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IMPROVING DISSOLVING WOOD PULP QUALITY USING BROWN-STOCK FRACTIONATION

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IMPROVING DISSOLVING WOOD PULP QUALITY USING BROWN-STOCK FRACTIONATION

Submitted in fulfilment of the requirements for the degree of Master of Engineering: Chemical in the Faculty of Engineering and Built Environment

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Co SUPERVISOR: Dr. JIMMY PAUCK

Dedication

I must express my very profound gratitude to my wife, Chrisanthia Potgieter, for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without her.

Declaration

I, **MARVIN SYDNEY POTGIETER** declare that:

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CO SUPERVISOR: ………………………
DR. JIMMY PAUCK

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I would also like to thank the experts who were involved in the validation survey for this research project: Mr Jonas Johakimu and Mr. Dereck Strobyl. Without their passionate participation and input, the validation survey could not have been successfully conducted.

Abstract

Dissolving wood pulp (DWP) contains high levels of cellulose and has various applications. Production of dissolving wood pulp is accompanied by various challenges such as equipment operational problems and high bleaching costs. These are mainly due to lignin and other impurities contained in wood. Further, these impurities impose threats to the dissolving pulps applications such as the viscose process and the manufacture of finished rayon products. Removal of these contaminants at the early production stages proved effective in meeting by the challenges.

Hydrocyclones achieve the separation of heavy and light pulp components in a process known as fractionation. In the case of dissolving wood pulp, hydrocyclones fractionate the pulp fibres into coarse fibres and fine fibres known as fines. Fines are the reject materials and are associated with impurities such as wood resins.

Wood pulp was fractionated at 0.8% consistency using a Kadant laboratory hydrocyclone at mass reject rates of 5% and 11%. Pulp properties and application properties were determined and compared to unfractionated pulp. The fractionated pulps showed higher cellulose contents and lower levels of fines and associated resins. Bleaching of the fractionated pulps under a standard ODEDH bleaching sequence showed higher levels of delignification, as measured by brightness, and more favourable application properties. These findings were used to optimise the bleaching sequence by reducing the amount of chlorine dioxide applied in the second chlorine dioxide stage. The optimised bleaching sequence produced pulps with satisfactory fibre and application properties.

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List of Abbreviations

DWP:	Dissolving wood pulps
D_1:	First chlorination bleaching stage in bleaching unit
D_2:	Second chlorination bleaching stage in bleaching unit
O_2:	Oxygen bleaching stage in bleaching unit
H(Hypo):	Hypochlorite stage in bleaching unit
K no:	Permanganate Number
CSF:	Canadian Standard Freeness
a.k.a:	Also known as
E:	Extraction stage in bleaching unit
ODEDH:	Oxygen, first chlorination, extraction, second chlorination and hypochlorite bleaching stages
AOX	Adsorbable organic halides

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Glossary

Bleaching:	Chemical processing applied to chemical and mechanical pulps in order to increase their brightness.
Hydrocyclone efficiency:	Efficiency of a hydrocyclone under a particular set of running conditions that can be described in terms of the “heavies” concentrations in the “lights” outflow as a percentage of the ‘heavies” loading in the total inflow.
Apex:	Refers to the taped end of the hydrocyclone where the thick pulp fibres exit which are the desired fraction known as the accepts.
Base:	Refers to the flat end of the hydrocyclone where the thin pulp fibres exit which are the rejected fraction known as the fines. These are also called rejects.
Mass reject rate:	Percentage of the fines mass flow rate, the rejected pulp, over the pulp feed mass flow rate.
Volumetric reject rate:	Percentage of the fines volume flow rate, the rejected pulp, over the pulp feed volume flow rate.
Consistency:	A term used to describe solid content of pulp during pulp processing
Bamboo:	A group of woody perennial evergreen plant in the true grass family.
Shives:	Fibre bundles that come from incompletely cooked wood.
Pitch:	Substances consisting of agglomerates of undissolved extractives.

Sack kraft:	A porous kraft paper with high elasticity and high tear resistance designed for packaging products with high demands for strength and durability
Pulp brightness	The measure of how much light is reflected by pulp under identified conditions and is usually described as a percentage of how much light is reflected, thus a higher number represents a brighter or whiter paper.
Bleachability:	Bleaching response of the pulp.
Pulp yield:	The amount of pulp, by weight that is produced from a given amount of raw material expressed as a percentage of the given amount of raw material
Wood density:	Mass of wood per unit volume. It is an important trait for understanding the function and ecology of woody species, as well as estimating stored biomass and carbon content
Xylem:	Plants transport tissue that transports water and solutes from the roots to the leaves.
Phloem:	Plants transport tissue that transports food from the leaves to the rest of the plant.
Lumina:	The central cavity of a tubular or other hollow structure in an organism or cell
Tracheids:	The a type of water-conducting cell in the xylem which lacks perforations in the cell wall

Knots:	The hard mass of wood at the point where a branch joins the trunk of a tree
Shives:	The small bundle of incompletely cooked wood fibres in the chemical pulp

1. Introduction

1.1 Statement of the problem

Dissolving pulp refers to a product made from wood fibres. The wood is pulped chemically to remove lignin and other impurities, leaving almost pure cellulose. This cellulose is sold to the chemical industry under the name “dissolving pulp” and is used to manufacture a wide range of products such as viscose or rayon, cellophane plastics, modified cellulose thickeners etc. Dissolving pulps are branded by a high content of cellulose, small amount of hemicelluloses and even smaller amounts of extractives, lignin and minerals. One such pulp is eucalyptus.

Remaining impurities, such as wood resins and silica, pose problems during the production and use of dissolving pulp. Dissolving pulp (*viz*. cellulose) is used as a raw material to manufacture viscose fibre. It has been shown that wood resin adversely affects the viscose process and the finished rayon products. A high resin content gives a low brightness to the finished rayon product and its stability becomes conspicuously lower (Croon, Jonsén and Olofsson 1957). The hydrophobic components of the resin have a tendency to solidify and form deposits which accumulate on production equipment such as wire presses, valves, tubes and spinning jets, which in time, leads to severe operational problems. Resin acids have a strong effect on viscose resin viscosity (Croon, Jonsén and Olofsson 1957). Resins remaining in the bleached pulp used to manufacture rayon products have been shown to precipitate as solidified impurities in the finished rayon products. Consequently, important properties such as stability of strength, colour on ageing, heating and treatment with ultra violet light (UV) are negatively affected. The stability against UV is of great importance to rayon products as they are incorporated into fabrics which are used for outside wear. Additionally, during the heating of rayon, coloured degradation products are formed which reduce the brightness of the product (Croon, Jonsén and Olofsson 1957; Asikainen *et al.* 2010).

One of the many process steps involved in manufacturing dissolving pulp is bleaching. During bleaching, the presence of resins increases the demand for bleaching chemicals (Fahmy *et al*. 2008). A large portion of resin is contained in the fines enriched fraction of the dissolving pulps, hence efficient removal of fines from the pulp furnish is necessary (Mosbye 2003). Sithole *et al.* (2010) examined three methods for improving deresination of sulphite pulps: alkaline washing, enzyme treatment and hydrocyclone fractionation. They established that the latter method was more viable. In 2002, a study on fibre fractionation was done in collaboration with a company called Kadant (formerly Noss) (Kurula and Karlsson 2007). The outcome of the work was promising and led to an improvement of pulp quality. Although the initial work was based on cleaning the final pulp it was demonstrated that the fines removal could be achieved by fractionation of the dissolved pulps using a hydrocyclone.

Hydrocyclones fractionate pulp fibres into distinctive fractions, one that is enriched with fines, and one that is enriched with coarse fibres (Brännvall *et al.* 2007; Johakimu and Bush 2010). A fractionation process or system that effectively removes the fines before the bleaching process promises to give improved dissolving pulp quality. The use of hydrocyclones to fractionate pulps has been increasing. Oleg and Bergström (2005) reported a shift of pulp and paper mills from relying on screens alone to utilizing the combination of screens and hydrocyclones for improving pulp quality.

Fibre fractionation has been shown to improve the strength and porosity of sack Kraft pulp (Olson et al. 2001). Fibres in pulp and paper industries can be fractionated using hydrocyclones according to their paper making potential (Bergström 2006). A comparative study conducted by Ouellet *et al.* (2004) proved the fractionation combination of screening and hydrocyclones to be slightly more efficient than screening alone.

1.2 Motivation for the study

According to Dey and Gupta (1992), returns on investments in the Pulp and Paper industry are very low as a result of intensive material and energy usage. As a result, it is necessary that broader strategies aimed at helping the industry to remain sustainable and competitive are initiated. In this study opportunities for potential cost savings in bleaching chemical costs through fibre fractionation were explored. Fibre fractionation was carried out using Kadant hydrocyclone test canister rig (AM80 – F). Subsequently, improvement in pulp quality and savings in bleaching chemicals (chlorine dioxide at the D2- bleaching stage) was determined.

1.3 Objectives

The overall objective of the project is to determine how brownstock fractionation contributes to product quality and savings in bleaching chemical costs.

Objective one:
To determine how the hydrocyclone operational conditions can be optimised to enhance fines separation.

Objective two:
To determine how the removal of fines impacts on bleaching chemical consumption.

Objective three:
To determine how the removal of fines impacts on dissolving pulp properties and application properties.

1.4 The Delimitations

The study will not investigate the following:

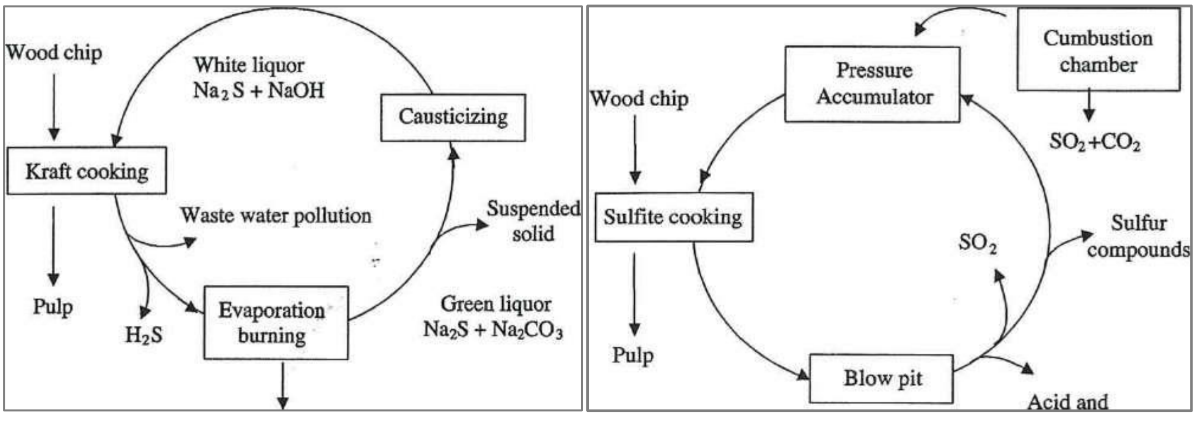
- Specific types of resins to be targeted
- Compare pulp types, pulping processes or various bleaching processes

2. Literature Review

2.1 Overview of pulping technologies used to produce dissolving pulp

The two predominant methods used to prepare dissolving pulps are the Prehydrolysis Kraft process shown in Figure 2.1a, and the acid bisulphite process shown in Figure 2.1b (Sridach 2010). Preparing dissolving pulp using the Prehydrolysis Kraft process, the hemicellulose removal is done prior to pulping using either steam or acidic reagents such as sulphuric acid. During subsequent pulping wood chips that have been extracted of hemicellulose are further treated with a mixture of sodium hydroxide and sodium sulphide that breaks the bonds that link lignin to the cellulose.

In the bisulphite process, a mixture of sulphurous acid and the bisulphite ion, with a chemical base of calcium, magnesium, sodium or ammonia, are used to attack and solubilize the lignin while the chemical structure of the cellulose is left largely intact. A pulp mill generally will consist of a wood preparation process, digesters, washing and screening processes and various bleaching processes. Figures 2.1a and 2.1b depict the Kraft and Sulphite processes, including the chemical recovery systems.



(a) (b)

Figure 2.1: (a) Kraft Process (Sridach 2010) (b) Sulphite Process (Sridach 2010)

Unbleached pulps exhibit a wide range of brightness depending on the pulping process and fibrous raw material used. The sulfite process produces the brightest pulp, up to 65% whereas the Kraft, soda and semi-chemical processes may produce pulp of only 15% brightness before bleaching (Bodhlyera 2014).

2.1.1 Wood processing, structure and composition

Handling of wood begins in the forest. This includes operations such as felling, transport (from forest to debarking plants) and storage. The wood is harvested and cut in the forest, and transported to the mill as logs. Eucalyptus and Pine are some of the dominant species of wood harvested by pulp and paper mills in South Africa. The logs are stored, and then chipped in preparation for pulping.

2.1.1 (a) Wood processing

The pulpwood is transported by truck or trains to the mills. Pulpwood usually arrives at the mill with bark. Wood must arrive fresh viz. as soon after felling as possible at the mill. Truck loads are measured on truck scale stations. These logs are measured by weight and volume. In some cases the moisture content of the wood is determined. The logs are cut into the desired length usually 2 to 3 meters. Usually the trend is to always procure logs that are longer.

Measurements can also be done when unloading the logs. Bridge cranes or wheel loader equipped with grapples unload the logs. They go directly to storage if they are not to be processed immediately. Although the storage time depends on local conditions, it should be as minimal as possible. Prolonged storage of wood causes decay, decreased basic density and pulp yield. Storage of huge quantities of wood is done temporally for special reasons such as seasonal supply problems. The storage area for wood at the mill is close to the process feed point.

Before debarking, logs can be cut if there is a need. This also decreases wood losses during debarking. Wood is debarked to remove the bark to the extent necessary for the quality of the finished product. Bark extractives cause problems in the production of bleached hardwood sulphite pulp (Fardim 2011).

Wood is sent to chippers to be cut into small uniform pieces. The logs are fed in at an angle into a rotating blade. This splits the wood and chip pieces break off. The complementary angle of the chipper influences the thickness of the chips. This is the angle between the front surface of the knife and the transverse surface to the fibre wood direction. The knife angle is normally between 32^0C and 40^0C. In hardwoods chips are normally about 20 mm long and 3 mm thick. Wood properties vary with moisture, and the moisture of the wood influences the wood chipping. Chipping the wood allows chemicals, water and heat to penetrate quickly. Delignification is strongly dependant on the thickness of the chips and this will be discussed in more detail in section 2.1.2. Chips are screened to ensure their sizes are uniform for cooking. Fines and oversized particles are removed. Chips that are oversized are rechipped and returned for screening again.

2.1.1 (b) Anatomy of wood

Trees are long lived with a unique rigid wooden structure of stems and branches. They are seed bearing plants and are classified into softwoods and hardwoods. Softwood seeds are produced in cones and are covered. Hardwood trees produce seeds that are covered within flowers. Softwood trees also have needle-like leaves which stay green throughout the year. Hardwood trees have blade-like leaves which are shed annually (deciduous) or continuously (evergreen).

Structural parts of a tree are the roots, branches, stem, bark and leaves displayed in Figure 2.2. For pulping only debarked stem wood is normally used. Wood is made up of specialised cells that perform mechanical functions that support water transport and metabolism.

Cells in the wood are heterogeneous. They are built up of polysaccharides such as cellulose and hemicellulose, and lignin. These substances are not uniformly distributed within the wood cell wall. Cell wall layers consist of the primary cell wall, the middle lamella, and the secondary cell wall. Secondary cell wall contains three layers S_1 being the outermost, S_2 the middle and S_3 the innermost. The S_1 layer and the outer part of the S_2 layer contain only slightly more cellulose than hemicellulose, while the innermost layer of the S_2 contain a large proportion of cellulose. Most of the lignin occurs in the middle lamella. In the outer part of S_3 layer the cellulose and hemicellulose contents increase and the lignin decreases.

On the outside of the cell walls non-structural components such as extractives and inorganic substances are normally found. These substances represent a minor fraction and are mainly composed of low molar mass compounds. In the cell walls are found trace amounts of compounds containing nitrogen i.e. proteins.

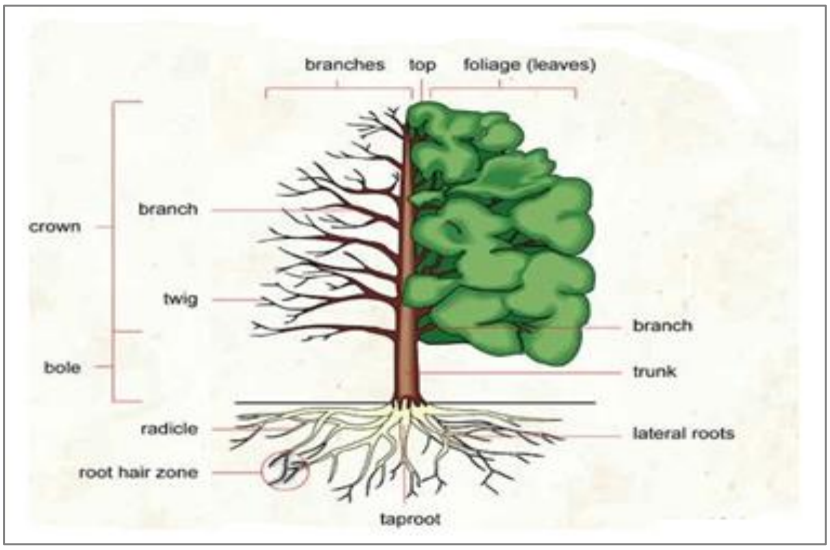


Figure 2.2: A tree structure (Arapahoetreeservice 2016)

2.1.1 (c) Wood morphology

A cross sectional view of a tree is displayed in Figure 2.3. Trees usually have about 15% total weight of bark. Bark consists of two layers, the inner bark and the outer bark. The inner bark has living cells and is narrower. The cells are called phloem cells and have a slow cell division rate. The outer bark is made up dead cells. These dead cells were part of the inner bark at an earlier stage. Protection is provided by the outer bark against mechanical damage, temperature and humidity.

A thin layer of tissue consisting of living cells called the cambium is found between the bark and the xylem. This is the section where cell division and radial growth of the tree occur. A new layer of xylem is produced annually, and forms what is commonly called the annual rings. Trees have more xylem than bark as phloem cells divide less often than cambium cells. Tree ages are calculated from the number of growth rings it possesses at the base of the stem (Fardim 2011).

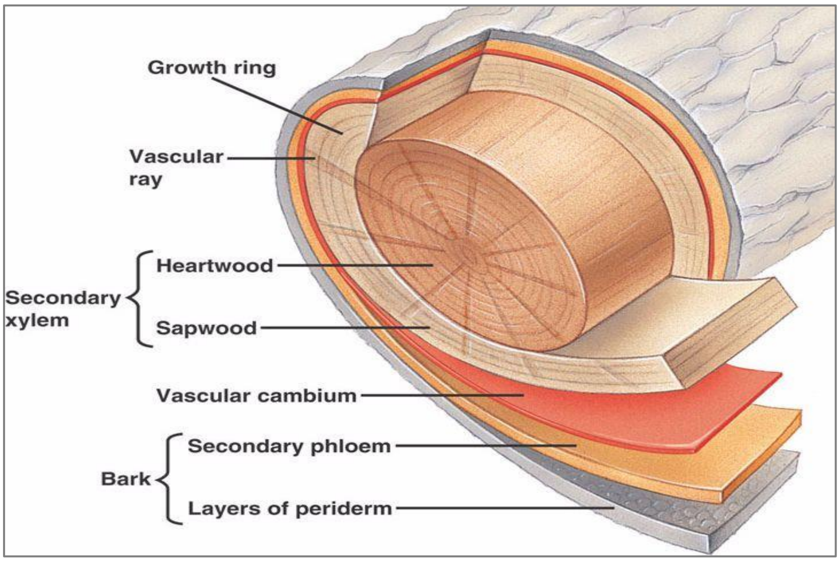


Figure 2.3: A tree diagram showing cambium, bark and xylem (Pinterest 2016)

The main structural elements of plants are their fibres. Fibres are long and narrow cells. Their length varies in the range 1-2mm (in hardwoods) with a diameter 0.01-0.05mm. They have closed ends which are mostly pointed as displayed in Figure 2.4. Fibre walls can be thick or thin and their lumina large or narrow as shown in Figure 2.4. These characteristics are helpful in fractionating pulp. The macroscopic structure of wood differs between softwoods and hardwoods and between different species. It differs also between different wood tissues within the same tree. Cells in the wood are elongated and are orientated in the longitudinal direction of the stem. The wood cells are interconnected with openings called pits. These allow for the flow of nutrients and water in the tree. Cells in softwoods are mainly tracheids as opposed to a broader variety of different specialised cell types in hardwoods such as fibres, vessels and parenchyma cells (Figure 2.4).

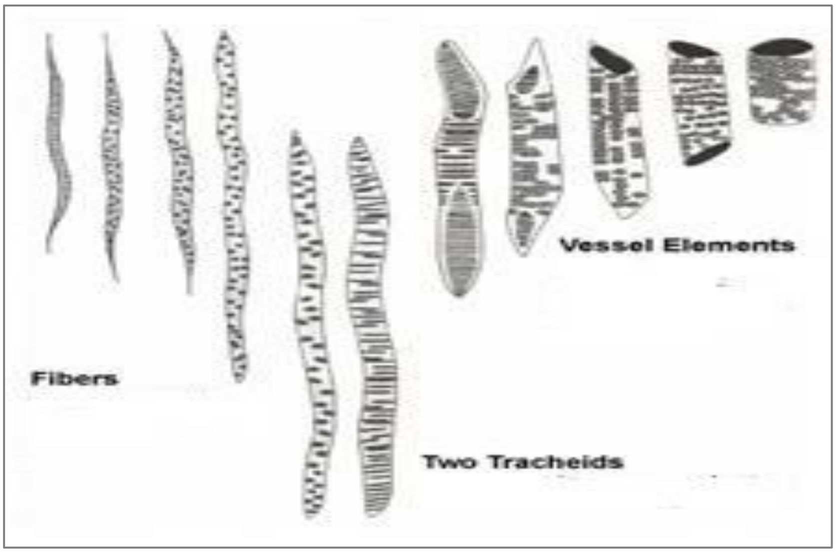


Figure 2.4: Wood fibres showing pits and lumina (Pinterest 2016)

2.1.1 (d) Structural components of wood

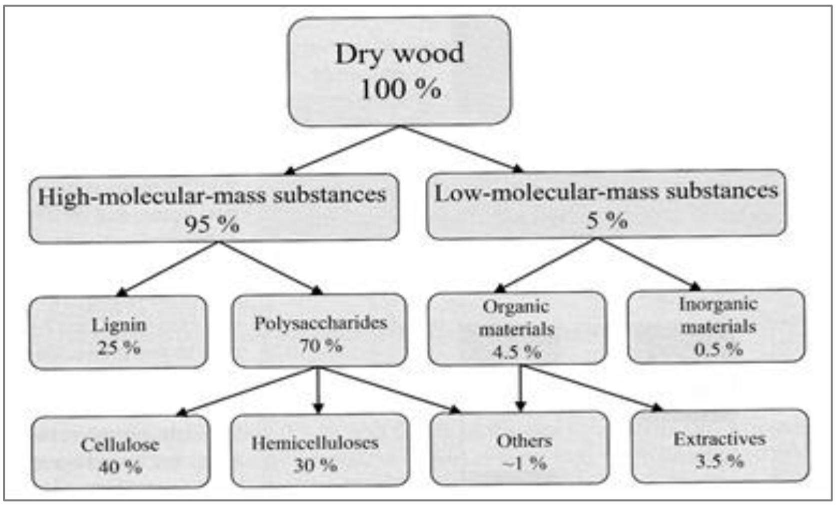


Figure 2.5: General classification and content of the chemical wood components (Asikainen and Alén 2011)

The structural substances of wood are cellulose, hemicellulose and lignin. These structural substances are shown in Figure 2.6 where their proportions in wood are quantified. The structure of hemicellulose differs between trees (i.e. softwoods and hardwoods) while the cellulose composition remains the same for all woods. Cellulose is the most abundant and important biopolymer worldwide. It is a naturally occurring carbohydrate based polymer. Cellulose is a homopolysaccharide. It is linked together by glyosidic bonds. Hemicellulose is another naturally occurring class of carbohydrate based polymers. They are heteropolysaccharides. Lignin is an amorphous polymer. Its irregular chemical structure differs clearly from other constituents of wood. Different structural elements are not linked to each other in any systematic order in lignin. Cellulose, hemicellulose and lignin are not uniformly distributed in wood cells. The distribution of chemical constituents remains uncertain (Fardim 2011).

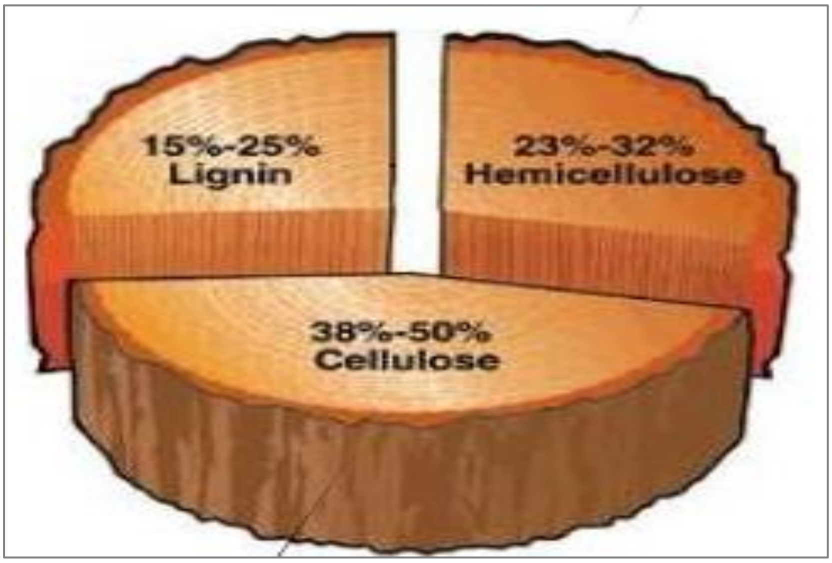


Figure 2.6: An outline of chemical composition of a tree (Forestbioenergy 2016)

(i) Cellulose and hemicellulose

The cellulose is composed of carbon, hydrogen, and oxygen in the form of sugars. It is the most abundant organic compound in the world, comprising 40%–50% of woody plant composition by weight. Cellulose is a linear polysaccharide of glucose units which is associated with hemicelluloses and lignin, and occurs mainly in the secondary cell wall (Smith, Faulkner and Powell 1994).

The structure of hemicellulose differs between trees (i.e. softwoods and hardwoods) while the cellulose composition remains the same for all woods. Hemicelluloses are comprised of carbohydrates with the monomers in the form of pentose, xylose, and hexose sugars. The hemicelluloses comprise 25%-35% of the dry weight of the wood. The proportion of hemicelluloses in softwood is smaller than that in hardwood. Generally, hemicelluloses differ from cellulose with respect to their greater solubility in alkali. This characteristic property is most commonly utilized when fractionating different polysaccharides in lignin-free samples (Vikash and Sigrid 2016).

(ii) Lignin

Lignin is derived mainly from wood and is a complex polymeric compound. Lignin is also a crucial component for fibre rigidity in plants. The properties of lignin and its composition contribute greatly to the properties of fibres and their use. Lignin is the main part of the secondary cell walls of wood as shown in Figure 2.7. Lignin has a very low solubility in water. Generally hard fibres are more lignified than soft fibres. Reliable quantification of lignin content is quite difficult. Lignin is also an abundant biological material, exceeded only by cellulose and hemicelluloses. Approximately 20%-30% of the wood structure is made up of lignin depending on the species of the wood. It is the cementing agent which binds the individual wood fibres together to form a substance of strength and hardness (Sjöström 1993).

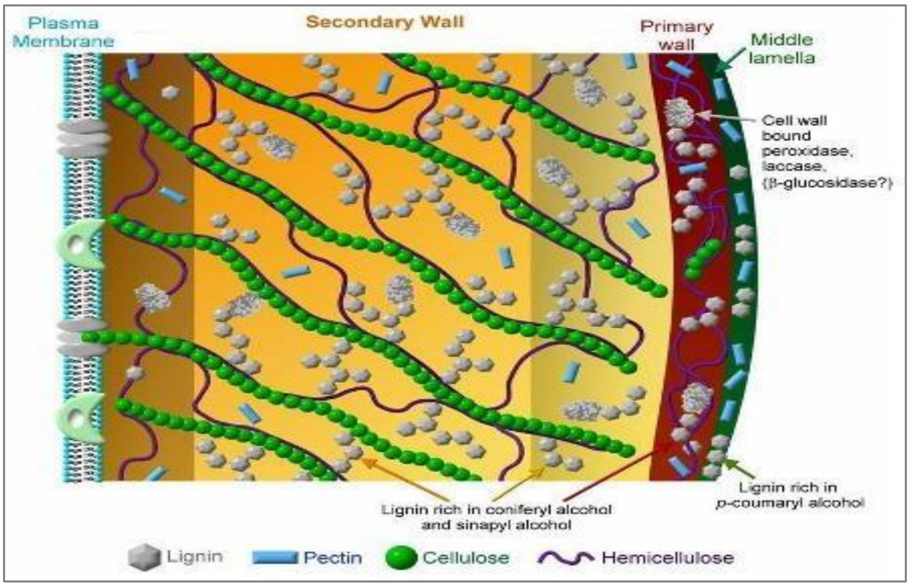


Figure 2.7:Diagram showing lignin/cellular composition in the secondary wall (Springer Science 2016)

2.1.1 (e) Non-structural wood components

As mentioned in section 2.1.1 (a) cellulose, hemicellulose and lignin are sometimes referred to as structural substances as shown in Figure 2.6. The other constituents referred to as non-structural substances are pectin, starch and proteins. These are present in smaller quantities as shown in Figure 2.5. Wood content can be divided into high and low molar mass substances. Non-structural compounds with low molar mass such as extractives and inorganics appear in small quantities.

Extractives may vary in amount and structure in softwoods and hardwoods. They contribute to wood properties such as colour, odour and taste. Extractives are also essential to maintain the differentiated biological functions of the tree.

2.1.1 (f) Extractives

Extractives are made up of many diverse substances of mainly low molar mass. The extractives are defined as lipophilic or hydrophilic. Lipophilic extractives are soluble in organic solvents and hydrophilic extractives are soluble in water. Lipophilic extractives are collectively called resins. Generally, hardwood pulps contain higher resin levels than softwood pulps. In softwood, a large portion of the resin is in the form of free fatty acids or rosin acids. Extractives composition will vary in different species and has been classified into various compounds as shown in Table 2.1.

(Fardim 2011; Yang and Jaakkola 2011)

Table 2.1: Classification of wood extractives (Yang and Jaakkola 2011)

Aliphatic and alicyclic compounds	**Phenolic compounds**	**Other compounds**
Terpenes and terpenoids	Simple Phenols	Sugars
Esters of fatty acids	Stilbenes	Cyclitols Amino acids
Fatty acids and alcohols	Lignans	Alkaloids
Alkanes	Isoflavones	Quinones
	Flavonoids	Coumarins

For production of organic chemicals, extractives play an important role as a valuable raw material. Trees with high extractives content provide substantial amounts of products such as crude turpentine and raw tall oils. These are produced as by products from alkaline pulping (Fardim 2011; Yang and Jaakkola 2011). Extractives give colour, taste and odour to wood. Wood also receives some protection from insect attack from resin components. In pulping, resins are directly released into the cooking liquor. This resin originates from thin walled resin canals that readily rupture during pulping., Resin pockets are also opened during chipping. However, during pulp bleaching extractives contribute to the consumption of bleaching chemicals negatively. The alkali in alkaline pulping processes is consumed by reaction with lignins, by degradation of the carbohydrates, and by reaction with organic acids and the extractives present in wood. Acidic and polyphenolic extractives react rapidly with NaOH so that the amount of alkali available for delignification is reduced. These extractives are also chemically altered during the reaction with bleaching chemicals. The major chemical transformations in pulp extractives composition and structure occur in the last bleaching stages (Freire , Silvestre and Pascoal Neto 2006).

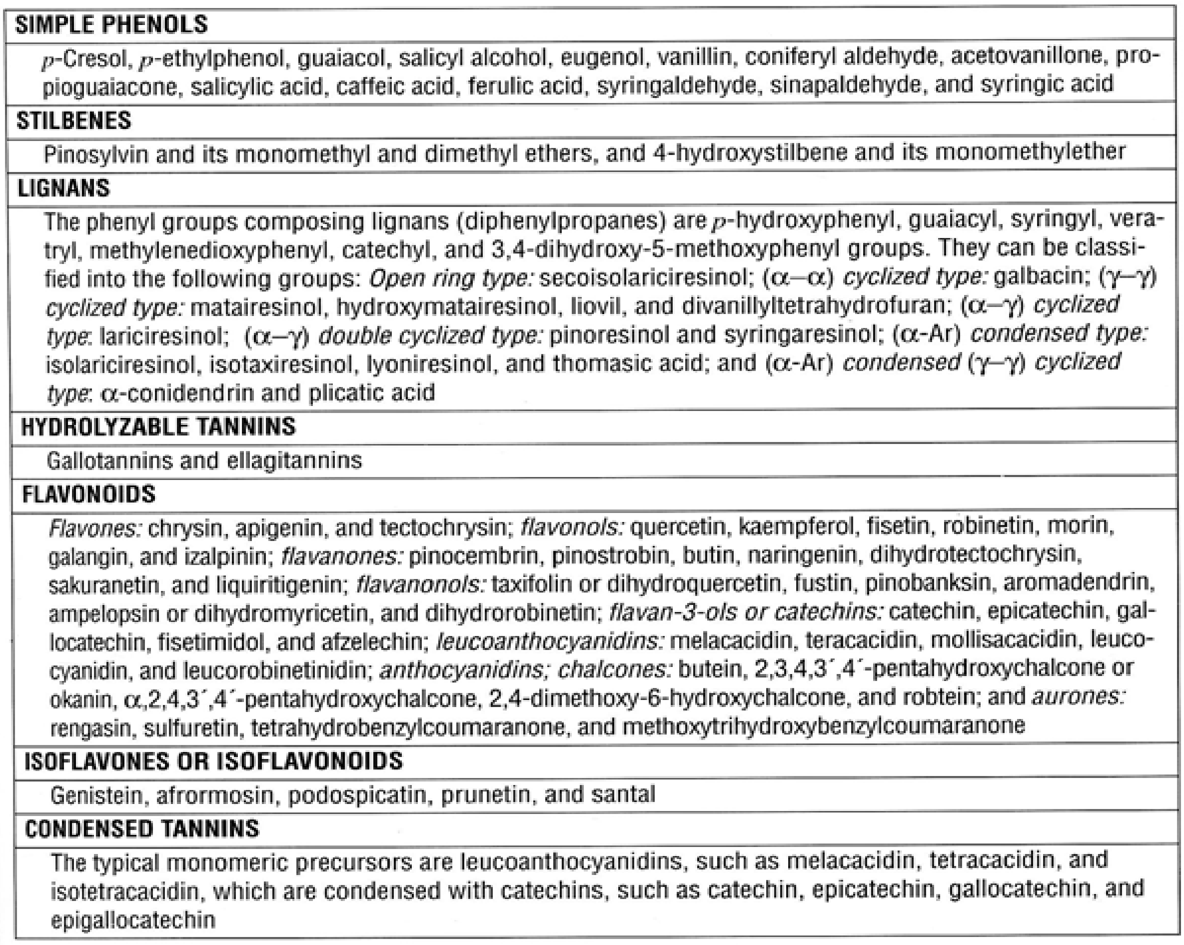
The resin content and chemical composition of the trees immediately begins to decrease and change, respectively after tree felling. The chemical composition of this fraction also changes. During storage of wood chips, extractives content decreases. Wood polysaccharides could also be biodegraded during lengthy storage which can result in reduced pulp yield and low pulp quality. Unwanted extractives can be removed from sulphite pulp by mechanical fibre fractionation (Fardim 2011). Extractives are divided into various groups. These have typical structural features. Terpenes, aliphatic extractives and aromatic extractives are some of the groups. Derivatives of terpenes contain a broad class of compounds that are widespread in plants, shown in Table 2.2. Aliphatic extractives comprise alkanes, fatty alcohols, fatty acids, fats and waxes, shown in Table 2.3. Alkanes, free alcohols and free fatty acids occur in lesser quantities in woods. Larger quantities of fatty acids and fatty alcohols are esterified in woods. Figure 2.8 displays some aromatic extractives known.

Table 2.2: Classification of main structural types of terpenes in wood tissue (Stenius 2000)

Name	**Number of ($C_{10}H_{16}$) units**	**Molecular formula**
Monoterpenes	1	$C_{10}H_{16}$
Sesquiterpenes	1.5	$C_{15}H_{24}$
Diterpenes	2	$C_{20}H_{32}$
Triterpenes	3	$C_{30}H_{48}$
Polyterpenes	1.4	$C_{40}H_{64}$

Table 2.3: Fatty alcohols and fatty acids in wood with their functions and location (Asikainen and Alén 2011)

Extractives	**Fats**
Subclasses	Triglyceride Fatty acids steryl esters sterols
Function in tree	Physiological
Occurrence	Parenchyma Cell
Tree species	All wood species



SIMPLE PHENOLS
p-Cresol, *p*-ethylphenol, guaiacol, salicyl alcohol, eugenol, vanillin, coniferyl aldehyde, acetovanillone, propioguaiacone, salicylic acid, caffeic acid, ferulic acid, syringaldehyde, sinapaldehyde, and syringic acid
STILBENES
Pinosylvin and its monomethyl and dimethyl ethers, and 4-hydroxystilbene and its monomethylether
LIGNANS
The phenyl groups composing lignans (diphenylpropanes) are *p*-hydroxyphenyl, guaiacyl, syringyl, veratryl, methylenedioxyphenyl, catechyl, and 3,4-dihydroxy-5-methoxyphenyl groups. They can be classified into the following groups: *Open ring type:* secoisolariciresinol; (α–α) *cyclized type:* galbacin; (γ–γ) *cyclized type:* matairesinol, hydroxymatairesinol, liovil, and divanillyltetrahydrofuran; (α–γ) *cyclized type*: lariciresinol; (α–γ) *double cyclized type:* pinoresinol and syringaresinol; (α-Ar) *condensed type:* isolariciresinol, isotaxiresinol, lyoniresinol, and thomasic acid; and (α-Ar) *condensed* (γ–γ) *cyclized type*: α-conidendrin and plicatic acid
HYDROLYZABLE TANNINS
Gallotannins and ellagitannins
FLAVONOIDS
Flavones: chrysin, apigenin, and tectochrysin; *flavonols:* quercetin, kaempferol, fisetin, robinetin, morin, galangin, and izalpinin; *flavanones:* pinocembrin, pinostrobin, butin, naringenin, dihydrotectochrysin, sakuranetin, and liquiritigenin; *flavanonols:* taxifolin or dihydroquercetin, fustin, pinobanksin, aromadendrin, ampelopsin or dihydromyricetin, and dihydrorobinetin; *flavan-3-ols or catechins:* catechin, epicatechin, gallocatechin, fisetimidol, and afzelechin; *leucoanthocyanidins:* melacacidin, teracacidin, mollisacacidin, leucocyanidin, and leucorobinetinidin; *anthocyanidins; chalcones:* butein, 2,3,4,3´,4´-pentahydroxychalcone or okanin, α,2,4,3´,4´-pentahydroxychalcone, 2,4-dimethoxy-6-hydroxychalcone, and robtein; and *aurones:* rengasin, sulfuretin, tetrahydrobenzylcoumaranone, and methoxytrihydroxybenzylcoumaranone
ISOFLAVONES OR ISOFLAVONOIDS
Genistein, afrormosin, podospicatin, prunetin, and santal
CONDENSED TANNINS
The typical monomeric precursors are leucoanthocyanidins, such as melacacidin, tetracacidin, and isotetracacidin, which are condensed with catechins, such as catechin, epicatechin, gallocatechin, and epigallocatechin

Figure 2.8: Aromatic extractives in wood (Stenius 2000)

2.1.2 Pulping

Chemical pulps are produced by chemically dissolving the lignin between and within the wood fibres. This process is called pulping and is carried out in chemical reactors. This enables the fibres to separate relatively undamaged. Most of the non-fibrous wood components are dissolved in the cooking liquor and removed. Kraft cooking liquor contains sodium hydroxide and sodium sulphide which dissolve the lignin from the cellulose fibres. Delignification needs several hours at temperatures of 170°C to 176°C. Hemicellulose degrades to provide fragments that are soluble in the liquors that are strongly basic. The cooking liquor contains lignin fragments and other inorganic salts.

Sulphite cooking liquor contains various salts of sulphurous acid to extract the lignin. The salts used are either sulphites, or bisulphites. Common counter ions are sodium, calcium, potassium, magnesium and ammonium. This results in the final yields in the order of 40 to 55% in these processes.

Digesters receive woodchips through conveyers by means of wood handling machinery. In the digesters the wood chips are submerged in the cooking liquor and they are cooked under pressure and set temperature with cooking liquor. The cooking liquor is present within the chips at the beginning of this stage. Delignification begins beyond temperatures of 145^0C-150^0C in the chip and cooking liquor mixture (Fardim 2011). It is at this point that the cooking chemicals within the chips start to react and deplete. During cooking diffusion of alkali into the chips occurs with simultaneous diffusion of solubilized components out of the wood. The fibres are freed from the wood matrix by dissolving the lignin. The fibres are freed from the wood matrix without damage once the lignin has been removed.

2.1.2 (a) Critical chip quality

The chips dimensions are of outmost importance for the pulp yield and quality. They have a large influence on the operation of the cooking process. The most critical dimension at this stage is the chips thickness. The thicker chips have a longer diffusion distance to the centres.

2.1.2 (b) Cavities in wood chips

Fresh woodchips have partially air and liquid in their cavities. Air in the wood cavities must be removed for the chips to be fully penetrated by cooking liquor. The process of removing air is usually done by pre-steaming the woodchips. The air then expands and a fraction of it is removed. The outward diffusion of the air and the inward diffusion of the steam reduce the air content further. The steamed woodchips are penetrated by the cooking liquor causing condensation of the steam inside the woodchips. This increases the pressure gradient between the free liquor and the woodchip interior, thereby facilitating impregnation. Process parameters that play an important role during pulping are chemical charge, cooking liquor composition, cooking time and temperature. Temperature plays a vital role in the reaction of lignin with cooking liquor. Figure 2.9 shows some influence of temperature during Kraft pulp cooking.

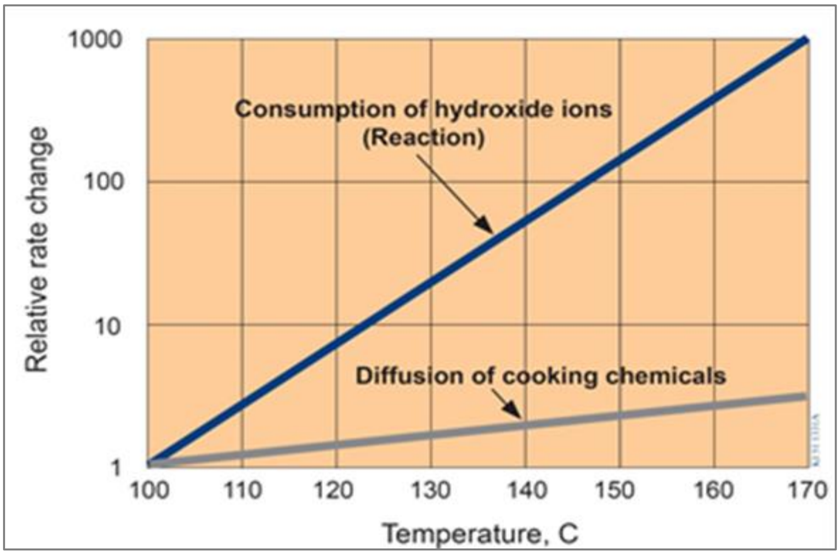


Figure 2.9: Temperature controls the rate of hydroxide ion consumption and the diffusion of cooking chemicals in the wood chips (Karlström 2009).

2.1.2 (c) Chip size influence

Diffusion into thicker chips is slower as result of the greater diffusion distance to the centre of the chip. Thicker chips will result in a larger delignification variation which leads to reduced strength and pulp yield. Strength of the pulp from thinner chips is higher. Thus thick chips will not be cooked sufficiently and thin chips can be overcooked (Tomlinson 1980). Chips are also not uniform in chemical composition. If chip impregnation is not complete the chemicals are completely consumed before they will reach the centre of the woodchips. As a result delignification is not uniform. Gullichsen, Hyvärinen and Sundqvist (1995) demonstrated more non uniformity in delignification of thick chips as compared to thin chips. Thicker woodchips require more alkali to reach the same level of delignification as thin woodchips. As a result larger chips size pulp more slowly than the smaller chips. They fail to pulp completely during the digesting process. This leads to a state where the central core of the chip passes out of the digester at the end of the pulping process as basically solid wood, and manifests and rejects in subsequent screening processes. On the other hand thinner chips have had all the lignin removed from between the individual fibres so that the fibres are liberated, and they might even be overcooked. This difference in degree of pulping has a weighty impact on pulp yield, pulp quality, digester operation, and subsequent pulp screening and cleaning, refining, and bleaching.

As mentioned earlier, the purpose of chemical pulping is to free fibres through delignification. Lignin becomes soluble in the alkaline solution. A side reaction occurs in the process which is undesirable. This is called lignin condensation in which dark masses of fibre are produced, which is difficult to bleach.

2.1.2 (d) The sulphite cooking process

Cooking liquor is prepared by reacting limestone with sulphur dioxide gas and water to form calcium bisulphite solution. This reaction takes place in a counter currently operated tower that is packed with limestone. Water is dripped down, and the sulphur dioxide is passed upwards through the tower. Calcium bisulphite solution is then formed by the contact of sulphurous acid with the limestone according to equation 2.1. The cooking liquor solution flows out the bottom section of the tower and is further strengthened by sulphur dioxide gas recovered from previous cooks.

$H_2O + SO_2 \rightarrow H_2SO_3$

$CaCO_3 + 2H_2SO_3 \rightarrow Ca(HSO_3)_2 + CO_2 + H_2O$

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

$Ca(OH)_2 + 2H_2SO_3 \rightarrow Ca(HSO_3)_2 + 2H_2O$ *Eqn no:* 2.1

The cooking liquor penetrates the woodchips thoroughly in the digesters. The contents in the digester are heated via circulation of the cooking liquor through a strainer and heat exchanger and back to the digester. This liquor circulation heating is at selected cooking temperatures of 125^0C – 140^0C. After a period of time the digester is degassed of excess SO_2, which is recirculated back to the liquor preparation stage. The contents in the digester are then discharged under pressure (blowing) into a blow tank, where further degassing and cooking takes place. The pulp is then sent for washing.

The three reactions involved in lignin breakdown are sulphonation, hydrolysis and condensation. Sulphonation and hydrolysis are directly responsible for delignification by lignin dissolution. Sulphonation makes the lignin more hydrophilic and hydrolysis breaks downs the lignin into soluble lignin fragments. Hydrolysis reactions are slow under neutral and alkaline pulping but faster under acidic sulphite conditions. Condensation increases with the decrease of the residual bisulphite concentration.

2.1.3 Washing

Washing of the pulp is an important unit operation in pulp mills. Effective washing entails removing products and impurities form previous reactions and modifying the fibres chemically and physically for the next treatments (Turner *et al.* 1996; Sillanpää *et al.* 2001).Typically pulp is washed in drum washers. The washing is done by diluting the fibre suspension with water and removing the water under suction, to produce a relatively dry pulp cake. Typical washing efficiencies are shown in Figure 2.10. Factors that affect washing efficiency are the fibre characteristics, shower characteristics, and operating factors. Showering parameters for washing are characterized by nozzles, temperature and shower distribution. The washing filtrate is returned to the process for recovery of chemicals. Washing reduces chemical losses from the pulping cycle and reduces the level of contaminants which might increase chemical consumption in the bleaching process. At the bleaching stage, the inter-stage washing operations reduce carry-over of unwanted substances to the next stage. They separate dissolved substances from the pulp after the bleaching reactions in order to prepare the pulp for the next treatment. Good washing between individual bleaching treatments allows higher quality, stable production and lower consumption of bleaching chemicals (Ala-Kaila and Poukka 2003).

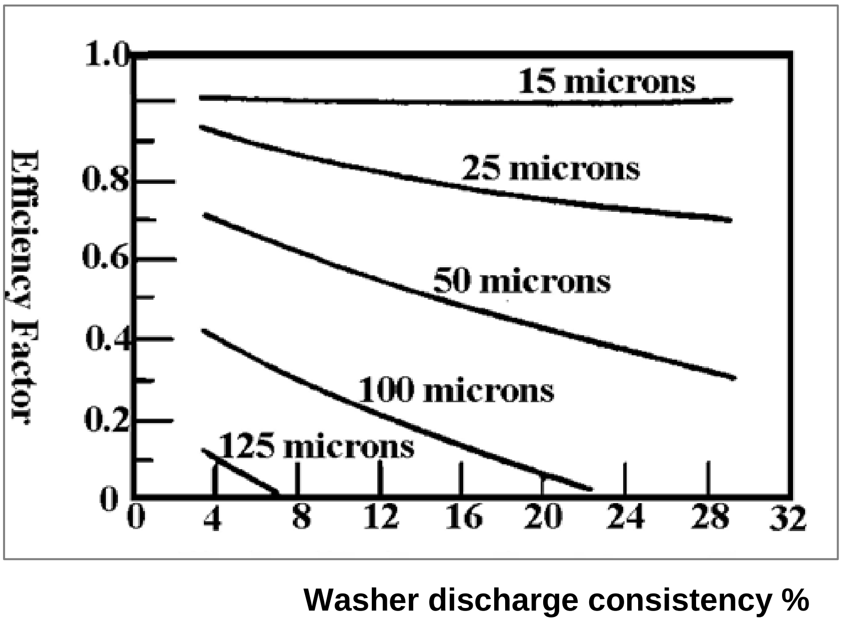


Figure 2.10: Diagram showing efficiency in various sieves sizes (Venditti 2015).

2.1.3 (a) Washing operations

Washing units are usually connected in series and the washing liquor travels counter-currently to the pulp being washed as shown in Figure 2.11. The counter-current water circulation principle is known both theoretically and practically to be an efficient way to achieve high recovery of chemicals and low dissolved-material carry over to the following process treatment stage (Ala-Kaila and Poukka 2003). The filtrate from one stage is used as wash water in the preceding stage. In the final stage the cleanest pulp will be washed by the cleanest water. This assists in minimising the dilution of cooking liquor flow to evaporation but still ensures that the pulp is as clean as possible.

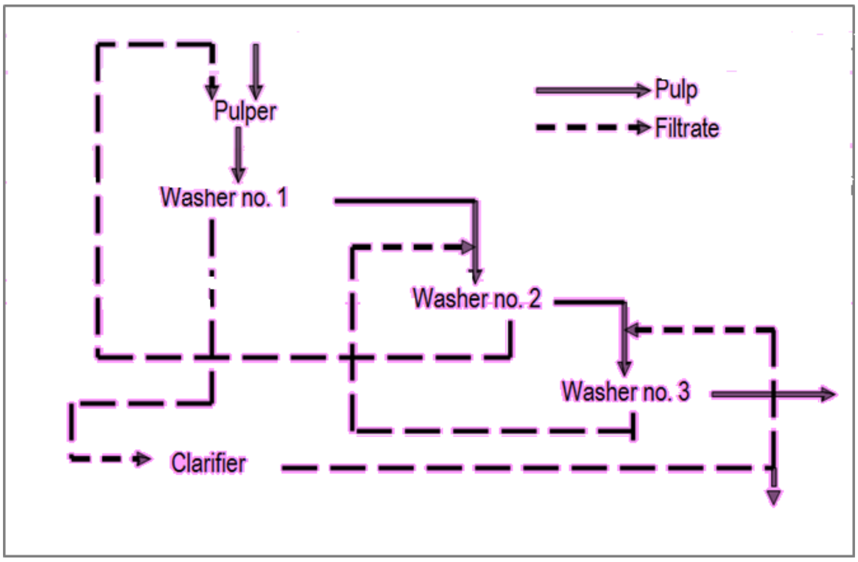


Figure 2.11: Block flow diagram of counter current washing (Venditti 2015).

2.1.4 Screening and Cleaning

Cooked pulp contains unwanted solid materials. These may be chips that are not cooked properly (a.k.a knots) or fibrous material that may not be completely separated into individual fibres (a.k.a. shives). Wood contaminants can also be present as non-fibrous solids. These larger unwanted particles can cause machine damage and need to be removed before washing. Such particles can also have an impact on bleaching chemical consumption.

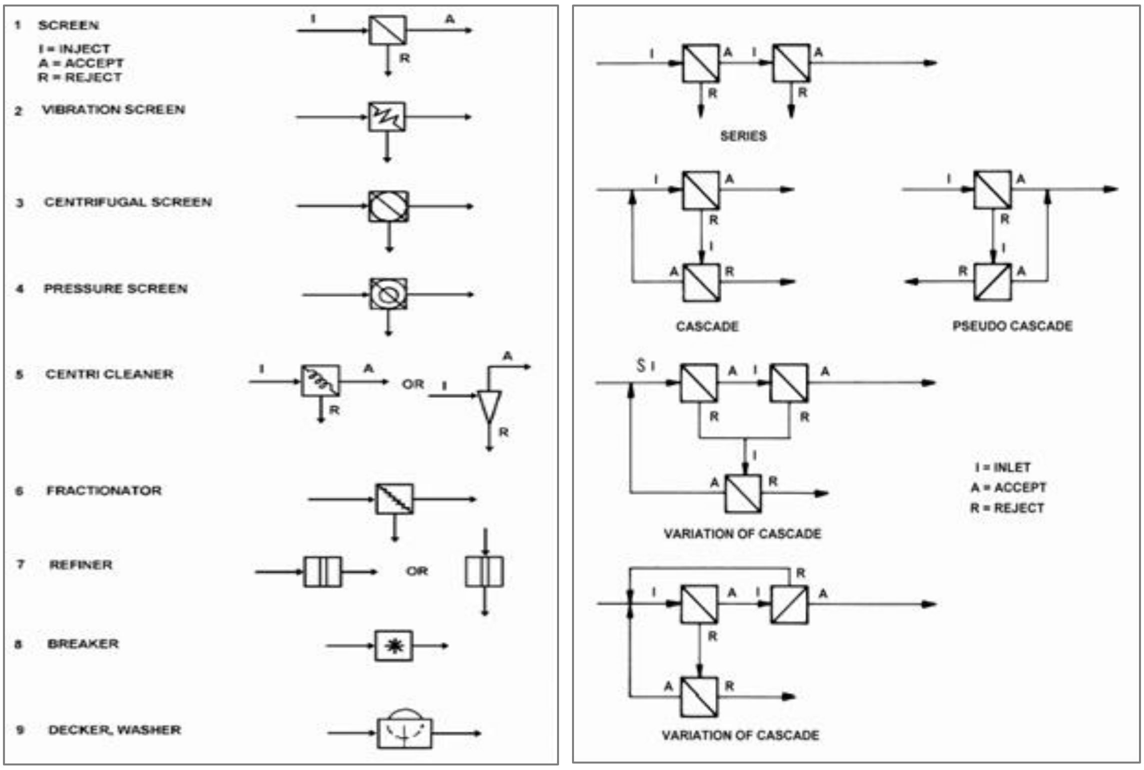
A combination of screens and cleaners (or hydrocyclones) are typically used to remove these impurities from the pulp stream. The performance of screens and hydrocyclones are governed by the properties of their fibres. Unfortunately screens do not have 100% selectivity. Hydrocyclones are also used in the mills to remove impurities and are sometimes referred as cleaners. Screens separate pulp fibres according to fibre length and flexibility while hydrocyclones separate according to particle specific surface area and density (Karnis 1997). Particles that will be removed fully are those that are too large to fit through screen apertures. Rejected particles are usually smaller than the screen aperture in one or two dimensions, thus their separation is based on probability screening.

Allison *et al.* (2003) showed that the fibre fractionation mechanism achieved by pulp screening was primarily based on fibre length. The shorter fibres pass more easily through screen apertures than long fibres. This makes the passage ratio for short fibres higher than long fibres. Screens have been used to divide pulp into different pulp fractions, based on different characteristics e.g. fibre length. This application is known as fractionation.

Some contaminants that are of similar in size to fibres may be removed on the basis of density. Cleaners use centrifugal forces to separate particles with different densities. Pilot plant trials performed to improve pulp quality for newsprint by comparing screens and hydrocyclones were done by Ouellet *et al.* (2004). Although hydrocyclone fractionation proved slightly better, the screens had lower operating costs. A more detailed description of the action of hydrocyclones is covered in Section 2.2.3.

2.1.4 (a) Industrial mill screening connections and operation

As mentioned in section 2.1.4 the basic purpose of screening and cleaning is to reduce rejectable material to suitably low concentrations so that the accept flow can be fed to the next process phase. Good fibres can occur in substantial amounts in the rejects stream when targeting maximum purity which may be costly. To avoid this situation, screening and cleaning systems are typically arranged in multi-stage cascading configurations. In cascading systems there is a primary stage that purifies the accepts according to requirement whilst the secondary stage reclaims the good fibres in the rejects. In the process it also concentrates the reject stream. The secondary stages' main goals are to minimise or possibly eliminate the loss of good fibre. In a study by Dumdie (1991), pressure screens under controlled conditions improved quality and efficiency and led to cost savings. Figure 2.12 depicts some typical screening and cleaning cascade arrangements. The symbols used are explained in Figure 2.12 (a) and typical cascading arrangements shown in Figure 2.12 (b)



(a) (b)

Figure 2.12: (a) Shows screening symbols that are used in flow diagrams and (b) possible arrangements of equipment that can be employed (Fardim 2011)

2.1.5 Bleaching

An overview of the bleaching process is given in this section and is covered in more detail in Section 2.4. The bleaching process decreases the colour and whitens the pulp. Lignin is the component that gives raw pulp its brown colour. The bleaching process uses various bleaching agents, but in particular chlorine dioxide to brighten the pulp by aiding the removal of lignin. A typical multistage bleaching process is shown in Figure 2.13. Large quantities of expensive chemicals are consumed in pulp bleaching processes.

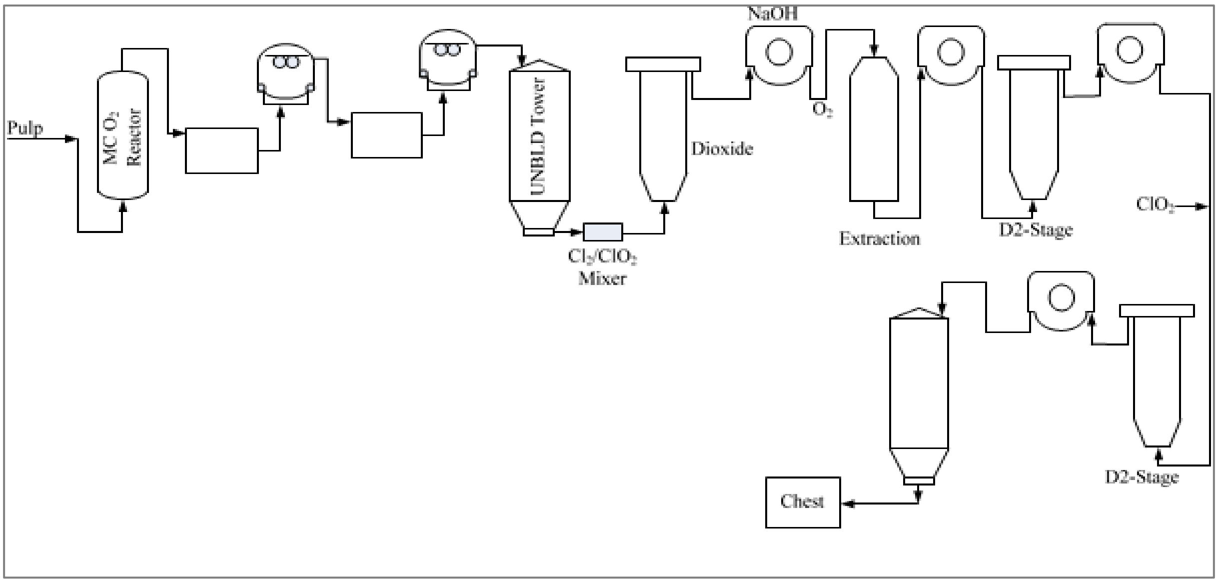


Figure 2.13: Bleaching process flow chart with chlorine dioxide (nptel 2015).

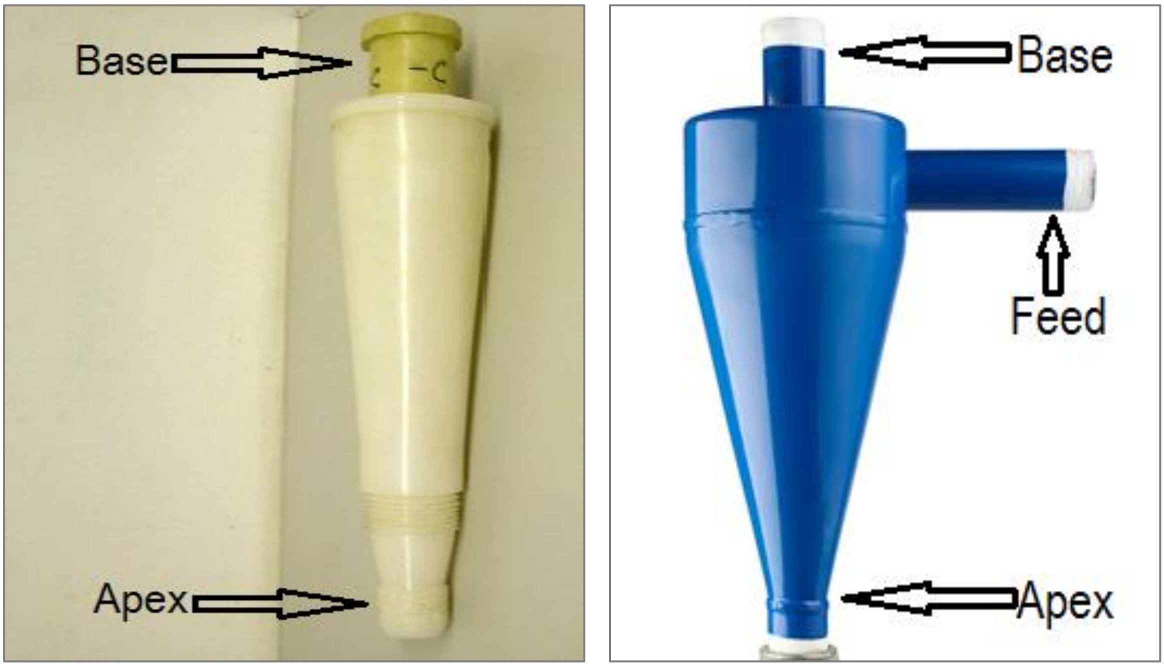
2.1.6 Pulp Drying

To prevent pulp properties deteriorating due to biological and chemical activities it is necessary that the pulp is dried after manufacture. Drying is also necessary for economic transportation of the pulp as it reduces the pulp moisture and hence the overall weight. The bleached pulp is dried, cut into sheets or rolls and sold as chemical cellulose

2.2 Dynamics of the Hydrocyclone

Hydrocyclones are commonly referred to as cyclones and have been widely utilized in the sorting of particles in comminution circuits. They are static devices that apply centrifugal force to liquid suspensions so as to promote separation of light and heavy components (CSI 2009).

The two basic components of the hydrocyclone are the inner cone shown in Figure 2.14 (a) and outer shell shown in Figure 2.14 (b). Hydrocyclones are commonly manufactured from steel with an internal rubber lining of 6 -12mm thickness (Neyrtec 2016). Alternative materials such as stainless steel, ceramic, and cast iron may be selected depending on the products to be treated and their corrosive or abrasive nature (Neyrtec 2016). The inner cone is typically made of wear resistance rubber. The practical range of classification for cyclones is 40 microns to 400 microns, with some remote applications as fine as 5 microns or as coarse as 1000 microns (Arterburn 2016). Despite their simplicity, hydrocyclones are very efficient when promoting solid-liquid separations. They utilize centrifugal force, a pseudo-force caused by inertia to separate the particles from the fluid. The success of these operations is based on the ratio of the suspension centripetal force to fluid resistance, which is high for dense and coarse particles and low for light and fine particles.



(a) (b)

Figure 2.14: (a) The inner cone referred to as the fractionator and (b) the outside shell known as the housing of a hydrocyclone (Ispat 2008).

2.2.1 Anatomy of a Hydrocyclone

The geometry of the hydrocyclone comprises the inlet area and shape, cylindrical section, the overall length, the cone angle, vortex finder and apex diameters. The exit dimensions are the overflow and the underflow diameters. The overflows and the underflows refer to base and apex flows respectively. Depending on the desired product they are referred to as accepts and rejects. This will be further clarified in the Section 3. Figure 2.15 below displays the internal view of a hydrocylone.

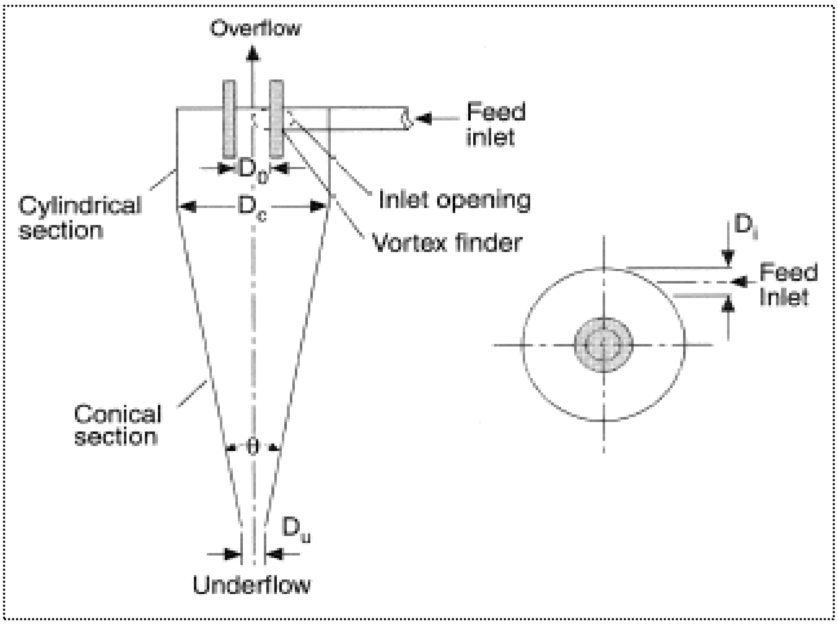


Figure 2.15: Scheme of a hydrocyclone (Bradley 2016)

2.2.2 Outline of hydrocyclone geometry

Statie, Salcudean and Gartshore (2001) investigated the effect of changes in the geometry of hydrocyclones, in particular cone angle, length of the cylindrical chamber, vortex finder, feed and exit diameter. Their findings enabled a better understanding of the flow of fluids and separation in hydrocyclones. The geometric relationships of the different sections of the hydrocyclones provide an understanding and some point of reference as to how a hydrocyclone performs in practise. Hydrocyclones have proper relationships between the hydrocyclone diameters, inlet area, vortex finder, and apex orifice, and sufficient length providing retention time to properly classify particles.

The most important parameter is the inside diameter of the cylindrical feed chamber. Statie, Salcudean and Gartshore (2001) discovered that overflow diameter had a vital geometrical influence on separation while the underflow diameter had more influence in the hydrodynamics of the hydrocyclone. Though, it was important that very small overflow diameters have high risks for flocculation. Feed inlet diameter was also found to have an important influence on fibre fractionation and separation performances inside the hydrocyclone. The effect of the overflow and inlet diameters on the hydrocyclone performance were evaluated and it was shown that changing the overflow diameter has more effect on the equivalent area factor (surface area of the imaginary gravity settling tank also called the equivalent settling area and known as the capacity factor of the separator) than the inlet diameter (Sabbagh *et al.* 2016). The equivalent settling area is a concept used to compare the performance and scaling up of different centrifugal separators. Sabbagh *et al.* (2015) discussed the performance of hydrocyclones in terms of the equivalent area and indicated that there was limited available information for developing the equivalent area. Changing the inlet and/or the outlet diameters changes the pressure drop, which affects the performance of the hydrocyclone.

The vortex finder functions to control both the separation and the flow leaving the hydrocyclone. It extends below the entrance of the feed. This is to prevent short circuiting of material directly into the overflow. It has a helical guide to direct the inlet flow from the tangential inlet towards the separating chamber. The diameter of the vortex finder is typically 0.35 times the cyclone diameter. The vortex finder is a tube that is an extension of the central exit tube inside the cyclone barrel. It projects downwards into the vortex of the hydrocyclone. It prevents the entering gas from escaping through the outlet directly. Statie, Salcudean and Gartshore (2001) showed that increasing vortex finder length improved the fractionation efficiency. This was because it increased the number of particles carried away. When fluid fills the hydrocyclone, the flow field becomes stable and the influence of the depth of the vortex finder becomes consistent. Yang *et al.* (2011) showed that the size of the vortex finder diameter has great influence on the distribution of the centrifugal separation factor, but the varying depth of vortex finder has little influence on the centrifugal separation factor. Furthermore, the greater the depth of vortex finder, the higher the degree of disturbance and the stronger the fluctuation of the tangential velocity gradient will be. They concluded that a smaller depth of vortex finder may benefit the liquid–liquid separation.

The cylindrical section is located between the feed chamber and the conical section. It has the same size diameter as the feed chamber and it lengthens the hydrocyclone and increases the retention time. The cylindrical chamber length was found to have no impact on separation or fibre fractionation (Statie, Salcudean and Gartshore 2001). A hydrocyclones cylindrical length is typically twice that of the cyclone diameter. The conical section is referred to as the cone section. The built-in angle of the cone section known as the cone angle is an important factor that will determine the size of the air core and affects the stability. Statie, Salcudean and Gartshore (2001) showed that the cone angle has no influence on fibre fractionation. The variation of the air core diameter with the cone angle shows that the air core has its maximum diameter at a specific cone angle. At the end of the conical section is the apex orifice and the critical dimension is the inside diameter at the discharge point. The orifice size is determined by the application involved. It must be large enough to permit the solids that have been classified into the underflow to exit the hydrocyclone without blocking. Minimum orifice size is 10% of the hydrocyclone diameter. It can however be as large as 35%.

The Kanant hydrocyclone used in this work has been optimised for fibre fractionation by the supplier.

2.2.3 Separation process

The operating efficiency of screens and hydrocyclones (cleaners) is based on the flows and properties of the feed, rejected pulp and on the accepted pulp. Some important parameters in the operation of screens and cleaners are the reject rate R_W, reject thickening factor and the cleaning efficiency. The reject rate is defined the ratio of rejected mass flow M_R to feed mass flow M_F displayed in equation 2.2.

$$R_W = \frac{M_R}{M_F} 100 \qquad \textit{Eqn no: } 2.2$$

Where: M_F is the feed pulp mass flow and

M_R is the reject pulp mass flow

Fluid passes the screens with greater ease than fibres and dirt. This causes the rejects to thicken. The reject thickening factor (K_{CR}) calculation is given in equation 2.3

$$K_{CR} = \frac{C_R}{C_F} \qquad \text{Eqn no: } 2.3$$

Where: C_F is the feed pulp consistency and

C_R is the reject pulp consistency

The cleaning efficiency E_C describes the decreased content of shives from those that were in the input material S_F to those that are in the accepts S_A. A gravimetric method is commonly used to measure the contents of the shives in pulp. Cleaning efficiency is defined in equation 2.4

$$E_C = \left(1 - \frac{S_A}{S_F}\right) x\ 100 \qquad \text{Eqn no: } 2.4$$

Where: S_A is the shives content in the accepts

S_F is the shives content in the input material

Materials which are similar in size to pulp fibres cannot be separated by screens. However these contaminants often differ in density to the pulp fibres. Therefore they can be separated using hydrocyclones. Hydrocyclones do consume high pumping energy and require a large amount of the equipment in major pulp flow lines. However they are still essential in separating sand and some difficult particles from pulp streams.

The actual separation takes place in the cylindrical chamber. This is located where a free vortex flow is expected to develop. The pulp suspension enters tangentially at high velocity into the cylindrical section of the vessel. Fluid pressure is converted into rotational movement as the pulp suspension is fed into the hydrocyclone. Material that is lower in density than water is discharged at the centre of the entrance end. The fraction that is coarser possesses more mass or inertia than the fines fraction. This allows the rotating suspension to be forced to spiral towards the centre to escape. This in turn causes differential movement of the materials suspended in the fluid. Thus, there is a radial inward flow in the suspension that is rotating. Particles in the hydrocyclone are exposed to two main opposing forces. The outward radial force is generated by centrifugal acceleration and the inward radial force emanates from the drag force of inward moving fluid as in equation 2.5 and 2.6. As stated above, , particles in hydrocyclones are subjected to two primarily forces: the centrifugal force and the drag force, which oppose each other (Kelly and Spottswood 1982). Additional lift, buoyancy and gravity forces also influence the particle movements. The particle rotates or spins as it moves in the hyrocyclone causing a pressure difference above and below the particle. Pressures above and below the particle are higher and lower respectively according to Bernoulli's equation. This creates downwards force that is perpendicular to the oncoming flow direction, and is referred to as the lift force. Buoyancy is an upward force exerted by the suspension in the hydrocyclone that is opposing the weight of the particle. Gravity force influences the flocculation tendency of the particle. In a column of fluid, pressure increases with depth as a result of the weight of the overlying fluid. Particles in the pulp suspension that are denser will move to the periphery of the rotating suspension. Less dense particle tend to move towards the rotational centre. They are moved towards one outlet or other by random impacts with other particles. The movement is a random whirlpool motion in a highly turbulent flow field inside the hydrocyclone. Conditions that define drag force equilibrium orbit are displayed in Equation 2.5 (Records and Sutherland 2001):

$$Drag\ force = 0.5 \times Cd(Vr - Ur)\rho f \times Ac \qquad \textit{Eqn no:}\ 2.5$$

where: Cd = drag coefficient

Vr = radial velocity of the fluid at a point in the hydrocyclone

Ur = radial velocity of the particle

ρf = fluid density

Ac = cross sectional area

In the time taken for a particle to make a single orbit in the hydrocyclone, the drag force is balanced by the centrifugal force due to the circulation motion. The particles move at their terminal settling velocities relative to the inward moving fluid. The movement in respect to the feed will appear to be in the direction of the wall of the hydrocyclone where it will collide and collect at the bottom. The degree of flocculation is minimal at consistencies less than 0.15% for long fibres (Jones, Cambell and Nelson 1966; Wood and Karnis 1979). Therefore the tendency to flocculate will increase with consistency. The less dense fraction (fines) concentrate in the center and exits from the top and the denser fraction concentrates outer towards the walls and exit at the bottom. The centrifugal force is given by equation 2.6 (Records and Sutherland 2001):

$$Centrifugal\ force = \frac{{V_\theta}^2}{r} Vp(\rho s - \rho f) \qquad \textit{Eqn no:}\ 2.6$$

Where: V_θ = tangential component of the particle velocity vector
r = radius of the tangential motion
Vp = volume of particle
ρs = density of solid
ρf = density of fluid

In the velocity field of the hydrocyclone, tangential velocity is predominant, which is an important factor in affecting the separation efficiency (Xu *et al.* 2015).

The three-dimensional view (3-D) in Figure 2.16 assists in the understanding of accurate particle separation and gives a better representation of the flow fields in the hydrocyclone. The centrifugal force that is exerted to particles in the rotational flow field is directly dependant on the tangential velocity (Anderson 2010). The performance of the hydrocyclone is vitally affected by precise determination of the tangential velocity (Statie, Salcudean and Gartshore 2001). Elshorbagy, Abdelrazek and Elsabaawy (2013) in their results indicated that on increasing the volume fraction the static pressure increases, the axial velocity decreases, the radial velocity decreases, and the tangential velocity remains almost unaltered. The separation efficiency increases, although it has in general relatively small values. In addition, the separation efficiency is affected by the volume fraction. Furthermore, an increase of volume fraction might increases the separation efficiency but it leads to an increase in the separated part (water) which was one part of the experiment and a decrease in the other separated part (oil). Three dimensional flow of fluid inside the hydrocyclone is shown in Figure 2.16.

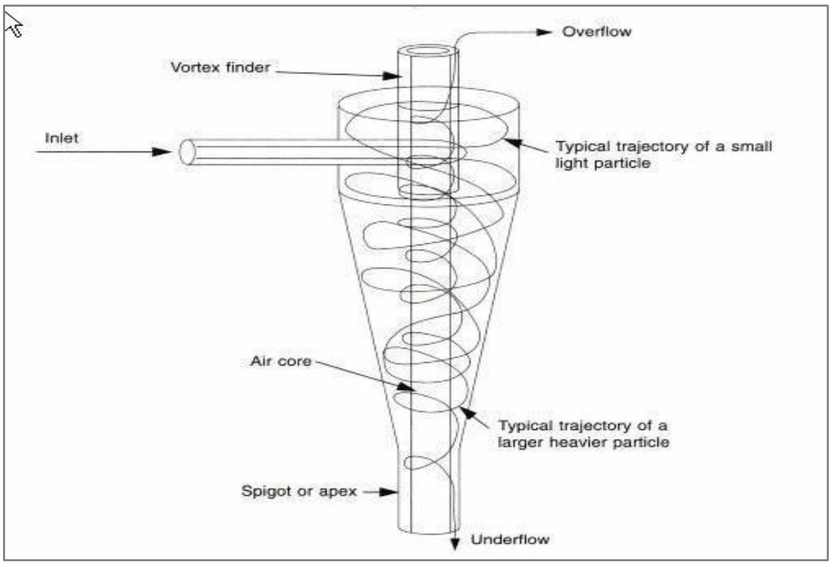


Figure 2.16: Three Dimensional (3-D) view of a hydrocyclone (Lenntech 2010)

The exit points of hydrocyclones are the apex or underflow (sometimes also called rejects) and the base or overflow (sometimes also called accepts), Figure 2.16. A study for softwood pulp showed fibre wall thickness was different for fibres in the accepts and rejects fractions from a hydrocyclone (Paavilainen 1993).

To better understand how the fractionation separation process occurs, it is best to characterise separated fines. Though, there are some characteristics that have no influence on this process, the type of pulp will also have significance influence in this area. Wood and Karnis (1977) and Wood and Karnis (1979) demonstrated the importance of specific surface in hydrocyclone separation for mechanical pulp, but this was not significant for chemical pulps. This was due to the uniformity of fibres in chemical pulps. Image analysis and confocal microscopy are some of the approaches used to determine fibre cross-section dimensions. Johnston *et al.* (1999) studied the fibre fractions that had been separated by a hydrocyclone. The work concluded that hydrocyclone separation was related to the apparent densities of the fibres. The fibres with similar densities and smoothness and larger cross-sectional areas are accepted, because these fibres are also subjected to a larger drag force.

Fibre fractionation to remove extractives may well be a technique to adopt over chemical removal at the bleaching stage. Fibre fractionation in screens is directed by probability separation as normal fibres have a diameter much less than the smallest aperture size. Though fibre fractionation comes with a high yield loss in removing fines, a study showed that up to two thirds of fines are lost along downstream processes (Odabas *et al.* 2016). Asikainen *et al.* (2010) have demonstrated that removing fines can lead to a 6% reduction in active chlorine in DEDED bleaching sequences. However, this work was not based on dissolving wood pulps (DWP) and the equipment used cannot be implemented in industrial process. From the abovementioned studies, the following can be concluded:

- A fractionation process/system that effectively removes the fines in the upfront (before bleaching units), may lead to cost savings and/or improving product quality.
- A hydrocyclone is the preferred method of fractionation.
- There is limited knowledge on fractionating DWP.

2.2.4 Pulp Separating Hydrocyclones

Hydrocyclones in pulp and paper mills are sometimes referred to as cleaners. Various types of hydrocyclones are used in pulp and paper industries. There are forward, reverse and parallel flow cleaners. Removal of denser particles is done by forward hydrocyclones. Forward cleaners are traditionally used in removing unwanted contaminants and objects. These cleaners can also be operated in reverse though they need a very high pressure drop and consume large amounts of energy (Biermann 1996). Reverse cleaners remove particles less dense than water. The overflow (accepts) in reverse hydrocyclones is at the apex and the underflow (rejects) at the base. In parallel flow hydrocyclones both accepts and rejects are removed in the apex and are sometimes referred to as through flow cleaners

2.2.4 (a) Conditions that favour separation

The centrifugal force has to be adequately high to achieve separation. Solids to be separated in the pulp should possess a density that is significantly different to the liquid phase. The different particles should be free to migrate within the pulp suspension. Lastly, the consistency of the pulp suspension must be low enough to ensure flocculation does not prevent particle separation in the flow field. Centrifugal cleaners are operated at low consistencies of 0.3% to 2% (Fardim 2011).

2.3 Fractionation

Fractionation in general is to divide or separate into parts. The definition may vary slightly accordingly to which field it is applied e.g. Geology, Biology, Medical and Industrial etc. For wood pulp, it implies separation of fibres based on size, width, length and density. In pulp mill fibre lines, fractionation produces pulp with better quality and uniformity.

2.3.1 Effects of feedstock consistency on hydrocyclone fractionation efficiency

It has been shown that feedstock consistency plays a vital role on hydrocyclone fractionation efficiency (Paavilainen 1992; Bergström and Vomhoff 2007; Johakimu and Bush 2010, 2011). It was further demonstrated that is also dependent on the hydrodynamic characteristics of the pulp being fractionated. Effective fractionation for TMP pulps was achieved at a feed stock consistency up to 1% (Bergström and Vomhoff 2007). Though for softwood chemical pulps the consistency required is less than 0.3% (Paavilainen 1992). However, in the initial trials conducted in 2002 by Kadant (using a Kadant hydrocyclone) a feedstock consistency of only 0.3% was applied (Noss 2002). As a result, there is limited data available on the effects of the feed stock consistency on fractionation efficiency of the dissolving pulps. Therefore, the effects of feedstock consistency were studied, to enable the mill to have a better understanding on what to expect if they install and operate the hydrocyclone at a particular feedstock consistency level. Though the implementation of such a consistency may be impractical in pulp mill fibre lines, this may not be the case for paper mill fibre lines.

2.4 Bleaching chemistry

Pulp is bleached to increase brightness and to control viscosity in the various stages (Kostamo and Kukkonan 2003; Zhang, He and Ni 2011; Loureiro *et al.* 2012). Bleaching is a multi-stage process that refines and brightens raw pulp. The bleaching sequence and number of stages are mostly governed by the requirement of brightness levels. The objective of bleaching is to dissolve the brown-coloured lignin that was not removed during pulping (cooking). At the same time the bleaching process has to maintain the integrity of the pulp fibres. Oxidative chemicals are used for these bleaching stages. These are chlorine dioxide, oxygen, ozone, sodium hypochlorite and hydrogen peroxide.

Factors such as pH, temperature, retention time, consistency, nature of the pulp, and method of chemical application determine the bleaching efficiency. Criteria for choosing a bleaching method are based on investments costs, operating costs, product quality of the pulp and discharge to the environment, health and safety (Jain and Mortha 2010). Moreover, for high purity pulp production several stages are required to eliminate extractives and hemicellulose while maintaining the viscosity of the pulp. Customized pulp is produced by varying the order, concentration and reaction time of the bleaching agents.

Chlorine dioxide bleaching is a well proven technology which is today universally used in the pulp industry. An example of a typical bleaching process for DWP is based on the five-stage bleaching process. The first stage is the oxygen stage (O_2) followed by the chlorination stage (D_1), next the extraction stage (E), followed by the second chlorination stage (D_2) and lastly the hypochlorite stage (H). This bleaching process is commonly referred as the ODEDH bleaching process. The first two stages complete the delignification process and are considered extensions of pulping. The individual bleaching stages are defined by their bleaching agent, pH (acidity), temperature and duration. After each bleaching stage, the pulp is washed with wash water to remove spent bleaching chemicals and dissolved lignin before it progresses to the next stage. Once the pulp leaves the last stage, it is then concentrated and conveyed to the storage tower. After the storage tower it is diluted and pumped through a series of screens and cleaners to remove any contaminants such as dirt or foreign particles and then moved to pulp machines for sheet information.

During the bleaching process some of the bleaching chemicals are wasted in side reactions. Lachenal, Chirat and Hamzeh (2006) demonstrated that at least 50% of ClO_2 would be wasted in side reactions in chlorine dioxide bleaching processes. Some of the chemical consumption is also due to the presence of constituents which are associated with extractives e.g. resins in the pulp fines. For these reasons, the bleaching process is accompanied by very high costs.

2.4.1 Oxygen stage

The process of oxygen delignification is the first stage in the bleaching unit and it reduces the consumption of bleaching chemicals of subsequent stages. The content of shives and extractives are significantly reduced after this oxygen stage. The oxygen bleaching process is less selective compared to the other bleaching agents. High temperature and pressure are required in this stage to attain a practical reaction as oxygen is a relatively weak reactive oxidant.

The oxygen molecule at its lowest energy contains two unpaired electrons; each of these electrons has an affinity to other electrons of opposite spin. It can therefore act as a free radical although at normal temperatures it is un-reactive, but at higher temperatures and alkaline conditions it has a strong tendency to react with organic molecules (Mill 2015).

2.4.2 Chlorine stage reactions

Pulp mills have since moved away from using elementary chlorine bleaching for environmental reasons, as discussed later in Section 2.4.2. Chlorine dioxide has been substituted for chlorine in the bleaching process. However, it is crucial to understand the chlorine bleaching chemistry as chlorine is formed in the reaction of chlorine dioxide and lignin.

Chlorine is gas at room temperature and its chemical formula is Cl_2. Dissolving Chlorine in water drops the pH of the water. Hypochlorous acid (ClOH) is formed as shown in equation 2.7.

$Cl_2 + \ H_2O \leftrightarrow ClOH + H^+ + Cl^-$ *Eqn no:* 2.7

Chlorine does not readily dissolve in water. As the temperature and pressure of the solution rises, the solubility of the chlorine gas tends to decrease. At the chlorine stage bleaching temperature of 60^0C the ClOH is the dominant species, but is unstable at higher temperatures(Turner *et al.* 1996; Fardim 2011; Mill 2016). This leads to the formation of radicals as shown in equations 2.8 and 2.9.

$ClOH \leftrightarrow Cl^{\cdot} + OH$ *Eqn no:* 2.8

$ClOH \leftrightarrow Cl^- + H^+ + \ O$ *Eqn no:* 2.9

Radicals are reactive species that can degrade cellulose and lead to depolymerisation and oxidation. For effective bleaching with chlorine, the pH should be about 2 with the lowest temperatures possible.

2.4.2 (a) Lignin reaction with chlorine

According to Fardim (2011) there are three supposed reactions of chlorine and lignin, shown in Figure 2.17. One such reaction is the hydrolysis of the ether groups. Another is the depolymerization of lignin using the departure of the lateral chain under conditions where there is a hydroxylic group. LachenaL, Fernandes and Froment (1995) demonstrated that chlorine has the capability to depolymerize the residual lignin while forming new free phenolic groups,. The other reaction is the chlorination of the aromatic ring. In the presence of excess chlorine, more than a single chlorine is fixed onto the aromatic ring. During this reaction some elemental chlorine is generated and is responsible for the formation of chlorinated organic compounds which are toxic compounds in the effluent. This reaction however does not contribute to delignification or solubilisation of the lignin.

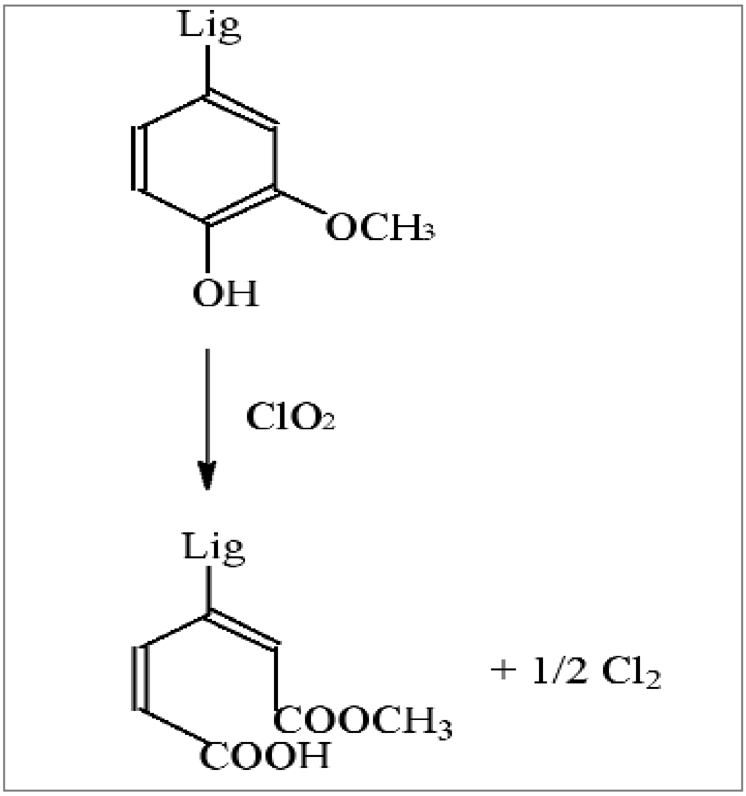


Figure 2.17: Reaction of chlorine with lignin (Lachenal, Chirat and Hamzeh 2006)

2.4.2 (b) Chlorine calculation for pulp application

The amount of lignin in the pulp determines the amount of chlorine needed for that bleaching stage. This calculation is based on the formula displayed in equation 2.10.

$$\%Cl_2 = chlorine\ factor \times kappa\ number \qquad \text{Eqn no: } 2.10$$

Where the chlorine factor is 0.2 and the kappa number is the quantification of the moieties in the pulp that consume permanganate (structures containing carbon-carbon double bonds).

2.4.3 Chlorine dioxide stages

Chlorine dioxide (ClO_2) is an extremely reactive greenish-yellow gas. It is toxic and corrosive. The gas explodes at high concentrations (10%) and is rapidly reduced to Cl_2 and O_2 in the presence of ultraviolet light. Chlorine dioxide (ClO_2) is a highly

selective chemical that can both de-lignify and brighten pulp. It oxidizes lignin, but does not add chlorine atoms onto lignin fragments. However, small amounts of elemental chlorine and other chlorine compounds formed during the chlorine dioxide bleaching process react with degraded lignin to form chlorinated organic compounds. Further chlorine dioxide attacks the lignin's phenolic group which foremost promotes the degradation of the lignin molecules and thus preserving the quality of the pulp (Zhu *et al.* 2016). The bleaching process can be summarized as the reaction of chlorine and lignin. During bleaching it is used as a ClO_2 solution in water. Chlorine and chlorine dioxide added together remove colored components from partially bleached pulps that have been rendered soluble in dilute warm alkali solution.
The water solution also becomes acidic. Chlorine dioxide exists as a radical as shown in equation 2.11.

$$O - Cl - O^o \qquad \textit{Eqn no:}\ 2.11$$

Chlorine dioxide has chemistry that is very different from that of chlorine gas.

- Chlorine gas (Cl_2) is made up of two chlorine atoms. Chlorine dioxide (ClO_2) is composed of one chlorine atom and two oxygen atoms. It is roughly 50 percent oxygen by atomic weight.
- During the pulp bleaching process, chlorine has a tendency to combine with lignin, which is the substance that cements the wood fibers together, to create chlorinated organics that end up in mill waste water.

In contrast, chlorine dioxide normally dignifies the pulp lignin, leaving behind organic compounds that are water soluble and very alike to those occurring naturally in the environment

2.4.3 (a) Lignin reaction with chlorine dioxide

The reaction of chlorine dioxide (ClO_2) with lignin is shown in Figure 2.18. The reaction of chlorine dioxide is predominantly with free phenolic groups. It takes place in three steps. The first would be an abstraction of one electron on the oxygen atom of the phenolic hydroxyl group. The ClO_2 is reduced to a chlorite ($HClO_2$). The second molecule will react on the quinone radical located on the third carbon in the aromatic ring. This will lead to an unstable ester. Last is the hydrolysis of the unstable product to muconic acid derivatives and hypochlorous (HOCl) acid is also formed in the process.

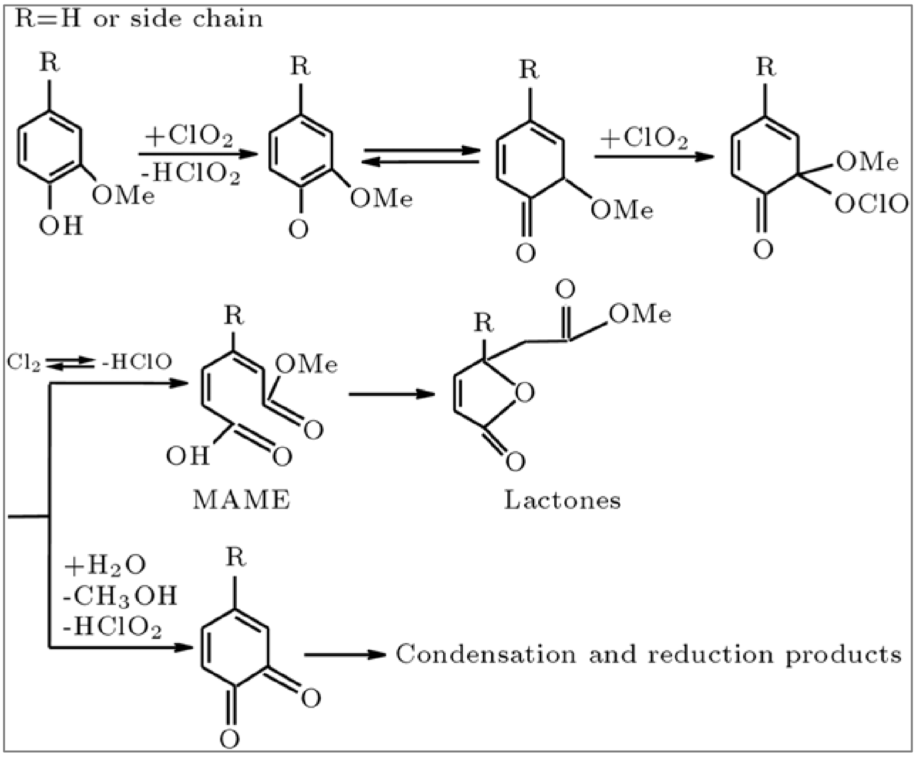


Figure 2.18: Reactions between phenolic lignin structures and chlorine dioxide (Liu and Zhou 2011).

2.4.3 (b) Chlorine formation and active chlorine

One Cl_2 molecule is formed when chlorine dioxide reacts with free phenolic lignin. The chlorine molecule cannot be quantified as it will readily react with the lignin thus leading to the formation of AOX. For practical purposes in many mills, the chlorine dioxide quantity is expressed in terms of active chlorine rather than chlorine dioxide. The active chlorine in ClO_2 is twice the active chlorine in Cl_2 gas.. These stages are designated as the D stages. The formula for calculation of amount of ClO_2 needed in delignification is displayed in equation 2.12.

$$\%ClO_2(as\ active\ chlorine) = kappa\ factor(e.g\ 0.2) \times kappa\ number$$ *Eqn no:* 2.12

2.4.3 (c) AOX formation in chlorine dioxide

During chlorine dioxide bleaching some chlorine is formed as a by-product. This leads to the formation of organochlorine compounds, although much less chlorine is present compared to that formed in elemental chlorine bleaching stages. This results in much less AOX resulting in much less toxic compounds in the effluent. The formula used to determine the amount of AOX formed in a bleaching stage is displayed in equation 2.13 (Nie *et al.* 2014).

$$AOX\left(\frac{kg}{ton}\,of\ pulp\right) = quantity\ of\ ClO_2\ (as\ active\ chlorine, \frac{kg}{ton}pulp)/50 \quad \textit{Eqn no: } 2.13$$

2.4.4 Alkaline Extraction stage

After the chlorine stage the pulp is washed to remove acidic and water soluble products to prevent high sodium hydroxide usage in the alkane extraction stage. It is necessary to remove chlorinated and oxidized lignin products from the pulp after the chlorine stages. The caustic soda is added to the pulp at medium consistency and applied uniformly to increase its effect on the lignin. Low caustic soda dosages may upset pH maintenance which is very crucial. The remaining lignin is reactivated for the next stage. The alkali soluble chlorinated lignins are washed out in water. Insoluble chlorinated lignin products are very difficult to remove. All other insoluble products dissolve in caustic soda solution. The caustic soda required for the alkaline stage is directly related to the chlorine consumed in the previous stage. This stage is designated as E.

2.4.5 Hypochlorite stage

Hypochlorite bleach is an oxidizing agent. Calcium hypochlorite and sodium hypochlorite bleaching agents are used in pulp and paper mills. The Hypochlorite stage comes after chlorination and alkali extraction stages. Chromophoric groups of the lignin are oxidized and decolorized at this stage. Furthermore, lignin and other impurities are solubilized in the pulp. The bleaching agent is non selective as it reacts not only the lignin but also cellulose. This requires that reactions are controlled properly.

The hypochlorite bleaching action is greatly affected by the pH value. At a pH value of 8 and below, the hypochlorite reacts with the cellulose and degrades the fibre. Operating at pH 9 – 11 is best with an ideal retention time of 1- 4 hours for this stage (Mill 2016). However in practise mills retain the pulp 1 - 2 hours in their bleaching units. Short retention times affect the bleaching action while lengthier periods of time may degrade the fibre. Temperature affects the bleaching agent consumption rate. Cellulose fibre is degraded at elevated temperatures although the reaction rate is increased and the hypochlorite consumption decreased. High consistency pulps increases production and reduce retention time and bleaching agent consumption while lower consistency increases retention time and bleach agent consumption. The hypochlorite bleaching stage is actually used as a final adjustment to the pulp viscosity, by utilising hypochlorite’s tendency to degrade cellulose.

2.4.6 Pulp constituents impact on bleaching

2.4.6 (a) Extractives

Fines and organic extractives, collectively known as resins negatively affect the quality of fully bleached dissolving pulps. Dissolving pulps consist of a bulk long fibre fraction and a fines fraction which comprises mainly ray cells enriched with resin and transition elements (Hink and Wallendahl 1999). According to Heijnesson-Hulten, Simonson and Westermark (1997) the reason for the higher content of extractives in the fines is due to the presence of ray cells , which are known to be a main source of extractives. Removal of the primary fines from dissolving pulp results in a fibre fraction having low metal contents and extractives. According to Dafchahi and Resalati (2012) all of the problematic wood components except for cellulose need to be removed during production. These include hemicellulose, lignin and extractives. Hink and Wallendahl (1999) extracted up to 4% of fines which led to reduced resin contents. They achieved up to 10% drop in bleaching chemical demand for removal of resins from unbleached pulp. Further, production rates were increased because the pulp was able to drain faster. Hence, extractives removal before and during bleaching enhances overall bleaching process performance.

2.4.6 (b) Pulp fibres

Fibre properties are changed during bleaching. The length of the fibre is not changed in bleaching, but due to yield loss the linear density of the fibre is reduced. Thus there are more fibres per unit weight of bleached pulp. This has a favourable effect on tear strength for instance. Due to the removal of lignin the fiber swells more easily and the pliability and flexibility of the fibres are increased. This facilitates the binding of the fibre network. Too great a loss of hemicellulose can on the other hand worsen the adhesive capacity of the points of contact, so that the end result may also be weakened pulp strength. The strength of the fibres is reduced as the carbohydrate chains are broken. However, a moderate weakening of viscosity is not considered a deterioration of pulp strength properties as a result of the contradictory factors mentioned above.

2.4.6 (c) Chromophoric group

Unbleached pulps exhibit a wide range of brightness depending on the pulping process and fibrous raw material used. The sulphite process produces the brightest pulp, up to 65% compared to Kraft, soda and semi-chemical that may produce pulp of only 15% brightness. Cellulose and hemi-cellulose are inherently white and do not contribute to colour. A chromophoric group is a chemical group that produces colour in a compound. In pulp it is the chromophoric groups in lignin which are responsible for colour.

There are two approaches used in the chemical bleaching of pulps. The one employs selective chemicals that terminate some of the chromophoric group which nonetheless do not attack lignin. The second approach is to virtually totally remove all lignin. The first approach provides around 70% brightness and retain high pulp yield, while second approach provides greater than 90% brightness but reduces pulp yield.

3. Methodology

3.1 Introduction

This research work was carried out in the laboratories of the Forestry and Forest Product Research Centre (FFP) at the Council for Scientific and Industrial Research (CSIR) campus in Durban, South Africa. This work was divided into two milestones as follows:

3.1.1 Determining the optimum hydrocyclone fractionation conditions

Determining the optimum fractionation conditions for the unbleached pulp required:

- Determining the optimum position to take samples (Section 3.2)
- Determining the optimum operating conditions of the laboratory hydrocyclone (Section 3.3).

Determining optimum hydrocyclone operating conditions required studying the effect of feedstock consistency, volumetric and mass rejects rates on the hydrocyclone fractionation efficiency. These conditions correspond to the flow rates and split ratios (ratio of underflow to overflow). Once the optimum fractionation conditions had been determined, the unbleached pulp was fractionated and bleached according the work flow scheme in Figure 3.1.

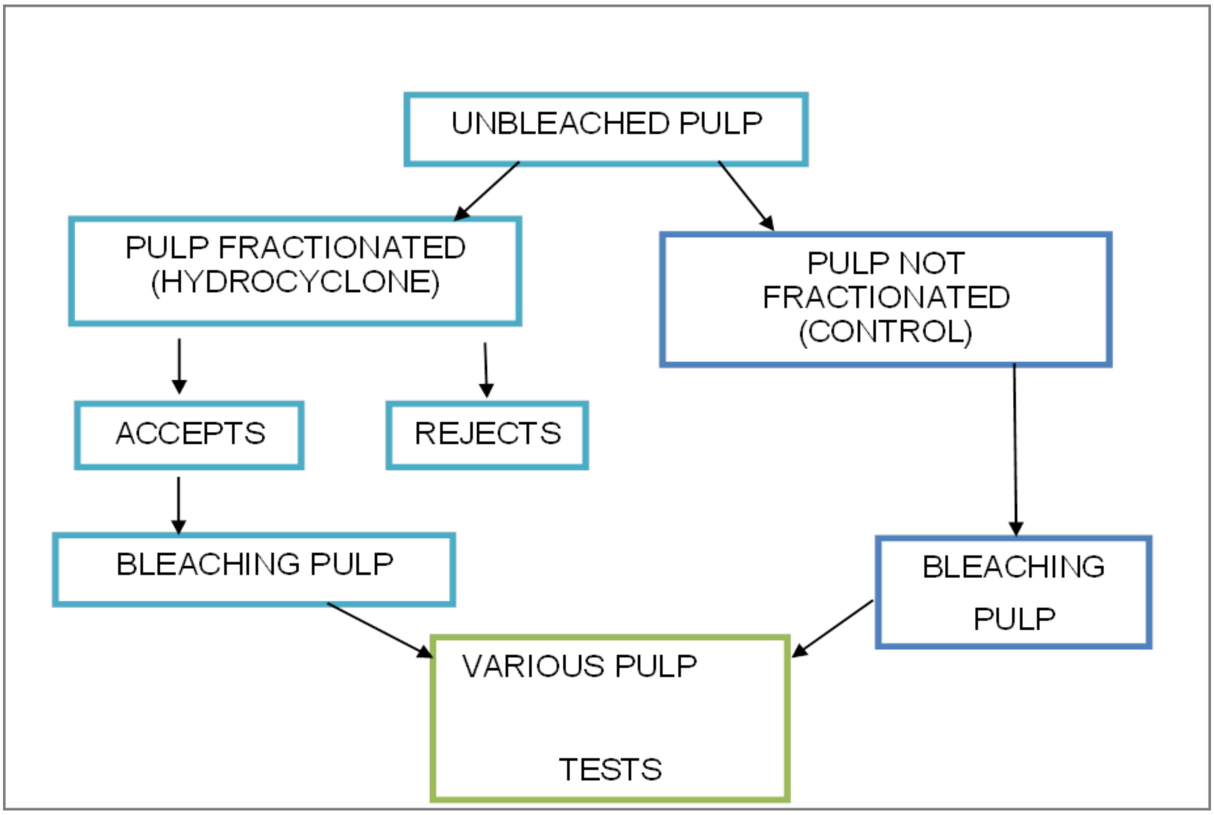


Figure 3.1: Brief overview of the method showing fractionated pulp and the unfractionated pulp, which is the control, subjected to bleaching process.

3.1.2 Evaluating the bleaching response of the fractionated pulps

This work required two parts *i.e.* determining the bleaching response of the accepts stream of the fractionated pulps (Section 3.4.1), followed by the optimization of the bleaching conditions (Section 3.4.2). The first part focused on comparing fractionated pulp against the unfractionated pulp (control). This determined whether the fines removal influences the bleaching response and properties of the dissolving pulps. The bleached pulp quality is represented in alpha (α) units which is its percentage purity (Section 3.5). Selected fractionated pulp samples at three levels of reject rates and the control pulp samples (unfractionated) were bleached to a standard 92 alpha (α) pulp quality (Section 4.3) using general bleaching conditions. Critical quality properties for dissolving pulp applications were determined. Thereafter, bleaching conditions were optimized with respect to the consumption of bleaching chemicals.

The following pulp tests were performed before bleaching on the coarse fibre enriched (accepts) fraction and fines enriched (rejects) fraction of the fractionated pulp, and on the unfractionated pulp (control):

- consistency
- freeness,
- fibre morphology
- extractives content

The following quality tests were performed on the bleached control and fractionated bleached coarse fibre enriched fraction:

- solubility
- copper number
- viscosity
- brightness
- K number
- extractives contents

3.2 Sampling

The unbleached pulp samples were collected from the post oxygen delignification bleaching stage at the mill and transported to the CSIR laboratory where fractionation and bleaching trials were performed. The process flow diagram for the pulp mill fibre line is illustrated in Figure 3.2. The pulp mill fibre line includes the following process stages: digester plant, pulp screening plant, pre- oxygen washer plant, oxygen delignification plant and the post oxygen washer, followed by the DEDH bleaching sequences. As can be seen in Fig 3.2, the ideal installation point identified for the fractionating cleaner system was between the screen and the pre-oxygen washer. However, the pulp samples were collected at the outlet of the pre oxygen washer, where the consistency was 10-12%. This was done to avoid the inconvenience of handling the large volumes of low consistency (3%) pulp samples at post screening. The problem with sampling in a different area to the desired installation point was the potential loss of fines in the pre-oxygen washer.

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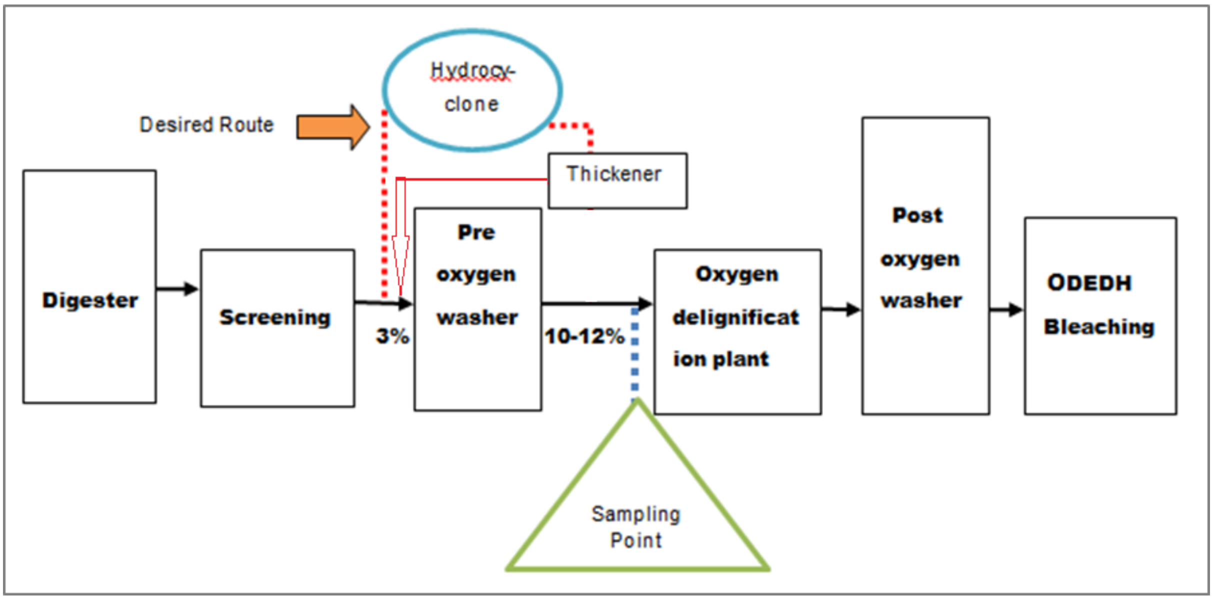


Figure 3.2 Simplified process flow diagram for the pulp mill fibre line indicating sampling point.

3.3 Determination of optimum fractionation conditions

The equipment used to fractionate the pulp was a test canister rig called the Kadant hydrocyclone (AM80-F) (kindly supplied by the Kadant company) shown in Figure 3.3.

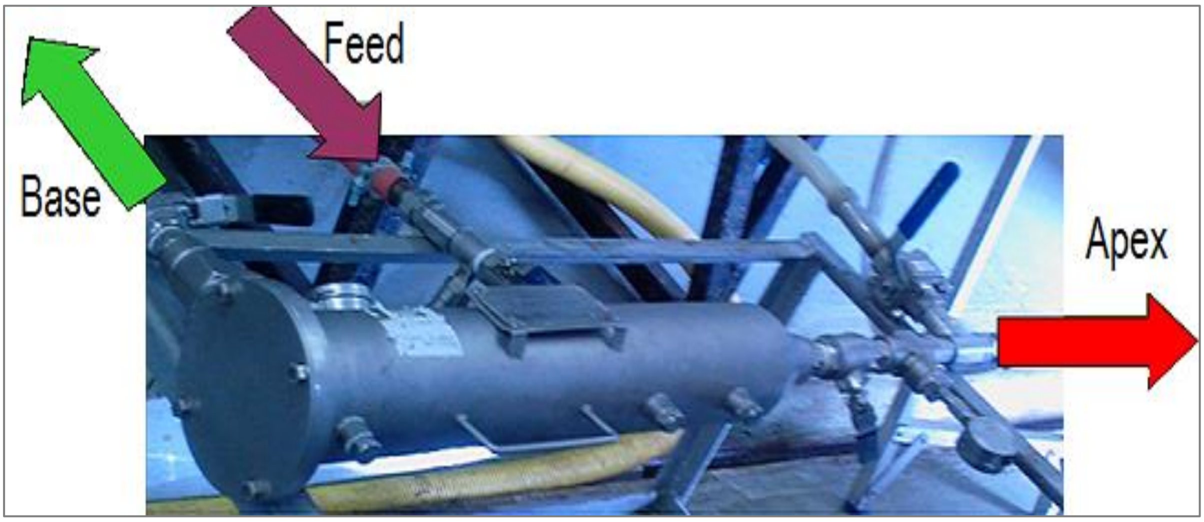


Figure 3.3: The Kadant Hydrocylone (AM80 –F) test canister rig used for the trials.

For mixing and circulating of the pulp suspension during a fractionation trial, the rig was connected to a tank and piping system shown in Figure 3.4. Pulp suspensions were prepared in the agitated tank with capacity of 400 litres. V2 and V3 are pneumatic valves and V1 is a manually operated valve. The electro-magnetic flow meter indicator (F1) and pressure gauge indicator (P1) were fitted in the feed line to the fractionator. Two X 50ℓ buckets and a stop watch timer were used to collect the fractionated samples.

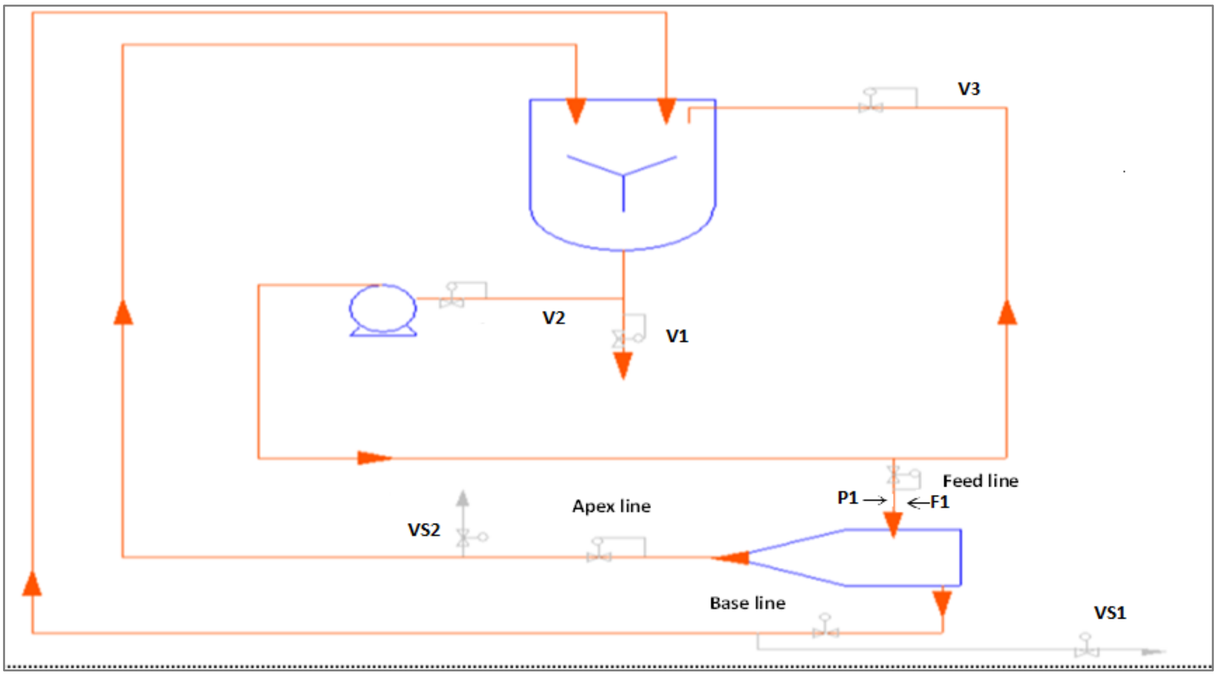


Figure 3.4: Flow diagram of the Kadant hydrocylone canister rig connected to perform the laboratory fractionation trials

At the desired consistency, the suspension was pumped from the tank to the hydrocyclone using a positive displacement pump (viz. the flow rate was independent of pressure). The slurry entering the hydrocyclone was subjected to centrifugal and drag forces (as discussed in Section 2.2.3) and was separated into thin and thick-walled fibre fractions. Usually the accept stream emerges from the base and reject stream from the apex. However, for these trials the hydrocyclone was operated in reverse mode “as a light weight cleaner”. Thus the base stream which was enriched with the thin-walled fibres and resin-containing fines will be referred as the *rejects* whereas the apex which was enriched with thick-walled fibres will be referred as the *accepts* stream.

Ideally operational parameters for fractionating pulp are standard. Consistency of the pulp suspension should be in the range of 0.7% to 1.0%. Attempting to fractionate at lower values down to 0.35% will depend on efficiency for an effective fractionation. Operational pressure should be at 220 kPa. Pressure in the rejects is lower than that in the accepts. The feed flow rate should be approximately 100ℓ/min. For this feed rate, the expected overflow and underflow flow rates are 30ℓ/min to 50ℓ/min and 60ℓ/min to 80ℓ/min respectively. Recommended flow rates for overflow and underflow are 30ℓ/min and 70ℓ/min respectively. Pulp fractionation using hydrocyclones are generally done at room temperature. The hydrocyclone used is AM80-F radiclone (Strobl 2013).

Softwood bleached chemithermomechanical pulp fibre was fractionated using a cylindrical hydrocyclone (Xiaojiang and Shijie 2006). Their work suggested the most significant parameter for fibre fractionation performance is the split ratio (the ratio of overflow to inlet flow), which was best between 0.14 and 0.2.

3.3.1 Consistency

The hydrocyclone operating conditions used to establish the desired feed stock consistency for fractionating DWP are summarized in Table 3.1. The mixture was pumped and recirculated through the hydrocylone at volumetric flow rate of 100-110 ℓ /min. The feed pressure was kept between 200 to 230kPa. The feed flow rate and pressure were hydrocyclone operating conditions specified by the supplier (Noss 2002). Fractionation was performed using five levels of feed stock consistency (0.1%, 0.3%, 0.5%, 0.8% and 1%) at a constant reject ratio of 27%.

Table 3.1: Hydrocyclone operating conditions used to establish the desired feedstock consistency

Experimental parameters	**Values**	**Test performed/evaluated**
Feed line pressure (kPa)	200 - 230	Freeness Consistency Fibre morphology Calculate mass reject rate
Stock consistency (%) varied	(Varied) 0.1 - 1	
Feed flow rate (ℓ/min)	100 - 110	
Volumetric (base/apex) ratios (%)	27 (maintained constant)	

At each feed stock consistency level, trials were duplicated and the standard error of the data was reported.

Pre-run equipment check list

1. Main control panel switch for agitators, pump, pneumatic valves and computer ensured on.
2. Mixing tank ensured clean.
3. Valve V1 ensured closed.

Feed preparation and loading

The specified mass of the pulp was diluted to the desired feed consistency in the mixing tank. The amount of dilution water to fill the tank was determined using the following formula as shown in equation 3.1:

$$W = \frac{P_o(C_o - C_i)}{C_i}$$

Eqn no: 3.1

Where: W = Amount of water required for dilution to the desired consistency (kg)
C_o = Initial consistency of wet pulp (%)
P_o = Mass of wet pulp (kg)
C_i = Desired consistency (%)

Various feed stocks were prepared to achieve a range of 0.1% to 1.0% consistencies. It is assumed the density of the low consistency pulp (P_o) was that of water.

1. Valves V2 and V3 were closed.
2. The inlet water valve was opened to allow the desired volume of water (*W*) to fill the agitated tank.
3. The weighed wet pulp (P_o) was added to the tank.

Mixing and circulation

1. Agitator was started and the speed was adjusted accordingly to allow complete mixing of water and pulp. The pulp suspension was allowed to mix for 20 minutes until all fibre bundles had been sufficiently dispersed.
2. The pneumatic valves V2 and V3 were opened and the pump started immediately thereafter.
3. The pulp suspension was allowed to circulate for 15 minutes.
4. A sample was taken for consistency determination prior to the start of fractionation.

Fractionation of the pulp using the Kadant hydrocyclone

1. The apex and base valves on the hydrocyclone were set to the closed position.
2. Pump speed was set to the desired flow rate of 1.66-2 ℓ/s (100 – 110 ℓ/min) in accordance with the operating specifications of the hydrocyclone.
3. The feed pressure was kept in the range of 2 to 230kPa. The feed flow rate and the pressure drop were according to the manufacture's specified hydrocyclone operating conditions.
4. A fixed apex/base ratio of 27% was set to be used for all consistency trials. The consistency level of 27% was arbitrary chosen as a starting point.
5. Two containers with a capacity of 50ℓ were placed each beneath the fibre fractionating lines, one at the apex and the other at the base line. To minimize variation in pressure drop the apex and base lines were maintained at the

same level. During sampling both apex (VS1) and base (VS2) valves were simultaneously opened. The time allowed to fill the 50ℓ containers was 10 seconds. This was timed using a stop watch. Again both valves were simultaneously closed and the timer stopped. Volumes of apex and base were measured using a scale and the corresponding apex/base volume split ratio was determined.

The pulp was sampled at the accepts, rejects and feed stream for testing. The balance of the pulp samples from each stream (feed, base and apex) were thickened by placing the pulp in a clean dry cloth bag and spun dried in a washing machine. and kept in a fridge at 4 °C until further analysis. The procedure was carried out for consistencies, 01%, 0.3%, 0.6%, 0.8% and 1.0 %. Pulp consistency was calculated based on Equation 3.2, assuming the density of the low consistency pulp was that of water.

$$Pulp\ consistency = \frac{oven\ dry\ weight\ of\ pulp}{weight\ of\ pulp+water}\ x\ 100 \qquad \textit{Eqn no: 3.2}$$

3.3.2 Reject rate

The experimental conditions used to study the effect of volumetric Base/Apex ratio on fractionation efficiency are summarized in Table 3.2. The hydrocyclone operating parameters, namely feed stock consistency and volumetric reject ratio were studied. As reported earlier, hydrocyclone was operated in reverse mode “ as the light weight cleaner”, thus the base, which will be enriched with the fines, will be referred to as the reject whereas, apex which will be enriched with the thick- walled fibres, will be referred to as the accept though out these studies.

Table 3.2: The Hydrocyclone operating conditions used to study the effect of volumetric Base/Apex ratio on fractionation efficiency

Experimental parameters	**Values**	**Test performed and evaluated**
Feed line pressure (kPa)	200 - 230	Freeness Fibre morphology Calculate mass reject rate Fibre morphology Extractive content (resins) Alkali Solubility Acid insolubles
Feed consistency (%) constant	0.8	
Feed flow rate (ℓ/min)	100 - 110	
Volumetric (Base/Apex) ratio (%) varied	17 - 65	

At each feed stock consistency level, trials were duplicated and the standard error was reported.

The same procedures reported in section 3.3.1 were followed, except that the consistency was kept constant at 0.8%. The desired mass reject rate was then calculated based on Equation 3.3.

Sampling of apex and base was carried out once the desired mass reject rate was achieved. The balance of the pulp samples from each stream (feed, base and apex) were thickened and kept in a fridge at 4 ^{o}C until further analysis. The procedure was carried out for reject rates, 5, 11, 16, 21, 25, 32, 36, 41, 45, and 52%.

$$base\ or\ apex\ mass\ reject\ rate = \frac{base\ or\ apex\ pulp\ mass\ flow}{total\ pulp\ mass\ flow}\ x\ 100$$

Eqn no: 3.3

Once these desired reject rates (refer to results Section 4.2) were obtained, the bleachability of the pulp trials commenced.

3.4 Pulp bleaching

The raw pulp was fractionated at a chosen consistency of 0.8% (Section 4.1.7) and at mass reject rate of 5% and 11% (Section 4.2.). These pulps were subsequently subjected to bleaching. The unfractionated pulp was also bleached under identical conditions and used as a control (Section 4.3). The ODEDH (D_1 stage (ClO_2 treatment), E stage (NaOH treatment), D_2 stage (ClO_2 treatment), and the H stage (hypochlorite treatment)) bleaching sequence was used to bleach the pulp The equipment used in this section of the trial consisted of a lab-scale digester and a water bath as shown in Figure 3.5.


(a) (b)

Figure 3.5: (a) Lab-scale pulping digester (b) Water bath

3.4.1 Bleachability of the pulp

Pulp was bleached to compare the fractionated pulp against the control (unfractionated) pulp. A range of general bleaching conditions are displayed in Table 3.3.

Table 3.3: Typical bleaching stages including parameters (Gullichsen et al. 1999):

Pulp bleaching	Chemical Dosage	Concentration %(w/w)	Time (min)	Pressure (Kpa)	Temperature (^{0}C)
Oxygen stage (O)	NaOH	1.8 – 2.8	60	450 gauge	85 - 105
Chlorine dioxide stage (D_1)	ClO_2	0.5 – 1.5	120 - 300	atmospheric	50 - 90
Extraction stage (E)	NaOH	2.5 – 5.0	60 - 120	atmospheric	55 - 80
Chlorine dioxide stage (D_2)	ClO_2	0.2 – 0.8	120 - 300	atmospheric	50 - 90
Hypochlorite stage (H)	NaOH	0.2 - 2	4 - 120	atmospheric	30 - 80

(a) Oxygen stage (O)

The pulp was weighed and then dosed with an active sodium hydroxide (NaOH) percentage of and subjected to a period of time in the autoclave under conditions in Table 3.1 for the O_2 stage. High pressure autoclave (reactor) was used for the oxygen stage as shown in Figure 3.5(a). It was heated to the desired temperature. The desired pressure was set. The temperature was maintained for the duration of the bleaching stage. The contents of the reactor were allowed to cool and decanted into a clean cloth. The sample was analysed for moisture in a “Ohaus, model MB45”, moisture analyser. From the moisture content the percentage dry mass of the pulp was calculated from equation 3.4.

$$\%\,Pulp\ dry\ mass = 100 - moisture\ content\ of\ the\ pulp \qquad \text{Eqn no: 3.4}$$

The pulp dry mass was then determined from the percentage pulp dry mass and the equivalent mass which was the actual weight of the initial sample. The pulp dry mass was calculated from equation 3.5.

$$pulp\ dry\ mass\ = \frac{\%\ pulp\ dry\ mass}{100}\ x\ equavilent\ mass \qquad \text{Eqn no: 3.5}$$

The decanted pulp was washed with deionised water making use of vacuum filtration utilizing a Buchner funnel fitted with a sieve. Washing was repeated until clear water was collected in the vacuum flask indicating that the pulp was now clean.

(b) Chlorine stage (D_1)

A water bath was used for the remaining bleaching stages D_1, E, D_2, and H, as shown in Figure 3.5(b). The mass of the pulp for this stage and the last three stages were calculated in the same procedure as the previous stage (Oxygen). Chlorine dioxide was dosed and kneaded into the pulp in the fume cupboard. The pulp was laid inside plastic bags and placed in the water bath under the conditions in Table 3.3. The pulp was then removed from the water bath for washing. The plastic bags were cut open and the pulp poured out into a Buchner funnel fitted with a sieve. The funnel containing the pulp was then placed on a vacuum flask. The pulp was washed (refer to the O stage process).

(c) Extraction stage (E)

NaOH was dosed and kneaded into the pulp. The pulp was laid inside plastic bags and placed in the water bath under conditions in Table 3.3. The pulp was then removed from the water bath for washing. The plastic bags were cut open and the pulp poured out into a Buchner funnel fitted with a sieve. The funnel containing the pulp was then placed on a vacuum flask. The pulp was washed (refer to the O stage process).

(d) Chlorine stage (D_2)

Chlorine dioxide was again dosed and kneaded into the pulp in the fume cupboard. The pulp was laid inside plastic bags and placed in the water bath under the conditions in Table 3.3. The pulp was then removed from the water bath for washing. The plastic bags were cut open and the pulp poured out into a Buchnner funnel fitted with a sieve. The funnel containing the pulp was then placed on a vacuum flask. The vacuum was activated. Deionised water was then poured over the pulp and the suction action of the vacuum drained the water into the vacuum flask. The pulp was washed (refer to the O stage process).

(e) Hypochlorite stage (H)

Hypochlorite was dosed and kneaded into the pulp. NaOH was then dosed and kneaded into the pulp. The pulp was laid inside plastic bags and placed in the water bath under conditions in Table 3.3. The pulp was then removed from the water bath and washed. The plastic bags were cut open and the pulp poured out into a Buchner funnel fitted with a sieve. The funnel containing the pulp was then placed on a vacuum flask. The pulp was washed (refer to the O stage process).

3.4.2 Bleaching optimization

Precise procedures and the parameters as in the bleaching response of the pulp were used for the bleaching optimization trials. To optimize the bleaching of the pulp the chlorine dioxide dosage was reduced by 33% (Section 4.4). This reduction was applied at the chlorine dioxide stages D_2. An unfractionated control sample was bleached in parallel with the pulp samples.

Table 3.4: Optimized bleaching conditions

Oxygen stage (O)	NaOH Dosage concentration	✘
	Time	✘
	Oxygen	✘
	Temp	✘
Chlorine stage (D_1)	ClO2 Dosage concentration	✘
	Temperature	✘
	Time	✘
Extraction stage (E_o)	NaOH Dosage concentration	✘
	Temperature	✘
	Time	✘
Chlorine stage (D_2) **Optimised stage**	ClO2 Dosage concentration	**33% dosage drop**
	Temperature	✘
	Time	✘
Hypochlorite stage (H)	NaOH Dosage concentration	✘
	OCl (hypochlorite) concentration	✘
	Temperature	✘
	Time	✘

3.5 Pulp testing

3.5.1 Pulp consistencies in each respective stream

One litre of pulp suspension (weight of BD pulp in 100g of pulp + water mixture) was collected from the feed line. The pulp suspension was vacuum filtered on a 0.5 micron pre-dried and pre-weighed filter paper. The fibres retained on the filter paper were dried in an oven for 24 hours at 110^{o}C. The mass of the dried filter cakes/papers was determined. This data was used to establish the consistency, which is the solid content of the pulp sample. The standard procedure of measuring pulp consistency (up to 25%) is laid out in Tappi T240. Consistency is an important process parameter in pulp and paper mills. Process equipment is designed to handle pulp at specific consistency. Higher consistency minimises dilution water usage which ends up as effluent and also helps in reducing the bleaching chemical consumption. However practical limitations of handling pulp at higher consistency specifically high viscosity make pulp flow very challenging.

3.5.2 Freeness of the pulp samples collected in each respective stream

The drainage time of pulp, also known as freeness or slowness of pulp is a commonly used measure of pulp processing in the industry. The drainage rate of unrefined pulp, can give an indication on the fibre length of pulp. Long fibre pulps have higher freeness compared to short fibre pulps. It is also important here that we are talking about one pulp, eucalyptus. The Canadian Standard Freeness (CSF) measurement was used in this work. The CSF of pulp gives a measure of the rate at which a dilute suspension of pulp (3 g of pulp in 1 L of water) drains. The freeness (drainage rate) is related to the surface conditions and swelling of the fibres. The results are also dependent on the test conditions. The standard procedure of measuring pulp freeness is laid out in Tappi 227 om-94

3.5.3 Pulp fibre morphology

The length of fibers is one of the most important parameters of pulp. Pulp strength is directly proportional to fiber length and dictates its final use. A long fiber pulp is good to blend with short fiber pulp to optimize on fiber cost, strength and formation of paper. Fines can have a significant impact on processing, particularly with regard to filtering or drainage operations. The fibre analysis was performed using a Morfi Compact Fibre Analyzer which is also commonly used. The fibre morphology measured fibre properties namely width, length, fines, and coarseness. The test also ascertained whether there was any fractionation of the pulp by the hydrocyclone. An additional measure of pulp particle size is the percentage of fines. This consists of particles measuring less than 0.2 mm in length as measured by a Morfi Compact Fibre Analyser.

3.5.4 Alkali solubility determination of the pulp

Pulps differ in their content of hemicelluloses and in the chemical composition of their hemicelluloses. The hemicellulose content of a pulp is an indicator of chemical differences originating from the tree and is also affected by the pulping process used. Hemicellulose helps with cellulose fibre bonding. Pulps which contain too much hemicellulose hydrate too fast and loose freeness before adequate strength is developed. However, lignin interferes with the extraction and determination of carbohydrates, and the method cannot be applied to unbleached pulps.

Alkali solubility is a measure of cellulose degradation, and also of loss or retention of hemicellulose during pulping and bleaching processes. A 10% sodium hydroxide solution (S_{10}) possesses maximum dissolving power and dissolves both degraded cellulose and hemicellulose; while in 18% NaOH (S_{18}), only the hemicellulose is soluble. Thus, the amount of degraded cellulose, which is the difference between (S_{10}) and (S_{18}), is represented by equation 3.6.

$$Degraded\ cellulose = S_{10}(\%) - S_{18}(\%) \qquad \textit{Eqn no: 3.6}$$

The α-cellulose was determined using equation 3.7.

$$Alpha(\alpha)cellulose\ = 100 - \frac{S_{10}(\%)+S_{18}(\%)}{2} \qquad \textit{Eqn no: 3.7}$$

Alpha cellulose refers thus to the percentage purity of the pulp.

S_{10} and S_{18} alkali solubilities were determined according to TAPPI method T235 OM-85. The method is based on the extraction of carbohydrates with sodium hydroxide followed by oxidation with potassium dichromate. . The S_{10} solubility was determined as follows:

1. Pulp sample of 1.6g was placed in 100 ml of 10% sodium hydroxide
2. The pulp and solution were stirred for 3 minutes and
3. The mixture was left at 20 ºC for a period of an hour.

4. There after the pulp sample was filtered under vacuum using a sintered glass crucible.
5. 10mL of 0.4N potassium dichromate and 30 mL of concentrated sulphuric acid were added to 10 ml of the filtrate.
6. This was followed by an addition of 500 mL of deionised water where after the solution was cooled.
7. Next 20 ml of 10% potassium iodide was added to the solution, and further cooled
8. After 5 minutes the solution was titrated with 0.1N sodium thiosulphate.
9. A blank, without pulp sample, was also titrated to give a blank titre.

   The S_{10} solubility was determine by equation 3.9.

$$Alkali\ Solubility = \frac{(Blank\ titre - sample\ titre)\ X\ 0.685\%}{weight\ of\ pulp\ sample} \qquad \textit{Eqn no: 3.8}$$

The S_{18} solubility was determined as follows:

1. Pulp sample of 1.6g was placed in 100 ml of 18% sodium hydroxide.
2. The pulp and solution were stirred for 3 minutes and
3. The mixture was left at 20 ºC for a period of an hour.
4. There after pulp sample was filtered under vacuum using a sintered glass crucible.
5. 10ml of 0.4N potassium dichromate and 30 ml of concentrated sulphuric acid were added to 10 ml of the filtrate.
6. This was followed by an addition of 500 ml of deionised water where the solution was cooled.
7. Next 20 ml of 10% potassium iodide was added to the solution further cooled
8. After 5 minutes the solution was titrated with 0.1N sodium thiosulphate.
9. A blank, without pulp sample, was also titrated to give a blank titre.

The S_{18} solubility was also determined by equation 3.8..

3.5.5 Extractives

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. Determination of extractives by solvent extraction of wood and pulp was performed according to Tappi test method T204 cm-97. The amount of extractives present in pulp samples were determined gravimetrically using Accelerated Solvent Extraction (ASE) Systems. The amount of solvent-soluble, non-volatile material in wood and pulp was obtained.

3.5.6 K number (permanganate number)

This is a chemical test performed on pulp to determine the degree of delignification.
The method is centered on the direct oxidation of lignin in pulp by standard potassium permanganate and back-titrating the excess permanganate with ferrous ammonium sulphate (Mohr's salt) standard solution.
The k number provided the relative "hardness" or bleachability of the pulp samples, thus assessing the lignin content after each stage. This is the amount of 0.1 N $KMnO_4$ consumed by 1 gm of moisture free pulp.
The k number was determined according to Tappi method UM 251. The k number was determined by equation 3.9

$$Permanganate\ number = (Sample\ titre - Blank\ titre) X\ 0.355 \qquad \textit{Eqn no: 3.9}$$

3.5.7 Brightness of the pulp

The brightness of pulp is the ability of a pulp sheet to reflect light directed onto it. It is the ratio of the reflectance of visible light from pulp compared to the corresponding reflectance of a magnesium oxide standard. This is affected by both the light absorption and light scattering of the pulp. The wavelength of 457 nm is used in measurements. The absorbance of visible light is usually associated with its lignin constituent. However other factors have influence on pulp brightness such as wood species, wood age, storage conditions and storage time. Test Method Tappi 452 om-08 was applied to determine the pulp brightness. This test determined the brightness of white or near-white bleached pulp.

3.5.8 Copper number

The copper number may be regarded as an index of those impurities in pulp, such as oxycellulose, hydrocellulose, lignin, and sugars, which possess reducing properties. It provides an indication of the reducing end groups in a pulp sample. It is useful for determining changes accompanying deterioration and may therefore be considered as a factor having an indirect bearing on the permanence of paper. The copper number is a measure of the reducing properties of the pulp and is defined as the number of grams of metallic copper reduced from the cupric (Cu^{++}) to cuprous (Cu^{+}) state in alkaline solution by 100 g cellulose under standard conditions. Copper number is defined as the number of grams of inorganic copper resulting from the reduction of $CuSO_4$ by 100.00 g of pulp fibres.
The copper number was determined according to Tappi method T 430 cm-09.

4. Results

4.1 Fractionation: Establishing the optimum feedstock consistency

This section presents the results of the influence of feed stock consistency and the reject rates on pulp fractionation using a hydrocyclone. The focus of the first part of this study was to determine the optimum operating consistency of the hydrocyclone.

4.1.1 Introduction

The overall objective of this study was to establish the optimum feedstock consistency to be used in the subsequent trials. Five levels of the feed stock consistency were studied at a constant volumetric reject rate of 27%. The volumetric reject rate of 27% was arbitrarily selected as a starting point for the study.

4.1.2 Consistency experiments

Preliminary trials were focused on determining the volumetric reject rate at which the hydrocyclone will be operated and understanding the repeatability of the fractionation. An arbitrary value of 27% was selected as a starting point. This then required that the base and the apex valves be set to provide a target volumetric rate of 27%. The volumetric reject rate is defined as follows:

$$\text{Volumetric reject rate} = \frac{Vol\ of\ base\ stream\ x\ 100}{Vol\ of\ feed\ stream} \qquad \textit{Eqn no: 4.1}$$

Whilst the volumetric accept rate is defined as follows:

$$\text{Volumetric accept rate} = \frac{Vol\ of\ apex\ stream\ x\ 100}{Vol\ of\ feed\ stream} \qquad \textit{Eqn no. 4.2}$$

It can be seen in Table 4.1 that the variations in volume collected over four trials was minimal and that the volumetric ratio was consistently close to 27%. This setting was kept the same and was applied during the evaluation of the effects of the feed stock consistency on pulp fractionation efficiency.

Table 4.1: Data for validation of the repeatability of the target volumetric reject rate (27)

	Volume collected (ℓ)		Time (s)	Feed Volume collected (ℓ)	Volumetric reject rate (Base/Feed)	Volumetric accepts rate (Apex/Feed)
Run	**Base**	**Apex**				
1	4.00	11.00	10	15.00	26.7	73.3
2	3.93	10.90	10	14.80	26.6	73.4
3	4.00	11.00	10	15.00	26.7	73.3
4	4.04	11.20	10	15.20	26.6	73.4

Fractionation efficiency was evaluated based on the freeness. Freeness measures the dewatering characteristics of the pulp slurry and has been shown to correlate with the amount of fines, flexible fibres or thick walled fibres present in the pulp samples (Karnis 1997; Noss 2002). As will be seen in Section 4.1.4 pulp samples enriched with fines or flexible fibres are characterized by lower freeness values, whereas pulp enriched with thick walled fibres behaves in the opposite fashion. (Karnis 1997; Johakimu and Bush 2011; Noss 2002).

4.1.3 Impact of consistency on fractionation

The first set of fractionation experiments examined the influence of the feedstock consistency on fractionation efficiency. Six levels of feed stock consistency (0.1%, 0.2%, 0.3%, 0.6%, 0.8% and 1%) were run at a constant volumetric reject ratio of 27%. The corresponding mass reject rate was 11% (Figure. 4.3). The overall objective of this study was to establish the optimum feedstock consistency to be used in subsequent trials.

The results for the effects of the feed stock consistency on fractionation efficiency are shown in Table 4.2: When comparing the fine fibre enriched fraction collected in the base stream with the feed stream, the highest freeness drop (144 units) was observed as the two lowest feed stock consistencies i.e. 0.1% and 0.3%. The result confirm that operating the hydrocyclone at lower feedstock consistency favours the separation of fines enriched pulps from the main feed stream (Paavilainen 1992; Johakimu and Bush 2011; Noss 2002).

Table 4.2: Effect of feedstock consistency on hydrocylone Fractionation Efficiency at reject ratio of 27%

Consistency (%)	Freeness (ml CSF)	Freeness (ml CSF)		CSF drop (Feed:Base)
	Feed	Base (reject)	Apex (accept)	
0.1	589±6.17	445±6.10	552±15.31	144
0.3	571±6.94	427±8.83	539±11.27	144
0.6	557±1.55	429±5.03	565±5.54	128
0.8	536±8.83	426±7.10	501±9.17	110
1.0	523±6.58	452±5.67	559±18.17	71

However, when comparing the fine fibre enriched fraction (base) at feed consistency of 0.8% and 1% with the feed stream, the freeness drops were 110 and 71 units respectively. The result suggested that fibre separation did take place but not as efficiently as when a consistency of 0.1% and 0.3% were applied. On the other hand, operating the hydrocyclone at feed consistency of 0.8% and 1% gave an passable freeness drop, an indication that almost similar fibre fractionation efficiency is also achieved at these consistencies. In terms of saving water and pumping energy costs a higher feedstock consistency is preferred.

In previous work (Paavilainen 1992; Bergström and Vomhoff 2007; Johakimu and Bush 2010, 2011), it has been shown that feedstock consistency plays a vital role on hydrocyclone fractionation efficiency. For example, effective fractionation of TMP pulps can be achieved when a feed stock consistency up to 1% is applied (Paavilainen 1992), whereas softwood chemical pulps require feedstock consistency less than 0.3% (Bergström and Vomhoff 2007). In the initial trials conducted in 2002 by Noss (now Kadant), only a feedstock consistency of 0.3% was applied (Noss 2002). As a result, there are no data for the effects of higher feed stock consistency on fractionation efficiency of the dissolving pulps. Therefore, this data could be useful for the operation of a fractionating system at higher consistency ranges.

4.1.4 Impact of consistency on freeness and freeness drop

As mentioned earlier in section 4.1.2 the fractionation efficiency was evaluated based on freeness values of base and apex relative to feed. The average freeness values for feed, apex and base displayed in Table 4.2 have been depicted graphically in Figure 4.1. As evident in Figure 4.1, the freeness values of the feed, base and apex are different. This is an indication that fractionation did take place, with the result that the two streams have fibres with different water drainage characteristics. For the entire range of feed consistency investigated, the base (reject) pulp samples exhibited relatively lower freeness values, an indication that the base stream was enriched with fines (Karnis 1997; Hanness and Karl-Johan 2002). The apex pulp samples gave freeness values that are not significantly difference to the feed. The freeness of the thick walled enriched pulp fibres in the apex stream was similar to the feed compared to the base stream with thin walled fibres.

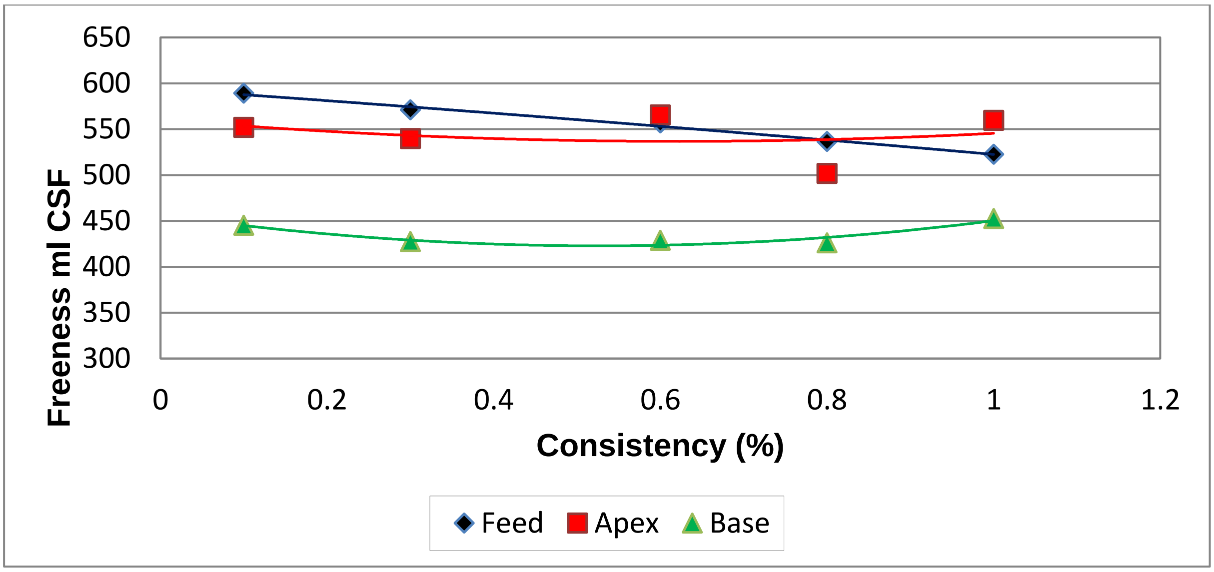


Figure 4.1: Influence of feed consistency on fibre fractionation efficiency (freeness)

This trend confirmed that operating the hydrocyclone at lower feedstock consistencies favours fractionation of the pulp fibres i.e. fines enriched pulps can be fractionated from the main feed stream (Paavilainen 1992; Johakimu and Bush 2011; Noss 2002). However, there were no major differences in freeness between the feed stream and the apex stream. No reasons were found in literature to explain this phenomena, therefore it can only be speculated that dissolving wood pulp (DWP) fibres are more likely to have homogenous fibre characteristics. According to previous studies (Paavilainen 1992; Karnis 1997; Bergström and Vomhoff 2007), pulp furnish having heterogeneous fibre characteristics such as TMP pulps and softwood have been reported to exhibit significant differences in freeness values. This can be explained by the fact that TMP pulps are characterised by mixture of fibrillated and unfibrillated fibres (Olson and Rehmat 2001; Bergström and Vomhoff 2007; Johakimu and Bush 2010), whereas softwood pulp is characterised by earlywood and latewood fibres (Paavilainen 1992; Karnis 1997). Early wood fibres are enriched with thin-walled fibres, whereas latewood fibres are enriched with thick-walled fibres (Paavilainen 1992; Karnis 1997). In Figure 4.2, the % Freeness drop as a function of feed consistency is shown. The % Freeness drop is defined as:

$$\% \text{ CSF drop} = \frac{(Feed\ freeness - base\ freeness)x\ 100}{Feed\ freeness}. \qquad \textit{Eqn no: 4.3}$$

Here it can be more clearly seen that at 0.8% consistency and below, freeness drops of over 20% were achieved, and above 0.8% consistency, the freeness drop decreased to below 20%. Similar findings on the effect of the feedstock consistency on fibre fractionation efficiency using hydrocyclone have been reported (Strobl 2013). Fibre fractionation takes place when there is movement of the fibres relative to each other, (Paavilainen 1992; Bergström and Vomhoff 2007). Thus increasing the feed consistency of the pulp, the fibres tend to act the opposite as this inhibits free fibre movement.

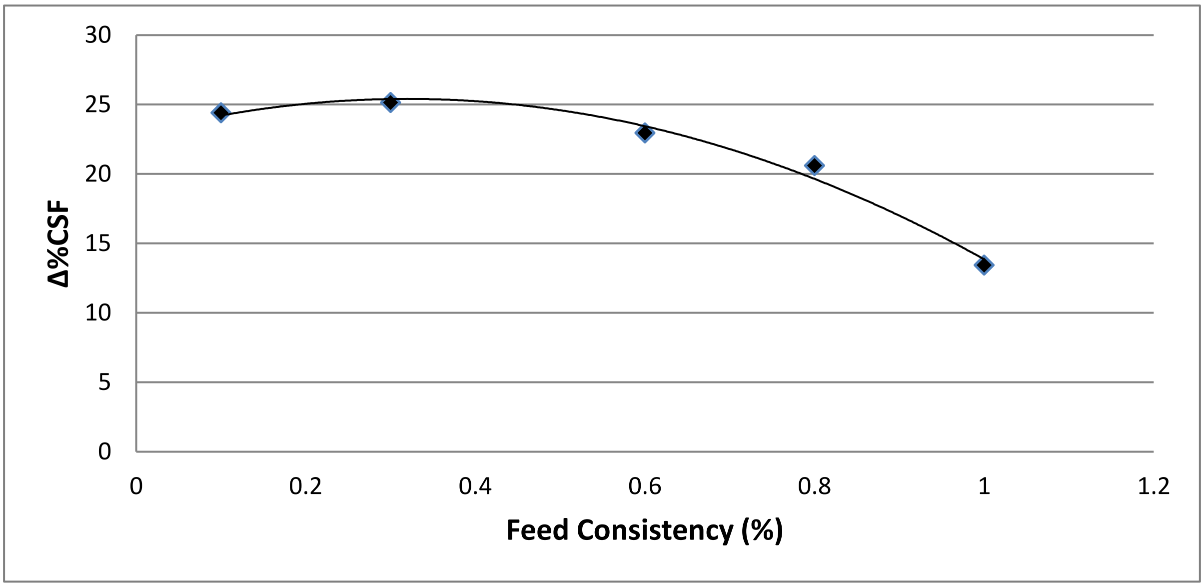


Figure 4.2: Influence of feed consistency on % CSF drop (fibre fractionation efficiency)

It was however noted that at feed consistency of 0.8% the freeness drop was still greater than 20% indicating that acceptable fibre fractionation was still achieved. In terms of saving water and pumping energy costs, a higher feedstock consistency is preferred. For this reason, operating the hydrocyclone using feed consistency in the range of 0.6 -1% could be more economical. Thus, a feed consistency of 0.8% was selected as a good practical compromise and was used in the subsequent experiments.

4.1.5 Impact of consistency on thickening factor

Table 4.3 shows the consistency data achieved in each stream at 27% volumetric reject rate. The consistency of the apex (accepts) stream was higher than the consistency of the feed stream, whereas the consistency of the base (rejects) was considerably lower. The base consistency is due to an increase in water volume that has lower fibre concentration. A thickening factor can be defined as:

$$\text{Thickening factor} = \frac{Consistency\ of\ apex\ stream}{Consistency\ of\ feed\ stream} \qquad \textit{Eqn no: 4.4}$$

The thickening factors at various feed consistencies are shown in Table 4.3. Thickening is necessary for fractionation to take place, thus the thickening factor, the apex/feed ratio, can also be used to predict fractionation (Olson and Rehmat 2001). In general, the lower the thickening factor the better the fractionation. It appears that at the selected feed consistency (0.8%), the thickening factor is 1.17, and is in the range of 1– 25 which indicates better fractionation (Olson and Rehmat 2001; Bergström and Vomhoff 2007).

Table 4.3: Streams and its corresponding consistencies (runs were repeated twice)

Consistency runs	**Feed stream (%)**	**Apex (accepts) stream (%)**	**Base (reject) stream (%)**	**Thickening factor**
0.1	0.112±0.070	0.119±0.003	0.086±0.061	1.07
0.3	0.314±0.001	0.352±0.008	0.176±0.007	1.13
0.6	0.605±0.008	0.696±0.019	0.211±0.083	1.15
0.8	0.758±0.040	0.884±0.002	0.244±0.026	1.17
1	0.971±0.008	1.181±0.003	0.292±0.004	1.22

4.1.6 Impact of consistency on fibre morphology

Fibre morphology data for the feed, base (rejects) and apex (accepts) pulp streams that were produced using a feed stock consistency of 0.8% are presented in Table 4.4. Fractionation resulted in pulp with different morphological properties. A higher proportion of fine fibres and short fibres were observed in base. This result supports the trend explained in the section 4.1.4 i.e., the fine fibre enriched base fraction exhibited lower freeness values while the coarse fibre enriched apex fraction exhibited higher freeness values.

As, expected, the fibre length data did not show major differences between feed, base (rejects) and apex (accepts) because hydrocyclones fractionate according to density/cell wall thickness and not on fibre length as the screening systems do (Karnis 1997). A comprehensive analysis on fibre morphology is reported in section 4.2.7

Table 4.4: Fibre morphology (sample fractionated using feed consistency of 0.8%)

	Feed	**Base(rejects)**	**Apex(accepts)**
Fibre length (μm)	691	595	688
Coarseness (mg/m)	0.10	0.05	0.10
Fibre amount (millions fibres/g)	39.2	54.7	40.0
Kinked fibres (%)	28.6	18.3	30.0
Curled fibres (%)	7.7	6.1	8.0
Fines (%)	4.0	8.8	3.8

4.1.7 Summary

- The effects of feedstock consistency on hydrocyclone fractionation efficiency for the dissolving pulps have been demonstrated. The pulp samples were fractionated at constant volumetric reject ratio of 27%. The corresponding mass reject rate was 11% (refer to Figure 4.3). The feedstock consistency levels were varied. The fractionation efficiency was evaluated based on the pulp streams' freeness data. The data acquired indicated that operating the hydrocyclone at feedstock consistency of 0.3% could favour better hydrocyclone fibre fractionation efficiency. When the samples collected in base (rejects) stream was compared to the control, a freeness drop of 144 units was achievable. These results suggested that a substantial amount of fines enriched pulp fibres were collected in the base (reject) stream and thus could be removed from the main brown stock pulps.

- On the other hand, operating the hydrocyclone at a feed stock consistency in the range of 0.8 – 1%, produced acceptable fractionation, as evidenced by a reasonable freeness drop of an average of 103 units, at consistencies that are within practical industrial range. Therefore, operational problems associated with operating hydrocyclone at extremely lower feedstock consistencies such as 0.1% and 0.3% could be avoided. For instance, in an existing pulp fibre line a low feedstock such as at 0.3% may require major process modification so as to accommodate the increased volume of water with associated increases in the pumping energy and/or the requirements for additional dewatering facilities.

- Based on these findings, it was proposed that in the subsequent trials, the feedstock consistency will be applied in the range of 0.8-1%. The effects of feedstock consistency on hydrocyclone fractionation efficiency of the dissolving wood pulps (DWP) had been determined. The consistency of 0.8% was identified as the optimal feed consistency. A feedstock consistency of 0.8% was to be used for subsequent trials.

4.2 Fractionation: Establishing the target mass reject rate

This section examines the effect of mass reject rates (MRR) on the hydrocyclone fractionation efficiency. The hydrocyclone critical operating parameter, the mass reject rate, was evaluated and optimised. Furthermore, freeness drop, thickening factor, extractives, acid insolubles, solubility and fibre morphology at the desired target mass reject rate were determined.

4.2.1 Introduction

Six levels of the mass reject rates were studied at a constant feed consistency of 0.8%. The overall objective of this study was to establish the optimum mass reject rates which were to be used in the subsequent bleaching trials.

4.2.2 Impact of mass reject rate

This work was conducted in two steps. The first step entailed varying valve settings of the base (rejects) and apex (accepts) lines, followed by determining the corresponding volumetric reject rates. Thereafter, the corresponding mass reject rate at each volumetric reject rate was determined. The volumetric reject rate was defined by Equation 4.1.

The relationship between volumetric reject rates and mass reject rate was calculated, and is represented graphically in Figure 4.3. As expected, increasing the volumetric reject rate resulted in an increase in mass reject rate. The volumetric flow is controlled through adjusting the valve opening, thus when the valve opening in the reject line is increased; the volumetric flow increases and subsequently more fibres collected in the base (reject) line. The target mass reject rate range of 5-41% was achieved when the hydrocyclone was operated using volumetric reject rate in the range of 17-65%.

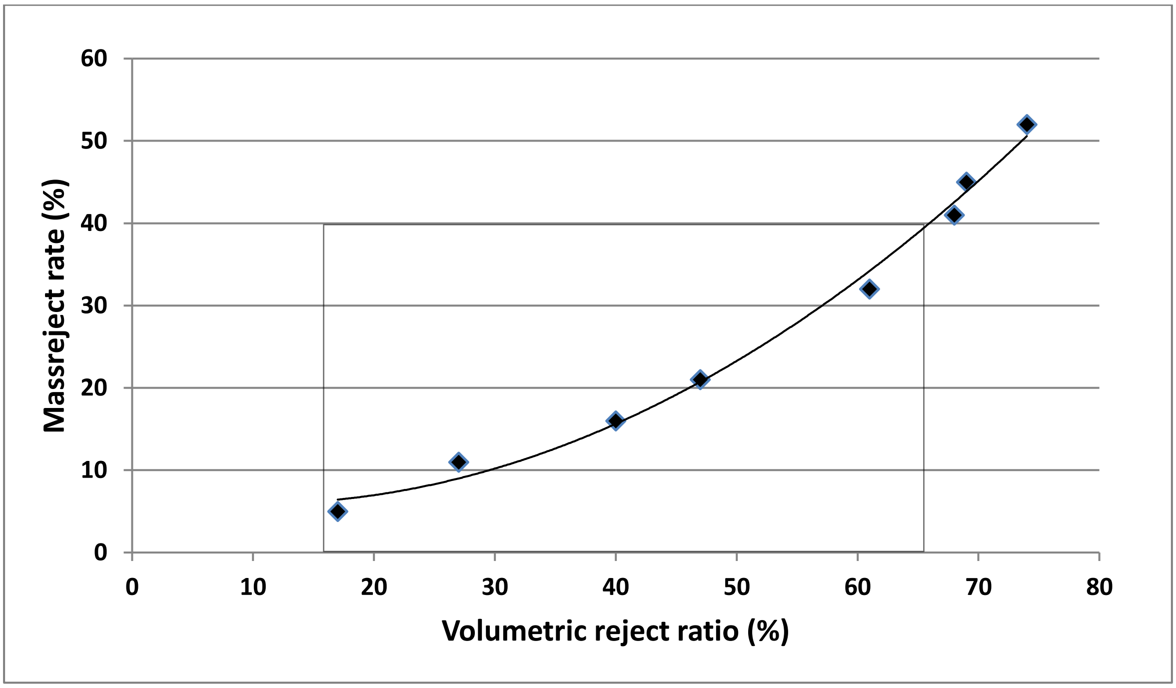
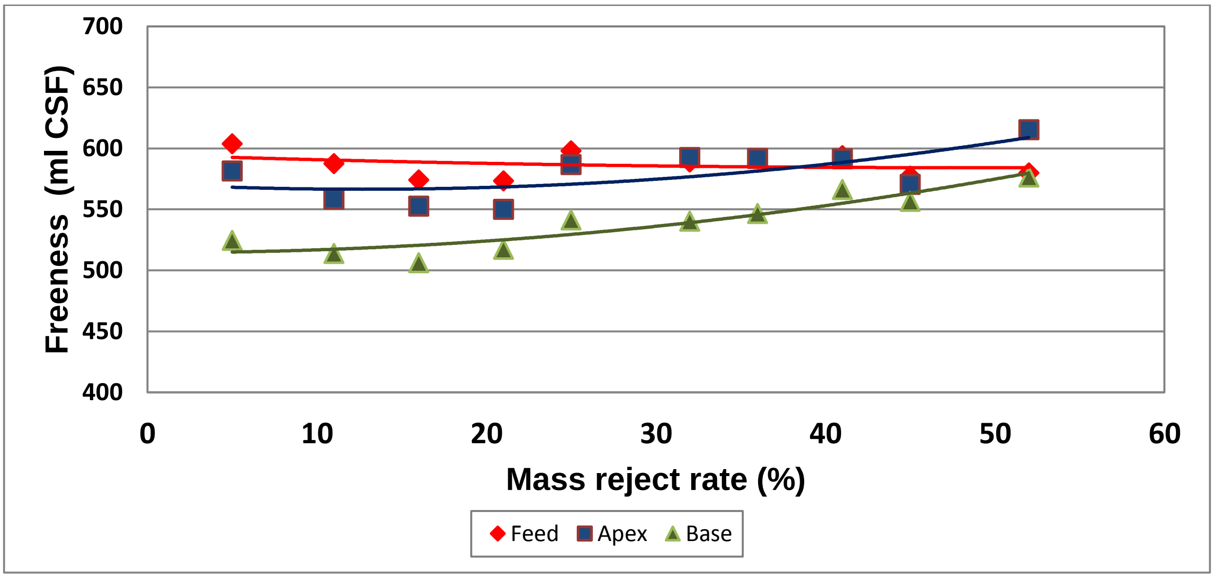


Figure 4.3: Impact of volumetric ratio on mass reject rate

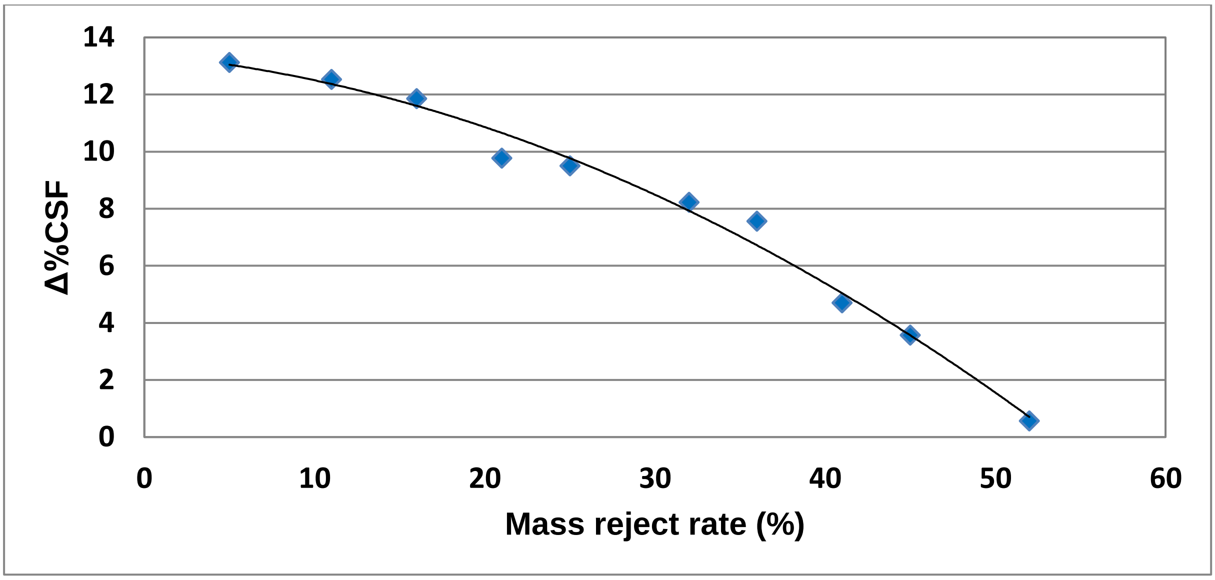
4.2.3 Impact of mass reject rate on freeness drop

As discussed in section 4.1.4, fractionation efficiency can be predicated using the freeness data. The freeness data corresponding to the various mass reject rates are shown in Figure 4.4(a). The freeness data of the base (rejects) and the apex (accepts) were compared graphically to that of the feed freeness data. Pulp samples collected from the feed and apex (accepts) streams had relatively higher freeness values than the samples collected in the base stream. This is an indication that fractionation did take place and a higher proportion of thin-walled and fines fibres were collected in base (rejects) stream (Karnis 1997; Hanness and Karl-Johan 2002). Thin-walled and fine fibres are characterised by poor water drainage characteristics and thus exhibits lower freeness values. The reason behind this phenomenon is that thin-walled fibre conforms and consolidates well among the fibres, resulting in a strong bond between the fibres with limited pores for water to penetrate, whereas thick-walled fibres behave in the opposite way. The graphical data also indicated that increasing the mass reject rate to high levels resulted in poorer fibre fractionation. Equation 4.3 in section 4.1.4 defines the calculation of ∆CSF drop.

In Figure 4.4(b), it is however very clear that better fibre fractionation can be achieved if the mass reject rate is maintained in the range of 5-16%. Beyond this range, as seen in Figure 4.4(a), apex freeness values tend to be closer to the feed, an indication that limited fibre fractionation occurred. At 35% mass reject rate and beyond there is little difference in the freeness values, indicating that little fractionation took place as shown in Fig 4.4(a).



(a)



(b)

Figure 4.4: Impact of mass reject rate on (a) freeness and (b) percentage change in freeness

4.2.4 Impact of mass reject rate on the thickening factor

Figure 4.5 shows the relationship between thickening factor and the mass reject rate. The thickening factor is defined in Equation 4.4 in section 4.1.5. It can be seen that an increase in mass reject rate resulted in an increase in thickening factor. Thickening factor refers to changes that occur in consistency as the pulp stream passes through the hydrocyclone. In general, the lower the thickening factor the better the fractionation. These data also supported the freeness data which also showed that an increase in mass reject rate has a negative effect on the fibre fractionation efficiency. However, it appears that at the selected mass reject rate of 5-41%, the thickening factor is in the range of 1- 2.5 which is within the acceptable range (Olson and Rehmat 2001; Bergström and Vomhoff 2007; Johakimu and Bush 2011).

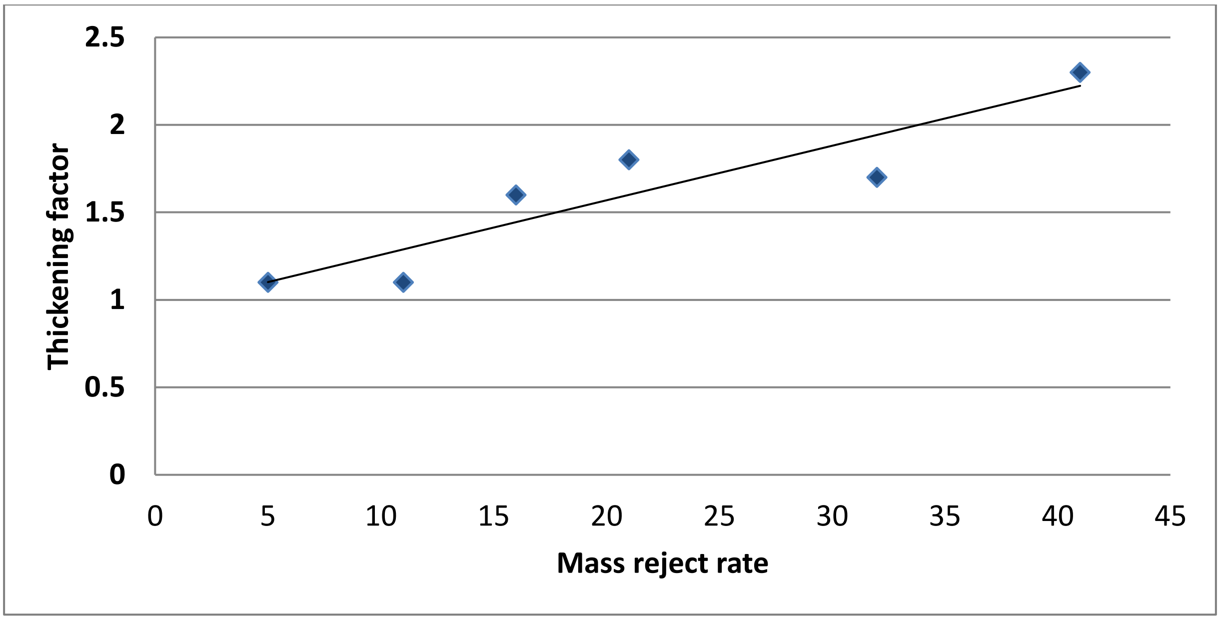


Figure 4.5: Impact of mass reject rate on the thickening factor

4.2.5 Impact of mass reject rate on alkali solubility

Alkali solubility is a measure of amounts of the hemicellulose and degraded cellulose in the fibres (refer to section 3.5). The alkali solubility data is presented in Table 4.5(a) and (b). Table 4.5(a) shows the S_{10} and S_{18} data, whereas Table 4.5(b) shows degraded cellulose and alpha (α) – cellulose data that were calculated based on the S_{10} and S_{18} data.

Table 4.5(a): Alkali solubility data of the various samples for S_{10} and S_{18} for the various pulp samples

Mass reject rate (%)	**S_{10}**			**S_{18}**		
	Feed	**Apex**	**Base**	**Feed**	**Apex**	**Base**
5	11.2	11.3	10.5	6.7	6.8	7.3
11	11.4	11.3	12.8	6.8	6.6	6.3
16	10.5	10.4	10.7	6.9	7.0	7.0
21	12.5	10.0	11.0	6.8	6.6	6.5
32	10.9	10.9	11.5	7.0	7.0	6.0
41	10.6	10.9	11.0	6.7	6.3	6.7

Table 4.5(b): Calculated degraded cellulose and alpha (α) – cellulose for the various pulp samples

Mass reject rate (%)	**Degraded cellulose (%)**			**Alpha (α) – cellulose (%)**		
	Feed	**Apex**	**Base**	**Feed**	**Apex**	**Base**
5	4.5	4.5	3.2	91.1	91.0	91.1
11	4.6	4.7	6.5	91.1	90.4	91.3
16	3.6	3.4	3.7	90.3	91.2	91.0
21	5.7	3.4	4.5	90.3	92.0	91.3
32	3.9	3.9	5.5	91.0	91.0	91.2
41	3.9	4.6	4.3	91.4	91.4	91.2

An indication of the total extractable material (degraded cellulose and hemicellulose) content in pulp is indicated by S_{10}, while S_{18} provides an indication of the total hemicellulose content in pulp (Bodhlyera 2014).The degraded cellulose is determined by the difference between the S_{10} and the S_{18} solubilities. For the entire study of the mass reject rate, degraded cellulose ranged from 3.1% to 6.5% and there was no clear trend to differentiate the impact of mass reject rate on the samples in the three streams; feed, apex and base. The α-cellulose was in the range of 90.3-92% and here too there was no clear trend to differentiate the impact of mass reject rate on the cellulose purity of these streams. No literature was found to explain this trend and therefore, it can only be speculated that the amount of degraded cellulose/ α-cellulose observed are the consequences of the pulping process rather than fibre fractionation. On the other hand, the result tends to suggest that fibre fractionation has no detrimental effect on the cellulose purity. This is especially true considering that the α-cellulose in the unfractionated pulp samples in the feed stream were almost the same as the fractionated samples in the apex (accepts) and base (rejects) streams.

4.2.6 Impact of mass reject rate on extractives

In previous studies (Bergström and Vomhoff 2007; Johakimu and Bush 2010), it has been reported that when pulp fibres are fractionated, substantial amounts of extractives can be found in the fines enriched stream. To confirm these claims, extractive tests, as discussed in section 3.5, were performed on the feed, apex and base samples. The extractive data is presented in Table 4.6.

Table 4.6: Impact of mass reject rate on extractives in pulp samples

Mass reject rate (%)	**Extractive (%)**		
	Feed	**Apex**	**Base**
5	1.13±0.7	0.30±0.1	0.57±0.2
11	1.07±0.4	0.33±0.1	0.46±0.5
16	0.59±0.4	0.20±0.2	0.36±0.3
21	1.35±0.3	0.69±0.1	0.71±0.1
32	1.3±0.8	0.56±0,1	0.60±0.5
41	1.23±0.4	0.64±0.9	0.58±0.3

Although at 16% mass reject rate, the feed value of 0.59% is much lower than the other feeds, the focus is the reference of the apex (accepts) and base (rejects) values relative to the total feed stream values. The first five mass reject rate values showed similar patterns. When their extractive data for the base (reject) samples were compared to the apex (accept) pulp samples, the base pulp samples exhibited a relatively higher amount of extractives. Thus, despite the differences in terms of level of fractionation i.e. mass reject rate the base streams are generally richer in extractives, except at very high reject rates. Mass reject rates 5 to 32% showed that the pulp fines were concentrated in the base stream (Section 4.2.3). This data suggests that there is a linkage between extractives and pulp fines. Hence, fibre fractionation appears to be a useful method for managing the fines and extractives (Johakimu and Bush 2010).

However, an increase in mass reject rate had an increasing effect on the extractive contents in the apex (accept) pulp samples. As discussed in 4.2.4 an increase in mass reject rate is also associated with poor fibre fractionation. A mass reject rate of 41% had 0.64% of extractives in the apex and 0.58% in the base. The apex extractives content was higher than in the base, which suggests poor fractionation at this point. Thus, pulp samples that are poorly fractionated will have more fines as well as extractives in the accept streams. It appears that to maximize the removal of extractives in dissolving wood pulp, the mass reject rate needs to be limited to the range of 5-16%.

4.2.7 Summary

- The effects of mass reject rate on hydrocyclone fractionation efficiency for the dissolving pulps have been demonstrated. The pulp samples were fractionated at a constant pre-determined consistency of 0.8%.
- The objective range of 5 – 40% mass reject rate was achieved by varying the volumetric reject rates. The hydrocyclone was operated using volumetric reject rates in the range of 17-65%, whilst maintaining all other input parameters within the target range. It appears that better fibre fractionation of the DWP can be achieved if the mass reject rate is maintained in the range of 5-20%. At optimum mass reject rates of 5 -16%, the apex (accepts) stream had a relatively lower amount of extractives. This may have a positive impact on the economics of the bleaching process. More importantly, it was also confirmed that fibre fractionation by hydrocyclones does not further degrade the cellulose, as all streams of the fractionated pulp samples had the same α-cellulose as the raw pulp samples.
- Based on these findings, it was proposed that in the subsequent experimental work, the mass reject rates would be applied in the range of 5 - 21%. The mass reject rates of 5% and 11% were identified as optimal and were used for the subsequent bleaching trials.

4.3 Bleaching: Bleaching response of the pulp

The main objective of this milestone was to examine the bleaching response of the fractionated pulp relative to unfractionated pulp, and evaluate potential savings in bleaching chemicals. Evaluating the bleaching response of the fractionated pulps required determining:

- The relative bleaching response of the fractionated pulps, and

- Optimizations of the bleaching process.

Pulp samples produced at mass reject rates of 5% and 11% and the control pulp samples (unfractionated) were bleached to a standard 92α pulp quality using typical bleaching conditions. Standard 92α pulp represents the percentage purity of the pulp. Critical quality properties for dissolving pulp applications were determined.

4.3.1 Impact of mass reject rate on K-number

K-number is the measure of residual lignin in pulps. K-number data for the control pulp samples (unfractionated) and pulp samples fractionated at mass reject rates of 5% and 11 % are presented in Figure 4.6, at various stages through the bleaching process. Comparatively, fractionated pulp samples exhibited lower k-numbers than the control pulp samples. Presumably, some of the lignin fragments were lost in the fines stream, as a result, the fractionated unbleached pulp had a lower residual lignin content than the control (unbleached). Subsequently, this effect was carried through in their respective bleached pulp samples. On the other hand, it can also be assumed that fractionated pulp samples respond much faster than the control pulp samples during bleaching. However, there was not much difference between the fractionated samples (5% and 11%), except in the D_2 and Hypo stages. This result tends to suggest that operating the hydrocyclone at a higher mass reject may be unnecessary, thus fibre loss resulting from a higher mass reject can be avoided. However, Bodhlyera (2014) established that the ideal k- number for 96 alpha pulp is 0.25 after bleaching. The 11% fractionated pulp here showed similar values for the k-number at 0.3.

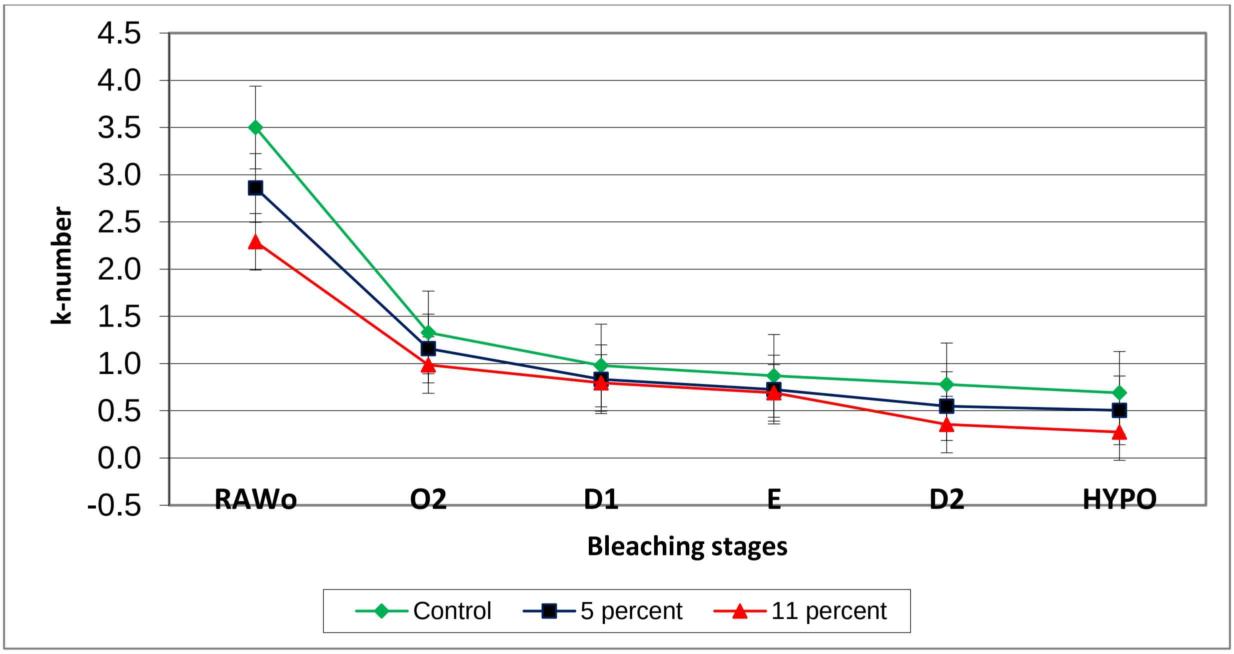


Figure 4.6: Impact of mass reject rate on the k-number at 5% and 11% reject rate

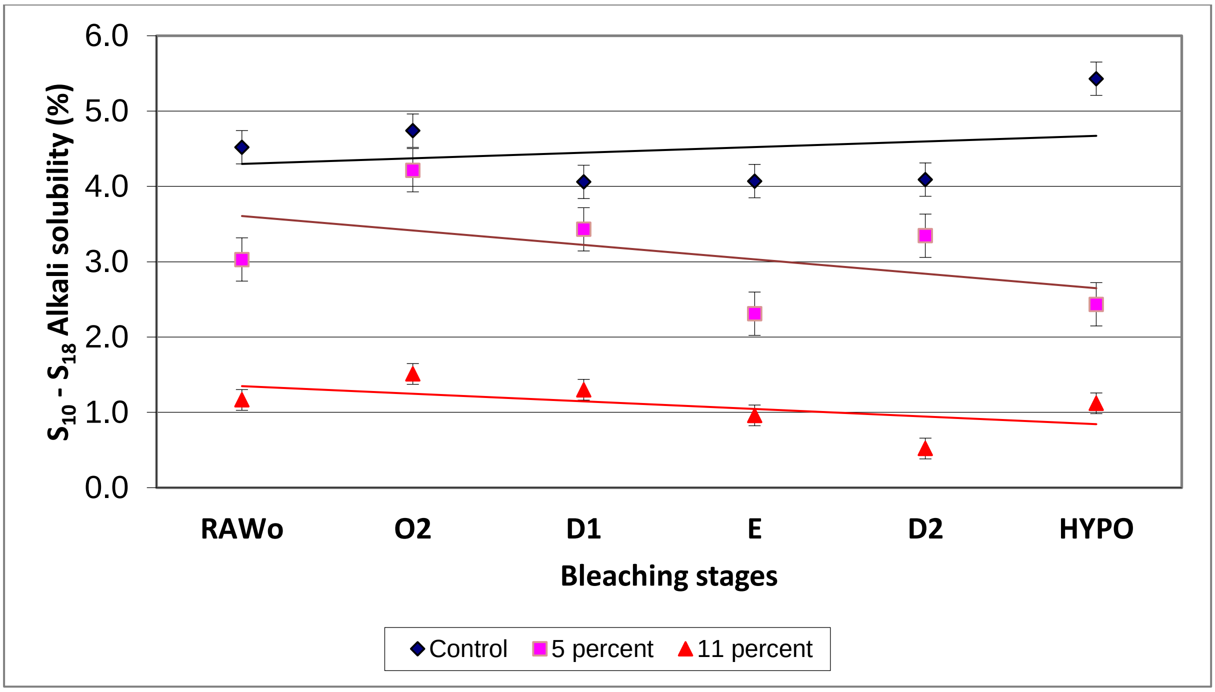
4.3.2 Impact of mass reject rate on alkali solubility

Alkali solubility is a measure of the amount of hemicellulose and degraded cellulose in a pulp sample. Low molecular weight carbohydrates (hemicellulose and degraded cellulose) can be extracted from pulp samples using sodium hydroxide (Bodhlyera 2014).The solubility data is presented in Table 4.7, Figure 4.7(a) and in Figure 4.7(b). Table 4.8 shows the S_{10} and S_{18} data, whereas Figure 4.7(a) shows the degraded cellulose data. It is not easy to draw firm conclusions about the relationship of the cellulose content between the fractionated and the control pulp though some consistent patterns in the data are evident.

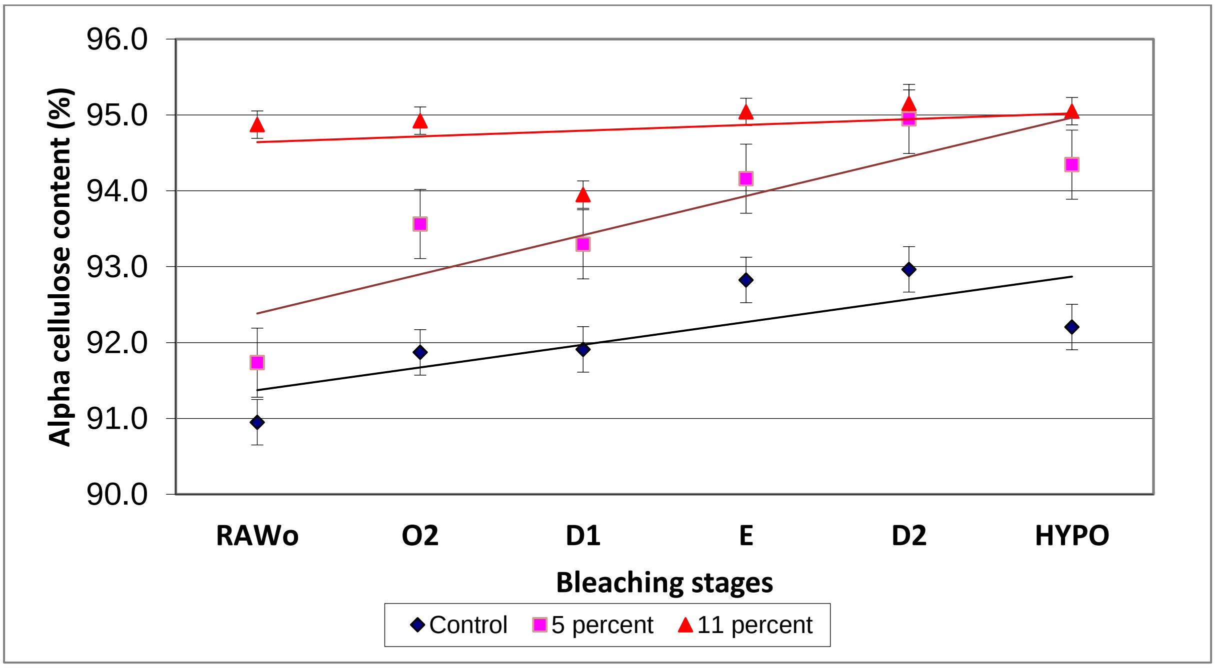
Solubility data, S_{10} and S_{18} values do not characterize dissolving pulp reactivity (Fischer, Schimdt and Fischer 2009). They are indicative of pulp alkali solubility and provide information regarding losses of material during pulp processing. The losses would comprise the low molecular weight carbohydrates that are soluble in 10% and 18% sodium hydroxide, respectively. Figure 4.7(b) shows the alpha (α) – cellulose data, calculated based on the S_{10} and S_{18} data. The control, 5% and 11% pulps attained 93, 94 and 95 alpha (α) cellulose respectively. The quality and hence the market value of the pulp is determined by α- cellulose content and solubility (Fischer, Schimdt and Fischer 2009). It is expected that D_1 stage would have the effect of slightly reducing the cellulose content but increase at the first and last stage (Bodhlyera 2014). Fractionated pulp samples exhibited relatively lower values of S_{10} and S_{18} (Table 4.7). Similarly, the amount of degraded cellulose was relatively lower in the fractionated pulp samples than in the control pulp samples. As a result, the fractionated pulp samples had a higher percentage of α-cellulose than the control pulp samples. The solubility of a pulp thus provides information on the degradation of cellulose and loss or retention of hemicellulose during bleaching processes (Bodhlyera 2014). The results suggested that fractionated pulps are characterised by a higher degree of selectivity during bleaching. Consequently, hemicellulose and lignin are selectively removed with minimum degradation on the cellulose. In comparison, it appears that the mass reject rate of 11% could deliver better pulp quality than the 5% mass reject rate and the control. On the other hand, the results tend to suggest that in order to maintain the same level of purity as the control pulp samples, bleaching conditions could be adjusted, e.g., reducing chemical dosage. This would lead to savings in bleaching chemicals.

Table 4.7: Impact of mass reject rate on bleaching response - solubility data (S_{10} and S_{18})

Bleaching stages	**S_{10}**			**S_{18}**		
	Control	**Mass reject 5%**	**Mass reject 11%**	**Control**	**Mass reject 5%**	**Mass reject 11%**
Raw	11.31	9.78	9.78	6.79	6.75	6.51
O_2	10.50	8.61	5.83	5.76	4.46	4.32
D_1	10.12	8.47	6.70	6.06	5.70	5.40
E	9.21	7.47	5.44	5.14	5.01	4.48
D_2	9.08	7.01	5.11	4.99	4.51	4.59
H	10.51	8.74	5.62	5.08	5.08	4.39



(a)



(b)

Figure 4.7: (a) Impact of mass reject rate on bleaching response - solubility data (Degraded cellulose), (b) Impact of mass reject rate on bleaching – solubility data (Alpha (α) – cellulose)

4.3.3 Impact of mass reject rate on brightness

The brightness on the final pulp samples were as follows: control (89.2%), 5% mass reject rate (89.5%) and 11% mass reject rate (90.2%). Brightness data for the 5% acquired at the D_2 stage appears to be superior to the 11% and control. Although the differences are not great, the brightness trend at 5% mass reject rate was superior to the control but was lower than at 11%. This indicates that the lower mass reject rate 5% could prove a better practical option to the higher mass reject rate of 11% in mill operation.

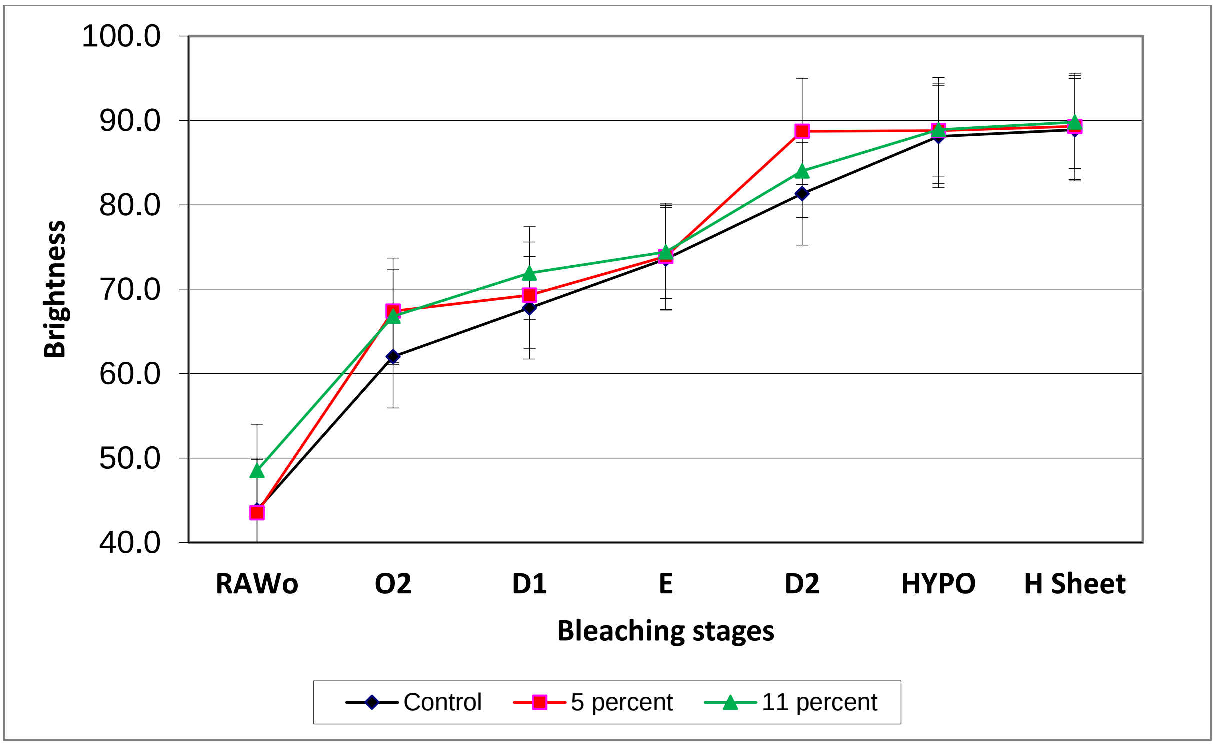


Figure 4.8: Impact of mass reject rate on bleaching response – pulp brightness

Furthermore, the higher brightness values of the fractionated pulps could be adjusted to that of the control value by chemical reduction in the bleaching process. This provides room for potential savings in bleaching chemicals. Brightness level differences were lower at the E and Hypo stages but more noticeable in the O_2, D_1 and D_2 stages. This data could assist later when choosing which bleaching stages to optimize e.g. O_2, D_1 and D_2 stages.

4.3.4 Impact of mass reject rate on copper number

The copper number, which is known to be inversely proportional to the viscosity of the pulp, shows that with a decrease in viscosity is associated with an increase in chain cleavage. Hence there are more reducing end groups. The copper number data is presented in Figure 4.9. It has been well established that hydrolyzed or oxidized cellulose is capable of reducing certain metallic ions to lower valence states, and reactions of this type have served to detect damage to cellulose and to estimate the quantity of reducing groups (Tappi 2016).

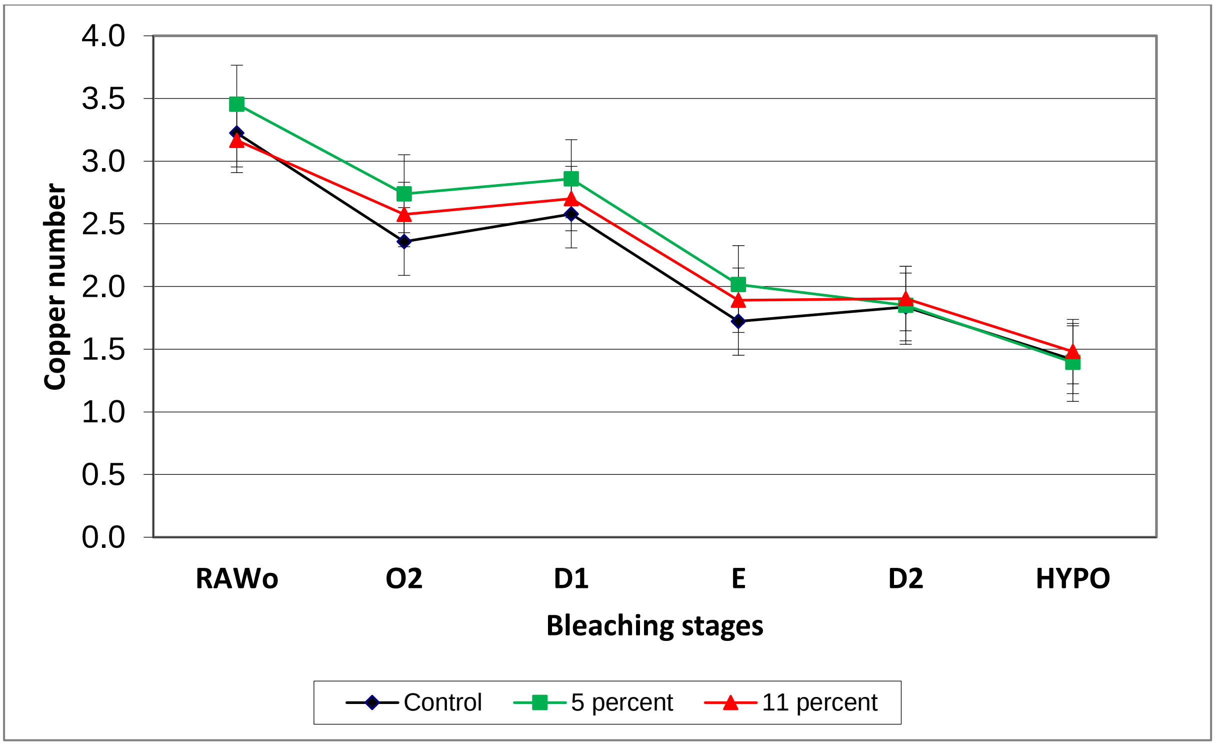


Figure 4.9: Impact of mass reject rate on bleaching response – copper number

The copper numbers decrease with each processing stage with the exception of the O and E stages. The fractionated pulps show higher values compared to the control suggesting higher presence of reducing groups in the pulp. However, there is not much difference in the fractionated and control values at the H stage of bleaching. Comparing the 5% to its superior counterpart the 11%, there does not seem to be a significance difference in their values. Thus a high mass reject rate of 11% could be avoided as it brings with it high water usage and fibre loss.

4.3.5 Summary

- The data for k-number (permanganate number) shows that fractionated pulp samples respond much faster than the control pulp samples during bleaching. As a result, to maintain the same level of k-number as in current bleaching practice, it may be possible to adjust the bleaching conditions, e.g., reduce the chemical dosage. This could result in chemical savings.
- Similarly, the solubility results tends to suggest that in order to maintain the same level of purity as the control pulp samples, bleaching conditions must be adjusted, e.g., reducing chemical dosage. This would lead to savings in bleaching chemicals.
- The copper number and the brightness values results might present considerable differences at the intermediate bleaching stages; however, there is no significant difference at the final H stages.
- It appears that the mass reject rate of 11% could deliver better pulp quality than the 5% mass reject rate. However the limitation could be excessive loss of pulp fibres. Pulp fractionation seems to improve pulp quality.

4.4 Optimization of the bleaching process

Optimizing bleaching conditions entailed identifying the bleaching stage that required adjustment of the bleaching conditions. The bleaching stage identified was D_2 from Table 4.8 where the chlorine dioxide dosage would be reduced by 33%. The mass reject rate of 5% was used for the optimization trials‘ based on the minimal differences observed between the 5% and the 11% results and the costs that would result with running the hydrocyclones at high mass reject rates. Lowering the bleaching requirements has not only been instrumental in making it possible to find alternatives to the traditional chlorine based bleaching but also to maintain critical pulp quality such as brightness (Chirat and Lachenal 1997).

The 5% fractionated and the control pulp (unfractionated) samples were bleached to a standard 92α pulp quality in two different bleaching conditions. The critical quality properties for dissolving pulp applications were tested for both bleaching conditions. The methods used have been described in sections 3.4.1 and 3.4.2. The optimised bleaching process conditions are also summarised in Table 4.8.

4.4.1 Impact of mass reject rate on k-number

The k-number data for the control pulp samples and the 5% MRR fractionated pulp samples bleached are presented in Table 4.8. In comparison, the 5% fractionated pulp samples exhibited lower k-numbers than the control pulp samples after O_2 bleaching. Apparently as mentioned in section 4.3.1, some of the lignin fragments were lost in the fines stream during fractionation, resulting in the 5% fractionated pulps having lower residual lignin contents than the control pulps. This effect was induced in their respective bleached pulp samples. It is observed that the k-number for both control and 5% fractionated are relatively higher at the D_2 stage. This is due to the reduced chlorine dioxide dosages (33%). The similar trend follows through at the H stage where the k values are higher for the 33% (less) ClO_2 pulp compared to the pulp at regular dosages. The 0.32 value for the 5% fractionated for the 33% reduction at the H stage is less than the control at regular dosage the H stage. This suggests that even at 33% chlorine dioxide reduction the 5% fractionated pulps are well within specification. Further this result tends to suggest that there is still room for more chlorine dioxide reduction as this value was less than the control without any chlorine dioxide reduction.

Table 4.8: Mass reject rate effect on bleachability – k-number

Bleaching process stages	**Control**	**5% MRR**
Raw pulp	2.11	2.4
O_2	1.28	1.34
D_1	0.93	0.74
E	0.82	0.46
D_2 **regular dosage**	0.44	0.37
33% (less)	0.66	0.44
H **regular dosage**	0.36	0.28
33% (less)	0.40	0.32

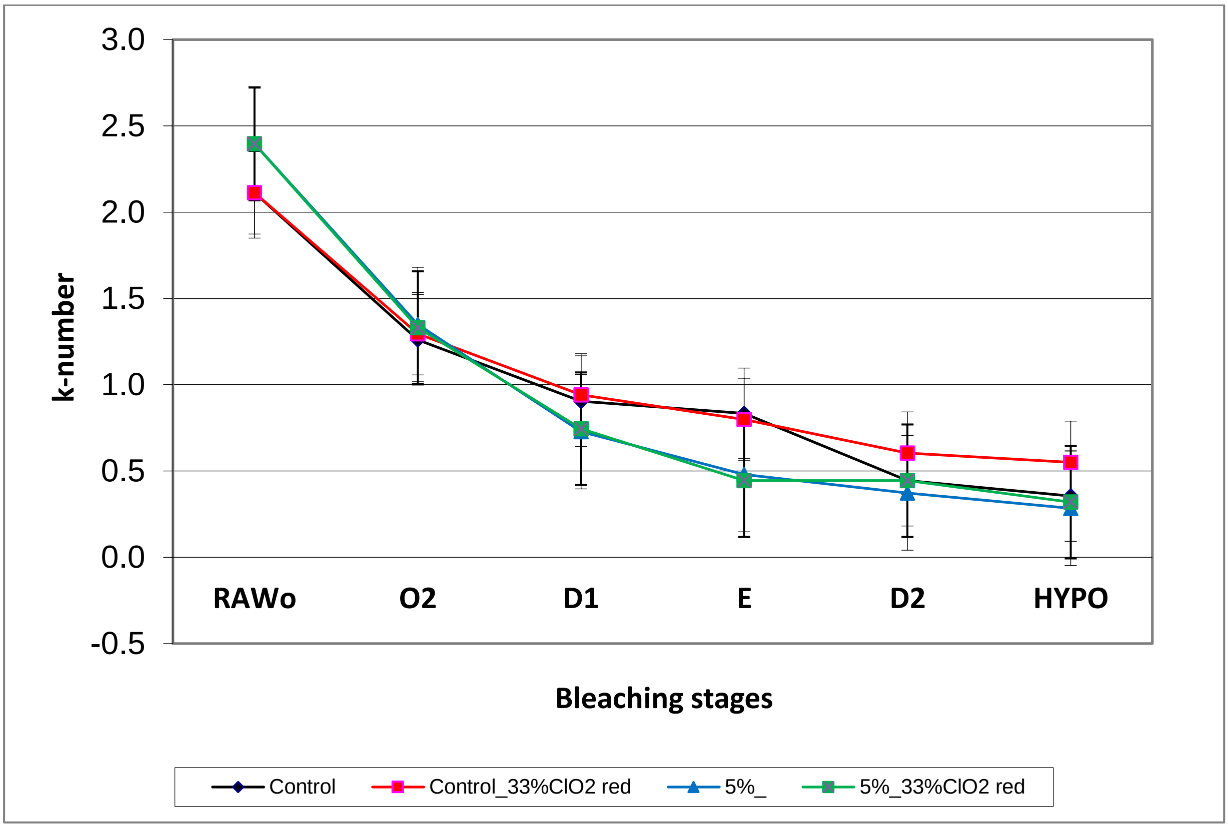


Figure 4.10: Impact of mass reject rate on bleaching response – k-number

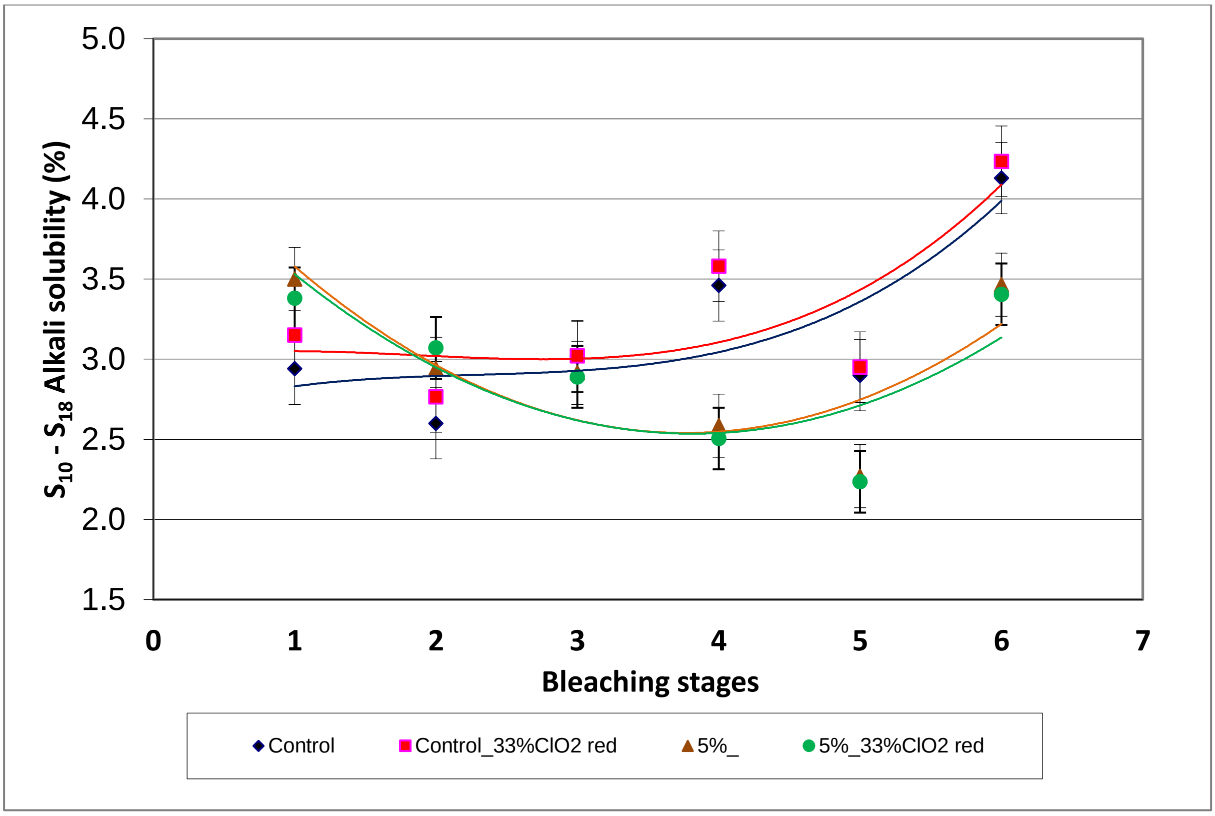
4.4.2 Impact of mass reject rate on Alkali solubility

Bleaching affects cellulose structure by the generation of oxidised positions and subsequent chain cleavage in pulp samples (Asikainen and Alén 2011; Fardim 2011). The solubility data is presented in Table 4.11, Figure 4.11(a) and (b). Table 4.11 shows the S_{10} and S_{18} data, whereas Figure 4.11(a) shows the degraded cellulose data. Figure 4.11(b) shows the alpha (α) – cellulose data, calculated based on the S_{10} and S_{18} data.

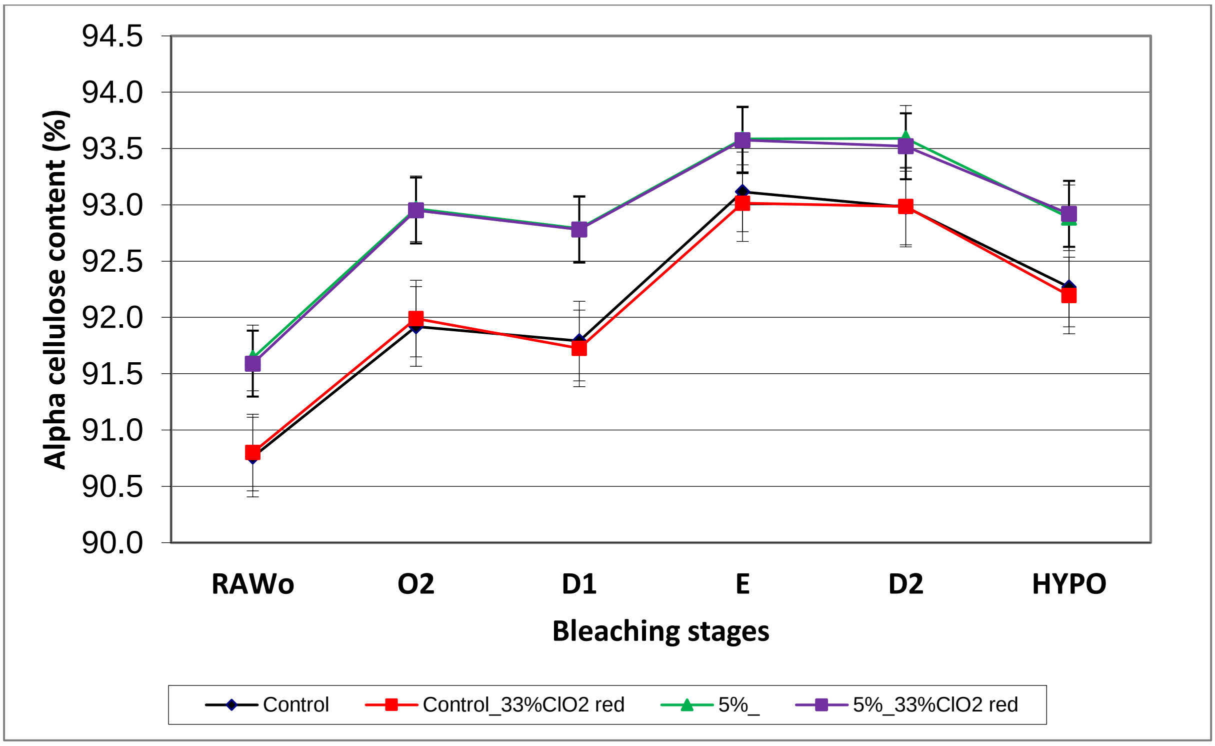
Alpha cellulose is closely associated with S_{18} cellulose and degraded cellulose and this is evident in Figure 4.11(a) which is more of an inverted version of the Figure 4.11(b). The 5% fractionated pulp samples exhibited relatively lower amounts of S_{10} and S_{18} (Table 4.9). For the (33% chlorine drop) these amounts are slightly higher as compared to the regular dosage. Similarly, the amount of degraded cellulose was relatively lower for the 5% pulp samples than in the control pulp samples (Figure 4.11(a)). As a result, the 5% pulp samples had a higher percentage of α-cellulose than the control pulp samples (Figure 4.11(b)). The results suggested that the 5% pulps are characterised by a higher degree of selectivity during bleaching. Consequently, hemicellulose and lignin are selectively removed with minimum degradation on the cellulose. In comparison to the control, it appears that the mass reject rate of 5% may well deliver better pulp quality. Furthermore the 5% pulp shows marginally better pulp quality at the 33% (less) chlorine dioxide compared to regular chlorine dioxide dosage. This is evident in Figure 4.11(b) as both 5% pulps at 33% (less) and regular dosage sit well above 92.5 gridline while the control samples are clearly below this line. This tends to suggest that in order to maintain the same level of purity as the control pulp samples, further adjustment in reducing the chlorine dioxide dosage may perhaps be possible. This would lead to further reduction in savings in bleaching chemicals.

Table 4.9: Impact of mass reject rate on bleaching response – solubility data

Bleaching process stages	**Control**		**5% MRR**	
	S_{10}	**S_{18}**	**S_{10}**	**S_{18}**
Raw pulp	10.74	7.69	10.11	6.67
O_2	9.39	6.70	8.53	5.51
D_1	9.75	6.74	8.56	5.48
E	8.70	5.17	7.70	5.16
D_2 regular dosage	8.45	5.53	7.54	5.23
33% (less)	8.51	5.58	7.61	5.42
H regular dosage	9.71	5.66	8.65	5.36
33% (less)	10.01	5.70	8.98	5.53


5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
S10 - S18 Alkali solubility (%)
0
1
2
3
4
5
6
7
Bleaching stages
Control
Control_33%ClO2 red
5%_
5%_33%ClO2 red

(a)


94.5
94.0
93.5
93.0
92.5
92.0
91.5
91.0
90.5
90.0
Alpha cellulose content (%)
RAWo
O2
D1
E
D2
HYPO
Bleaching stages
Control
Control_33%ClO2 red
5%_
5%_33%ClO2 red

(b)

Figure 4.11: (a) Impact of mass reject rate on bleaching response – solubility data (degraded cellulose), (b) Impact of mass reject rate on bleaching response – solubility data (alpha cellulose)

4.4.3 Impact of mass reject rate on pulp brightness

As expected the brightness of the 5% fractionated pulp remains superior to the unfractionated pulp, (Figure 4.12). Brightness levels are seen to decrease for lower chlorine dioxide dosages. In the first four bleaching stages the 5% fractionated pulps for both regular dosage and 33% (less) chlorine dioxide stages clearly are dominant showing higher levels of brightness. The control pulps at 33% (less) chlorine dioxide have poor brightness at the hand sheet stage showing clearly compromised quality. However, the final stage brightness quality is not compromised for both the 5% pulps at 33% less and regular dosage. Closer inspection of Table 4.10 shows that even with lower chlorine dioxide dosages the final pulp brightness for the 5% remained superior to the control final pulp brightness without chlorine dioxide reduction. This quantifies the potential in saving bleaching chemicals.

Table 4.10: Hand sheet brightness levels for control and 5% pulps

Bleaching process stages	**Percentage ClO_2**	**Control**	**5% MRR**
Brightness	Regular dosage	91.52	92.19
	33% (less)	88.37	91.59
Yellowness	Regular dosage	1.97	2.77
	33% (less)	4.66	3.21
whiteness	Regular dosage	5.54	9.66
	33% (less)	0	2.88

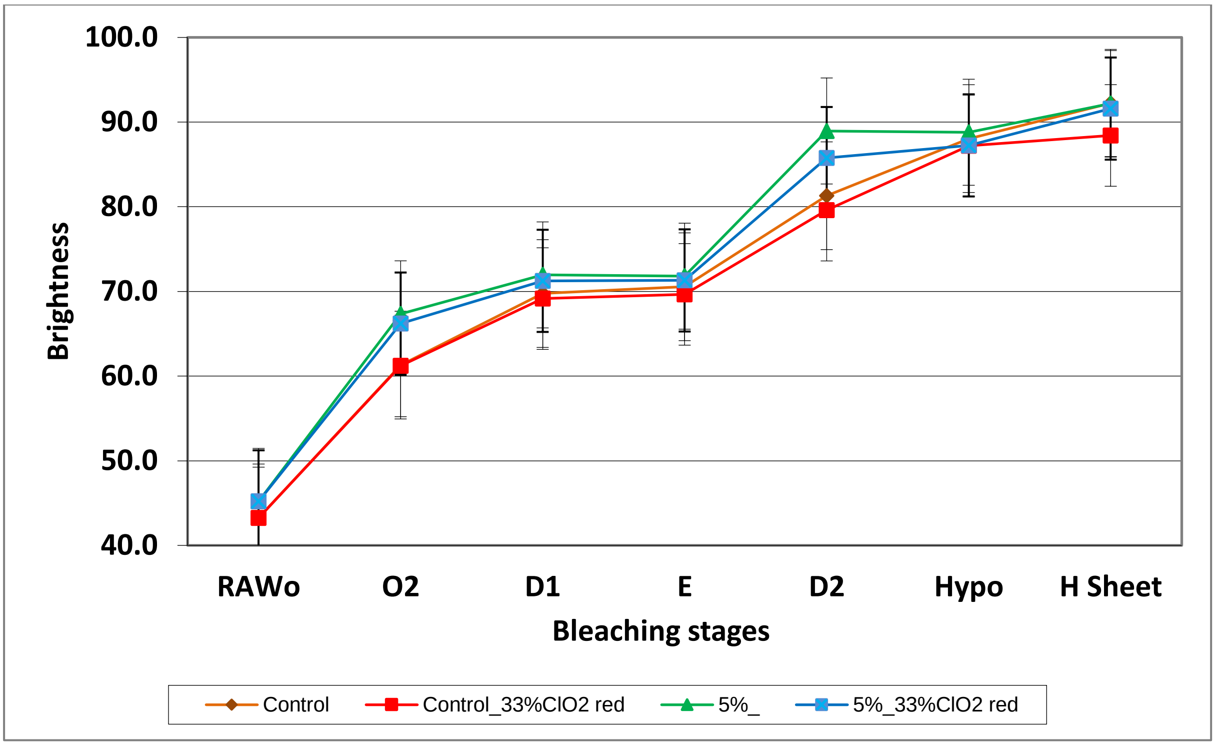


Figure 4.12: Impact of mass reject rate on bleaching response – pulp brightness

4.4.4 Impact of mass reject rate on Copper number

The copper number also serves as an index of reducing impurities in pulp, such as oxycellulose, hydrocellulose, lignin and monosaccharides, which possess reducing power as mentioned in section 3.5. The copper number is an index indicating changes accompanying deterioration in pulps. The copper number data for the 5% fractionated and unfractionated pulp at 33% (less) and regular chlorine dioxide dosage is presented in Figure 4.13 At the D_2 stage the copper number for the 5% fractionated pulp drops lower to that of the control. Results reported in section 4.3.4 presented the control values to be less than both the 5% and 11% at this bleaching stage. For the H stage the 5% fractionated values were less than that of the unfractionated which was expected. The data for 5% fractionated pulp for both 33% (less) and the regular chlorine dioxide dosage bleaching are very close. Thus the

33% chlorine reduction possibly had little effect on the copper number. Perhaps a further reduction could be applied.

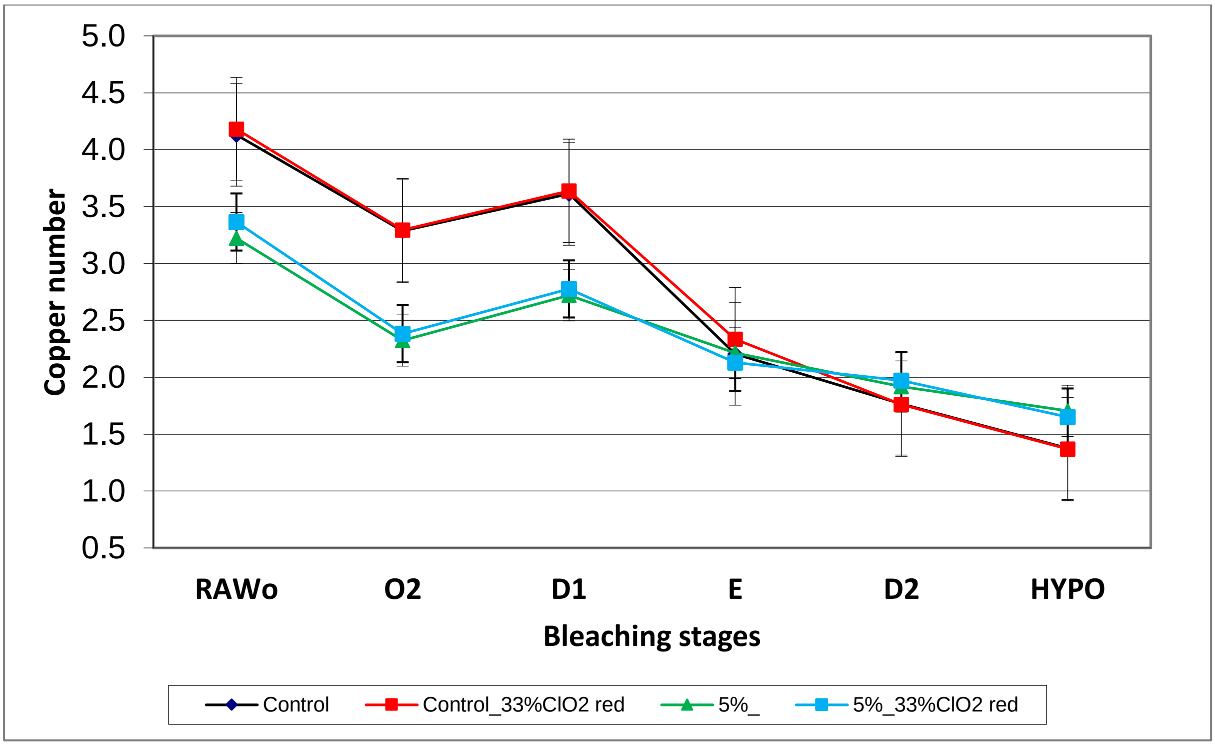


Figure 4.13: Impact of mass reject rate on bleaching response – copper number

4.4.5 Summary

- Bleaching conditions were optimised and potential saving in bleaching chemicals were evaluated.
- The impact of reducing chlorine dioxide dosage at the D_2 stage on critical quality properties namely; k-number, solubility, brightness and copper number has been demonstrated.
- The data acquired indicated that fractionation of dissolving pulp at mass reject rate 5% followed by reducing chlorine dioxide dosage at the D_2 stage by 33% in the bleaching process would not negatively affect the critical pulp quality properties.

5. Conclusions and Recommendations

Operating the hydrocyclone at feedstock consistencies of 0.6% up to 1% produced an acceptable fractionation efficiency which could be practical at industrial level. A feedstock consistency of 0.8% was identified as the optimal feed consistency and was used for all experimental work.

The effects of mass reject rate on hydrocyclone fractionation efficiency for the dissolving pulps were determined.

Maintaining the mass reject rate at a range of 5 - 16% produced better fibre fractionation of the dissolving wood pulps. In this range the hydrocyclone accepts samples held a comparatively lower amount of extractives and acid insoluble material. Mass reject rates of 5% were subsequently used for the bleaching trials. It was also discovered that the cellulose remains intact and is not degraded any further during fractionation by the hydrocyclone. Fractionated pulp samples had the same α-cellulose as the raw pulp samples.

The bleaching properties of the pulp showed that fractionated pulp samples responded better than the unfractionated pulp samples to bleaching. As a result, to maintain the same pulp quality level achieved by unfractionated pulp in normal bleaching conditions, it was then possible to adjust these bleaching conditions. This was done by reducing the bleaching chemical dosage which creates potential chemical savings.

Fractionating at mass reject rate of 5%, and reducing chlorine dioxide at the D_2 stage did not negatively affect the critical pulp quality properties of k-number, solubility, brightness and copper number.

This suggests chlorine dioxide reduction would compromise pulp quality, the pulp was nonetheless within the acceptable production rate. It appears that 33% savings in chlorine dioxide may be achievable

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Appendices

Appendix A: Fractionation of the pulp

	Consistency experiment: Average moisture content (%)				
Sample	**0.1**	**0.3**	**0.6**	**0.8**	**1**
Feed	85.22	87.16	88.06	72.92	83.88
	85.60	86.98	88.85	72.35	87.13
Apex	74.30	68.01	72.61	82.02	72.92
	76.12	75.05	72.34	81.40	72.35
Base	77.96	82.02	77.59	80.09	82.02
	78.59	79.90	76.04	75.25	81.40

Sample	**Mass reject rates experiment: Average moisture content (%)**									
	5	**11**	**16**	**21**	**25**	**32**	**36**	**41**	**45**	**52**
Feed	87.17	84.55	84.55	85.21	86.59	88.63	86.22	88.30	86.83	87.85
	85.21	86.78	86.78	88.23	85.26	88.48	91.15	88.55	88.44	86.44
Apex	70.86	77.04	77.04	76.55	78.18	79.67	76.87	78.46	76.92	75.21
	69.72	78.15	78.15	78.89	78.32	82.38	78.89	75.63	73.56	77.86
Base	78.65	83.52	83.52	76.90	81.76	84.09	79.46	81.12	89.44	77.33
	80.36	79.51	79.51	74.04	85.88	86.13	77.19	81.85	90.75	77.77

	Establishing required consistency (%)				
Sample	**0.1**	**0.3**	**0.6**	**0.8**	**1**
Feed	0.1161	0.3148	0.5995	0.7865	0.9655
	0.1068	0.3134	0.6107	0.7794	0.9761
Apex	0.121	0.3463	0.6842	0.9021	1.1874
	0.1173	0.3576	0.7087	0.8651	1.1839
Base	0.0816	0.1712	0.1975	0.2431	0.2951
	0.0912	0.1809	0.2237	0.2453	0.2894

Sample	Establishing target mass reject rate: Mass Split obtained (%)									
	5	**11**	**16**	**21**	**25**	**32**	**36**	**41**	**45**	**52**
Feed	100	100	100	100	100	100	100	100	100	100
Apex	94	90	84	79	73	69	65	59	55	48
Base	6	10	16	21	27	31	35	41	45	52

Freeness data ml CSF					
	Consistency (%)				
	0.1	0.3	0.6	0.8	1
Feed	589	571	557	536	523
Apex	552	539	565	501	559
Base	445	427	429	426	452
%CSF change	24.415	25.15	22.95	20.60	13.45

Freeness data ml CSF										
	FII B	FI BI	FI BII	FII BII	FI BIII	FI BIV	FII BIII	FI BV	FII BIV	FII BV
	5	11	16	21	25	32	36	41	45	52
Feed	604	588	574	573	598	589	591	594	577	580
Apex	582	558	553	550	587	593	592	592	571	615
Base	525	514	506	517	541	540	547	566	557	577
%CSF change	13.12	12.52	11.85	9.77	9.50	8.22	7.57	4.70	3.57	0.57

Mass reject rate (%)	**S10**			**S18**		
	Feed	**Apex**	**Base**	**Feed**	**Apex**	**Base**
5	11.20	11.30	10.50	6.70	6.80	7.30
11	11.40	11.30	12.80	6.80	6.60	6.30
16	10.50	10.40	10.70	6.90	7.00	7.00
21	12.50	10.00	11.00	6.80	6.60	6.50
32	10.90	10.90	11.50	7.00	7.00	6.00
41	10.60	10.90	11.00	6.70	6.30	6.70
92 α – cellulose pulp	9.7±0.2			6.6±0.1		

Mass reject rate (%)	**Degraded cellulose (%)**			**α – cellulose (%)**		
	Feed	**Apex**	**Base**	**Feed**	**Apex**	**Base**
5	5.60	5.50	3.10	91.10	91.00	91.10
11	4.70	6.50	3.60	91.10	90.40	91.30
16	3.60	3.30	3.50	90.30	91.20	91.00
21	5.70	3.20	3.40	90.30	92.00	91.30
32	3.70	3.80	5.50	91.00	91.00	91.20
41	4.00	4.60	4.30	91.40	91.40	91.20
92 α – cellulose pulp	3.1±0.2			91.9±0.1		

Appendix B: Bleachability of the pulp

Control

Wet chemistry analysis	RAWo	O2	D1	E	D2	HYPO	
Viscosity/cP R1	484.00	389.20	429.80	539.20	446.50	525.80	
Viscosity/cP R2	484.00	389.20	429.80	539.20	446.50	525.80	
Average	**484.00**	**389.20**	**429.80**	**539.20**	**446.50**	**525.80**	
std	0.00	0.00	0.00	0.00	0.00	0.00	
se	0.00	0.00	0.00	0.00	0.00	0.00	
Lignin (K-number) R1	3.50	1.33	0.98	0.87	0.78	0.69	
Lignin (K-number) R2	3.50	1.33	0.98	0.87	0.78	0.69	
Average	**3.50**	**1.33**	**0.98**	**0.87**	**0.78**	**0.69**	
std	0.00	0.00	0.00	0.00	0.00	0.00	
se	0.00	0.00	0.00	0.00	0.00	0.00	
(β+γ) - cellulose content (S10) R1	11.31	10.50	10.12	9.21	9.08	10.51	
(β+γ) - cellulose content (S10) R2	11.31	10.50	10.12	9.21	9.08	10.51	
Average	**11.31**	**10.50**	**10.12**	**9.21**	**9.08**	**10.51**	
std	0.00	0.00	0.00	0.00	0.00	0.00	
se	0.00	0.00	0.00	0.00	0.00	0.00	
γ - cellulose content (hemicellulose) R1	6.79	5.76	6.06	5.14	4.99	5.08	
γ - cellulose content (hemicellulose) R2	6.79	5.76	6.06	5.14	4.99	5.08	
Average	**6.79**	**5.76**	**6.06**	**5.14**	**4.99**	**5.08**	
std	0.00	0.00	0.00	0.00	0.00	0.00	
se	0.00	0.00	0.00	0.00	0.00	0.00	
β - cellulose content (degraded cellulose) R1	4.52	4.74	4.06	4.07	4.09	5.43	
β - cellulose content (degraded cellulose) R2	4.52	4.74	4.06	4.07	4.09	5.43	
Average	**4.52**	**4.74**	**4.06**	**4.07**	**4.09**	**5.43**	
std	0.00	0.00	0.00	0.00	0.00	0.00	
se	0.00	0.00	0.00	0.00	0.00	0.00	
α - cellulose content R1	90.95	91.87	91.91	92.83	92.97	92.21	
α - cellulose content R2	90.95	91.87	91.91	92.83	92.97	92.21	
Average	**90.95**	**91.87**	**91.91**	**92.83**	**92.97**	**92.21**	
std	0.00	0.00	0.00	0.00	0.00	0.00	
se	0.00	0.00	0.00	0.00	0.00	0.00	
Copper number R1	3.22	2.36	2.58	1.72	1.84	1.42	
Copper number R2	3.22	2.36	2.58	1.72	1.84	1.42	
Average	**3.22**	**2.36**	**2.58**	**1.72**	**1.84**	**1.42**	
std	0.00	0.00	0.00	0.00	0.00	0.00	
se	0.00	0.00	0.00	0.00	0.00	0.00	
							H Sheet
Brightness R1	43.80	62.00	67.80	73.60	81.30	88.10	88.90
Brightness R2	43.80	62.00	67.80	73.60	81.30	88.10	88.90
Average	**43.80**	**62.00**	**67.80**	**73.60**	**81.30**	**88.10**	**88.90**
std	0.00	0.00	0.00	0.00	0.00	0.00	0.00
se	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Average results	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/cP	484.00	389.20	429.80	539.20	446.50	525.80	
Lignin (K-number)	3.50	1.33	0.98	0.87	0.78	0.69	
(β+γ) - cellulose content (S10)	11.31	10.50	10.12	9.21	9.08	10.51	
γ - cellulose content (hemicellulose)	6.79	5.76	6.06	5.14	4.99	5.08	
β - cellulose content (degraded cellulose)	4.52	4.74	4.06	4.07	4.09	5.43	
α - cellulose content	90.95	91.87	91.91	92.83	92.97	92.21	
Copper numbers	3.22	2.36	2.58	1.72	1.84	1.42	
Brightness	43.80	62.00	67.80	73.60	81.30	88.10	88.90

se	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/cP	0.00	0.00	0.00	0.00	0.00	0.00	
Lignin (K-number)	0.00	0.00	0.00	0.00	0.00	0.00	
(β+γ) - cellulose content (S10)	0.00	0.00	0.00	0.00	0.00	0.00	
γ - cellulose content (hemicellulose)	0.00	0.00	0.00	0.00	0.00	0.00	
β - cellulose content (degraded cellulose)	0.00	0.00	0.00	0.00	0.00	0.00	
α - cellulose content	0.00	0.00	0.00	0.00	0.00	0.00	
Copper numbers	0.00	0.00	0.00	0.00	0.00	0.00	
Brightness	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Mass reject 5%

Wet chemistry analysis	RAWo	O2	D1	E	D2	HYPO	
Viscosity/cP R1	598.60	555.50	605.00	619.40	606.90	617.30	
Viscosity/cP R2	600.00	564.90	604.60	601.50	628.00	632.20	
Average	599.30	560.20	604.80	610.45	617.45	624.75	
std	0.99	6.65	0.28	12.66	14.92	10.54	
se	0.70	4.70	0.20	8.95	10.55	7.45	
Lignin (K-number) R1	2.86	1.12	0.75	0.69	0.62	0.55	
Lignin (K-number) R2	2.86	1.20	0.92	0.76	0.48	0.46	
Average	2.86	1.16	0.84	0.73	0.55	0.51	
std	0.00	0.06	0.12	0.05	0.10	0.06	
se	0.00	0.04	0.09	0.04	0.07	0.05	
(β+γ) - cellulose content (S10) R1	9.78	8.61	8.47	7.47	7.01	6.85	
(β+γ) - cellulose content (S10) R2	9.78	8.48	8.37	6.52	6.44	6.91	
Average	9.78	8.55	8.42	7.00	6.73	6.88	
std	0.00	0.09	0.07	0.67	0.40	0.04	
se	0.00	0.06	0.05	0.48	0.29	0.03	
γ - cellulose content (hemicellulose) R1	6.75	4.46	5.70	5.01	4.51	4.38	
γ - cellulose content (hemicellulose) R2	6.75	4.20	4.28	4.36	2.25	4.49	
Average	6.75	4.33	4.99	4.69	3.38	4.44	
std	0.00	0.18	1.00	0.46	1.60	0.08	
se	0.00	0.13	0.71	0.33	1.13	0.06	
β - cellulose content (degraded cellulose) R1	3.03	4.15	2.77	2.46	2.50	2.47	
β - cellulose content (degraded cellulose) R2	3.03	4.28	4.09	2.16	4.19	2.40	
Average	3.03	4.22	3.43	2.31	3.35	2.44	
std	0.00	0.09	0.93	0.21	1.20	0.05	
se	0.00	0.07	0.66	0.15	0.85	0.04	
α - cellulose content R1	91.74	93.47	92.92	93.76	94.24	94.39	
α - cellulose content R2	91.74	93.66	93.68	94.56	95.66	94.30	
Average	91.74	93.56	93.30	94.16	94.95	94.35	
std	0.00	0.14	0.54	0.57	1.00	0.06	
se	0.00	0.10	0.38	0.40	0.71	0.05	
Copper number R1	3.62	2.59	2.85	1.78	1.75	1.37	
Copper number R2	3.29	2.89	2.87	2.25	1.95	1.42	
Average	3.45	2.74	2.86	2.02	1.85	1.39	
std	0.23	0.21	0.01	0.33	0.14	0.03	
se	0.16	0.15	0.01	0.23	0.10	0.02	
							H Sheet
Brightness R1	43.5	67.4	69.3	73.9	88.7	88.8	89.3
Brightness R2	43.5	67.4	69.3	73.9	88.7	88.8	89.3
Average	43.50	67.40	69.30	73.90	88.70	88.80	89.30
std	0.00	0.00	0.00	0.00	0.00	0.00	0.00
se	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Average results	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/cP	599.30	560.20	604.80	610.45	617.45	624.75	
Lignin (K-number)	2.86	1.16	0.84	0.73	0.55	0.51	
(β+γ) - cellulose content (S10)	9.78	8.55	8.42	7.00	6.73	6.88	
γ - cellulose content (hemicellulose)	6.75	4.33	4.99	4.69	3.38	4.44	
β - cellulose content (degraded cellulose)	3.03	4.22	3.43	2.31	3.35	2.44	
α - cellulose content	91.74	93.56	93.30	94.16	94.95	94.35	
Copper numbers	3.45	2.74	2.86	2.02	1.85	1.39	
Brightness	43.50	67.40	69.30	73.90	88.70	88.80	89.30

se	RAWo	O2	D1	E	D2	HYPO		H Sheet
Viscosity/cP	0.70	4.70	0.20	8.95	10.55	7.45	4.38	
Lignin (K-number)	0.00	0.04	0.09	0.04	0.07	0.05	4.549	
(β+γ) - cellulose content (S10)	0.00	0.06	0.05	0.48	0.29	0.03		
γ - cellulose content (hemicellulose)	0.00	0.13	0.71	0.33	1.13	0.06		
β - cellulose content (degraded cellulose)	0.00	0.07	0.66	0.15	0.85	0.04		
α - cellulose content	0.00	0.10	0.38	0.40	0.71	0.05		
Copper numbers	0.16	0.15	0.01	0.23	0.10	0.02		
Brightness	0.00	0.00	0.00	0.00	0.00	0.00		0.00

Mass reject 11%

Wet chemistry analysis	RAWo	O2	D1	E	D2	HYPO	
Viscosity/cP R1	498.80	481.90	527.90	552.70	497.20	450.20	
Viscosity/cP R2	497.10	485.60	528.80	547.90	498.80	443.80	
Average	497.95	483.75	528.35	550.30	498.00	447.00	
std	1.20	2.62	0.64	3.39	1.13	4.53	
se	0.85	1.85	0.45	2.40	0.80	3.20	
Lignin (K-number) R1	2.29	0.85	0.76	0.71	0.37	0.28	
Lignin (K-number) R2	2.29	1.12	0.83	0.67	0.34	0.27	
Average	2.29	0.99	0.80	0.69	0.36	0.28	
std	0.00	0.19	0.05	0.03	0.02	0.01	
se	0.00	0.13	0.04	0.02	0.02	0.01	
(β+γ) - cellulose content (S10) R1	5.71	5.83	6.70	5.44	5.11	5.40	
(β+γ) - cellulose content (S10) R2	5.71	5.83	6.70	5.44	5.11	5.62	
Average	5.71	5.83	6.70	5.44	5.11	5.51	
std	0.00	0.00	0.00	0.00	0.00	0.16	
se	0.00	0.00	0.00	0.00	0.00	0.11	
γ - cellulose content (hemicellulose) R1	4.58	4.30	5.42	4.48	4.54	4.36	
γ - cellulose content (hemicellulose) R2	4.51	4.34	5.38	4.48	4.64	4.42	
Average	4.55	4.32	5.40	4.48	4.59	4.39	
std	0.05	0.03	0.03	0.00	0.07	0.04	
se	0.04	0.02	0.02	0.00	0.05	0.03	
β - cellulose content (degraded cellulose) R1	1.13	1.53	1.28	0.96	0.57	1.04	
β - cellulose content (degraded cellulose) R2	1.20	1.49	1.32	0.96	0.47	1.20	
Average	1.17	1.51	1.30	0.96	0.52	1.12	
std	0.05	0.03	0.03	0.00	0.07	0.11	
se	0.04	0.02	0.02	0.00	0.05	0.08	
α - cellulose content R1	94.86	94.94	93.94	95.04	95.18	95.12	
α - cellulose content R2	94.89	94.92	93.96	95.04	95.13	94.98	
Average	94.87	94.93	93.95	95.04	95.15	95.05	
std	0.02	0.01	0.01	0.00	0.04	0.10	
se	0.02	0.01	0.01	0.00	0.02	0.07	
Copper number R1	3.22	2.35	2.58	1.72	1.84	1.42	
Copper number R2	3.11	2.80	2.83	2.06	1.97	1.55	
Average	3.17	2.57	2.70	1.89	1.90	1.48	
std	0.08	0.32	0.17	0.24	0.09	0.09	
se	0.06	0.22	0.12	0.17	0.07	0.06	
							H Sheet
Brightness R1	48.5	66.8	71.9	74.4	84.0	88.9	89.8
Brightness R2	48.5	66.8	71.9	74.4	84.0	88.9	89.8
Average	48.50	66.80	71.90	74.40	84.00	88.91	89.80
std	0.00	0.00	0.00	0.00	0.00	0.00	0.00
se	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Average results	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/cP	497.95	483.75	528.35	550.30	498.00	447.00	
Lignin (K-number)	2.29	0.99	0.80	0.69	0.36	0.28	
(β+γ) - cellulose content (S10)	5.71	5.83	6.70	5.44	5.11	5.51	
γ - cellulose content (hemicellulose)	4.55	4.32	5.40	4.48	4.59	4.39	
β - cellulose content (degraded cellulose)	1.17	1.51	1.30	0.96	0.52	1.12	
α - cellulose content	94.87	94.93	93.95	95.04	95.15	95.05	
Copper numbers	3.17	2.57	2.70	1.89	1.90	1.48	
Brightness	48.50	66.80	71.90	74.40	84.00	88.91	89.80

se	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/cP	0.85	1.85	0.45	2.40	0.80	3.20	
Lignin (K-number)	0.00	0.13	0.04	0.02	0.02	0.01	
(β+γ) - cellulose content (S10)	0.00	0.00	0.00	0.00	0.00	0.11	
γ - cellulose content (hemicellulose)	0.04	0.02	0.02	0.00	0.05	0.03	
β - cellulose content (degraded cellulose)	0.04	0.02	0.02	0.00	0.05	0.08	
α - cellulose content	0.02	0.01	0.01	0.00	0.02	0.07	
Copper numbers	0.06	0.22	0.12	0.17	0.07	0.06	
Brightness	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix C: Bleaching Optimization

Control (unfractionated) at 0.6% ClO

Wet chemistry analysis	RAWo	O2	D1	E	D2	HYPO	
Viscosity/ R1	738.90	642.90	571.20	540.00	631.20	561.00	
Viscosity/ R2	729.70	653.80	579.70	552.40	643.60	550.80	
Average	734.30	648.35	575.45	546.20	637.40	555.90	
std	6.51	7.71	6.01	8.77	8.77	7.21	
se	4.60	5.45	4.25	6.20	6.20	5.10	
Lignin (K-number) R1	2.13	1.28	0.92	0.82	0.43	0.32	
Lignin (K-number) R2	2.09	1.24	0.89	0.85	0.46	0.39	
Average	2.11	1.26	0.91	0.83	0.44	0.36	
std	0.03	0.03	0.03	0.03	0.03	0.05	
se	0.02	0.02	0.02	0.02	0.02	0.04	
(β+γ) - cellulose content (S10) R1	10.70	9.38	9.83	8.79	8.44	9.59	
(β+γ) - cellulose content (S10) R2	10.77	9.29	9.80	8.53	8.46	9.83	
Average	10.74	9.34	9.82	8.66	8.45	9.71	
std	0.05	0.06	0.02	0.18	0.01	0.17	
se	0.04	0.05	0.01	0.13	0.01	0.12	
γ - cellulose content (hemicellulose) R1	7.77	6.69	6.80	5.13	5.52	5.70	
γ - cellulose content (hemicellulose) R2	7.62	6.53	6.76	5.24	5.54	5.61	
Average	7.70	6.61	6.78	5.19	5.53	5.66	
std	0.05	0.06	0.01	0.04	0.01	0.03	
se	0.04	0.04	0.01	0.03	0.01	0.02	
β - cellulose content (degraded cellulose) R1	2.94	2.69	3.03	3.57	2.92	3.89	
β - cellulose content (degraded cellulose) R2	2.94	2.51	3.00	3.35	2.88	4.37	
Average	2.94	2.60	3.02	3.46	2.90	4.13	
std	0.00	0.06	0.01	0.08	0.01	0.17	
se	0.00	0.04	0.01	0.05	0.01	0.12	
α - cellulose content R1	90.76	91.96	91.69	93.08	93.02	92.35	
α - cellulose content R2	90.76	91.88	91.89	93.15	92.94	92.19	
Average	90.76	91.92	91.79	93.12	92.98	92.27	
std	0.00	0.03	0.07	0.02	0.03	0.06	
se	0.00	0.02	0.05	0.02	0.02	0.04	
Copper number R1	4.13	3.53	3.62	2.31	1.77	1.36	
Copper number R2	4.13	3.04	3.60	2.10	1.76	1.39	
Average	4.13	3.29	3.61	2.21	1.77	1.38	
std	0.00	0.35	0.01	0.14	0.00	0.03	
se	0.00	0.25	0.01	0.10	0.00	0.02	
							H Sheet
Brightness R1	43.50	61.20	70.10	69.80	81.40	88.20	92.94
Brightness R2	43.00	61.40	69.40	71.30	81.20	87.90	91.52
Average	43.25	61.30	69.75	70.55	81.30	88.05	92.23
std	0.35	0.14	0.49	1.06	0.14	0.21	1.00
se	0.25	0.10	0.35	0.75	0.10	0.15	0.71

Average results	RAWo	O2	D1	E	D2	HYPO	H Seet
Viscosity/ml/g	734.30	648.35	575.45	546.20	637.40	555.90	
Lignin (K-number)	2.11	1.26	0.91	0.83	0.44	0.36	
(β+γ) - cellulose content (S10)	10.74	9.34	9.82	8.66	8.45	9.71	
γ - cellulose content (hemicellulose)	7.70	6.61	6.78	5.19	5.53	5.66	
β - cellulose content (degraded cellulose)	2.94	2.60	3.02	3.46	2.90	4.13	
α - cellulose content	90.76	91.92	91.79	93.12	92.98	92.27	
Copper numbers	4.13	3.29	3.61	2.21	1.77	1.38	
Brightness	43.25	61.30	69.75	70.55	81.30	88.05	92.23

se	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/ml/g	4.60	5.45	4.25	6.20	6.20	5.10	
Lignin (K-number)	0.02	0.02	0.02	0.02	0.02	0.04	
(β+γ) - cellulose content (S10)	0.04	0.05	0.01	0.13	0.01	0.12	
γ - cellulose content (hemicellulose)	0.04	0.04	0.01	0.03	0.01	0.02	
β - cellulose content (degraded cellulose)	0.00	0.04	0.01	0.05	0.01	0.12	
α - cellulose content	0.00	0.02	0.05	0.02	0.02	0.04	
Copper numbers	0.00	0.25	0.01	0.10	0.00	0.02	
Brightness	0.25	0.10	0.35	0.75	0.10	0.15	0.71

Control (unfractionated) at 0.4% ClO

Wet chemistry analysis	RAWo	O2	D1	E	D2	HYPO	
Viscosity/ R1	738.90	664.40	571.70	528.30	659.10	572.10	
Viscosity/ R2	729.70	660.50	572.20	540.80	658.00	581.60	
Average	734.30	662.45	571.95	534.55	658.55	576.85	
std	6.51	2.76	0.35	8.84	0.78	6.72	
se	4.60	1.95	0.25	6.25	0.55	4.75	
Lignin (K-number) R1	2.13	1.28	0.92	0.82	0.64	0.57	
Lignin (K-number) R2	2.09	1.31	0.96	0.78	0.57	0.53	
Average	2.11	1.30	0.94	0.80	0.60	0.55	
std	0.03	0.03	0.03	0.03	0.05	0.03	
se	0.02	0.02	0.02	0.02	0.04	0.02	
(β+γ) - cellulose content (S10) R1	10.70	9.38	9.61	8.53	8.50	9.99	
(β+γ) - cellulose content (S10) R2	10.77	9.50	9.77	8.79	8.52	10.02	
Average	10.74	9.44	9.69	8.66	8.51	10.01	
std	0.05	0.08	0.11	0.18	0.01	0.02	
se	0.04	0.06	0.08	0.13	0.01	0.01	
γ - cellulose content (hemicellulose) R1	7.77	6.86	6.61	5.18	5.62	5.62	
γ - cellulose content (hemicellulose) R2	7.62	6.73	6.77	5.17	5.45	5.77	
Average	7.70	6.80	6.69	5.18	5.54	5.70	
std	0.11	0.09	0.11	0.01	0.12	0.11	
se	0.07	0.06	0.08	0.00	0.09	0.07	
β - cellulose content (degraded cellulose) R1	3.15	2.76	3.04	3.55	2.92	4.22	
β - cellulose content (degraded cellulose) R2	3.15	2.77	3.00	3.61	2.98	4.25	
Average	3.15	2.77	3.02	3.58	2.95	4.24	
std	0.00	0.00	0.01	0.02	0.02	0.01	
se	0.00	0.00	0.01	0.01	0.01	0.01	
α - cellulose content R1	90.80	92.09	91.72	92.98	93.00	92.28	
α - cellulose content R2	90.80	91.89	91.73	93.05	92.97	92.11	
Average	90.80	91.99	91.73	93.02	92.99	92.20	
std	0.00	0.07	0.00	0.02	0.01	0.06	
se	0.00	0.05	0.00	0.02	0.01	0.04	
Copper number R1	4.18	3.47	3.65	2.32	1.76	1.35	
Copper number R2	4.18	3.12	3.63	2.34	1.76	1.39	
Average	4.18	3.29	3.64	2.33	1.76	1.37	
std	0.00	0.24	0.01	0.01	0.01	0.03	
se	0.00	0.17	0.01	0.01	0.00	0.02	
							H sheet
Brightness R1	43.50	61.50	69.80	69.50	79.80	86.90	88.47
Brightness R2	43.00	60.90	68.50	69.80	79.40	87.50	88.37
Average	43.25	61.20	69.15	69.65	79.60	87.20	88.42
std	0.35	0.42	0.92	0.21	0.28	0.42	0.07
se	0.25	0.30	0.65	0.15	0.20	0.30	0.05

Average results	RAWo	O2	D1	E	D2	HYPO
Viscosity/ml/g	734.30	662.45	571.95	534.55	658.55	576.85
Lignin (K-number)	2.11	1.30	0.94	0.80	0.60	0.55
(β+γ) - cellulose content (S10)	10.74	9.44	9.69	8.66	8.51	10.01
γ - cellulose content (hemicellulose)	7.70	6.80	6.69	5.18	5.54	5.70
β - cellulose content (degraded cellulose)	3.15	2.77	3.02	3.58	2.95	4.24
α - cellulose content	90.80	91.99	91.73	93.02	92.99	92.20
Copper numbers	4.18	3.29	3.64	2.33	1.76	1.37
Brightness	43.25	61.20	69.15	69.65	79.60	87.20

se	RAWo	O2	D1	E	D2	HYPO
Viscosity/ml/g	4.60	1.95	0.25	6.25	0.55	4.75
Lignin (K-number)	0.02	0.02	0.02	0.02	0.04	0.02
(β+γ) - cellulose content (S10)	0.04	0.06	0.08	0.13	0.01	0.01
γ - cellulose content (hemicellulose)	0.07	0.06	0.08	0.00	0.09	0.07
β - cellulose content (degraded cellulose)	0.00	0.00	0.01	0.01	0.01	0.01
α - cellulose content	0.00	0.05	0.00	0.02	0.01	0.04
Copper numbers	0.00	0.17	0.01	0.01	0.00	0.02
Brightness	0.25	0.30	0.65	0.15	0.20	0.30

Mass reject 5% at 0.6% ClO

Wet chemistry analysis	RAWo	O2	D1	E	D2	HYPO	
Viscosity/ R1	572.10	496.80	559.00	537.10	529.50	447.30	
Viscosity/ R2	564.10	497.50	555.70	534.10	536.90	461.00	
Average	568.10	497.15	557.35	535.60	533.20	454.15	
std	5.66	0.49	2.33	2.12	5.23	9.69	
se	4.00	0.35	1.65	1.50	3.70	6.85	
Lignin (K-number) R1	2.38	1.31	0.75	0.50	0.39	0.28	
Lignin (K-number) R2	2.41	1.38	0.71	0.46	0.36	0.28	
Average	2.40	1.35	0.73	0.48	0.37	0.28	
std	0.03	0.05	0.03	0.03	0.03	0.00	
se	0.02	0.04	0.02	0.02	0.02	0.00	
(β+γ) - cellulose content (S10) R1	10.11	8.46	8.63	7.74	7.52	8.66	
(β+γ) - cellulose content (S10) R2	10.10	8.61	8.64	7.65	7.55	8.64	
Average	10.11	8.54	8.64	7.70	7.54	8.65	
std	0.01	0.11	0.01	0.06	0.02	0.01	
se	0.00	0.07	0.00	0.04	0.02	0.01	
γ - cellulose content (hemicellulose) R1	6.61	5.61	5.75	5.05	5.18	5.46	
γ - cellulose content (hemicellulose) R2	6.72	5.59	5.72	5.11	5.27	5.26	
Average	6.67	5.60	5.74	5.08	5.23	5.36	
std	0.08	0.01	0.02	0.04	0.06	0.14	
se	0.05	0.01	0.02	0.03	0.04	0.10	
β - cellulose content (degraded cellulose) R1	3.50	2.85	2.88	2.69	2.34	3.40	
β - cellulose content (degraded cellulose) R2	3.50	3.03	2.95	2.48	2.20	3.53	
Average	3.50	2.94	2.92	2.59	2.27	3.47	
std	0.00	0.06	0.02	0.07	0.05	0.05	
se	0.00	0.04	0.02	0.05	0.03	0.03	
α - cellulose content R1	91.64	92.97	92.81	93.60	93.65	93.04	
α - cellulose content R2	91.64	92.96	92.77	93.57	93.53	92.73	
Average	91.64	92.97	92.79	93.59	93.59	92.89	
std	0.00	0.00	0.01	0.01	0.04	0.11	
se	0.00	0.00	0.01	0.01	0.03	0.08	
Copper number R1	3.22	2.24	2.69	2.12	1.86	1.64	
Copper number R2	3.22	2.40	2.75	2.31	1.98	1.77	
Average	3.22	2.32	2.72	2.22	1.92	1.71	
std	0.00	0.11	0.04	0.13	0.09	0.09	
se	0.00	0.08	0.03	0.09	0.06	0.06	
							H Sheet
Brightness R1	45.10	67.60	72.00	72.10	88.90	88.60	92.26
BrightnessR2	45.30	67.10	71.90	71.50	89.00	89.00	92.12
Average	45.20	67.35	71.95	71.80	88.95	88.80	92.19
std	0.14	0.35	0.07	0.42	0.07	0.28	0.10
se	0.10	0.25	0.05	0.30	0.05	0.20	0.07

Average results	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/ml/g	568.10	497.15	557.35	535.60	533.20	454.15	
Lignin (K-number)	2.40	1.35	0.73	0.48	0.37	0.28	
(β+γ) - cellulose content (S10)	10.11	8.54	8.64	7.70	7.54	8.65	
γ - cellulose content (hemicellulose)	6.67	5.60	5.74	5.08	5.23	5.36	
β - cellulose content (degraded cellulose)	3.50	2.94	2.92	2.59	2.27	3.47	
α - cellulose content	91.64	92.97	92.79	93.59	93.59	92.89	
Copper numbers	3.22	2.32	2.72	2.22	1.92	1.71	
Brightness	45.20	67.35	71.95	71.80	88.95	88.80	92.19

se	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/ml/g	4.00	0.35	1.65	1.50	3.70	6.85	
Lignin (K-number)	0.02	0.04	0.02	0.02	0.02	0.00	
(β+γ) - cellulose content (S10)	0.00	0.07	0.00	0.04	0.02	0.01	
γ - cellulose content (hemicellulose)	0.05	0.01	0.02	0.03	0.04	0.10	
β - cellulose content (degraded cellulose)	0.00	0.04	0.02	0.05	0.03	0.03	
α - cellulose content	0.00	0.00	0.01	0.01	0.03	0.08	
Copper numbers	0.00	0.08	0.03	0.09	0.06	0.06	
Brightness	0.10	0.25	0.05	0.30	0.05	0.20	0.07

Mass reject 5% at 0.4% ClO

Wet chemistry analysis	RAWo	O2	D1	E	D2	HYPO	
Viscosity/ R1	572.10	515.10	576.90	460.40	560.80	476.80	
Viscosity/ R2	564.10	508.00	587.80	473.00	565.50	473.40	
Average	568.10	511.55	582.35	466.70	563.15	475.10	
std	5.66	5.02	7.71	8.91	3.32	2.40	
se	4.00	3.55	5.45	6.30	2.35	1.70	
Lignin (K-number) R1	2.38	1.31	0.71	0.43	0.43	0.32	
Lignin (K-number) R2	2.41	1.35	0.78	0.46	0.46	0.32	
Average	2.40	1.33	0.75	0.44	0.44	0.32	
std	0.03	0.03	0.05	0.03	0.03	0.00	
se	0.02	0.02	0.04	0.02	0.02	0.00	
(β+γ) - cellulose content (S10) R1	10.11	8.55	8.70	7.67	7.57	9.03	
(β+γ) - cellulose content (S10) R2	10.10	8.56	8.69	7.71	7.65	8.92	
Average	10.11	8.56	8.70	7.69	7.61	8.98	
std	0.01	0.01	0.01	0.03	0.06	0.08	
se	0.00	0.00	0.00	0.02	0.04	0.05	
γ - cellulose content (hemicellulose) R1	6.61	5.59	5.75	5.19	5.37	5.50	
γ - cellulose content (hemicellulose) R2	6.72	5.52	5.83	5.24	5.46	5.56	
Average	6.67	5.56	5.79	5.22	5.42	5.53	
std	0.08	0.05	0.06	0.04	0.06	0.04	
se	0.05	0.04	0.04	0.02	0.04	0.03	
β - cellulose content (degraded cellulose) R1	3.38	3.02	2.92	2.54	2.28	3.45	
β - cellulose content (degraded cellulose) R2	3.38	3.12	2.86	2.47	2.19	3.36	
Average	3.38	3.07	2.89	2.51	2.24	3.41	
std	0.00	0.04	0.02	0.02	0.03	0.03	
se	0.00	0.02	0.01	0.02	0.02	0.02	
α - cellulose content R1	91.59	92.90	92.82	93.62	93.59	93.08	
α - cellulose content R2	91.59	93.00	92.74	93.53	93.45	92.76	
Average	91.59	92.95	92.78	93.58	93.52	92.92	
std	0.00	0.04	0.03	0.03	0.05	0.11	
se	0.00	0.02	0.02	0.02	0.04	0.08	
Copper number R1	3.36	2.44	2.80	2.09	1.87	1.56	
Copper number R2	3.36	2.33	2.76	2.16	2.07	1.74	
Average	3.36	2.38	2.78	2.13	1.97	1.65	
std	0.00	0.07	0.03	0.05	0.14	0.13	
se	0.00	0.05	0.02	0.03	0.10	0.09	
							H Sheet
Brightness R1	45.10	66.50	71.60	71.40	83.60	86.90	91.09
Brightness R2	45.30	65.90	70.90	71.20	87.90	87.60	92.10
Average	45.20	66.20	71.25	71.30	85.75	87.25	91.60
std	0.14	0.42	0.49	0.14	3.04	0.49	0.71
se	0.10	0.30	0.35	0.10	2.15	0.35	0.50

Average results	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/ml/g	568.10	511.55	582.35	466.70	563.15	475.10	
Lignin (K-number)	2.40	1.33	0.75	0.44	0.44	0.32	
(β+γ) - cellulose content (S10)	10.11	8.56	8.70	7.69	7.61	8.98	
γ - cellulose content (hemicellulose)	6.67	5.56	5.79	5.22	5.42	5.53	
β - cellulose content (degraded cellulose)	3.38	3.07	2.89	2.51	2.24	3.41	
α - cellulose content	91.59	92.95	92.78	93.58	93.52	92.92	
Copper numbers	3.36	2.38	2.78	2.13	1.97	1.65	
Brightness	45.20	66.20	71.25	71.30	85.75	87.25	91.60

se	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/ml/g	4.00	3.55	5.45	6.30	2.35	1.70	
Lignin (K-number)	0.02	0.02	0.04	0.02	0.02	0.00	
(β+γ) - cellulose content (S10)	0.00	0.00	0.00	0.02	0.04	0.05	
γ - cellulose content (hemicellulose)	0.05	0.04	0.04	0.02	0.04	0.03	
β - cellulose content (degraded cellulose)	0.00	0.02	0.01	0.02	0.02	0.02	
α - cellulose content	0.00	0.02	0.02	0.02	0.04	0.08	
Copper numbers	0.00	0.05	0.02	0.03	0.10	0.09	
Brightness	0.10	0.30	0.35	0.10	2.15	0.35	0.50

Mass reject 11% at 0.6%

Wet chemistry analysis	RAWo	O2	D1	E	D2	HYPO	
Viscosity/CED R1	498.80	481.90	527.90	552.70	497.20	450.20	
Viscosity/CED R2	497.10	485.60	528.80	547.90	498.80	443.80	
Average	497.95	483.75	528.35	550.30	498.00	447.00	
std	1.20	2.62	0.64	3.39	1.13	4.53	
se	0.85	1.85	0.45	2.40	0.80	3.20	
Lignin (K-number) R1	2.29	0.85	0.76	0.71	0.37	0.28	
Lignin (K-number) R2	2.29	1.12	0.83	0.67	0.34	0.27	
Average	2.29	0.99	0.80	0.69	0.36	0.28	
std	0.00	0.19	0.05	0.03	0.02	0.01	
se	0.00	0.13	0.04	0.02	0.02	0.01	
(β+γ) - cellulose content (S10) R1	5.71	3.25	5.20	6.19	5.04	5.40	
(β+γ) - cellulose content (S10) R2	5.71	5.83	6.70	5.44	5.11	5.62	
Average	5.71	4.54	5.95	5.82	5.08	5.51	
std	0.00	1.82	1.06	0.53	0.05	0.16	
se	0.00	1.29	0.75	0.38	0.04	0.11	
γ - cellulose content (hemicellulose) R1	3.00	4.32	5.40	4.48	4.59	4.39	
γ - cellulose content (hemicellulose) R2	3.00	4.32	5.40	4.48	4.59	4.39	
Average	3.00	4.32	5.40	4.48	4.59	4.39	
std	0.00	0.00	0.00	0.00	0.00	0.00	
se	0.00	0.00	0.00	0.00	0.00	0.00	
β - cellulose content (degraded cellulose) R1	2.71	-1.07	-0.20	1.71	0.45	1.01	
β - cellulose content (degraded cellulose) R2	2.71	1.51	1.30	0.96	0.52	1.23	
Average	2.71	0.22	0.55	1.34	0.49	1.12	
std	0.00	1.82	1.06	0.53	0.05	0.16	
se	0.00	1.29	0.75	0.38	0.04	0.11	
α - cellulose content R1	95.65	96.22	94.70	94.67	95.19	95.11	
α - cellulose content R2	95.65	94.93	93.95	95.04	95.15	95.00	
Average	95.65	95.57	94.33	94.85	95.17	95.05	
std	0.00	0.91	0.53	0.27	0.02	0.08	
se	0.00	0.65	0.38	0.19	0.02	0.05	
Copper number R1	3.22	2.35	2.58	1.72	1.84	1.42	
Copper number R2	3.11	2.80	2.83	2.06	1.97	1.55	
Average	3.17	2.57	2.70	1.89	1.90	1.48	
std	0.08	0.32	0.17	0.24	0.09	0.09	
se	0.06	0.22	0.12	0.17	0.07	0.06	
							H Sheet
Brightness R1	48.80	67.30	72.20	72.80	88.30	89.50	91.57
Brightness R2	48.80	67.30	72.20	72.80	88.30	89.50	91.57
Average	48.80	67.30	72.20	72.80	88.30	89.50	91.57
std	0.00	0.00	0.00	0.00	0.00	0.00	0.00
se	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Average results	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/CED	497.95	483.75	528.35	550.30	498.00	447.00	
Lignin (K-number)	2.29	0.99	0.80	0.69	0.36	0.28	
(β+γ) - cellulose content (S10)	5.71	4.54	5.95	5.82	5.08	5.51	
γ - cellulose content (hemicellulose)	3.00	4.32	5.40	4.48	4.59	4.39	
β - cellulose content (degraded cellulose)	2.71	0.22	0.55	1.34	0.49	1.12	
α - cellulose content	95.65	95.57	94.33	94.85	95.17	95.05	
Copper numbers	3.17	2.57	2.70	1.89	1.90	1.48	
Brightness	48.80	67.30	72.20	72.80	88.30	89.50	91.57

se	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/CED	0.85	1.85	0.45	2.40	0.80	3.20	
Lignin (K-number)	0.00	0.13	0.04	0.02	0.02	0.01	
(β+γ) - cellulose content (S10)	0.00	1.29	0.75	0.38	0.04	0.11	
γ - cellulose content (hemicellulose)	0.00	0.00	0.00	0.00	0.00	0.00	
β - cellulose content (degraded cellulose)	0.00	1.29	0.75	0.38	0.04	0.11	
α - cellulose content	0.00	0.65	0.38	0.19	0.02	0.05	
Copper numbers	0.06	0.22	0.12	0.17	0.07	0.06	
Brightness	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Mass reject 11% at 0.4%

Wet chemistry analysis	RAWo	O2	D1	E	D2	HYPO	
Viscosity/CED R1	498.80	481.90	527.90	552.70	497.20	450.20	
Viscosity/CED R2	497.10	485.60	528.80	547.90	498.80	443.80	
Average	497.95	483.75	528.35	550.30	498.00	447.00	
std	1.20	2.62	0.64	3.39	1.13	4.53	
se	0.85	1.85	0.45	2.40	0.80	3.20	
Lignin (K-number) R1	2.29	0.85	0.76	0.71	0.37	0.28	
Lignin (K-number) R2	2.29	1.12	0.83	0.67	0.34	0.27	
Average	2.29	0.99	0.80	0.69	0.36	0.28	
std	0.00	0.19	0.05	0.03	0.02	0.01	
se	0.00	0.13	0.04	0.02	0.02	0.01	
(β+γ) - cellulose content (S10) R1	5.71	3.25	5.20	6.19	5.04	5.40	
(β+γ) - cellulose content (S10) R2	5.71	5.83	6.70	5.44	5.11	5.62	
Average	5.71	4.54	5.95	5.82	5.08	5.51	
std	0.00	1.82	1.06	0.53	0.05	0.16	
se	0.00	1.29	0.75	0.38	0.04	0.11	
γ - cellulose content (hemicellulose) R1	3.00	4.32	5.40	4.48	4.59	4.39	
γ - cellulose content (hemicellulose) R2	3.00	4.32	5.40	4.48	4.59	4.39	
Average	3.00	4.32	5.40	4.48	4.59	4.39	
std	0.00	0.00	0.00	0.00	0.00	0.00	
se	0.00	0.00	0.00	0.00	0.00	0.00	
β - cellulose content (degraded cellulose) R1	2.71	-1.07	-0.20	1.71	0.45	1.01	
β - cellulose content (degraded cellulose) R2	2.71	1.51	1.30	0.96	0.52	1.23	
Average	2.71	0.22	0.55	1.34	0.49	1.12	
std	0.00	1.82	1.06	0.53	0.05	0.16	
se	0.00	1.29	0.75	0.38	0.04	0.11	
α - cellulose content R1	95.65	96.22	94.70	94.67	95.19	95.11	
α - cellulose content R2	95.65	94.93	93.95	95.04	95.15	95.00	
Average	95.65	95.57	94.33	94.85	95.17	95.05	
std	0.00	0.91	0.53	0.27	0.02	0.08	
se	0.00	0.65	0.38	0.19	0.02	0.05	
Copper number R1	3.22	2.35	2.58	1.72	1.84	1.42	
Copper number R2	3.11	2.80	2.83	2.06	1.97	1.55	
Average	3.17	2.57	2.70	1.89	1.90	1.48	
std	0.08	0.32	0.17	0.24	0.09	0.09	
se	0.06	0.22	0.12	0.17	0.07	0.06	
							H Sheet
Brightness R1	47.90	66.90	71.50	69.80	84.60	87.90	91.36
Brightness R2	47.90	66.90	71.50	69.80	84.60	87.90	91.36
Average	47.90	66.90	71.50	69.80	84.60	87.90	91.36
std	0.00	0.00	0.00	0.00	0.00	0.00	0.00
se	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Average results	RAWo	O2	D1	E	D2	HYPO	H Sheet
Viscosity/CED	497.95	483.75	528.35	550.30	498.00	447.00	
Lignin (K-number)	2.29	0.99	0.80	0.69	0.36	0.28	
(β+γ) - cellulose content (S10)	5.71	4.54	5.95	5.82	5.08	5.51	
γ - cellulose content (hemicellulose)	3.00	4.32	5.40	4.48	4.59	4.39	
β - cellulose content (degraded cellulose)	2.71	0.22	0.55	1.34	0.49	1.12	
α - cellulose content	95.65	95.57	94.33	94.85	95.17	95.05	
Copper numbers	3.17	2.57	2.70	1.89	1.90	1.48	
Brightness	47.90	66.90	71.50	69.80	84.60	87.90	91.36

se	RAWo	O2	D1	E	D2	HYPO	H sheet
Viscosity/CED	0.85	1.85	0.45	2.40	0.80	3.20	
Lignin (K-number)	0.00	0.13	0.04	0.02	0.02	0.01	
(β+γ) - cellulose content (S10)	0.00	1.29	0.75	0.38	0.04	0.11	
γ - cellulose content (hemicellulose)	0.00	0.00	0.00	0.00	0.00	0.00	
β - cellulose content (degraded cellulose)	0.00	1.29	0.75	0.38	0.04	0.11	
α - cellulose content	0.00	0.65	0.38	0.19	0.02	0.05	
Copper numbers	0.06	0.22	0.12	0.17	0.07	0.06	
Brightness	0.00	0.00	0.00	0.00	0.00	0.00	0.00