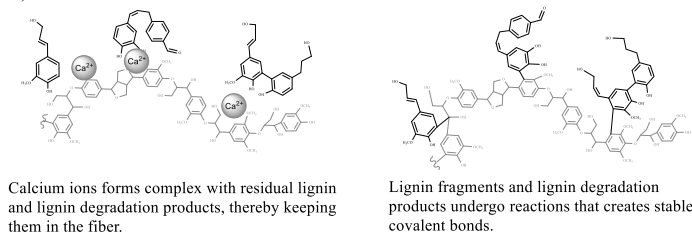


Figure 14: Mechanisms explaining the negative effect of calcium on lignin degradation.

The adverse effects are concentrated in the early stages of pulping. One possibility is that the calcium oxalate crystals in the lumen dissolve quickly when they encounter the high pH in the pulping liquor. The calcium ions then move into the cell wall, disrupting the liquor. The calcium ions then move into the cell wall, disrupting pulping in two ways, as described above. Later in the pulping process, calcium either leaves the cell wall or becomes "inactive" due to the formation of stable crystals (Figure 8). Calcium oxalate solubility tends to increase with temperature, and it seems that high pH can aid in crystal dissolution (Nancollas & Tomazic, 1979). Calcium ions are also known to have an affinity for cellulose, lignin, and hemicellulose (Torre et al., 1992). As a result, it seems plausible that calcium ions may move from the lumen into the cell wall faster in the pulping process. As a result, a calcium-rich layer will form. Calcium could then disrupt delignification and catalyze alkaline hydrolysis, as discussed below (Figure 15).

Moreover, when organic black liquor products are created, the calcium may form a stable complex with the components present, resulting in chemical inactivation, but the damage has already occurred (Figure 15). Saltberg (2010) discovered a similar effect, more substantial when eucalypt was used than when other hardwoods were used. Eucalyptus black liquors contain more calcium than other hardwoods (Linden et al., 1996).

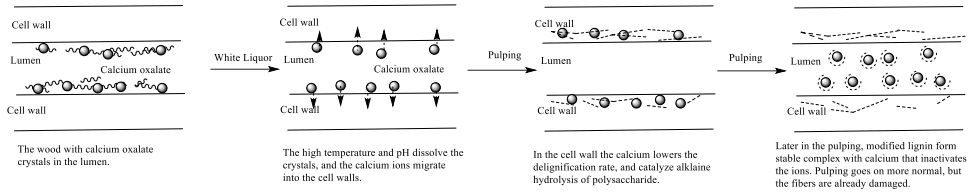


Figure 15: Mechanism explaining the negative effect of calcium ions is concentrated at the beginning of pulping (Vegunta et al., 2022).

## 5.2. Understanding the impact of calcium in polysaccharide degradation (paper1)

The cause of yield loss concerning calcium content is significant and probably caused not solely by calcium crystal dissolution (Figure 8 and Table 2). The most probable explanation for slower delignification with higher calcium content is attributed to polysaccharide degradation. As a result, the pulps were subjected to carbohydrate analysis. Figure 12 shows that cellulose is degraded. However, the lines appear parallel, indicating that critical effects also occur early in the pulping process. The carbohydrate losses throughout kraft pulping are primarily caused by three types of reactions: alkaline hydrolysis (Jansson & Lindberg, 1960), peeling reaction (Hansson & Hartler, 1970), and dissolutions (Aurell & Hartler, 1965).

The alkaline hydrolysis reaction can indirectly induce the other two responses, i.e., the reducing ends created in alkaline hydrolysis will be starting points for the peeling response, and shorter polysaccharides have generally higher solubility (Sjöström, 1993). Because only short cellulose oligosaccharides are soluble, the dissolution reaction primarily affects hemicellulose (Correia et al., 2014). Moreover, if the yield losses are caused mainly by alkaline hydrolysis stimulated by calcium ions, the viscosity of the pulp, i.e., the degree of polymerization of polysaccharides, is expected to decrease with increasing calcium content in the wood (Figure 17). However, such an effect is not assumed if increased peeling is the cause. As a result, viscosity measurements were taken to see if the calcium concentration affected the cellulose polymerization degree (Figure 16) (Vegunta et al., 2022).

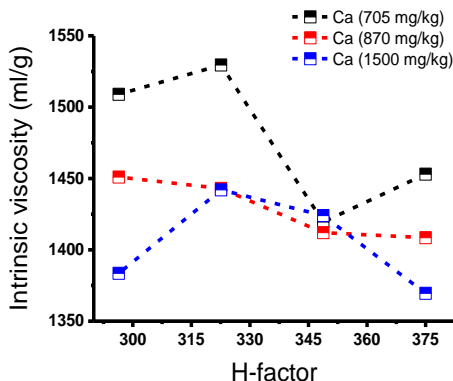


Figure 16: Intrinsic viscosity (ml/g) of unbleached pulp produced using white liquor with different calcium-containing *E. dunnii* wood chips as a function of H-factor.

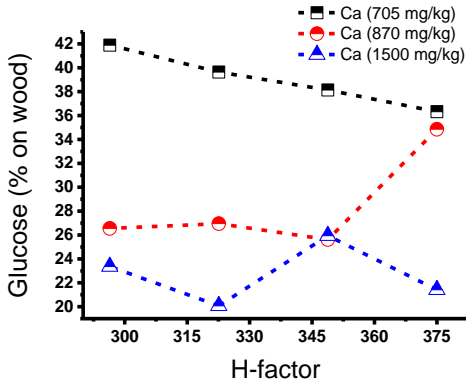


Figure 17: Glucose (% on wood) of unbleached pulp produced with white liquor using different calcium-containing *E. dunnii* wood chips as a function of *H*-factor.

### 5.2.1. Suggestion for a possible mechanism for calcium on polysaccharide degradation (Paper 1)

The ability of calcium to degrade polysaccharides can be explained by the fact that calcium ions catalyze polysaccharide degradation. This effect of the catalytic activity of calcium salts has already been reported (Marques et al., 2013). Figure 18 depicts a hypothetical mechanism of alkaline hydrolysis catalysis by calcium (II) ions. The tool below explains that the calcium ions form a complex with a glycosidic bond of cellulose by removing hydrogen ions. A positive charge of the calcium ion stimulates the deprotonation of alcohol, making it a strong nucleophile. This strong nucleophile attacks C1 carbon and breaks the glycosidic bond, and water molecules form stabilized reaction products.

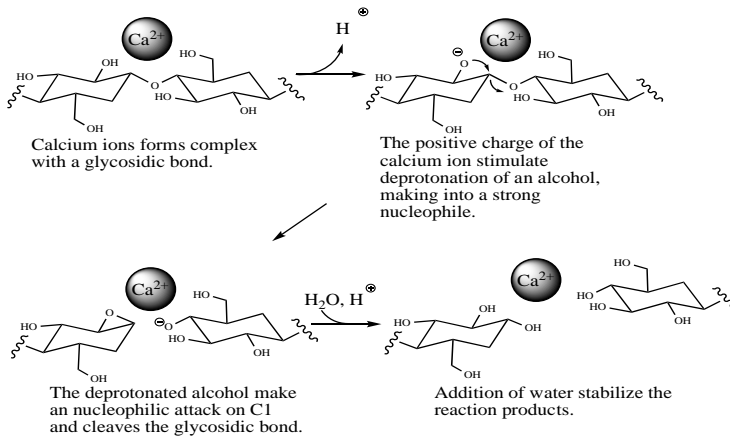


Figure 18: Mechanism explaining the role of calcium ions in alkaline hydrolysis of polysaccharides.

### 5.3. Investigation of the role of different cooking liquors during the impregnation stage and kraft pulping

As mentioned in section 14.3, the adverse effects on yield are mainly present in the initial pulping stage. Based on this hypothesis, the calcium content in the spent black liquor during the impregnation stage. In this work, the *E. dunnii* wood chips containing a calcium content of 3368 mg/kg were investigated. The cooking liquor conditions EA (18%), sulfidity (35%), and impregnation temperature (110 °C) are kept the constant throughout the study. The spent black liquor was collected at different points (20, 40, 60, and 90 minutes) throughout the impregnation stage. The impregnation liquors subjected are white liquor (reference), black + white liquor, and green liquor (synthetic). The preparation of these liquors is discussed in Material and methods. The impregnation study is focused on the characterization of spent black liquor lignin precipitation (wt %), dry solids (%), ash content (%), residual alkali (mol/l), and oxalic acid. All experiments are done in duplicate.

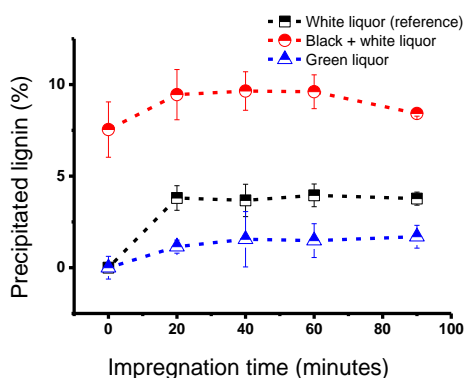


Figure 19: Precipitated lignin (%) in spent black liquor drained from chips after impregnation as a function of impregnation time (minutes).

The precipitated lignin content (%) concerning impregnation time in the spent black liquor during impregnation is investigated (figure 19). There is no significant change observed over time. However, lower lignin precipitation from spent black liquor obtained from green liquor (synthetic) is observed. One of the reasons could be that under applied conditions, the rate of reaction is slow, leading to the lower dissolution of lignin. On the other hand, a higher amount of lignin precipitation is observed from spent black liquor obtained from black + white liquor because there is a certain amount of lignin in black liquor from the beginning.

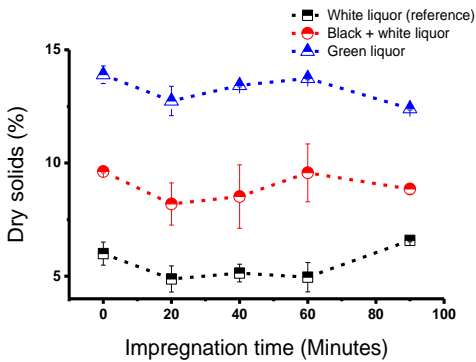


Figure 20: Dry solids (%) in spent black liquor drained from chips after impregnation as a function of impregnation time (minutes).

Dry solids concerning impregnation time present in the spent black liquor during impregnation are investigated (figure 20). Increased dry solids (%) are observed in spent liquor produced using green liquor. One of the reasons could be the higher amounts of carbonates and sodium present initially in the green liquor (synthetic). However, after 20 minutes of all spent black liquor, there is a decrease in dry solids, which explains one of the reasons for the penetration of sodium ions into wood chips.

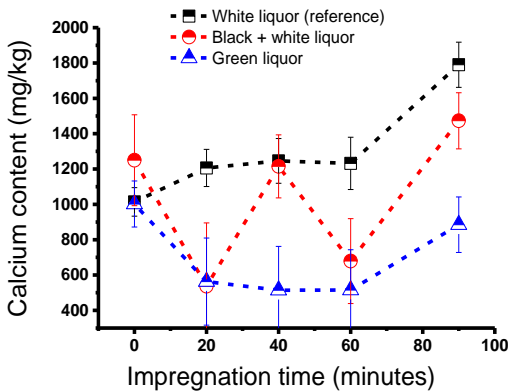


Figure 21: Calcium content in black liquor (mg/kg) in spent black liquor drained from chips after impregnation as a function of impregnation time (minutes).

Calcium content concerning impregnation time present in the spent black liquor during impregnation is investigated (figure 21). No significant change was observed in calcium content for 40 minutes, regardless irrespective of cooking liquor. However, as time increases to 60 minutes, the calcium content increases in spent black liquor, irrespective of cooking liquor. This shows that the calcium content in spent black liquor increases after 60 minutes during the impregnation stage. The lower calcium content observed in spent black liquor produced using green liquor (synthetic) could be why more calcium follows the fiber line during the impregnation stage.

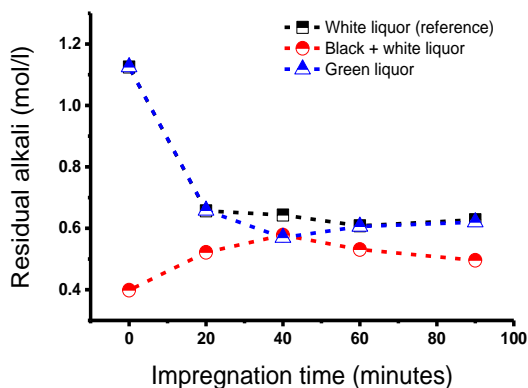


Figure 22: Residual alkali (mol/l) in spent black liquor drained from chips after impregnation as a function of impregnation time (minutes).

Residual alkali (mol/l) concerning impregnation time present in the spent black liquor during impregnation was investigated (figure 22). No significant change was seen in our study's residual alkali with regard to cooking time. Previous studies have shown increased alkali consumption with an increase in time. However, the reason might need to be explained clearly in this case.

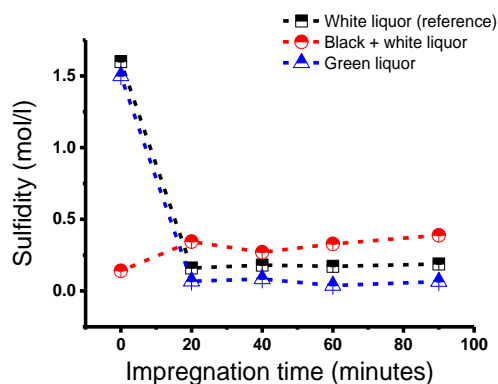


Figure 23: Sulfidity (mol/l) in spent black liquor drained from chips after impregnation as a function of impregnation time (minutes).

The sulfidity (mol/l) of the impregnated spent black liquor is investigated with respect to impregnation time (figure 23). There is no noticeable change in sulfidity over time. However, spent black liquor made from green liquor has less sulfidity. This also explains how green liquor impregnation offers a chemical reaction foundation for increasing selective delignification during the impregnation process by activating sulfate ions. By using selective delignification, the  $\beta$ -O-4 bonds of lignin and methyl groups are broken.

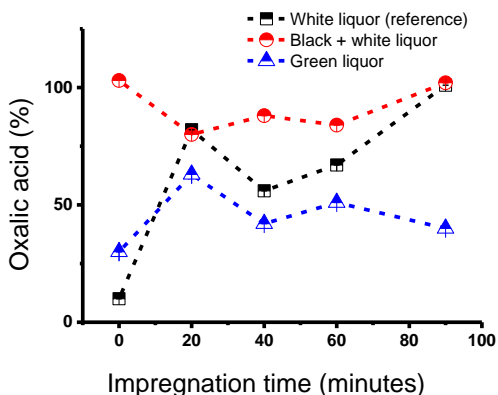


Figure 24: Oxalic acid (wt%) in spent black liquor drained from chips after impregnation as a function of impregnation time (minutes).

The oxalic acid (wt%) of the impregnated spent black liquor is investigated with regard to impregnation time (figure 24). Compared to white liquor (reference), green liquor impregnation has a lower oxalic acid content. However, there is a slight increase in oxalic acid content above 60 minutes observed in spent liquor obtained from white liquor (reference) and black + white liquor impregnation. The chemistry of wood components with cooking liquor could explain this.

### 5.3.1. Role of different cooking liquors on kraft pulping (Paper 2)

As we saw at the beginning of the study (section 5.2), calcium content leads to slower delignification and more cellulose degradation using *E. dunnii* with varying calcium content (705, 870, and 1500 mg/kg) and presents possible mechanisms explaining these effects. Even under extreme conditions, kraft pulping with lab-made white liquors was nearly impossible for samples with more significant calcium than 3000 mg/kg. However, high calcium content had less impact on industrial-scale pulping, though severe problems did arise. The difference between lab and industrial scale is that black liquor is typically added to wood chips, whereas white liquor may be polluted/contaminated with green liquor because of insufficient causticization. As a result, before pulping, we tested impregnation (section 5.4) and subjected to kraft pulping with lab scale-made white liquor, black +white liquor, and green liquor. The black liquor we produced has similar [OH]<sup>-</sup> and [HS]<sup>-</sup> concentrations compared to industrial black liquor (appendix 1).

Kraft pulping was accomplished by aiming the pulp with similar kappa number. The cooking temperature used had a varying H-factor to achieve the desired kappa number. Temperatures were raised from 138 °C to 140 °C, 145 °C, 155 °C, 165 °C and 170 °C. In this study, *E. dunnii* wood chips with a calcium content of 3368 mg/kg were used. Green liquor (synthetic) pulps produced a higher yield than white liquor (reference) and black + white liquor at the targeted kappa number. Figure 25 illustrates the overall change in screened pulp yield. Green liquor significantly influenced the rate of delignification of high calcium-content wood chips. Even with a lower H-factor, using green liquor it was possible to pulp high calcium-containing wood chips with lower rejects to achieve lower kappa (Figures 26 and 27). Several studies have found that green liquor induced kraft pulping significantly impacts the delignification rate and pulp quality (Andrews & Chang, 1985; Ban et al., 2004); Klevinska & Treimanis, 1997; Svedman & Tikka, 1998). Our present study also found this pattern, except that we used wood chips with a high calcium content (3368 mg/kg).

According to our hypothesis, the high carbonate content in the green liquor binds to calcium and forms complexes, causing the lignin moieties to detach. Therefore, using green liquor as a cooking liquor could lead to a boost in delignification rate and pulp strength. As a result, adding green liquor

is a way to significantly improve the kraft pulping of wood with high calcium content. On the other hand, the study hypothesized that the calcium ions could reduce delignification by different mechanisms (section 5.2.1) and catalyze the alkaline hydrolysis of cellulose (section 5.3). However, the impact on viscosity could be more evident regarding H-factor, which could be explained by the fact that defibrillation occurred much earlier in the pulping process for the green liquor-treated samples.

Moreover, at a given kappa number, the viscosity is much higher for the green liquor pulp samples (figure 28), indicating significantly improved selectivity of pulping. Therefore,  $\text{Na}_2\text{CO}_3$  in the green liquor (synthetic) probably inactivates the calcium ions, making carbonate ions a likely candidate. Figure 29 below illustrates a speculative explanation for this. The central idea is that calcium forms inert, stable, and insoluble calcium carbonate crystals that do not interfere with kraft pulping. However, if this is correct, calcium should remain in the fiber during the kraft cook and not be transferred to the pulping liquor in significant amounts. Indeed, the data in figure 28 shows that green liquor-treated pulp contains significantly more calcium than white and black liquor-treated pulp.

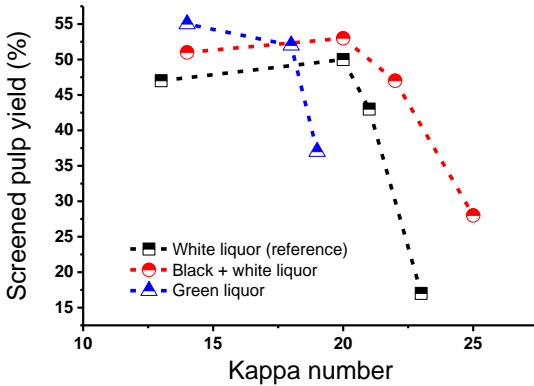


Figure 25: Screened pulp yield (%) of unbleached kraft pulp produced using different cooking liquors as a function of kappa number.

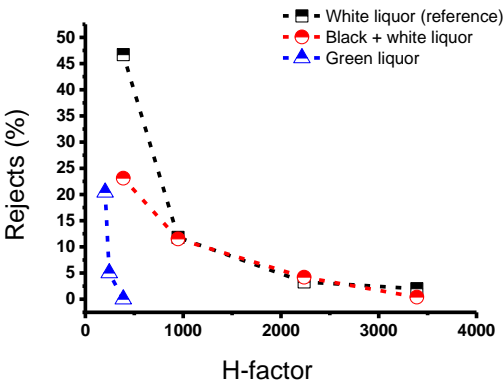


Figure 26: Reject (%) of unbleached kraft pulp produced using different cooking liquors as a function of H-factor.

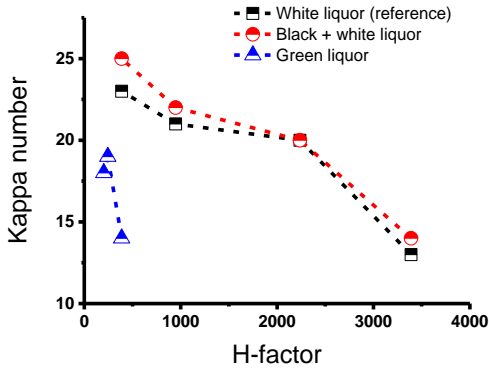


Figure 27: Kappa number of unbleached kraft pulp produced using different cooking liquors as a function of H-factor.

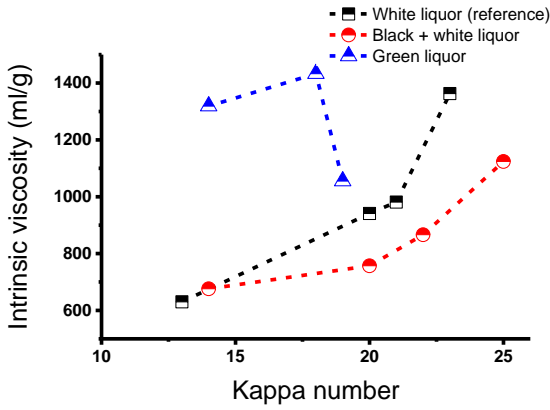


Figure 28: Intrinsic viscosity (ml/g) of unbleached kraft pulp produced using different cooking liquors as a function of kappa number.

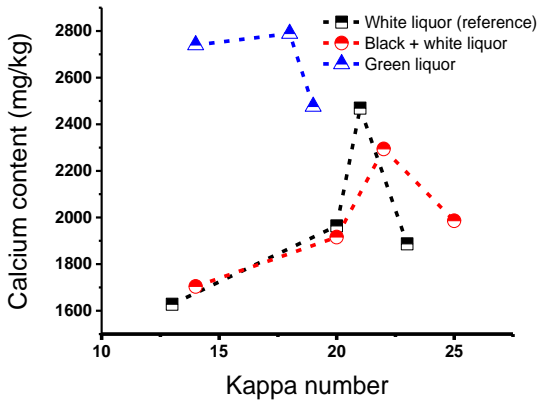


Figure 29: Calcium content of unbleached kraft pulp (mg/kg) produced using different cooking liquors as a function of kappa number.

Figure 28 shows the hypothetical explanation of the chemistry of cooking liquors concerning calcium oxalate ions in wood chips. Previous studies have shown that calcium oxalate exists in the lumen of wood (figure 6) (Adadi et al., 2003). When these wood chips are subjected to kraft pulping with highly alkaline white liquor, oxalate and calcium ions are degraded into the cell wall. These calcium ions speed up polysaccharide degradation while slowing delignification by damaging products that form calcium complexes and are transferred into the black liquor. As a result, the cell wall has been completely damaged, and polysaccharides have been damaged. Calcium oxalates are also degraded in green liquor kraft pulping due to similar alkaline conditions. Carbonate ions in green liquor form stable and inert calcium carbonate crystals and remain in the lumen. As a result, calcium does not interfere with kraft pulping or polysaccharide degradation.

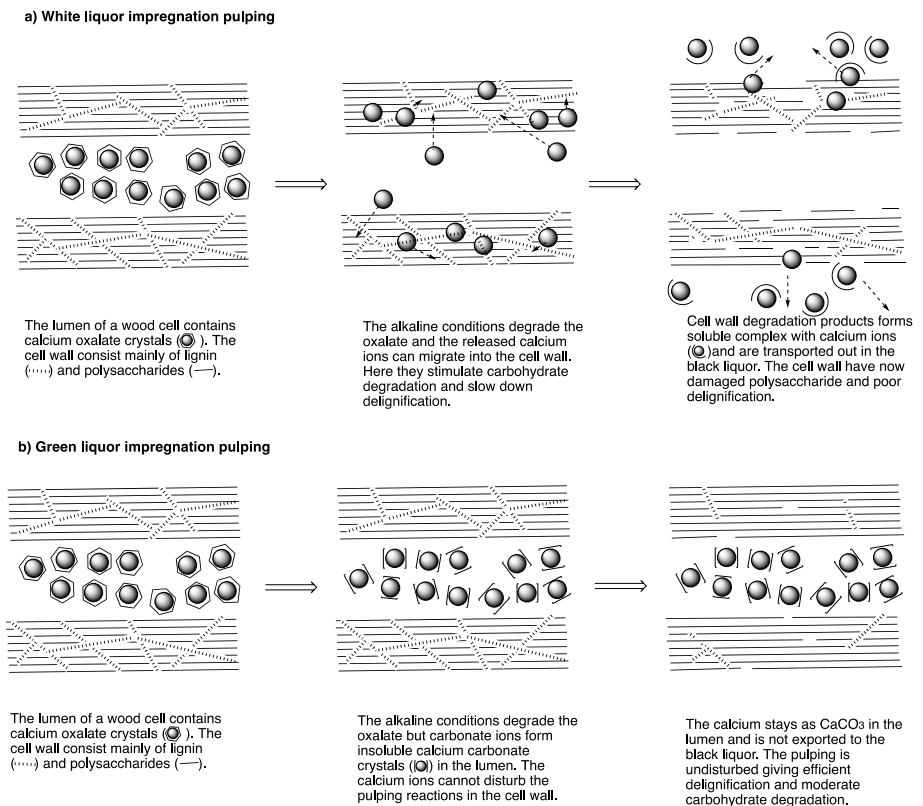


Figure 30: Hypothetical explanation for the strong positive effect of green liquor impregnation.

To determine if the effect was similar, we performed kraft pulping on wood chips with a high calcium content (4668 mg/kg). These wood chips cannot be pulped (mostly rejects (%)) under these cooking conditions when white liquor is used. However, under similar conditions, wood chips can be pulped with green liquor (Table 4). The cooking liquor conditions are EA 18%, sulfidity 35% and liquor to wood ratio 4:1. The kraft cooking conditions used are impregnation (110 °C, 90 minutes) and kraft cook (145 °C, 210 minutes). Ramping time took 10 minutes.

Table 4: Details regarding pulp produced using high calcium-containing wood chips (4668mg/kg) using green liquor.

<b>Green liquor (synthetic) 100% (0.66M)</b>	
<b>Rejects (%)</b>	0.1
<b>Total yield (%)</b>	52
<b>Screened pulp yield (%)</b>	52
<b>Kappa number</b>	18.6
<b>Dry solids in black liquor (%)</b>	18
<b>Ash content in black liquor (%)</b>	59
<b>Precipitated lignin (%)</b>	4.7
<b>Glucose on wood (%)</b>	31.8
<b>Xylose on wood (%)</b>	9.4
<b>Klason lignin (%)</b>	3.97
<b>Viscosity (ml/g)</b>	1369
<b>Calcium content in pulp sample (mg/kg)</b>	4138
<b>HexA in unbleached pulp (<math>\mu\text{mol/g}</math>)</b>	11.5
<b>HexA in bleached pulp(<math>\mu\text{mol/g}</math>)</b>	11

#### 5.4. Comparison of bleaching of kraft pulps obtained using different cooking liquors (Paper 2)

Section 5.4 showed that green liquor positively affects the kraft pulping of high calcium-content wood chips. One potential issue would be if the high mineral content interfered with pulp bleaching. As a result, additional batches of pulp with high calcium content were prepared as a control and subjected to bleaching experiments. Pulp was produced at a specific kappa number to investigate the effect of pulp quality and strength. This bleaching experiment used wood chips with a calcium content of 3758 mg/kg. Using three different impregnation liquors, the wood chips were kraft cooked to a similar kappa number.

Table 5: Characterization of kraft cooks subjected to bleaching experiments.

	<b>White liquor (reference)</b>	<b>Black + white liquor</b>	<b>Green liquor (synthetic)</b>
<b>Rejects (%)</b>	1.3	0	0
<b>Total yield (%)</b>	45.7	46.3	51.5
<b>Screened pulp yield (%)</b>	44.4	46.3	51.5
<b>Kappa number</b>	17	16	16.1
<b>Dry solids in black liquor (%)</b>	14	23	16
<b>Ash content in black liquor (%)</b>	59	60	59
<b>Precipitated lignin (%)</b>	5.1	9.2	5.7
<b>Viscosity (ml/g)</b>	882	896	1364
<b>Calcium content in pulp sample (mg/kg)</b>	1925	2362	2580
<b>HexA in unbleached pulp (<math>\mu\text{mol/g}</math>)</b>	22.5	31.3	13.5

The pulp yield, reject content, kappa number, klason lignin, precipitated lignin, dry solids, and ash content in the black liquor, Hexenuronic acid, and viscosity of unbleached pulps are summarized in table 5. At the same kappa number, the kraft cook performed with green liquor impregnation showed higher pulp yield, delignification rate, and pulp viscosity, i.e., similar tendencies as in the above-described experiments (section 5.4). When using green liquor impregnation, the total yield increased by 5%. The pulps were kraft pulped under similar chemical conditions but with a different H-factor

to achieve similar kappa numbers. Under similar cooking H-factor, good kraft cooks are not produced using white liquor (reference) and black + white liquor (section 5.4).

The total inorganic metals present in the unbleached pulp samples produced using different impregnation liquors are shown in table 5. The calcium content of unbleached pulp produced by green liquor impregnation is slightly higher than that of unbleached pulp produced by white and black + white liquor (table 5). That indicates that the calcium content is following the fiber line rather than being washed with black liquor while using green liquor. Bleaching experiments using the sequence DEDED were performed on pulps with similar kappa numbers treated with white liquor. The pulps produced using green liquor can bleach without affecting the pulp properties. Although calcium ions do not appear to interfere significantly with bleaching stages, there is a risk that calcium carbonate crystals in the pulp could trap transition metal ions that could disrupt bleaching.

The intrinsic viscosity of pulp samples impregnated with green liquor was much higher than that of white, black, + white liquor. Which means it is a good indication of the pulp's improved mechanical properties. These findings are consistent with the figure (see figures 32 and 33) tensile strength and tear index results obtained from the unbleached and bleached pulp. At a given kappa number, the viscosity (figure 29) of unbleached and bleached pulp produced with white and black + white liquor is lower than that of green liquor impregnated pulp. One reason for low viscosity is the higher H-factor used in the production of pulp from white liquor and black + white liquor. The results in figure 31 clearly show that most of the benefit of green liquor treatment in high viscosity was retained after bleaching, which was also reflected in the improved tensile index (figure 32) and tear index (figure 33) for bleached pulps that had previously been treated with green liquor. PFI refining improves pulp fiber paper-making properties, allowing pulp fibers to bond better and improving pulp strength. Figure 35 shows unbleached and bleached pulps going through PFI refining at 3000 revs (revolutions). Green liquor-impregnated pulp has a high tensile index and tear index in both cases. The improved strength properties of green liquor treated pulps may be due to a high hemicellulose content on the fiber surfaces green liquor treatments allow for faster pulping and less alkaline hydrolysis, resulting in increased fiber-fiber interaction. However, this may result in increased drainage resistance, which appears to be the case (figure 34). The data in figure 35 shows that bleaching worked just as well for the green liquor-treated pulps as it did for controlling brightness development. The data in figure 29 indicates that calcium carbonate crystals in pulps do not pose a significant problem in bleaching.

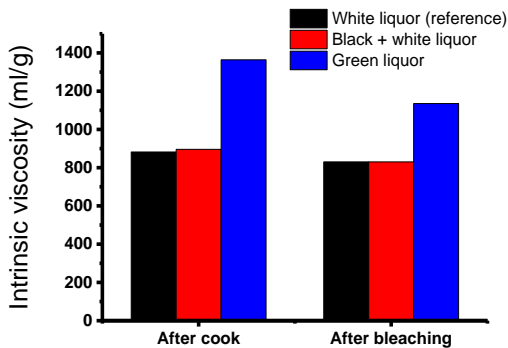


Figure 31: Intrinsic viscosity (ml/g) of kraft pulps (unbleached and bleached DEDED) produced at targeted kappa number using different cooking liquor.

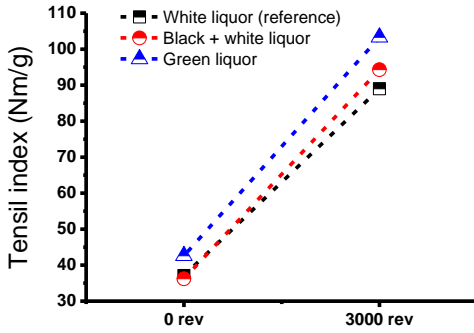


Figure 32: Tensile index (Nm/g) of pulps produced at targeted kappa number using different cooking liquor.

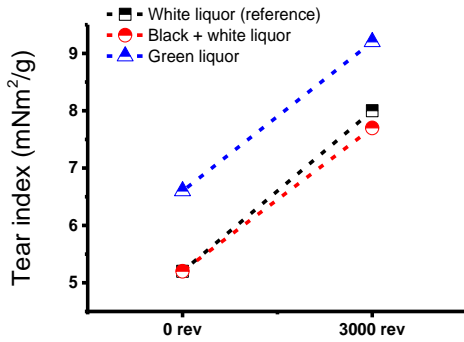


Figure 33: Tear index (mNm<sup>2</sup>/g) of kraft pulps produced at targeted kappa number using different cooking liquor.

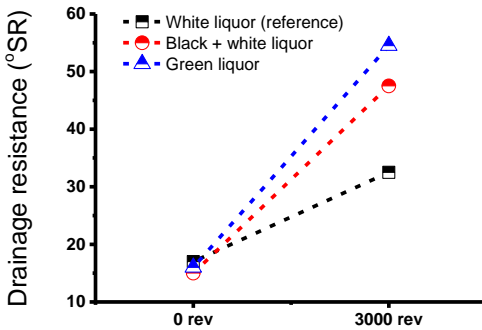


Figure 34: Drainage resistance of kraft pulps produced at targeted kappa number using different cooking liquor.

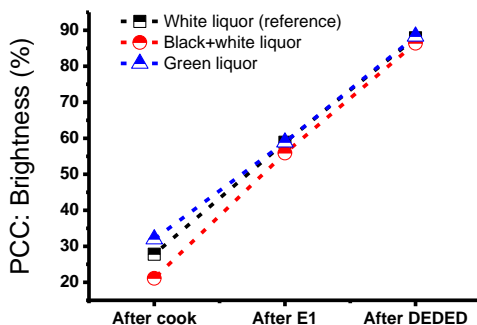


Figure 35: PCC brightness of kraft pulps (unbleached and bleached DEDED) produced at targeted kappa number using different cooking liquor.

## 5.5. Investigation of reduced concentration of green liquor during kraft pulping and bleaching

Lab scale kraft pulping of high calcium content wood chips (4668 mg/kg) were carried out using two types of green liquor (synthetic). The two types of green liquor were marked as 100% green liquor (0.66M concentration of  $\text{Na}_2\text{CO}_3$ ) and the other green liquor was marked as 50% green liquor (0.33M concentration of  $\text{Na}_2\text{CO}_3$ ). The table-6 below shows kraft pulp yield, rejects, kappa number, viscosity, calcium content, and HexA range in the pulp sample. Table 6 also displayed the dry solids, ash content, and precipitated lignin content in spent black liquor. When *E. dunnii* with high calcium content were subjected to kraft pulping with white liquor under similar conditions, the wood chips were difficult to pulp. This study confirmed that the calcium content in the wood chips, as described in Section 5.2, significantly influenced their behavior. Comparing the total yield of kraft pulps using different concentrations of green liquor (table 6) revealed that lower concentrations increased output yield by 1%. Despite a slightly lower yield with higher concentrations, 100% green liquor has more calcium in the pulp than 50% green liquor.

This study was performed to see if green liquor shows a similar effect even at lower concentrations of green liquor. Moreover, reduced concentrations of green liquor can pulp high calcium-containing wood chips without affecting their pulp properties. One reason could be that lower concentrations of green liquor slow down hemicellulose dissolution rates and increase delignification (Bykova et al., 1997). This can be demonstrated by investigating the carbohydrate content of the unbleached and the bleached pulp. The HexA pulps are compared before and after bleaching of pulps made with 100% and 50% green liquor, respectively. After bleaching, the score is reduced by about 0.5 points for HexA in both cases, and higher levels of HexA were found in pulps produced with 100% green liquor versus 50% green liquor. This result demonstrates that the yield increase in the latter case was not due to HexA. That is significant because we know that lignin and HexA are both removed during bleaching. Therefore, their weights are not to be considered during yield calculations.

Table 6: Characterization of kraft cooks produced using 100% and 50% Green liquor.

<b>Green liquor (synthetic)</b>	<b>100% (0.66M)</b>	<b>50% (0.33M)</b>
<b>Rejects (%)</b>	0.1	0.2
<b>Total yield (%)</b>	52	53
<b>Screened pulp yield (%)</b>	52	53
<b>Kappa number</b>	18.6	18
<b>Dry solids in black liquor (%)</b>	18	17
<b>Ash content in black liquor (%)</b>	59	60
<b>Precipitated lignin (%)</b>	4.7	5.6
<b>Viscosity (ml/g)</b>	1340	1396
<b>Calcium content in pulp sample (mg/kg)</b>	4138	3063
<b>HexA in unbleached pulp (<math>\mu\text{mol/g}</math>)</b>	11.5	10.9
<b>HexA in bleached pulp (<math>\mu\text{mol/g}</math>)</b>	11	0.8

The figures below show the pulp characteristic such as viscosity (Figure 36), brightness (Figure 37), yield (Figure 38), and kappa number (Figure 39) of unbleached and bleached pulps. Lower concentrations of green liquor demonstrated good pulp qualities before and after bleaching experiments. With a lower concentration of green liquor (50% in this work), the brightness, yield, intrinsic viscosity were significantly higher and lower kappa number was achieved. Several factors could be responsible for this, namely hemicellulose dissolution and removal of HexA during bleaching at higher concentrations of green liquor. Investigating the monosaccharide content (glucose and xylose) of pulps produced at these concentrations will aid in better understanding the phenomenon.

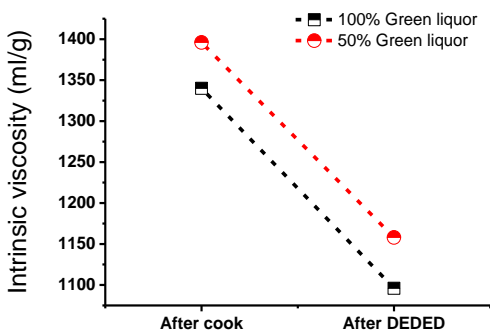


Figure 36: Intrinsic viscosity (ml/g) of pulps after kraft pulping (unbleached) and after DEDED (bleaching).

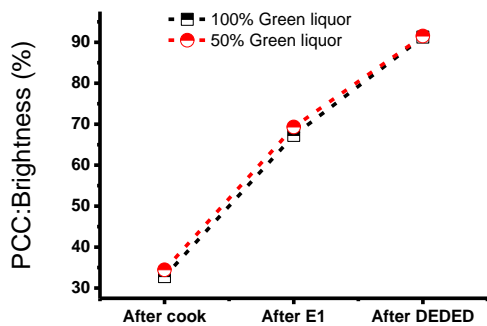


Figure 37: PCC: brightness (%) of pulps after kraft pulping (unbleached) and after DEDED (bleaching).

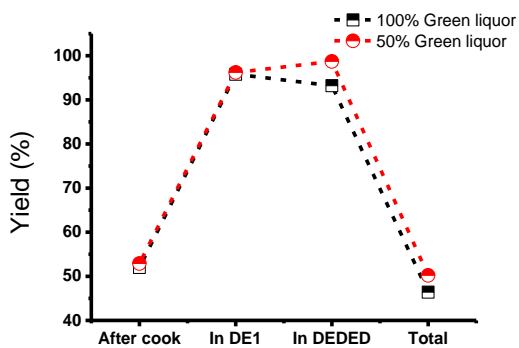


Figure 38: Total yield (%) of pulps after kraft pulping (unbleached) and after DEDED (bleaching).

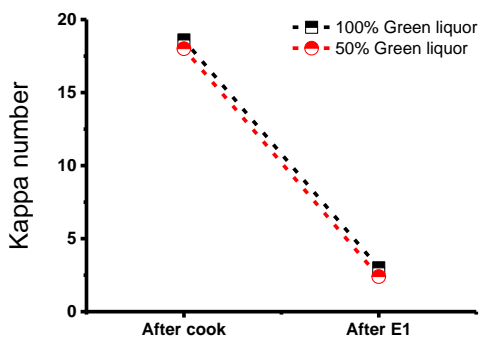


Figure 39: Kappa number of pulps after kraft pulping (unbleached) and after E1 (alkali extraction bleaching).

## 5.6. Laboratory trials for comparing synthetic and industrial green liquor on *E. dunnii* wood chips with different calcium content

A preliminary study comparing and investigating the effect of industrial green liquor versus synthetic green liquor was conducted. White liquor is taken as a control. Different calcium-containing wood chips were considered to compare with current mill working conditions. The calcium content in wood chips used for this work were 1419 mg/kg, 2061 mg/kg, and 2539 mg/kg. The cooking liquor conditions used for this work were EA (18%), sulfidity (33%), and liquor-to-wood ratio (4:1). Impregnation was carried out for 90 minutes at 110 °C, and kraft pulping was performed for 210 minutes at 145 °C. A significant decrease in kappa number (figure 40) and an increase in yield (figure 41) was observed with synthetic green liquor compared to industrial green liquor. At the same time, little scattering was observed in intrinsic viscosity (figure 42) for comparison to previous findings i.e., higher viscosity with high calcium content. One of the reasons could be the unknown cellulose content in wood chips, irrespective of calcium. Despite this, white liquor (control) shows less polysaccharide degradation compared to green liquor (synthetic) and green liquor (industrial). One explanation could be that the kraft pulping conditions are longer for these wood chips at this high? calcium level leading to alkaline hydrolysis. The solution for this problem would be to reduce the cooking time and perform kraft pulping which can be considered as future work. Green liquor (industrial) did not show a similar effect as green liquor (synthetic). One of the explanations is the impurity and other inorganic components in green liquor (Industrial) leading to alkaline hydrolysis. Ionic strength also influences the rate of delignification, so we performed some conductivity on green liquor (industrial) = 145.6 mS/Cm, green liquor (synthetic) = 217 mS/cm, and green liquor (industrial) used for kraft pulping with mixing with white liquor = 184 mS/cm. This shows that the ionic strength of industrial green liquor is relatively low compared to green liquor (synthetic). Pulps with high calcium content wood chips (calcium 2539 mg/kg) have higher kappa numbers irrespective of cooking liquors. That shows that the higher calcium content is sensitive toward delignification. The result is in line with the previous work (Vegunta et al., 2021). Selective filtration and purifying green liquor help improve the results on an industrial scale.

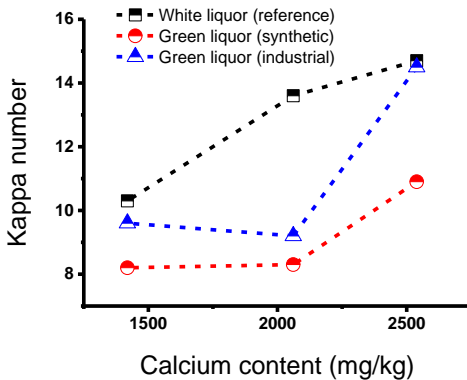


Figure 40: Kappa number as a function of calcium content (mg/kg) in the wood produced using white liquor (reference), green liquor (synthetic), and green liquor (industrial).

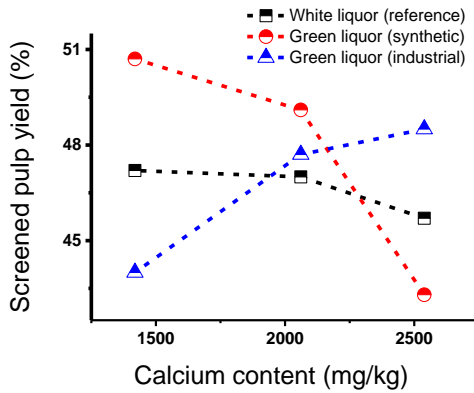


Figure 41: Screened pulp yield (%) as a function of calcium content in the wood (mg/kg) in the wood produced using white liquor (reference), green liquor (synthetic), and green liquor (industrial).

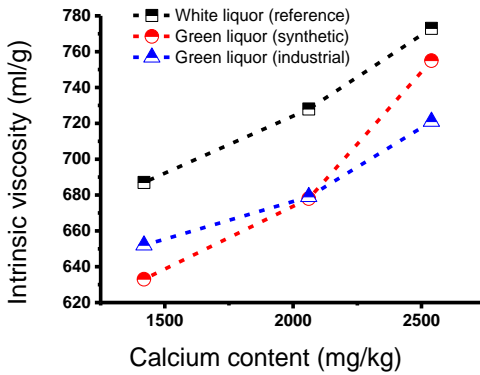


Figure 42: Intrinsic viscosity (ml/g) as a function of calcium content in wood (mg/kg) in the wood produced using white liquor (reference), green liquor (synthetic), and green liquor (industrial).

## 5.7. Supporting work for proving calcium effect on cellulose degradation using cotton linters

The effect of calcium ion concentration on accelerating alkaline hydrolysis during kraft pulping has been investigated in this work. Kraft pulping is performed on cotton linters with a different calcium concentration of calcium sulfate and calcium chloride salts. The viscosity of produced pulps using cotton linters is considered to express the degree of polymerization concerning the concentration of calcium salts. This work showed a decrease in the degree of polymerization of cellulose with an increase in the concentration of calcium salts (figure 43). This theory is in line with earlier studies (Vegunta et al., 2021) showing that calcium catalyzes alkaline hydrolysis during kraft pulping (Andersson, A., 2021; Master's thesis work, Karlstad).

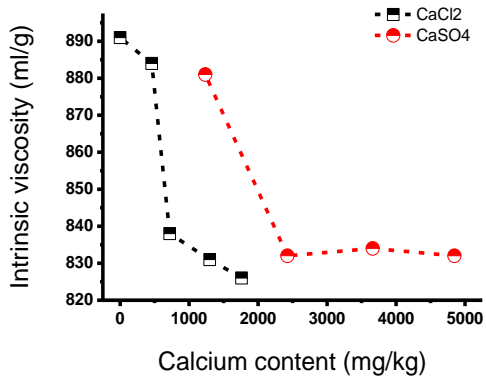


Figure 43: Intrinsic viscosity (ml/g) as a function of calcium content (mg/kg) of kraft pulped cotton linters using Calcium sulfate ( $\text{CaSO}_4$ ) and calcium chloride ( $\text{CaCl}_2$ ).

## 6. Conclusions

1. The chemical composition of *E. dunnii* wood with different calcium—affects the rate of delignification
2. The rate of delignification and polysaccharide degradation during kraft pulping of *E. dunnii* wood increased with increased calcium content.
3. Lower lignin, calcium, sulfidity, and oxalic acid content in spent black liquor were obtained with green liquor impregnation.
4. Increased rate of delignification with lower (13) kappa number and lower polysaccharide degradation were observed when using green liquor in kraft pulping.
5. A higher amount of calcium is carried through the fiber line using green liquor for kraft pulping.
6. Increased brightness, tensile, and tear index of the pulps were observed using green liquor during kraft pulping.
7. With lower concentrations of green liquor during pulping a Slightly increased rate of delignification was observed.
8. Synthetic green liquor increased the rate of delignification and lowered polysaccharide degradation compared to industrial green liquor.

## Future studies

From a chemistry perspective, one should consider the following factors for further study in this area:

- Identify the form of calcium oxalate complexes present in the wood, which will help us understand the chemistry of calcium formed with cooking chemicals and other wood components.
- Monitor lignin degradation products through the pulping process using NMR spectroscopy; to know how many hydroxyl groups were degraded and  $\beta$ -O-4 bonds were affected during pulping.

Even though several studies have been performed on green liquor usage in kraft pulping, they have yet to study the chemistry between cooking liquor and wood components occurring during this process. Therefore, understanding the chemistry to get more benefits from this process regarding biorefinery and optimizing the method to the respective pulp mill is important.

From a technical perspective, one should consider the following factors for further study in this area.

- To monitor the stability of soluble calcium, oxalates, carbonates, and ionic strength in spent liquor while using green liquor. As we know, soluble calcium forms complexes with oxalates and carbonates, leading to scale problems.
- Monitor sulfide content in the liquor as industrial green liquor is more in sulfide content for chemical balances in the recovery process.

## Industrial significance

By using green liquor on a lab scale, we have seen an exceptional result with wood chips that can be pulped under normal cooking conditions. Despite that, we observed improvements in brightness and strength properties with increased pulp yield for the same wood quantity feed in the pulping process. Of course, this method must be optimized for each wood species to minimize the detrimental effects of inorganics on the pulp mill recovery section and degradation of important components like cellulose. However, one should consider the following factors for using this method on an industrial scale to get its full benefits.

- Modeling the inorganics and pulping liquor balance will help to optimize the green liquor charge required for effective pulping and evaluate chemical balance in the chemical recovery system.
- Monitor the inorganic and organic flow to the recovery boiler for handling spent green liquor and scaling problems.

## Acknowledgement

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### Appendix 1:

Table 1: Comparison of industrial green liquor to black liquor at KTH produced for impregnation and kraft cooking using black + white liquor.

<b>Analysis</b>	<b>Black liquor (Industrial)</b>	<b>Black liquor (KTH)</b>
<b>Dry solids (%)</b>	15.82±0.26	13.24±0.35
<b>Lignin content (%)</b>	5.54±0.25	2.78±0.07
<b>Ash (%) dry solids</b>	69.42±0.75	65.69±3.04
<b>[OH]<sup>-</sup></b>	0.25±0.05	0.36±0.008
<b>[HS]<sup>-</sup></b>	0.13±0.03	0.18±0.002