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**Investigating the effects of wood chemistry and cooking conditions
on pulp properties at a dissolving wood pulp mill**

by

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PREFACE

The research contained in this thesis was completed by the candidate while based in the Discipline of Chemical Engineering, School of Engineering of the College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Howard College Campus, South Africa. Sappi financially supported the research.

The contents of this work have not been submitted in any form to another university and, except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.

Signed: Prof. Bruce Sithole

Date:

DECLARATION 1: PLAGIARISM

I, Zininzi Khatshane, declare that:

- (i) the research reported in this thesis, except where otherwise indicated or acknowledged, is my original work;
- (ii) this thesis has not been submitted in full or in part for any degree or examination to any other university;
- (iii) this thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons;
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 - a) their words have been re-written, but the general information attributed to them has been referenced;
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- (v) where I have used material for which publications followed, I have indicated in detail my role in the work;
- (vi) this thesis is primarily a collection of material, prepared by myself, published as journal articles or presented as a poster and oral presentations at conferences. In some cases, additional material has been included;
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ABSTRACT

Pulp viscosity is the main criteria used to determine the endpoint of the pulping process in acid bisulphite pulping for production of dissolving pulp (DP). However, pulping performance is highly dependent on the relative abundance, structure, and reactivity of wood chemical components, mainly cellulose, hemicellulose and lignin. Thus, the chemistry of wood components has become an important factor when selecting wood species for use in the production of DP. It is believed that the chemical composition of wood components in tree species can be used to predict the pulp properties after pulping the wood. Although this correlation has been reported in Kraft pulping studies, there is very limited knowledge of such correlations in the acid sulphite pulping processes.

This study entailed an investigation to ascertain if there are correlations between wood chemistry components and the resulting pulp properties from acid sulphite pulping process. The study was conducted on wood samples from Eucalyptus species, coded in this study as (*E.001*, *E.002*, *E.003*, *E.004*), *Acacia mearnsii* (Wattle) and additional clones and hybrids of eucalyptus species (W962-71, G438-105, A189-97, 100 GN). The samples were pulped using the magnesium acid sulphite cooking process, at wood specific base charge of 2.5 and 3.0. The wood chemistry of the trees and properties of their resultant brown pulp samples were determined. The results showed that there were variations in wood chemical composition among the Eucalyptus species that were evaluated. A lower base ratio of 2.5 produced pulps with lower viscosity and lower kappa than those produced at base ratio 3.0. These pulping conditions resulted in about 1 to 2% lower pulp yields than those reported for standard mill pulping conditions.

Comparison of data on wood chemistry composition and pulp properties seemed to indicate good correlations on samples cooked at base ratio of 3.0 with a correlation coefficient (r) maximum of 0.71: the correlation was between alpha cellulose and total pulp yield. Correlation coefficients above 0.5 are considered significant. The results suggested that for some eucalyptus species pulped at base ratio of 3.0, a higher syringyl to guaiacyl S/G ratio in wood resulted in a higher delignification rate, resulting in lower residual lignin (K number) and higher pulp brightness. Eucalyptus wood samples with higher total lignin produced lower total pulp yields and brightness values whereas those with higher alpha cellulose content produced higher pulp

yields with higher brightness values. Analysis of a combination of various wood components, namely, S/G ratio, hemicellulose content, and alpha cellulose content led to derivation of a formula that showed these parameters could be used to predict the viscosity of resultant pulps: the correlation coefficient was approximately 0.7 was obtained at base ratio 3.0, whereas 0.67 was obtained at base ratio 2.5.

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GLOSSARY

Absorbance units	AU
Anthraquinone	AQ
Correlation coefficient	R
Consistency	Cons
Cupriethylenediamine	CED
Degree of polymerization	DPol
Dichloromethane	DCM
Dissolving pulp	DP
Gas Chromatography with Flame Ionisation Detector	GC-FID
High-Performance Liquid Chromatography	HPLC
Kappa number	K.no
Neutral Sulphite-Semi Chemical	NSSC
Paper Manufacturers Association of South Africa	PAMSA
Prehydrolysis Kraft	PHK
Pulsed Amperometric Detection	PAD
Sappi Technology Centre	STC
South African Pulp and Paper Industry	Sappi
Sulphur dioxide	SO ₂
Syringyl to Guaiacyl	S/G
Uridine diphosphate	UDP
Technical Association of the Pulp and Paper Industry	TAPPI

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CHAPTER 1: INTRODUCTION

1.1 Introduction

Wood is known as an extremely heterogeneous material and its synthesis and structural characteristics depend upon the individual species, environmental conditions, and growth site (Macdonald and Franklin, 1969). Wood used primarily as raw material in the production of pulp is from either softwood or hardwood trees. The hardwood's demand for the manufacturing of Dissolving Pulp (DP) has slowly accumulated over the past twenty years because of its lesser cost and greater accessibility in comparison to softwoods (Sixta *et al.*, 2004). Wood is comprised of cellulose, hemicellulose and lignin together with small amounts of extractives, pectin and proteins (Panshin and De Zeeuw, 1964). The composition of wood is important for selection of species for better pulping properties as desired by the mill.

Wood, among other components, contains extractives, parts of which are lipophilic. Lipophilic wood extractives, also called wood resin, have negative impacts on the pulp and paper making process because of their formation of pitch deposits (Sithole *et al.*, 2010a; Speranza *et al.*, 2002). Most of the wood resin is saponified, solubilised and washed out in alkaline pulping. In acid pulping, however, no such saponification takes place and the wood resin accumulates to form sticky deposits called pitch. Pitch is disadvantageous as it affects negatively on the quality of the pulp and paper properties. This is because of resinous extractives blocking responsive gatherings on the outside of the fibres and distressing inter-fibre holding (Sefara and Birkett, 2004). Pitch can disturb several pulp and paper machine activities by reducing the effectiveness of pulp screening, washing, cleaning, centrifugation, and pulp refining (Vercoe *et al.*, 2005). The problem of lipophilic extractives is more pronounced in acid sulphite pulping where the acid conditions are not conducive to their removal via saponification (Kilulya, 2012). Thus, the DP process is plagued with pitch deposition problems and the pitch also results in higher consumption of bleaching chemicals (Back and Allen, 2000). The fines in the DP have high amount of resin, thus their elimination from DP pulp can be helpful. For example, a study by Sithole *et al.* (2010b) evaluated three strategies that can be applied to reduce the resin content of sulphite pulps, and pulp fractionation was very effective in removal of extractives albeit with loss of fibres. Prior to that, a report by Kurula and Karlsson (2007) showed that cleaning of DP using hydrocyclone cleaning resulted in improved pulp quality when the fines were removed.

In hardwood species such as Eucalyptus, lignin is mainly composed of syringyl and guaiacyl (S/G) moieties (Robinson and Mansfield, 2009). Lignin structure, mainly S/G ratio, affects wood processing such as delignification of wood during pulping as reported in many studies (Ohra-aho and Tamminen, 2011). According to Studer *et al.* (2011) a high S/G ratio enhances the efficiency of Kraft pulping. A study by Ventorim *et al.* (2014) showed that increasing the S/G ratio of Kraft pulped Poplars and eucalyptus species improved the ease of delignification (EOD). However, it is important to note that all these studies were done on Kraft pulping. Thus examining the effects of wood chemistry components and cooking conditions on pulp properties at a dissolving pulp mill is essential.

In South Africa, Sappi (South African Pulp and Paper Industry) Saiccor in the KwaZulu-Natal province is a main producer of DP, annually producing 800 million tons from Eucalyptus, Wattle and clones by means of acid bi-sulphite pulping with magnesium or calcium as a base. In this study, magnesium bisulphite pulping was used to pulp all wood samples in two base ratios of 2.5 and 3.0 at pulping time and pulping temperature of four hours 53 minutes and 140 °C, respectively. The effect of base ratio in resultant pulp viscosity was investigated.

Pulp viscosity is the key quality criteria the mill uses to control its pulping process, with lower and upper limits at 680 and 830 ml/g, respectively. Measurements of pulp viscosity using Cupriethylenediamine (CED) solution may be used as an indirect estimate of the degree of polymerization (DPol) or cellulose degradation as a result of wood processes such as pulping or bleaching (TAPPI, 1999; Oglesby *et al.*, 2016). Thus, ascertaining correlations between wood chemistry properties and resultant dissolving pulp properties would provide valuable information for the mill.

In South Africa, *E. grandis* is the most commonly used species of wood and studies on its wood chemistry have previously been done (Gutierrez, *et al.*, 1999). However, few studies have been carried out on other Eucalyptus species, *Acacia mearnsii* (Wattle) and clones/ hybrids. Since these species are used by South African mills, it is important to gather data that could be used to optimise their pulping in the manufacture of DP. In the present study, hardwood species, viz., *Eucalyptus species*, Wattle, hybrids and clones used in a South African dissolving pulp mill were evaluated.

1.2 Research Aims, Objectives, Hypothesis and Key Questions

1.2.1 Aim

This research project is aimed at investigating if wood chemistry can be used to predict the DP properties that would result from acid sulphite pulping of the wood. The information will benefit the mill by enabling optimisation of each sulphite cook, minimising burnt and failed cooks. This strategy can increase pulp production, hence reducing production costs. Full analysis of wood chemistry can be used to predict pulp properties prior to pulping. Based on this, the mill can select wood species for pulping according to the desired DP properties.

1.2.2 Objectives

The following research aims were addressed in order to meet the objectives of the study:

- Determine the wood chemistry of tree species used at Sappi Saiccor.
- Categorise the wood species, based on pulping CED viscosity results obtained, as being Fast (< 680 ml/g), Medium (680 m/g to 830 ml/g), or Slow cookers (>830 ml/g).
- Effect of varying base ratios (2.5 vs. 3.0) and pulping time on pulp properties
- Select wood chemistry properties that can predict resultant CED viscosity
- Determine effect of wood chemistry components such as S/G ratio, alpha cellulose, sugars, extractives on pulping properties such as yield, kappa, viscosity using statistical analysis

1.2.3 Hypothesis

Wood chemistry properties such as cellulose, hemicellulose, lignin and lipophilic extractives can be used to predict DP properties of the wood at 95% confidence level.

1.2.4 Key questions

1. What is the wood chemical composition of species used in the mill to produce dissolving wood pulp? And can the wood chemistry composition of the species be used to select better species for pulp production?
2. Which of the species used in the mill pulp better at lower base ratio of 2.5 and at higher base ratio of 3.0? Which base ratio is recommended for better pulping?
3. Which of the species can be categorised as fast, medium and slow cookers based on the pulp viscosity data obtained?

4. Which wood chemistry parameters can be controlled to predict viscosity?

1.3 Thesis Structure

The six chapters shown below add to the understanding of the effects of wood chemistry parameters and cooking conditions on pulp properties at a dissolving wood pulp mill. The thesis has one reference listing at the end.

Chapter 1: introduction This chapter provides a brief overview description of the literature surrounding the research objectives. It presents the rationale, hypotheses, aims, and essential research questions to meet the objectives of the study.

Chapter 2: literature review This chapter presents an assessment of the literature on wood chemistry composition, with major focus on chemical composition of wood major components such as cellulose, hemicellulose, lignin and lipophilic extractives. The second part of the chapter reviews the chemical pulping methods used in the mill with major focus on the acid sulphite pulping process used in this study.

Chapter 3: materials and methods Highlights the materials and methods used to determine the wood chemistry components of Eucalyptus, Wattle, clones /hybrids and the materials and methods used in the sulphite pulping.

Chapter 4: Discusses the wood chemistry results of the various wood samples tested and the pulping results obtained. Conclusions based on wood chemistry and the pulping results obtained are highlighted.

Chapter 5: data modelling, this chapter correlates the wood chemistry properties obtained with pulp properties to find out if wood chemistry properties can be used to predict sulphite pulp properties. Based on these results, a model predicting wood viscosity is developed using the wood chemistry properties of interest. This chapter also provides conclusions based on the results obtained when wood chemistry and pulp properties were correlated.

Chapter 6: This final chapter outlines crucial findings in the entire thesis and reflects on the wood chemistry of species prior to cooking and after pulping. Here, strategies are recommended for wood chemistry parameters and cooking conditions on pulp properties at a dissolving wood pulp mill. In addition, results from this study showed gaps in understanding sulphite pulping process and gives recommendations guidance for future research needs to address these limitations.

This can add to our knowledge of wood chemistry parameters and cooking conditions on sulphite pulp properties.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

South Africa is amongst the top twenty paper and pulp producers in the world (PAMSA, 2021). This R28bn per annum industry has undergone extensive restructuring in recent years by reduced demand for printing and writing papers caused by increased digital alternatives. This reduction has led to some of the paper manufacturers moving away from their core business and diversifying into non-traditional markets. However, despite this, certain grades of packaging, paper and pulp, including dissolving pulp (DP) remain robust. Sappi (South African pulp and paper industry) has established itself as the world's leading producer of DP and exports over one million tons of DP per annum (Sappi, 2020). DP is used in the production of various consumer products across a diverse range of industries. According to Sappi DP is an extremely purified form of cellulose taken from sustainably grown and responsibly managed trees using unique cellulose chemistry technology.

Sappi uses only hardwood species to produce DP. The demand for these hardwoods for DP manufacturing has improved moderately over the past twenty years, because it's cheaper and easily available compared to softwoods (Sixta *et al.*, 2006). This tremendous demand for hardwood species explains the massive investment in studies to enhance and better understand the resultant pulp properties (Abreu *et al.*, 2009).

Trees are classified into softwoods or hardwoods. Softwood trees are called gymnosperms and hardwoods are referred to as angiosperms (Wiedenhoeft, 2010). The word "gymnosperm" is derived from Greek word translated as "naked". Gymnosperms are trees that don't have bounded seeds but are borne naked, subtended by scales or fleshy structure (Panshin and De Zeeuw, 1964). Gymnosperms are native to colder regions and are usually characterised by needle-shaped leaves. Examples are spruce, larch, fir, cedar and pine (Macdonald and Franklin, 1969). Angiosperms are flowering plants that have broad leaves and are the largest and most diverse group within the kingdom Plantae. They typically lose their leaves annually. There are about 3000 different angiosperms representing approximately 80% of all known living green plants now living (Jones, 1951). Examples of angiosperms are *Pterocarpus angolensis* (Umvangazi), *Dalbergia armata* (Umlungulu), *Colophospermum mopane* (Mopane) etc. However, local trees are not suitable for the forestry products industry, hence introduction of plantations of non-native trees such as eucalyptus species.

2.2 Physical properties of wood

Trees, both gymnosperms and angiosperms, are comprised of an external layer bark, phloem, cambium, sapwood, heartwood and pith. Bark is the dark outer layers of stems of woody plants located outside the vascular cambium (Biermann, 1996). It comprises of two notable layers, namely the “outer bark” and the “inner bark”. The “outer bark” comprises mostly of non-living cells, while the “inner bark” has living cells (Macdonald and Franklin, 1969). Cambium consists of a layer of living cells between wood and the bark; from its inner surface it deposits new wood while its outer surface produces a layer of bark (Panshin and De Zeeuw, 1964). The secondary wood structure of trees consists of the outer, living layers called Sapwood which transports minerals and water to the top of the tree. Sapwood is more easily permeated by liquids and cells have no deposits of dark material because they contain more water. Heartwood is the non-living, “inner wood” with cells that have dark coloured material or tannins. It comprises most of a stem's cross-section (Macdonald and Franklin, 1969). Sapwood is distinguished from heartwood by its lighter colour. During the initial growth, the light-coloured earlywood (or springwood) is formed which consists of thinner walls and larger cells (Torbensohn *et al.*, 2016). The latewood (or summerwood) is formed as the season progresses. It is the darker, firmer part at the outside of the growth ring (Macdonald and Franklin, 1969). Pith is the first formed portion of the stem of tree consisting entirely of cellular tissues. When the tree is young, the pith contains an extensive amount of fluid which nourishes the tree.

The cell wall comprises of the “primary wall (P)” and the “secondary wall (S)”. These are formed in layers having different compositions of chemical constituents and microfibrils orientations. The primary wall is the portion formed while the cell was enlarging from the cambial initial, whereas the secondary cell wall forms after the cell enlargement is complete.

The thickness of the primary wall of the living tree is approximately 0.1 micron and contains approximately 72 percent of water. The secondary cell wall comprises of S1, S2 and S3. S1 is the outer thin layer, S2 is the middle thick layer and S3 is the thin inner layer as shown in Figure 1 (Panshin and De Zeeuw, 1964). The peripheral contains roughly 10% of cell wall thickness, the middle layer involves around 85% of the thickness, and the deepest layer includes around 1% of the secondary wall thickness (Sjöström, 1993). The lignin-rich middle lamella between the strands ties the filaments together. The secondary wall contains, principally, cellulose, hemicellulose and lignin while the primary wall additionally contains a

lot of pectin, xyloglucan and protein (Sjöström, 1993; Côté, 1967). The information about the ultra-auxiliary plan inside wood fibres is vital for understanding tree (wood) composition and structure.

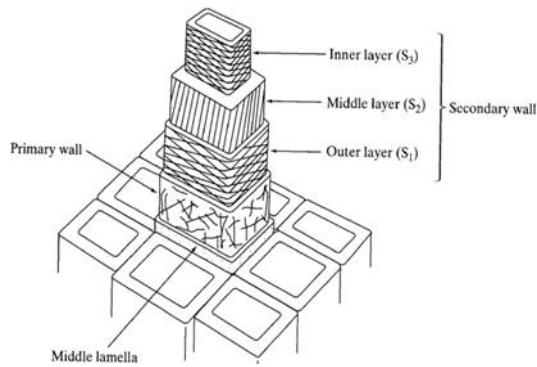


Figure 1: Basic structure of the wood wall showing the middle lamella and the layers of the cell wall (Côté, 1967)

2.3 Chemical composition of wood

Wood is composed primarily of four chemical constituents, cellulose, hemicelluloses, lignin and extractives. Generally, wood comprises of 38-50% cellulose, 20-30% hemicelluloses, 15-25% lignin, and 3-10% extractives based on the dry wood (Macdonald and Franklin, 1969) as shown in Figure 2. However, the amounts change depending on the wood type (softwood versus hardwood) and the species of the tree. There is ample published information on chemical composition of various species. Conventional chemical investigation can differentiate angiosperms and gymnosperms. Unfortunately, these methods cannot be utilised to differentiate singular species due to the variety and similitudes inside and among various species. Wood chemistry analysis methods are time-consuming and require numerous analyses for complete characterisation of wood.

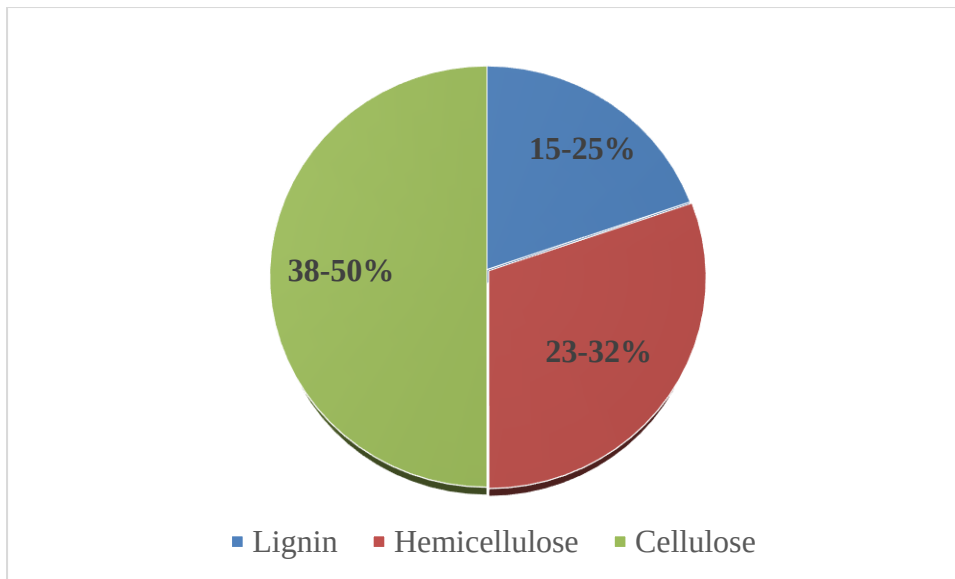


Figure 2: Major components and structure of wood

Additionally, wood as an organic material is also comprised of three chemical elements, namely carbon (C), oxygen (O) and hydrogen (H). It is observed that wood also contains about 0.1% to 0.3% nitrogen (N) whereas wood ash contains inorganic elements such as potassium (K), sodium (Na), magnesium (Mg), calcium (Ca), and silicon (Si). These wood elements are essential growth factors that are mainly involved in the metabolism of the living cells during wood formation and growth. Protein compounds contain N and serve as nutrients and tree defence (in certain tree species). Wood comprises of 50% carbon, 44% oxygen, and 6% hydrogen, and small quantities of metal ions (Unger, 2001). Two major and important wood components in chemical pulping are lignin, whose concentration in trees varies from 15 to 25% and carbohydrate which varies from 65 to 75%. The other components, hemicellulose and extractives, are removed during the pulping operations and are not meant to be part of the final product.

2.3.1 Extractives

These are non-structural wood constituents that are a minor fraction of wood. They account for about 3 to 10 % of dry wood. Softwoods have 5 to 8% whereas hardwoods have 2 to 4% extractives. According to Pettersen (1984), extractives are a variety of organic compounds including waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilage, gums, resins, terpenes, starches, glycosides, saponins, and essential oils. According to Yang and Jaakkola (2011), extractives include both inorganic and organic components, but

the organic components are higher than inorganic components. Macdonald and Franklin (1969) and Yang and Jaakkola (2011) agree that extractives are not an essential part of the structure of cell wall, therefore Macdonald and Franklin (1969) described extractives as all none-cell wall components of wood whether or not the materials are soluble in solvents.

Many wood species are characterised by their extractive materials. The utility and even undesirability of certain extractive species for the paper and the chemical industries is strongly influenced by these materials. This means that certain wood species can be preferred for use over others based on their extractive contents. Extractives can be undesirable during certain processes such as pulping and bleaching. Anatomical structures would be the only remaining differentiating features (Panshin and De Zeeuw, 1964). It has been reported that often, the effects and significance of extractives far outweighs the amount present, however, considering the differences between the softwood and hardwood extractives content, amounts should also be considered.

2.3.1.1 Location of wood extractives

Wood extractives are not uniformly distributed in the tree or in the fibre cell walls. According to Yang and Jaakkola (2011), extractives content is higher in bark, leaves and roots than in the wood stem. The food reserves such as fats are in the ray cells. The resin acids and terpenes are found around and inside the resin ducts in softwoods where they are generated, especially when the wood becomes heartwood and the resin acids assume a wood-preservation function (Beentje, 2010). Many phenolic compounds found in heartwood of certain species are toxic to fungi. Constituents soluble in water such as sugars are found in the tree's sapwood. Hardwoods may contain considerable resin materials in the vessels of the heartwood (Caron-Decloquement, 2010). Wood rays from some softwoods may contain approximately 20% extractives which, with sulphite pulping are not dissolved or solubilised (Spark, 2004). Release of these resins and fatty acids during fibre processing is a common source of the sticky deposits in pulp plants (Megown *et al.*, 2000). The amount and type of extractives vary within species and are site specific (Ucar *et al.*, 1995). Megown *et al.* (2000), considered the impact of tree age and site index on extractives in *E. grandis*. It was discovered that extractives content became higher with increasing tree age and diminishing site index.

2.3.1.2 Classification of wood extractives

According to Vercoe *et al.* (2004), extractives are low sub-atomic weight constituents in wood and can be classified into lipophilic and hydrophilic extractives. Caron-Decloquement, (2010) also classified wood extractives into lipophilic and hydrophilic, with the emphasis that the classification is based on the solvent used in the extraction step. However, Yang and Jaakkola (2011), reported that organic extractives can also be classified into compounds such as alicyclic, aliphatic, phenolic etc. They have been similarly characterised as material that can be excluded from paper by a specific dissolvable or dissolvable framework within Soxhlet extraction (Casey, 1952).

i) Lipophilic extractives

Lipophilic extractives are compounds that are soluble in non-polar organic solvents such as pentane, hexane, petroleum ether, dichloromethane (DCM), chloroform or toluene (Caron-Decloquement, 2010). These compounds are comprised mainly of resin acids, diterpenyl alcohols, fatty acids, sterols, steryl esters and triglycerides (Kilulya ,2012). In this study, four examples of lipophilic extractives namely, resin and fatty acid fractions, terpenes and terpenoids, steroids and glycerides and waxes were discussed.

a) Resin and fatty acid fractions

Resin is a hardened mucus or exudate from wounded stem or leaves of softwoods that is soluble in alcohol but not in water (Beentje, 2010). The term resin and rosin are regularly utilized as an aggregate name for those lipophilic wood extractives that are soluble in “non-polar” natural solvents but water insoluble (Spark, 2004). There are eight regular resin acids found in softwoods. These can be separated into three classes namely, sweet-smelling, conjugated diene and alkene, and can be exploited as a significant value chain. According to Vercoe *et al.* (2004) they are routinely recovered from tall oil-fermented Kraft alcohol. However, there is wide variation in the composition and amount of resin like material present in wood, with the softwood species and the heartwood portions of wood containing more lipophilic material than in the hardwoods and sapwood portions. This fraction is considered as an important source of commercial products and plays a role as a determining factor in the utility of pulps for papermaking.

b) Terpenes and terpenoids

Terpenes are pure hydrocarbons, usually with intramolecular linkages that form one or more ring structures. Terpenoids incorporate several five carbon isoprene units with functional groups such as carboxylic acids, hydroxyl, carbonyl, etc. Terpenes are found in essential oils that have direct applications as feedstocks in the flavour and scent industry. Terpenes have other potential applications because of their natural properties (Zwenger and Basu, 2008). They are developed based on associated isoprene units (2-methyl-1, 3-butadiene) and, along these lines, contain various carbon atoms. Terpenoids are chemically transformed terpenes with, for example, alcohols, epoxides, ketones, aldehydes, carboxylic acids and esters (Bruneau *et al.*, 2018).

c) Steroids

Steroids are cyclic triterpenes derived from the precursor squalene. They are biosynthesized from squalene oxide. They are compounds containing cyclo-pentano-per, hydro-phenanthrene Lewis structure. Sterols may occur as fatty acid esters or glycosides (Verk *et al.*, 2016).

d) Glycerides and waxes

Esters of glycerol containing fatty acids are glycerides, whereas a combination of aliphatic compounds including fatty acids, fatty alcohols, hydrocarbons and their derivatives forms waxes (Verk *et al.*, 2016).

ii) Hydrophilic extractives

Hydrophilic wood extractives are low molecular weight carbohydrates. Verk *et al.* (2016) noted that hydrophilic compounds are usually further extracted by using more polar solvents, such as methanol, acetone, ethanol, water, etc. Some well-known representatives of hydrophilic extractives are soluble sugars (e.g. xylose, mannose, sucrose) and various simple phenolics, such as stilbenes, lignans, flavonoids and tannins (Caron-Decloquement, 2010).

a) Flavonoids

Flavonoids are diphenyl propane compounds created from phenylpropane precursors (Figure 3). They are widely distributed in the plant. Flavonoids have various biological activities, which include flower pigmentation and antioxidant activities.

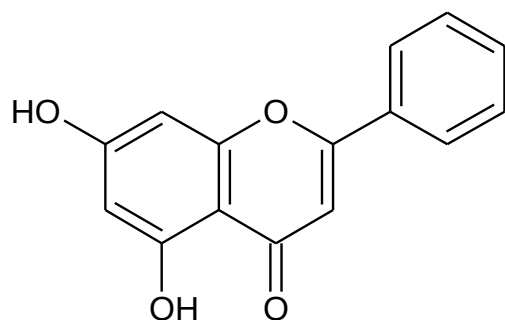


Figure 3: Example of a Flavonoid structure produced using Chem structure software

b) Lignans

Lignans are phenylpropanoids covalently bonded between two propane side chains (Figure 4). Lignan occurs when the linkage is C8-C8' (b-b), whereas a neolignan occurs in any C-C bond linkage (Caron-Decloquement, 2010).

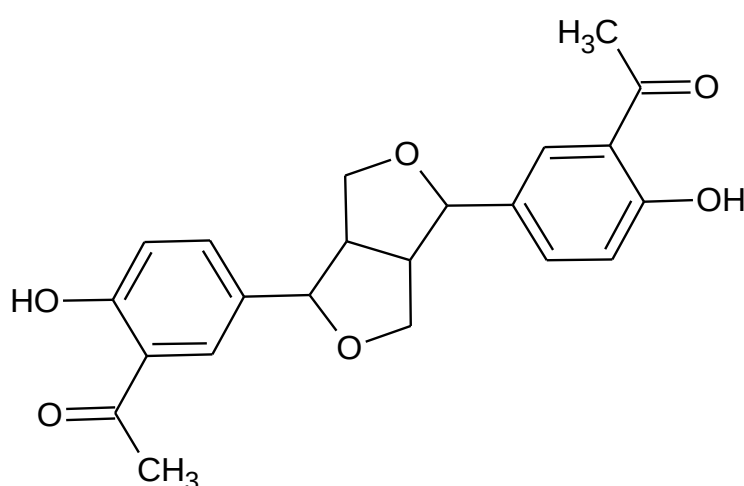


Figure 4: Example of a lignan structure produced using Chem structure software.

c) Tannins

According to Caron-Decloquement (2010), tannins are oligomeric and polymeric, water-soluble polyphenolic compounds (Figure 5). They can be categorised into hydrolysable and condensed tannins. Condensed tannins have several biological functions and are involved in plant defence mechanisms (Caron-Decloquement, 2010). Large concentrations of tannins are obtained in the bark and heartwood.

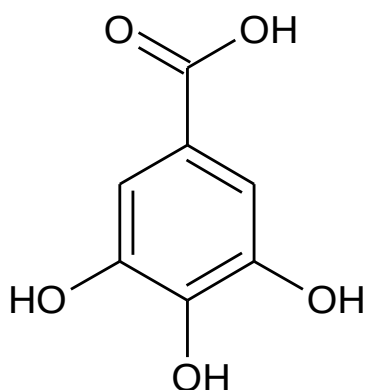


Figure 5: Example of a Tannin structure produced using Chem structure software.

d) Stilbenes

Stilbenes are compounds based on the 1, 2-diphenylethene structure (Figure 6). Some stilbenes are formed as a response to external stresses such as fungal infection or ultraviolet light. Pinosylvin and pinosylvin monomethyl ether, take part in the mechanism's inhibition of sulphite pulping (Caron-Decloquement, 2010).

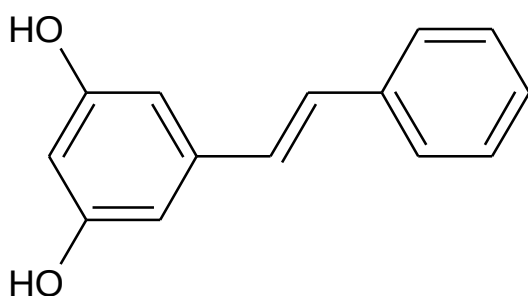


Figure 6: Example of a Stilbene structure produced using Chem structure software

2.3.1.3 Impact of wood extractives on pulping

Various authors have reported on the fate of lipophilic wood extractives during pulping and bleaching processes in pulp mills. Various extractives classes have different chemical behaviour during and after pulping. In acidic to neutral pulping, the lipophilic extractives are hard to remove, compared to alkaline pulping, where they are much easier to remove (Gutiérrez *et al.*, 1999). Lipophilic wood extractives negatively affect the pulp and paper-making process

because of their formation of pitch deposits (Sithole, 2000). The non-polar nature of lipophilic extractives leads to their adherence onto hydrophobic surfaces of paper machines and build up to form pitch deposits. The problem of lipophilic extractives is more pronounced in acid sulphite pulping, where the acid conditions are not conducive to their removal via saponification (Kilulya, 2012). Thus, the DP process is plagued with pitch deposition problems and the pitch also results in higher consumption of bleaching chemicals (Back and Allen, 2000). Dissolving pulp's fines contain a substantial part of resin, thus their elimination from the pulp can be helpful. A study by Sithole *et al.* (2010b) was conducted where he evaluated three strategies that can be applied to reduce the resin content of sulphite pulps, and pulp fractionation was very effective in removal of extractives albeit with loss of fibres. Prior to that, a report by Kurula and Karlsson (2007) showed that cleaning of DP using hydrocyclone cleaning resulted in improved pulp quality when the fines were removed.

2.3.2 Lignin

Lignin is the cell-wall component that distinguishes wood from other cellulosic materials formed by nature (Tsoumis, 1968). Lignin has a content of 20 to 40% in wood. However, Panshin and De Zeeuw (1964) reported that lignin forms about 15 to 35% of woody cell wall, whereas Macdonald and Franklin (1969) reported that lignin comprised 20 to 35% of wood cell-wall. These differences could be caused by different provenance of the wood sources. Softwoods contain 26 to 32% lignin whereas hardwoods contain 20 to 26%. Lignin content not only varies between hardwoods and softwoods but also from one species to another and within the same species (Panshin and De Zeeuw, 1964). Lignin appears to be a polymer built up through condensation of structural units of few similar types. Primarily, these units are of the phenyl propane (C_6C_3) type, but they may be combined in a variety of ways (Browning, 1967). According to BaOsman (1996), phenylpropane building units of lignin are bonded to each other with ether and carbon-carbon linkages. The complicated phenylpropane units are nonlinearly and randomly linked (Chen, 2014). The phenylpropane units are identified in isolated lignin in two characteristic forms, namely Syringyl (S) and Guaiacyl (G) (Zhu, 2013). Lignification, namely deposition of lignin, constitutes the last stage of cell wall development (Chen, 2014).

2.3.2.1 Location of lignin in wood

Around 70% of softwood lignin and 60% of hardwood lignin are found in the secondary cell wall (Zhu, 2013). The highest and lowest lignin concentrations are in the middle lamella and

secondary wall (S2), respectively. However, due to S2's thickest layer compared to thin middle lamella, S2 therefore contains the majority of lignin (Obst, 1990). Lignin's cell wall in its natural state is sometimes called protolignin: this distinguishes it from chemically isolated lignin. Lignin is in charge of the strengthening of plants (Sluiter *et al.*, 2010), thus, without it, trees would fall because of gravity (Abreu *et al.*, 2009). The molecular structure, composition and spatial orientation of lignin contribute to wood properties. Lignin forms a cementing matrix that holds together the cellulose fibrils in the tracheid cells and between the tracheid cells and imparts considerable mechanical strength and assists with the growth of plant structures (BaOsman, 1996). The lignin's primary physical property is its stiffness and rigidity it provides to the cell walls.

2.3.2.2 Classification of lignin

Lignin is derived primarily from the hydroxycinnamyl alcohols p-coumaryl, coniferyl, and sinapyl alcohol (Zhao *et al.*, 2010; Chen, 2014) as shown in Figure 7. These three compounds are the main monomers of lignin. The addition of one methoxyl group to the aromatic (phenol) ring produces a syringyl unit, whereas two methoxyl groups results in a guaiacyl unit. Due to lignin's different monomers, it can be divided into the following types namely:

- Syringyl lignin, which is polymerized by syringyl propane,
- Guaiacyl lignin, which is polymerized by guaiacyl propane, and
- Hydroxy-phenyl lignin which is polymerized by hydroxy-phenyl propane (Abreu, Latorraca *et al.*, 2009).

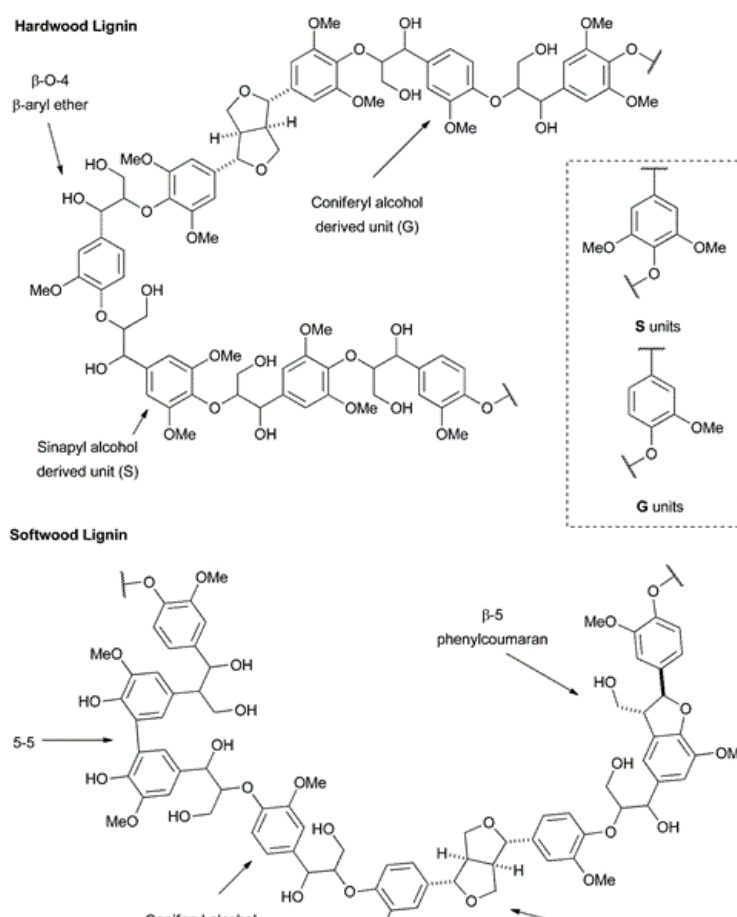


Figure 7: Structural representations of sections of hardwood and softwood lignins showing the most abundant units (S/G) and linkages found in each, adapted from Lancefield and Westwood (2015)

In softwoods, guaiacyl units (as the phenyl part of the phenyl propane units) appear to be the basic building units, whereas in hardwoods the lignin is made up of both guaiacyl and syringyl units (Panshin and De Zeeuw, 1964; Browning, 1967; Santos *et al.*, 2013). The thioacidolysis reaction is mostly used for establishing lignin's basic composition (Robinson and Mansfield, 2009). This method determines the concentration of lignin's monomers (S, G, H) that maybe split from the polymer. This procedure is well established, however, it requires a significant amount of time and resources. (Rolando *et al.*, 1992).

According to Robinson and Mansfield (2009), proportional content of lignin composition in terms of S, G and H may affect wood processing i.e., delignification efficiency such as, lignin residual content, pulp yield and the ability to bleach pulp as seen in chemical pulping. For

example, in chemical pulping, the lignin monomer ratio has been shown to have a significant impact on the efficiency of delignification, such as pulp yield, residual lignin content and the ability to bleach pulp. The lignin portion of the cell wall cannot be isolated quantitatively without severe degradation because of its high reactivity and molecular weight. In the sulphite pulping process, lignin can be dissolved by acid hydrolysis following sulphonation, whereas in Kraft and soda processes, lignin can be dissolved using a hot alkali (Macdonald and Franklin, 1969). During the bleaching process of pulp, lignin can be dissolved by chlorination, oxidation and hydrolysis. During analysis, lignin can also be classified as acid-Insoluble and acid-soluble lignin. Acid-insoluble lignin (Klason lignin) is defined as lignin residues remaining after 72% sulphuric acid hydrolysis of a wood sample (Zhu and Theliander, 2011). The Klason lignin method is considered to be more precise than conventional methods for determining the lignin concentration of the samples (Zhu and Theliander, 2011). Acid soluble lignin is defined as a portion of the lignin that is solubilized during the 72% sulphuric acid hydrolysis of the wood sample.

2.3.2.3 Impact of lignin in pulping

Lignin structure plays a very important role during pulping process. During chemical pulping, chemicals react with lignin blocks to release cellulose fibres. Bleached pulp properties depend on the pulping process, sequences used during bleaching process, delignification efficiency and wood species. The main aim of pulping is to get rid of lignin while minimising cellulose and hemicellulose losses. However, chemical conditions applied in the pulping process determine the lignin, hemicellulose and cellulose degradation (Rydholm, 1965; Antonsson *et al.*, 2009). The total pulp yield obtained from the pulping process is important, as a result, additives to improve yield by means of stabilising glucomannan are commonly used. These can be either oxidizing or reducing chemicals. For example, sodium borohydride (NaBH_4) was previously used as a reducing additive yielding stable alcohol groups (Rydholm, 1965). However, sodium borohydride is very toxic and less convincing in yield benefit, as a result, it is hardly used. Anthraquinone is a widely used yield increasing additive / catalyst.

During sulphite pulping, lignin dissolves in the liquor as it depolymerises through the cleavage of ether linkages. During the benzilium ion formation, α -hydroxyl and α -ether groups are cleaved (Sixta, 2006). The cleavage of the open α -aryl ether linkages represents the fragmentation of lignin during acid sulphite pulping. The benzilium ions are sulphonated by

attack of hydrated sulphur dioxide or bi-sulphite ions, resulting in increased hydrophilic nature of the lignin molecule. The extent of delignification depends on the degree of sulphonation and the depolymerisation.

2.3.3 Hemicellulose

Hemicelluloses are heterogeneous polysaccharides which are formed through biosynthetic routes different from those of cellulose. Polysaccharide polymers in hemicellulose have a degree of polymerisation (DPol) between 100-200. Hemicelluloses are mixtures of polysaccharides synthesized in wood almost entirely from glucose, mannose, galactose, xylose, arabinose, 4-O methylglucuronic acid, and galacturonic acid residues (Macdonald and Franklin 1969; Pettersen 1984). They constitute the portion of the total polysaccharides in wood which in some parts can be soluble or dissolved in weak or dilute alkali solutions and can be hydrolysed in dilute acid to form sugars and sugar acids (Panshin *et al.*, 1949). A basic hemicelluloses fractionation from wood can be achieved by using a gradient elution at varying alkali concentrations (Rowell, 2012). Acidification by means of acetic acid can be used to precipitate hemicelluloses from the alkaline solution. According to Sjöström (1981), a complete hemicellulose precipitation can be improved by further treating the neutralized solution with a neutral organic solvent such as ethyl alcohol.

2.3.3.1 Location of hemicelluloses

Hemicellulose have random and amorphous structures, and are located within the cellulose and between the cellulose and lignin (Zhang *et al.*, 2015). According to Panshin *et al.* (1949), hemicelluloses constitute from 35% to 50% of the polysaccharides in the cell wall substance and from 20% to 35% of the total dry weight of the wall. Hemicellulose location within the cell wall has an impact on the pulping reactions and the resultant final pulp properties (Pettersen, 1984). The low molecular weight and amorphous structure of hemicelluloses contribute to their high solubility and susceptibility to hydrolysis compared to cellulose. In softwoods, Kilian (2007) observed a chemical combination between lignin and hemicelluloses, only few and easily hydrolysable bonds which also connect several hemicelluloses together via lignin.

2.3.3.2 Classification of hemicelluloses

Hemicelluloses consist of six hemicellulose monomers including xylose, glucose, galactose,

mannose with minor amounts of arabinose and rhamnose Figure 8. Hardwood hemicelluloses are composed mainly of xylans whereas softwood hemicelluloses are comprised of mainly mannans. Hardwood xylose has D-xylosyls which are connected to each other to form homopolymer linear molecules as the main chain. Hemicelluloses dissolve in alkali and can be easily hydrolysed by acids (Pettersen, 1984). This resultant hemicellulose fraction is composed of two general classes of substances namely;

Xylans: xylans have molecules which are produced by polymerization of the anhydro forms of pentose sugars.

Glucomannans: have molecules formed by polymerisation of anydro forms of hexose sugars, mainly glucose and mannose.

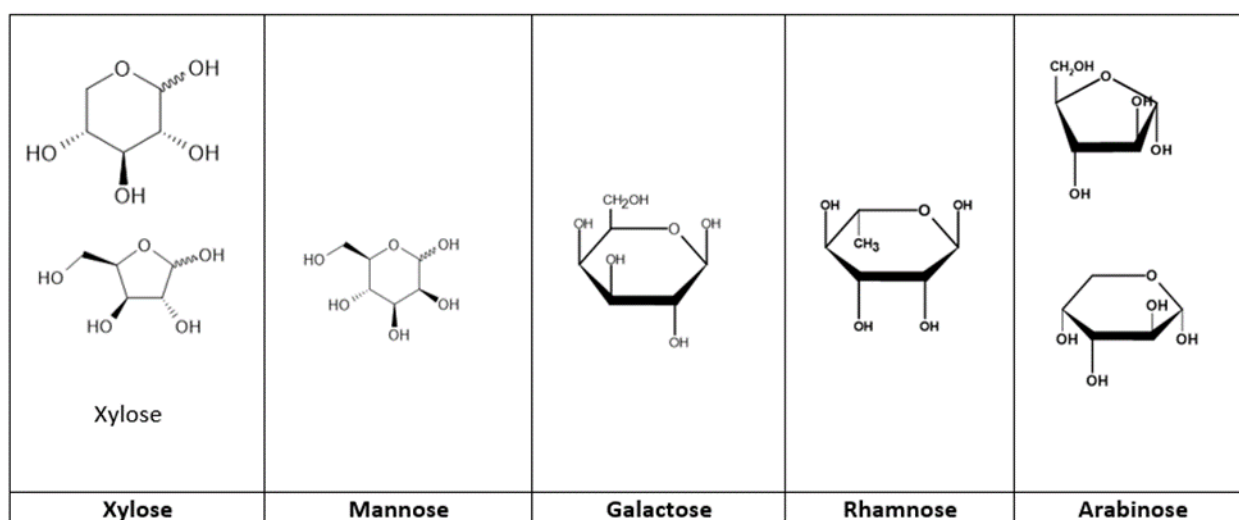


Figure 8: Examples of hemicellulose monomers produced using Chem structure software

Hardwood hemicelluloses is usually referred to as glucuronoxylans. This polysaccharide has a xylan backbone of D-xylopyranose units linked β -(1 $\rightarrow$ 4) with acetyl groups at C-2 or C-3 of the xylose units on an average of seven acetyls per ten xylose units (Sjöström 1981). Softwoods hemicelluloses comprises of a backbone polymer of D-galactose, D-glucose, and D-mannose (Sjöström 1981). The galactoglucomannan makes up 20% as the primary hemicellulose with a linear or possibly slightly branched chain with β -(1 $\rightarrow$ 4) linkages (Rowell, 2005) .

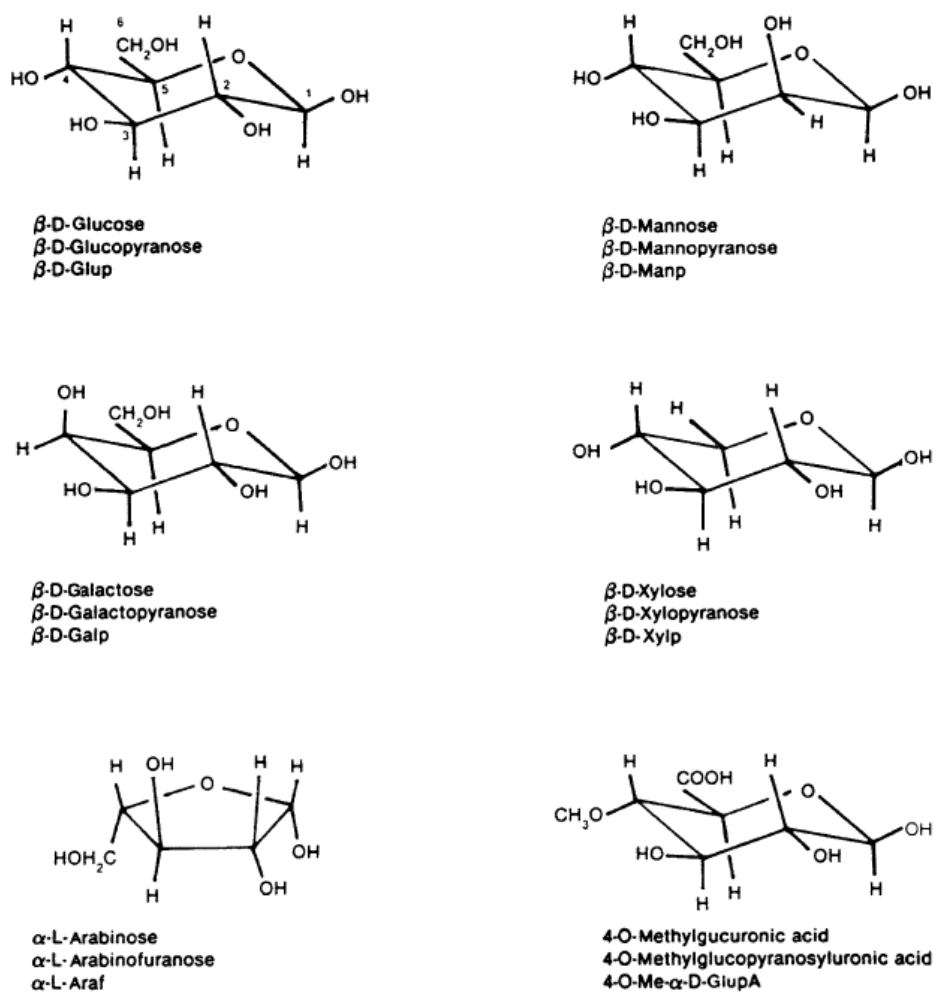


Figure 9: Sugar monomer components of hemicellulose, adapted from Rowell, 2012.

2.3.3.3 Impact of hemicellulose in pulping

Hemicelluloses are dissolved from wood in the early stages of acid sulfite pulping thus, hemicellulose removal plays an important role in chemical pulping. When hemicelluloses are retained in the wood during pulping, the delignification is characteristically slow. However, when hemicelluloses are removed in the early stages of pulping, delignification is much more rapid (Kerr and Goring, 1975). The remaining hemicelluloses are of significance in paper pulps in assuring desirable paper making properties, however, in chemical pulps, the presence of hemicellulose is harmful. The composition of hemicelluloses that remain in the pulp may be related to the pulping process, e.g. arabinose and galactose units are easily removed from polysaccharides containing them by an acid cook. Therefore, the hemicellulose content and the nature of hemicelluloses are important in the investigation of dissolving pulps (Browning,

1967). According to Kilian (2007), during the pulping , components of hemicellulose location may change and be closely associated with the cellulose, e.g. glucomannan in some types of sulphite cooking.

2.3.4 Cellulose

Cellulose is a polysaccharide consisting of a linear chain of biopolymers (Festucci-Buselli et al., 2007). It is a versatile commodity product because of its availability and unique structural properties (Festucci-Buselli et al., 2007). Cellulose is insoluble in water and is characterised by a firm linear structure composed of β (1-4) - linked glucose residues and uridine diphosphate. The linear cellulose molecules are connected laterally by hydrogen bonds to form linear bundles, giving rise to a crystalline structure (Seyedmohammadi et al., 2011). The crystalline regions are interrupted every 60 nm by a non-crystalline amorphous region (Seyedmohammadi et al., 2011). A single long chain cellulose molecule can connect several of the crystalline regions because the chains have a degree of polymerization between 1,000 to 10,000 (Haslach, 2000). Cellulose content usually accounts for 38 to 50 % of dry wood weight.

2.3.4.1 Location of cellulose

In nature, cellulose is the main structural component of the cell wall, located in seed fibres of certain plants. Cellulose content varies depending on the plant source, for example, wood contains 40 to 50% of cellulose compared to 97-98% found in the cotton plant.

2.3.4.2 Classification of cellulose

According to Alam *et al* (2014) ,cellulose has two terminal glucose residues namely:

- Reducing end group which contains a reducing hemiacetal group in the position C11
- Non-reducing end group which contains an extra secondary hydroxyl group in the position C4.

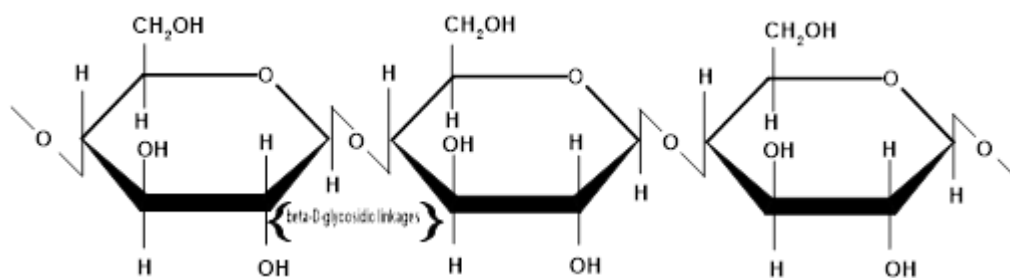


Figure 10: Cellulose structure produced using Chem structure software

The glucosyl ring of cellulose has three active hydroxyls: one primary hydroxyl group and two secondary hydroxyl groups (Figure 23). Cellulose reactivity is attributed to the reactivity these functional groups on the cellulose ring (Chen, 2014). The hydroxyl groups can form hydrogen bonds between molecules, and this impacts on cellulose chain's reactivity and morphology. These hydrogen bonds can enforce the linear integrity and rigidity of the cellulose molecules and make molecule chains arrange closely to form highly ordered crystalline regions (Chen, 2014).

Cellulose content in wood has been assessed based on Alpha-, beta- and gamma-cellulose. Separation of the cellulose in pulp into alpha (α)-, beta (β)- and gamma (γ)-cellulose fractions is an empirical procedure originally developed by Cross and Bevan in 1912, and later adopted by Willets in 1931 as a TAPPI standard. The procedure is used in the pulp and paper industry extensively, to evaluate pulps for many purposes, such as aging characteristics and response to refining operations. Alpha-cellulose shows undegraded, higher-molecular-weight cellulose content in pulp; beta-cellulose shows degraded cellulose; and the gamma-cellulose indicates mainly hemicellulose. To determine the alpha cellulose, wood samples are usually treated in a two-step process to selectively remove lignin and hemicellulose to produce pure α -cellulose (Tappi,1999). According to Chen (2014), cellulose with different degrees of polymerization dissolves in sodium hydroxide solution of different concentrations and temperatures . Based on changes in solubility under different conditions, cellulose can be divided into three types namely: α -cellulose, β -cellulose and γ -cellulose.

- i) α -cellulose: cellulose which is soluble in 16.5% concentration of sodium hydroxide solution at 20 °C. Alpha-cellulose has a high DP_{ol} of above 200. The α -cellulose content is the primary factor of DP, because chemical properties of the molecular structure of cellulose are essential to the final products. Alpha-cellulose is not pure

and may contain residuals of hemicelluloses and lignin. The higher the α -cellulose amount, the better the DP quality. Thus alpha cellulose is indicative of purity of dissolving wood pulp.

- ii) β -cellulose: cellulose, which is deposition extracted after neutralizing the acid solution and the remaining alkaline solution. This cellulose is soluble in 18% NaOH but regenerated in acetic acid. β -cellulose has a DP_{ol} of 10 to 200.
- iii) γ -cellulose: is the dissolved material which remains soluble in neutral or slightly acidic solutions. In general, γ -cellulose has a DP_{ol} of less than 10.

A summary of major wood chemistry components, including subunits, bonds and composition is shown in Table 1.

Table 1: Summary of major wood biochemistry components, including subunits, bonds, and composition.

	Cellulose	Hemicellulose	Lignin
Subunits	D-pyran glucose units	D-xylose, mannose, L-arabinose, galactose, glucuronic acid	Guaiacylpropane (G), Syringylpropane (S), Hydroxyphenylpropane
Bonds types between the units	-1,4-Glycosidic bonds	-1,4-Glycosidic bonds in main chains; -1.2-, -1.3-, -1.6-glycosidic bonds inside chains	Various ether bonds and carbon-carbon bonds, mainly -O-4 ether bond
Bond types between three components	Hydrogen bond	Chemical bond with Lignin	Contain chemical bond with hemicellulose
Composition	Three-dimensional linear molecular composed of crystalline and amorphous regions	Three-dimensional nonhomogeneous molecule with a small crystalline region	Amorphous, nonhomogeneous, nonlinear three-dimensional polymer

2.4 Pulping

Pulping is a process that extracts fibrous material, mainly cellulose, from wood or other raw material, as a prelude to papermaking. The main aim of pulping is to detach cellulose fibres from other chemicals and impurities in the wood or other fibrous source such as bagasse, straw (Sixta, 2006). A product of pulping process is a pulp, defined as a fibrous material resulting from complex manufacturing processes that involve the chemical and/or mechanical treatment of various types of plant material (Sixta, 2006). Pulping can be done either by mechanical, chemical, or semi-mechanical (a combination of mechanical and chemical) means (Sixta, 2006; Gellerstedt, 2009).

2.4.1 Mechanical pulping

Mechanical wood pulp, also called ground wood pulp, is obtained by grinding fibre material with mechanical means (Sixta *et al.*, 2013). The mechanical wood pulp contains a high lignin content and short fibres, making it more delicate than chemical pulp. Mechanical pulping involves the pre-treatment of wood with steam (and sometimes also with aqueous sulphite solution) prior to the separation into fibrous material by abrasive refining or grinding (Sixta, 2006). Water is added to the process to lessen wood damage because of heat and friction. Mechanical pulps with yields of 96% to 98% are produced by two different commercial processes, in which wood is processed either as logs treated in grinders, or as wood chips that are converted to pulp by mechanical work in a refiner (Sixta, 2006; Gellerstedt, 2009).

During mechanical pulping process, lignin is not removed. As a result, its presence is primarily responsible for fragility and yellowing of mechanical pulp with age. Mechanical pulp has a lot of properties that makes it perfect for printing, however, it has drawbacks for example low brightness, strength, and permanency, as well as the tendency to yellow with time due to the presence of lignin that reacts with light to form chromophores. Additionally, mechanical pulping has high energy demand (Sjostrom, 1993). Paper made from mechanical pulp also exhibits imperfections because of so-called shives, or un-fiberised bundles of fibre torn from the wood during grinding (Sixta, 2006). Many permutations entailing partial treatment of chips by thermal or chemicals prior to mechanical pulping have been developed in order to improve paper quality. They are summarised in Figure 11.

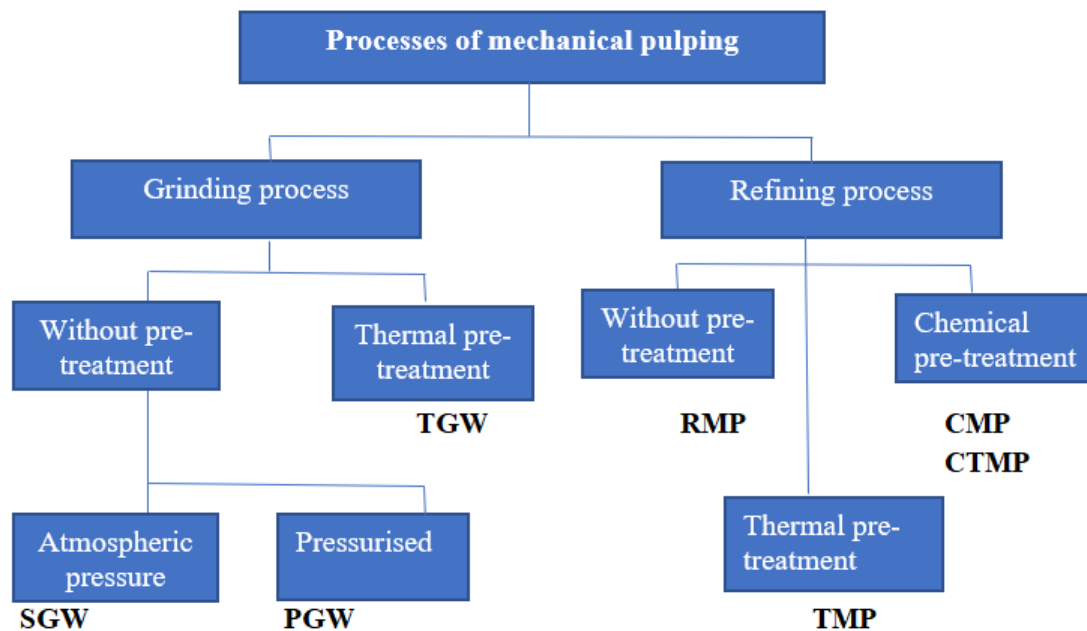


Figure 11: Example of mechanical pulping stages

2.4.2 Chemical pulping

Historically, chemical pulping became popular in the mid-1800s. Watt and Burgess in 1851 discovered that it was feasible at higher temperatures to extract lignin from wood by means of strong alkaline solutions such as sodium hydroxide (Gullichson and Fogelholm, 1999). In 1854 Burgess set up a factory in the United States of America where chips (poplar) were pulped using sodium hydroxide to produce pulp. Tilghman designed the sulphite procedure in 1866, and in 1879 Dahl created the sulphate or Kraft process. These procedures, invented in the twentieth century, resulted in rapid developments in the pulp and paper industry to produce a wide range of industrial and consumer products for modern society. The key commercial chemical pulping processes are the sulphate or Kraft, the acid sulphite, and the soda processes.

2.4.2.1 Kraft (sulphate)

Kraft (sulphate) pulping is commonly used to produce strong paper products. In Kraft pulping, the lignin is chemically dissolved using an aqueous solution of sodium hydroxide and sodium sulphide under high temperature and pressure conditions (Kuenen *et al.*, 2013). The lignin

dissolves in the pulping liquor depolymerises primarily through the cleavage of the ether linkages. The pulping temperature is critical to the rate of the pulping process and is in the range 150° C to 180°C. Pulping time is usually up to 4 hours ,under pressure (800kPa). Pulp yield obtained in Kraft pulping is between 45% to 60%. Unbleached Kraft pulp fibres can be used, after washing, to make packaging papers (e.g., cement bags) because of their high strength properties. The pulp is usually bleached to remove residual lignin and produce a white pulp that can be used in a wide variety of products such as hygienic products, printing and writing papers, paper cups, tissue products, etc. Advantages of Kraft pulping include its ability to pulp almost every wood type and its ability to produce a strong pulps (Sixta, 2006). The kraft pulping process offers the ability to recover the chemical used in the process through its efficient chemical and heat recovery system thereby reducing pulping costs. The chemical recovery process is an effective technology that offers for recycling of the pulping chemicals, effectual generation of steam and electrical power from the fuel value of the black liquor, and effective disposal of dissolved wood substances (Tran and Vakkilainen, 2008). Kraft recovery cycle is shown in Figure 12. Additional advantages of Kraft pulping include the ability to produce dissolving pulp by adding a preceding acid prehydrolysis stage (Kuenen *et al.*, 2013). Disadvantages of Kraft process are however the odour emissions which are still concern even to date.

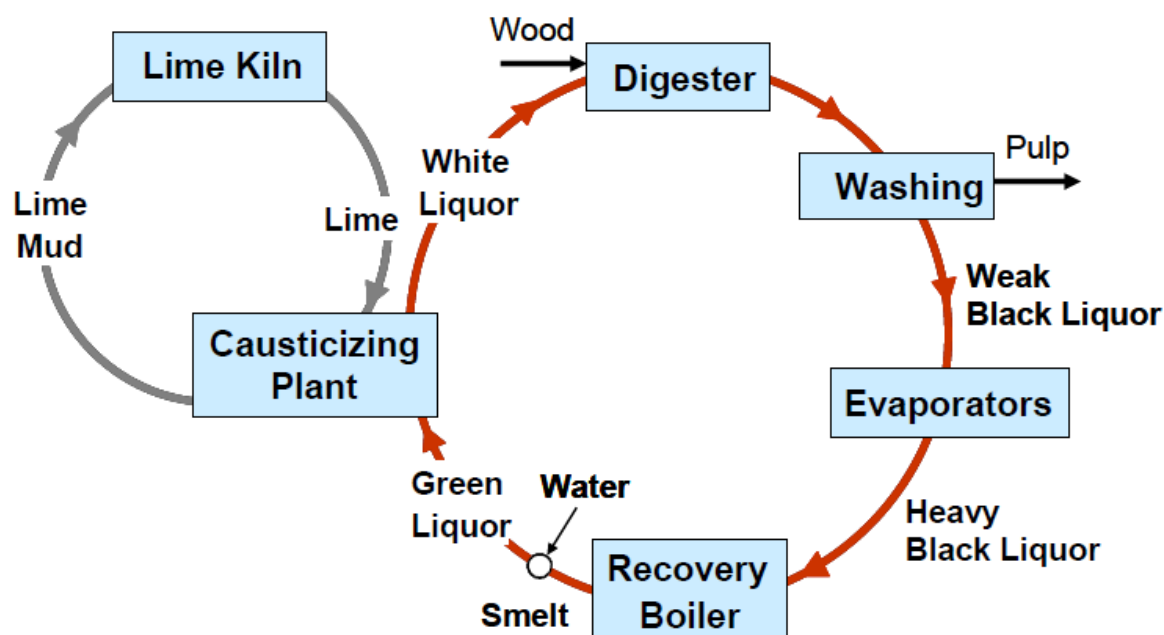


Figure 12: Kraft Recovery Process, Adapted from (Tran and Vakkilainen, 2008)

2.4.2.2 Soda process

Soda pulping is a chemical pulping procedure that uses sodium hydroxide as its delignification chemical. In the soda process, the digestion of wood chips is achieved by caustic soda to manufacture pulp for paper products. Soda pulping was one of the first chemical pulping methods invented by Burgess and Watts in 1851, and the first mill was started in USA in 1866. In the soda process, anthraquinone (AQ) may be used as a pulping additive to protect carbohydrate degradation. Soda pulping produces pulp with lower tear strength compared to Kraft process, but still has limited use for easy to pulp materials such as straw and some hardwoods (Casey, 1951). Although caustic soda is the main ingredient in soda process, it is difficult to maintain the system completely free of sulphide since sulphur that can be introduced with the wood, water, and fuel oil accumulates in the system and is converted to sulphide in the recovery furnace.

2.4.2.3 Sulphite Pulping Process

Three unique procedures for sulphite pulping developed were all based on corrosive bisulphite forms and utilized calcium, magnesium, and sodium bases separately. Prior to 1950, the

calcium bisulphite process was favoured considering its economic base and its overall simplicity of activity without recuperation of the cooking synthetic concoctions (Casey, 1952). A fourth base which significantly increased the sulphite pulping business was the ammonium base that was introduced in the USA and Japan after 1900. The Sulphite pulping industry is primarily characterised by the type of base chemical used with sulphurous acid to effect delignification of hardwoods. Previously, calcium was the base of choice used with sulphurous acid, however, recently magnesium has become a preferred choice because chemical and heat recovery can be achieved more economically (Linero and Lahre, 1977). Magnesium sulphite pulping is popular in Europe, with a couple of mills using sodium as base. Both magnesium and sodium pulping processes allow the chemical and heat recovery (Kuenen *et al.*, 2013). The lignosulphonates generated in the cooking liquor can be used as a raw material for producing different value added chemical products. In ammonium base operations, heat can be recovered by combusting the spent liquor, but the ammonium base and sulphur are lost.

In sulphite pulping, sulphur dioxide (SO_2) is adsorbed in a base of calcium, sodium, and magnesium or ammonium counter ion solutions that dissolve lignin and liberate cellulosic fibres (Kuenen *et al.*, 2013; Gellerstedt 2009). The sulphite cooking process results in a weaker pulp than other pulping types.

Sulphite pulping is characterised by several processes, differing mainly in the base chemical used and levels of chemical and heat recovery practiced (Linero, 1977). Delignification of wood chips is performed in large cylindrical vessels of up 170 m^3 capable of handling 80 tons of wood chips. In an acidic sulphite pulping, a certain amount of bisulphite ions must always be available in the liquor to obtain a lignin sulphonation reaction. Otherwise, the wood residue will turn dark with no dissolution of lignin because of a predominance of lignin condensation reaction.

Acid sulphite pulping is the process in which the pulping acid used has a high free SO_2 (excess SO_2) percentage and initial pH below 2 (Macdonald and Franklin, 1969). This excess is relieved from the digester and recovered by dissolving it in fresh cooking liquor for reuse (Casey, 1951). Sulphite pulping of wood, where the goal is to make paper products, can be carried out under acidic, neutral or alkaline conditions. However, if dissolving pulp is targeted, only acidic conditions may be employed because of the high level of cellulose purity expected.

The hemicellulose amount should also be low since these molecules are best removed at low pH.

i) Neutral sulphite semi-chemical (NSSC) pulping

Neutral sulphite semi-chemical pulping (NSSC) is a semi-chemical pulping process combining both chemical and mechanical pulping methods. Chemically, wood chips are treated to weaken inter-fibre bonding by removal of some hemicelluloses and a portion of the lignin. This is achieved through a partial delignification of wood using a buffered sodium sulphite solution, (Kuenen *et al.*, 2013). The second stage is a mechanical treatment which converts the chemically treated material into individual fibres and bundles of fibres. The NSSC pulping process produces a pulp yield between 70 to 85%, and is characterised by stiff fibres which are used for corrugated board, roll cores and container products.

ii) Calcium as a base

Calcium was the initial base-of-choice in the sulphiting industry where there was good availability of low resin spruce, fir and hemlock. According to Ingruber *et al.* (1970), in the years between 1870s until the mid-1950s, calcium has since been replaced by ammonia, sodium and magnesium bases (Kuenen *et al.*, 2013). When calcium is used, chemical and heat recovery are usually not considered because of formation of scale in the evaporation steps preliminary to recovery, as well as formation of calcium sulphate ash in the furnace (Linero and Lahre, 1977).

iii) Magnesium as a base

Along with ammonia, magnesium base pulping is one of the most commonly used sulphite pulping processes today. Its advantages include:

- Higher production rates can be attained using high reaction temperature if proper pH control is maintained.
- Wide variety of pulps can be made.
- Pulping operations are simplified because the need for the side relief step is lessened and consideration may be given to use of continuous digesters.
- A simple system is available for recovery of heat and total chemical magnesium and sulphur dioxide.

Magnesium base liquor is burnt to produce carbon-free MgO ash and SO₂. The gases pass through cyclones where the ash is collected and flushed with water to a retention tank. The

MgO slurry is then converted to $\text{Mg}(\text{OH})_2$ in the slaking system and used for absorption of the SO_2 in a series of venturi scrubbers. The overall chemical recovery of sulphur and $\text{Mg}(\text{OH})_2$ is around 80% (Kuenen *et al.*, 2013). Magnesium, sodium and ammonium base recovery systems all use absorption systems to recover SO_2 from sources such as the recovery furnaces, acid fortification towers and multiple effect evaporators. These recover over 95% of the sulphur for reuse, by scrubbing with the base chemical slurry or solution (Kuenen *et al.*, 2013).

2.5 Sulphite pulping reaction pH of different bases (Mg, Ca, Na, NH_4)

According to the pH, sulphite pulping can be divided into Acid bi-sulphite, Bi-sulphite, Neutral sulphite (NSSC) and Alkaline sulphite as illustrated in Table 2. At pH below 6, the sulphite in the cooking liquor is represented as hydrosulphite ion (HSO_3^-), while above this pH it is represented as a sulphite ion (SO_3^{2-}). The calcium and sulphite combination are insoluble in aqueous solution of pH above 2. Hence, calcium sulphite cooking liquors are restricted to the acid sulphite process (Linero and Lahre, 1977). At cooking temperatures, the calcium hydrogen sulphite decomposes to calcium sulphite and hydrated SO_2 . Thus, high charges of free SO_2 and low cooking temperatures must be maintained to stop the precipitation of calcium sulphite (Sixta, 2006). Mg sulphite is soluble in solutions whose pH is below approximately 7, and it may be used in acid sulphite bisulphite and over the lower end of the neutral sulphite range of pH (Linero and Lahre, 1977). Ammonium sulphite is soluble in solutions of a pH below 9, whereas sodium sulphite is soluble across the entire pH range. The desired range of pH for the cooking liquor will dictate the type of cooking chemicals which can be used (Linero and Lahre, 1977) as shown in Table 2.

Table 2: Sulphite pulping methods and conditions according (Sjostrom, 1993; Sixta, 2006)

Process	pH range at 25 °C	Base alternatives	Active reagents	Max. temp °C
Acid sulphite	1-2	Ca^{2+} , Mg^{2+} , Na^+ , NH_4^+	H^+ , HSO_3^-	125-145
Bisulphite (magnephite)	3-5	Mg^{2+} , Na^+ , NH_4^+	H^+ , HSO_3^-	150-170
Neutral sulphite (NSSC)	6-9	Na^+ , NH_4^+	HSO_3^- , SO_3^{2-}	160-180
Alkaline sulphite	10-13.5	Na^+	SO_3^{2-} , OH^-	160-180

For this study, the acid sulphite pulping with magnesium as a base was used. This is because it simulated the pulping processes at a dissolving pulp mill under investigation. The main unit operations during sulphite pulping, namely steaming, impregnation, as well as side relief are discussed below.

2.5.1 Impregnation

Steaming and impregnation of wood with the cooking chemicals are common operations prior to cooking, to make the delignification more efficient. There are various pulping processes which use different chemicals, depending on the desired pulp properties and level of delignification. The pulping begins with an impregnation stage after the chips have been immersed in the cooking liquor (Sjostrom, 1993). This is to ensure that the liquor is brought into intimate contact with the wood substrate (Macdonald and Franklin, 1969). The impregnation stage involves both liquid penetration into wood cavities and the diffusion of dissolved cooking chemicals. The penetration rate depends on the pressure gradient and proceeds fairly quickly, whereas diffusion is controlled by the concentration of dissolved chemicals and occurs slowly (Sjostrom, 1993). Free sulphur dioxide, in acid sulphite liquors enters wood more rapidly than does combined sulphur dioxide so that at some stage, the centre of a chip may contain sulphur dioxide but no base. This is not important at low temperatures, but at temperatures above 110°C such a chip becomes brown in the centre and is soon rendered practically un-cookable “burnt cook” (Macdonald and Franklin, 1969). Black cook is undesirable, and it happens if the transport of chemicals into the chips is still incomplete after the cooking temperature has been reached. Unwanted reactions catalysed by hydrogen ions occur, e.g., if the concentration of the base in an acid sulphite cook is deficient, the sulphonic acids formed are not neutralised and the cooking liquor pH suddenly drops. As a result, reactions leading to lignin condensation and decomposition of the cooking acid are accelerated in the chips interior, resulting in dark hard cores (Sjostrom, 1993). To obtain adequate penetration, a substantial fraction of the pore volume must be filled with liquor or if the wood is very wet, time must be allowed for bisulphite to diffuse into water in the pores and in the swollen cell walls (Macdonald and Franklin, 1969).

2.5.2 Side relief

A complete digester filling leads to a high liquor-to-wood ratio (4-5:1 for softwoods, 3-5:1 for hardwoods) causing an excessive steam consumption for heating to maximum temperature, and high spent liquor dilution. Through a side relief, cooking liquor is withdrawn until a target

liquor-to-wood ratio is attained, if liquor circulation is ensured. Maximum side relief of up to 30% is possible, and this decreases the liquor-to-wood ratio to about 3.5:1 for softwoods and to 2.5:1 for dense hardwoods (Sixta, 2006).

2.6 Wood reactions during chemical pulping

Chemical pulping relies mostly on chemical reactants and heat energy to soften and dissolve lignin in the plant material, so that the pulp fibres have little lignin content (Haslach, 2000). Chemical delignification is an important process during pulping and includes all processes resulting in partial or total removal of lignin from wood by the action of suitable chemicals (Haslach, 2000; Kuenen *et al.*, 2013). Chemical pulping results in near to complete removal of lignin and other non-fibre constituents of wood (Sixta, 2006). In chemical pulping, lignin is degraded and dissolved through chemical reactions at raised temperatures, which can range from 130°C to 170°C (Sixta, 2006). The fibres can be separated without further mechanical defibration only after about 90% of the lignin has been removed (Sixta, 2006). The dissolution of wood components during pulping is characteristic for each pulping process which, at a given residual lignin content, is reflected in the carbohydrate yield and composition (Kuenen *et al.*, 2013). The total fibre yield ranges from 45% to 55% (at a given extent of delignification of about 90%), depending on the wood source and the pulping process applied. Continuing cooking beyond a certain extent of delignification ultimately results in extremely large yield losses due to preferred carbohydrate degradation (Sixta, 2006). Hence, the chemical reactions must be stopped at a point when the lignin content is low enough for fibre separation, and where acceptable yield can still be achieved (Sixta, 2006).

Cellulose is preserved in sulphite pulps, whereas xylan is most stabilised in Kraft pulps. The high resistance of xylan towards alkali is mainly the reason for the yield advantage of Kraft over sulphite pulps in case of hardwoods. On the other hand, galactoglucomannan (GGM) is less degraded during sulphite pulping, which contributes to the higher yield of softwood sulphite pulps as compared to Kraft pulps. The yield advantage even increases when the pH is shifted to neutral conditions in the first stage of a two-stage sulphite process because of an increased retention of glucomannan (Sixta *et al.*, 2013). Neutral conditions have been proven to be sufficient at elevated temperatures to account for almost complete deacetylation of glucomannan. In this state, glucomannan may bind more closely via hydrogen bonds to the cellulose microfibrils, thus being more resistant toward acid hydrolysis. The hemicellulosic

fraction is hydrolysed to sugars (being xylose the major monomer), and the pentoses generated are decomposed in part to furfural in the reaction medium (Parajó and Santos, 1995). The relative amounts of pentoses and furfural obtained are dependent on the operational conditions and pulping method used in experiments.

The wood chemistry composition is important in the sulphite pulping process. As a result, many softwood species are considered being less suited to acid sulphite pulping. The poor pulping results obtained in sulphite pulping process are connected to the availability of large amounts of wood extractives. It has been reported that resin, in a wood species with high resin content, reacts with lignin to form a condensation product that prevents delignification. The highest DCM extractives contents in certain species relate to high pitch problems during further processing of the corresponding unbleached pulps. The presence of an excessive amount of hemicelluloses in dissolving pulp can have negative effects on the subsequent rayon production process, for example, poor filterability of viscose, and incomplete xanthation of cellulose (Christov and Prior, 1993; Ibarra *et al.*, 2010b). Hemicelluloses, particularly xylose, also cause discoloration of the viscose products (Sixta, 2006). Alpha cellulose content is the most important feature of dissolving pulp, therefore the higher α -cellulose content in DP pulp is accompanied by an improvement of the end product quality.

2.7 Statistical analysis

Correlation analysis is used to report statistical methods of summarizing research data (Akoglu, 2018). It dictates if the relationship between two different variables exists, and if so, how crucial or strong the relationship is (Taylor, 1990). The correlation coefficient is the best known and subject to statistical testing. The coefficient of determination is defined as the percent variation in the values of the dependent variable (y) that can be explained by variations in the value of the independent variable (x) (Akoglu, 2018). Regression is a way of describing how one variable, the outcome, is numerically related to predictor variables. The regression model is a statistical method that allows a researcher to determine the linear, or straight line, relationship that relates to two or more variables. This linear relationship summarizes the amount of change in one variable that is associated with change in another variable or variables. In this study, the correlation coefficient (R^2) was determined to assess the relationship between wood chemistry properties and pulp properties obtained after sulphite pulping of Eucalyptus species using base ratios 3.0 and 2.5. Correlation R^2 above 0.5 were of major interest. In this

study, Excel Data Analysis ToolPaK (corelation and regression) were used for data analysis at 95% confidence level.

2.8 Conclusion

It is believed that knowledge of wood chemistry properties such as S/G ratio, alpha cellulose, lignin of species, can be used to predict the resultant pulp properties. The higher S/G ratio has been reported to increase the ease the delignification (Santos, 2013; Robinson and Mansfield, 2009; Venter *et al.*, 2014), thereby saving chemicals and pulping time. These correlations have been reported in many Kraft pulping related studies, however, limited knowledge is known about such correlations in the acid sulphite pulping processes, especially regarding South African wood species and wood mills. There are no current reports regarding this study in South Africa. In this study, wood chemistry of various species used in the manufacturing of DP was tested, and these properties were later correlated with pulp properties obtained to see in any correlations exists.

CHAPTER 3: MATERIALS AND METHODS

3.1 Wood

The wood chemistry study was conducted on 67 wood samples consisting of Eucalyptus species (*E.001*:21 samples, *E.002*:13 samples, *E.003*: 11 samples, *E.004*:6 samples), *Acacia mearnsii* (Wattle) , and additional clones and hybrids of Eucalyptus (16 samples). The samples were obtained from various Sappi plantations which conducted the debarking as well as the chipping of the logs. After chipping, the wood samples were sent to Sappi Shaw Research Centre in KwaZulu-Natal, where a 5kg (oven dry) composites of each sample (*E.001*:6 samples, *E.002*:7 samples, *E.003*: 6 samples, *E.004*:5 samples), Wattle, and additional clones and hybrids of Eucalyptus (11 samples) were prepared and sent to STC for sulphite pulping. The 66 wood samples for wood chemistry analysis were ground and milled to 200 wire-mesh size at Sappi Shaw Research and also sent to STC for wood chemistry analysis.

The age rotation and site quality of the wood species were not investigated in this study.

3.2 Wood properties

3.2.1 Wood moisture content

The moisture content was determined by measuring the mass of samples before and after drying the samples in an oven set at a temperature of 105°C for 12 hours according to the TAPPI test method T204 om-12 (TAPPI, 2012).

$$\text{Consistency (\%)} = [(W_{\text{dry weight}} - W_{\text{wet weight}}) \times 100] \quad (1)$$

3.3 Wood chemistry components

The following wood chemistry components were analysed:

- Wood extractives (lipophilic) using DCM as a solvent
- Lignin (soluble, insoluble, total, and S/G ratio)
- Hemicellulose
- Cellulose

3.3.1 Determination of wood extractives

Determination of lipophilic wood extractives by solvent extraction of wood was performed according to TAPPI test method T204 cm-97 (TAPPI, 1997). Dichloromethane (DCM) was used as the extraction solvent. In this experiment, 10 mg of milled wood was weighed into an extraction thimble which was later loaded into the Soxhlet extractor and placed in the Soxhlet apparatus. A total of 200 mL of DCM was added in the round bottom flask where the DCM was heated to boiling point and refluxed for 5 hours. The extracts in the round-bottom flask were transferred to a 50 mL beaker, which was left on the bench to dry overnight and later oven dried at ~70°C. The quantity of lipophilic extractives was determined gravimetrically based on the mass difference before and after evaporation. The residue from the extraction thimble of all the samples were collected and used for further wood chemistry analysis such as carbohydrates, lignin (soluble, insoluble, total lignin), S/G ratio of lignin and alpha cellulose. Extractives were calculated as follows:

$$\text{Extractives (\%)} = [(We - Wb) \div Wp] \times 100 \quad (2)$$

Where, We = oven-dry weight of extract (g), Wp = oven-dry weight of wood (g), Wb = oven-dry weight of blank residue (g).

3.3.2 Determination of wood lignin

3.3.2.1 Acid soluble and acid insoluble lignin

Acid insoluble and acid soluble lignin were determined together with hemicellulose (see section 3.3.3 Hemicellulose and Lignin). Acid insoluble lignin was determined gravimetrically with reference to the Klason method and TAPPI method T 222 “Acid-insoluble lignin in wood and pulp” (Tappi, 2002). Acid-soluble lignin was determined using TAPPI T UM 250 “Acid-soluble lignin in wood and pulp” method (Tappi, 1991).

$$\text{Acid insoluble Lignin (\%)} = A 100 \div W \quad (3)$$

where: A = weight of lignin (g), W = oven-dry weight of test specimen (g)

3.3.2.2 S/G ratio

The thioacidolysis reaction was used to determine the monomeric composition of wood lignin to enable evaluation of S/G ratio. S/G ratio of lignin was determined by using gas chromatography with flame ionisation detection (Thermo Scientific, Trace 1310). Extractive-free wood samples of 20 mg were weighed into glass vials. The reaction mixture consisting of Boron trifluoride etherate (BF₃), Ethanthiol and 1,4-Dioxane of 1.0 mL was added to the

sample vial, purged with nitrogen gas and sealed tightly. The samples were then placed into a pre-heated heating block at 100°C for 4 hours and agitated every hour. After 4 hours, the reaction was stopped by placing the samples in a freezer (-20°C) for five minutes. Internal standard (Tetracosane 10 mg/ml) of 200 µL was added to the samples.

Sodium bicarbonate of 0.4 M was added to bring the reaction pH to between 3 and 4. Water (2.0 mL) and methylene chloride (1.0 mL) were added to each sample to extract the reaction products from the aqueous mixture into the organic phase. The samples were vortexed and allowed to settle into aqueous (upper) phase and the organic (lower) phase. An aliquot (1.0 mL) of the organic phase was removed and passed through a Pasteur pipette packed with a small tissue-paper plug and granular anhydrous (Na)₂SO₄ (50 mg) into a polypropylene microfuge tube (2.0 mL). The samples were evaporated to dryness in an Eppendorf Vacufuge for 2 hours at (45°C) and re-suspended dried samples in 300 µL of methylene chloride.

Derivatisation was done by adding 20 µL of pyridine to each insert and 100 µL of N,O-bis(trimethylsilyl) acetamide (derivitisation agent) to the inserts. The previously prepared samples were added (20 µL) to derivitisation mixture in the insert and GC vials capped and incubated for at least 2 h at room temperature and analysed the reaction product (2 µL) on a GC-FID. S/G ratio was calculated using the following equation based on Figure 13 as follows:

$$\text{S/G ratio equation} = \text{Sum (S peaks)} \div \text{Sum (G peaks)} \quad (4)$$

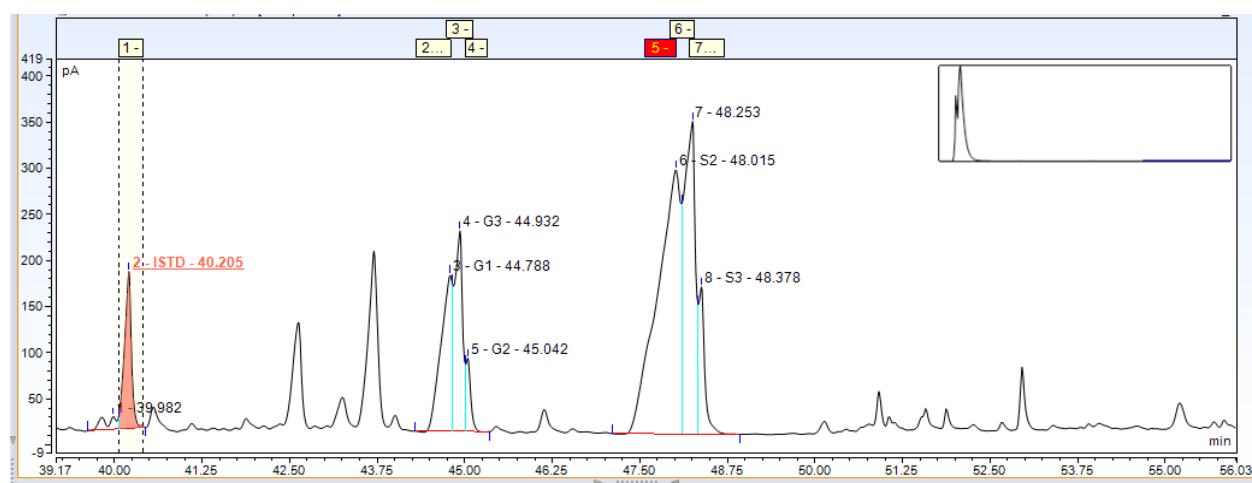


Figure 13 : Integrated S peaks (S1,S2 and S3) and G peaks (G1,G2 and G3) used to determine S/G ratio per sample.

3.3.3 Hemicellulose (wood sugars) and lignin (acid soluble and insoluble lignin)

Sulphuric acid was used to hydrolyse wood polysaccharides into their constituting monosaccharides. To achieve this, 3 mL of 72% sulphuric acid was added into accurately weighed 0.2 g of wood samples and left to hydrolyse for two hours. After the hydrolysis, High-Performance Liquid Chromatography (HPLC) grade water (111.0 mL) were added to stop the reaction. Internal standard selected as ribose sugar of 1 mL was then added, and the samples were capped and later autoclaved at 161°C for 90 minutes, for further hydrolysis. In this study, the quantification of arabinose and rhamnose, galactose, glucose, xylose and mannose were done. The hydrolysates obtained were cooled to room temperature and filtered quantitatively under vacuum through a 0.45µm crucible, using deionised water to rinse the serum bottle. The filtrate was further diluted ten times (1:10 times) and filtered prior to injection on HPLC with Pulsed Amperometric Detection (PAD) Dionex ultimate. The chromatograms as shown in Figure 14 were integrated and sugars quantified.

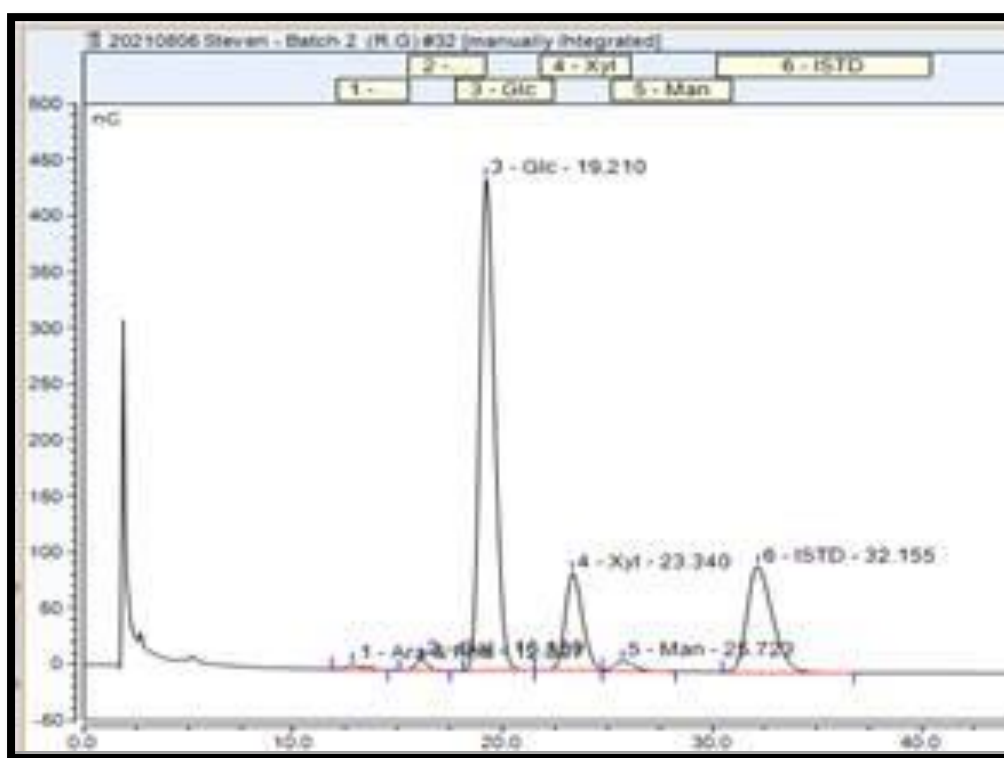


Figure 14: Graph showing various sugar peaks prior to integration

The remains from the crucible were used to gravimetrically measure the acid insoluble lignin known as Klason lignin by drying in an oven at 105°C according to TAPPI method T 222 (Tappi, 2002).

$$\text{Acid insoluble Lignin (\%)} = A \cdot 100 \div W \quad (5)$$

where: A = weight of lignin (g), W = oven-dry weight of test specimen (g)

For the determination of acid soluble lignin, the filtrate was further diluted with 2% H₂SO₄ to obtain an absorbance reading between 0.200 to 0.700 Absorbance Units (AU) at 205 nm on a spectrophotometer. The lignin in the filtrate was then quantified by measuring absorbance at 205 nm and quantified using a calibration curve as described in TAPPI T UM 250 (Tappi, 1991).

3.3.3.1 HPLC principle of operation

The HPLC system used in this study (Thermo scientific, Ultimate 3000) consists of an auto-sampler and injector that introduces the sample into the system, a quaternary-pump that provides the mobile phases to separate the monosaccharides and equilibrate the columns, a column compartment that houses the guard and analytical columns on which the monosaccharides are separated, an electrochemical detector for quantification and an auxiliary pump. The auxiliary pumps (post-column pump) functions to add NaOH post-column to the sample, to increase the hydroxide concentration that is required for an adequate signal in the detector. Additional components that provide back pressure (piping loops and columns) and flow switching valves are also integral to the system.

3.3.4 Cellulose

Cellulose content in this study wood was assessed based on Alpha-cellulose. To determine the alpha cellulose, wood samples were treated in a two-step process to selectively remove lignin and hemicellulose to produce pure α-cellulose (Tappi, 1999). About 400 mg of extracted wood powder was weighed into a serum bottle and 10.5 mL of buffer solution (NaOH) and 4.5 mL of 20% NaClO₂ were added. The sample bottles were capped and placed in a shaking incubator with temperature controlled at 50°C and shaking speed of 100 rpm for 16 h. After 16 hours, the reaction was stopped by placing the bottles in ice, and the reaction mixture was carefully removed without disturbing wood particles. The second cycle of the extraction was performed

by adding 10.5 mL buffer solution (NaOH), 4.5 mL of 20% NaClO₂ and incubating the samples for 16 hours, as in the previous step. The reaction was quenched by placing the bottles on ice and the contents were vacuum-filtered through a pre-weighed sintered-glass crucible. The residual contents from the bottle were washed with 1% glacial acetic acid (300 mL) into the crucible, which was then washed with 30 mL of acetone and oven-dried overnight at 50°C, and the contents were quantified. About 200 mg of the dried contents were weighed into 50 mL centrifuge tubes and left for 30 min to allow moisture equilibration. Exactly 16 mL of 17.5% NaOH were added to the sample and reacted at room temperature for 30 min, after which 16 mL of H₂O was added. The mixture was mixed by vortex for 1 minute and reacted at room temperature for 30 min and vacuum-filtered through a sintered-glass crucible. About 300 mL of water was used to wash the residual sample from the tube into the crucible, which was later soaked in 30 mL of 1.0 M acetic acid and washed with another 300 mL of water. The crucible was then oven-dried overnight at 50°C and the alpha cellulose determined gravimetrically.

$$\text{Alpha cellulose (\%)} = [(W_{c+acel} - W_c) \div W_h] \times 100 \quad (6)$$

Where, W_{c+acel} = weight of crucible+acellulose (g), W_c = weight of empty crucible (g), W_h = oven-dry weight of holocellulose (g).

3.4 Sulphite pulping process

Thirty five wood samples were pulped at standard mill conditions (temperature 140°C, time for four hours and 53 minutes pulping time). The pulping was carried out using a pilot digester (CRS Twin Digester). A magnesium acid sulphite pulping recipe consisting of 0.85% magnesium oxide and 8% sulphur dioxide in place at the mill was used. Wood chips moisture content, as well as packing densities were determined. For each cook, the equivalent of 2 kg of bone-dry wood chips were used.

3.5 Wood chips preparation and analysis

3.5.1 Wood chips screening/sorting

Wood chips for this study were obtained from the Shaw Research Centre in KZN. The chips screening was done at the Sappi Technology Centre (STC) using the 8.0 mm aperture screen to remove large knots and small sized (pin-chips) chips.

3.5.2 Wood moisture

Wood moisture was determined as described in section 3.3.1 *Wood moisture and consistency Moisture*.

3.5.3 Wood density

A Scan – N46:92 Wood Chips for Pulp Production - Bulk Density method was used to determine the bulk density. According to the procedure, the upper section of the pipe was closed by inserting the pull-out slide to keep the wood chips in the upper part of the pipe. The pre-weighed collection tray was placed underneath. Wood chips were transferred into the upper pipe section using the 2-litre scoop until it was full of chips, as shown in Figure 15 (a). Once the wood chips were full, the pull-out slide was quickly removed / withdrawn to let the chips to fall into the lower pipe section. The wooden disc was also dropped to freefall into the pipe, as shown in Figure 15(b). The chip column height from the pipe bottom to the bottom edge of the wooden disk was measured on opposite sides of the pipe and calculated as Scan – N46:92 Wood Chips for Pulp Production - Bulk Density.



Figure 15: Bulk density measurement set-up a) wood chips in the “upper pipe” section b) wood chips in the “lower” pipe section , Z. Khatshane 09 March 2021

3.6. Magnesium bisulphite liquor preparation and analysis

Magnesium bisulphite ($\text{Mg}(\text{HSO}_3)_2$) liquor was prepared by slaking 502 g magnesium oxide (MgO) powder in 40 litres of water. The resultant mixture was then bubbled with sulphur dioxide (SO_2) resulting in the formation of the solution of magnesium bisulphite ($\text{Mg}(\text{HSO}_3)_2$) with a pH value between 1 and 2. The target specifications of the liquor were 8% for total SO_2 and 0.85% active MgO . The cooking liquor was analysed and adjusted to obtain such

concentrations, determined by iodometric titration, followed by another titration with NaOH. The Palmrose method derived from Tappi T 604 cm-09 “Sulphur dioxide in sulfite cooking liquor “ was used for the liquor analysis (Tappi, 2009). Pressurised liquor tanks were used to store and charge the liquor into the digester (Figure 18).

3.7 Sulphite pulping process

The sulphite pulping process followed consists of various stages presented in Figure 16.

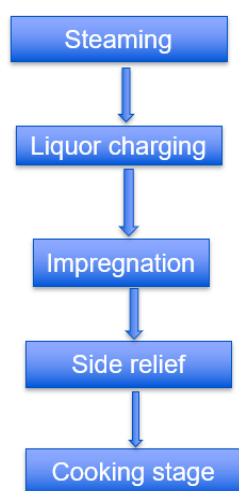


Figure 16: Process flow diagram used during the pulping process

3.7.1 Steaming

The pulping was carried out in the CRS pilot scale Twin digester. Wood chips of 2 kg, on an oven dry basis, were loaded into the pilot scale pressure vessel. The load was pre-steamed for 10 min at a temperature of 105°C as shown in Figure 19.

3.7.1.1 CRS twin digester principle

The CRS Twin Digester is designed for the delignification of wood chips or other cellulosic materials to produce pulp. Delignification involves chemically dissolving lignin and hemicellulose materials, enabling them to be removed during subsequent washing. The digester is presently being used to simulate the Saiccor pulping process for exclusively (magnesium-based sulphite cooks). The Twin Digester is operated semi-automatically using the Programmable Logic Computer (PLC), with two operational modes which are Twin mode and Pilot mode. The digester has two vessels - Digester A and Digester B connected by four-way

pneumatic valves, with two separated electric heat exchangers for each digester. Both systems are a mirror image of each other and can be operated as individual recirculation digesters (Twin mode). In the Pilot mode, both loops are interlinked and Digester A acts as digester, while Digester B fills the function of a liquor accumulator. Each digester loop is equipped with a centrifugal pump that circulates the liquor from digester to heat exchanger and back to digester. The lifts are used to lift the basket into the digester and open and close the heavy stainless-steel lid of the digester. A picture of the Twin Digester is given in Figure 17.



Figure 17: CRS Twin digester used for sulphite pulping, Z. Khatshane 09 May 2021

3.7.2 Liquor charging

Pressurized liquor tanks shown in Figure 18 were used to charge the liquor into the digester. The consequence of doing this dropped the temperature inside the pressure vessel. The heating of the liquor in the pressure vessel took was via an external heat exchanger



Figure 18: Pressurised liquor tanks used to charge liquor into the digester, K. Makgale 21 August 2017

3.7.3 Impregnation

A fixed temperature profile was followed, as shown in Figure 19 during the impregnation stage, where the pressure vessel was heated to a temperature of 110°C. Impregnation ensures that the cooling liquor is brought into contact with the wood chips.

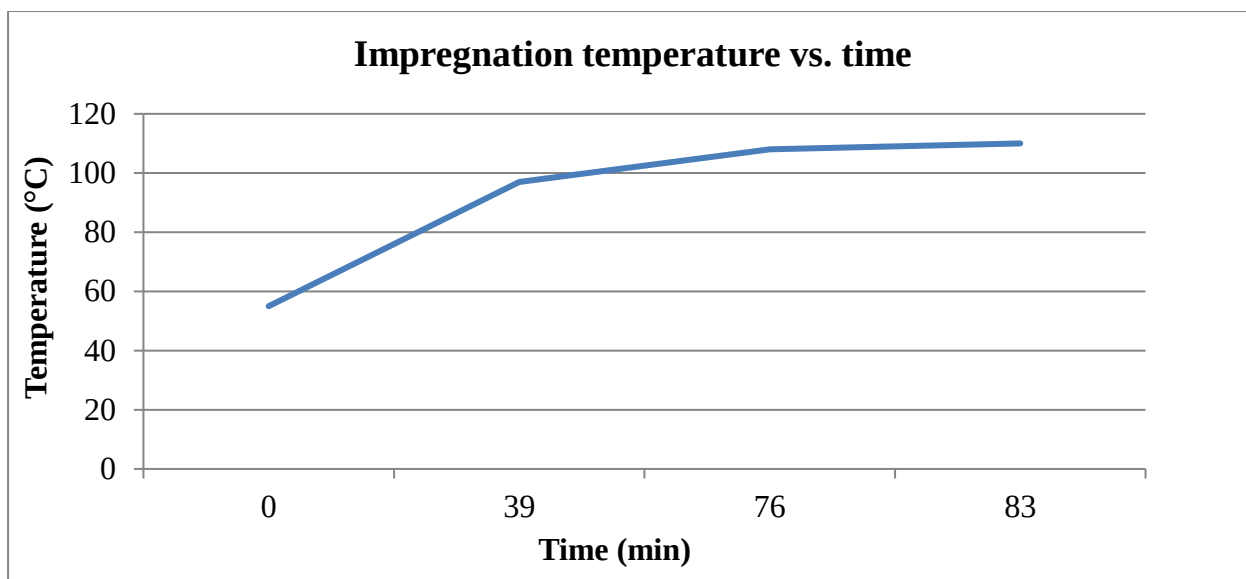


Figure 19: Impregnation stage of an acid sulphite pulping

3.7.4 Side relief and pulping

Side-relief followed the impregnation stage and where liquor was removed from the pressure vessel to balance the base (magnesium) in the digester. The amount removed because of the side relief action was determined according to the base ratio used in the cook (base ratios of 2.5, and 3.0, were used). The duration of the side relief was approximately 20 minutes, (approximately 8 litres removed) in which the pressure dropped to about 5 bars. The temperature was then gradually ramped up to the maximum temperature for the pulping experiment (140°C) and the pressure was increased using nitrogen to between 8.2 to 8.6 bars pressure. When the prescribed pulping time was reached, the temperature inside the pressure vessel was rapidly cooled to stop the reactions occurring within the digester by adding cold water to the digester. The side relief and the pulping stage is shown in Figure 20.

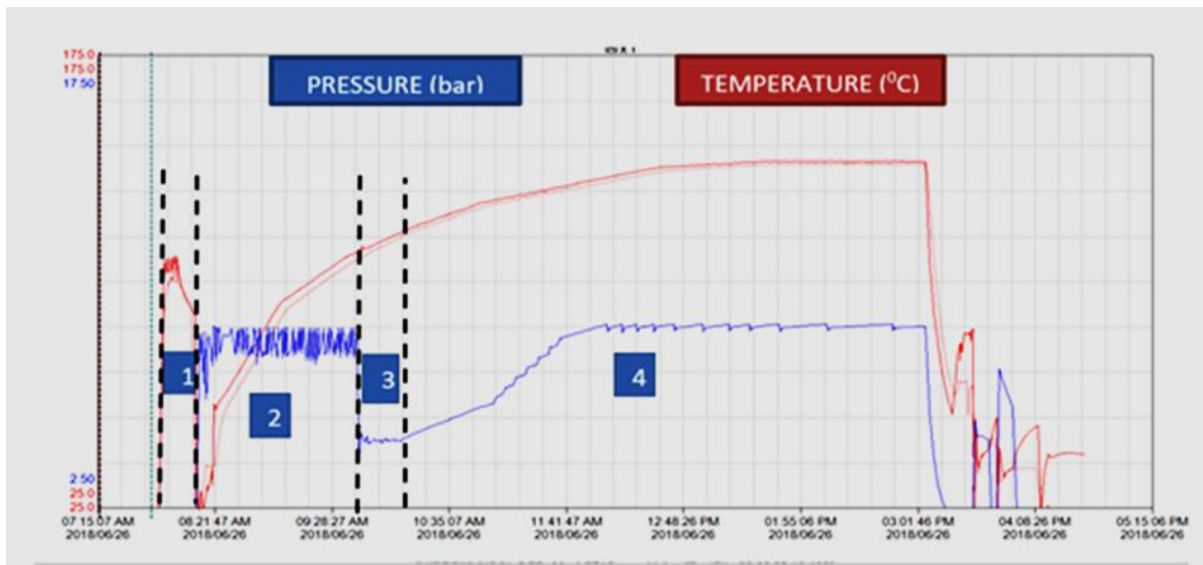


Figure 20: Example of a typical cook where 1 represents the STEAMING phase, 2 IMPREGNATION, 3. SIDE RELIEF phase, and 4 is the COOKING phase, Z. Khatshane 26 June 2018

3.7.5 Pulping conditions

All wood samples were pulped in two base ratios of 2.5 and 3.0 and a pulping temperature and pulping time of 140°C and four hours and 53 minutes , respectively. The effect of varying base ratio was investigated.

3.8 Pulp testing

Pulp was tested for the following properties:

3.8.1 Pulp Yield

A sample mass of 100 g (wet pulp) was dried in the oven for 12 hours at 105°C. The pulp yield was determined based on the mass and consistency of the wet pulp obtained and the oven-dry equivalent mass of the material charged to the digester. The pulp yield was determined by the following equation:

$$\text{Pulp yield (\%)} = (\text{mass of oven dried pulp} / \text{mass of oven dried wood chips}) \times 100 \quad (7)$$

3.8.2. Viscosity of cellulose

Measurements of pulp viscosities using Cupriethylenediamine (CED) solution (TAPPI, 1999). The amount of sample mass depends on the target viscosity for the pulp samples. For an unknown sample, 150 mg of pulp sample was weighed into a 50 ml sample bottle to which 25 ml of water was added, and the bottle was placed in a shaking device to mix and disintegrate the pulp for 25 minutes. CED solution of 25 ml was added and samples shaken for another 25 minutes. The samples were then conditioned in a water bath at 25°C for an hour. A portion of the sample was drawn into the viscometer by suction and the solution allowed to drain. When the meniscus was at the upper mark, the timer was started to measure the efflux time, which is the time it took the meniscus to fall from the upper to lower mark as shown in Figure 21.



Figure 21: Viscosity CED analysis set-up used during the analysis of pulp viscosity using Cupriethylenediamine solution, Z. Khatshane 09 May 2021

The following equation was used to calculate the pulp viscosity.

$$\text{Viscosity CED } [\eta] \text{ (ml/g)} = \lim \eta - \eta^0 \div \eta^0 c \quad (8)$$

where η is the viscosity of the sample solution (ml/g), η^0 is the viscosity of the solvent (ml/g), c is the concentration of pulp (g/ml)

3.8.3 Micro Kappa number and K number

The Tappi standardized method (T 236 om-13) for “Kappa number of pulp” and the laboratory procedure for K number (Tappi, 1999) were used to determine Micro Kappa and K number (K No) which reports the permanganate number. The amount of sample mass depends on the target kappa for the pulp samples. For unknown sample, 0.2 g of sample was disintegrated with 500 mL of water and transferred to a 2L flask. Deionised water was added to bring the mixture to approximately 800 mL and about 100 of potassium permanganate and 100 mL of sulfuric acid were added to the pulp mixture. After 10 minutes, the reaction was stopped by adding 20 mL of the potassium iodide and titrated with sodium thiosulphate till the endpoint was reached. Kappa was calculated as follows:

$$\text{Kappa (ml)} = (p \times f \div w) \times T \quad (9)$$

where f factor for correction to a 50% permanganate consumption, dependent on the value of p , w is the weight of moisture-free pulp in the specimen, (g), p is the amount of 0.1N permanganate actually consumed by the test specimen (ml), T is the temperature correction factor

3.8.4 Xylose, mannose and glucose

The hemicelluloses were determined using HPLC with reference to the SCAN standard method SCAN-CM 71:09 “Pulps: Carbohydrate composition” (SCAN, 2009). Pulp samples of 90 mg were weighed into serum bottles and 1 mL of 75% H_2SO_4 was added. The sample was left to hydrolyse for an hour, after which 23 mL of water as well as 1mL of the ribose internal standard were added. The samples and the calibration standards were placed in a pre-heated autoclave for digestion at 121°C for 60 min. After the autoclave reached 90°C, the sample was removed and left to cool. The sample was then diluted with HPLC grade water, filtered, and injected into the instrument. The sugars were quantified by integrating the chromatograms as previously described.

3.8.5 Pulp brightness

Brightness was determined using the Technidyne Colour Touch 2 (Poly Test CTH-150) instrument according to Tappi Test Method, T452; Brightness of Pulp, Paper and Paperboard. Kappa hand-sheets were used for the brightness analysis. A hand-sheet was placed in the Technidyne equipment, and two readings recorded on both sides, average was recorded.

3.9 Data analysis

Data analysis tool correlation was used to evaluate the correlation between the wood chemistry and pulp properties, whereas data analysis tool regression was used to develop the equation for prediction of viscosity. These statistical tools, based on Excel (at 95% confidence level), were chosen because of the limited number of data points (below 50 points) compared to well-known modelling methods that require many data points, typically above 100.

Statistical analysis to determine the significant differences (Q-values) could not be performed due to the limitation in wood chips, since only one bag of wood chips was available per wood sample, making it impossible to pulp the wood sample multiple times. Long cook hours of 8 hours approximately per one cook, also contributed as many cooks could not be performed to collect numerous data for statistical analysis.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Wood chemistry of the Eucalyptus samples

4.1.1 Extractives

Lipophilic wood extractives for the Eucalyptus samples were quantified using dichloromethane as the solvent are presented in Figure 22. It is apparent from the results that there was a variation in terms of extractives within the Eucalyptus species. Overall, the *E.003* species had the highest extractives of 0.5%. However, if outliers are removed, it can be deduced that, in general, the extractives content of Eucalypts are about 0.3%. As expected, these values are much lower than those of softwoods values that are at least 10 times over (Back and Allen, 2000) as softwoods are known to contain very high extractives. The results obtained in this study were similar to those obtained by Kilulya (2012) on South African hardwoods.



Figure 22: Extractives content of the eucalyptus samples.

4.1.2 Lignin

4.1.2.1 Syringyl/ guaiacyl (S/G) ratio

Figure 23 summarises the S/G ratio results of the Eucalyptus species tested. The results showed that *E.004* had higher S/G ratios among the tested species. The S/G ratio results obtained in this study were higher than those reported by Ramadevi *et al.* (2016) on *E. grandis* (sourced from India) where they ranged between 2.1 to 3.0%. The differences are most probably due to the different origins of the wood samples. It is well known that site locations affect S/G ratios (Robinson and Mansfield, 2009). However, in a study by Rencoret *et al.* (2006), the S/G ratio results obtained for three different Eucalyptus species from Pontevedra (Spain) were 3.6%, 4.6% and 4.0%. All these results were within the range obtained in this study.

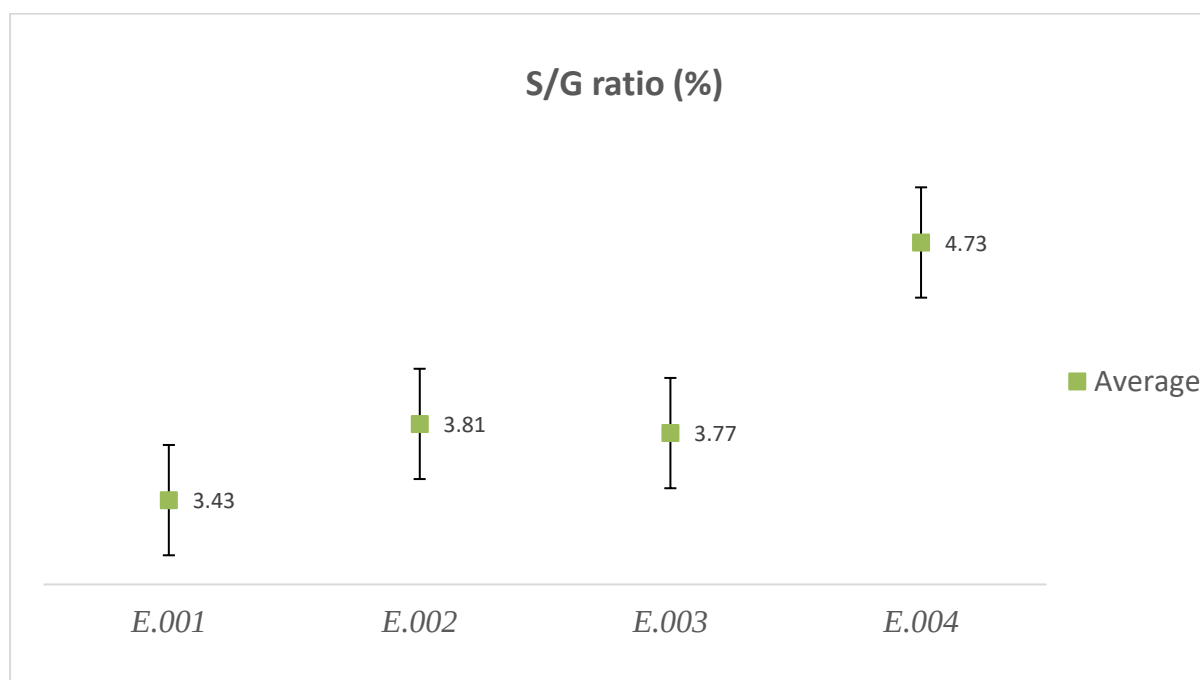


Figure 23: Syringyl/ Guaiacyl (S/G) ratio content of the Eucalyptus samples

4.1.2.2 Total lignin

Total lignin was calculated as the sum of Klason lignin (insoluble lignin) and acid soluble lignin. The *E.001* and *E.002* wood samples had the minimum total lignin content of approximately 19% (Figure 24) and maximum total lignin of approximately 30% and 28%, respectively. *E.003* had total lignin between 20% and 29%. In summary, *E.001*, *E.002* and

E.003 had similar total lignin average of 25.5%. *E.004* had the lowest total lignin content of all the Eucalyptus samples with values between 18.8% and 24.6%.

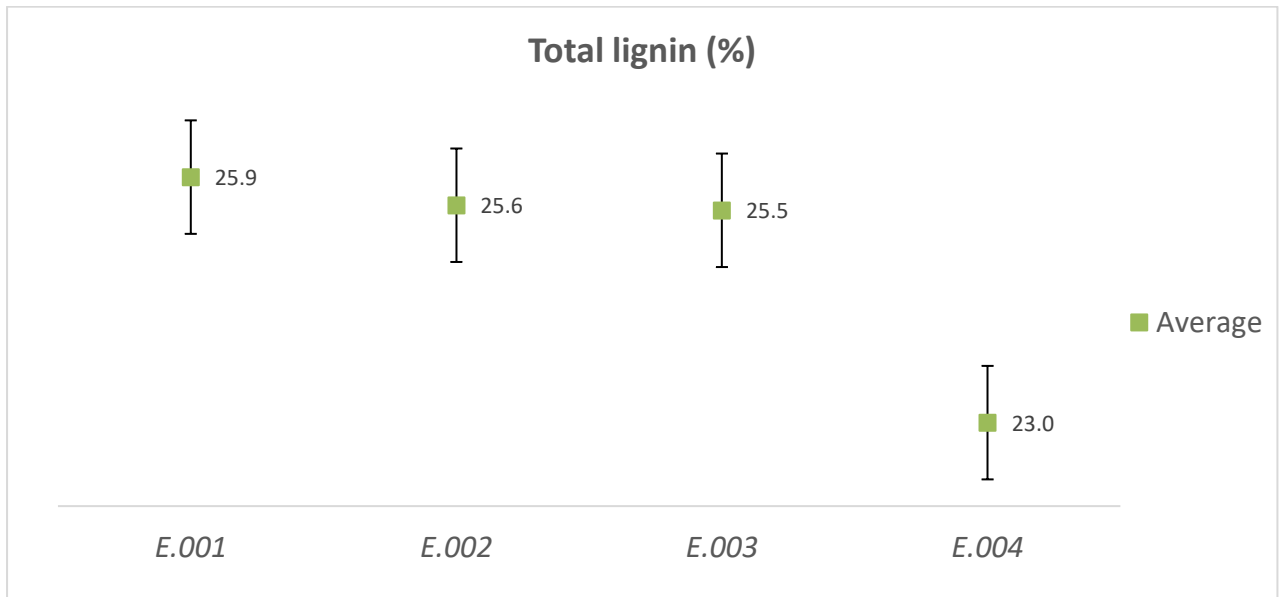


Figure 24: Total lignin ratio content of the Eucalyptus samples

4.1.2.3 Acid soluble lignin

The maximum soluble lignin for the eucalyptus samples was 4% (*E.003*) followed by 3.8 (*E.002* and *E.004*). The lowest soluble lignin was approximately 1.9% obtained for both *E.001* and *E.003*, as shown in Figure 25.

4.1.2.4 Insoluble lignin (Klason lignin)

Klason lignin for the *E.001* samples ranged from 17.4 to 27.1%. In a study by Rencoret *et al.* (2006) Klason lignin contents obtained for three Eucalyptus species were 21.1%, 22.5% and 21.6%. In the current study, similar results were obtained for sample *E.001*-36, which had 21%, *E.003*- 51 with 22.4% and *E.002*-10, which had 21.8% as shown in Appendix A, Figure 56. In general, *E.001* had the highest maximum Klason lignin content of 27%, whereas *E.004* had the lowest Klason lignin of 16%.

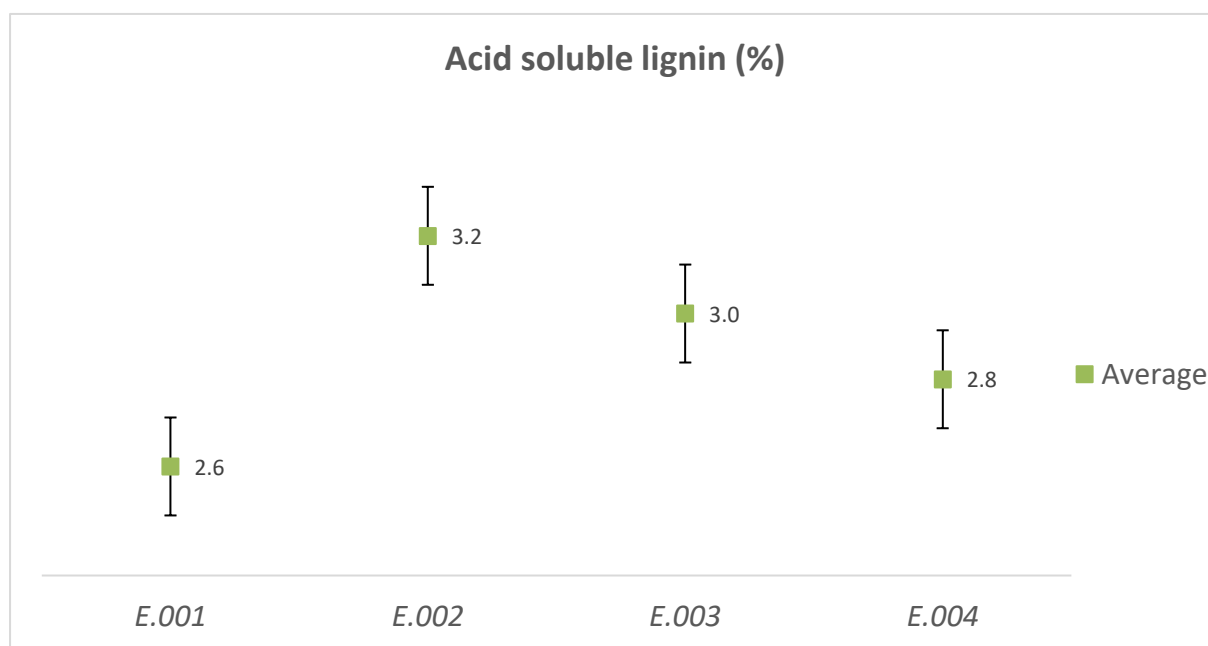


Figure 25: Soluble lignin ratio content of the Eucalyptus samples

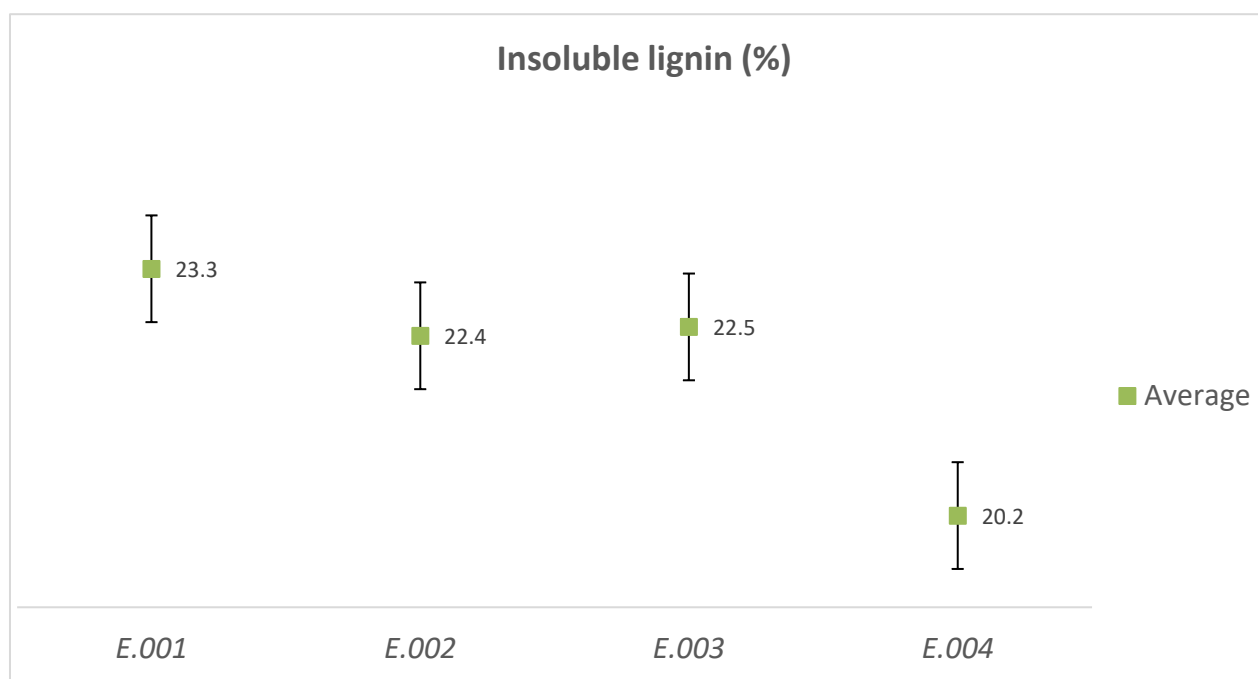


Figure 26: Acid insoluble lignin ratio content of the Eucalyptus samples

4.1.3 Sugars

The sugars were comprised mainly of glucose and hemicelluloses whose major components were xylose with smaller amounts of mannose, galactose, arabinose, and rhamnose Appendix A, Figure 57, Figure 58 and Figure 59. The xylose contents of the Eucalyptus species were high and ranged from 8 to 14% and the contents of the other hemicellulose compounds were low at around 2%. This confirms the notion that hardwoods are an excellent source of xylose. In general, *E.003* had the highest xylose content among the Eucalyptus samples. Both *E.002* and *E.004* had a similar range of xylose content between 9% to 12% (Figure 27). As can be seen in Figure 28, the glucose content values of the eucalyptus samples ranged between a minimum of 39% (*E.003*) and a maximum of 64% (*E.004*).

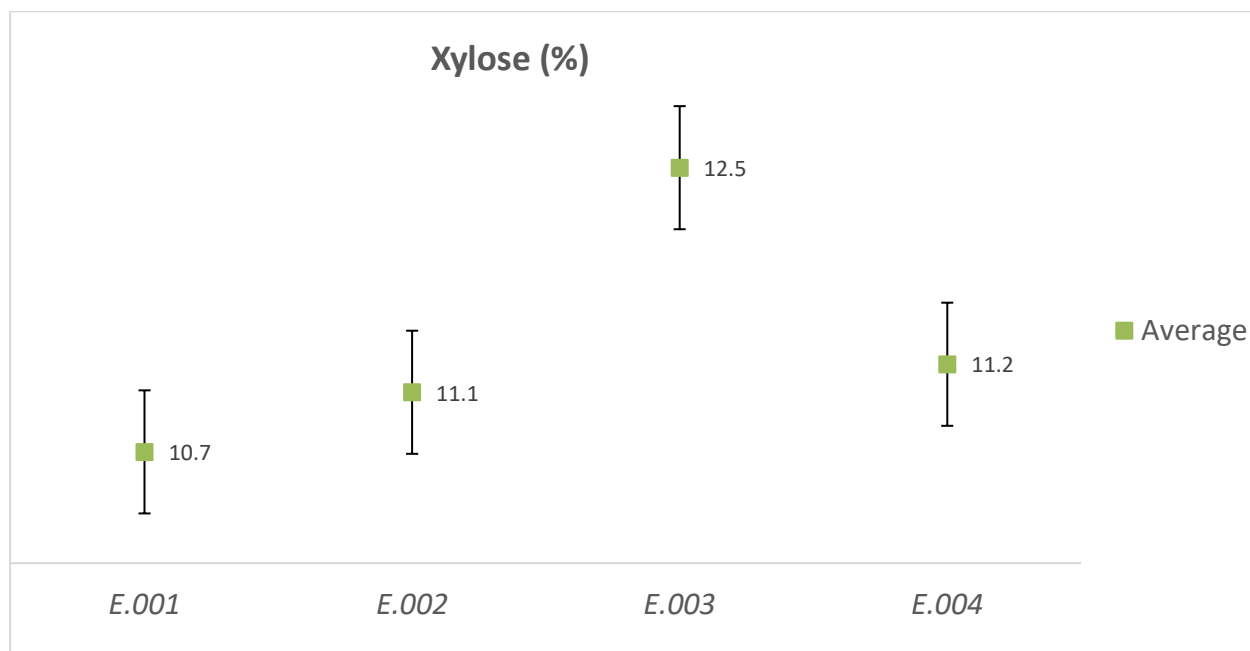


Figure 27: Xylose content of eucalyptus samples

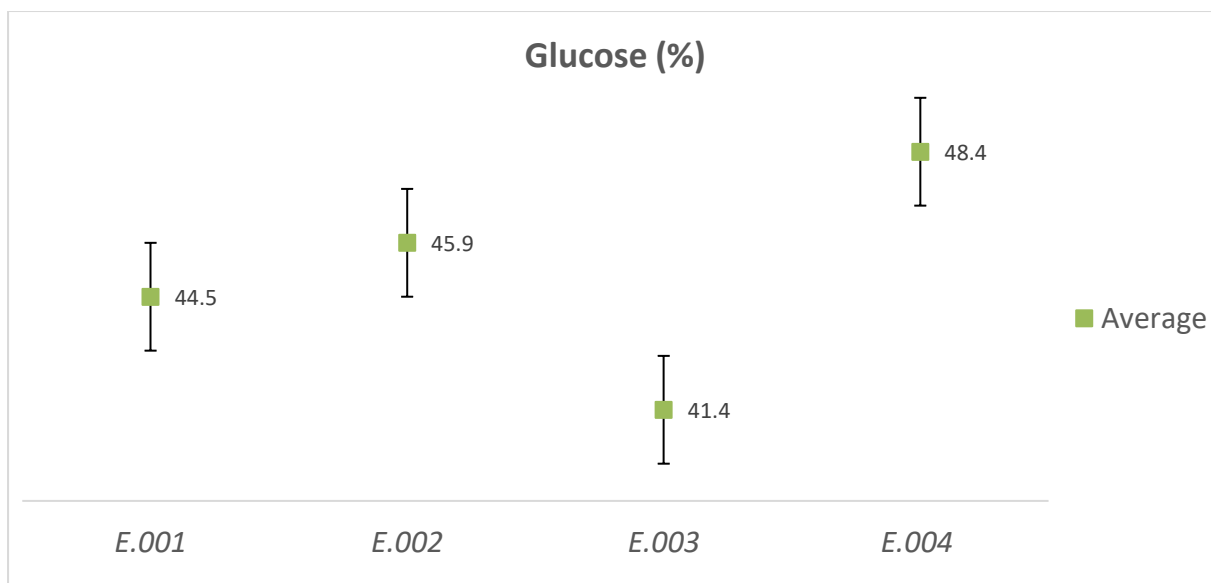


Figure 28: Glucose content of eucalyptus samples

4.1.4 Alpha cellulose

The alpha cellulose of the Eucalyptus samples varied between 41 and 50.7% as shown in Figure 29, *E.001* and *E.002* had a similar range between 43 to 48% and 42 to 48%, respectively, *E.003* had 41 to 45%. The results were similar to those reported on similar species by Ona *et al.* (1995). The results indicate that site provenance has no impact on alpha-cellulose content since the studies by Onal *et al.*(1995), were on samples bought in Japan.

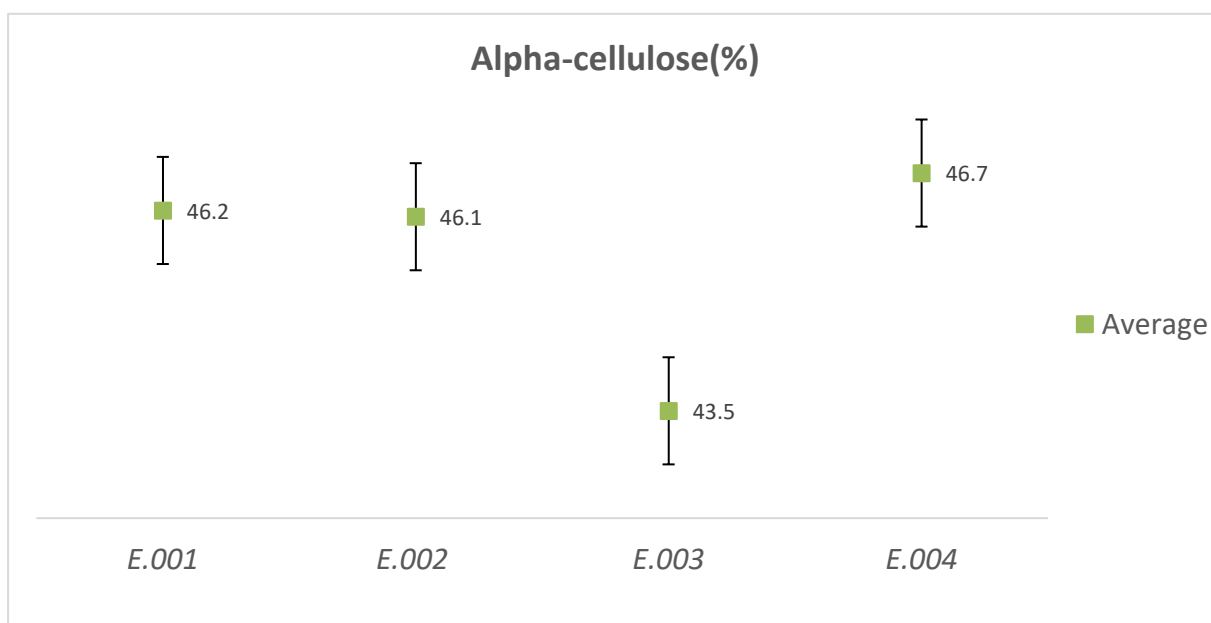


Figure 29: Alpha-cellulose content of eucalyptus samples

4.1.5 Summary of the Eucalyptus samples

The summary of the eucalyptus results is shown in Table 3 below.

Table 3: Summary of the statistical average of eucalyptus wood chemistry components

Sample ID	<i>E.001</i>	<i>E.002</i>	<i>E.003</i>	<i>E.004</i>
DCM Extractives (%)	0.25	0.24	0.32	0.27
Soluble lignin (%)	2.64	3.15	2.89	2.71
Insoluble lignin (%)	23.28	22.43	22.83	20.98
Total lignin (%)	25.92	25.58	25.72	23.69
S/G ratio (%)	3.43	3.81	3.81	4.79
Arabinose + Rhamnose (%)	0.62	0.66	0.85	0.82
Galactose (%)	1.27	1.33	1.25	1.34
Glucose (%)	44.48	45.93	41.70	48.14
Xylose (%)	10.69	11.06	12.37	10.97
Mannose (%)	0.57	0.64	0.57	0.80
Alpha cellulose (%)	46.23	46.14	43.47	46.58

4.2 Wood chemistry results of the Wattle samples

Wattle (*Acacia mearnsii*) had DCM extractive content between 0.18 (Wattle 43) and 0.2% (Wattle 45) as shown in Table 4. The S/G ratio was between 2.3 (Wattle 45) and of 4.1% (Wattle 41). Wattle had a Klason lignin range between 18.2 (Wattle 45) and 26.9% (Wattle 43). Klason lignin results in the current study were similar to those reported previously by Widiatmoko (2006) with Klason lignin of 27.1% for Wattle (*Acacia mangium*). In another study by Santos *et al.* (2012), the Klason lignin obtained was between 19.5 to 22.4% for Wattle (*Acacia melanoxylon*), this range was lower than what was obtained in the current study. The xylose content obtained in this study was between 10.9 and 16%, while glucose content was between 40.6% and 48.4%. The xylose and glucose content reported by Widiatmoko (2006) for Wattle was 10.9% and 48% respectively, which was similar to the results obtained in the current study. However, the glucose content obtained in this study was higher than the range reported by Santos *et al.* (2012) of 45.5 to 49.6% based on Wattle (*Acacia melanoxylon*). Wattle 41 had the highest alpha-cellulose content of 49.1%.

Table 4: Wood composition of Wattle samples

Sample ID	Wattle 41	Wattle 43	Wattle 44	Wattle 45
DCM Extractives (%)	0.19	0.18	0.19	0.20
Soluble lignin (%)	2.11	2.28	2.50	2.69
Insoluble lignin (%)	21.85	26.88	24.69	18.20
Total lignin (%)	23.96	29.17	27.19	20.89
S/G ratio (%)	4.10	2.65	2.41	2.29
Arabinose + Rhamnose (%)	0.84	0.76	0.66	0.89
Galactose (%)	1.34	1.02	0.69	1.25
Glucose (%)	44.21	43.34	40.59	48.41
Xylose (%)	10.87	15.09	16.09	15.60
Mannose (%)	0.49	1.39	1.13	1.25
Alpha cellulose (%)	49.12	48.73	45.78	48.32

4.3 Eucalyptus and Wattle Clones and hybrids

Various eucalyptus and Wattle clones were analysed for wood chemistry components and the results are shown in Table 5, full data results are shown in Appendix A, Table 14. W962 had extractives between 0.21 and 0.30% while the S/G ratio was approximately 3%. W962-71 had the lowest xylose content of 9.59% and the highest total lignin and alpha-cellulose of 28 and 47%, respectively. G438 had S/G ratio of approximately 3.4% and alpha cellulose of 45%. The maximum S/G ratio of the GN samples was 3.3%, xylose was 11% while the alpha cellulose content was 48%.

Table 5: Wood composition of clones and hybrids

Sample ID	Extractives (%)	Soluble lignin (%)	Insoluble lignin(%)	Total lignin (%)	S/G ratio	Glucose (%)	Xylose (%)	Alpha cellulose (%)
W962 71	0.21	3.01	25.96	28.97	3.04	47.33	9.59	47.10
W962-72	0.30	1.68	19.92	21.60	3.26	46.09	13.97	44.89
W962-73	0.20	2.13	20.37	22.49	3.45	44.63	10.51	46.05
G438-103	0.24	3.09	25.40	28.49	3.36	45.69	10.80	45.00
G438-105	0.19	2.19	17.33	19.52	3.51	45.15	12.03	45.95
GN 101	0.19	1.88	23.37	25.25	3.38	46.94	11.11	46.97
GN 98	0.24	1.95	22.82	24.77	2.85	46.57	9.65	46.39
GUW 1035-96	0.24	3.10	28.55	31.64	2.77	42.41	11.81	45.80
A189-97	0.31	2.63	19.21	21.84	3.74	41.11	11.72	44.06
100 GN	0.24	2.14	19.68	21.82	2.89	46.98	11.01	48.92
GN018b 30431	0.27	3.01	28.37	31.38	3.37	41.94	10.59	42.14
PP2107 30434	0.36	1.92	22.46	24.38	3.59	49.84	9.88	43.17

4.4 Wood moisture

Wood moisture results for 40 Eucalyptus species are shown in Appendix B Table 15 whereas those for Wattle as well clones samples are presented in Appendix B Table 16. Wood moisture content for Eucalyptus ranged between 41.1% (E.005- 99) for the wood chips as fresh timber, to 13.6% (E.001-23), almost air-dry. Moisture content for Wattle and clones ranged between 14.5% (W962-72) to 36.3% (GN-98). However, these differences had no impact on this study. According to Casey (1951) knowledge of moisture content of chips is important as it enables pulp mills to correctly assess the true wood input into digesters. Additionally, optimum pulping controls can be achieved only if liquor-to-wood ratios and chemical concentrations in the liquor are constant for all cooks. Variations in wood chips moisture content can cause significant fluctuations.

4.5. Packing / bulk density

The bulk density of chips is expressed as the weight per unit volume of chips, usually in kg per m³ loose volume (Kofman, 2006). The denser the wood, the more of it that can be charged into the digester. However, one needs to assure adequate chemical charge to pulp it. E.004- 63 had the highest bulk density of 221.11 kg.m⁻³, whereas E.001-39 had the lowest bulk density of 109.8 kg/m³ compared to all Eucalyptus samples, as shown in Appendix B Table 17. In

clones, GN-98 had the bulk density of 211.88 kg/m³ while 100 GN had the lowest bulk density of 127.85 kg.m⁻³ Appendix B Table 18.

4.6 Pulping Properties

4.6.1 Total yield

4.6.1.1 Eucalyptus species

The average total yield range of the eucalyptus samples was between 43.37 to 53.06% in base ratio 2.5, as can be seen in Figure 30. When the base ratio was increased to 3.0, the total yield range increased from 44.03 to 55.07% (Figure 31). *E.001* had a yield range of 43 to 50% and 46 to 51% at base ratio 2.5 and 3.0, respectively. The yield for *E.002* was between 45 to 50% in both base ratios, whereas that of *E.003* was between 44 to 48% also in both base ratios. This implies that there is a variation within the same Eucalyptus samples, as well as within the species. Amongst all the eucalyptus species, *E.004* had the highest total yield range of 53.06 and 55.07% in base ratios of 2.5 and 3, respectively. According to Casey (1951), in the acid sulphite pulping process, the unbleached pulp yields for bleachable grades are in the range of 45 to 50%, whereas in bisulphite pulping the yield is in the range of 48 to 53%. The yield of 45 to 50% was only observed with the *E.002* samples in this study. In the current study, 71% of the Eucalyptus species had a higher pulp yield at base ratio 3.0 compared to base ratio 2.5%.

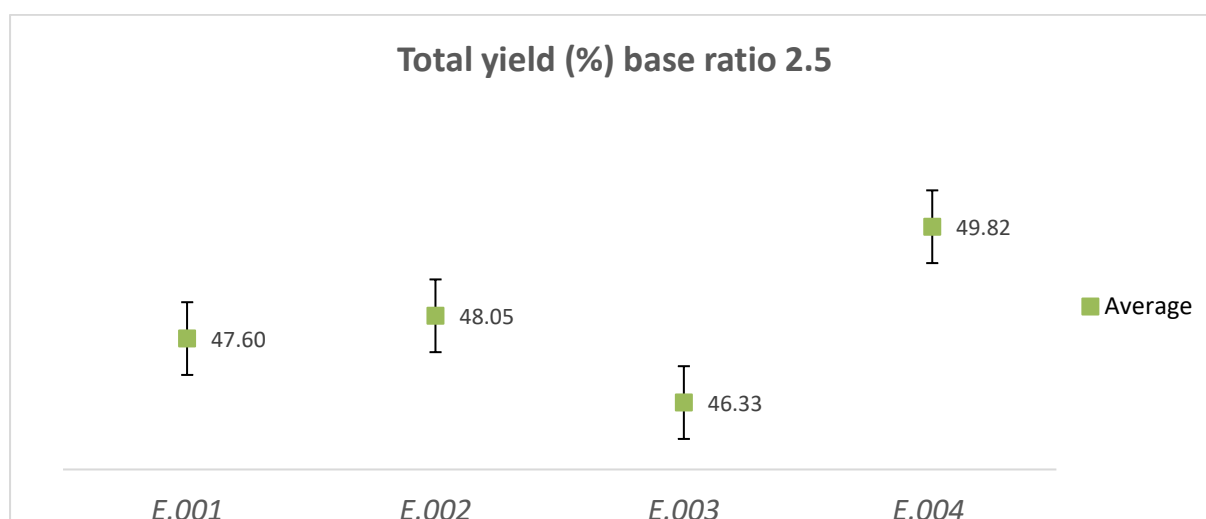


Figure 30: Total yield of the Eucalyptus species pulped at base ratio 2.5

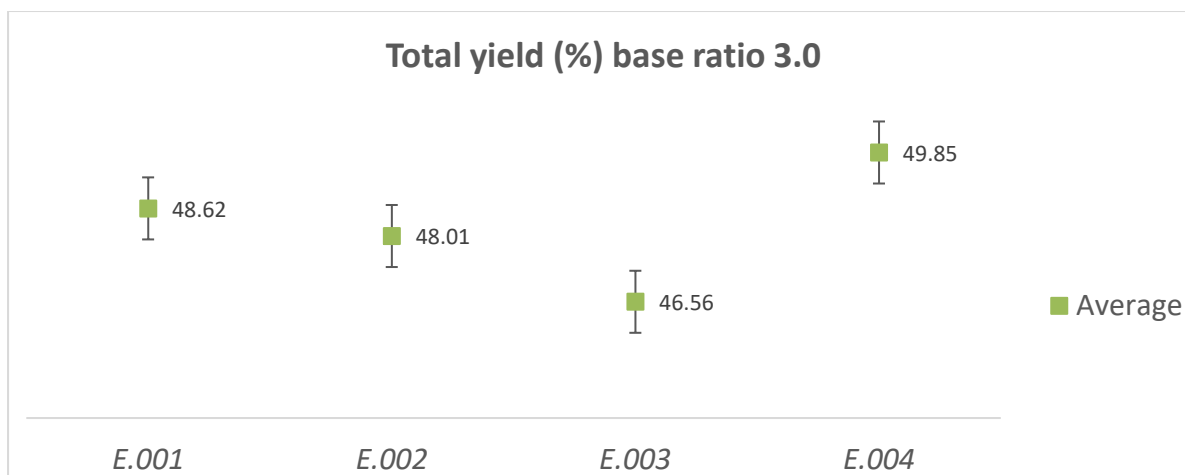


Figure 31: Total yield of the Eucalyptus species pulped at base ratio 3.0

4.6.1.2 Wattle and clones

Wattle 41 had a total yield of approximately 53% at base ratio 2.5 and 54% at base ratio 3, Figure 32. Wattle 42 had a total yield of approximately 51% in both base ratios. Amongst the clones, GN 98 had the highest total yield of approximately 52%, whereas W962-72 had the lowest total yield of 45% compared to all the clones. On average, about 89% of Wattle and clones had higher total pulp yield at base ratio 3, compared to base ratio 2.5. Only GN 98 had higher pulp yield at base ratio 2.5 compared to other clones.

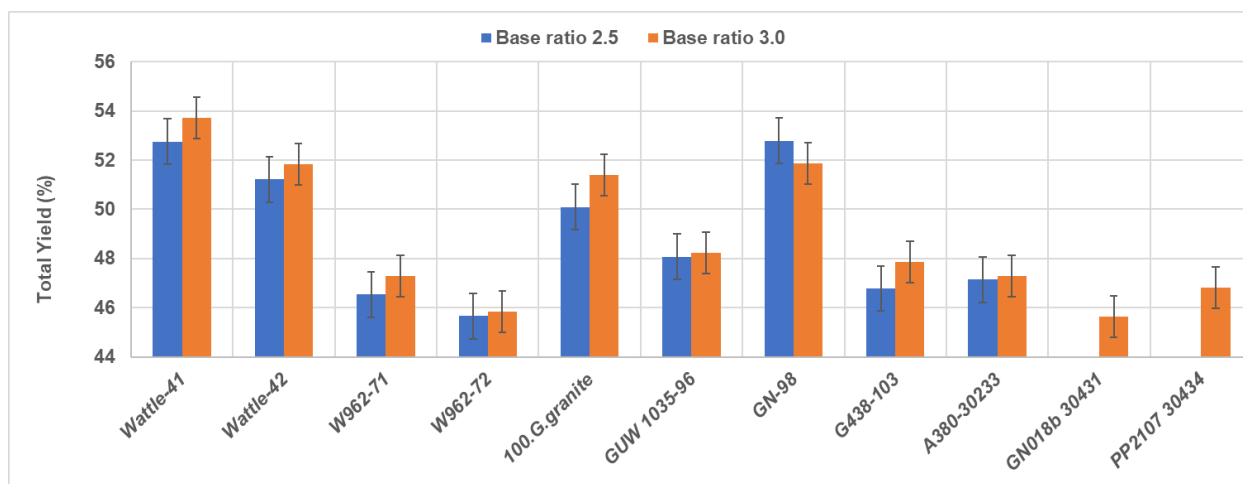


Figure 32: Total yield of Wattle and clones species pulped at base ratios 2.5 and 3.0

4.6.2 Kappa number

4.6.2.1 Micro-kappa Eucalyptus

Kappa number is used in the pulp and paper industry to estimate the lignin content remaining in the pulp after the pulping process. Kappa number can also determine the rate of delignification during pulping. In the current study, the micro kappa and K. number methods were used to determine the kappa content as preferred by the mill under study. Micro kappa and K. number methods are similar and comparison of the results between the two methods had a correlation coefficient R^2 of 0.93. The maximum target micro kappa and K. number for the mill is 7 and 3 ml, respectively. In all species, some samples had microkappa below 7ml, however, *E.002* had the lowest microkappa of 4.5 ml, whereas *E.001* had the highest microkappa of 18 ml and 19 ml in base ratio 2.5 and 3, respectively as shown in Figure 33 and Figure 34.

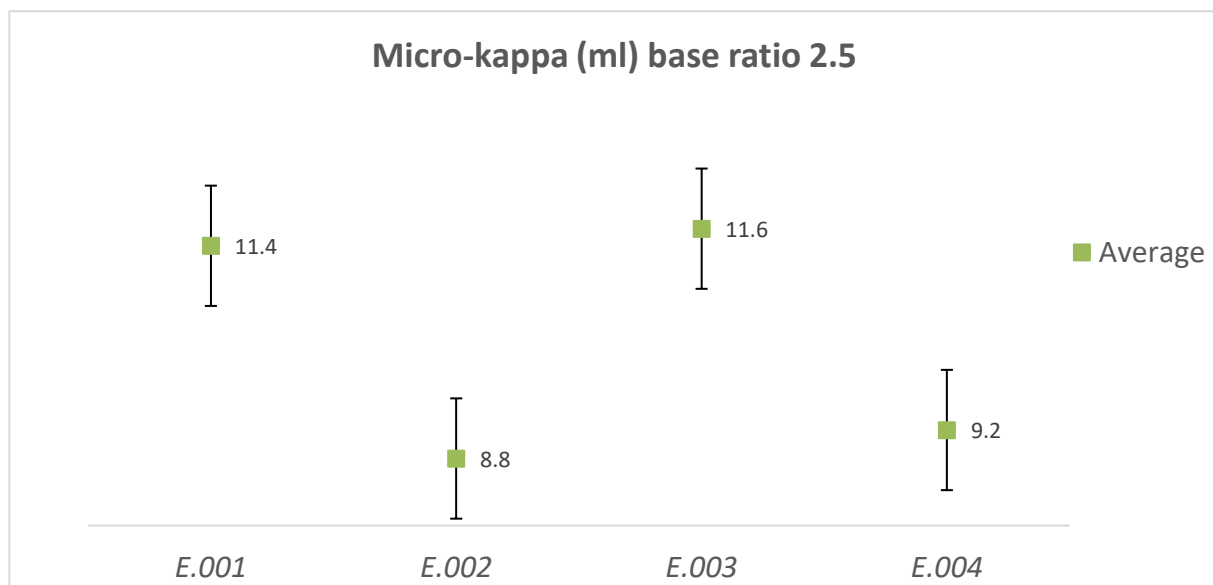


Figure 33: Micro-kappa of the Eucalyptus species pulped at base ratio 2.5

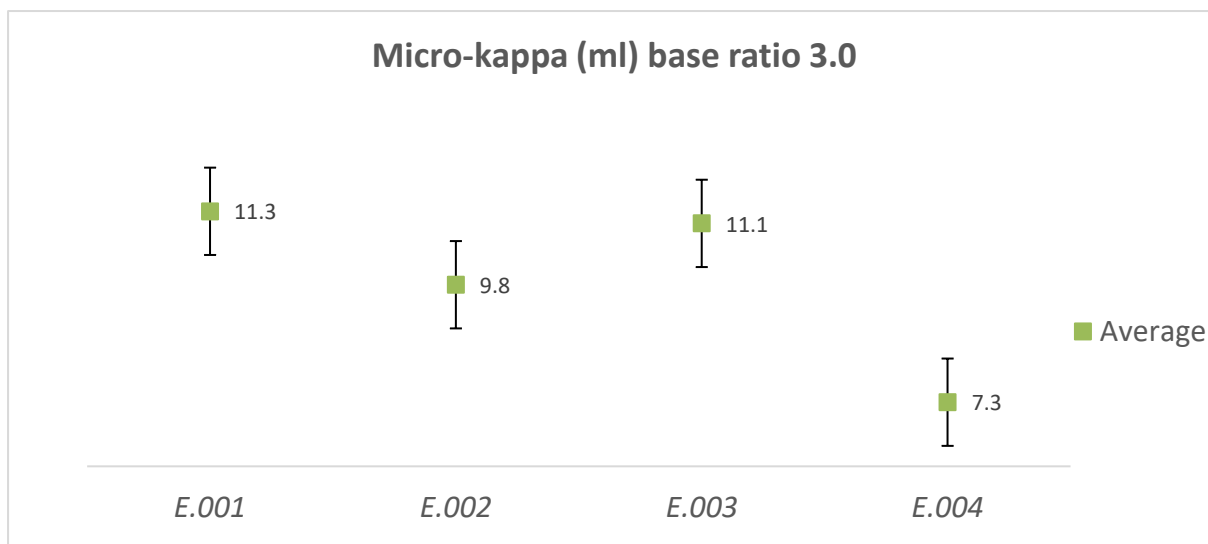


Figure 34: Micro-kappa of the Eucalyptus species pulped at base ratio 3.0

4.6.2.2 K.number Eucalyptus

The highest K. number obtained in the eucalyptus samples was 5.7 ml and 6.2 ml (both *E.001* at base ratio 2.5 and 3, respectively (Figure 35 and Figure 36). About 65% of the eucalyptus samples had higher kappa at base ratio 3 compared to base ratio 2.5 and 75% of the eucalyptus samples had higher k. number at base ratio 3,0. This means that pulping at base ratio 2.5 gave lower micro kappa and K. number results.

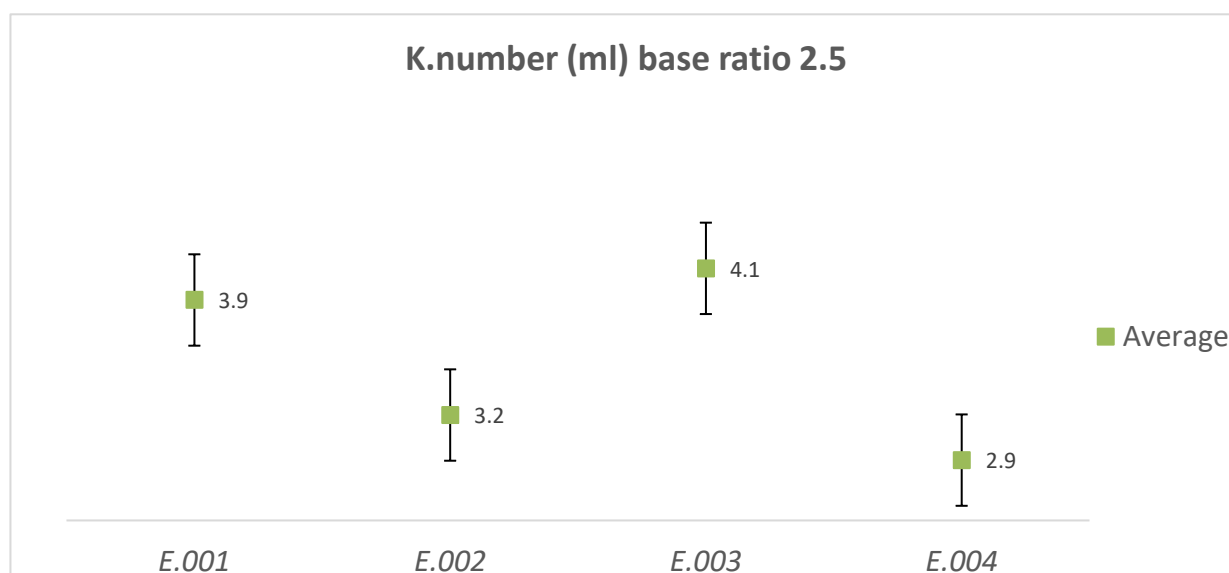


Figure 35 : K.number of the Eucalyptus species pulped at base ratio 2.5

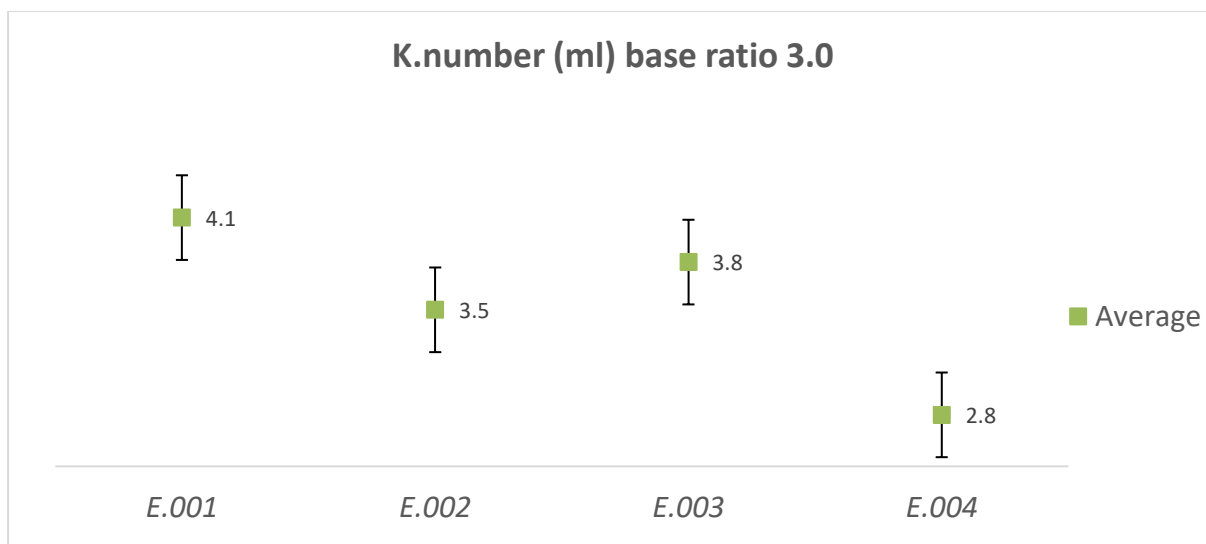


Figure 36: K.number of the Eucalyptus species pulped at base ratio 3.0

4.6.2.3 Wattle and clones

Wattle had micro kappa values of approximately 8 to 13 ml and K. number of 3 to 4 ml in base ratios 2.5 and 3.0, respectively as shown in Figure 37. A380 30233 had the highest micro kappa and K. number of all the clones evaluated. Only few clones had target K. numbers below 3ml: these were W962-72, G438-103 (base ratio 2.5) and PP 2107 30434 as shown in Figure 38. Approximately 78% of Wattle and clones had higher kappa at base ratio 3 than at base ratio 2.5.

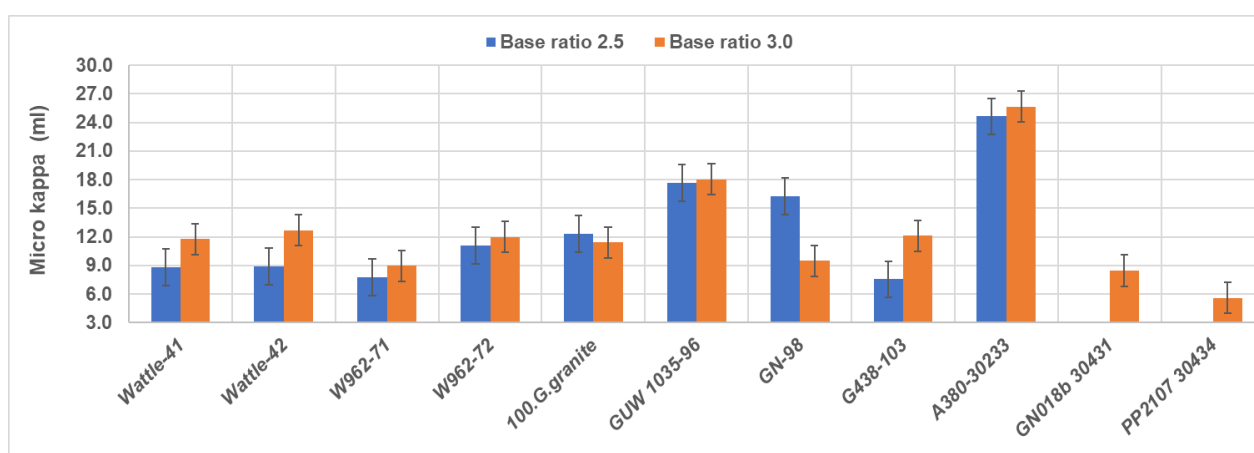


Figure 37: Micro kappa of Wattle and clones species pulped at base ratios 2.5 and 3.0

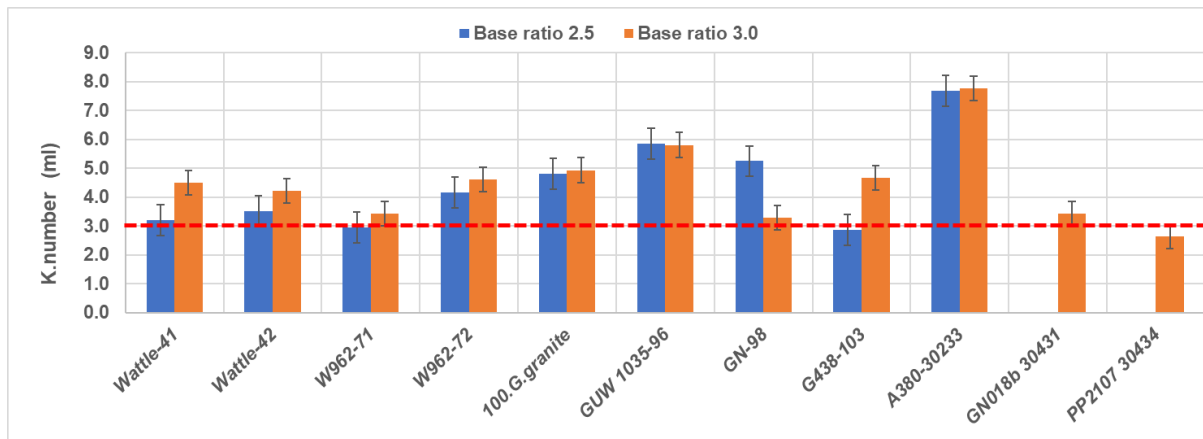


Figure 38: K. number of Wattle and clones species pulped at base ratios 2.5 and 3.

4.6.3 Viscosity in CED solution

4.6.3.1 Eucalyptus

The mill has a target CED viscosity between 680 ml/g to 830 ml/g. Based on the viscosity obtained, the wood samples can be categorised as fast cookers, medium cookers, or slow cookers. Fast cookers are wood species with a pulp viscosity below 680 ml/g, medium cookers are those with a viscosity between 680 ml/g and 830 ml/g, and slow cookers are those with a viscosity above 830 ml/g. At base ratio 2.5, fast cookers were *E.002-2* and *E.004-65*, whereas at base ratio 3.0, only *E.004-65* was the fast cooker as shown in Table 6. The medium cookers in base ratio 2.5 were *E.001-22*, and *E.002-1*. At base ratio 3.0, medium cookers were *E.001-30432*, and *E.002-2*. The rest of the samples were slow cookers since their viscosities were above 830 ml/g. The average viscosity range for all species at base ratio 2.5 was between 877 ml/g and 938 ml/g, and between 874 ml/g and 974 ml/g for base ratio 3.0 as shown in Figure 39 and Figure 40. At base ratio 2.5, only 20% of the eucalyptus samples exhibited viscosity results that were within the target range (below 830 ml/g) whereas at base ratio 3.0, only 13% of the samples had viscosity results below 830 ml/g. This means that most of the eucalyptus samples (above 70%) exhibited high viscosity values thus, implying that the wood samples would be problematic for pulping at the mill. About 70% of the eucalyptus samples had higher

viscosity when pulped at base ratio 3.0 compared to 25% of the samples that were pulped at base ratio 2.5.

Table 6: Categorisation of Eucalyptus species in terms of fast, medium and slow cookers based on pulp viscosity

	Fast cookers	Medium cookers	Slow cookers
Base ratio 2.5	<i>E.002-2, E.004-65</i>	<i>E.001-22, E.002-1</i>	<i>E.001-21, E.001-30, E.001-31, E.001-39, E.002-3, E.002-4, E.002-5, E.002-6, E.003-53, E.003-54, E.003-55, E.003-57, E.003- 59, E.004-61, E.004-62, E.004-63.</i>
Base ratio 3.0	<i>E.004-65</i>	<i>E.001-30432, E.002-2</i>	<i>E.001-21, E.001-22, E.001-30, E.001-31, E.001-39, E.002-1, E.002-3, E.002- 4, E.002-5, E.002-6, E.002-30436, E.003-53, E.003-54, E.003-55 E.003-57, E.003-59, E.003-30433, E.004-61, E.004-62, E.004-63, E.004-30435.</i>

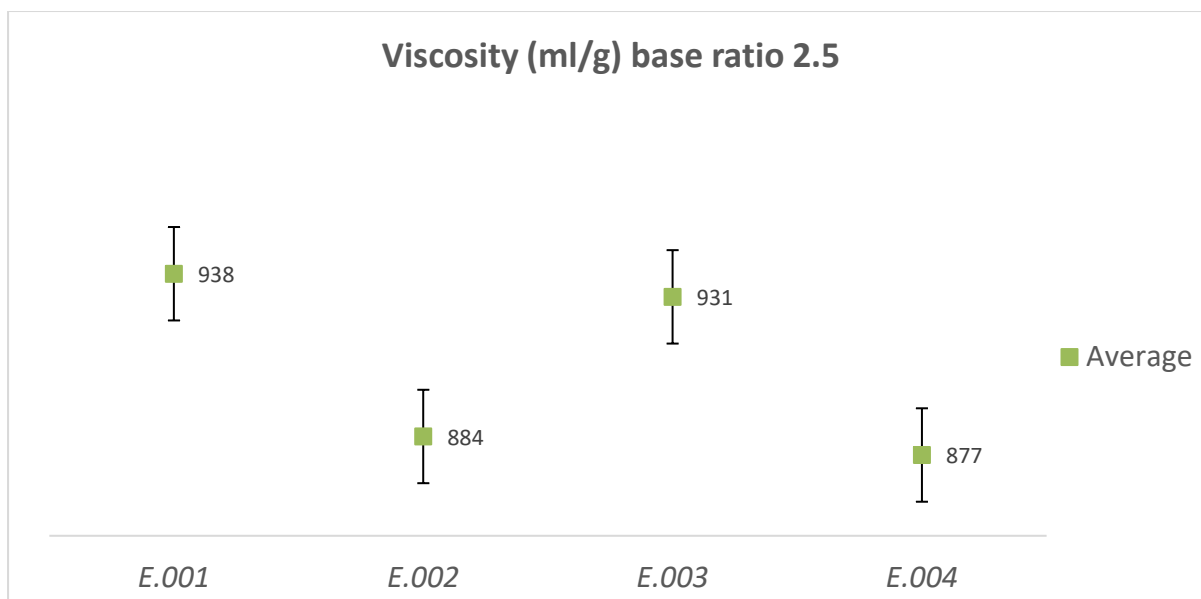


Figure 39: Cupriethylenediamine (CED) viscosity of the Eucalyptus species pulped at base ratio 2.5

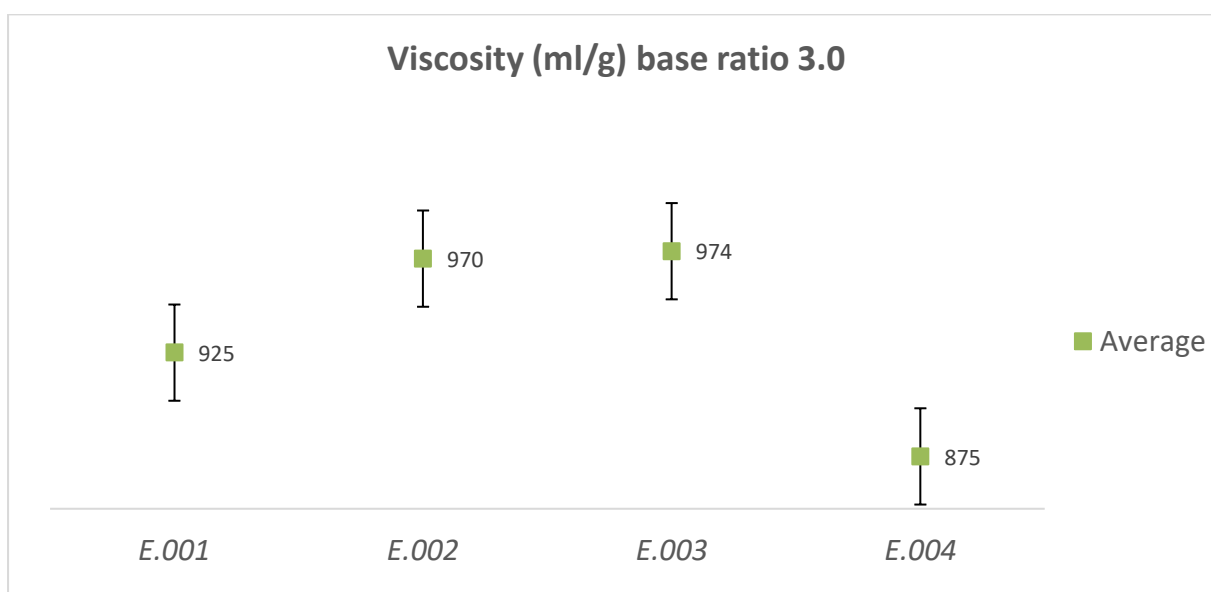


Figure 40: Cupriethylenediamine (CED) viscosity of the Eucalyptus species pulped at base ratio 3.0

4.6.3.2 Wattle and clones

Different viscosity results were observed between Wattle 41 and 42. Wattle 41 had a viscosity of 1004 ml/g and 603 ml/g in base ratio 2.5 and 3.0, respectively (Figure 41). Wattle 42 had a viscosity of 959 ml/g and 1018 in base ratio 2.5 and 3.0, respectively. W962 -71 and G438-103

can be categorised as medium cookers in base ratio 2.5, while Wattle and other clones can be categorised as slow cookers (Table 7). In base ratio 3.0, Wattle 41 can be categorised as a fast cooker, while Wattle 42 and other clones can be categorised as slow cookers. About 56% of the clones had higher viscosities at base ratio 3.0 compared to base ratio 2.5.

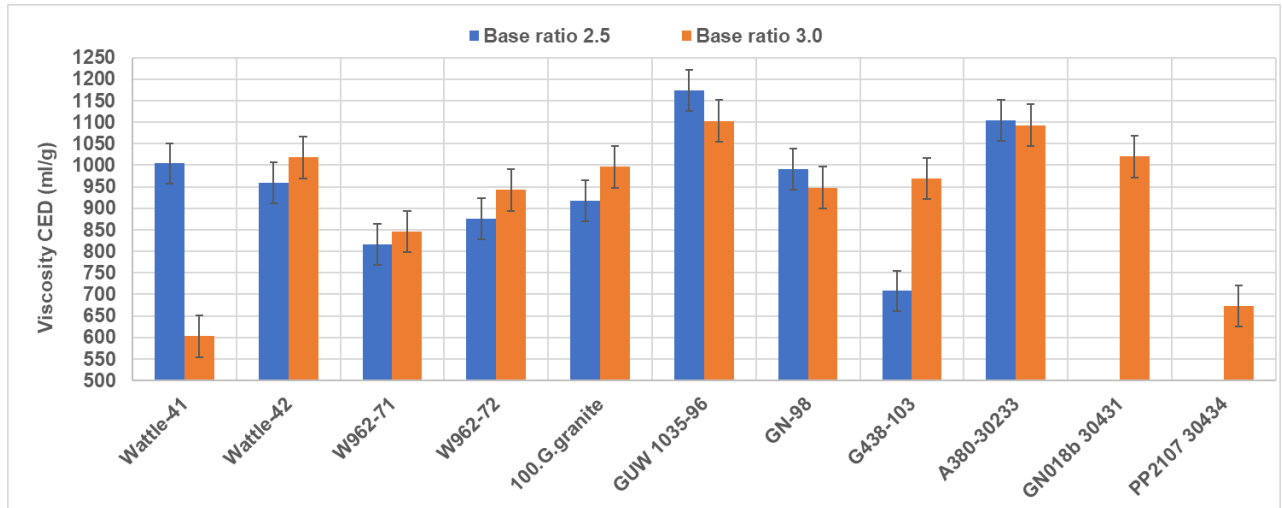


Figure 41: Cupriethylenediamine (CED) viscosity of Wattle and clones species pulped at base ratios 2.5 and 3.0

Table 7: Categorisation of Wattle and clones in terms of in terms of fast, medium and slow cookers based on pulp viscosity.

	Fast cookers	Medium cookers	Slow cookers
Base ratio 2.5	<i>None</i>	W962-71, G438-103	Wattle-41, Wattle-42, W962-72, 100.G. granite, GUW 1035-96, GN-98, A380-30233
Base ratio 3.0	PP2107, (30434), Wattle-41	<i>None</i>	Wattle-42, *W962-71, W962-72, 100.G. granite, GUW 1035-96, GN-98, G438-103, A380-30233, GN018b and (30431)

4.6.4 Pulp brightness

4.6.4.1 Eucalyptus

The sulphite pulping process is characterised by a higher brightness content compared to other pulping processes such as soda, Kraft process etc. Brightness measurements are indicative of

residual lignin in pulps after pulping. Desirable brightness levels of unbleached sulphite pulps are around 65%. As shown in Figure 42 and Figure 43, the average brightness of the eucalyptus samples was between 54 % and 59 % (base ratios 2.5) and between 55% and 61% at base ratio 3.0. *E.002* and *E.004* had brightness levels above 61% at base ratio 2.5 and 3.0. *E.001* and *E.002* had higher maximum brightness at base ratio 2.5 compared to base ratio 3.0, whereas *E.003* had higher maximum brightness at base ratio 3 compared to base ratio 2.5. *E.004* had similar maximum brightness at both base ratios.

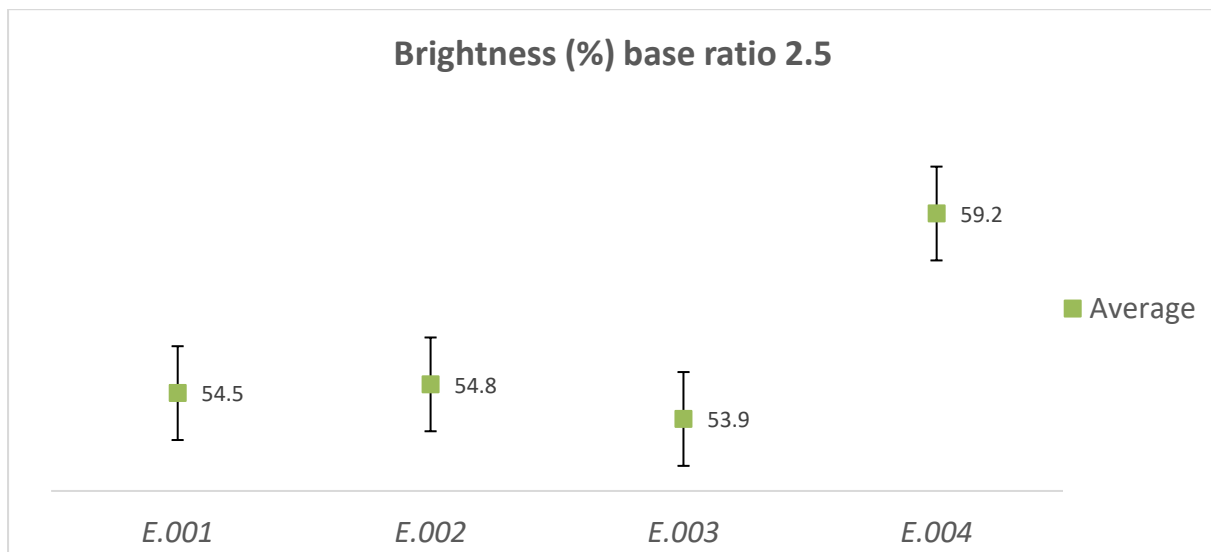


Figure 42: Brightness of the Eucalyptus pulped at base ratios 2.5

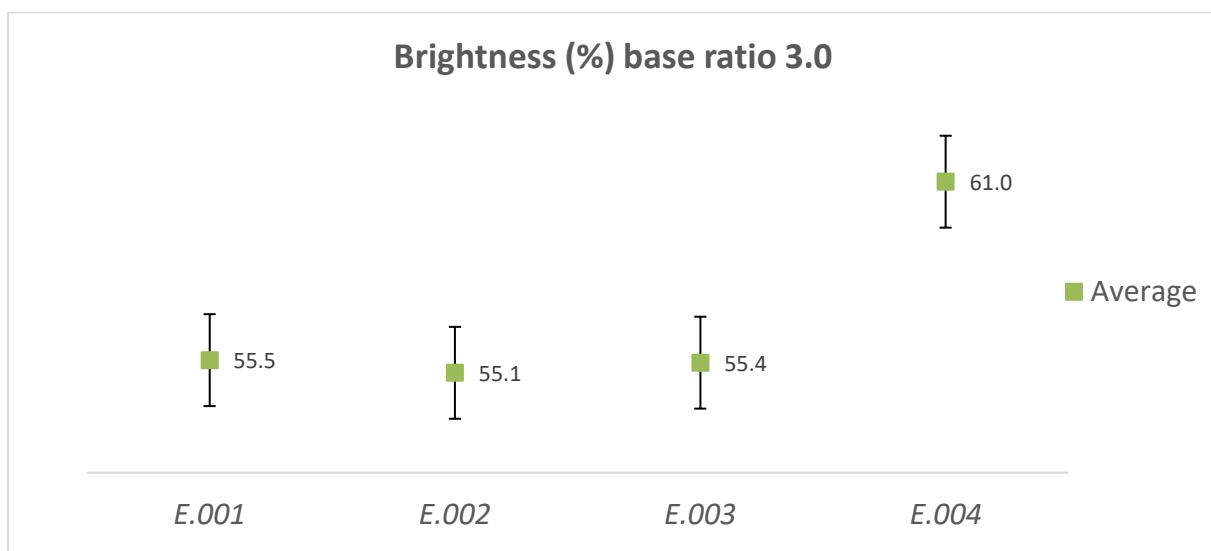


Figure 43: Brightness of the Eucalyptus pulped at base ratios 3.0

4.6.4.2 Wattle

Wattle 41 had a brightness of approximately 51% in both base ratios, while Wattle 42 had a brightness of 49% in base ratio 2.5 and 48% in base ratio 3.0 as shown in Figure 44. W962-71, 100.G. granite and GN 98 had brightness levels of approximately 54% at base ratio 2.5. GN 98 had the highest brightness of 56% at base ratio 3.0. The lowest brightness on the clones was obtained in G438-103, which was approximately 50% and 47% in base ratios 2.5 and 3.0, respectively. About 56% of clones and Wattle had higher pulp brightness at base ratio 2.5 compared to 44% at base ratio 3.0.

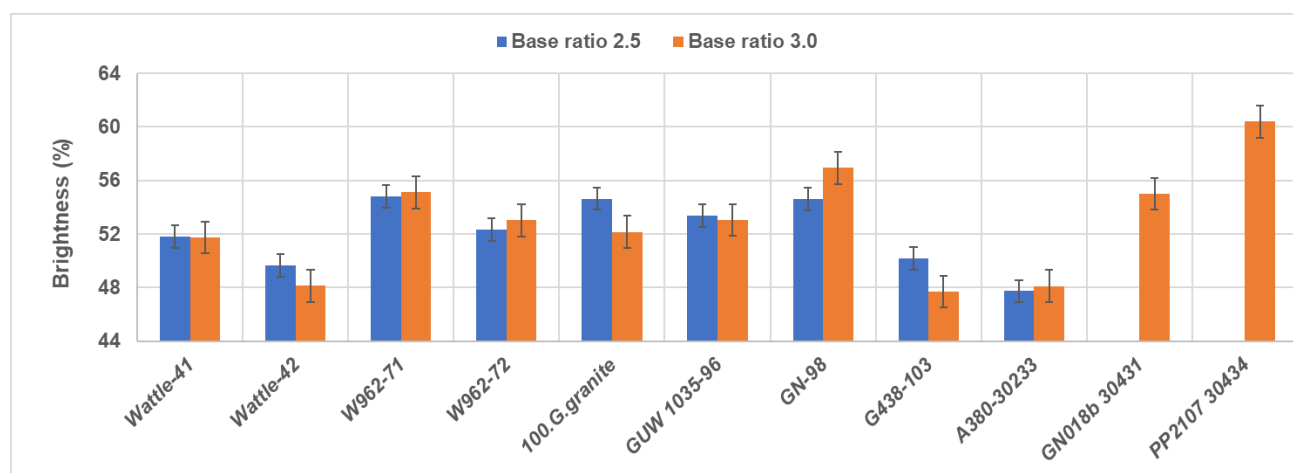


Figure 44: Brightness of Wattle and clones species pulped at base ratios 2.5 and 3.0

4.6.5. Sugar analysis (xylose, mannose and glucose)

4.6.5.1 Eucalyptus

Sugars are formed because of hydrolysis of hemicellulose (Llano, 2016). Xylose and mannose were measured in the pulp to give the hemicellulose content of the pulp. The hemicellulose content in the dissolved wood pulp, mainly the xylose and mannose components, should be minimised to a total content target lower than 5%. In hardwood species such as Eucalyptus samples, the xylose content is usually higher than the mannose content, whereas in softwood species, the mannose is higher than the xylose content. The measurement of the xylose and mannose content is important in the dissolving pulps because it shows the hemicellulose degradation during the pulping process. Minimum xylose content at base ratio 2.5 was obtained

with the *E.001* species of 2.9%. *E.003* had the highest xylose content of above 7% in both base ratios, as shown in Figure 45 and Figure 46.

The highest mannose content obtained at base ratio 2.5 was 1.6% for the *E.003*, however at base ratio 3.0, this reduced to 1.3% at base ratio 3.0 both *E.001* and *E.004* had the highest mannose content of 1.6% (Figure 47 and Figure 48). About 65% of the eucalyptus samples had higher xylose at base ratio 3.0 compared to base ratio 2.5.

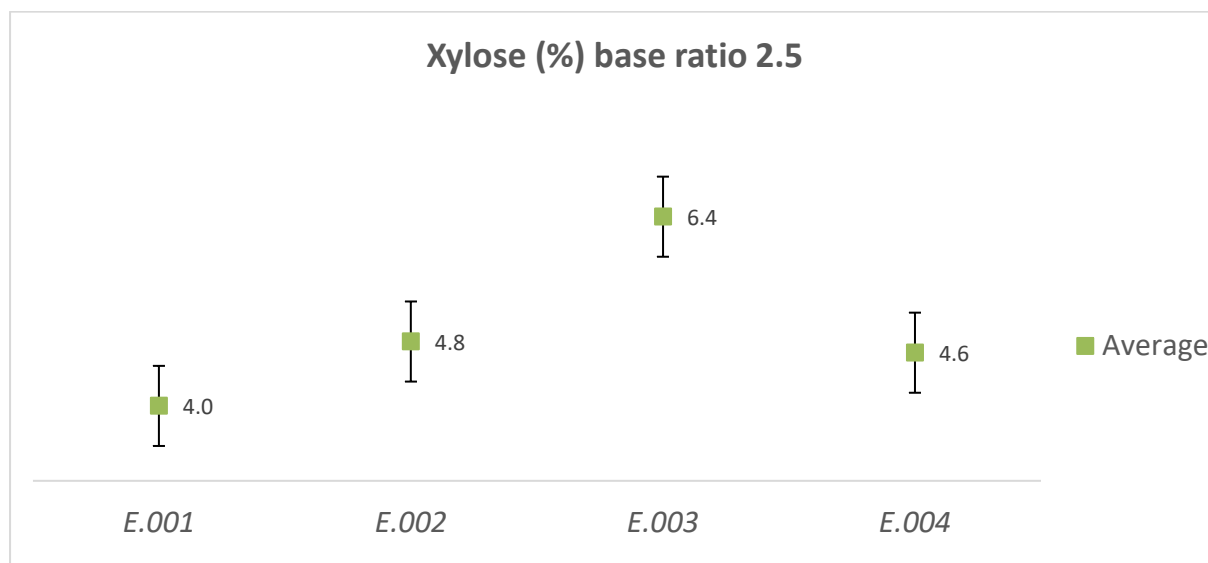


Figure 45: Xylose content of the Eucalyptus species pulped at base ratio 2.5



Figure 46: Xylose content of the Eucalyptus species pulped at base ratio 3.0

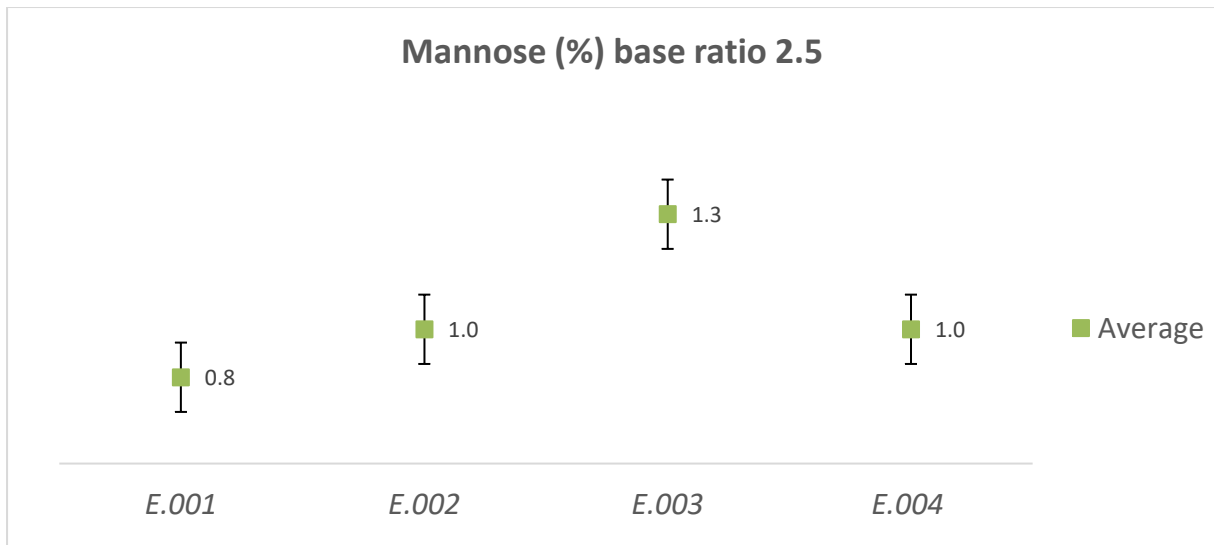


Figure 47: Mannose content of the Eucalyptus species pulped at base ratio 2.5

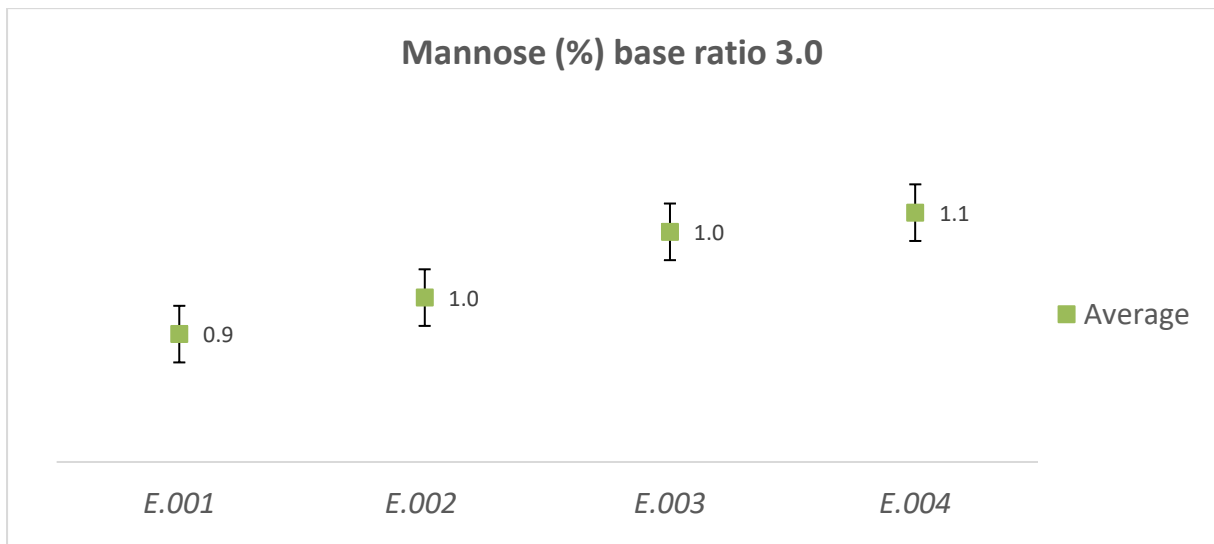


Figure 48: Mannose content of the Eucalyptus species pulped at base ratio 3.0

E.001 had a highest average glucose content of 95% in both base ratios. *E.003* had a minimum glucose content of approximately 91% in base ratio 2.5 and 3.0 as shown in Figure 49 and Figure 50. *E.003*, *E.002* and *E.004* had similar maximum glucose contents of 95.5%. There is a strong negative correlation between the xylose and glucose contents ($R^2=0.7$), pulps with higher xylose content had the lowest glucose content; this implies that higher xylose content indicates poor cooking.

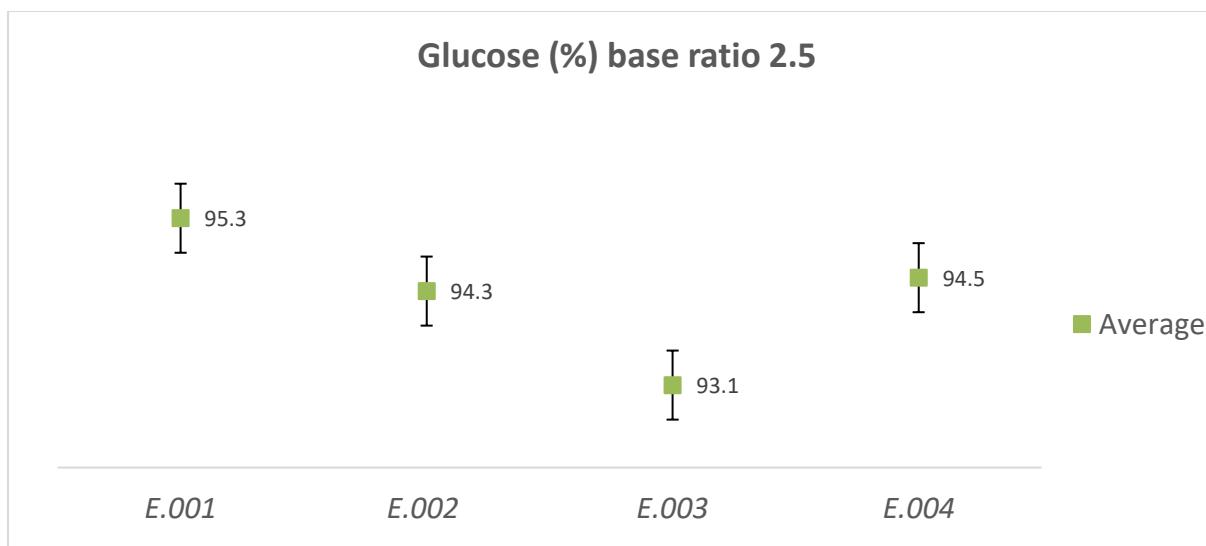


Figure 49: Glucose content of the Eucalyptus species pulped at base ratio 3.0



Figure 50: Glucose content of the Eucalyptus species pulped at base ratio 3.0

4.6.5.2 Wattle and clones

Wattle had xylose and mannose contents of 6.9% and 1.4%, respectively, in base ratio 2.5 (Figure 51 and Figure 52), and a slightly higher xylose content of 7.5% in base ratio 3.0. Clones had xylose contents between 3.5% (G438-103) and 5.4% (A380-30233) with base ratio 2.5, and 3.3% (GN-98) and 6.0% (GN018b 30431) with base ratio 3.0. Lower glucose contents were obtained on the Wattle samples because of high xylose contents in Figure 53.

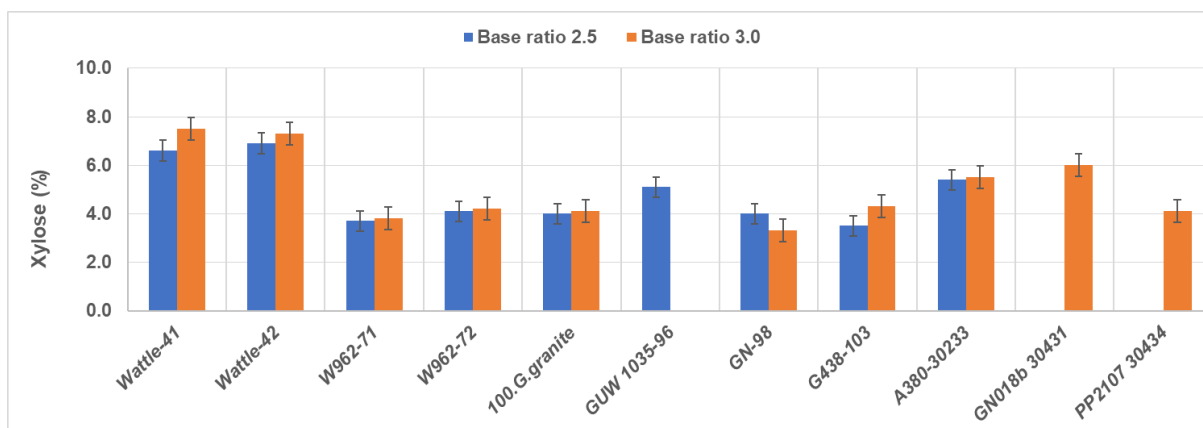


Figure 51: Xylose content of wattle and clones pulped at base ratio 2.5 and 3.0

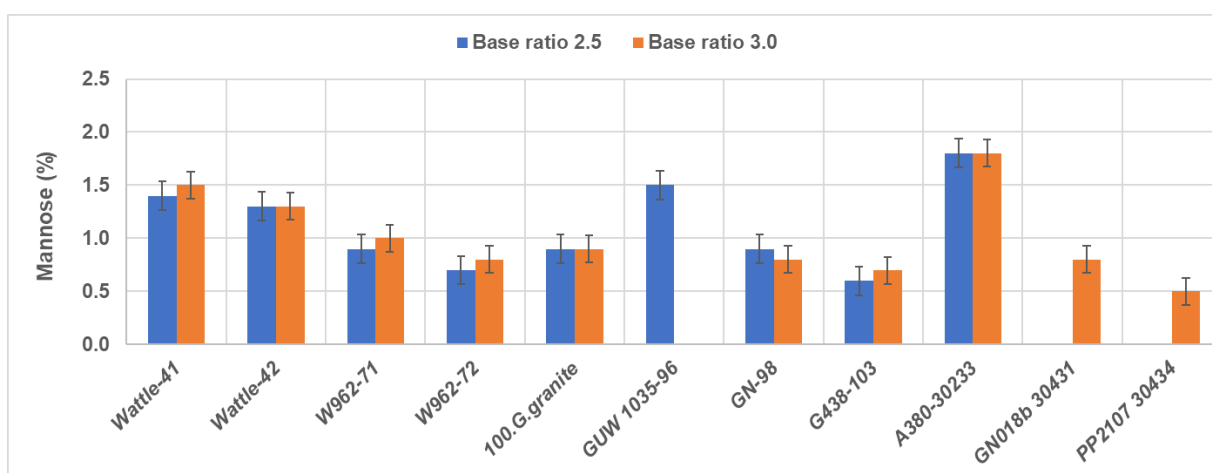


Figure 52: Mannose content of wattle and clones pulped at base ratio 2.5 and 3.0

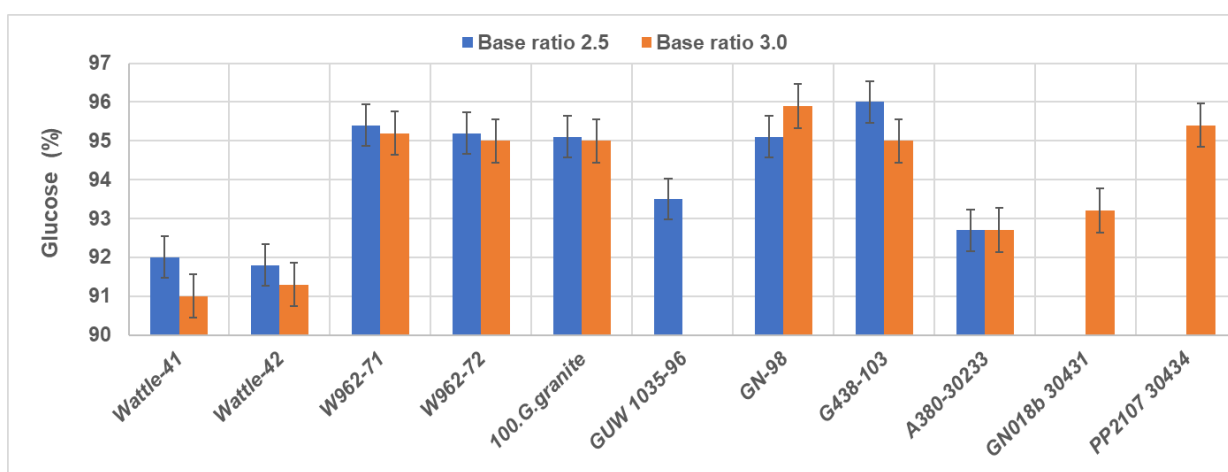


Figure 53: Glucose content of wattle and clones pulped at base ratio 2.5 and 3.0

DISCUSSION AND CONCLUSION ON WOOD CHEMISTRY AND PULPING EXPERIMENTS

The statistical average of the Eucalyptus species (*E.001*, *E.002*, *E.003*, *E.004*) is presented in Table 3. Based on the results, it can be concluded that, on average, *E.004* had the highest S/G ratio and alpha cellulose content of approximately 4.8 and 46.5% respectively compared to all the eucalyptus samples. As reported previously by Ventorim *et al.* (2014), a high S/G ratio enables fast delignification during Kraft pulping. However, there are currently no known studies to confirm such correlations regarding sulphite pulping process. If we assume such correlations to be true also under sulphite pulping, *E.004* would then be best suitable for better delignification and its higher alpha cellulose content would improve pulp yield. *E.001* and *E.002* also exhibited higher alpha cellulose contents of approximately 46% similar to *E.004*. However, the higher S/G ratio content obtained for the *E.002* and lower extractive content compared to *E.001* would favour better pulping of *E.002* over *E.001*. Wood extractives are important in selection of the wood species for sulphite pulping as these affect the washing of pulp. The higher DCM-extractives may cause pitch problems during further processing of unbleached pulps (Sixta, 2006). A study by Sixta (2006) showed that a higher content of DCM extractives can cause cross-links with lignin during acid sulphite pulping, thereby, preventing delignification. The lower extractives of the *E.002* favour better pulp quality. *E.003* had the highest xylose content of approximately 12% compared to other species. This makes the *E.003* more suitable for sugar production, such as xylitol, xylonic acid and furfural because of high xylose content compared to other Eucalyptus species. A study by Sixta (2006) showed that the amount of pentose present in the spent liquor is proportional to the xylan content in the wood. However, the highest extractives obtained for the *E.003* would be a disadvantage if better pulp quality is desired, as these extractives can affect the pulp quality, washing and screening process. For better delignification, higher yield and better quality, the eucalyptus species can be selected in the order: *E.004*, >*E.002*>*E.001* and for higher xylose or C5 carbon sugar selection, *E.003* can be selected provided care will be taken to deal with higher extractive content.

Based on the statistical average, Wattle had the lowest DCM extractives range between 0.19% to 0.20% and higher alpha cellulose of 48%. The xylose content of 14.4% compared to 12% on the Eucalyptus samples would allow the Wattle samples to be better selected for better sugar

extraction, better pulp quality, higher alpha cellulose content compared to the eucalyptus samples.

Different clones and hybrids had different wood chemistry components, as expected. *G438-105* and *GN 101* had the lowest extractive content which is good for sulphite pulping as extractives have shown to cause problems during pulping.

The effect of pulping at base ratio 2.5 vs 3.0 was also studied and it can be concluded that pulping at base ratio 2.5 was advantageous with respect to lower kappa, lower viscosity, and lower xylose and mannose contents. However, the base resulted in lower total yield. Since lower viscosity is desired in a sulphite pulping process, it can therefore be concluded that base ratio 2.5 can be selected for better pulp properties compared to base ratio 3, albeit with higher yield loss of approximately 1 to 2%.

CHAPTER 5: DATA MODELLING

5.1.1 Statistical analysis

In this study, correlation was determined to assess the relationship between wood chemistry properties and pulp properties obtained during the sulphite pulping of *Eucalyptus* species using base ratios 3.0 and 2.5. R^2 above 0.5 were of major interest. Based on the R^2 results obtained, a regression model was developed using wood chemistry variables of interest to predict the viscosity of the pulp species for base ratios 3.0 and 2.5%. The R^2 was then used to assess the predicted viscosity versus the actual laboratory measured viscosity.

5.1.2 Data analysis tool

Data analysis tool correlation was used to evaluate the correlation between the wood chemistry and pulp properties, whereas data analysis tool regression was used to develop the equation for prediction of viscosity. These statistical tools, based on Excel, were chosen because of the limited number of data points (below 50 points) compared to well-known modelling methods that require many data points, typically above 500.

5.2 Viscosity prediction using wood properties.

The degree of polymerization (DPol) describes the length of the individual cellulose chains on the fibres, and variations to DP indicate the extent to which the cellulose chains have been degraded. The measurements of pulp viscosities may be used as an indirect estimate of the average DPol of the pulp (Oglesby *et al.*, 2016). Pulp viscosity is the criteria the mill uses to control its pulping process, with lower and upper limits of viscosity set at 680 and 830 ml/g, respectively. Viscosity results for pulps give a direct relative indication of cellulose degradation (decrease in cellulose molecular weight) resulting from pulping or bleaching (TAPPI, 1999). Based on the viscosity values obtained, wood samples can be categorised as fast cookers, medium cookers, or slow cookers. Considering the standard for Saiccor cooks, fast cookers are wood species with a pulp viscosity below 680 ml/g. Medium cookers are the species with a viscosity between 680 ml/g and 830 ml/g, and slow cookers are those with viscosity above 830 ml/g.

5.2.1 Fast Medium Slow (FMS) prediction number

FMS is a number in the range 0-10 that can categorise viscosity of wood species pulped using the sulphite pulping process in base ratio of 2.5 and 3.0. The number from 0-6.8 is classified as fast cooker, 6.8-8.3 as medium cooker and values above 8.3 as slow cookers.

In order to obtain the FMS number, wood chemistry properties of interest namely, S/G ratio, galactose, xylose and alpha cellulose contents were used to predict viscosity of Eucalyptus samples, as well as the (R^2) for the actual laboratory measured viscosity values and the predicted viscosity values for the Eucalyptus species.

5.3 Wood chemistry properties and pulp properties

5.3.1 Wood extractives

Wood extractives were determined using the Dichloromethane (DCM) as the extraction solvent. Extractives, which are low molecular weight carbohydrates, also indicate the extent of cellulose degradation during pulping and bleaching processes, which may affect pulp strength and other properties. Wood extractives are known to negatively affect the pulp and paper making forms (Speranza *et al.*, 2002; Blom and Bergström, 2006). Even though larger part of the extractive mixes breaks down in cooking alcohols amid pulping, some are persisted in the fading procedures and collect to frame sticky deposits called pitch. Pitch is disadvantageous as it impacts on the quality properties of the paper. This is because of resinous extractives blocking responsive gatherings on the outside of the fibres and distressing inter-fibre holding (Sefara and Birkett, 2004). Pitch deposits can likewise debilitate item quality by causing earth, gaps, and scabs (Kostamo and Kukkonen, 2003). Pitch diminishes the proficiency of pulp washing, screening, centrifugation, cleaning and refining and can disturb many paper machine activities (Hubbe *et al.*, 2006; Vercoe *et al.*, 2005). Wood extractives in this study had poor correlation coefficient with all the pulp properties at base ratios 2.5 and 3.0 as shown in Table 8 and Table 9. This is because their concentrations are too small to be of any concern.

5.3.2 Lignin

5.3.2.1 S/G ratio of lignin

In hardwood species, such as Eucalyptus, lignin is mainly composed of guaiacyl and syringyl moieties (Robinson and Mansfield, 2009). Several studies have shown that the structure of

lignin, mainly S/G ratio, affects the processability of the wood, such as the delignification of wood during pulping (Ohra-aho and Tamminen, 2011). A high S/G ratio enhances the efficiency of Kraft pulping (Studer *et al.*, 2011). However, it is important to note that all these studies were done on Kraft pulping. The results of the current study showed that S/G ratio had a negative correlation coefficient of 0.5 with K. number at base ratio 3.0 (Table 8) and a weak negative correlation coefficient of 0.3 with eucalyptus samples pulped at a lower base of 2.5 (Table 9). The S/G ratio measures the ratio of the main lignin contents of wood, whereas K. number measures the remaining lignin after pulping. This means that for some eucalyptus species pulped at base ratio 3.0, a higher S/G ratio in the wood sample resulted in a higher delignification rate, hence the lower residual kappa number. A study by (Ventorim *et al.*, 2014) showed that there was an improvement in the ease of delignification (EOD) for Kraft pulped Poplars and eucalyptus species when the S/G ratio was increased from a low to a moderately high value. In this study, one can expect a lower K. number after sulphite pulping, making a wood sample with a higher S/G ratio more ideal in achieving lower K. numbers.

S/G ratio was also correlated with pulp brightness. The results showed that S/G ratio had a positive correlation coefficient of 0.7 with pulp brightness at base ratio 3.0 and 0.6 at base ratio 2.5. A study by Lima *et al.* (2000) showed a linear correlation between the pulp brightness and kappa, with greater values for sample brightness acceptably correlating to lower residual lignin contents in the pulp (kappa number). (Brogdon, 2014) proposed a linear relationship that related the pulp's extracted kappa number (~2-8) to its brightness. Based on the correlation results obtained between the S/G ratio and pulp brightness, it can be suggested that wood samples with higher S/G can produce brighter sulphite pulps, due to lower residual lignin (K number, kappa) content.

5.3.2.2 Soluble, insoluble and total lignin

Soluble lignin had no correlation with all the pulp properties. Insoluble lignin and total lignin both had a negative R^2 of 0.6 with pulp yield at base ratios of 2.5 and 3.0, as shown in Table 8 and Table 9. At base ratio 3.0, total and soluble lignin had a negative correlation coefficient of 0.5 with pulp brightness. Eucalyptus samples with higher total lignin can be expected to produce lower pulp yield with darker pulps (lower brightness).

5.3.3 Hemicellulose

Arabinose + rhamnose, galactose, glucose, xylose and mannose were correlated with wood pulp properties. Galactose had an interesting negative R^2 of 0.6 and 0.4 with viscosity at base ratios 3.0 and 2.5, respectively (Table 8 and Table 9). Glucose had a R^2 of 0.5 with brightness at base ratio 3.0. There was a poor correlation between arabinose and rhamnose, xylose, mannose with all the pulp properties.

5.3.4 Alpha cellulose

Alpha cellulose had a positive R^2 of 0.7 with total pulp yield at base ratios of 3.0 and 2.5 (Table 8 and Table 9). It was noted that Eucalyptus species with higher alpha cellulose contents produced higher total pulp yields. Alpha cellulose also had a positive R^2 0.5 with pulp brightness. Eucalyptus wood species with higher alpha cellulose content produced brighter pulps.

Table 8: Correlation coefficients for wood and pulp properties of the Eucalyptus species at base ratio 3.0

Wood chemistry properties	Pulp properties				
	Yield (%)	Micro kappa (ml)	K Number (ml)	Viscosity (CED) (ml/g)	Brightness (%)
Extractives	0.097	-0.159	-0.241	0.016	0.296
S/G	0.270	-0.474	-0.534	-0.398	0.679
Soluble lignin	-0.273	0.070	0.114	-0.081	-0.179
Insoluble lignin	-0.608	0.089	0.132	0.028	-0.560
Total lignin	-0.615	0.095	0.144	0.011	-0.553
Ara + Rha	-0.196	-0.068	-0.103	0.140	0.183
Galactose	0.180	0.088	0.079	-0.649	-0.107
Glucose	0.241	-0.176	-0.168	-0.144	0.517
Xylose	-0.120	0.099	-0.011	0.311	0.176
Mannose	-0.210	-0.280	-0.267	0.146	0.273
Total sugar	0.159	-0.136	-0.165	-0.060	0.518
Alpha cellulose	0.711	-0.263	-0.265	-0.447	0.544

Table 9: Correlation coefficient for wood and pulp properties of the Eucalyptus species at base ratio 2.5.

Wood chemistry properties	Pulp properties				
	Yield (%)	Micro kappa(ml)	K. Number (ml)	Viscosity (CED) (ml/g)	Brightness (%)
Extractives	0.206	0.280	0.339	0.276	-0.066
S/G	0.462	-0.323	-0.339	-0.399	0.567
Soluble lignin	-0.342	-0.138	-0.145	-0.058	-0.118
Insoluble lignin	-0.640	-0.004	0.060	0.087	-0.439
Total lignin	-0.658	-0.030	0.028	0.070	-0.430
Ara + Rha	-0.120	0.016	-0.159	0.276	-0.033
Galactose	-0.047	-0.035	0.047	-0.489	-0.043
Glucose	0.227	-0.167	-0.385	-0.220	0.280
Xylose	-0.173	0.186	0.187	0.186	-0.011
Mannose	-0.118	-0.234	-0.440	0.081	0.097
total sugar	0.139	-0.117	-0.333	-0.165	0.251
Mannose	-0.118	-0.234	-0.440	0.081	0.097
Alpha cellulose	0.690	-0.361	-0.387	-0.447	0.574

5.4 Viscosity prediction results

Base ratio 2.5 and base ratio 3 results were used to predict the viscosity using wood chemistry properties namely S/G ratio, xylose & galactose and alpha cellulose. In each base ratio, 75% of data points shown in Table 10 and Table 11(i) were used to obtain the linear equation as:

$$\text{Predicted Viscosity} = [a(10 \times G/S) + b(100 \times g/x) + c(al/10) + d] \quad (9)$$

where a , b , c and d are constants

Based on the equation obtained, the 25% remaining data in Table 10 and Table 11 (ii) was later used to verify the robustness of the model using the equation obtained. The obtained calculated viscosity based on the equation was plotted against the actual laboratory CED viscosity to determine the correlation.

Using the 75% data for base ratio 2.5, and base ratio 3, the following equation and constants were obtained, at base ratio 2.5 and 3, respectively.

$$a=86.83371831; 28.14432524, b=-18.71142985; -16.07316877, c=-116.2149893; -138.0518266$$

$$d=1413.43337; 1678.409889 \quad (10)$$

$$\text{Predicted viscosity (base ratio 2.5)} = [86.83372 (10^*G/S) - 18.7114 (100^*g/x) - 116.215 (al/10) + 1413.433] \quad (11)$$

$$\text{Predicted viscosity (base ratio 3.0)} = [28.1443 (10^*G/S) - 16.073169(100^*g/x) - 138.0518 (al/10) + 1678.4099] \quad (12)$$

Table 10: Viscosity prediction using wood and pulp properties at base ratio 2.5

	i)75% DATA (used for prediction)			
Species	10*G/S	100/xg	al/10	Viscosity (CED)
E.001-21	2.896	13.703	4.419	910
E.001-31	3.502	13.097	4.785	875
E.002-1	2.794	7.397	4.666	830
E.002-2	2.260	14.502	4.782	621
E.002-6	3.526	16.066	4.506	859
E.003-53	2.656	7.440	4.268	862
E.003-54	2.811	12.557	4.346	905
E.003-55	2.685	10.492	4.308	995
E.003-57	2.685	14.963	4.349	883
E.004-61	2.017	9.275	4.705	886
E.004-62	3.393	6.404	4.599	1113
E.004-65	1.637	23.289	5.074	600
W962-71	3.285	12.496	4.710	816
GUW 1035-96	3.606	9.004	4.580	1174
GN-98	3.513	11.309	4.639	991
E.003-59	2.131	8.688	4.504	1008
E.001-39	2.798	11.570	4.549	1096
E.005-81	2.588	21.696	4.525	694
E.006-99	3.344	18.023	4.228	852
	ii) 25% DATA (used for validation)			
Species	10*G/S	100/xg	al/10	Viscosity (CED)
E.001-30	3.282	14.132	4.540	1025
E.004- 63	2.424	7.860	4.596	910
W962-72	3.071	6.438	4.489	876
100.GN	3.458	11.176	4.892	917
E. 002-3	2.600	13.470	4.439	1038
Wattle-41	2.441	12.370	4.912	1004

Table 11: Viscosity prediction using wood and pulp properties at base ratio 2.5

i) 75% DATA (used for prediction)				
Species	10*G/S	100/xg	al/10	Viscosity (CED)
E.001-21	2.896	13.703	4.419	910
E.001-31	3.502	13.097	4.785	875
E.002-1	2.794	7.397	4.666	830
E.002-2	2.260	14.502	4.782	621
E.002-6	3.526	16.066	4.506	859
E.003-53	2.656	7.440	4.268	862
E.003-54	2.811	12.557	4.346	905
E.003-55	2.685	10.492	4.308	995
E.003-57	2.685	14.963	4.349	883
E.004-61	2.017	9.275	4.705	886
E.004-62	3.393	6.404	4.599	1113
E.004-65	1.637	23.289	5.074	600
W962-71	3.285	12.496	4.710	816
GUW 1035-96	3.606	9.004	4.580	1174
GN-98	3.513	11.309	4.639	991
E.003-59	2.131	8.688	4.504	1008
E.001-39	2.798	11.570	4.549	1096
E.005-81	2.588	21.696	4.525	694
E.006-99	3.344	18.023	4.228	852
ii) 25% DATA (used for validation)				
Species	10*G/S	100/xg	al/10	Viscosity (CED)
E.001-30	3.282	14.132	4.540	1025
E.004- 63	2.424	7.860	4.596	910
W962-72	3.071	6.438	4.489	876
100.GN	3.458	11.176	4.892	917
E. 002-3	2.600	13.470	4.439	1038
Wattle-41	2.441	12.370	4.912	1004

The remaining 25% data was used to determine the calculated viscosity from the predicted viscosity equation for base ratio 2.5 and 3.0, respectively. At base ratio 2.5, the R^2 of 0.67 (Figure 54) was obtained for the actual viscosity and the calculated viscosity, with the standard deviation % error between 1.5% and 14% (Table 12). At base 3, R^2 of 0.71 was obtained for the actual viscosity and the calculated viscosity Figure 55 with standard deviation % error between 0.8 to 25.6% (Table 13).

The viscosity prediction has been proven successful based on the correlation coefficient of above 0.7 for base ratios 3.0 when the laboratory and calculated viscosities were compared. This means that the FMS was also a success. However, more work needs to be done to refine the model for base ratio of 2.5 pulp properties.

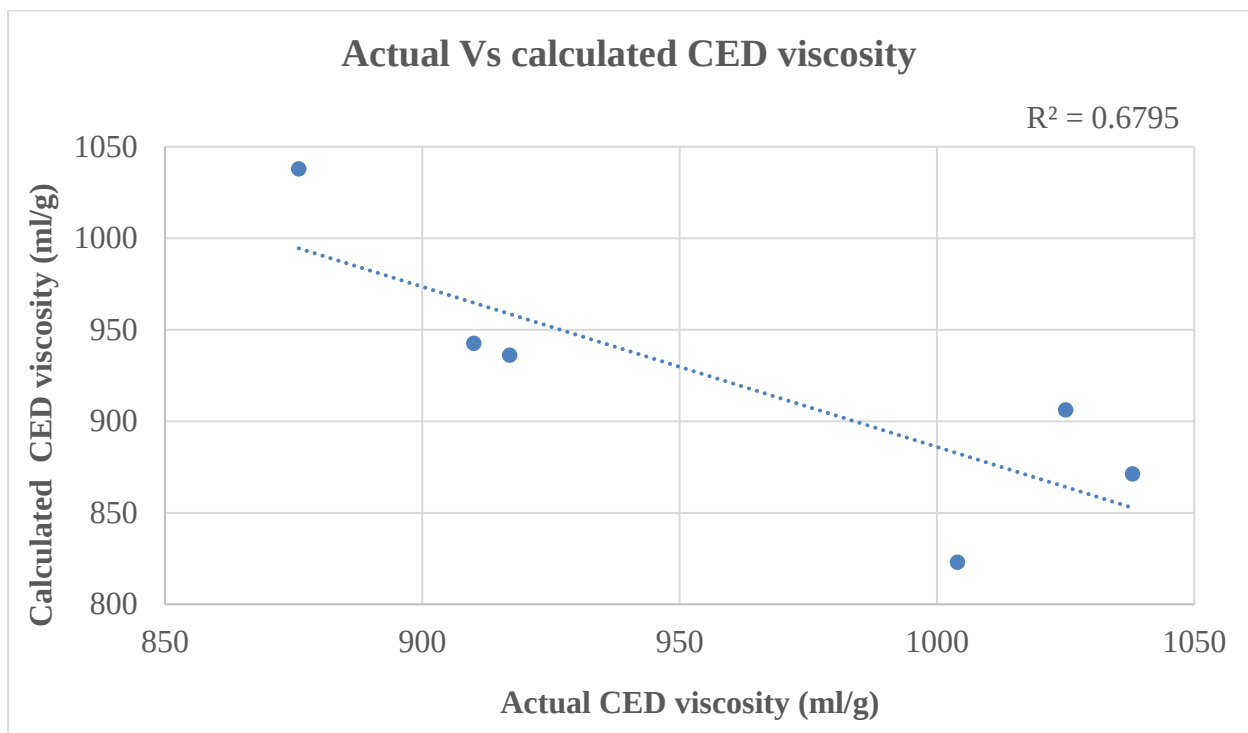


Figure 54: Actual laboratory measured CED viscosity and the Calculated CED viscosity for base ratio 2.5 pulps at 95% confidence level.

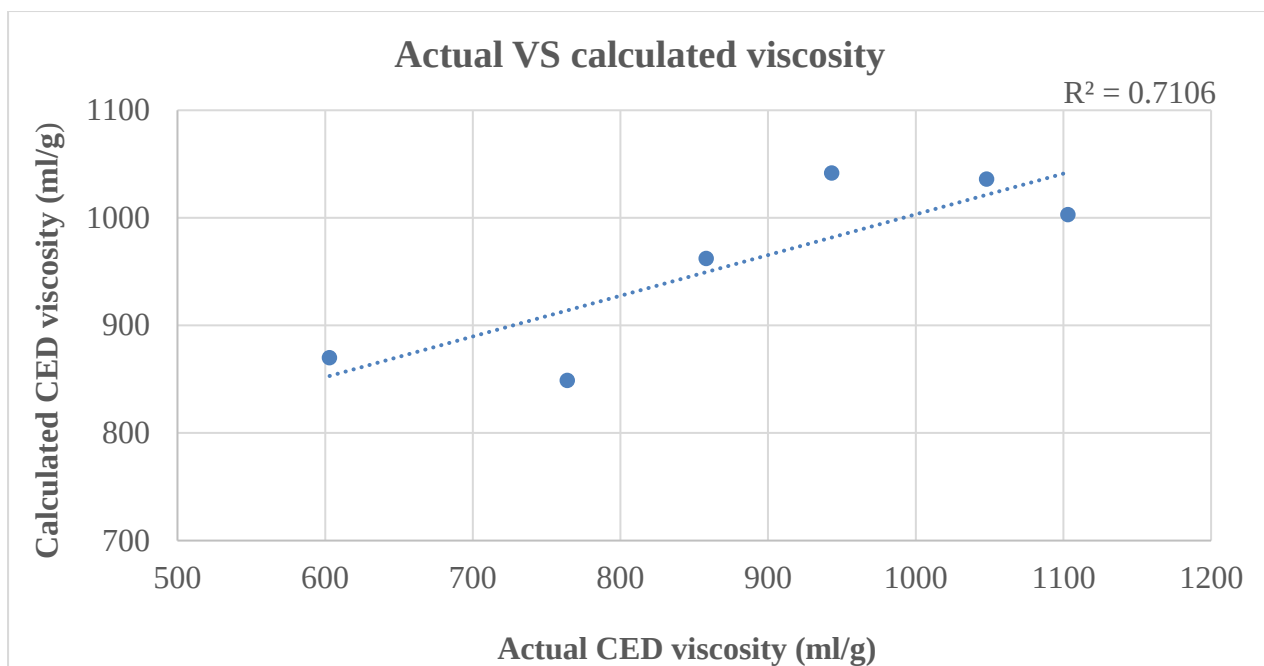


Figure 55: Actual laboratory measured CED viscosity and the Calculated CED viscosity for base ratio 3.0 pulps at 95% confidence level.

Table 12: Std deviation % error between calculated and actual viscosity at base ratio 2.5

Species	a	10* G/S	b	100/x g	c	al/10	d	Calculated viscosity	Actual Viscosity	Average	std dev	std% dev
E.001-30	86.8	3.3	-18.7	14.1	-116.2	4.5	1413.4	906	1025	966	83.9	8.7
E.004-63	86.8	2.4	-18.7	7.9	-116.2	4.6	1413.4	943	910	926	23.1	2.5
W962-72	86.8	3.1	-18.7	6.4	-116.2	4.5	1413.4	1038	876	957	114.5	12.0
100.GN	86.8	3.5	-18.7	11.2	-116.2	4.9	1413.4	936	917	927	13.5	1.5
E.002-3	86.8	2.6	-18.7	13.5	-116.2	4.4	1413.4	871	1038	955	117.9	12.4
Wattle-41	86.8	2.4	-18.7	12.4	-116.2	4.9	1413.4	823	1004	914	127.9	14.0

Table 13: Std deviation % error between calculated and actual viscosity at base ratio 3.00

Species	a	10* G/S	b	100/x g	c	al/10	d	Calculated viscosity	Actual Viscosity	Average	std dev	std% dev
E.001-22	28.1	3.22	-16.1	10.07	-138.1	4.67	1678	962	858	910	73.7	8.1
E.002-2	28.1	2.26	-16.1	14.5	-138.1	4.78	1678	849	764	806	60	7.4
E.004-62	28.1	3.39	-16.1	6.404	-138.1	4.6	1678	1036	1048	1042	8.4	0.8
Wattle-41	28.1	2.44	-16.1	12.37	-138.1	4.91	1678	870	603	737	189	25.6
GUW 1035-96	28.1	3.61	-16.1	9.004	-138.1	4.58	1678	1003	1103	1053	70.8	6.7
W962-72	28.1	3.07	-16.1	6.44	-138.1	4.49	1678	1042	943	992	69.8	7.0

CONCLUSIONS

Better correlations were obtained at base ratio 3.0 compared to base ratio 2.5.

Wood extractives had no correlation with any of the pulp properties evaluated, such as pulp yield, micro kappa, K. number, viscosity and pulp brightness.

S/G ratio correlation with kappa number suggests that for some Eucalyptus species pulped at base ratio 3.0, a higher S/G ratio in the wood sample resulted in a higher delignification rate, hence the lower residual lignin (K. number).

S/G ratio had a positive correlation coefficient of 0.7 and 0.6 with pulp brightness at base ratio 3.0 and 2.5. Based on the correlation results obtained between the S/G ratio and pulp brightness, it can be suggested that wood samples with higher S/G can produce brighter sulphite pulps, due to lower residual lignin (Kappa) content. Wood with higher S/G ratio is ideal for pulping.

Higher total lignin in wood samples produced pulp with lower total yields and lower pulp brightness.

Wood samples with higher galactose content had lower viscosity after pulping. Glucose had a positive correlation of 0.5 with brightness at base ratio 3.0. There was poor correlation between arabinose and rhamnose, xylose, mannose with all pulp properties.

Alpha cellulose had a positive correlation coefficient of 0.7 with total pulp yield and a positive correlation coefficient of 0.5 with pulp brightness. Eucalyptus species with higher alpha cellulose content produced higher total pulp yields and brighter pulps.

The CED viscosity prediction models using S/G ratio, xylose, galactose and alpha cellulose were successful with strong correlations, above of 0.7 (base ratio 3), between actual laboratory measured and calculated viscosities. Lower correlations were observed at base ratio 2.5. This study showed that categorizing wood samples by species, e.g. *E.001*, *E.003*, *E.004*, *E.002*, and Wattle for pulping purposes is not adequate as wood samples of the same species have different quantities of wood chemistry components.

CHAPTER 6: OVERALL SUMMARY AND FUTURE WORK

This study showed that:

6.1.1 The effect of pulping at base ratio 2.5 vs 3.0

Base ratio 2.5 had advantages such as the low kappa, viscosity, xylose and mannose. However, lower total yield was obtained. Since lower viscosity is desired in a sulphite pulping process, it can be concluded that base ratio 2.5 can be selected for better properties compared to base ratio 3, although minimum yield loss of approximately 1 to 2% can be expected.

6.1.2 Using wood chemistry properties to predict pulp properties

Wood chemistry properties such as S/G ratio, xylose, galactose and alpha cellulose were successfully used to predict the CED viscosity with a strong correlation above of 0.7 between the predicted and laboratory measured viscosity. This work can be used as basics for bigger modelling projects. More work involving the forest research team and the mill is recommended for testing the robustness of the model using the data produced in the mill. The limitations in this study were the fewer data points available because of the longer hours (approximately 8 hours) involved in sulphite pulping process.

Wood chemistry can be used to predict resultant pulp properties prior to sulphite pulping. This was proven by strong correlations such as (alpha cellulose vs total yield, S/G ratio vs kappa, S/G ratio vs brightness).

6.2 Limitations in this study

Wood species data: the minimal availability of key wood chips information such as age and plantation. This is because the wood chips were supplied to the Forest research team by various plantation companies and a result, were only sent to the Sappi Technology Centre by the Forest research team with minimal information as received.

Wood chips: Only one bag of wood chips was available per wood sample, making it impossible to pulp the wood sample multiple times. As a result, the effect of increasing pulping time using one wood sample was not possible.

Statistical analysis: because of a limitation in wood chips, as well as the long hours of 8 hours approximately per one cook, many cooks could not be performed to collect numerous data for statistical analysis. Software modelling techniques require at least a minimum of 100 data points.

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APPENDICES

APPENDIX A (Wood chemistry results)

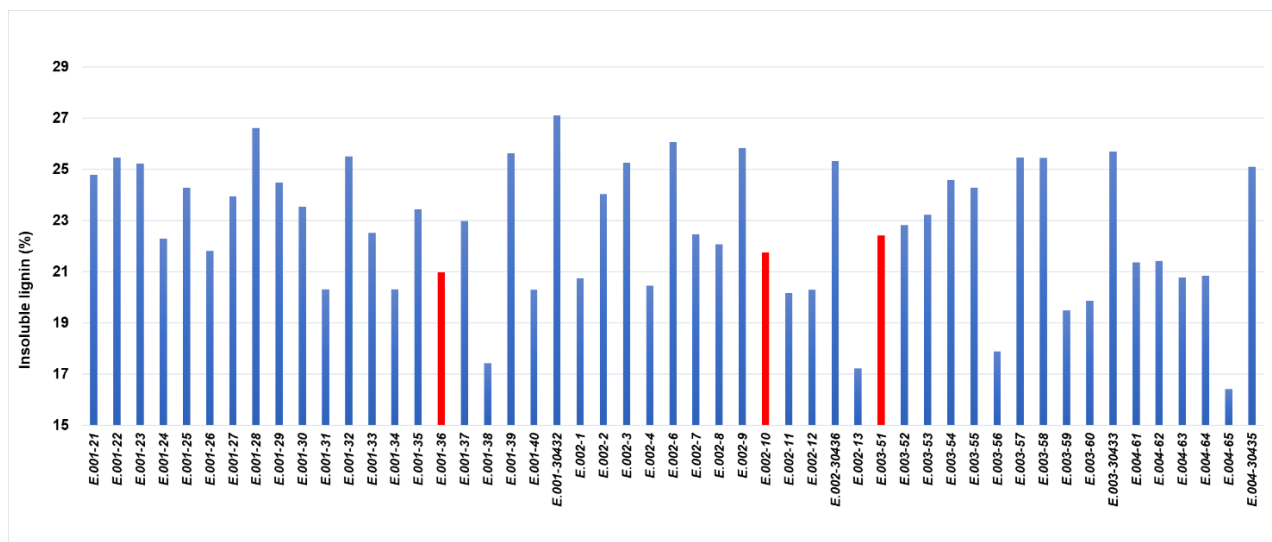


Figure 56: Insoluble lignin of the eucalyptus samples

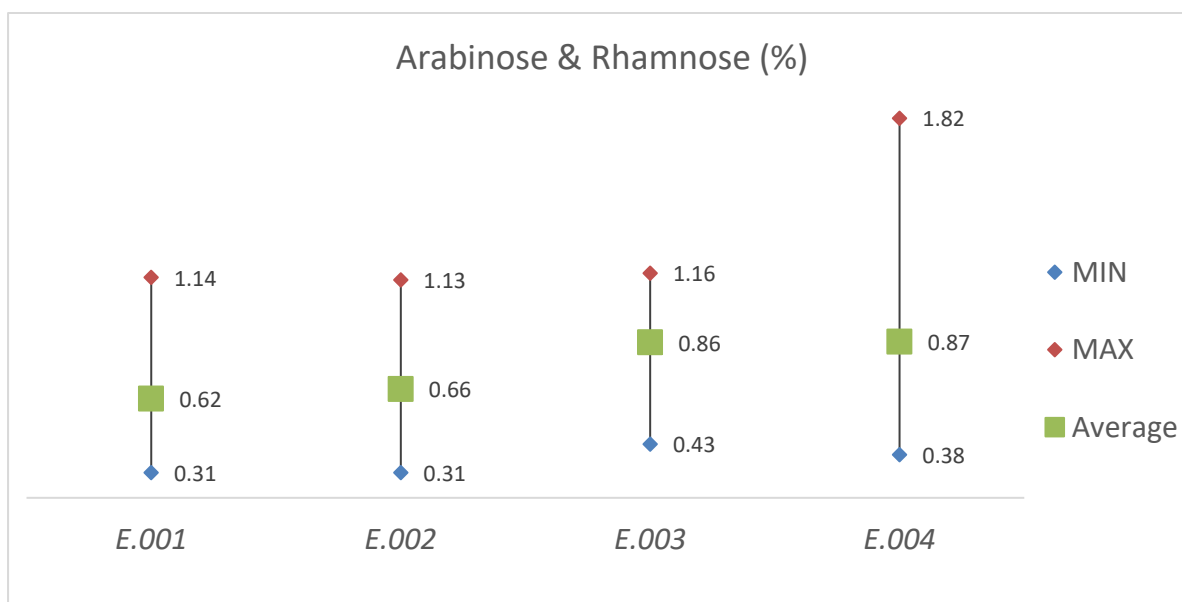


Figure 57: Arabinose and rhamnose content of eucalyptus samples

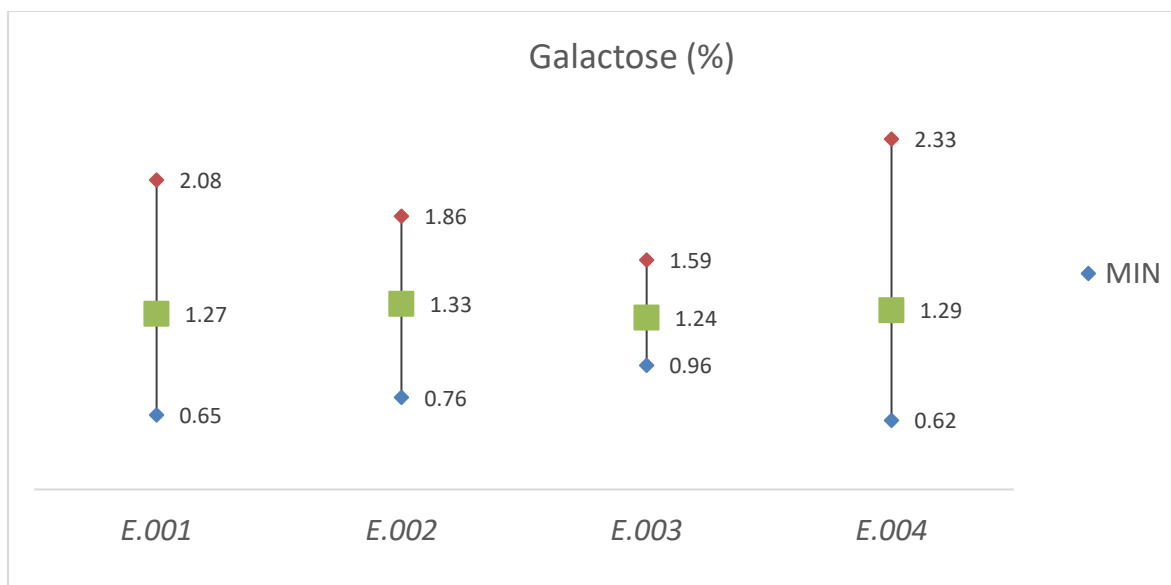


Figure 58: Galactose content of eucalyptus samples

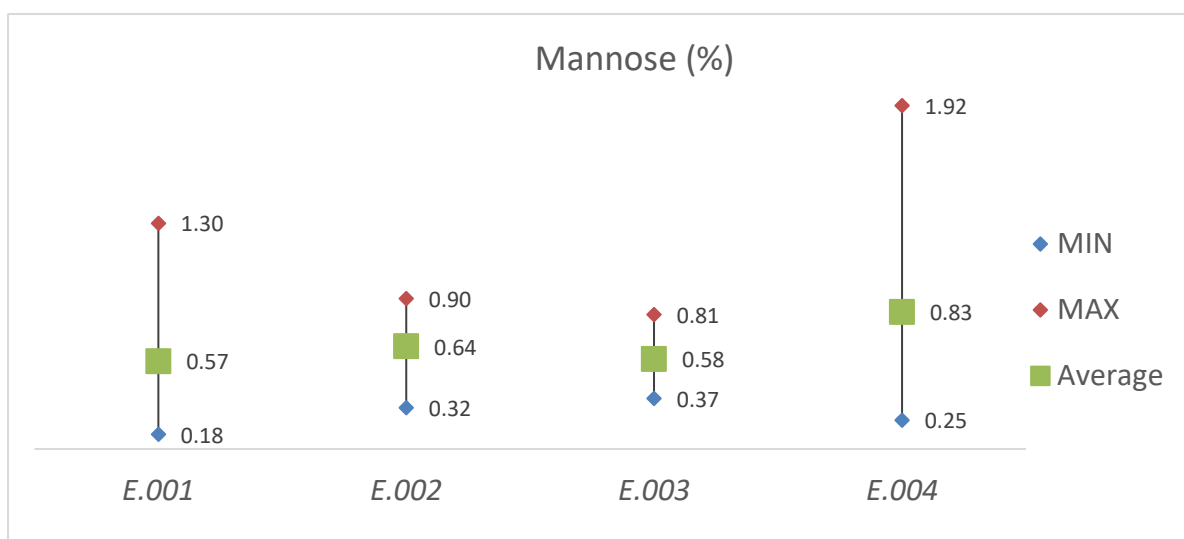


Figure 59: Mannose content of eucalyptus samples

Table 14: Full data results for clones and hybrids.

	DCM Extr (%)	Lignin (%)				Wood sugars (%)					Cellulose (%)
Sample ID	Extr	sol	insol	tol lig	S/G ratio	Ara + Rha	gal	glu	Xy	man	alph
W962 71	0.21	3.01	25.96	28.97	3.04	0.63	1.20	47.33	9.59	0.55	47.10
W962-72	0.30	1.68	19.92	21.60	3.26	1.08	0.90	46.09	13.97	0.84	44.89
W962-73	0.20	2.13	20.37	22.49	3.45	0.65	1.58	44.63	10.51	0.21	46.05
G438-103	0.24	3.09	25.40	28.49	3.36	0.62	1.23	45.69	10.80	0.67	45.00
G438-105	0.19	2.19	17.33	19.52	3.51	1.06	1.66	45.15	12.03	0.71	45.95
GN 101	0.19	1.88	23.37	25.25	3.38	0.57	1.23	46.94	11.11	0.38	46.97
GN 98	0.24	1.95	22.82	24.77	2.85	0.54	1.09	46.57	9.65	0.65	46.39
GUW 1035-96	0.24	3.10	28.55	31.64	2.77	0.46	1.06	42.41	11.81	0.50	45.80
A189-97	0.31	2.63	19.21	21.84	3.74	0.79	1.21	41.11	11.72	0.93	44.06
100 GN	0.24	2.14	19.68	21.82	2.89	0.60	1.23	46.98	11.01	0.35	48.92
GN018b 30431	0.27	3.01	28.37	31.38	3.37	0.83	1.04	41.94	10.59	0.51	42.14
PP2107 30434	0.36	1.92	22.46	24.38	3.59	0.66	2.12	49.84	9.88	0.29	43.17

*Extractives, soluble, insoluble, total lignin, arabinose, rhamnose, glucose, xylose, mannose and alpha cellulose

APPENDIX B (Showing pulping results)

Table 15: Wood moisture of Eucalyptus samples

Sample name	Wood moisture (%)	Sample name	Wood moisture (%)
E.001-21	17.2	E.002-1	20.9
E.001-22	24.5	E.002-2	26.6
E.001-30	29.0	E.002-3	31.7
E.001-31	20.8	E.002-4	34.9
E.001-39	29.7	E.002 -5	19.1
E.001-30432	20.85	E.002-6	26.6
E.001-23	13.6	E.002-30436	37.8
E.001-24	27.6	E.002-7	38.9
E.001-26	30.4	E.002-9	26.9
E.001-28	35.3	E.002-10	21.3
E.001-32	17.4	E.004-61	31.1
E.001-36	18.8	E.004--62	23.7
E.001-37	15.9	E.004-63	17.4
E.003-53	20.2	E.004-65	24.8
E.003-54	15.7	E.004-30435	37.0
E.003-55	18.9	E.004-64	28.0
E.003-57	17.0		
E.003-59	17.9		
E.003- 30433	30.2		
E.003-60	15.4		

Table 16: Wood moisture of Wattle and clones

Sample name	Wood moisture (%)
Wattle-41	16.1
Wattle-42	18.5
Wattle-43	23.2
Wattle-45	18.4
W962-71	27.1
W962-72	14.5
W962-73	19.0
Other GN -98	36.3
Other GN -101	15.0
GN018b 30431	30.8
G438-103	28.9
G438-105	22.1
GUW1035-96	19.1
100 G. Granite	35.5
PP2107 30434	30.8

Table 17: Packing wood density of Eucalyptus samples

Sample name	bulk density (Kg/m3)	Sample name	bulk density (Kg/m3)
*E.001-21	-	E.002-1	168.4
E.001-22	145.0	E.002-2	176.3
E.001-30	167.5	*E.002-3	-
E.001-31	137.7	*E.002-4	-
E.001-39	109.8	E.002-5	163.7
E.001-30432	152.0	E.002-6	147.6
E.001-23	136.2	E.002-30436	178.2
E.001-24	122.0	E.002-7	167.5
E.001-26	183.4	E.002-9	136.7
E.001-28	146.7	E.002-10	168.6
E.001-32	132.7	E.004-61	176.1
E.001-36	139.7	*E.004-62	-
E.001-37	195.7	E.004-63	221.1
E.003-53	125.5	E.004-65	196.4
E.003-54	175.6	E.004-30435	186.4
E.003-55	171.8	E.004-64	175.5
E.003-57	140.7		
E.003-59	180.3		
E.003-30433	189.6		
E.003-60	171.3		

*Packing density of the wood chips was not tested

Table 18: Packing wood density of clone samples

Sample name	Bulk density (Kg/m³)
Wattle-41	177.3
Wattle-42	162.0
Wattle-43	203.3
Wattle-45	191.4
W962-71	150.7
W962-72	187.4
W962-73	156.1
Other GN -98	211.9
Other GN -101	151.3
GN018b 30431	160.2
*G438-103	Nt
G438-105	161.7
GUW1035-96	182.5
100 G. GN	127.9
PP2107 30434	170.6

*Packing density of the wood chips was not tested

Table 19: Eucalyptus, Wattle and clones pulped using sulphite pulping process (Total:31)

Eucalyptus (Total 24)			
<i>E.001-21</i>	<i>E.002-1</i>	<i>E.003-53</i>	<i>E.004-61</i>
<i>E.001-22</i>	<i>E.002-2</i>	<i>E.003-54</i>	<i>E.004-62</i>
<i>E.001-30</i>	<i>E.002- 3</i>	<i>E.003-55</i>	<i>E.004-63</i>
<i>E.001-31</i>	<i>E.002- 4</i>	<i>E.003-57</i>	<i>E.004-65</i>
<i>E.001-39</i>	<i>E.002-5</i>	<i>E.003-59</i>	<i>E.004-30435</i>
<i>E.001- 30432</i>	<i>E.002-6</i>	<i>E.003-30433</i>	
	<i>E.002-30436</i>		
Wattle and clones (Total 11)			
<i>Wattle-41</i>	<i>GN -98</i>	<i>G438-103</i>	
<i>Wattle-42</i>	<i>GN -101</i>	<i>G438-105</i>	
<i>PP2107 30434</i>	<i>GN018b 30431</i>	<i>GUW1035-96</i>	
	<i>A380-30233</i>	<i>100 G. GN</i>	