

# **Simultaneous Neutral Sulphite Semichemical Pulping of Hardwood and Softwood**

By

Floris Antonides

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## Abstract

The work described in this thesis was aimed at obtaining a better understanding of the neutral sulphite semichemical pulping process employed by Mondi Kraft's Piet Retief mill, and to investigate ways to improve this process. The unique feature of the process in this mill is that hardwood and softwood species are pulped simultaneously in a continuous digester. The pulping trials described were carried out in a laboratory batch digester which was built as a part of this project. Pulps were evaluated for yield, Hypo number as an indication of the residual lignin content and strength properties. The first part of the experimental work focused on the effect that different pulping variables have on the process and the resulting pulp. Variables investigated were the chemical charge, pulping temperature, chip composition and anthraquinone dosage. The second part of the work was to investigate ways in which the process can be improved. In particular it was investigated whether it would be advantageous to pulp hardwood and softwood separately and mix the two pulps together after pulping. The effect of changing to an alkaline sulphite process was also briefly investigated.

It was found that the current process is optimized as far as the chemical charge and pulping temperature is concerned. Increasing the softwood percentage used to 50 % (from current value of 41 %) increases the tear strength, whilst decreasing it to 30 % increases the tensile strength of the resulting pulp. It was also determined that increasing the AQ dosage from 0.1 % to 0.5 % might bring savings in chemical costs. It is suggested that this is investigated in a mill trial.

It was further found that pulping the two species separately improves the tear strength of the pulp by about 20 % compared with that which was pulped simultaneously. The results indicate that no benefits concerning the chemical costs, pulping temperature, pulp yield, burst strength or tensile strength are to be gained from separate pulping.

Preliminary results indicated that significant strength increases and possible chemical cost savings are to be gained by changing from a neutral sulphite to an alkaline sulphite process. Further work to determine the reproducibility of these results, as well as the effect of different chemical charge and ratios is suggested.

## Preface

I, the undersigned, hereby declare that, unless specifically indicated to the contrary in the text, the work contained in this thesis is my own original work, and has not been submitted in part, or in whole to any other university. The research work described in this thesis was carried out at the University of Natal in Durban, Mondi Kraft in Richard's Bay and the Forestry and Forest Products Research Centre of the CSIR in Durban. This project was initiated by Mondi Kraft in Piet Retief in order to improve their pulping process, and was supervised by John Hunt, senior research fellow at the University of Natal, Durban.

Signature:



F.E. Antonides

Date:

23 / 03 / 01

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## Glossary

Alkaline sulphite pulping:	Pulping process in which sodium sulphite and sodium hydroxide are used as pulping chemicals.
Anthraquinone:	Organic compound used as pulping catalyst.
Black liquor:	Spent liquor from pulping reaction.
Beating:	Process in which pulp fibres are subjected to mechanical forces in order to fibrillate fibres to increase bonding between individual fibres.
Burst index:	Indication of the burst strength of paper.
Canadian Standard Freeness:	Unit of measurement of pulp freeness.
Cellulose:	Linear organic constituent of wood, aggregated to form fibres.
Cooking liquor:	Solution of cooking chemicals in water used in pulping.
Delignification:	Removal of lignin from wood by means of chemical pulping.
Digester:	Pressure vessel in which pulping takes place.
Freeness:	An indication of the rate at which water drains from a given pulp suspension.
Furnish:	Pulp suspension used for papermaking.
Hemicellulose:	Branched organic constituent of wood, closely associated with cellulose in fibre cell walls.
Hypo number:	Indication of the residual lignin left in pulp after pulping. The reaction of sodium hypochlorite with residual lignin is used in the determination of the Hypo number.
Kappa number:	Indication of the residual lignin left in pulp after pulping. The reaction of potassium permanganate with residual lignin is used in the determination of the Kappa number.
Lignin:	Amorphous organic constituent of wood which is dissolved in chemical pulping in order to separate fibres.
Neutral sulphite pulping	Pulping process in which sodium sulphite and sodium carbonate are used as pulping chemicals.
Refined yield:	Pulp yield determined after refining.
Refining:	Process in which pulp fibres are separated by means of mechanical action provided by metal discs or grindstones.
Sulphite charge:	Amount of sodium sulphite used in pulping, expressed as % $\text{Na}_2\text{O}$ on oven dry wood.
Sulphite percentage:	Percentage sodium sulphite of total cooking chemicals, expressed as $\text{Na}_2\text{O}$ .
Tear index:	Indication of tear strength of paper.
Tensile index:	Indication of tensile strength of paper.

Total alkali:

Total amount of sodium sulphite, sodium carbonate, sodium hydroxide and sodium sulphide present in cooking liquor, expresses as  $\text{Na}_2\text{O}$ .

Yield:

Mass of oven-dry pulp produced per oven-dry mass of wood charged.

## Abbreviations

AA	Active alkali, which is the sum of NaOH and Na <sub>2</sub> S, expressed as Na <sub>2</sub> O, in a batch of cooking liquor.
AS	Alkaline sulphite
AQ	Anthraquinone
ASSC	Alkaline sulphite semichemical
CSF	Canadian Standard Freeness.
HW	Hardwood
NS	Neutral sulphite
NSSC	Neutral sulphite semichemical
O.D.	Oven-dry, i.e. moisture free
SEM	Scanning electron microscope
SW	Softwood
TA	Total alkali, which is the sum all the NaOH, Na <sub>2</sub> SO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> and Na <sub>2</sub> S, expressed as Na <sub>2</sub> O, in a batch of cooking liquor.

# 1. Introduction

Mondi Kraft's Piet Retief mill produces linerboard by means of the neutral sulphite semichemical anthraquinone process. In this process sodium sulphite and sodium carbonate are used as cooking chemicals, and anthraquinone is added as a catalyst. Pulping is done in a single continuous digester. Originally only hardwood species were pulped at the mill, but softwood was subsequently introduced to improve the tear strength of the pulp. Currently, a 50/50 volumetric ratio of hardwood to softwood is used. This is a unique feature of this mill since hardwood and softwood species are generally pulped separately due to the different pulping rates of the two species. The process conditions employed by the mill are summarized in Table 1.1.

Table 1.1: Current pulping conditions at Mondi Kraft's Piet Retief mill

Pulping temperature	179 °C
Total alkali (TA) charge	9.5 % as Na <sub>2</sub> O on oven dry wood
Sulphite charge	8.5 % as Na <sub>2</sub> O on oven dry wood
Na <sub>2</sub> SO <sub>3</sub> / Na <sub>2</sub> CO <sub>3</sub> ratio	10/1 (kg Na <sub>2</sub> SO <sub>3</sub> /kg Na <sub>2</sub> CO <sub>3</sub> )
Anthraquinone (AQ) dosage	0.1 % on oven dry wood
Hardwood/softwood ratio	50/50 on a volumetric basis
Target Hypo number	18

The aim of this project was two-fold. Firstly to investigate the effect of various process variables on the process. This was done to determine how the different variables effect the refined yield and quality of the pulp produced. Variables investigated were the chemical charge, pulping temperature, wood chip composition and anthraquinone dosage. The second part of this project was focused on determining how the process could be improved with regards to the cost of the pulp produced as well as the resultant pulp quality. The focus was particularly on whether it would be beneficial to pulp the two wood species separately before combining them for refining and linerboard making. The effect of substituting the sodium carbonate with sodium hydroxide in the cooking liquor, and thus changing to an alkaline sulphite cooking process was also investigated.

A laboratory scale batch digester was build at the University of Natal, Durban in order to carry out the experimental work. Further experimental work was done at Mondi Kraft's Richards Bay mill and the Forestry and Forest Products Research Centre of the CSIR in Durban. Funding was provided by Mondi Kraft, the Technology and Human Resources for Industries Program (THRIP) of the Department of Trade and Industries and the National Research Foundation (NRF).

## 2. Background

### 2.1. History of pulping

The Ancient Egyptians invented papyrus, from which the term paper was derived, around 3000 BC [1]. Papyrus was the world's first writing material and was made by beating and pressing together thin layers of the stem of the papyrus plant. The applied pressure ensured that the layers were held together by natural glues in the reed. There was, however, no complete defibering, the main characteristic of true papermaking [2].

The first authentic paper was made by Ts'ai Lun of China in 105 AD. His first paper was made from hemp rags, ropes, fishing nets and other domestic articles which were beaten in a mortar and drained on a piece of loosely woven cloth [3]. Within 20 years he produced paper by treating the bark of mulberry trees with lime. Papermaking was developed into a highly skilled art by the Chinese over the next seven hundred years, during which time it was kept a closely guarded secret [4].

In the early 700s the Arabs came in contact with papermaking when they captured a Chinese city containing a paper mill [1]. Through the Arabs, the art of papermaking spread through the Middle East and later reached Europe, where cotton and linen rags became the most widely used raw materials [2]. By the beginning of the 15<sup>th</sup> century a number of paper mills existed in Spain, Italy, Germany and France.

The concept of using wood as a raw material was first reported in 1719 by a René de Réaumur, a French physicist, who noticed the American wasp constructing its fibrous, paper-like nest from wood fibres [5]. The first paper made entirely from wood was only produced in the early 1800s by Matthias Koops, who reduced wood to a pulp by maceration with lime [3]. He started his own paper mill, which went bankrupt in 1804. In 1840, Anselme Payne, a French chemist, used nitric acid to isolate a fibrous substance from wood, which he called cellulose [6]. The use of nitric acid, however, caused too much damage to the fibres to be used commercially.

Friedrich Keller introduced the concept of producing groundwood pulp in 1843 after watching children grind cherry pits against a wet stone with a piece of wood, which was gradually fiberized under the influence of water and pressure [5]. As a result of the work by Heinrich Voelter and Johann Voith in 1847 on Keller's concept, groundwood mills sprung up throughout Germany and other European countries. In 1869 M. Behrend introduced the steaming of logs before grinding [5]. Thus the basis was laid for the development of modern mechanical and thermomechanical pulping processes.

Chemical pulping came into its own as an independent process in the mid-1800s. In 1851 Watt and Burgess found that it was possible to remove lignin, which binds wood fibres together, from wood at elevated temperatures using strongly alkaline solutions based on sodium hydroxide ([7], [8]). In 1854 Burgess set up a mill in the USA in which poplar chips were cooked with sodium hydroxide, called the soda process [8]. In 1866 Tilghman invented the sulphite process, and the sulphate or kraft process was developed by Dahl in 1879 [6]. Numerous refinements of these three processes in the twentieth century have led to the rapid growth and adaptation of paper not only for writing and printing, but also for wrapping, packaging and a variety of disposable products.

## **2.2. Wood anatomy**

Within living trees, wood is produced to perform the roles of support, conduction and storage. The support role enables the tree stem to remain erect despite the heights to which a tree grows. Because of these heights, wood also must perform the role of conduction, that is the transport of water from the ground to the upper parts of the tree. Finally, food is stored in certain parts of the wood until required by the living tree.

### **2.2.1. Wood chemistry**

The chemical components of wood can be divided into two main categories: macromolecular components and components with a low molecular mass. The former can be divided into polysaccharides, namely cellulose and hemicellulose or polyose, and lignin, whilst the low molecular components consist of organic and inorganic components, also referred to as extractables and ash respectively.

Cellulose is the chief component of wood, contributing between 40 and 50% of the total dry mass of wood, depending on the species [7]. Cellulose consists of linear beta-D-glucopyranose polymers with a chain length or degree of polymerization (DP) of between 600-12000 units, depending on the species [6]. The chemical structure of a cellulose molecule is shown in Fig. 2.1. It constitutes the fibrous part of wood (and other plant material) and has a white colour. It is insoluble in water and other organic solvents and has a very high tensile strength.



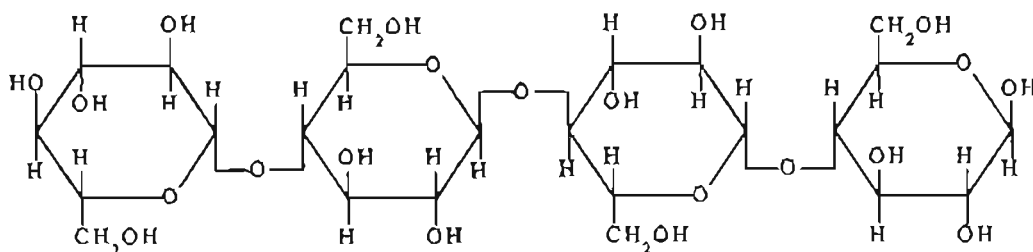


Fig. 2.1: Chemical structure of a cellulose molecule [5].

Hemicellulose is found in close association with cellulose in the cell walls and has a lower average DP value (50 – 300, [5]) and a more branched structure than cellulose. Hemicellulose are much more soluble and susceptible to chemical degradation than cellulose [1].

Hemicellulose consists of a number of diverse substances. The two principal components are the cellulosans and the polyuronides, whilst other substances include gums, degradation products of cellulose, derivatives of sugars, and mixtures of hexosans. The cellulosans include both hexosans, (e.g. mannan, galactan, and glucosan) and pentosans (e.g. xylan and araban). Some of these cellulosans are strongly associated with the cellulose in wood and are not readily removed by alkali. The polyuronides are amorphous substances which contain large amounts of hexuronic acids, some methoxyl and acetyl groups, and some free carboxylic acid groups. The polyuronides are mainly associated with the lignin, although some association exists with the cellulose. The simplified structures of the major hemicelluloses in wood are shown in Fig. 2.2. The total hemicellulosic content of wood varies from about 15 to 18 % (in softwoods) to about 22 to 34 % (in hardwoods) [9].

For practical reasons, cellulose in wood pulp has traditionally been classified according to its solubility in an alkali solution [9]:

Alpha cellulose:	non-soluble in aqueous 17.5 % NaOH
Beta cellulose:	soluble in above mentioned solution, precipitates after neutralization
Gamma cellulose:	soluble fraction after neutralization

It has been suggested that a 17.5 % NaOH solution dissolves chains up to a DP of 200 [8]. Since the DP of hemicellulose in wood ranges between 50 and 300, a large part of the beta- plus gamma-cellulose in reality is hemicellulose and not cellulose chains shortened during the pulping process. The terms alpha-, beta- and gamma cellulose are however still used despite this discrepancy.

<i>Hemicellulose Type</i>	<i>Simplified structure</i>																								
Galactoglucomannan	$\begin{array}{ccccccc} G & - & M & - & M & - & G & - & M & - & M & - & M & - & - \\   & &   & &   & &   & & & &   & & & & \\ GAL & & Ac & & Ac & & & & & & GAL & & & & \end{array}$																								
Glucomannan	$G - M - M - G - M - - -$																								
Arabinoglucuronoxylan	$\begin{array}{ccccccc} X & - & X & - & X & - & X & - & X_5 \\ & &   & & & &   & & \\ & & Ga & & & & A & & \end{array}$																								
Glucuronoxylan	$\begin{array}{ccccccc} X & - & X & - & X & - & X & - & - & - \\   & & & &   & & & & & \\ Ac & & & & Ga & & & & & \end{array}$																								
Arabinogalactan	$\begin{array}{ccccccc} GAL & - & GAL & - & GAL \\   & &   & &   \\ GAL & & R & & A \\   & &   & &   \\ GAL & & \vdots & & A \end{array}$																								
Abbreviations:	<table><tr><td>G</td><td>- Glucose</td><td>X</td><td>- xylose</td></tr><tr><td>GAL</td><td>- galactose</td><td>A</td><td>- arabinose</td></tr><tr><td>M</td><td>- mannose</td><td></td><td></td></tr><tr><td>Ac</td><td>- acetyl group (CH<sub>3</sub>CO)</td><td></td><td></td></tr><tr><td>Ga</td><td>- 4-O-methyl-glucuronic acid</td><td></td><td></td></tr><tr><td>R</td><td>- usually galactose</td><td></td><td></td></tr></table>	G	- Glucose	X	- xylose	GAL	- galactose	A	- arabinose	M	- mannose			Ac	- acetyl group (CH <sub>3</sub> CO)			Ga	- 4-O-methyl-glucuronic acid			R	- usually galactose		
G	- Glucose	X	- xylose																						
GAL	- galactose	A	- arabinose																						
M	- mannose																								
Ac	- acetyl group (CH <sub>3</sub> CO)																								
Ga	- 4-O-methyl-glucuronic acid																								
R	- usually galactose																								

Fig. 2.2: The types and simplified structures of the major hemicelluloses in wood [10].

Other types of cellulose have also been defined according to the method by which they were isolated, e.g. holocellulose and Cross and Bevan cellulose [9]. These cellulose differ in degree of purity, i.e. the amount of other wood material, mainly lignin and hemicellulose, isolated together with the cellulose.

The third macromolecular component of wood, lignin, is an amorphous, aromatic polymer consisting of phenyl propane units. The three building units of lignin are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol and are shown in Fig. 2.3.

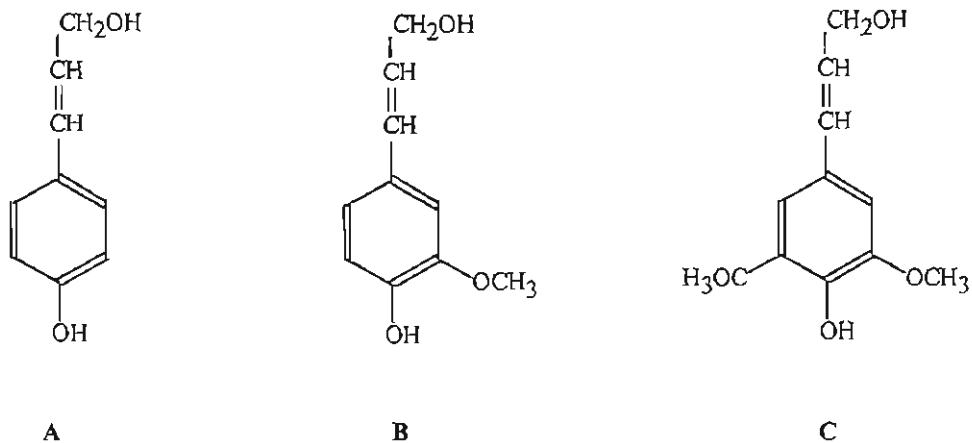
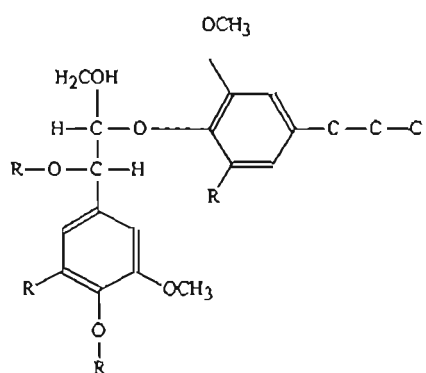


Fig. 2.3: The building units of lignin: A: p-coumaryl alcohol, B: coniferyl alcohol and C: sinapyl alcohol [5].

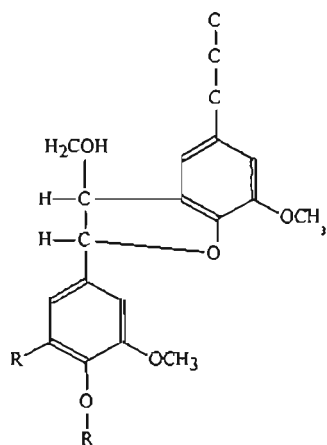
These units are linked together in many different ways, mainly by oxygen (ether) bridges connecting the alpha or beta carbons of the side chain of one unit with the phenyl ring of the other. These bonding types are shown in Fig 2.4.

The units form complex macro-molecules which strengthen the wood structure, and can be seen as the “glue” which keeps the polysaccharides together. Softwood generally contains more lignin (25 - 31 %) than hardwoods (16 - 24 %) [2]. Lignin is insoluble in water in its natural state.

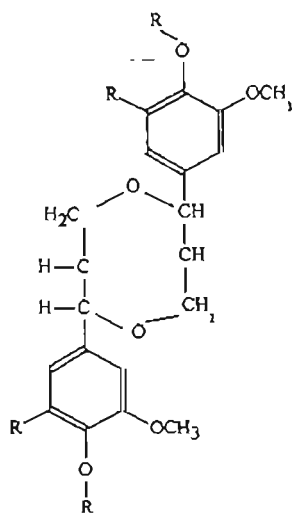
The low molecular components are very diverse and differ from species to species. The organic compounds can be divided into aromatic compounds, terpenes, aliphatic acids and alcohols. They are also often classified according to the method by which they can be extracted, e.g. alcohol/benzene extractives or hot water extractives. Inorganic ash consists of potassium, calcium, magnesium and silicon.



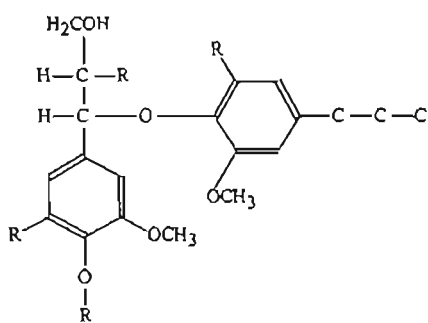
A: 50 (62)



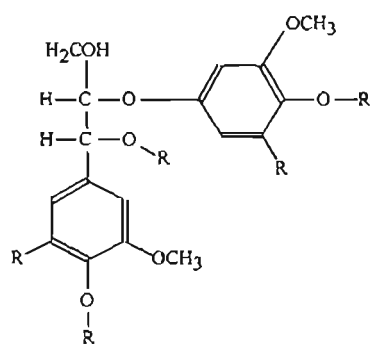
B: 11 (5)



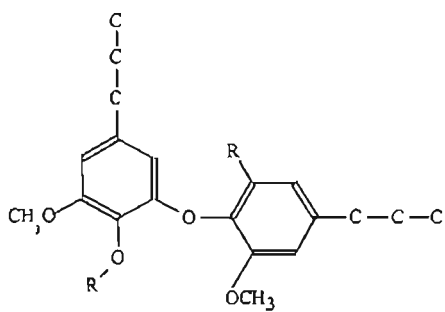
C: 0 (4)



D: 7 (6)



E: 2 (2)



F: 4 (7)

Fig. 2.4: Bonding types between lignin units. The values beneath each bonding type indicate the frequency per 100 phenylpropane units in spruce and, in brackets, birch [11].

### 2.2.2. Cell wall structure

Cellulose molecules are aggregated into threadlike structures approximately 3,5 nm in diameter, containing both crystalline and amorphous regions [1]. These are encased in a shell of hemicellulose molecules and are called microfibrils [12]. In the fibre wall, these microfibrils occur in small bundles or "macrofibrils". These form thin sheets or "lamellae", which gives the wall a layered texture [5]. A diagrammatic sketch of a typical fibre is shown in Fig. 2.5. A cementing layer, the middle lamella, holds the individual fibres in the structure together and is composed mainly of lignin. The middle lamella is important in any pulping process since it has to be broken or removed to separate individual cells to produce single fibres [13].

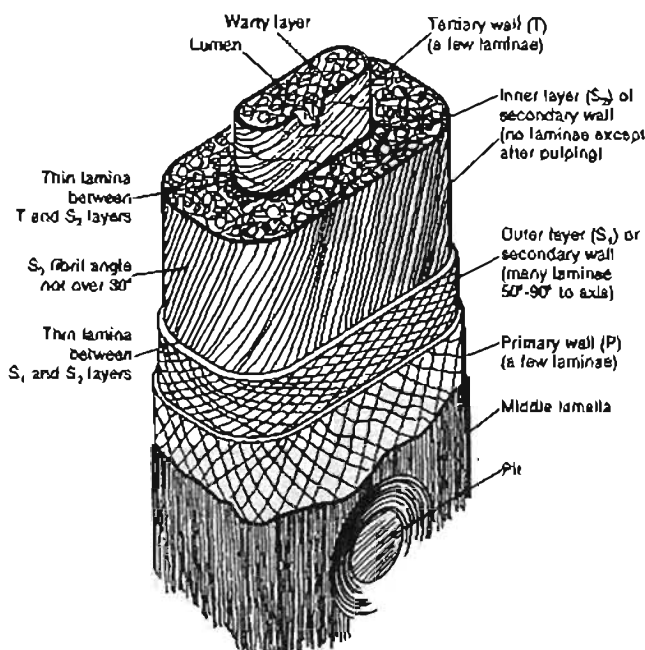


Fig. 2.5: Diagrammatic sketch of a typical fibre (softwood tracheid) [14].

Fibres in all plants grow from the outside inwards. When growth of an individual cell begins, the primary cell wall is formed and is initially filled with liquid. It is about 0.1 µm thick and has a netlike structure of microfibrils in an interwoven pattern [12]. The microfibrils are orientated at an angle of about 85° with the cell axis. The primary wall is estimated to consist of only 10 % cellulose embedded in an amorphous plastic matrix of hemicellulose, extractives and lignin [5].

The multi-layered secondary wall is formed after further growth. The outer layer of the secondary layer, called the S<sub>1</sub>-layer, is about 0.1 to 0.2 µm thick with a microfibril angle between 50 -70° [12]. The S<sub>1</sub>-layer is rich in lignin and closely resembles the primary wall to which it is closely attached, therefore also is

known as the transition layer. The central secondary wall, the  $S_2$ -layer, is attached much less firmly to the  $S_1$ -layer. A continuous envelope of hemicellulose between these layers is thought to cause this lesser cohesion [13]. The  $S_2$ -layer contains more cellulose and less lignin than the  $S_1$ -layer, whilst the microfibril angle is between 10 and 30°[12]. It forms the bulk of the fibre and is about 2 to 6  $\mu\text{m}$  thick [5].

The tertiary wall is the innermost component of the cell wall and the surrounds the central canal called the lumen. The tertiary wall is very thin, about 0.1  $\mu\text{m}$ , and is rich in hemicellulose [2, 12].

### **2.2.3. Wood classification**

Trees are classified into two major groups, namely softwoods (gymnosperms) and hardwoods (angiosperms). The botanical basis for classification is whether or not the tree seed is naked as in softwoods or covered as in hardwoods. The major difference with regard to wood anatomy is the presence of vessels in hardwoods. Vessels are structures composed of cells created exclusively for the conduction of water. Softwoods lack vessels but have cells termed longitudinal tracheids which perform a dual role of conduction and support. In general, softwood fibres are more than twice as long as hardwood fibres [2].

#### **2.2.3.1. Softwood anatomy**

The anatomy of softwoods is a lot less complex than that of hardwoods. The two main cell types which constitute softwoods are tracheids and parenchyma. Tracheids are long, tapering cells which are orientated in the longitudinal direction, i.e. parallel to the vertical axis of the tree [2]. Depending on species, most softwoods have tracheids ranging from 2.5 mm to 7 mm in length [1]. The tracheids are a lot longer in length than the parenchyma cells, and constitute 90 % or more of the volume of wood in the tree [5]. The tracheids perform the roles of water conduction and support within a tree [12].

Parenchyma are responsible for storing various extractives, including starch, polyphenols, oils, fats, etc., as well as inorganics, e.g. K, Mg, Mn, Ca and Si. The parenchyma cells are orientated in the transverse direction, at right angles to the vertical tree axis, and are very short, chunky, thin-walled fibres. Ray tracheids, which are similar in size to parenchyma, and longitudinal parenchyma cells are found in small quantities in some softwood species.

#### **2.2.3.2. Hardwood anatomy**

Hardwoods have a more complex anatomy since more than two kinds of cells are present. Specific characteristics of the hardwoods are a lack of radial alignment of cells, variable size and composition of cells, abundance of rays and the presence of pores or vessel elements [12]. The four major cell types are

fibres, vessel elements, tracheids and parenchyma cells. The relative quantities of the different types of cells vary significantly from tree to tree and give each species its specific characteristics.

Vessels perform the role of water conduction in hardwoods. They are structures composed of vessel elements stacked on top of each other. Vessel elements are short, thin-walled cells with large diameters and perforated ends. They occupy a large cross-sectional area and can often be detected with the unaided eye [12].

Fibres, known as libriform fibres in hardwood, occupy 40 – 75% of the wood volume, and perform the role of supporting a tree. They are orientated in the longitudinal direction and are thick-walled, elongated cells with closed pointed ends. Fibre lengths are in the order of 0.9 mm to 1.5 mm [1]. The term fibre is also commonly used for all woody cells used in the pulp and paper industry [12].

Hardwood tracheids occur in small amounts in some species. These are small, longitudinal conducting cells which act as transition elements between major cell types [12].

Longitudinal and ray parenchyma cells are present in hardwoods [2]. They constitute a larger volume (about 20 % on average) than do softwood parenchyma cells [5]. These cells perform the storage role in a tree, as is the case with softwood parenchyma.

### **2.2.3.3. Growth rings**

Growth rings, or annual increments, are detectable due to differences in the wood produced early and late in the growing season. Growth in a tree occurs at the cambium layer, which is a thin layer of tissue situated between the bark and the wood of a tree [2]. The rate of cambial growth varies during the growing season, causing deposition of thin-wall fibres in the early season and more dense thick-walled fibres towards the end of the growing season [2]. The cambium layer is dormant outside of the growing season. The wood produced early, called earlywood or springwood, is considerably lighter in color than the wood termed latewood or summerwood which is produced late in the growing season. The color difference is due mainly to the different kinds of cells produced either early or late in the growing season.

The inner portion of wood in a tree eventually dies and is called heartwood. Heartwood is generally drier than the outer part of the trunk which contains living cells, called sapwood.

#### 2.2.3.4. Reaction wood

Reaction wood forms because of external mechanical forces, caused by wind and geotropic erection, as well as the presence of branches. The anatomical, physical and chemical characteristics of reaction wood differ from the normal wood tissue. Reaction wood is formed as a self-regulating response to provide support and reorientate the deviated growth of the tree due to the above external forces.

Hardwood trees form tension wood, while compression wood is the reaction wood of softwoods. Compression wood develops typically on the underside (compression side) of leaning or misformed stems, branches and beneath branch insertions. The main characteristics are its dark color and high density as compared to normal wood. This is caused by a relatively high lignin content and a modification of the cell wall. The tracheids are 30–40 % shorter and the cell walls are considerably thicker. Compression wood in a mechanical pulping process leads to inferior paper properties due to the inability of the fibres to fibrillate under normal refining circumstances. In chemical pulping, the high lignin content causes the yield to be lower and the chemical requirements to be higher than for normal wood from the same tree [5, 12].

In hardwoods, the reaction wood tissue is commonly located on the upper side of branches and leaning stems. The structural characteristics of tension wood are less definitive than those of compression wood [5]. A prominent feature of tension wood is its increased fibre volume and above average cellulose content. Another feature is an additional, loosely attached cell wall layer at the fibre lumen. This layer, called the G-layer, is composed of almost pure cellulose and has a microfibril angle close to the fibre axis. In mechanical pulping, the thickened fibre walls and lower lignin content promote defibration and enhance sheet properties. Chemical pulp from tension wood has a high yield because of the high cellulose content, but the strength is inferior to that of pulp from normal wood from the same tree [5].

#### 2.2.4. Wood as a source for pulp

Two factors should be taken into account when wood is considered as a source for producing pulp and paper, namely the yield of fibre per given weight of wood and the quality of the resulting fibre [13]. The former depends on the characteristics of wood prior to pulping and the process employed in its conversion to pulp, while the latter is mainly a result of morphological features of the individual fibres and their modification due to the pulping process.

Fibre quality is also a variable quality in the sense that interpretations of the quality aspects of fibres depend on the specific requirements of the final product to be made from the pulp. The question of wood pulp quality is still further complicated by the lack of agreement among the technical people and producers of pulp products on the interpretation of the qualitative features of fibres, and by the difficulties



encountered in determining these features in a practical way [13]. The qualities of the resulting fibres depend on the wood structure, i.e. the types of cells, and to a lesser extent on the chemical composition of the cell wall material.

The fibre variables responsible for determining the physical characteristics and quality of pulp and paper are classified under fibre morphological aspects. The most important of these variables are cell wall thickness and fibre length [2]. Other variables include fibre coarseness (weight per unit length of a fiber), fibre strength and interfibre bonding.

#### **2.2.4.1. Cell wall thickness**

Thick walled cells, such as found in the latewood of softwoods, resist the compacting forces and tend to maintain their original cross-sectional shape during sheet formation. This results in open, absorbent and bulky papers. Strength properties associated with fibre bonding, such as bursting and tensile strength are appreciably reduced, whilst tearing resistance is relatively high. Thin walled cells on the other hand collapse readily to form dense, well-bonded papers, low in tear but high in burst, tensile and other strength properties [1].

#### **2.2.4.2. Fibre length**

Fibre length is important because a minimum length is required to provide sufficient bonding surface between different fibres. Paper made from fibres that are too short will have insufficient common bonding area between fibres; as a result there will be points of weakness within the sheet and the paper will be low in strength.

The tearing resistance of paper is virtually proportional to fibre length, i.e. the longer the fibres, the higher the tearing resistance [2]. Burst and tensile strength properties are effected by both fibre length and fibre bonding [2]. Long fibres with a high coarseness do not collapse easily during refining and sheet formation, giving bulkier, more open structures with less bonded contact area and lower burst and tensile strengths [15]. Therefore, burst and tensile strength are more dependent on fibre coarseness than on fibre length.

Another important factor is the degree of variation in fibre lengths found in pulpwood. Although the longer fibre lengths are an important plus factor as far as strength is concerned, their significance is affected by the fact that any portion of a tree will contain a range of fibre lengths, with many short fibres included. These short fibres have a negative influence on the strength of the paper, but cause a more regular sheet formation with reduced bulk and smooth texture.

## 2.3. Neutral sulphite semichemical (NSSC) pulping

There are two main categories of modern pulping techniques, chemical and mechanical pulping. They produce pulps with significantly different fibre characteristics. In chemical pulping cellulose fibres are separated by dissolving the lignin with a chemical solution called the cooking liquor. In mechanical pulping fibre bundles are separated through mechanical action provided by an abrasive stone or metal discs. Fibres obtained by chemical pulping are longer, more flexible and considerably stronger than mechanical pulp fibres, since the fibres undergo a lot less physical damage during the pulping process. The yield for chemical pulping typically lies in the 45 to 50% range due to the loss of lignin, hemicellulose and some cellulose, whilst for mechanical pulp it usually is higher than 90%. The yield is defined as the mass of moisture free pulp produced divided by the weight of moisture free wood used to produce the pulp, expressed as a percentage.

Chemical pulping is traditionally categorized as either sulphite or alkaline pulping, although alkaline sulphite processes have been developed over the last few decades. Alkaline pulping consists of soda and kraft pulping. In soda pulping caustic soda is the only cooking chemical, whilst sodium sulphide and caustic soda are used as delignification agents in kraft pulping.

Semichemical pulping combines chemical and mechanical pulping methods. The pulping process occurs in two stages. In the first stage wood chips (or other lignocellulosic materials) are chemically treated to weaken interfibre bonding by removal of some hemicelluloses and a portion of the lignin. The second stage is a mechanical treatment which converts the chemically treated material into individual fibres and bundles of fibres. The yield obtained usually is in the range of 70 - 85%.

### 2.3.1. Development of sulphite pulping

The sulphite pulping process was first developed in 1866 by an American named Benjamin Chew Tilghman [8]. Whilst inspecting wooden wine vats in Paris, Tilghman observed that the wine barrels became fiberized on the inside after repeated use and disinfections with sulphur dioxide. After further experiments using sulphurous acid and wood, he discovered that fibres could be isolated if the mixture was kept at a high temperature and under pressure. To prevent the formation of free sulphuric acid and consequent damage to the pulp, he added lime to the cooking liquor. The pulp obtained was suitable for the manufacture of paper.

The first commercial sulphite mill, using magnesium bisulphite solution as the cooking agent, was established in Bergvik, Sweden in 1874 under the direction of a Swedish chemist, C.D.Ekman [8, 9]. Ekman discovered the sulphite process in 1872 without knowledge of the Tilghman patent whilst studying

bisulphite as a bleaching chemical. At the same time in Austria, Carl Kellner accidentally invented the acid sulphite process when his technician performing soda pulping experiments in the laboratory, accidentally took a bottle containing sodium bisulphite from a shelf and used it, instead of the prescribed caustic soda, for liquor preparation [10]. Kellner, together with Eugen Ritter, further developed the process and had it operating in their mills from about 1878.

Since about 1890, the sulphite process has been well established as a commercial pulping process and was the most important chemical pulping process until about 1937, when it was surpassed in importance by the sulphate (kraft) process, in which the cooking liquor contains sodium sulphide and caustic soda [9].

The three original processes by Tilghman, Ekman and Kellner were all acid bisulphite processes, and used calcium, magnesium and sodium bases respectively. Before 1950 the calcium bisulphite process was preferred because of its inexpensive base and its relative ease of operation without recovery of the cooking chemicals [10]. A fourth base which was to gain significant commercial importance, ammonium, appeared only after 1900. The first suggestion of ammonium bisulphite pulping was patented in the United States using gaseous sulphur dioxide, ammonia, and steam, but the first clear proposal of the acid ammonium bisulphite process is found in patents granted to Marusawa in 1917 in Japan and the United States [10].

Modifications of the sulphite process, away from the original acid bisulphite process and into higher pH levels, began to appear after 1930. These modifications came as a result of pressure on the calcium bisulphite process through environmental concerns, increasing shortage of the commonly used spruce wood and paper strength demands. The first of these modifications was high yield neutral sulphite pulping, mainly of hardwoods, for packaging material. After 1950, sulphite technology moved closer to a neutral pH with the development of bisulphite high yield pulps mainly for the news sector. In the seventies expansion into ultra high yield sulphite pulping followed, with yields from wood in the 90 % range. The semi-soluble magnesium base and soluble sodium and ammonium bases were introduced on a larger scale, resulting in new processes with recovery of chemicals, which became known under the names of Magnefite, Weyerhaeuser FB and HO, Stora, Rauma and others.

In the late sixties technological investigation began to open up in the area of sulphite pulping in the alkaline field. The alkaline sulphite process was developed which challenged the kraft process as far as paper strength was concerned and offered easy bleaching and operation without the offensive smell of the kraft process. In 1976 a sulphite process at lesser alkalinity but with anthraquinone as pulping catalyst was patented [16]. Pulps produced by this process were better delignified, brighter, less degraded and stronger than kraft pulps, except for tear strength. These developments meant that the sulphite processes could provide a wide variety of pulp grades required for paper manufacture [10].

### 2.3.2. Development of semichemical pulping

The concept of semichemical pulping first emerged in 1874 when it was proposed by A. Mitscherlich that chips be treated with sulphurous acid or bisulfite, followed by grinding or rubbing to produce a pulp. In 1880 C.F. Cross described the advantages of cooking in neutral or slightly alkaline solution with sodium sulphite. Implementation of the process was however delayed because of a lack of demonstrated use for the pulp and lack of suitable equipment, especially for defiberizing. The neutral sulphite semichemical (NSSC) process was developed in the early 1940s [1] for the manufacture of corrugated medium as a result of research by the U.S. Forest Products Laboratory on a profitable use for chestnut chips from which the tannin had been extracted [17]. Soon several similar mills were in operation.

Sodium is the most commonly used base. During the sixties ammonium came into use because it leaves no residual that would require additional processing if the spent liquor is disposed of by burning. However due to factors such as corrosion, increased cost of ammonia and the complexity of the recovery process, by 1980 very few ammonium base NSSC mills were in operation [10].

The increasing paper and paperboard requirements ensures that further growth in semichemical pulping is to be expected, because of the unrivaled compression strength that hardwood imparts to corrugated containers [10]. Since the mid-seventies, many NSSC mills have been converted to non sulphur (sodium carbonate and sodium hydroxide) semichemical pulping in order to reduce environmental impacts. These impacts include air pollution through the emission of  $\text{SO}_2$  and other gases, and water pollution through the discharging of spent cooking liquor containing lignosulphonates and, depending on the wood species, small amounts of toxic materials. The NSSC operation of many integrated kraft-NSSC mills were also switched over to kraft green liquor semichemical pulping. Several small NSSC mills were shut down because pollution problems could not be solved at acceptable cost. Chemical recovery can significantly reduce water pollution caused by small mills, but capital costs of recovery for small mills are uneconomical [10].

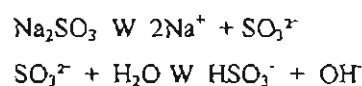
### 2.3.3. Neutral sulphite semichemical process

In general, when using sodium sulphite and sodium carbonate the process is referred to as neutral sulphite pulping, whilst when sodium sulphite and sodium hydroxide are used, it is called alkaline sulphite pulping [13]. Other sources classify sulphite pulping processes according to the cooking liquor pH, with a pH of 10 and higher being regarded as alkaline [7]. This leads to some confusion, since the cooking liquor pH for a sodium sulphite and sodium carbonate solution can be higher than 10 [18], as was also the case in some of the cooks done in this project. In this thesis the former definition was used.

### 2.3.3.1. Pulping reactions

The pulping chemicals used in neutral sulphite pulping are sodium sulphite and sodium carbonate. The sulphite is the delignification agent whilst the carbonate is used as a buffer to control the pH by neutralizing acids released by the wood [10].

$\text{HSO}_3^-$  ions are formed in a solution of sodium sulphite in water in the following manner [19]:



Limited delignification in the NSSC process is achieved through the combined effects of sulphonation by the  $\text{HSO}_3^-$  ion and hydrolysis (removal of a water molecule) [7]. Sulphonation acts to soften the lignin and make it more hydrophylic. Hydrolysis breaks lignin bonds so that new and smaller soluble lignin fragments are formed [7]. The sulphonation and hydrolysis reaction is shown in Fig. 2.6.

The modification of lignin by sulphonation is the most important reaction in sulphite pulping. Lignin is insoluble in water and is converted to soluble liginosulphonate during sulphonation. Both K- and 2-arylether bonds are sulphonized and are broken by hydrolysis (loss of water molecule). The introduction of sulphonic acid groups into the phenyl propane structure of lignin causes the formerly neutral and ionically inactive compound to become a strong organic acid.

The lignin is thus transformed into a large multi-branched macro anion with increased hydrophilic properties. The cell walls swell up during pulping due to the increase of sulphonate groups present [20]. The macro lignin anions dissolve in the water medium of the pulping liquor. A large quantity of the lignin is still embedded in the chips and is only removed once the fibres are separated during refining. The liquor carries an equivalent amount of positive base ion ( $\text{Na}^+$ ). When the water is removed, the positive base ions join the negative macro ion and form liginosulphonate salt [10].

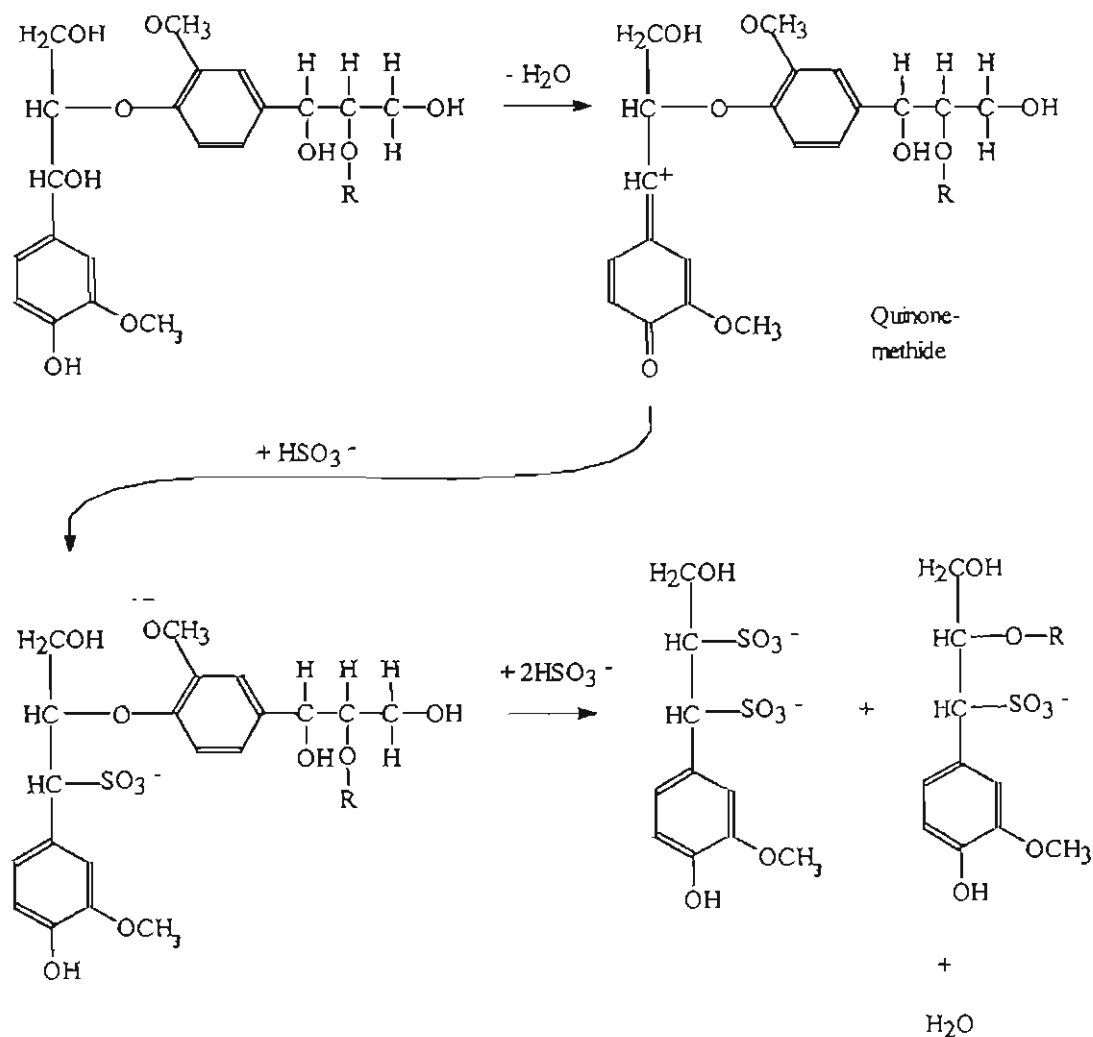


Fig. 2.6: Sulphonation and hydrolysis of lignin in neutral sulphite pulping [10].

A certain amount of polysaccharide material is also lost [21]. The cellulose and hemicellulose undergo hydrolysis when exposed to hot cooking liquor. These hydrolytic reactions split main chains and eliminate side units, leading to carbohydrate losses. In neutral sulphite pulping, hydrolysis of polysaccharide material is reduced, as opposed to acid or strongly alkaline pulping. This results in the pulps having a high hemicellulose content, promoting bonding and strength as required for stiff corrugated board [10].

### 2.3.3.2. Pulping variables

#### 2.3.3.2.1. Temperature

The pulping rate is controlled by the temperature, with the rate roughly doubling for an increase of 10 °C [10]. Increasing the temperature also decreases the selectivity, i.e. the relative amounts of lignin and polysaccharides removed from the wood, although cellulose losses are not excessive. The selectivity for neutral sulphite pulping is more temperature dependant than that of kraft pulping, in which case the selectivity stays relatively constant as the temperature is increased [22]. The neutral sulphite process is more selective in its action than kraft pulping, removing a larger portion of lignin at an equivalent yield, where yield is the mass of pulp produced per unit mass of wood pulped [22, 23]. This causes neutral sulphite pulp to have a higher yield than kraft pulping at a similar residual lignin level [24, 25].

Obstacles encountered when using higher temperatures in the NSSC process lie in securing sufficiently rapid liquor penetration and chemical distribution, and in the increase in pressure (nearly 690 kPa when temperature is increased from 190 °C to 210 °C) [10].

The reaction rate for anthraquinone-catalyzed neutral sulphite (NS-AQ) pulping is lower than for kraft pulping [24]. The neutral sulphite delignification rate rigidly obeys the Arrhenius equation  $K = Ae^{-E_a/RT}$  [26]. Wilder & Han [22] however suggest that delignification of aspen chips with neutral sulphite occurs in at least two stages. Initially, the lignin removal can be represented by a rapid reaction order ~2.5 with respect to lignin. This then changes to a lower reaction order ~1.2.

It was found that alpha-cellulose removal in NSSC pulping takes place in two steps: a rapid initial reaction followed by a reaction of zero order with respect to the amount of material present [22]. This latter reaction has a higher temperature coefficient than either delignification reaction, leading to the speculation that an increase in temperature would yield an inferior pulp at the same overall yield level. The removal of hemicellulose in the form of pentosans in NSSC pulping also takes place in at least two steps, the latter being zero order with respect to the pentosans remaining in the wood.

The H-factor is a variable that combines time and temperature into a single variable. It was developed by Vroom [27] and has been successfully employed in kraft pulping [7]. It was also shown to be valid in sulphite pulping for pH 7.5 and lower by Nye et al [28] when using black spruce chips. Correlations between the H-factor, yield and residual lignin content in the NSSC pulping of various hardwoods were determined by Mašura [26]. However, the maximum temperature used in developing the correlations was held constant at 170 °C, with only the cooking time being varied. Thus it can be concluded that there is a

correlation between the cooking time (not necessarily the H-factor) and yield and residual lignin. No references to the successful application of the H-factor at pH levels above 7.5 have been found.

#### *2.3.3.2.2. Liquor to wood ratio*

The ratio of liquor to wood in the digester generally ranges from 1.5:1 to 4:1 [10]. When a low liquor ratio is used, the chips are impregnated under high pressure in an excess of liquor at temperatures as high as the maximum pulping temperature. Subsequently the free liquor is drained and steam is added to the chips to complete the digestion. When the digester is heated by circulating the liquor through an external heat exchanger, a higher liquor to wood ratio is required. A low liquor to wood ratio reduces steam consumption, since less is required to heat the digester charge and to evaporate the spent liquor.

The liquor to wood ratio is determined by the chemical charge on the dry wood chips on one hand, and by the chemical concentration on the other hand. This is discussed in the next section.

#### *2.3.3.2.3. Chemical charge*

For the production of corrugating medium at yields between 75 and 85 %, sodium sulphite charges between 8 and 15 %, expressed as  $\text{Na}_2\text{O}$ , on oven dry wood is needed. The amount of sodium sulphite should be enough to give a residual of from 5 to 10 g/L in spent liquor. If the chemical is completely exhausted before the chips are discharged, the pulp darkens [10].

Sodium sulphite to sodium carbonate ratios vary and ratios between 2.56:1 and 10:1 (chemicals expressed as g  $\text{Na}_2\text{O}$ ) are used [26]. At 80 – 85 % sodium sulphite and 15 – 20 % sodium carbonate or sodium hydroxide (all chemicals expressed as g  $\text{Na}_2\text{O}$ ) in the cooking liquor, pulp yield of softwood cooks is at a maximum and both lignin content and carbohydrate degradation are at their minima [10]. This is confirmed by Ojanen [24] and Virkola [29]. Virkola further states that the optimum ratio of sodium sulphite to sodium sulphite plus sodium carbonate is between 0.80 and 0.85 (i.e sulphite percentage of 80 to 85 %) for both birch and pine wood chips. A study, using a sulphite percentage of 85% along with a liquor to wood ratio of 12.5:1 was conducted by Keskin & Kubes [30] to investigate the effect of liquor concentration on the rate of delignification in neutral sulphite and neutral sulphite-anthraquinone pulping of black spruce wafers. A concentration range of 54 - 82 g sodium sulphite per liter was used. Anthraquinone dosage was 0.5 % (on o.d. wood) and cooking times were varied to obtain yields between 50 and 80 %. The effect of liquor concentration on the delignification rate expressions for both processes was investigated. It was observed that the reaction rate orders with respect to sodium sulphite charge were 0.28 and 0 for the delignification rate of NS and NS-AQ respectively. The experiments extended to lower liquor-to-wood ratios (5/1) for



NS-AQ pulping. A negligible effect of liquor concentration on NS-AQ pulping was observed. Lower liquor to wood ratios were found to be more efficient for delignification.

Virkola et al [29] discovered during softwood NS-AQ cooking trials on both laboratory and mill scale that the most important factors influencing the result of NS-AQ cooking were total alkali charge, alkali ratio and amount of AQ on wood. The sodium sulphite charge had a greater influence on delignification than the total alkali charge. The properties of the NS-AQ pulps were quoted as being exceptional compared with conventional sulphite pulps, whilst one of the most interesting aspects of the NS-AQ process was found to be the very high pulping yield.

Sodium carbonate is used as a buffer in the cooking process. This is to counteract a fast and clear drop in pH at the beginning of a cook, which is probably due to the neutralization of acetyl groups in wood chips [24]. A minimum amount of buffer chemical, sufficient for a spent liquor pH of just over 7 produces the brightest pulp, whilst a pH of 8 to 9 provides faster pulping, some improvement in pulp strength and reduced corrosion in equipment. Some mills pulp to a spent liquor pH of as low as 5.5 to save on buffer chemicals and to enhance pulp drainage [10].

In a study on the reactions of lignin during sulphite pulping at various pH levels, Gellerstedt [11] found that at the neutral pH-level a selective sulphonation of phenolic lignin is operative, in part leading to lignin fragmentation by sulphitolytic rupture of  $\beta$ -aryl ether bonds. Phenylpropane units containing carbonyl groups, whether phenolic or not, are also sulphonated under these conditions. Such structures, if part of a  $\beta$ -aryl ether system, are degraded to a large extent by cleavage of the  $\beta$ -aryl ether bond. Elimination of hydrogen and/or formaldehyde from intermediately formed methylene quinones gives rise to conjugated structures of the styrene and stilbene types. Furthermore, cleavage of methyl aryl ether bonds creates catechol groups in initial phenolic structures. The conjugated structures formed may in subsequent reactions give rise to chromophoric systems.

#### *2.3.3.2.4. Wood species*

Semichemical pulping has been limited almost entirely to the hardwoods, although some softwoods deliver excellent pulps [10]. The drawbacks to softwood semichemical pulping are that its chemical consumption is higher and it requires considerably more energy for fiberizing and refining. Species which have high resin contents are also likely to produce pitch problems in a paper mill. Pine species specifically have been found difficult to pulp using sulfite as delignification agent. The large resin content of pine is a major cause of equipment operating problems [31]. Pine heartwood contains a class of phenolics which retards sulphite pulping. Pinosylvin and related phenolic substances present in pine heartwood apparently condense with lignin under acidic pulping conditions to form insoluble products, even after lignin

sulphonation had taken place. It was found that wood can be pulped by pretreatment with an alkaline sulphite solution prior to acidic sulphite pulping.

Softwood lignin is sulphonated to a greater degree than hardwood lignin by neutral sulphite liquor [10]. However, softwood reacts slower and a larger charge of chemicals is required for a given degree of delignification. This is mainly due to the greater lignin content of softwood, its inaccessability in the cell wall and its higher molecular weight.

#### 2.3.3.2.5. *Anthraquinone*

The introduction of anthraquinone (AQ) as a catalyst has brought great improvements to the NSSC pulping process, since it has made the use of softwood economically viable [32]. AQ accelerates the delignification rate dramatically [33] and stabilizes wood carbohydrates in the pulping process [32, 34]. At a constant residual lignin level, NSSC-AQ pulps have higher yields than NSSC pulps, indicating that AQ also protects the carbohydrate portion of wood during pulping. Physical strength properties of NSSC-AQ pulp are also significantly higher than that of NSSC pulps [33]. This was confirmed by Virkola et al [29], who found that the properties of the NS-AQ pulps were quoted as being exceptional compared with conventional sulphite pulps, whilst one of the most interesting aspects of the NS-AQ process was found to be the very high pulping yield. A mill in New Zealand has achieved a 25 % increase in its production capacity with the introduction of AQ [32]. AQ was found to permit much faster delignification of hardwoods. It can be used for a variety of objectives, including to decrease the cooking time and to decrease the alkali charge [32].

The most important factors influencing the result of NS-AQ cooking are the total alkali charge, alkali ratio and amount of AQ on wood [29]. The sodium sulphite charge has a greater influence on delignification than the total alkali charge. This was found during softwood NS-AQ cooking trials on both laboratory and mill scale.

The most prominent feature for bulk delignification in neutral sulphite anthraquinone (NS-AQ) cooks is its good selectivity [24]. This was shown during trials on neutral sulphite anthraquinone cooking of pine and birch chips (0.1 % AQ on wood) to produce paper pulps. A 0.1% AQ on oven dry wood is commonly used [24, 28, 35], though dosages from 0.05 % [36] to 1 % [37] AQ on wood have been successfully used. For a 0.5 % AQ dosage, used in neutral sulphite pulping of pine (*Pinus radiata*), the kappa number dropped by half under given pulping conditions. For *Pinus taeda*, the optimum AQ charge was found to be 1 % [38].

Delignification rate expressions for neutral sulphite semichemical (NSSC) and neutral sulphite semichemical anthraquinone (NSSC-AQ) pulping of black spruce were developed by Keskin & Kubes

[33]. The rates take into account the effects of temperature and reaction times on the rates of delignification.

It was found that addition of AQ affects the delignification rate in two ways. First, it increases the reaction order in lignin from 1.7 to 2.1. Second, the reaction rate constant increases. It was also determined that the NSSC process is more temperature dependent than the NSSC-AQ process. Therefore, a temperature rise would favour the delignification in the NSSC process more than in the NSSC-AQ process.

Anthraquinone is believed to enhance delignification during the initial phases of sulphite-AQ pulping by promoting the cleavage of free phenolic Beta-aryl ether linkages [39]. Anthraquinone is reduced in the pulping liquor to anthrahydroquinone (AHQ), which in turn is ionized and dissolves as the AHQ anion with a dark red color, as shown in Fig. 2.7.

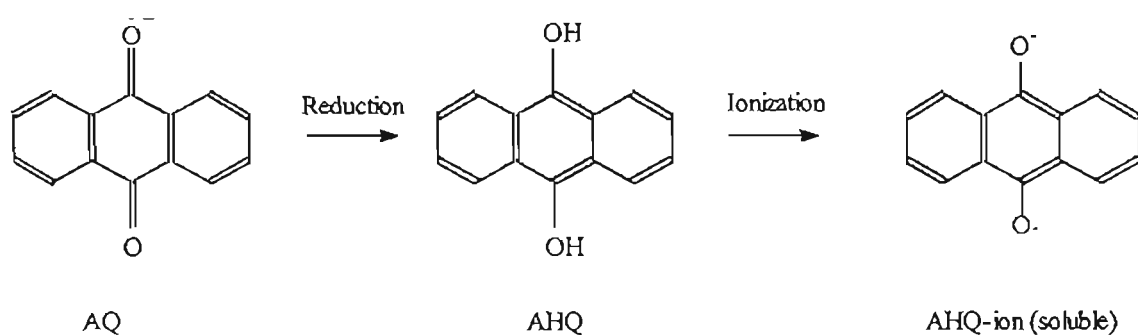


Fig. 2.7: Reduction of anthraquinone to anthrahydroquinone and subsequent ionization [10].

Wood sugars act as the reducing agent [39]. These reduced forms of AQ promote cleavage of free phenolic 2-arylether linkages under sulphite AQ conditions. The mechanism proposed for a three carbon 2-ether model, in which the 2-ether linkage is cleaved via a reduced anthraquinone-quinone methide adduct, is shown in Fig. 2.8. Coniferyl alcohol (B) is formed from the adduct (A), and the sulphonates C and D are formed during the reaction of this alcohol with  $\text{HSO}_3^-$  ions.

AQ also very effectively promotes bulk phase delignification. Three possible roles for anthraquinone in the bulk phase have been identified and were discussed by Suckling [39]. Additional work is still required to establish the role AQ actually plays in the bulk phase.

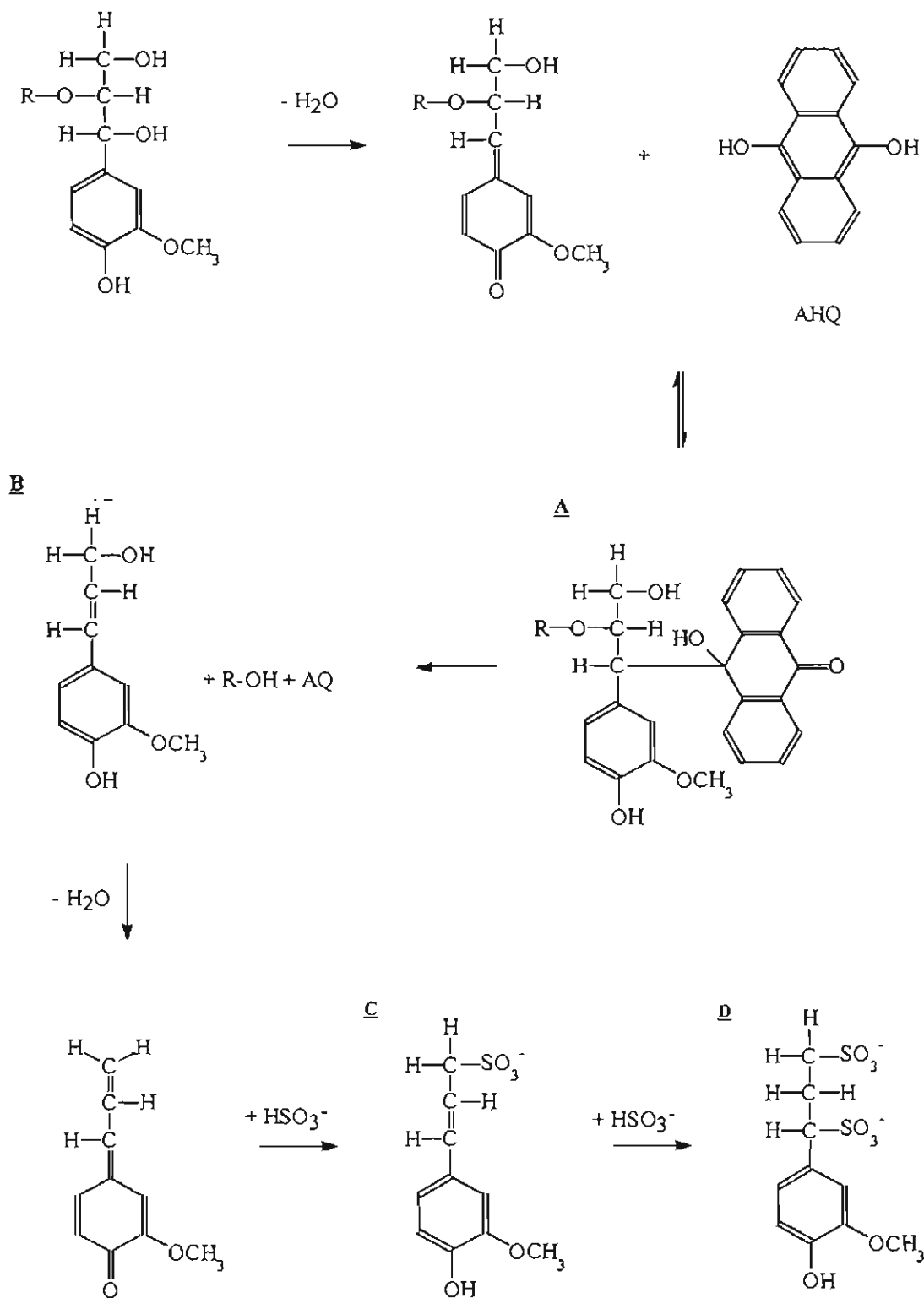


Fig. 2.8: Proposed mechanism for initial delignification in sulphite-AQ pulping [39].

The advantage of using AQ as an additive was also practically shown by McArthur [36]. He listed the following improvements in the NSSC process at Whakatane Board Mills, where *Pinus radiata* is used, which were achieved when 0.05% AQ was introduced to their existing NSSC process:

- Reduction of time at pressure from 135 to 30 min
- The quantity of sodium sulphite employed has been reduced by 11.5 %.
- A reduction of 60 % in primary refining energy
- Increase in plant capacity by 31 %.
- The pulp presented to the paperboard machine stock preparation system was of higher freeness and tearing resistance but of lower bursting and tensile strengths; a less developed fibre allowing greater flexibility in its end use.

#### 2.3.4. Properties of NSSC pulps

Pulp yields for neutral sulphite pulp are generally higher than that for kraft at a similar residual lignin level. At a similar degree of delignification, the yield for both pine (*Pinus silvestris*) and spruce (*Picea abies*) pulp is 6 to 12 % higher than in kraft pulping [29]. According to Ojanen [24] the total yield in pine NS-AQ cooking is 8 to 10 % higher than that in pine kraft cooking, whilst in birch NS-AQ cooking the yield advantage is 6 to 8 % compared with birch kraft cooking.

Hardwood NSSC pulps contain more pentosans than pulps cooked by any other common process. This is largely due to the neutral nature of the pulping liquor, which restrains hydrolysis and dissolution of the hemicelluloses during pulping. Both yield and strength benefit from high retention of hemicelluloses. With light mechanical processing, the pentosans on the surface of the fiber swell rapidly and furnish additional bonding. Although some disagreement appears to exist on the effect of the yield on the strength properties, the general conclusion is that the lower the yield, the better the average strength [10].

Semichemical pulp for corrugating medium contains 15% to 20% lignin depending on wood species and pulping conditions. As a result of the high amount of lignin retained, semichemical fibres are heavier than fully pulped fibres. Consequently, a sheet of standard weight contains fewer fibres. The semichemical fibres are also stiffer, because of the large hemicellulose content, than comparable chemical pulps prepared from the same species [10]. As the yield is reduced by extended pulping, higher chemical charge or higher cooking temperature, the increasing number of fibres per gram and increasing flexibility contribute to greater bonding within the sheet. Sheet density, when pressed under similar conditions, also increases as the fibres become less rigid.

NSSC hardwood pulps respond to refining in a similar way to other pulps except that they increase somewhat in tear strength as freeness is reduced [10]. Other properties such as density, flat crush (Concora), ring crush and tensile strengths also benefit from freeness reduction, while caliper, bulk and stock drainage rate decrease.

In tests done on NS-AQ pulp from pine slabwood and corewood [40] it was found that the presence of the compound middle lamella on fibre surfaces and its general resistance to disruption and fibrillation by pulp refining are properties unique to the neutral sulphite-anthraquinone pulps. These pulps are of substantially higher yield than kraft pulps of roughly the same strength qualities, are easily refined and have the potential to be rapid draining on paper machine wires. Furthermore such pulps could be made into highly consolidated and dense webs of high porosity because of the development with refining of highly bondable fibres with essentially unfibrillated surfaces. Web porosity will, therefore, largely depend on factors which influence fibre morphology (length, diameter, wall thickness) and degree of fibre collapse and packing arrangement within the paper web. Fines content will remain low in webs made from neutral sulphite-anthraquinone pulps since interfibre voids will not be filled by such material.

### **2.3.5. Use of NSSC pulps**

The main product made from NSSC pulp is corrugated medium. A small amount of NSSC pulp is used in the base sheet duplex linerboard as low cost furnish component, which imparts good compression strength. The quality of NSSC pulp has to be high enough to meet the requirements in three areas. They are paper machine runnability, corrugator runnability and end use as component of corrugated containers.

### **2.3.6. Simultaneous pulping of hardwood and softwood**

Very little information is available on simultaneous pulping of hardwood and softwood. This is mainly because technically it is preferable to pulp hardwood and softwood separately. There are, however, a variety of circumstances which make it technically and/or economically advantageous to pulp mixtures of hardwoods or HW/SW blends even though the components have quite different pulping properties [41].

Some investigations into the simultaneous pulping of hardwood and softwood species by means of other chemical processes have been reported. Long term mill operating experience has shown that hardwood and pine can be successfully mixed pulped by the countercurrent soda-AQ process [42]. During simultaneous hardwood and softwood kraft and soda-AQ pulping trials, it was found that hardwood was severely overcooked in all cases. This is because hardwoods pulp more easily than softwoods, because of the different chemical nature of the lignin of the two species, as well as the lower lignin content of hardwood [41].

A way to minimize the overcooking of HW chips is by manipulating the chip thickness, especially the pine chip thickness [42]. Increasing the hardwood chip thickness or decreasing that of the softwood decreases the difference of the extent of delignification of the two species.

Mixed pulp yield was found to be less than would arise from separate pulping to the same degree of delignification [41, 42]. The yield advantage of separate pulping during kraft and soda-AQ pulping was found to be at a maximum with 50:50 mixtures of hardwood and softwood and was lowest with pine rich mixtures. Therefore, since hardwood chips give higher yield than softwood chips at a given degree of delignification, there could be practical circumstances where mixed pulping of high pine content mixtures, could be an attractive option [41].

The chemical requirement for mixed pulping of hardwoods (eucalyptus, wattle and myrtle) and pine (*Pinus radiata*) was found to be higher than for separate pulping [41]. This difference increased with increasing hardwood content. A linear additive mixing rule, using the fractions of hardwood and softwood charged, did not apply for total pulp yield or alkali requirement.

In kraft pulping trials done on a variety of hardwood and softwood species, it was found that a furnish obtained by blending the pulps of individual species, including hardwood and softwood species, and those obtained by cooking the mixture of all the species give almost similar strength properties [43]. This indicates that there is no advantage to be gained when pulping hardwood and softwoods separately as opposed to simultaneously. However, this was determined for the kraft process, and the pulps compared had different residual lignin levels. Therefore the basis for comparison of the separately and simultaneously pulped mixtures was not clear.

## 2.4. Alkaline sulphite pulping (AS-AQ)

Alkaline sulphite-AQ pulping is the fifth and newest member of the family of sulphite processes. It uses sodium sulphite and sodium hydroxide as cooking chemicals. It has met with increasing interest in since 1989 [44]. The addition of AQ to alkaline sulphite liquor considerably accelerated delignification, improved its selectivity and allowed for pulping at much lower alkalinity than the original process (single-stage alkaline sulphite process). The improved selectivity leads to higher yields at a given degree of delignification when compared with kraft pulping [44, 45], with yields up to 10 % higher than kraft pulp being reported [45, 46].

An advantage of the AS-AQ process is that the pulp can be produced at a high yield (70 %) while maintaining easy fiberization and high strength characteristics. AS-AQ liner at 70 % yield gives combined

board properties that were equal to, or better than, those obtained with kraft liner at 54 % yield, except for a slightly lower tear strength [47]. An added advantage of the AS-AQ process is the lack of kraft odor. AS-AQ pulps are also easily bleached to high brightness [44].

Although at its present state of development the cooking rate of AS-AQ is somewhat deficient relative to kraft [35], full process evaluations have confirmed economic advantages in capital investment and production cost. However, improving the rate of cooking is a desirable objective and investigations are continuing in Scandinavia, Canada, the United States and elsewhere. The same delignification rate as in kraft cooking can be reached through the AS-AQ process if an AQ dosage of 0.1% on wood is used and the temperature is increased by 9 C ° from 166 to 175 °C [44].

Compared with NS-AQ pulping, the AS-AQ process uses a smaller chemical charge and shorter cooking time for pulp with a high degree of delignification (i.e. full chemical pulp), whilst the NS-AQ pulps have a higher yield and reduced bleaching costs. [48]. For pulp with a low degree of delignification, as in semichemical pulping, the NS-AQ process is preferred because of the higher yield, although it is not suitable when a pulp with a high tear strength is desired.



## 2.5. Process description of NSSC process at Mondi Kraft, Piet Retief

Block diagrams of the process are presented in Fig. 2.9 to 2.11.

### 2.5.1. Chip preparation

Hardwood is delivered to the mill in the form of debarked logs originating from forests in the surrounding area. These logs are debarked since bark consumes chemicals and persists in the pulp as dark specs, which can be difficult to remove. The logs are chipped in a 1.68 m (66 inch) Norman chipper and stored in chip piles. Softwood is delivered in the form of chips from several saw mills in the area. These chips are stored in separate chip piles. Chips from the chip piles are loaded into chip loading bins by means of front-end loaders. Screw feeders transport the chips from the loading bins onto two vibrating screens, where undersized and oversized chips are removed. The ratio of hardwood to softwood is controlled by the relative rates of the screw feeders. The chip accepts from the screens are transported to a chip hopper by means of a conveyer belt.

From the chip hopper the chips go through a chip meter and a low pressure feeder into a steaming vessel. This steaming vessel is in the form of a screw-type conveyer and is used to impregnate the chips with steam at 100 kPa. The purpose of steaming is to remove air from the chips. When the steam-impregnated chips are exposed to the high pressure inside the digester, the steam condenses. This causes the cooking liquor to effectively be sucked into the chips to fill the volume left by the condensed steam, resulting in more effective liquor impregnation.

### 2.5.2. Pulping

From the steaming vessel the chips go via a chip chute into a high pressure feeder. Circulating cooking liquor from the digester is used to transport the chips from the high pressure feeder to the top separator at the top of the digester. The temperature of the cooking liquor and chip mixture fed to the top separator is about 100°C. The top separator is an inclined screw conveyor, which feeds the chips to the digester. Excess cooking liquor from the high pressure feeder is pumped through a sand separator and an inline strainer to remove solid materials. The excess cooking liquor as well as fresh cooking liquor and AQ dispersion from mixing tanks is subsequently pumped to the top separator. The closed nature of this liquor circulation loop ensures that no cooking liquor is wasted.

The digester, built in 1970, is a 30 m Kamyr type continuous digester with a diameter of 3 m at the base. It can be divided into three zones, the impregnation zone, the cooking zone and the countercurrent washing zone. The impregnation zone starts in the top separator, where the chips are impregnated with the cooking

liquor. The chips descend down the digester where the cooking zone starts. The heat is supplied by high pressure (11 to 13 bar) steam at 220 to 250 °C injected near the top of the digester, where the temperature is at its maximum value of 179 °C. The digester temperature is controlled by the steam flow rate. There are four sets of screens down the length of the digester where the liquor is extracted. The liquor from the top set of extraction screens can be circulated through a heat exchanger and pumped back to the top of the digester. This system is not used at the mill.

The spent cooking liquor is extracted from either of the middle two extraction screens, where the temperature is about 165 °C. The washing zone starts below the bottom extraction screens. Here the pulping reaction is stopped by countercurrent wash water moving upwards through the chip column. The wash water is pumped through a heat exchanger where it is heated up to 130 °C and pumped back to the bottom of the digester. Water from external pulp washers is pumped into the digester through nozzles located below the washing zone extraction screens to provide countercurrent washing. The temperature in this zone is about 80 °C.

The cooked chips leave the digester via an outlet device at the bottom. This device has rotating paddle arms which break up the chip mass. The chips leave the digester through a valve and the Kamyr blow unit, and are blown into a blow cyclone.

### 2.5.3. Stock preparation

The cooked chips from the blow tank are sent through two parallel rotary Contra Shears, which are rotating drum filters for draining black liquor from the pulp. This pulp is sent to a storage chest where it is diluted and agitated. From here the pulp is fed through two Asplund raffinators in parallel to break down the cooked chips, after which it goes through two parallel Sund slurry presses. In the slurry presses excess water is removed before the pulp is stored in a pile.

From these piles, pulp is fed to a Grubbens pulper where the pulp is diluted and disintegrated. The pulp is fed through another set of raffinators for further fibre separation and stored in the pre-refining chest. From here the pulp is refined to develop pulp strength. The pulp is stored in the refined chest where the freeness is measured. The freeness is an indication of the rate of which water drains from the pulp and determines the speed at which the paper machine can be operated. It is also an indication of the degree of refining and thus the pulp strength. Pulp from the refined chest is fed to the blend chest where waste paper pulp is added. The ratio of NSSC pulp to waste paper pulp is 55:45. Pulp from the blend chest is sent to the paper machine. Linerboard is formed on the paper machine and stored in rolls which are cut to size to suit the customer.

#### 2.5.4. Spent liquor treatment

The extracted black liquor is flashed in a cyclone, with the flashed steam used for chip impregnation in the low pressure steaming vessel. The black liquor is subsequently pumped to black liquor dams where water is allowed to evaporate. Black liquor from the dams is pumped through a fibre filter to remove large solid materials. The filtered black liquor is concentrated in five evaporators, two of which are in parallel, from a solids content of about 15 % to about 30 %. The concentrated liquor is stored in an intermediate storage tank. From this storage tank the liquor is pumped through a venturi scrubber, where the liquor is concentrated to about 50 % by the flue gasses from a Copeland fluidized bed incinerator. This heavy black liquor is again stored in an intermediate storage tank.

The heavy black liquor is fed to the Copeland fluidized bed incinerator which operates at a temperature of 700 °C. The black liquor is introduced into the space above the fluidized bed as a conical spray with air dispersion. Air supplied by a blower is used to fluidize the bed. The organic constituents of the black liquor are converted to carbon dioxide, water vapour and various other pyrolysis products through combustion, whilst the inorganic constituents are oxidised to  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  which is sold as a by-product as salt cake (chemical data sheet in appendix A). The reactor gases are sent through the venturi scrubber and then through a water scrubber to reduce emission carry-over, before being released to the atmosphere.

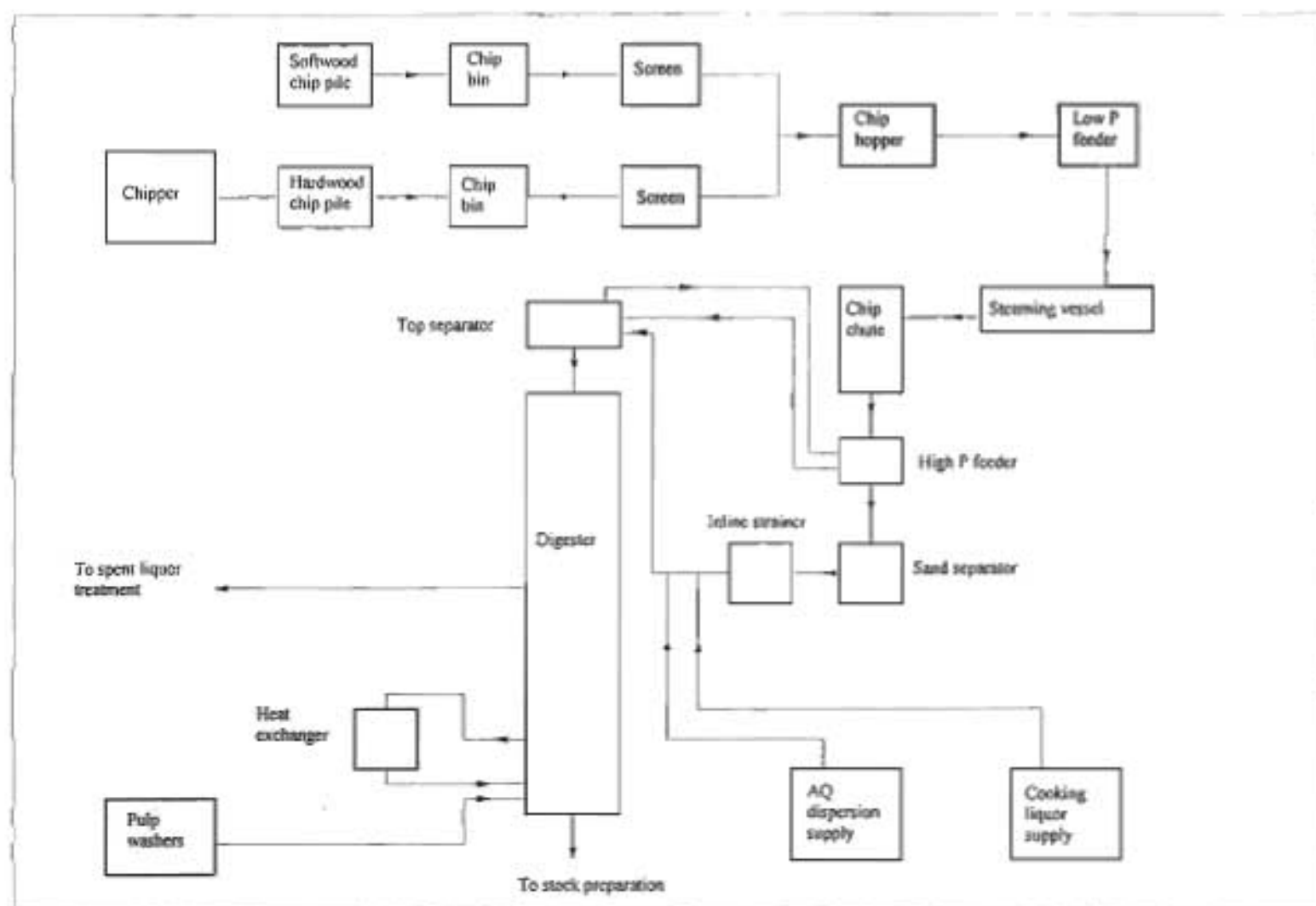


Fig 2.9: Block diagram of chip preparation and pulping at Mondi Kraft, Piet Retief.

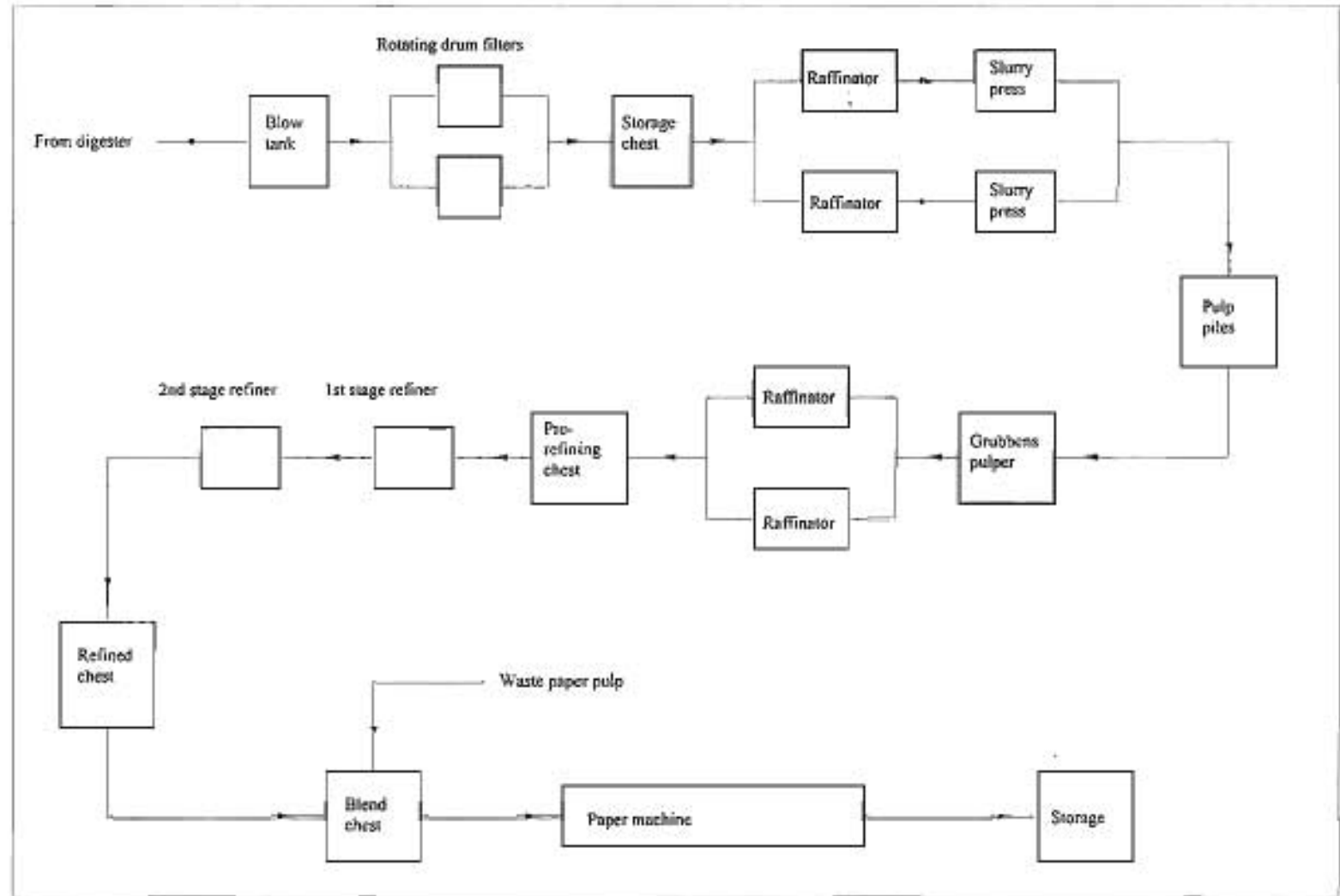


Fig 2.10: Block diagram of stock preparation and linerboard making at Mondi Kraft, Piet Retief.

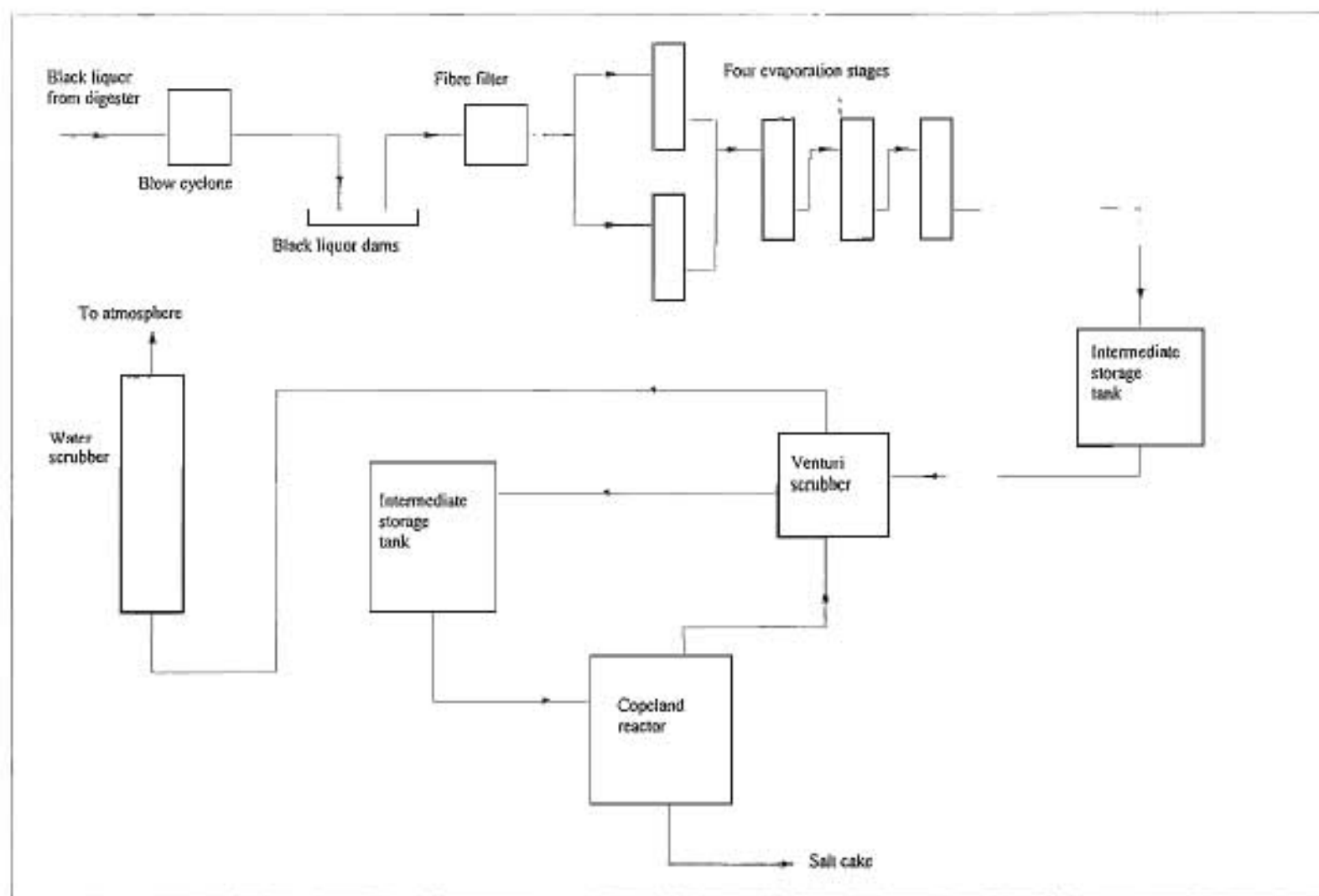


Fig 2.11: Block diagram of spent liquor treatment at Mondi Kraft, Piet Retief.

## 3. Experimental

### 3.1. Laboratory digester

A laboratory digester with liquor circulation system was constructed for pulping experiments. The design was based on a pilot-scale digester used at Mondi Kraft's Richards Bay Mill. Mondi's pilot-scale digester is a modified version of a unit supplied by Aurora. Although the digester was build for this project, the design is versatile and allows for other cooking processes.

#### 3.1.1. Hardware description

A schematic drawing of the digester is shown in Fig. 3.1. The digester vessel is a pressure vessel made of 316L stainless steel with a wall thickness of 10 mm. The inside diameter of the vessel is 203 mm, whilst the height is 420 mm, giving a volume of 13.6 liters. The vessel has a 316 stainless steel lid of 16 mm thickness, which is fastened by 12 M20x75 stainless steel bolts. Wood chips are loaded into a basket made of 316L stainless steel sieve plate with 3.2 mm holes which fits into the digester vessel. The basket prevents solid material being pumped through the circulation line. The liquor is pumped from the bottom of the vessel by means of a magnetically driven pump through 12 mm stainless steel piping. This type of pump has no seals which enables operation under high temperatures and pressures and with highly corrosive liquids. The liquor is pumped through a vertical cooling jacket and is returned to the digester vessel via a manual ball valve (V9). A distribution nozzle is inserted on the inlet to the digester above the chip level to ensure even distribution of the liquor return.

A smaller cooling jacket is located before the pump inlet, and the cooling water is connected in series with the vertical cooling jacket. The cooling jackets are used for temperature control and to cool down the circulating liquor after completion of the cook. The ball valve (V9) located on the liquor circulation line is used to regulate the flow of the liquor to ensure even distribution over the chips. A magnetic flow meter (FI1) is installed on the top circulation line for flow measurement.

On the bottom horizontal part of the liquor circulation line two other lines are connected, one of which leads to the drain, whilst the other is connected to a fresh water supply header. These lines are used for washing the pulp, draining spent liquor out of the system and flushing the system after completion of a cook. Both these lines are fitted with pneumatically activated solenoid valves (V1 & V3) whilst a similar valve (V2) is fitted between the connections of the drain and water lines on the circulation line. This valve is closed whilst the system is being flushed.

A sampling system is connected on the top horizontal part of the circulation line. This consists of a 6 mm stainless steel line, which tees off from the circulation line and goes through a

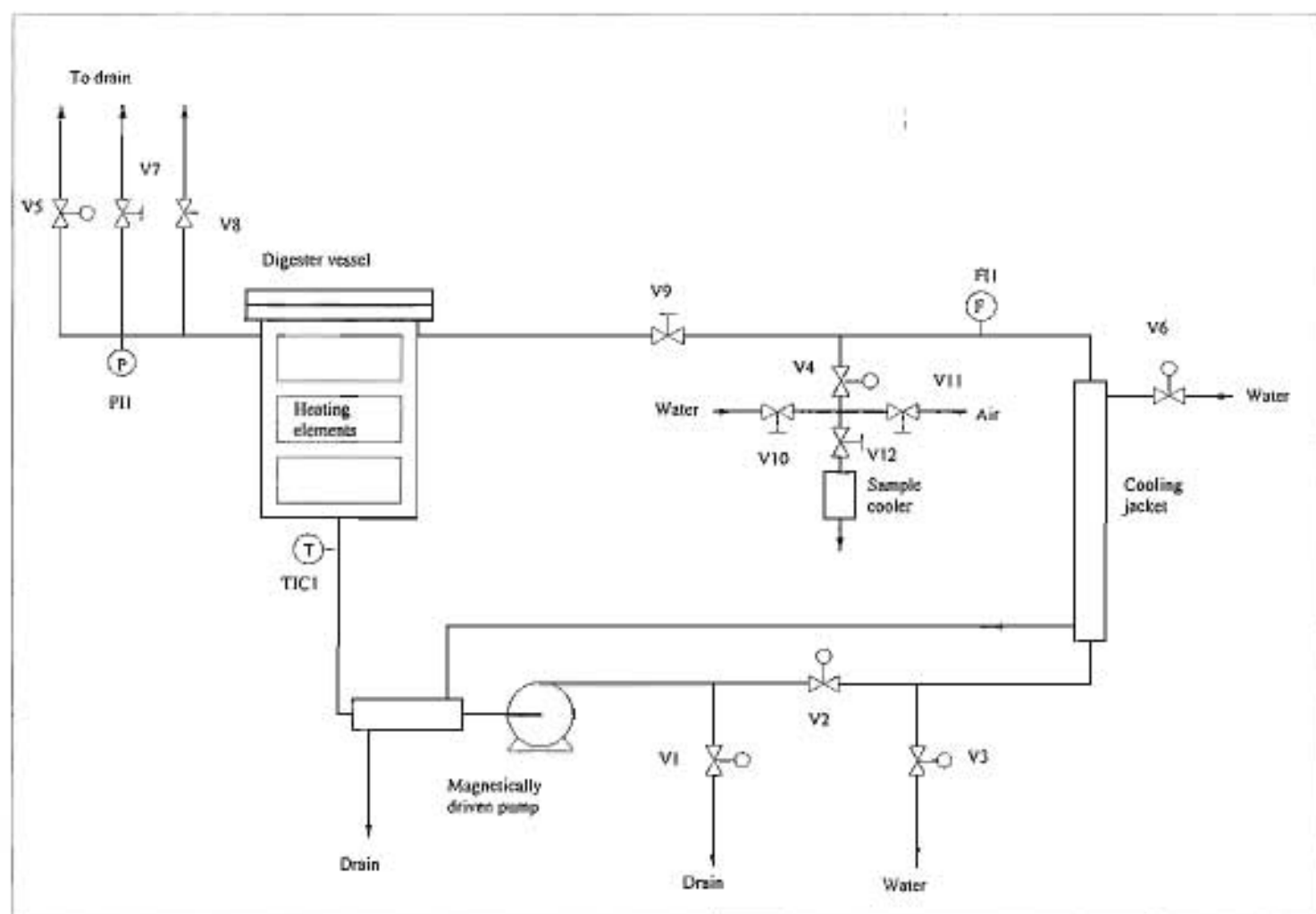


Fig. 3.1: Schematic drawing of Laboratory digester.



pneumatically operated solenoid valve (V4), a manual needle valve (V12) and cooling jacket. The needle valve is used to control the flow through the sampling system and also for isolation of the sampling system if required. The piping in the cooling jacket is in the form of a coil and has a total length of approximately 2 m. At the outlet a beaker is used to collect the sample. Two 6 mm stainless steel lines are connected between the needle valve and the solenoid valve. One of these lines is connected to the water supply header, whilst the other is connected to an air supply header. These lines are used to clean the sampling system after a cook and are both fitted with manual needle valves (V10 & V11). The air supply header also supplies compressed air for the pneumatically operated solenoid valves. An air regulator is fitted before the header, and controls the air supply at 350 kPa.

A venting system is connected to the vessel. This consists of a 12 mm stainless steel line connected near the top of the vessel. This line tees off into three different lines, which contain a pneumatically operated solenoid valve (V5), a safety relief valve (V8) set at 13 bar, and a manual needle valve (V7) respectively. The solenoid valve is used for non-condensable gas purging during the cook, whilst the manual valve is fitted as back-up for the solenoid valve. A pressure gauge (PI1) and pressure transducer are fitted before the needle valve.

Water for the cooling jackets on the circulation line as well as on the sampling system is supplied by the water header. A solenoid valve (V6) is fitted at the inlet to the vertical cooling jacket on the liquor circulation line to control the water flow through the cooling jacket. The inlet is located at the top of the cooling jacket with the outlet at the bottom, to ensure that, whilst the cooling jacket is deactivated, there will be no standing water in the jacket, which would slow down the heating up process of the liquor.

Heat is supplied to the vessel by three banks of heating elements, consisting of three elements each. These heating elements are bands fitted around the vessel, and each is capable of delivering 900 Watts power, which gives a total power capability of 8.1 kW. Each of the three banks of heating elements is fitted with a high temperature trip switch set at 270 °C. These trip switches prevent overheating of the heating elements. A thermocouple is fitted at the bottom of the vessel for measuring the digester temperature (TIC1). The whole system was designed for a maximum pressure of 15 bar and a maximum temperature of 220 °C, with the pressure relief valve set at 13 bar.

### **3.1.2. Control process**

#### **3.1.2.1. Software description**

The process is controlled by a Siemens S5 115U Programmable Logic Controller (PLC) and Turbolink is used for the man-machine interface. The PLC consists of a power supply module, a central processing unit, an expansion module, an analogue input module, a digital input module and a digital output module. The different inputs and outputs of the process are listed below

Digital outputs:

3 Heating element temperature trip switches on/off

Digital inputs:

Pump on/off

3 banks of heating elements on/off

Drain line solenoid valve open/closed

Wash water line solenoid valve open/closed

Main circulation line solenoid valve (isolation valve) open/closed

Sampling solenoid valve open/closed

Venting line solenoid valve open/closed

Cooling jacket solenoid valve open/closed

Analogue outputs:

Digester temperature

Digester pressure

All the above mentioned inputs and outputs are cyclically communicated with the PLC, with the scan time being between 2 and 6 ms. Turbolink, the man-machine interface software, allows the operator to enter various cooking parameters and to control the process via a PC. Data between the PLC and Turbolink is cyclically exchanged at a frequency of every 600 to 700 ms. A list of the various Turbolink inputs is given below:

Ramp time:	Duration of the ramping stage.
Cook time:	Duration of the cooking at maximum temperature stage.
Cook temperature:	Maximum cooking temperature.
H-Factor control:	This is switched on if the cook is ended when a certain H-factor is reached, instead of after a specified time.
Target H-factor:	H-factor at which the cook is ended, if H-factor control is used.
Purge time:	Time for which the venting solenoid is opened when the temperature reaches 110 °C.
Sampling time:	Time for which sampling solenoid is opened when the temperature reaches 90 °C during the cooling down stage.
M:	H-factor constant (described in appendix C)
N:	H-factor constant
Start:	Switch to start the process.
Reset:	Switch used to reset all the parameters used in the control process in order to start a new cook. It can also be used as an emergency stop.

Manual:	Switched on to enable the operator to manually operate the pump and drain, wash water and isolation valves.
Drain:	Opens and closes the drain valve.
Isolate:	Opens and closes the isolation valve.
Wash:	Opens and closes the wash water valve.
Pump:	Switches pump on and off.
Sample:	Switched on to enable sampling of the liquor at any stage during a cook.

### 3.1.2.2. The cooking process

Each run or cook can be divided into three different phases, the ramp time, the cooking time at maximum temperature and the cooling down time. When the process is started, only the pump and the bottom bank of heating elements are switched on. When the temperature reaches a value of 40 °C, the ramp time is started. In this phase the temperature is increased at a constant rate towards the maximum cooking temperature in the specified ramp time (usually 60 min). When a temperature of 110 °C is reached, the venting line solenoid is activated by the PLC for the specified purging time. This is done to purge non-condensable gases. Once the ramping time is over, the temperature is controlled at the cooking temperature for the specified cooking time. When the time at cooking temperature has elapsed, the heating elements are switched off and the cooling jacket is activated. This is the cooling down phase. While the liquor is cooling down and when it reaches a value of 90 °C, the sample solenoid is opened for the specified sampling time and a sample of the spent liquor is collected. The circulating liquor is cooled down to a temperature of 40 °C, at which stage the pump is switched off and the cooling jacket is deactivated. At this stage the cook is completed.

During the cook, the H-factor is calculated. The H-factor was developed by Vroom [27] and is described by the following equation:

$$\text{H-factor} = \int e^{(M - N/T)} dt,$$

where T is the temperature in Kelvin, and M and N are constants for a specific pulping reaction. The following values for M and N for neutral sulphite pulping were calculated using activation energies as determined by Eagle and McDonough [38] and Keskin and Kubes [33]

	M	N (K)
Hardwood	35.7	13229
Softwood	41.9	15635
Mixture, 41 % softwood	38.0	14192

The derivation of M and N is shown appendix B.

Instead of pulping for a specified time, it is also possible to cook to a certain H-factor. This is used extensively in kraft pulping [7]. The H-factor has not been successfully employed in neutral and alkaline sulphite pulping at this stage, and the H-factor control option was not used during the experimental work described in this thesis. A print-out of both the PLC step 5 program and the Turbolink program, along with a detailed description of the control process is given in appendix C.

### 3.1.2.3. Temperature control

Temperature control by the PLC occurs during the ramping and cooking at maximum temperature stages of each cook. A simple feedback on/off control loop is used. The digester temperature is measured by the digester thermocouple, with the temperature signal being sent to the PLC. The PLC subsequently adjusts the temperature by switching the heating bands on or off and activating the cooling jacket for short periods.

During the ramping stage, the temperature is increased at a constant rate. The setpoint is recalculated every 10 seconds. The calculation of the setpoint is done in the Turbolink program because of software limitations of the S5 PLC. Following a trial and error procedure, the following control procedure for the ramp time was found to be satisfactory: All three banks of heating elements are on as long as the temperature is 0.2 C ° above the setpoint or lower. If the temperature is between 0.2 and 1 C ° above the setpoint, only the bottom bank is switched on. If the temperature is more than 1 C ° above the setpoint, the cooling jacket is activated for half a second.

During the cooking at maximum temperature stage, the setpoint is simply the specified cooking temperature. The control procedure in this phase differs from that used during the ramp time. While the temperature is equal to or below the setpoint, all three banks of heating bands are switched on. When or if the temperature reaches a value of 0.7 C ° above the setpoint, the cooling jacket is activated for one second. This procedure allowed the temperature to be controlled to within one degree of the setpoint. The temperature profile for an entire cook with the setpoint for the cooking temperature at 179 °C is shown in Fig. 3.2. A close-up of the temperature profile as the ramp stage ends and the constant temperature stage starts is shown in Fig. 3.3.

As described earlier, a high temperature trip switch is connected to each bank of heating elements. These trip switches overwrite the control program to prevent overheating of the heating elements. A bank of heating elements are switched on again ten seconds after the temperature of that bank drops below 270 °C.

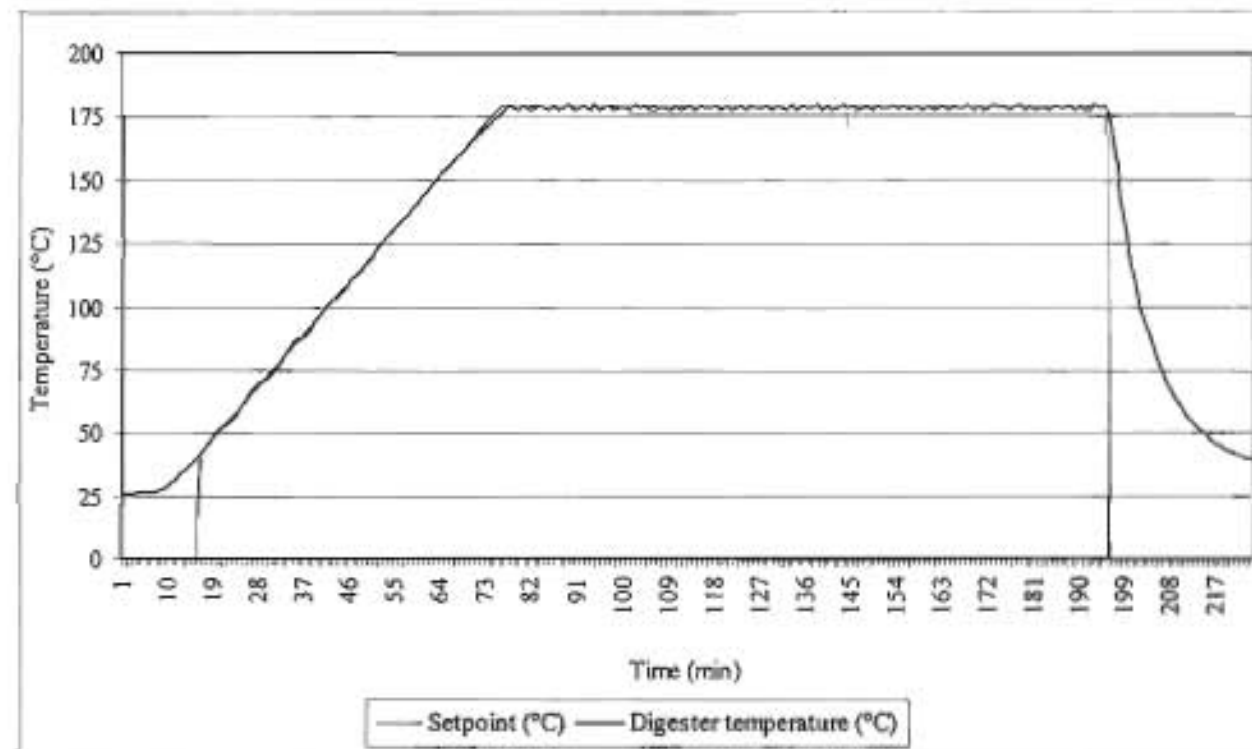


Fig. 3.2: Temperature profile for a cook with cooking temperature setpoint at 179 °C.

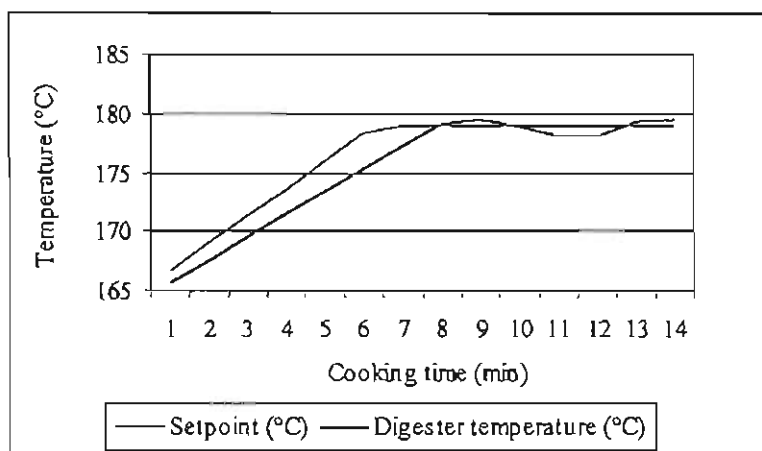


Fig. 3.3: Temperature profile for period when ramp stage is completed and constant temperature stage starts.

## 3.2. Experimental procedure

### 3.2.1. Chip preparation

In the process at Piet Retief the softwood chip feed is made up of various pine species, including *Pinus patula*, *Pinus taeda*, and *Pinus elliotti*, whilst the hardwood chips are a mixture of *Eucalyptus* species, including *E.grandis* and *E.saligna*. For the experimental work *P. patula* and *E. grandis* were used since these make up the bulk of the softwood and hardwood chip feeds respectively. Single species were used to eliminate the variability derived from the inherent differences between different species of the same genus.

*P.patula* from the Natal Midlands area and *E.grandis* from northern Kwazulu Natal was delivered as logs. Three different batches of wood were used for the pulping trials. The *P.patula* logs used were between 16 and 17 years old, whilst ten year old *E.grandis* logs were used. The logs were debarked and cut by means of a hand held chainsaw into discs of thicknesses between 15 and 20 mm. These discs were chipped by means of a laboratory chipper which has a guillotine type action, and produces chips with a uniform thickness of about 3 mm ( $\pm 0.5$  mm). At high pH values the chip thickness is the most important dimension of the chip from a mass transfer perspective [1]. Using these chips with a uniform thickness reduced the effect of chip variability on the process.

The chips were left to dry out for a week after chipping. This was done to allow the moisture content of the chips to come into equilibrium with that of the ambient air, as done by Chen et al [49]. After seven days, the moisture content of the batch of chips was determined according to Tappi Test Method

T 258 om-94 [50]. The chips were stored in a sealed plastic bag to ensure the moisture content was not effected by atmospheric changes. If the moisture content of the chips is measured before it has come into equilibrium with that of the air, the moisture content of the chips decreases inside the bag, due to condensation on the sides of the bag. This leads to inaccuracy in the weight of oven dry chips charged to the digester, and subsequently in all chemical charges and yield determinations. Before each run the chips were sorted to remove under- and oversized, as well as damaged chips.

### 3.2.2. Liquor preparation

A liquor to wood ratio of 5:1 was used for all the runs since this ensured that most of the chips in the basket were covered with liquor. This is not crucial since with a good liquor distribution over the chips, variability is not affected [51]. Commercial grade sodium sulphite and sodium carbonate, as well as commercial grade anthraquinone (AQ) from the Piet Retief mill was used for liquor preparation. Laboratory data sheets for the chemicals are given in appendix A. Tap water was used to dissolve 220 g of sodium sulphite and 22 g of sodium carbonate to ensure a 10:1 ratio of sodium sulphite to sodium carbonate, as is used by the mill. The mixture was stirred for at least 24 h since the sodium sulphite concentration was near its saturation value. After stirring, the total alkali and sulphite percentage of the liquor was measured according to Mondi Kraft Laboratory Standard Methods WPI.004 and WPI.005 (see appendix D), which are based on Tappi Test Method T 624 cm-00 [50]. The sulphite percentages of various liquor batches varied between 84 and 86 %, whilst the total alkali (TA) was between 118 and 124 g/L expressed as grams of  $\text{Na}_2\text{O}$  per litre. The sulphite concentration varied between 101 and 104 g/L expressed as grams of  $\text{Na}_2\text{O}$  per litre, a variation of about 3 %. The TA of the cooking liquor was measured regularly to account for oxidation of the sulphite. However, the decrease in TA of the cooking liquor was found to be insignificant.

The AQ was delivered by Buckmann Laboratories as a dispersion in water of 419 g/L strength. For each run, the cooking liquor needed to give the desired TA charge on oven dry wood was calculated, as well as the volume of AQ dispersion needed to give the desired AQ dosage. The AQ and cooking liquor were added together, and the volume of tap water needed to give a total volume of 5 L in the digester, including the moisture in the wood chips, was calculated and added. The mixture was stirred well before adding to the digester. The pH of selected cooking liquors were measured at this stage.

### 3.2.3. Cooking

For each run the chips and liquor were added to the digester and after all the parameters had been set on Turbolink, the run was started. Sample calculations for the chip and liquor charges are shown in appendix E. The flow control valve was adjusted until an even distribution of liquor over the chips was obtained before the lid was closed. The cook was subsequently controlled by the control system as described earlier.

After the completion of the cook, the black liquor sample was transferred to a flask and stored. Selected black liquor samples were later tested for residual TA and pH. The rest of the black liquor was drained out of the vessel and the pulped chips were washed for 5 min by closing the isolation valve and opening the drain and wash water valves. After 5 min the wash water valve was closed and the water allowed to drain out of the vessel while the lid was opened. After washing, the pulped chips were removed from the basket and excess water was removed by spinning it for five minutes in a spin drier with a diameter of 300 mm at a speed of 300 rpm. The pulped chips were stored in plastic bags.

#### **3.2.4. Refining**

Since the pulped chips from the digester were still in chip form, the chips had to be refined before handsheet making. This simulates the refining process in the mill. The refining was done in a 12 inch disc refiner at Mondi Kraft's Richards Bay mill at room temperature. Each batch of pulp was given two passes through the refiner, with the discs set at 0.5 mm apart. Tap water was used to flush the pulp through the refiner. The purpose of this refining was to separate the individual fibres and not to develop pulp strength. After refining the pulp was drained and spun dry in the spin drier described previously for five minutes.

#### **3.2.5. Pulp evaluation**

The yield of the refined pulp was determined after spin drying. The total mass of refined pulp was weighed and the moisture content of the pulp determined according to Tappi Test Method T 258 om-94 [50]. This was done to determine the weight of oven dry pulp produced. The yield was calculated by dividing the weight of oven dry pulp by the weight of oven dry wood charged to the digester originally.

The Hypo number of the pulp was determined according to a slightly modified version of Tappi Test method T 253 wd-98 [50]. The Hypo number is an indication of the degree of delignification of the pulp, similar to the more frequently used Kappa number. The advantage of the Hypo number is that it can be used for all grades of unbleached pulps without limitation in respect to their yield [50], whereas the Kappa number is only applicable to pulps with a yield of less than 70 %. The Hypo number testing method was changed slightly from the prescribed method. Instead of using a positive pressure in the separating funnel to force the potassium iodide solution into the reaction flask, a vacuum was created inside the flask before any chemicals were added. This vacuum was used to suck all the reagents into the flask through the separating funnel. This method was found to be easier to carry out and resulted in the potassium iodide entering the reaction vessel more rapidly, producing more reproducible results. A comparison of the Hypo number results when using the original and the modified test methods is given in appendix F.

Handsheets for testing pulp strength properties were made at the CSIR's Forestry and Forest Product Research Centre. Each batch of pulp was beaten to various extents using a PFI mill according to Tappi



Test method T 248 sp-00 [50]. After beating the Canadian Standard Freeness (CSF) was measured as described in Tappi Test method T 227 om-99 [50] and 6 handsheets were made on a laboratory handsheet maker for each different beating level, according to Tappi Test method T 205 sp-95 [50]. After conditioning in a humidity controlled room for at least 24 h, the handsheets were weighed, cut into several pieces and the tensile, burst and tear strength measured, as described in Tappi Test method T 220 sp-96 [50].

### 3.3. Reproducibility

To investigate the reproducibility of the results obtained, four cooks were repeated under the same conditions. These cooks were done using the a mixture of hardwood and softwood in the same ratio as used by the mill, with the cooking parameters kept at the standard mill values. These refined yields and Hypo numbers of these cooks were determined, and the results analyzed for reproducibility. The standard deviation and repeatability, as described by Tappi Test Method T 1200 sp-00 [50], for both the refined yield and the Hypo number is shown in Table 3.1.

Table 3.1: Hypo number and yield reproducibility results for four cooks produced under the same conditions

	Refined yield (%)	Hypo number
Average	72.9	18.0
Standard deviation	0.61	0.15
Repeatability (%)	1.04	1.03

The repeatability refers to a limit within which agreement may be expected 95 % of the time between two test results obtained under essentially the same conditions and from the same homogeneous sample of material. In the case of the Hypo number, the repeatability was found to be 1.03 %, which is less than the value of 2.6 % for the Hypo number testing method as reported in Tappi Test Method T 253 wd-98 [50]. This indicates that experimental variations other than that caused by the Hypo number testing method are insignificant. For the yield, the repeatability was calculated as 1.04 %, which means a 95 % confidence interval of 0.7 percentage points above or below a certain value, which was also deemed satisfactory.

## 4. Results and Discussion

### 4.1. Current process

In this section the effect of various operating variables on the current cooking process is described.

#### 4.1.1. Effect of cooking time on refined yield and Hypo number

The residence time in a continuous digester, as used at the plant, and the cooking time in a batch digester, as used in this project, are not directly related because of the inherent differences between the two types [52]. Therefore a basis for comparing the different pulping variables had to be established. It was decided to determine the cooking time needed to produce a pulp with the mill target Hypo number of 18, using the standard mill pulping conditions. This cooking time was then used in all the subsequent cooks done in this project.

Nine cooks using the standard mill conditions as described in Table 1.1 (repeated below) were done using various cooking times at constant cooking temperature. The cooking time values stated exclude the 60 minute period at the start of each cook in which the temperature is ramped at a constant rate from 40 °C to 179 °C.

Table 1.1: Current pulping conditions at Mondi Kraft's Piet Retief mill

Pulping temperature	179 °C
TA charge	9.5 % as Na <sub>2</sub> O on oven dry wood
Sulphite charge	8.5 % as Na <sub>2</sub> O on oven dry wood
Na <sub>2</sub> SO <sub>3</sub> / Na <sub>2</sub> CO <sub>3</sub> ratio	10/1 (kg Na <sub>2</sub> SO <sub>3</sub> /kg Na <sub>2</sub> CO <sub>3</sub> )
AQ dosage	0.1 % on oven dry wood
Hardwood/softwood ratio	50/50 on a volumetric basis
Target Hypo number	18

The 50/50 volumetric ratio of hardwood to softwood was determined to be equivalent to a 41/59 softwood/hardwood ratio on an oven-dry wood base due to differing wood moisture contents. This oven-dry softwood weight percentage of 41 was used in the digester charge when pulping a mixture of hardwood and softwood in this project.

The refined yields and Hypo numbers obtained for the various cooking times are shown in Fig. 4.1 and 4.2. Tables with raw data, including operating conditions and results, for all the cooks described in this thesis are given in appendix G.

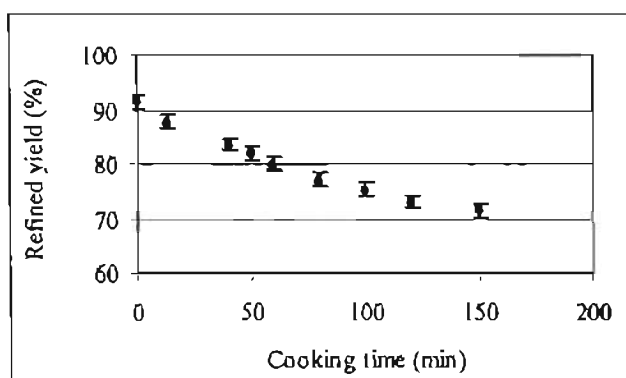


Fig. 4.1: Effect of the cooking time at constant temperature on the refined yield.

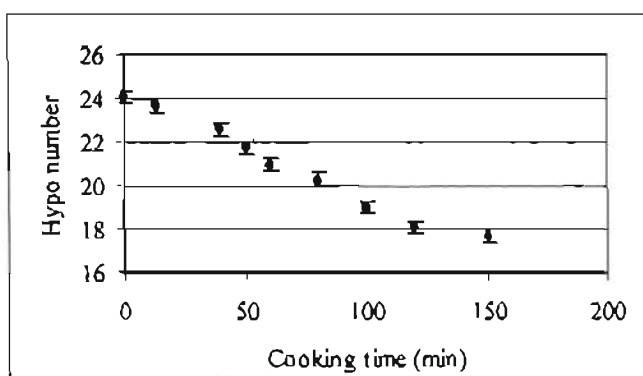


Fig. 4.2: Effect of the cooking time at constant temperature on the Hypo number.

Error estimates are presented in Fig 4.1 and 4.2 as two standard deviations above and below an experimental value. These error estimates are the same for all refined yield and Hypo number graphs, and are not indicated in further graphs to prevent these from becoming congested.

Both curves display a similar form, indicating a correlation between degree of delignification and yield. This is confirmed by Fig. 4.3, where refined yield is plotted against the Hypo number. Linear regression was applied and the degree of correlation was found to be  $r^2 = 0.97$ . The linear regression

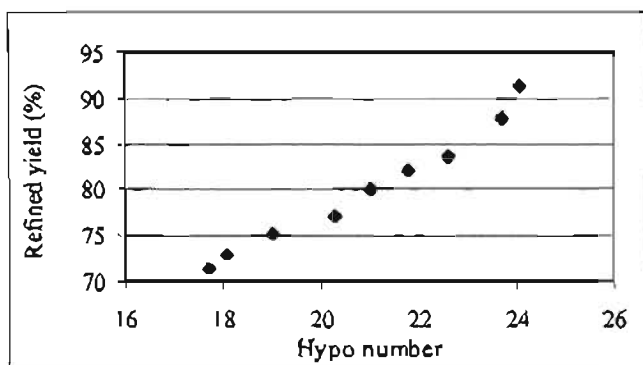


Fig. 4.3: Correlation between refined yield and Hypo number.

technique, as well as the formula for calculating  $r^2$  is shown in appendix H. Both the curves in Fig. 4.1 and 4.2 show a linear relationship between the refined yield and Hypo number, and the cooking time up to a cooking time of about 100 min ( $r^2 = 0,98$  and  $0,99$  respectively), where the slope of the curve reduces. It indicates that the depletion of cooking chemicals starts effecting the pulping reaction rate after this point. The curves also show that a cooking time of 120 min will yield a pulp with a Hypo number of 18, with a corresponding yield of 73 %. An increase in the cooking time of 10 minutes will decrease the Hypo number by about 0.1 to 0.2 units and yield by about 1 % whilst a reduction of similar magnitude in cooking time will increase both the Hypo number and refined yield by about 0.5 units and 1 to 2 percentage points respectively. It follows that a decrease in cooking time has a more significant effect on the degree of delignification than an increase of similar magnitude.

#### 4.1.2. Effect of total alkali charge on refined yield and Hypo number

Six cooks were done, using TA charges of 1, 4, 7, 9.5, 12.5 and 16 % respectively, whilst the standard mill conditions applied for the other parameters. The refined yield is plotted against the TA charge in Fig. 4.4, whilst the Hypo number and black liquor TA results are illustrated in Fig. 4.5. Because of the previously determined linear relationship between the refined yield and the Hypo number, the curve of the refined yield versus TA charge has a similar shape to that of the Hypo number versus TA charge.

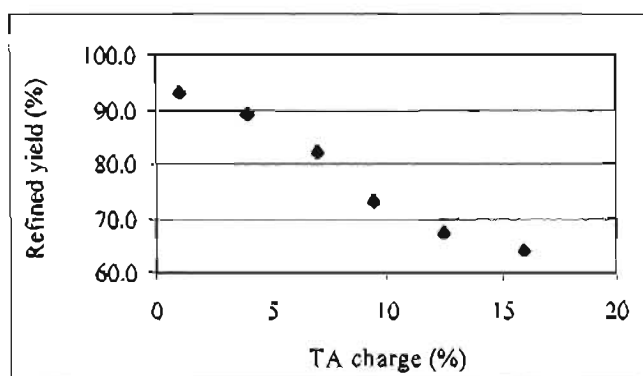


Fig. 4.4: Effect of the TA charge (% as  $\text{Na}_2\text{O}$  on O.D. wood) on the refined yield.

The Hypo number curve in Fig. 4.5 has a decreasing gradient up to about a 9 % TA charge, after which the slope of the curve reduces. In the first part of the curve, the extent of the pulping reaction is obviously limited by the amount of chemical present. This is illustrated by the fact that for the cook with a 1% TA charge, the residual black liquor had no measurable TA left. The flattening out of the curve from about 9 % TA charge onwards is probably due to the fact that at those TA charge values an excess of chemicals is present, as indicated by the relatively high black liquor TA value. It is concluded that the extent of the pulping reaction is at this point dependent on the pulping temperature and mass transfer efficiency rather than the chemical availability.

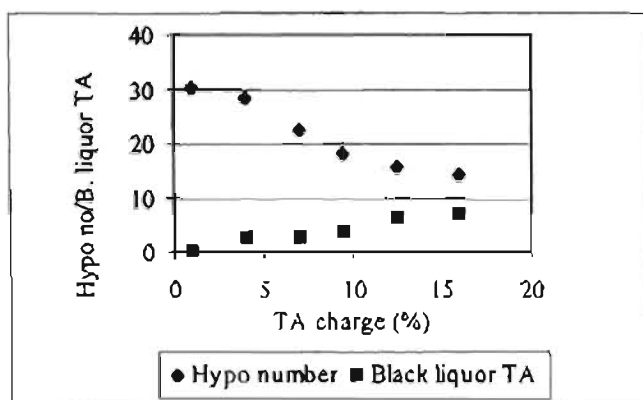


Fig. 4.5: Hypo number and black liquor TA in g/l  $\text{Na}_2\text{O}$  as a function of TA charge, expressed as percent  $\text{Na}_2\text{O}$  on O.D. wood.

The current operating point at the Piet Relief mill, 9.5% TA, is located just within the temperature and mass transfer controlled zone. This will mean that a decrease of about 1% in the TA charge will have a more significant effect on the Hypo number (about 1.5 to 2 units increase) than will an increase of 1 % (0.5 units decrease). According to Ingruber et al [10], the lower the residual lignin in pulp, i.e. the lower the Hypo number, the stronger the pulp will be. This is confirmed by Fig. 4.6, where the burst and tear index at 400 Canadian Standard Freeness (CSF) of pulp made from a mixture of hardwood and softwood, as at Piet Relief, is plotted against the Hypo number. A graph of the tensile index versus the Hypo number is presented in appendix 1. It follows a similar trend to the burst index. The burst, tear and tensile index versus PFI mill revolutions and CSF for individual pulps at different Hypo numbers used to construct the graphs mentioned previously are also shown in appendix 1.

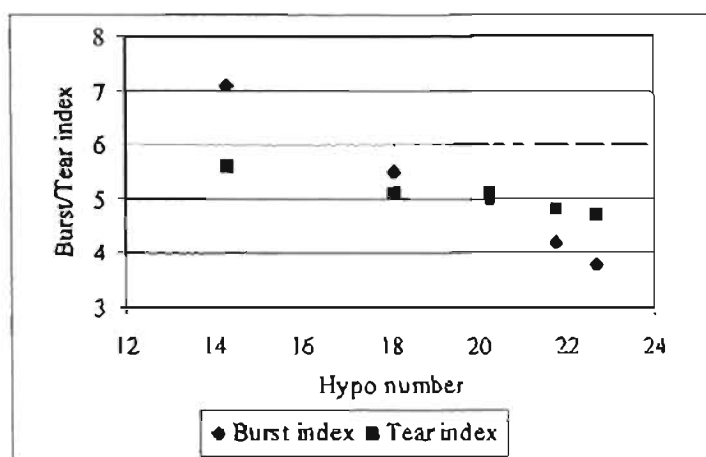


Fig. 4.6: Burst index in  $\text{kPa}\cdot\text{m}^2/\text{g}$  and Tear index in  $\text{mN}\cdot\text{m}^2/\text{g}$  plotted against the Hypo number of a simultaneously pulped hardwood/softwood mixture.

An economic model was developed to determine the changes in sodium sulphite and sodium carbonate costs, as well as total raw material costs, when pulps with different Hypo numbers, and subsequent

different strength properties, are produced by changing the TA charge. The derivation of this model is shown in appendix J. From Fig. 4.5 and 4.6 can be seen that if the Hypo number is decreased by 0.5 by increasing the TA charge by 1 % (from 9.5 % to 10.5 %), the burst index will increase by about 0.2 kPa.m<sup>3</sup>/g, a rise of 3.5 %. Using the economic model, it was calculated that this will increase the sodium sulphite and sodium carbonate costs by about 11% when compared with the cost when using the current TA charge of 9.5%. The increase in total raw material costs was calculated as about 7.5 %.

Decreasing the TA by 1 % will increase the Hypo number to between 19.5 and 20. According to Fig. 4.6, this will result in a decrease of about 0.5 kPa.m<sup>3</sup>/g (9 %) in the burst index. The accompanying saving in sodium sulphite and sodium carbonate costs was calculated as about 10 % and the raw material cost savings as about 7 %. The reduction in strength has to be weighed up by the mill's personnel against the reduction in chemical costs and the increase in refined yield (4 to 5 % at TA charge of 8.5 % according to Fig. 4.4).

#### 4.1.3. Effect of temperature on refined yield and Hypo number

To investigate the effect of the temperature on the process, five cooks were done using different temperatures, whilst the other parameters were again held constant at the current mill conditions. Temperatures used were 169, 174, 179, 184 and 189°C. The refined yield and Hypo numbers are plotted against the temperature in Fig. 4.7 and 4.8 respectively.

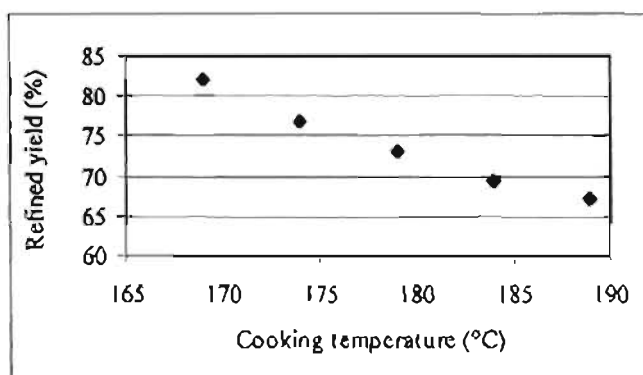


Fig. 4.7: Effect of cooking temperature on the refined yield.

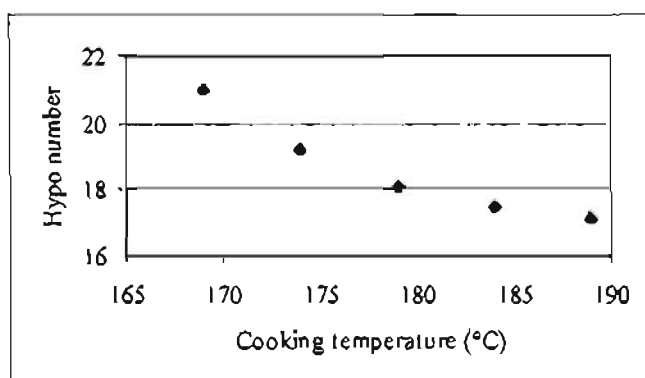


Fig. 4.8: Effect of cooking temperature on the Hypo number.

As expected, increasing the temperature reduces the refined yield and Hypo number, since increasing the temperature increases the reaction rate [10]. The flattening out of the curve is assumed to be due to the fact that, at the higher temperature, the chemicals get depleted at an earlier stage due to the higher reaction rate, and the reaction rate becomes limited by the chemical availability. Another reason may be the limitations that mass transfer effects impose on the reaction rate, as suggested by Eagle and McDonough [38].

In this case, similar to what was observed while investigating the TA charge, an increase in the temperature will have a less dramatic effect on the degree of delignification than will a decrease. Decreasing the temperature by 10 °C from the current 179 °C will increase the Hypo number by about 3 units, whilst increasing the temperature by 10 °C causes a decrease of about 1 unit in Hypo number. From Fig. 4.6 the effect of increasing the Hypo number by 3 units to 21 on the burst index is indicated as being a decrease of about 18 % (from ~ 5.6 to ~ 4.6 kPa.m<sup>3</sup>/g). If the Hypo number is decreased to about 17 by increasing the temperature to 189°C, the burst index increases by about 9 % (from ~ 5.6 to ~ 6.1 kPa.m<sup>2</sup>/g). However the tear index only improves by about 4 % (from ~ 5.2 to ~ 5.4 mN.m<sup>2</sup>/g).

The refined yield is plotted against the Hypo number in Fig 4.9. It can be seen that in this case the relationship is not linear as in Fig. 4.3. This is probably due to the fact that at higher temperatures, the selectivity of the neutral sulfite reaction decreases [10]. Therefore the slope of the curve increases with decreasing Hypo number (i.e. increasing temperature).

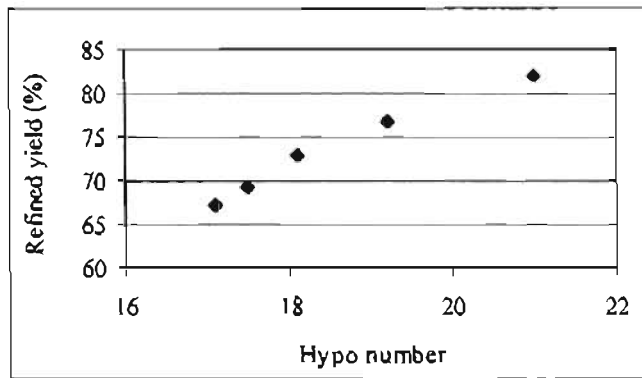


Fig. 4.9: Refined yield (%) as a function of Hypo number for cooks done at different temperatures.

From Fig. 4.8 can be seen that at 189 °C, a Hypo number of 17.1 is reached in the cooking time of 120 minutes. Therefore it is concluded that increasing the temperature at the mill would increase the production rate since a lower residence time would be needed to reach the current Hypo number of 18. The process at the mill is however limited by the speed of the paper machine, not by the digester. There is thus no need for increasing the temperature from a production rate point of view.

#### 4.1.4. Effect of wood species on refined yield and Hypo number

Seven cooks were done at the standard pulping conditions with softwood percentages of 0, 15, 30, 41, 50, 75 and 100 % to determine the effect of the chip composition on the pulping process. The resulting refined yields and Hypo numbers are plotted against the softwood percentage (on O.D. wood basis) of the chips charged in Fig. 4.10 and 4.11.

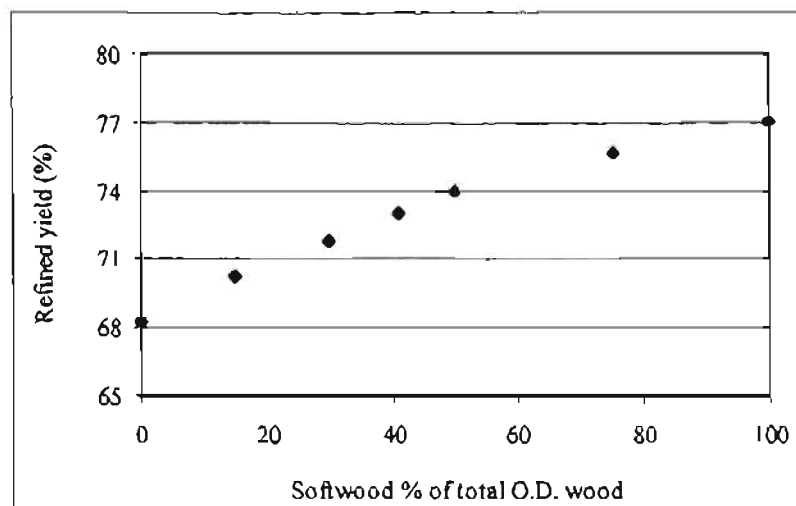


Fig. 4.10: Refined yield as a factor of chip charge composition.



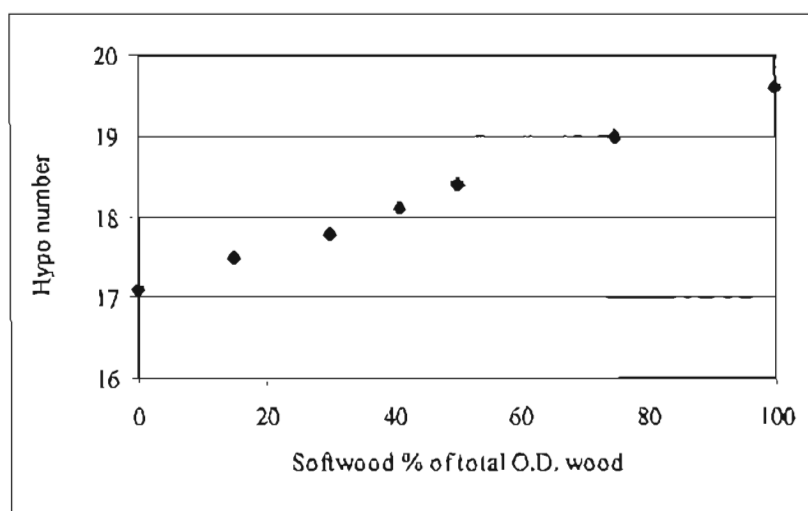


Fig. 4.11: Hypo number as a factor of chip charge composition.

As shown, under the same conditions, pine pulps to a Hypo number of about 19.6, whilst *Eucalyptus* reaches a value of about 17.0, a difference of 2.6 Hypo number units, showing that the pine is undercooked and the *Eucalyptus* overcooked relative to the target Hypo number of 18. These results warrant further investigation into the effect on the pulp quality if both species are pulped separately, each to a Hypo number of 18, and the pulps mixed afterwards.

The results in both Fig. 4.10 and 4.11 indicate that there is a linear relationship between the softwood mass percentage and the Hypo number ( $r^2 = 0.97$  and  $1.00$  respectively). This suggests that there are no significant interactions between the two wood species when pulped simultaneously.

The pulps produced from different chip compositions were evaluated for the strength properties in order to determine the optimum ratio of hardwood to softwood at the current operating conditions as far as the pulp strength is concerned. The burst, tear and tensile indexes at a freeness of 400 CSF are plotted against the softwood percentage of the chip charge in Fig. 4.12 to 4.14. Graphs of the strength properties plotted against the freeness for each individual pulp are shown in appendix I. The interfibre bonding of the fibres of the pulp made from softwood only was insufficient to allow for handsheet making, even at high beating levels. This is probably due to the low degree of delignification of the pulp. Therefore no strength properties for the pulp made from softwood only is reported.

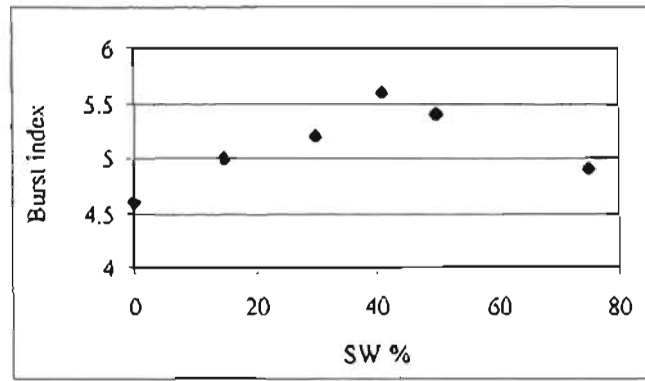


Fig. 4.12: Burst index (kPa.m<sup>2</sup>/g) at 400 CSF versus softwood percentage of the chip charge.

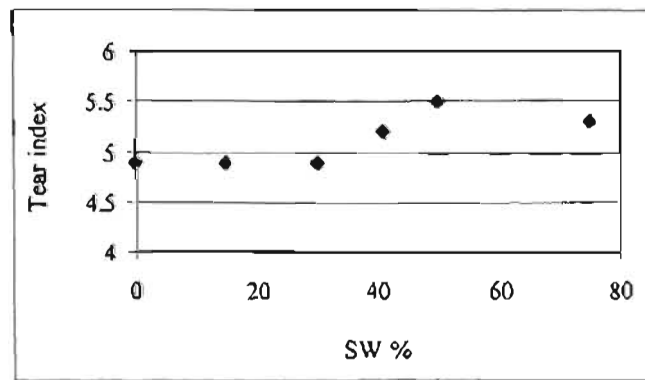


Fig. 4.13: Tear index (mN.m<sup>2</sup>/g) at 400 CSF versus softwood percentage of the chip charge.

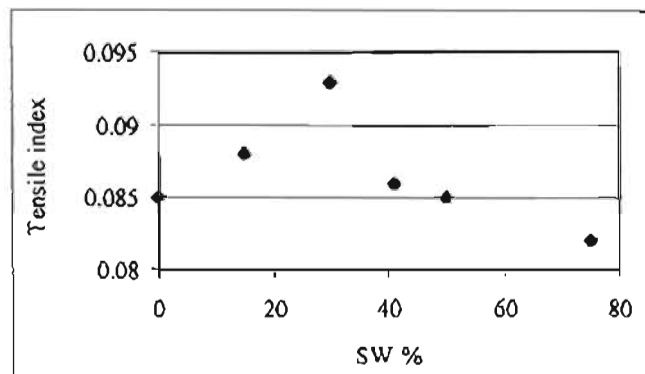


Fig. 4.14: Tensile index (Nm/g) at 400 CSF versus softwood percentage of the chip charge.

From Fig. 4.12 it follows that the current softwood proportion of around 41 % yields pulp with a maximum burst strength. The tear strength reaches an optimum at about 50 % softwood (Fig. 4.13), whilst the tensile strength maximum lies at a softwood percentage of about 30 % (Fig 4.14). In all three cases a pulp mixture of hardwood and softwood displays better strength properties than either hardwood or softwood pulp. The hardwood is pulped to a lower Hypo number than the softwood and

the fibres are more readily fibrillated during refining because of the lower residual lignin level. Therefore the interfibre bonding of the hardwood will be better than in the case of softwood. Softwood fibres are longer and generally stronger than hardwood fibres [12], but the interfibre bonding is weaker due to the lower degree of delignification. The better bonding of the hardwood fibres combined with the stronger softwood fibres cause the hardwood/softwood pulp mixture to be stronger than either pure hardwood or softwood pulp. The increase in tear strength that a higher softwood percentage causes can be explained by the fact that the fibre length is a more important variable as far as tear strength is concerned [2]. Tensile and burst strength are measures of the bonding ability of pulp [24] therefore the better bonding ability of the hardwood causes the maxima for the burst and tensile strength to lie at softwood percentages lower than in the case of the tear strength. The effect of hardwood and softwood fibres on the pulp strength properties is further discussed in section 4.2.

#### **4.1.5. Effect of AQ dosage on refined yield and Hypo number**

To determine the effect of AQ on the degree of delignification in the NSSC process, fifteen cooks were done. The first five were done using a mixture of species, using AQ dosages of 0, 0.05, 0.1, 0.2 and 0.5 % respectively. The remaining ten cooks consisted of five each for hardwood and softwood, using the same AQ dosage as in the case for the mixture. The resulting refined yields and Hypo numbers are shown in Fig. 4.15 and 4.16. Refined yields for the softwood cooks with AQ dosages of 0.05 and 0.2 % were inaccurate as a result of the loss of pulp during the experimental procedure, and are therefore not indicated on Fig.4.15.

The curves in Fig. 4.15 indicate that the refined yield reaches a maximum at an AQ dosage of about 0.1 % in all three cases. Therefore the mill currently uses an optimum AQ charge as far as the refined yield is concerned. The increase in refined yield when using an AQ dosage of 0.1% as opposed to pulping without AQ is probably due to the stabilizing effect the AQ has on the polysaccharide fraction of wood [32, 34]. This stabilizing effect is more evident in softwood, as can be seen by the increase in refined yield by about 4 percentage points, as compared with hardwood, where the increase is about 1.5 percentage points. At AQ dosages higher than 0.1 %, the refined yield decreases with increasing AQ dosage. This is due to the higher degree of delignification the chips undergo at higher AQ levels, as can also be seen on Fig. 4.16.

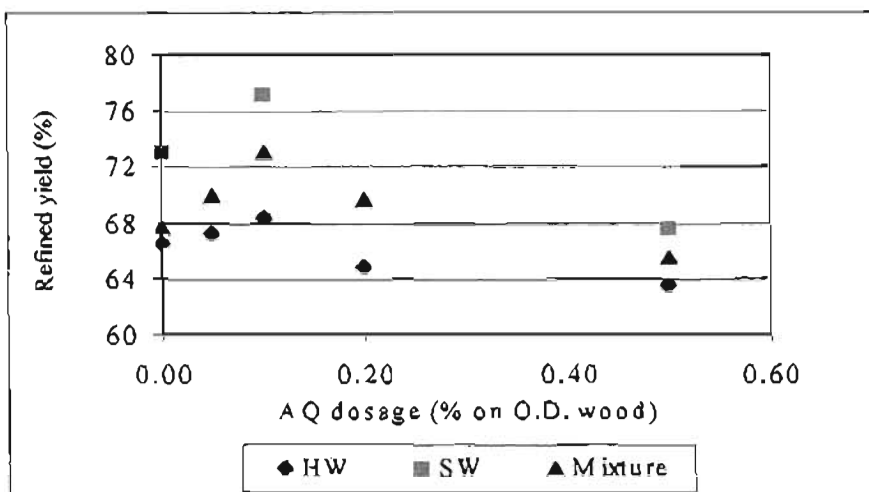


Fig. 4.15: Refined yield (%) as a function of AQ dosage for hardwood, softwood and a mixture of the two species.

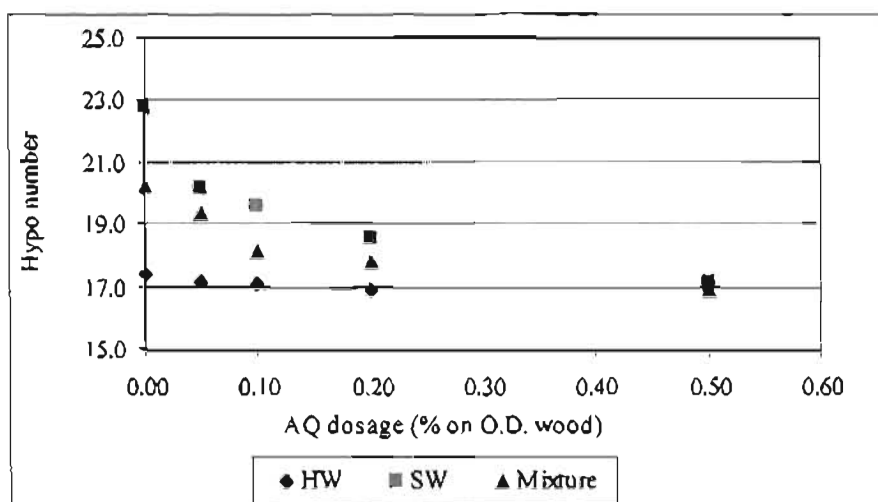


Fig. 4.16: Hypo number as a function of AQ dosage for hardwood, softwood and a mixture of the two species.

Fig 4.16 indicates that the anthraquinone has very little effect on hardwood delignification. However, as far as softwood is concerned, the addition of 0.1 % AQ, as is used currently by the mill, leads to a drop of 3.2 points in the Hypo number, a decrease of 14 %. The curve for the mixture lies between those for the hardwood and softwood, since this is in effect a mixture of the two pulps.

All three curves seem to converge to a Hypo number of about 17. Since the hardwood and softwood pulps have a similar Hypo number at this point, the pulp produced when using an AQ dosage of 0.5 % will be the same as that produced by separate pulping of hardwood and softwood to a Hypo number of 17. This leads to the speculation that by using an AQ dosage of 0.5 %, the advantages of using

softwood and hardwood pulp at similar Hypo numbers produced by separate pulping may be obtained without actually pulping the species separately. The burst and tear strengths of the pulp obtained when using a 0.5 % AQ dosage were 6 kPa.m<sup>2</sup>/g and 5,4 mN.m<sup>2</sup>/g at a freeness of 400 CSF respectively. These values compare with the values at a Hypo number of 16.9 when using an AQ dosage of 0.1 %, as indicated on Fig. 4.6. The different Hypo numbers in Fig 4.6 were obtained by varying the cooking time at constant temperature. This indicates that, at a Hypo number of 16.9, a higher AQ dosage does not improve the strength of the pulp, but only increases the rate of delignification.

Since increasing the AQ dosage from 0.1 to 0.5 % causes the Hypo number of a hardwood/softwood mixture to drop from 18,1 to 16,9; an increase in the AQ dosage may lead to a saving in chemical costs. This can be done by using an AQ dosage of 0.5 % and decreasing the TA charge so that a Hypo number of 18 is reached. It is proposed that the mill do a trial using an AQ charge of 0.5 % to assert whether savings in chemical costs can be made, in order to determine the optimum operation conditions.

The linerboard the mill produces has to meet certain specifications as far as the strength properties are concerned, depending on the desired quality of the final product. When a large volume of produced linerboard falls below one of the strength specifications, the mill has to decide whether to change the TA charge, temperature or AQ dosage in order to improve the NSSC pulp strength. The NSSC pulp strength is not directly comparable with the linerboard strength, since waste paper is added to the linerboard furnish, and thus the NSSC pulp strength properties can't be compared with the linerboard strength property specifications. The factors influencing the cost of these changes discussed under each of these variables have to be taken into account in order to find the most economical option. Similarly, when pulp is produced with strength properties much higher than the specifications, the TA charge, temperature or AQ dosage can be reduced in order to reduce the cost of producing the pulp. Again the different factors discussed before have to be weighed up against each other to find the most attractive alternative.

## 4.2. Simultaneous versus separate pulping

The second part of the experimental investigations was aimed at determining whether it would be beneficial to pulp hardwood and softwood separately before mixing the pulps and refining simultaneously. The separately cooked pulps were refined simultaneously since this would be done at the mill, as it does not have the equipment to refine the pulps separately.

In order to determine the pulping conditions to achieve a Hypo number of 18, different runs for both species were done varying the chemical charge as well as the temperature. These variables were selected since they can readily be varied in the mill process. The cooking time was not varied, since a constant cooking time of 120 min is used as a basis for comparing different cooks, as discussed previously. For the hardwood, chemical charges of 7.5 and 8.5 % TA (as Na<sub>2</sub>O) on oven dry wood

were used whilst the other pulping parameters were held at the standard mill conditions. Similarly, cooks with temperatures of 159 and 169 °C were done, again keeping all the other parameters at the standard mill conditions. The results are shown in Fig. 4.17 and 4.18.

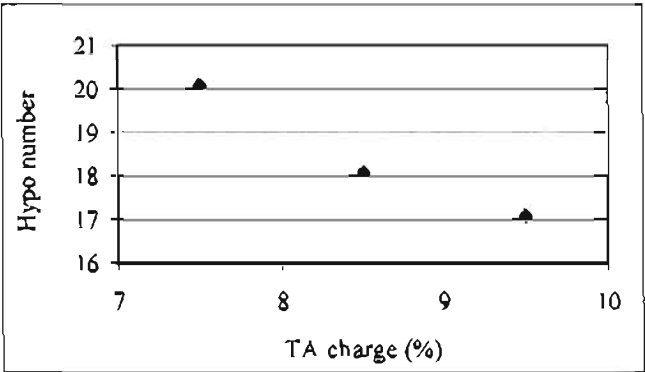


Fig. 4.17: Hardwood Hypo number versus TA charge (% as  $\text{Na}_2\text{O}$  on oven dry (O.D.) wood)

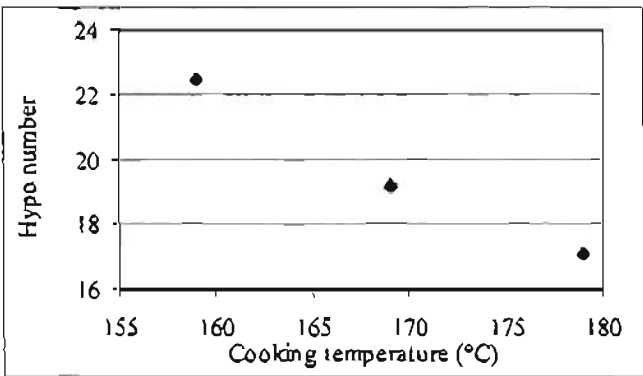


Fig. 4.18: Hardwood Hypo number versus Cooking temperature.

From Fig. 4.17 it can be seen that using a TA charge of 8.5 % on oven dry wood, a pulp with a Hypo number of 18.1 is obtained. Fig. 4.18 indicates that using a pulping temperature of 174 °C will yield a pulp with a Hypo number of about 18.

For the softwood, runs were done with TA charges of 11.5 and 12 % on oven dry wood, with the other pulping parameters kept at the standard values. Similarly, at a pulping temperature of 189 °C, TA charges of 9.5, 10.5 and 11.5 % were used, with the other parameters for each cook again held at the standard mill conditions. Higher pulping temperatures were not used since the pressure would then rise above 13 bar, the level at which the digester safety relieve valve is set, and also because selectivity is reduced at higher temperatures [10]. The results for the Hypo numbers obtained are shown in Fig. 4.19.

From Fig. 4.19 it follows that using a pulping temperature of 179 °C and a TA charge of 11.5 % on oven dry wood, a softwood pulp with a Hypo number of 17.8 is produced. When using a pulping temperature of 189 °C, a TA charge of 11 % yields a pulp with a Hypo number of about 18.

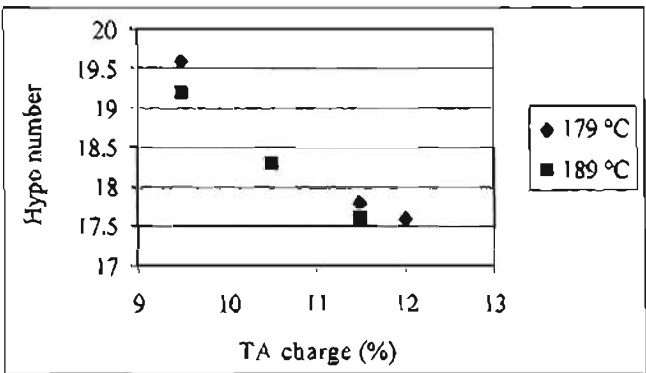


Fig. 4.19: Softwood Hypo number as a function of TA charge (% as Na<sub>2</sub>O on O.D. wood) at two different temperatures.

The hardwood pulp with a Hypo number of 18.1 and the softwood pulp with a Hypo number of 17.8 were used to make handsheets. Handsheets of both the pulps were made for different beating revolutions in the PFI mill. Handsheets were also made from a mixture of the two pulps, mixed in a ratio of 41 % softwood: 59 % hardwood, the same as the ratio of oven dry wood fed to the digester at the mill. Pulp with a Hypo number of 18.1, made from pulping hardwood and softwood simultaneously at the standard mill conditions was used to make handsheets. Softwood pulps were beaten to levels between 10 000 and 26 000 PFI revolutions. At beating levels of less than 10 000 revolutions, the strength development of the pulp was insufficient for the making of handsheets. At PFI revolutions higher than about 26 000, the CSF values became very low, resulting in the drainage time being unacceptably long (longer than 10 min). For hardwood handsheets the pulps were beaten up to a level of about 10 000, whilst mixtures were beaten between 4 000 and 15 000 revolutions. These handsheets were tested for burst, tear and tensile strength, and the results, along with some scanning electron microscope (SEM) images are shown in Fig 4.20 to 4.31. Since the SEM images are taken of only a few fibres, several pictures were taken for a given sample to show that the images are representative of the entire sample. The replicate pictures for each sample are shown in appendix K.

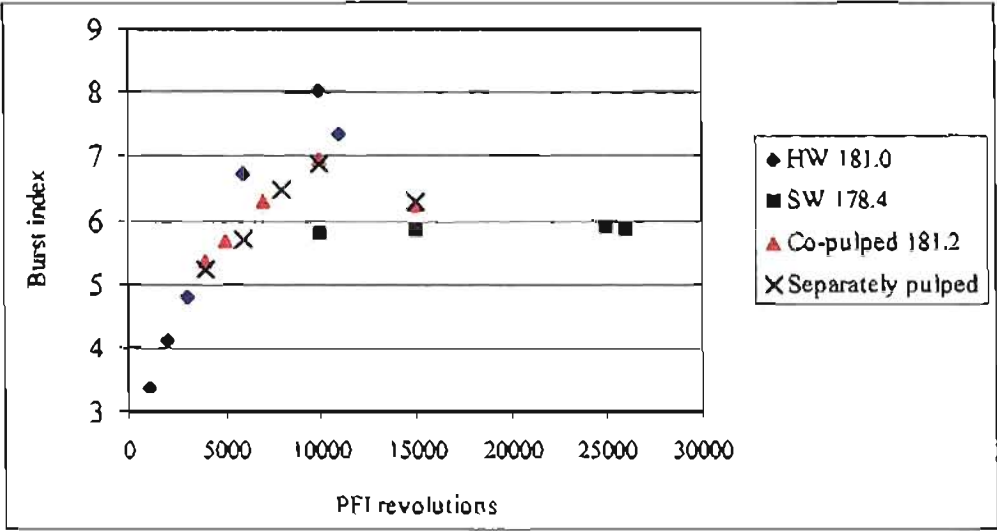


Fig. 4.20: Burst index (kPa.m<sup>3</sup>/g) versus PFT mill revolutions.

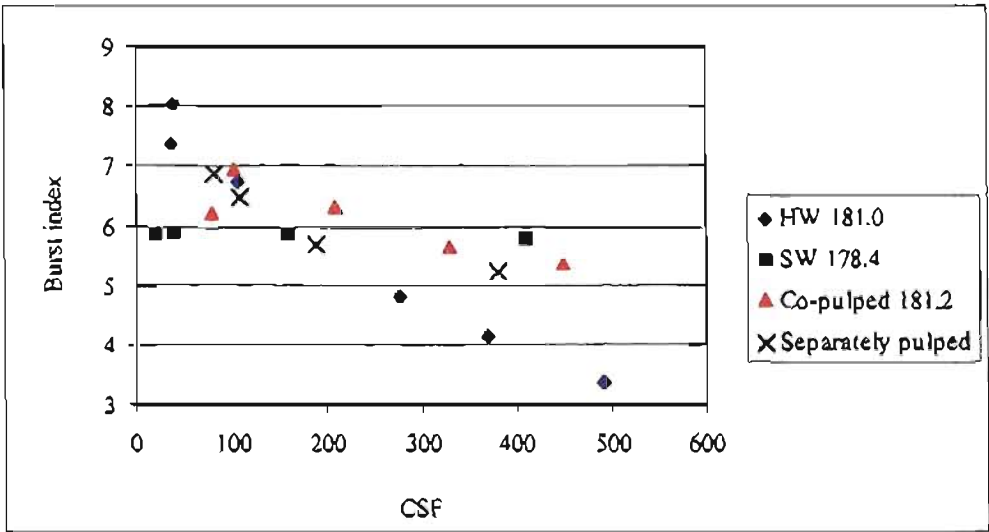


Fig. 4.21: Burst index (kPa.m<sup>3</sup>/g) versus Freeness.



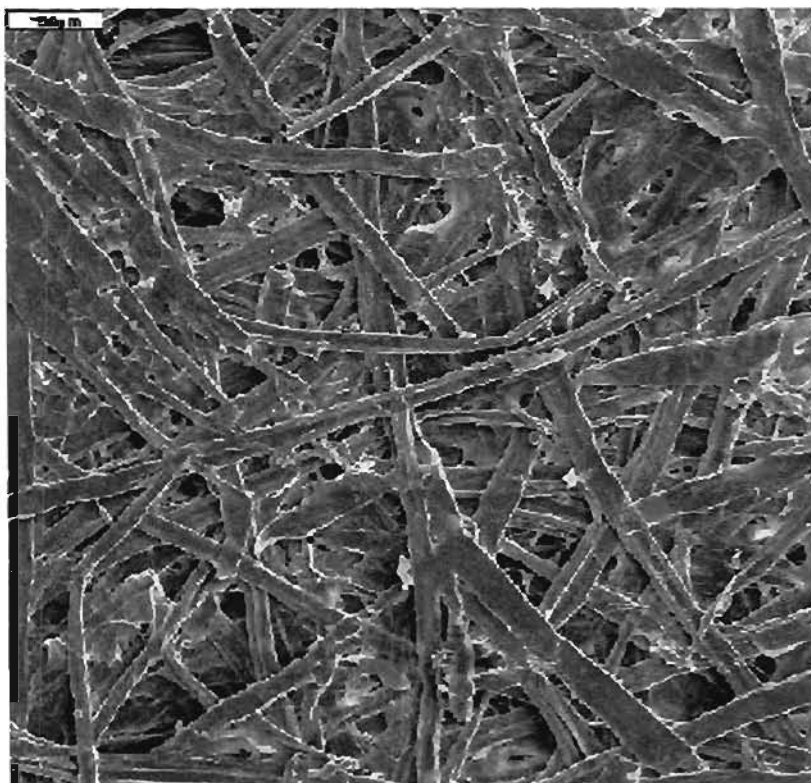


Fig. 4.22: SEM image of a handsheet of hardwood pulp, Hypo number 18.1; 2 000 PF1 mill revolutions; 371 CSF (white bar in top left corner = 50  $\mu\text{m}$ ).

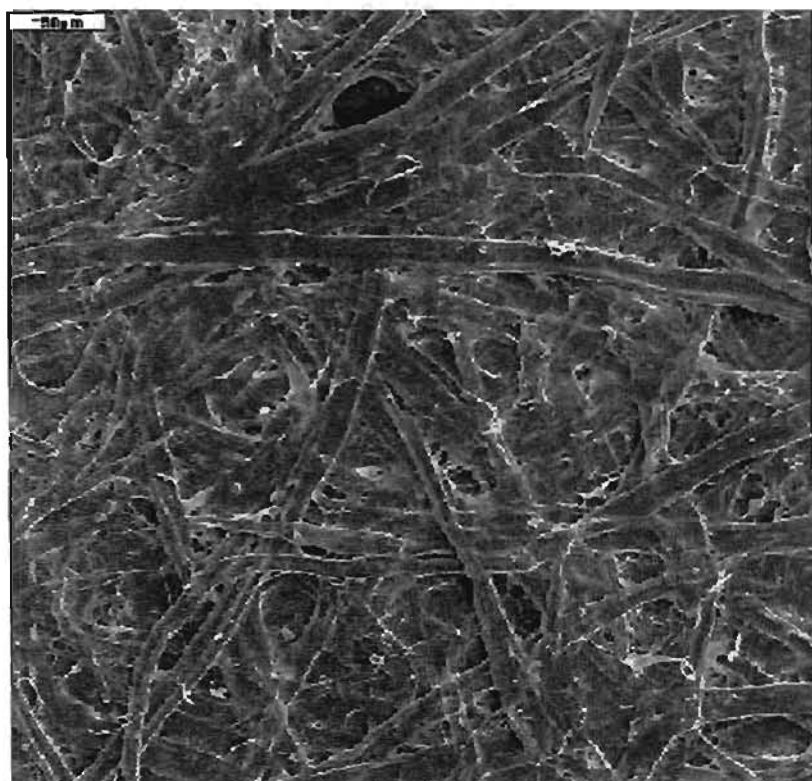


Fig. 4.23: SEM image of a handsheet of hardwood pulp; Hypo number 18.1; 11 000 PF1 mill revolutions; 38 CSF (white bar = 50  $\mu\text{m}$ ).

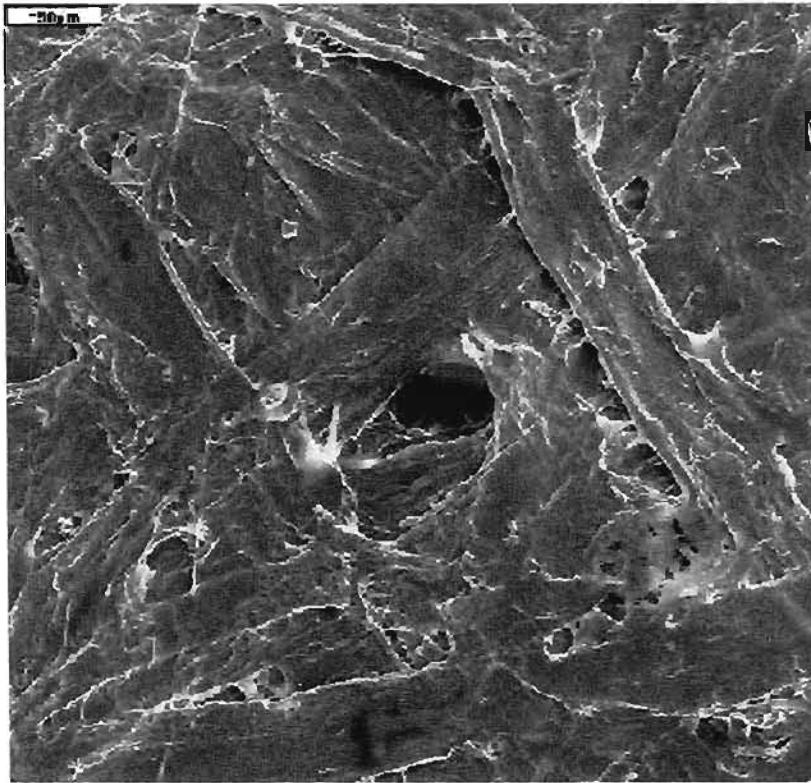


Fig. 4.24: SEM image of a handsheet of softwood pulp; Hypo number 17.8; 10 000 PFI mill revolutions; 411 CSF (white bar = 50 μm).

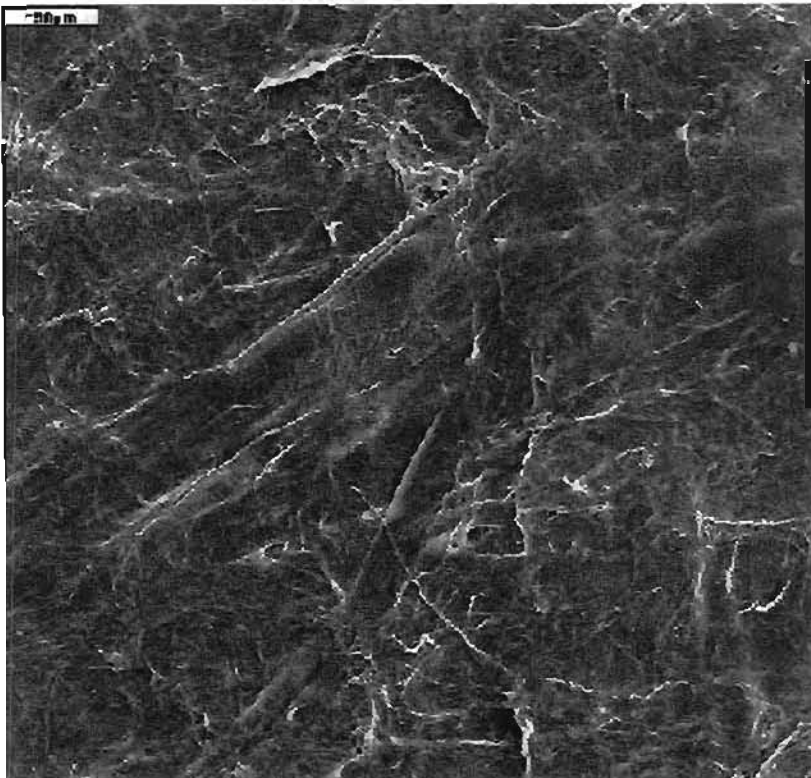


Fig. 4.25: SEM image of a handsheet of softwood pulp; Hypo number 17.8; 25 000 PFI mill revolutions; 40 CSF (white bar = 50 μm).

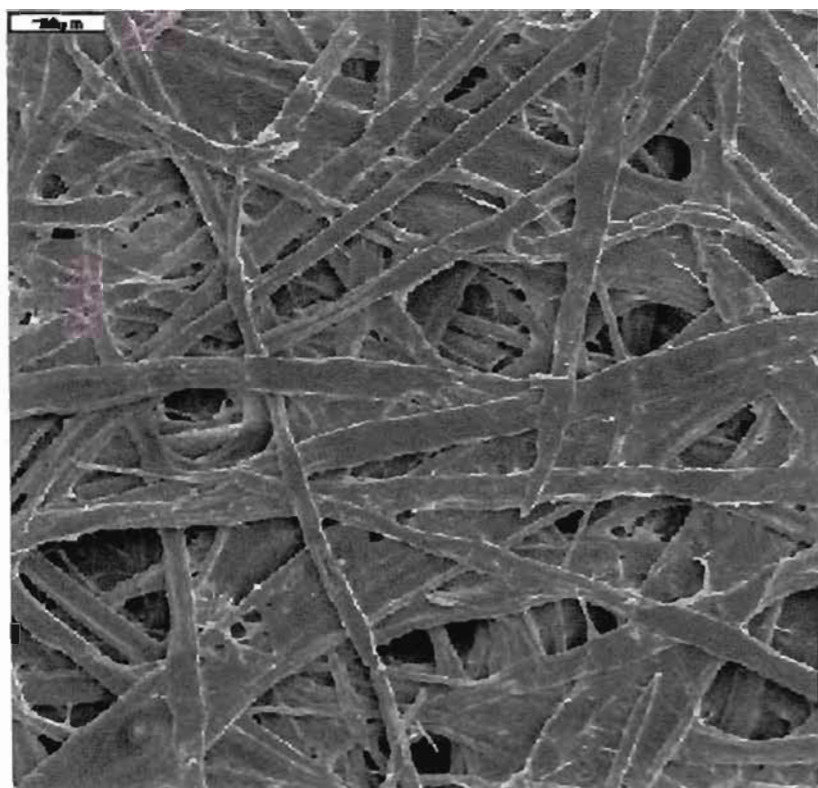


Fig. 4.26: SEM image of a handsheet of a simultaneously pulped mixture of hardwood and softwood; Hypo number 18.1; 4 000 PFI mill revolutions; 451 CSF (white bar = 50  $\mu\text{m}$ ).

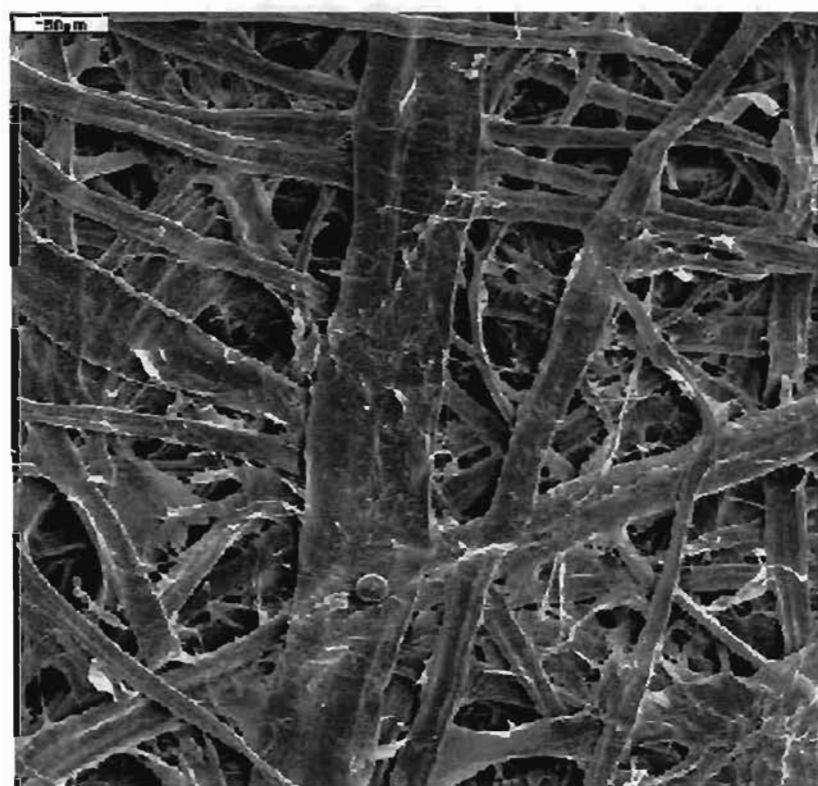


Fig. 4.27: SEM image of a handsheet of a mixture of separately pulped hardwood (Hypo number 18.1) and softwood (Hypo number 17.8); 4 000 PFI mill revolutions; 380 CSF (white bar = 50  $\mu\text{m}$ ).

Fig 4.20 indicates that there is definite strength development as far as the hardwood pulp is concerned, whilst the softwood pulp shows no strength development at all. The strength development of the hardwood can be attributed to the higher degree of fibrillation at the higher beating levels. This can be seen on the SEM images of hardwood pulp at beating levels of 2 000 and 11 000 respectively (Fig. 4.22 and 4.23). The fibres at the higher beating level are clearly more fibrillated, which ensures better interfibre contact, which is reflected in the higher burst index. A comparison between the SEM pictures of the softwood pulps beaten to 10 000 and 25 000 revolutions respectively (Fig. 4.24 and 4.25) indicates that in this case at the higher beating level, the fibres are more fibrillated as well, but also seem to be a lot more damaged, i.e. cut into smaller pieces. It is concluded that in the case of the softwood, the positive effect of having a higher surface area available for bonding at the higher beating level is negated by the negative effect of having shorter and more damaged fibres. This results in the net effect of beating on the burst strength being practically zero.

It is also interesting to note that the hardwood pulp reaches a maximum burst strength of about 40 % higher than that of the softwood ( $8.1 \text{ kPa}\cdot\text{m}^2/\text{g}$  as compared with  $5.8 \text{ kPa}\cdot\text{m}^2/\text{g}$ ). However, looking at Fig. 4.21 it can be seen that the higher hardwood strength values are obtained at CSF values of below 200, at which the drainage rate is lower than that used at Piet Relief. At a CSF value of 400, the softwood pulp is significantly stronger than the hardwood pulp, by about 45 %.

It can further be seen that the mixture of separately cooked pulp produces a slightly higher burst strength than the simultaneously pulped pulp. However, this difference is only about 4 % at a freeness level of 400 CSF.

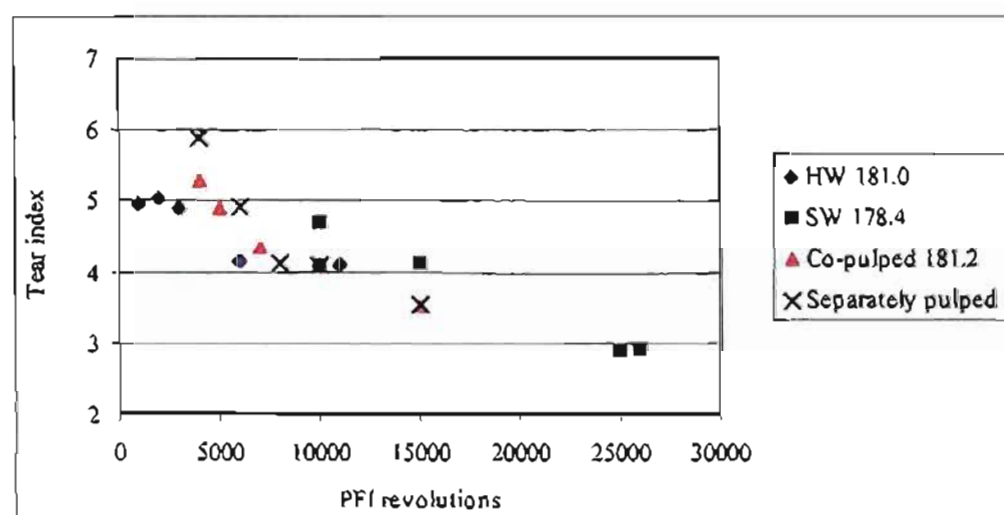


Fig. 4.28: Tear index ( $\text{mN}\cdot\text{m}^2/\text{g}$ ) versus PFI mill revolutions.



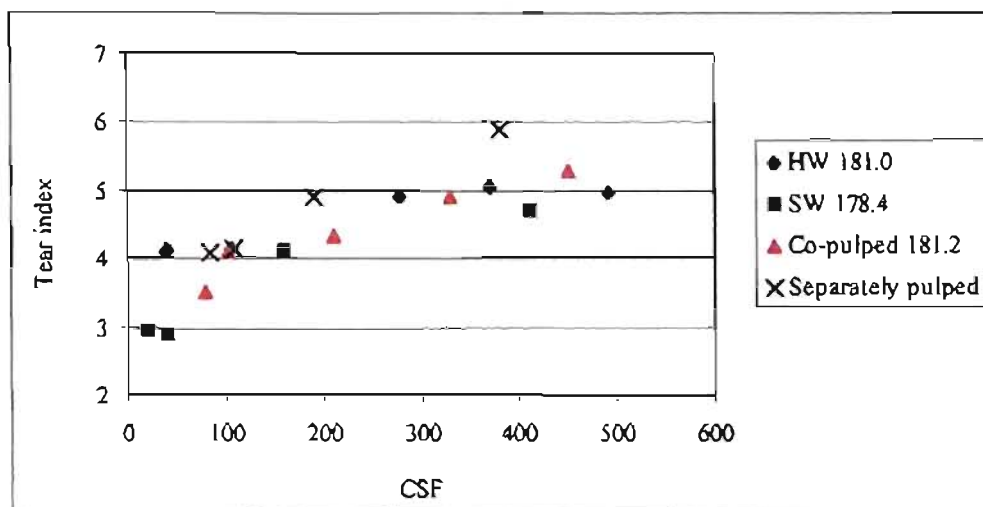


Fig. 4.29: Tear index ( $\text{mN.m}^2/\text{g}$ ) versus Freeness.

Fig. 4.28 indicates that as far as tear strength is concerned, the hardwood pulp also reaches a higher strength than the softwood, but only slightly so. The graph also shows a significant difference between the separately pulped and simultaneously pulped mixtures. This is indicated more clearly when plotted against the freeness, as done in Fig 4.29. At a freeness level of 400 CSF, there is a difference of about 20 % ( $6.1 \text{ mN.m}^2/\text{g}$  as opposed to  $5.1 \text{ mN.m}^2/\text{g}$ ). The SEM images of the two pulps (Fig. 4.26 and 4.27) indicate that there is no significant difference between the degree of fibrillation of the two pulps, which explain the similar burst and tensile strengths. A possible explanation for the higher tear strength in the separately pulped mixture is the following: Since the softwood fibres in the simultaneously pulped mixture have a higher residual lignin level, the fibres are more strongly bound together when fed to the refiner. This means that more refining energy is used to separate these fibres, which would lead to more damage to the fibres, with the fibres being cut to a greater extent and the average fibre length being reduced. Since tear strength is virtually proportional to fibre length [2], the shortened fibres would cause the tear strength to decrease.

At a freeness of 400 CSF, the hardwood pulp's tear strength is slightly higher than that of the softwood pulp, but slightly lower than that of the simultaneously pulped pulp, whilst the separately pulped pulp is 22 % stronger in tear strength than the hardwood pulp. It seems that, because of the way the hard- and softwood pulp fibres bind, a pulp is produced which is stronger than the two pulp types from which it is made. A possible explanation may be this: The bonding between fibres in softwood pulp is lower because of the lack of fibrillation. In the case of a mixture, the hardwood fibres act as substitutes for the fibrillated parts of softwood fibres, i.e. the hardwood fibres act to bind the softwood fibres together, ensuring better bonding between individual softwood fibres. This combined with the fact that softwood fibres are bigger and therefore (presumably) possess more inherent strength than hardwood fibres, provide for a pulp with a tear strength greater than that of the sum of its parts.

As far as the tensile index is concerned, it can be seen from Fig. 4.30 that the hardwood pulp again reaches a significantly higher value than the softwood pulp, but this is only slightly higher than that of both the separately and simultaneously pulped mixtures. Fig. 4.31 shows that, at a freeness of 400 CSF, the hardwood and softwood pulp tensile strengths are very similar. Both the separately and simultaneously pulped mixtures are significantly stronger than hardwood and softwood pulp as far as tensile index is concerned, with both pulps being about 16 % stronger than the hardwood pulp. There seems to be no difference in strength between the two mixtures, indicating that separate pulping does not improve the tensile strength of the pulp produced. This is supported by the SEM images of Fig. 4.23 and 4.24, where there seems to be very little difference in the degree of interfibre bonding between the separately and simultaneously pulped mixtures.

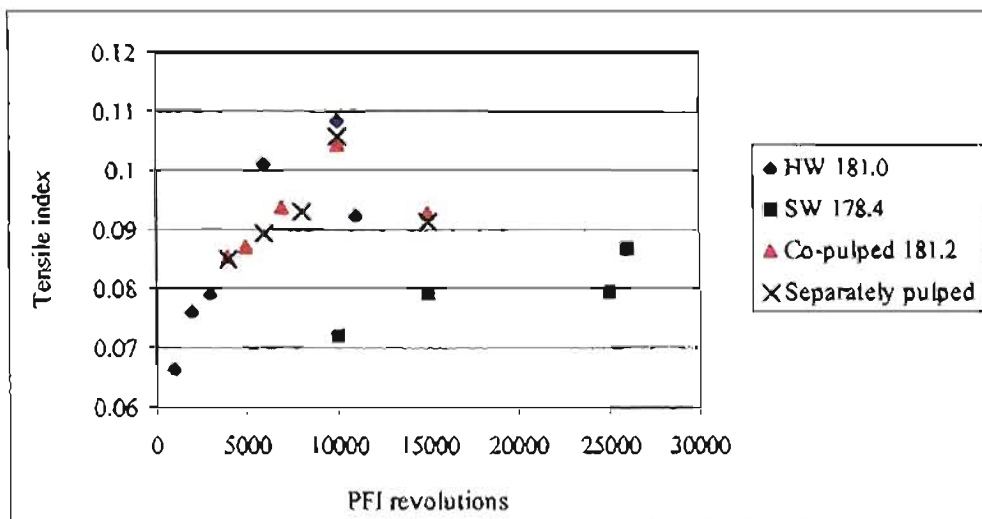


Fig. 4.30: Tensile index (Nm/g) versus PFI mill revolutions

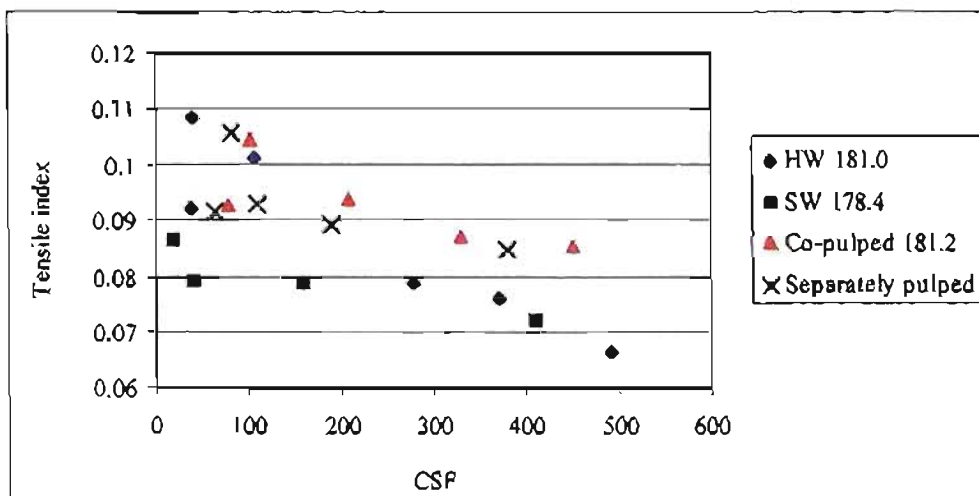


Fig. 4.31: Tensile index (Nm/g) versus Freeness.

Fig. 4.32 shows the relationship between the CSF and PFI mill revolutions. The softwood needs a lot more beating than hardwood does. The separately pulped mixture seems to be slightly easier to refine than the simultaneously pulped mixture, however this improvement is barely significant.

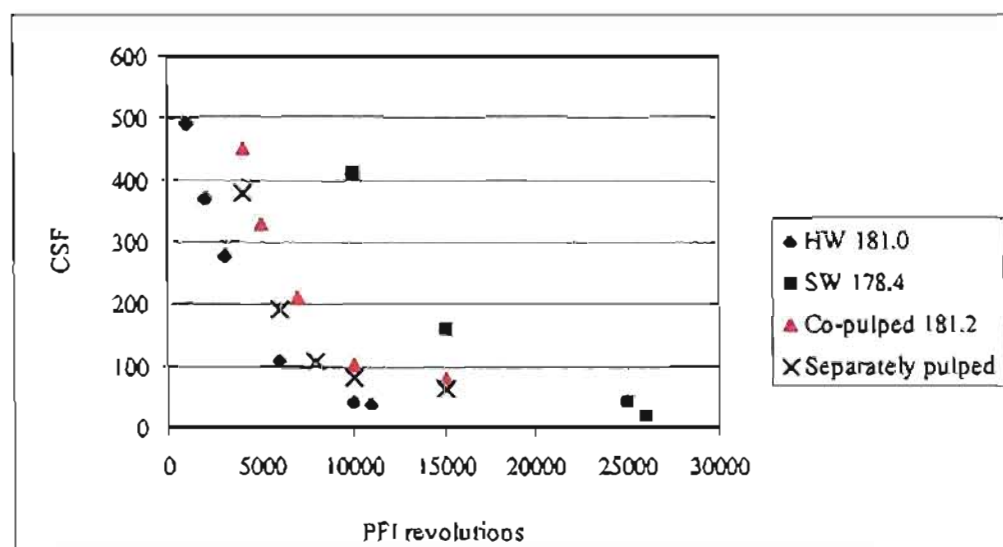


Fig. 4.32: Canadian Standard freeness versus PFI mill revolutions.

From the results presented above, it is concluded that separate pulping brings a significant improvement to the tear strength, with no significant improvement as far as burst and tensile strength is concerned.

Since a TA charge of 8.5 % is needed to produce a hardwood pulp with a Hypo number of 18, and 11.5 % TA charge is needed in the case of softwood, with 41 % of the final pulp mixture consisting of softwood pulp, the average TA charge can be calculated:

$$\begin{aligned}\text{Average TA charge} &= 11.5 \% \times 41 \% + 8.5 \% \times 59 \% \\ &= 9.7 \%\end{aligned}$$

This value is slightly higher than the currently used TA charge of 9.5 %. This indicates that there are no savings to be made as far as chemicals are concerned by changing to separate pulping.

As far as the refined yield is concerned, softwood and hardwood pulped to a Hypo number of about 18 give refined yields of 70.1 and 71.4 % respectively. The average refined yield for a mixture of the two pulps, mixed in the same ratio as currently used in the digester charge (41/59 softwood/hardwood) can be calculated as follows:

$$\begin{aligned}\text{Average refined yield} &= 0.41 \times 71.4 \% + 0.59 \times 70.1 \% \\ &= 70.6 \%\end{aligned}$$

Compared to the refined yield of 73.0 % obtained for pulp with a Hypo number of 18 using simultaneous pulping, this gives a reduction of 2.4 %.

In order to determine whether separate pulping should be employed, the mill's personnel should weigh up the advantage of an improvement in the tear strength with the changes in mill operation associated with running the mill on a campaign basis, e.g. pulping softwood and hardwood alternatively in the digester. This mode of operation will result in the production of substantial quantities of "twilight pulp", i.e. pulp produced while switching from a hardwood to a softwood digester charge, which might differ in quality with respect to the normal pulp.

### 4.3. Substituting sodium carbonate with sodium hydroxide

In addition to the previous work described, one cook was done to determine the effect of substituting sodium carbonate with sodium hydroxide, thus changing from an NSSC-AQ to an alkaline sulphite semichemical-AQ (ASSC-AQ) pulping process. For this cook the TA and sulphite charges were kept at the current levels of 9.5 % and 8.5 % as  $\text{Na}_2\text{O}$  on oven dry wood respectively. The other cooking parameters were kept at the current mill values. The Hypo number obtained for this cook was 17.3, indicating that the presence of NaOH accelerates the pulping reaction if compared with the value for the neutral sulphite process of 18.1. The refined yield was found to be 71.4 %, which is 1.6 % lower than the current value. This corresponds with the findings of Sanborn et al [48]. The strength properties for the ASSC-AQ pulp at a freeness of 400 CSF is compared with that of the current process in Table 4.2. Graphs of the burst, tear and tensile indexes versus CSF for the ASSC-AQ pulp and the NSSC-AQ pulp are given in appendix I.

Table 4.1: Strength properties of NSSC-AQ and ASSC-AQ pulp at 400 CSF produced under the same pulping conditions.

	Hypo number	Burst index (kPa.m <sup>2</sup> /g)	Tear index (mN.m <sup>2</sup> /g)	Tensile index (Nm/g)
ASSC-AQ	17.3	6.3	6.9	0.107
NSSC-AQ	18.1	5.6	5.2	0.086

The results indicate that the introduction of NaOH increases the burst, tear and tensile strengths by 13%, 33 % and 24 % respectively. The big increases in strength properties indicate that this process may prove to lead to major strength increases in the pulp produced. It also indicates that a lower chemical charge with accompanying cost savings may be needed to obtain the current strength properties. Further work is required to confirm these results and to determine the effect of different TA charges as well as  $\text{Na}_2\text{SO}_3$  to NaOH ratios on the pulp strength.



## 5. Conclusion and Recommendations

The experimental work indicates that the process at the mill is optimized as far as the chemical charge and pulping temperature is concerned. Therefore, as far as the current process is concerned, it was found that there is no incentive for changing the TA charge or the temperature whilst the produced pulp complies with the specifications. It was further determined that the current hardwood/softwood ratio (59/41 on an O.D. mass basis) produces pulp with a maximum burst strength. A maximum tear strength is obtained at an O.D. softwood percentage of 50 %, whilst for the tensile index the maximum lies at 30 % O.D. softwood.

It was found that increasing the AQ dosage from 0.1 to 0.5 % causes the Hypo number of a hardwood/softwood mixture to drop from 18.1 to 16.9. Therefore an increase in the AQ dosage may lead to a saving in chemical costs. This can be done by using an AQ dosage of 0.5 %, and decreasing the TA charge so that a Hypo number of 18 is reached. It is recommended that this is investigated in a mill trial.

The results obtained indicate that separate pulping produces pulp with a tear strength 20 % higher than that of the current simultaneous pulping process. As far as burst and tensile strength is concerned, there are no significant differences between the two processes. Pulp strength data indicate that the softwood fibres undergo very little strength development with refining at a Hypo number of 18, whilst hardwood burst and tensile strength properties are readily developed at a similar Hypo number. Separately and simultaneously pulped mixtures of hardwood and softwood produced pulps with higher strength properties than either hardwood or softwood pulp at a similar freeness level. It was suggested that this because of the effect of the better interfibre bonding of hardwood fibres combined with the greater inherent strength of the softwood fibres.

It was determined that the separate pulping process needs the equivalent of a 9.7 % TA charge to pulp batches of hardwood and softwood to a Hypo number of 18 in order to obtain a mixture of pulp mixed in the same ratio as is currently used in the digester feed. This value of 9.7 % is slightly higher than the current TA charge of 9.5 %, therefore there are no savings in chemicals to be obtained. The refined yield of a separately pulped mixture is 2.4 % lower than that obtained using the current process (70.6 % when compared to 73.0 %).

The only improvement the separate pulping process brings seems to be with regards to the tear strength. However, the drop in yield, lack of chemical savings and production of twilight pulp when switching from pulping one wood species to the other in the mill involved with separate pulping do not seem to justify changing from the status quo, i.e. simultaneous pulping.

The results from the single ASSC-AQ cook done, indicate that substituting sodium carbonate with sodium hydroxide produces pulp that is more delignified than NSSC-AQ pulp when using a similar TA charge (Hypo number = 17.3 compared to 18.1). The refined yield obtained was 71.4 % compared to 73.0 %. The resulting pulp had significantly higher burst, tear and tensile indexes, with increases of 13%, 33% and 24% respectively obtained when compared with NSSC-AQ pulp at a Hypo number of 18.1. More work is recommended to determine the reproducibility of these results and also to investigate the effect of different TA charges and chemical ratios on the pulp strength properties. The results suggest that chemical savings can be made, since 25 % less sodium hydroxide than sodium carbonate is needed to produce a similar TA charge. The results also indicate that a lower TA charge is needed to reach a Hypo number of 18 when using the ASSC-AQ process, which indicate that further chemical savings can be made. These savings will depend on the relative costs of sodium carbonate and sodium hydroxide.

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## **Appendix A:**

### **Chemical data sheets**

Chemical data sheets are presented for:

Anthraquinone dispersion (Busperse 2262)

Sodium sulphite

Sodium carbonate (soda ash)

Salt cake (Sodium sulphate and sodium carbonate)

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**BUCKMAN LABORATORIES (PTY) LTD.****MATERIAL SAFETY DATA SHEET****BUSPERSE 2262**

Buckman Laboratories (Pty) Ltd.  
P.O.Box 591, Hammarsdale 3700 Natal  
Telephone: 0325-363010  
Fax: 0325-61593

Revision Date: 3/4/97

For Emergencies After Hours, Please Call:  
(031) 2034077

**SECTION 1****OSHA HAZARD CLASSIFICATIONS**

Irritating to the eyes.

**SECTION 2****COMPONENTS**

Proprietary Information.

**SECTION 3****PHYSICAL AND CHEMICAL PROPERTIES**

Appearance.....	Grey dispersion
Odour.....	Bland
pH (neat).....	7,0 - 8,0
Density at 25 °C.....	1,14 - 1,18
Boiling Point:.....	>100 °C
Solubility.....	Dispersible in water

**SECTION 4****FIRE AND EXPLOSION INFORMATION**

Flammable limits: Not applicable  
Extinguishing media: Water fog, carbon dioxide, foam, dry chemical.  
Special firefighting procedures: None

**SECTION 5****REACTIVITY INFORMATION**

Stability: Stable

Incompatibility: None known

Hazardous Decomposition Products: None known

**SECTION 6****TOXICOLOGICAL INFORMATION**

Acute effects: Not tested. Expected to be moderately toxic based on components.

Irritant effects: Expected to be irritating to the eyes and skin.

Sensitization effects: Not tested. None expected.

Carcinogenic potential: Not listed in any of OSHA Standard, Section 1910.1200 sources as carcinogenic; not tested by Buckman Laboratories, Inc.

Other health effects: None known

**SECTION 7****HANDLING PRECAUTIONS**

Rubber gloves and safety glasses or goggles required.

Eye wash fountains in the work place are strongly recommended.

Body-protective clothing and shoes are recommended.

**SECTION 8****FIRST AID INFORMATION**

Eye exposure: Flush immediately with copious amounts of tap water or normal saline solution for a minimum of 15 minutes. Take exposed individual to a physician, preferably an ophthalmologist, for further evaluation.

Skin exposure: Wash exposed area with plenty of soap and water. Repeat washing. Remove contaminated clothing and wash thoroughly before reuse. If irritation persists consult a physician.

Inhalation: If exposure by inhalation is suspected, immediately move exposed individual to fresh air. If individual experiences nausea, headache, dizziness, has difficulty in breathing or is cyanotic, seek medical attention immediately.

Ingestion: DO NOT INDUCE VOMITING. Rinse with copious amounts of water or milk, first. Irrigate the esophagus and dilute stomach contents by slowly giving one (1) or two (2) glasses of water or milk. Avoid giving alcohol or alcohol related products. In cases where the individual is semi-comatose, comatose or convulsing, DO NOT GIVE FLUIDS BY MOUTH. In case of intentional ingestion of the product seek medical assistance immediately; take individual to nearest medical facility.

NOTE TO PHYSICIAN: No product specific antidote is known. Probable mucosal damage may contraindicate the use of gastric lavage. Treat Symptoms.

**SECTION 9****SPILL, LEAK, AND DISPOSAL PROCEDURES****SPILL AND LEAK RESPONSE GUIDELINES**

Large Spills: Dam area to prevent spill from spreading. Minimise adverse effects on the environment. Recover as much as possible of the pure product into appropriate containers. Later, determine if this recovered product can be used for its intended purpose. Clay, soil, or commercially available absorbents may be used to recover any material that cannot be recovered as pure product. Dispose of as provided below.



Small Spills: Flushing of residual material to an industrial sewer, if present at the site of a spill or leak, may be acceptable if authorized approval is obtained. If this is the case, ensure that the product does not come into contact with incompatible materials.

Product Disposal: Product is not a hazardous waste. Dispose in an approved landfill.

Container Disposal: Offer empty drums for recycling or triple rinse and dispose of in an approved landfill.

**SECTION 10****TRANSPORTATION AND SHIPPING INFORMATION**

DOT Shipping: Non-hazardous

**SECTION 11****REGULATORY INFORMATION**

EPA Registration

Not applicable

TSCA Regulations

All components are included in the inventory

FDA Regulations

21 CFR 176.170

The information on this Material Safety Data Sheet reflects the latest information and data that we have on hazards, properties, and handling of this product under the recommended conditions of use. Any use of this product or method of application which is not described in the Product Data Sheet is the responsibility of the user.

OM

# Sodium sulphite

## Grade 5060 and 5062

### Grade 5060

Sodium sulphite (technical anhydrous)  $\text{Na}_2\text{SO}_3$

#### Specification

Appearance	Buff-pink powder
Sodium sulphite (gravimetric method)	90% w/w min
Sodium sulphate (gravimetric method)	9% w/w max
Iron oxide (gravimetric method)	0.3% w/w max
Water (Olsen and Stark method)	0.3% w/w max
Undissolved solids (gravimetric method)	0.4% w/w max

#### Typical analysis Grade 5060

Sodium sulphite	94% w/w
Sodium sulphate	5% w/w
Iron oxide	0.2% w/w
Water	0.2% w/w
Undissolved solids	0.3% w/w

### Grade 5062

Sodium sulphite liquor  
Specification

Sodium sulphite	20% w/w min
Cresol	0.1% w/w max
pH	7.0 min

#### Typical analysis Grade 5062

Sodium sulphite	20.3% w/w
Cresol	0.05% w/w
pH	7.5

#### Uses

Sodium sulphite is a mild reducing agent.

It has been used as a pulping medium during hard wood and straw pulping.

It has been used for bleaching pulp and textiles.

It has been used in boiler water where its affinity for oxygen assists against corrosion and scale formation.

Sodium sulphite has also had an application in ore flotation techniques eg in copper mining.

#### Packaging

Grade 5060

Multi-ply 50 kg net bags or road tankers  
Road tankers or  
Rail Tankers

Grade 5061

Grade 5062

#### Shipping classification

Brussels nomenclature	28.37
Hazard label	non-hazardous

In giving or expressing opinion, the Company disclaims liability for damage or injury of any kind arising therefrom.

## Health and safety information

#### Physical properties (5060)

Formula	$\text{Na}_2\text{SO}_3$
Appearance	buff-pink powder
Odour	slight
Bulk density	about 1.25
Solubility in water	max 28%

5062 is a 20% solution of the above in water SG 1.23

This information is supplied for safety purposes and may include data on the pure material. It does not constitute a specification.

#### Hazardous properties and general information

The material is non inflammable and is mildly toxic if taken in large quantities, although small amounts in the stomach are soon oxidised and neutralised. The powder is non corrosive but mildly irritating to the skin especially in combination with perspiration. Prolonged exposure in these conditions can promote soreness and irritation of the skin. Breathing in large quantities of dust should be avoided.

#### Safety precautions

##### Storage and handling

Anhydrous sodium sulphite may be handled in bulk or in multi walled paper sacks. The sacks should be stored in dry building, sheltered from rain, risk of mechanical damage and not near sources of heat or fire.

#### Protective equipment

Because of its dry nature, the product can create a dust problem, and in such cases a suitable dust-mask should be worn.

Goggles should give complete protection to the eyes and rubber or plastic gloves and boots should be worn.

First Floor, East Wing  
Yellow Wood Place  
Momentum Park  
143 Western Service Road  
Woodmead 2157  
South Africa

P.O. Box 54313  
Highlands North 2057  
South Africa  
Telephone: (011) 202-2020  
Fax: (011) 802-1642

**BORDIC**  
(Pty) Ltd

# Sodium sulphite

Grade 5060 and 5062

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## First aid

### Personal Injury

Sulphite on the skin should be washed away with plenty of water.

### Eye contamination

The eyes should be flooded or irrigated with plenty of cold or lukewarm water.

### Ingestion

Drink plenty of water, tea or milk etc. Any contaminated clothing should be laundered before re-use.

### Spillages

The material can be safely shovelled and swept up, provided the usual precautions of wearing protective clothing are taken. Sulphite in inaccessible places can be safely swilled away with plenty of water but care must be taken to avoid undue contamination of drains or water courses.

### In case of fire

There is no fire risk, but if the sulphite is strongly heated there may be some toxic fumes evolved.

# Material Safety Data Sheet

## Soda Ash

### PRODUCT IDENTIFICATION

Brand Name..... soda ash  
 Chemical Name..... Sodium carbonate  
 Common Name..... Soda ash  
 Formula.....  $\text{Na}_2\text{CO}_3$   
 OCT Proper  
 Shipping Name..... Not applicable  
 OCT Hazard  
 Class..... Not applicable  
 OCT I.D. Number..... Not applicable  
 Stable Quantity (RQ)..... Not applicable  
 CAS Number..... 497-19-8

### PHYSICAL AND CHEMICAL PROPERTIES

State..... Granular solid  
 Melting Point C..... 851  
 Boiling Point C..... Decomposes  
 Colour..... White  
 Odour..... None  
 Bulk Density, lb/cu. ft..... 50 - 65  
 Weight Per Gallon..... Not applicable  
 Specific Gravity @ 20C..... 2.5  
 Water Solubility, % by sl. @ 20C..... 22.6  
 Flash Point and Method..... Not applicable  
 pH..... Not applicable

### HAZARDOUS INGREDIENTS

Chemical Name	Common Name(s)	CAS Number	Hazard
Sodium carbonate	Soda ash	497-19-8	Irritant to eyes, mucous membranes and skin

### PHYSICAL HAZARD INFORMATION

Explosive: No Upper Explosive Limit: Not applicable Lower Explosive Limit: Not applicable  
 Phosphoric No  
 Flammable No Flammability Class: Not applicable  
 Combustible: No Organic Peroxide: No  
 Oxidiser: No Compressed Gas: No  
 Reactivity: Normally stable. May react violently with strong acids. Carbon dioxide gas and large quantities of heat can be evolved. Reacts with hydrated lime in the presence of moisture to form caustic soda, a corrosive.  
 Incompatibilities: Keep away from aluminium powder, fluorine, phosphorus pentoxide, sulphuric acid, ammoniacal silver nitrate and molten lithium.  
 Hazardous Decomposition: Soda ash decomposes at temperatures above 1000C, releasing carbon dioxide gas ( $\text{CO}_2$ ). Carbon dioxide is an asphyxiant and may affect respiration rate or interfere with breathing. The sodium oxide residue sublimes at 1275C, forming vapours and mists of caustic soda on contact with moisture or water.  
 Conditions to Avoid: Do not expose to intense heat.

Reported As a Potential Carcinogen ☐ Not applicable: ☐ National Toxicology Programme  
 or Carcinogen ☐ OSHA ☐ International Agency for Research on Cancer

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## PRECAUTIONS FOR SAFE HANDLING AND USE

Avoid contact with eyes, skin, and clothing.  
Avoid breathing dust.  
Use with adequate ventilation.  
Keep container closed when not in use.  
Wash thoroughly after handling

---

## SPILL AND LEAK PROCEDURES

Soil Release	Shovel and sweep up. Dispose of in a chemical waste facility as permitted by federal (RCRA), state and local regulations.
Water Spill:	Dilute and disperse with water jets, propellers or similar agitation techniques.
Air Spill:	Keep upwind. Treat impact site as appropriate for soil or water spill.
Occupational Spill:	Shovel and sweep up. As permitted, small spills may be washed to an industrial sewer. Large amounts can be disposed of in a chemical waste facility as permitted by federal, state and local regulations.
RCRA Waste Nuclear	Not applicable

---

## ENGINEERING CONTROLS AND PERSONAL PROTECTIVE EQUIPMENT

Ventilation:	Use general dilution and local exhaust ventilation techniques to meet nuisance dust exposure limit.
Respirator:	Use NIOSH/MSHA approved dust type respirator.
Eye Protection:	Use safety glasses or safety goggles. Ensure eyewash fountain is located in immediate work area.
Gloves:	Use gloves that will not allow alkaline solutions to penetrate.
Clothing:	Wear easily washable clothing. Change daily or more often if contaminated. Wash clothing before reuse.

---

## HEALTH INFORMATION

Precautionary Information:	Caution! Causes irritation. This product is a severe irritant to the eyes and a moderate irritant to the nose and skin.
Symptoms of Exposure:	Eye, nose or skin irritation. Burning sensation to nose, throat and eyes. Redness of the skin. Sneezing and coughing.
Restrictive Medical Conditions:	Eye or skin disease and breathing or respiratory disorders will be aggravated by exposure to this chemical

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## PRIMARY ROUTE(S) OF ENTRY

Eye and skin contact, Inhalation (breathing), and Ingestion (swallowing).

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## TOXICITY INFORMATION

Oral - Rat LD<sub>50</sub> 2483 mg/kg; Intraperitoneal - mouse LD<sub>50</sub> 117 mg/kg  
Skin Irritation - rabbit 50 mg / 24 hour, Moderate; Eye Irritation - rabbit 100 mg / 24 hour, severe

---

## EXPOSURE LIMITS

OSHA: Not established  
ACGIH: Not established  
Other: ACGIH - TLV - TWA for nuisance dust is 10 mg / m<sup>3</sup> total dust or 5 mg / m<sup>3</sup> respirable dust.

---

## EMERGENCY PROCEDURES

Fire: This product is not flammable and does not support combustion.  
Spill or Leak: Sweep up and shovel into containers for later disposal.

---

## FIRST AID PROCEDURES

Ingestion: If swallowed, do not induce vomiting. Give large quantities of water. Never give anything by mouth to an unconscious person. Call a physician.

Inhalation: If inhaled, remove to fresh air. If not breathing give artificial respiration, preferably mouth-to-mouth. If breathing is difficult, give oxygen. Call a physician.

Skin Contact: Flush with plenty of water. Wash clothing before reuse. Thoroughly clean shoes before reuse.

Eye Contact: Immediately flush eyes with plenty of water for at least 25 minutes. Call a physician.

Note to Physician: The chemical of exposure is sodium carbonate which is alkaline in solution.

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P.O. Box 100

## TYPICAL LABORATORY ANALYSIS

PRODUCT: SALT CAKE ( SODIUM SULPHATE)

CHEMICAL FORMULA:  $\text{Na}_2\text{SO}_4$  (Anhydrous)

DESCRIPTION : TYPICAL ANALYSIS ON SALT CAKE EX-COPELAND  
REACTOR ( FLUIDISED BED ) AS BY- PRODUCT ,  
EX-MONDI KRAFT, PIET RETIEF MILL

### SCREEN ANALYSIS :

	%
Mesh 10	4.2
Mesh 20	31.1
Mesh 30	24.8
Mesh 40	23.1
Mesh 50	10.2
Mesh - 50	6.5

### CHEMICAL ANALYSIS :

	%
Sodium Sulphate ( $\text{Na}_2\text{SO}_4$ )	75.3
Sodium Carbonate ( $\text{Na}_2\text{CO}_3$ )	22.3
Sodium Chloride ( $\text{NaCl}$ )	0.18
Iron (Fe)	0.04
Fluoride (F)	0.005
Aluminium (Al)	0.012
Magnesium (Mg)	0.046
Potassium (K)	0.43
Phosphorus (P)	0.025
Insolubles ( $\text{H}_2\text{O}$ )	1.2

## Appendix B:

### Calculation of H-factor constants

The equation for the H-factor is as follows:

$$\text{H-factor} = \int e^{(M - Nt)} dt$$

The constants M and N are calculated as follows, according to Mašura [26]:

$$M = E_a/373R \text{ and}$$

$$N = E_a/R,$$

Where  $E_a$  = activation energy for the pulping reaction in question (kJ/mol)

$R$  = Universal gas constant (kJ/mol.K)

Mašura [26] used a value of 110 kJ/mol as the activation energy for NSSC pulping of hardwoods. This value was taken as the average of a range of values between 103 and 117 kJ/mol, as reported by Eagle and McDonough [38]. Although these values were determined for the NSSC process without the addition of AQ, it was decided to use the value of 110 kJ/mol, since it was suspected (and subsequently shown) that the AQ doesn't have much effect on hardwood NSSC pulping.

Contradicting activation energy values for softwood NSSC pulping are reported. Eagle and McDonough [38] report activation energy values for sulphite pulping of loblolly pine (*Pinus taeda*) of 122 kJ/mol without and 155 kJ/mol with the addition of AQ. Keskin and Kubes [34] determined activation energy values of 130 kJ/mol for NSSC-AQ and 181 kJ/mol for NSSC pulping. In the first case the presence of AQ seems to cause an increase in activation energy, whilst in the second instance the activation energy drops with the addition of AQ. Since it was unclear which sulphite process was used in Eagle and McDonough's work, it was decided to use the value of 130 kJ/mol reported by Keskin and Kubes.

Substituting these activation energy values into the equations for M and N produces the following equations for the H-factor for hardwood and softwood:

Hardwood: 
$$\text{H-factor} = \int e^{(35.7 - 13229/T)} dt$$

Softwood: 
$$\text{H-factor} = \int e^{(41.9 - 15635/T)} dt$$



In cooks where a mixture of hardwood and softwood was used, the activation energy was calculated by multiplying each of the activation energies with the mass fraction of the specific wood in the digester charge, and adding the two values together. For a 50/50 volumetric blend (as used by the mill), which translates to a 41/59 softwood/hardwood mass ratio, the activation energy was calculated as 118 kJ/mol.

Using this value to calculate the constants M and N, the following equation for the H-factor for NSSC-AQ pulping of a mixture of softwood and hardwood resulted:

$$\text{H-factor} = \int e^{(38.0 - 14192/T)} dt$$

## Appendix C:

### Digester control program and description

In this appendix, printouts of both the Siemens S5 115U PLC Step 5 program and the Turbolink control program are given.

Communication between the PLC and Turbolink occurs through data block (DB) 10. At the end of each PLC program cycle, the following words and bits are transferred between the PLC and Turbolink (the PLC addresses and corresponding Turbolink tag names are given):

PLC to Turbolink:

Digital:

PLC	Turbolink	Description
I 0.0	TOPHEATS	Top heater bank trip switch signal
I 0.1	MIDHEATS	Middle heater bank trip switch signal
I 0.2	BOTHEATS	Bottom heater bank trip switch signal
Q 4.0	PUMPI	Pump status
Q 4.1	HEATBOT	Bottom heater bank status
Q 4.2	HEATMID	Middle heater bank status
Q 4.3	HEATTOP	Top heater bank status
Q 4.4	V1	Wash water valve status
Q 4.5	V2	Isolation valve status
Q 4.6	V3	Drain valve status
Q 4.7	V4	Sampling valve status
Q 5.0	V5	Venting valve status
Q 5.1	V6	Cooling jacket valve status
F 101.0	RAMPING	On when ramp stage is in progress
F 101.1	COOKING	On when constant temperature stage is in progress
F 101.2	COOLING	On when cooling stage is in progress
F 101.3	END	On when cook is completed
F 102.4	BATTFAIL	On in case of battery failure

Analogue:

PLC	Turbolink	Description
DW 6	RAMPLEFTD	Fixed point value of ramp time left
DW 12	C/HLEFTD	Fixed point value of time at constant temperature left
DW 14	C/HTRGTD	Fixed point value of constant temperature stage target time.
DW 16	COOLLEFTD	Fixed point value of cooling time left
DW 18	COOLTRGT	Cooling stage target time in seconds
DW 22	TEMPHEX	Temperature signal fixed point value
DW 24	PRESSHEX	Pressure signal fixed point value

Turbolink to PLC:

Digital:

Turbolink	PLC	Description
OPTHFACT	F 120.0	H-factor control option
SMFLAG	F 120.1	Manual sampling switch
RESET	F 120.2	Reset switch
START	F 120.3	Start switch
DRAIN	F 120.5	Manual drain valve switch
WASH	F 120.6	Manual wash water switch
ISOLATE	F 120.7	Manual isolation valve switch
PUMPMAN	F 121.0	Manual pump switch
MANUAL	F 121.1	Manual control option

Analogue:

Turbolink	PLC	Description
RAMPTIMED	DW 100	Fixed point ramp time value
COOKTIMED	DW 102	Fixed point cooking time value
COOK10	DW 104	Cooking temperature in °C x 10
TARGETH	DW 106	Target H-factor
PURGE2D	DW 110	Fixed point purge time value
SAMPLED	DW 112	Fixed point sample time value
SP10	DW 114	Ramp stage setpoint in °C x 10
HFACTOR	DW 116	Current H-factor
TIC10	DW 118	Current temperature in °C

## PLC Step 5 program:

Note: OB 21, OB 22, FB 1, FB 200, FB 201 and FB 202 were programmed by Philip Lombard of Design Technologies

	OB 1	Description
: NAME : :	JU FB 1 TIMERS	FB 1 is used in communicating data with Turbolink (Programmed by P. Lombard).
: NAME : :	JU FB 19 ANALOGIN	Analog input signals from the PLC are converted to fixed point numbers in FB 19.
: NAME : :	JU FB 42 LOADTIME	Timers for the ramping, cooking and cooling down stages are loaded and started in FB 42.
: NAME : :	JU FB 49 STARTUP	The cook is started in FB 49.
: NAME : :	JU FB 41 TIMING	The extend of the cooking process is managed in FB 41.
: NAME : :	JU FB 43 TIMESTAT	The status of the timers are converted and loaded into DB 10 in FB 43.
: NAME : :	AN F 0.1 JC FB 9 MANSAMP	If automatic sampling is not in progress, go to FB 9 where manual sampling is controlled.
: NAME : :	JU FB 11 RESETS	Flags and digital outputs are reset in FB 11.
: NAME : :	JU FB 26 DIGSTAT	The status of the cook (i.e ramping, cooking, cooling, end) is determined and sent to Turbolink in FB 26.
: :	A Q 4.1 JC FB 35	If the bottom bank of heating elements is on, go to FB 35 where the bottom heating bank

NAME :	TRIP3			interlock is controlled.
:				
:	A	Q	4.2	If the middle bank of heating elements is on,
:	JC	FB	34	go to FB 34 where the middle heating bank
NAME :	TRIP2			interlock is controlled.
:				
:	A	Q	4.3	If the top bank of heating elements is on,
:	JC	FB	33	go to FB 33 where the top heating bank
NAME :	TRIP1			interlock is controlled.
:				
:	A	F	121.1	If the manual control switch is switched on in
:	JC	FB	2	Turbolink, go to FB 2.
NAME :	MANUAL			
:				
:	O	F	101.5	If the thermocouple reading is out of range or
:	O	F	101.6	negative (determined in FB 19), go to FB 5.
:	JC	FB	5	
NAME :	TCOUPINT			
:				
:				
:	JU	FB	201	FB 201 is used in communicating data with
NAME :	L1-RX			Turbolink (Programmed by P. Lombard).
:				
:	JU	FB	202	FB 202 is used in communicating data with
NAME :	L1-TX			Turbolink (Programmed by P. Lombard).
:				
:	BE			
	OB21			Programmed by P.Lombard.
:	L	KF	+255	
:	G	DB	10	
:				
:	C	DB	10	
:				
:	L	KH	0001	
:	T	-L1-COMMS		
:				

```

:      JU      FB      200
NAME :      SETUPL1
:
:      BE

```

OB22

Programmed by P. Lombard.

```

:      L      KF      +255
:      G      DB      10
:
:      C      DB      10
:  ---
:      L      KH      0001
:      T      -L1-COMMS
:
:      JU      FB      200
NAME :      SETUPL1
:
:      BE

```

OB23

```

:      A      Q      4.1
:      R      Q      4.1
:      A      Q      4.2
:      R      Q      4.2
:      A      Q      4.3
:      R      Q      4.3
:      A      Q      4.0
:      R      Q      4.0
:
:      STP
:      BE

```

When a time-out has occurred during individual access to the S5 bus, the pump and heating elements are switched off and the PLC is stopped.

OB34

```
: A -ALWAYS_1 When a battery failure has occurred, F 22.7 = 1.
: S F 22.7
: BE
```

FB1

Programmed by P. Lombard.

NAME : TIMERS

```
: A -ALWAYS_1
: ON -ALWAYS_1
: = -ALWAYS_1
:
: AN -ALWAYS_1
: = -ALWAYS_0
:
: AN -SCAN_PLS
: = -SCAN_PLS
:
: AN -100mS
: L KT 001.1
: SD T 120
: A T 120
: = -100mS
:
: AN -1SEC
: L KT 010.1
: SD T 121
: A T 121
: = -1SEC
:
: AN -2SEC
: L KT 020.1
: SD T 122
: A T 122
: = -2SEC
:
```

```

:      AN      -30SEC
:      L      KT      300.1
:      SD      T      123
:      A      T      123
:      =      -30SEC
:
:      AN      -1MIN
:      L      KT      060.2
:      SD      T      124
:      A      T      124
:      =      -1MIN
:
:      AN      -2MIN
:      L      KT      120.2
:      SD      T      125
:      A      T      125
:      =      -2MIN
:
:      BE

      FB2
NAME :      MANUAL

:      A      F      120.5      If the drain valve switch in Turbolink is
:      =      Q      4.6      switched on, the drain valve is opened, and
:                               vice versa.
:
:      A      F      120.6      If the wash water valve switch in Turbolink is
:      =      Q      4.4      switched on, the wash water valve is opened, and
:                               vice versa.
:
:      A      F      120.7      If the isolation valve switch in Turbolink is
:      =      Q      4.5      switched on, the isolation valve is opened, and
:                               vice versa.
:
:      A      F      121.0      If the pump switch in Turbolink is switched on,
:      =      Q      4.0      the pump is turned on, and vice versa.
:
:      BE

```



	FB5			
NAME :	TCOUPINT			
:				
:	A	-ALWAYS_0		If the thermocouple reading is faulty, all heating
:	=	Q	4.1	elements are switched off.
:	=	Q	4.2	
:	=	Q	4.3	
:				
:	BE			

	FB9			
NAME :	MANSAMP			
:				
:	C	DB	10	
:				
:	JU	FB	241	The sampling time value from Turbolink is
NAME :	COD:16			converted to BCD code and loaded into FW 138.
DUAL :		DW	112	
SBCD :		F	20.6	
BCD2 :		FY	52	
BCD1 :		FW	138	
:				
:				
:	A	F	120.1	If manual sampling has been selected in
:	L	FW	138	Turbolink, the sampling time is loaded and
:	SP	T	6	timer 6 started. The sampling valve V4 is open
:	A	T	6	while timer 6 is running.
:	=	Q	4.7	
:				
:	BE			

```

NAME : FB11
      RESETS

      : C      DB      10
      :
      : AN      F      120.2      If the Turbolink reset switch is switched off,
      : JC      =AN1      go to AN1.
      :
      : L      KH      0000      All the listed flags are set to zero.
      : T      FW      0
      : T      FW      2
      : T      FW      4
      : T      FW      20
      : T      FW      22
      : T      FY      101
      : T      FW      102
      : T      FW      150
      : T      FW      90
      :
      : A      -ALWAYS_1      All the digital outputs are set to zero.
      : R      Q      4.0
      : R      Q      4.1
      : R      Q      4.2
      : R      Q      4.3
      : R      Q      4.4
      : R      Q      4.5
      : R      Q      4.6
      : R      Q      4.7
      : R      Q      5.0
      : R      Q      5.1
      :
      : BE

```

	FB15			
NAME :	SPRAMP			
:	C	DB	10	The temperature setpoint for the ramp time
:	L	DW	114	calculated in Turbolink is loaded and transferred
:	T	FW	44	to FW 44.
:				
:	BE			

	FB16			
NAME :	SPCOOK			
:	C	DB	10	The temperature setpoint for the constant
:	L	DW	104	temperature phase from Turbolink is loaded
:	T	FW	44	and transferred to FW 44.
:				
:	BE			

	FB17			
NAME :	PURGING			
:	L	KF	+1100	When the temperature reaches 110 °C during
:	L	FW	6	the ramp time, F 2.2 is set = 1.
:	<=F			
:	S	F	2.2	
:				
:	JU	FB	241	The purge time from Turbolink is converted to
NAME :	COD:16			BCD code and loaded into FW 26.
DUAL :		DW	110	
SBCD :		F	21.0	
BCD2 :		FY	54	
BCD1 :		FW	26	
:				
:	A	F	2.2	When the temperature reaches 110 °C, the purge
:	L	FW	26	time is loaded and timer 2 started. The venting
:	SP	T	2	valve V% is opened while timer 2 is running.
:	A	T	2	
:	=	Q	5.0	

```

:
:      BE

      FB19
NAME :    ANALOGIN

:      C      DB      10
:
:      L      PW      194      The mA input signal from the thermocouple
:      SRW          3          is represented by a binary word. This word
:      T      FW      220      is shifted to the right to convert it to a fixed point
:                               number.
:
:
:      A      F      220.4      If bit F 220.4 equals 1, the mA value from
:      =      F      101.5      the thermocouple is negative, and not processed.
:      JC      =M001
:
:      L      FW      220      The thermocouple's range is 0 – 300 °C. A
:      L      KF      +514      temperature of °C is represented by the fixed
:      -F          point number 514, and 250 °C by 2562. To
:      T      FW      222      ensure both scales start at 0, 514 is subtracted
:                               from the fixed point number.
:
:
:      L      FW      222      The fixed point number is checked for being
:      L      KF      +0      less than 0. If it is, the value is not processed.
:      <F
:      =      F      101.5
:      JC      =M001
:
:
:      L      FW      222      The value is checked to determine if it exceeds
:      L      KF      +2048      the upper limit. If it does, it is not processed.
:      >F
:      =      F      101.6
:      JC      =M001
:
:
:      L      FW      222      The fixed point value is send to DW 22 in DB10
:      T      DW      22      for further processing in Turbolink. In Turbolink
:                               This value is converted to °C x 10.

```

	:	L	DW	118	The temperature in °Cx10 calculated in
	:	T	FW	6	Turbolink during the previous cycle is loaded
	:				into the PLC program.
	:				
M001	:	L	PW	196	The pressure signal is processed similarly to
	:	SRW		3	the temperature signal. In this case the
	:	T	FW	224	pressure range is 0 – 16 bar. The pressure
	:				signal fixed point value is loaded into DW 24
	:	A	F	224.4	for further processing in Turbolink.
	:	=	F	102.2	
	:	JC	=M002		
	:				
	:	L	FW	224	
	:	L	KF	+514	
	:	-	-F		
	:	T	FW	226	
	:				
	:	L	FW	226	
	:	L	KF	+0	
	:	<	<F		
	:	=	F	102.2	
	:	JC	=M002		
	:				
	:	L	FW	226	
	:	L	KF	+2048	
	:	>	>F		
	:	=	F	102.1	
	:	JC	=M002		
	:				
	:	L	FW	226	
	:	T	DW	24	
	:	BE			

	FB26				
NAME :	DIGSTAT				
:	C	DB	10		
:					
:	A	F	1.2	If ramp stage is in progress, set F 101.0 = 1.	
:	=	F	101.0		
:					
:	A	F	3.4	If constant temperature stage is in progress, set	
:	AN	F	1.4	F 101.1 = 1.	
:	=	F	101.1		
:					
:	A	F	1.4	If cooling stage is in progress, set F 101.2 = 1.	
:	AN	F	1.7		
:	=	F	101.2		
:					
:	A	F	1.7	If the run is finished, set F 101.3 = 1.	
:	=	F	101.3		
:					
:	A	F	22.7	In case of battery failure, set F 102.4 = 1.	
:	=	F	102.4		
:					
:	BE				
	FB33				
NAME :	TRIP1				
:	AN	I	0.0	When the top heater bank trip switch signal is 0,	
:	=	F	180.0	F 180.0 = 1.	
:					
:	A	F	180.0	After the top heater bank trip switch signal	
:	L	KT	100.1	changes from 0 to 1, timer 30 is started to delay	
:	SD	T	30	the top heater bank being switched on by 10	
:	NOP	0		seconds.	
:	NOP	0			
:	NOP	0			
:	A	T	30		
:	=	Q	4.3		
:					

: BE

FB34

NAME : TRIP2

```
: AN    I    0.1    When the middle heater bank trip switch signal is
: =     F    180.1   0, F 180.1 = 1.
:
: A     F    180.1   After the middle heater bank trip switch signal
: L     KT   100.1   changes from 0 to 1, timer 31 is started to delay
: SD    T    31      the middle heater bank being switched on by 10
: NOP   0                      seconds.
: NOP   0
: ~     NOP   0
: A     T    31
: =     Q    4.2
:
: BE
```

FB35

NAME : TRIP3

```
: AN    I    0.2    When the middle heater bank trip switch signal is
: =     F    180.2   0, F 180.2 = 1.
:
: A     F    180.2   After the bottom heater bank trip switch signal
: L     KT   100.1   changes from 0 to 1, timer 32 is started to delay
: SD    T    32      the bottom heater bank being switched on by 10
: NOP   0                      seconds.
: NOP   0
: NOP   0
: A     T    32
: =     Q    4.1
:
: BE
```

		FB41			
NAME :		TIMING			
	:	C	DB	10	
	:				
	:	A	F	1.1	If the temperature is greater than or equal to
	:	AN	F	3.6	40 °C, load the ramp time and start timer 4.
	:	L	FW	16	F 1.2 = 1 as long as timer 4 is running.
	:	SP	T	4	
	:	A	T	4	
	:	=	F	1.2	
	:				
	:	AN	F	1.2	If timer 4 is not running, but the cook has been
	:	A	F	1.1	started (i.e. ramp time is finished), F 3.4 = 1.
	:	=	F	3.4	
	:				
	:	A	F	3.4	If the ramp time has elapsed and the H-factor
	:	A	F	120.0	option is used, load a value of 900x10 seconds
	:	AN	F	3.6	and start timer 13.
	:	L	KT	900.3	
	:	SP	T	13	
	:				
	:	AN	F	120.0	If the H-factor option is not used, go to AN1.
	:	JC	=AN1		
	:				
	:	L	DW	106	Compare the current H-factor with the target
	:	L	DW	116	H-factor. If the target is reached, F 1.4 = 1.
	:	<=F			
	:	S	F	1.4	
	:				
	:	JU	=AN2		
	:				
AN1	:	A	F	3.4	If the ramp time has elapsed, and cooking time
	:	AN	F	120.0	control option is used, the cooking time is loaded
	:	AN	F	3.6	and timer 5 is started. F 1.3 = 1 while timer 5 is
	:	L	FW	18	running.
	:	SP	T	5	
	:	A	T	5	
	:	=	F	1.3	
	:				



	:	A	F	3.4	When the cook time has elapsed, F 1.4 = 1.
	:	AN	F	1.3	
	:	=	F	1.4	
	:				
AN2	:	A	F	1.4	When the constant temperature stage
	:	L	KT	720.3	is finished, load 720x10 seconds and
	:	SP	T	14	start timer 14.
	:				
	:	A	F	1.2	During the ramp time, go to FB 15 where the
	:	JC	FB	15	setpoint for the ramp time is loaded.
NAME	:	SPRAMP			
	:				
	:	A	F	3.4	During the constant temperature stage, go to
	:	AN	F	1.4	FB 16 where the constant temperature setpoint is
	:	JC	FB	16	loaded.
NAME	:	SPCOOK			
	:				
	:	A	F	1.1	During the ramp and constant temperature stages
	:	AN	F	1.4	go to FB 51 where the temperature is controlled.
	:	JC	FB	51	
NAME	:	TCONT			
	:				
	:	JU	FB	17	The purging of non-condensable gases is
NAME	:	PURGING			controlled in FB 17.
	:				
	:	A	F	1.4	When the constant temperature stage has
	:	JC	FB	47	finished, go to FB 47, where the heating
NAME	:	END2			elements are switched off.
	:				
	:	L	KF	+900	If a temperature of 90 °C is reached during
	:	L	FW	6	the cooling down period, F 1.5 = 1.
	:	>=F			
	:	=	F	1.5	
	:				
	:	JU	FB	241	The sampling time from Turbolink is converted
NAME	:	COD:16			to BCD format to be used in the PLC's timers,
DUAL	:		DW	112	and loaded into FW 138.
SBCD	:		F	20.6	
BCD2	:		FY	52	
BCD1	:		FW	138	

NAME :	BE			
	FB42			
NAME :	LOADTIME			
	C	DB	10	
	JU	FB	241	
NAME :	COD:16			
DUAL :		DW	100	
SBCD :		F	20.3	
BCD2 :		FY	50	
BCD1 :		FW	16	
	A	F	120.0	
	JC	=AN1		
	JU	FB	241	
NAME :	COD:16			
DUAL :		DW	102	
SBCD :		F	20.5	
BCD2 :		FY	50	

[illegible]

SBCD : F 21.3  
DUAL : DW 12

:  
: JU =AN2

AN1 : LD T 5  
: T FW 28

Cook time control option:

The status of the constant temperature stage timer for the cook time control option is loaded into FW 28.

: JU FB 240  
NAME : COD:B4

The time value in FW 28 is converted to a fixed point number and loaded into DW 12.

BCD : FW 28  
SBCD : F 21.4  
DUAL : DW 12

Cook time and H-factor control options:

AN2 : LD T 14  
: T FW 136

The status of the cooling down stage timer is loaded into FW 136.

: JU FB 240  
NAME : COD:B4

The time value in FW 136 is converted to a fixed point number and loaded into DW 16.

BCD : FW 136  
SBCD : F 21.6  
DUAL : DW 16

:  
: BE

FB46  
NAME : END

: AN F 1.4  
: JC =AN1

If the constant temperature stage has not finished, go to AN1.

: L KF +400  
: L FW 6

If the temperature is equal to or below 40 °C, F 1.7 = 1.

: >=F  
: S F 1.7

:	A	F	1.4	When the temperature is below 40 °C, the pump is switched off and the cooling jacket valve (V6) closed. F 3.6 is set = 1.
:	A	F	1.7	
:	R	Q	5.1	
:	R	Q	4.0	
:	S	F	3.6	
:				
AN1	:	BE		

FB47  
NAME : END2

:	A	F	1.4	When the constant temperature stage has finished, the heating elements are switched off.
:	R	Q	4.1	
:	R	Q	4.2	
:	R	Q	4.3	
:				
:	A	F	1.4	The cooling jacket valve (V6) is opened when the constant temperature stage is completed and the temperature is above 40 °C.
:	AN	F	1.7	
:	S	Q	5.1	
:				
:				
:				
:	BE			

FB49  
NAME : STARTUP

:	A	F	120.3	If F120.3 (Start switch in Turbolink) is 1, all the valves are set to there 0 positions, i.e. all closed except the isolation valve V2. F 1.0 is set to 1 and the pump and bottom bank of heating elements are switched on.
:	R	Q	4.4	
:	R	Q	4.5	
:	R	Q	4.6	
:	R	Q	4.7	
:	R	Q	5.0	
:	R	Q	5.1	
:	S	F	1.0	
:	S	Q	4.0	
:	S	Q	4.1	
:				
:	AN	F	1.0	If the cook has not been started, jump to AN1.
:	JC	=AN1		

:	:				
:	:	L	KF	+400	If the temperature is equal to or greater than
:	:	L	FW	6	40 °C, set F 1.1 = 1.
:	:	<=F			
:	:	S	F	1.1	
:	:				
ANI	:	BE			
		FB51			
NAME	:	TCONT			
	:				
:	:	L	FW	6	The setpoint (SP) is subtracted from the actual
:	:	L	FW	44	temperature (T) value and the result loaded into
:	:	-F			FW 146.
:	:	T	FW	146	
:	:				
:	:	L	KF	+10	If T – SP is smaller than 1 °C, F 0.2 = 1.
:	:	L	FW	146	
:	:	>=F			
:	:	=	F	0.2	
:	:				
:	:	A	F	0.2	During the ramp time, if T – SP < 1 °C,
:	:	A	F	1.2	the bottom bank of heating elements is
:	:	=	Q	4.1	switched on.
:	:				
:	:	A	F	1.2	If the temperature is ramping, go to M001.
:	:	JC	=M001		
:	:				
:	:				<u>Constant temperature stage:</u>
:	:	L	KF	+7	If T – SP > 0.7 °C, F 150.2 = 1.
:	:	L	FW	146	
:	:	<=F			
:	:	=	F	150.2	
:	:				
:	:	A	F	150.2	If T – SP > 0.7 °C, Timer 20 is used to open
:	:	L	KT	100.0	the cooling jacket valve for 1 second.
:	:	SP	T	20	
:	:	A	T	20	
:	:	=	Q	5.1	

	:					
	:	L	KF	+0	If $T - SP < 0\text{ }^{\circ}\text{C}$ , F 150.1 = 1.	
	:	L	FW	146		
	:	>=F				
	:	=	F	150.1		
	:					
	:	JU	=M002			
	:					
	:				<u>Ramping stage:</u>	
M001	:	L	KF	+10	If $T - SP > 1\text{ }^{\circ}\text{C}$ , F 150.2 = 1.	
	:	L	FW	146		
	:	<=F				
	:	=	F	150.2		
	:					
	:	--	A	F	0.4	If $T - SP > 1\text{ }^{\circ}\text{C}$ , and it is more than 15 seconds
	:		A	F	150.2	since the cooling jacket valve has been opened,
	:		L	KT	050.0	timer 20 is used to open the cooling jacket valve
	:		SP	T	20	for half a second.
	:		A	T	20	
	:		=	Q	5.1	
	:					
	:		AN	Q	5.1	When the cooling jacket valve is closed, timer 17
	:		L	KT	150.1	is used to set F 0.4 = 0 for 15 seconds.
	:		SD	T	17	
	:		A	T	17	
	:		=	F	0.4	
	:					
	:	L	KF	+2	If $T - SP < 0.2\text{ }^{\circ}\text{C}$ , F 150.1 = 1.	
	:	L	FW	146		
	:	>=F				
	:	=	F	150.1		
	:					
M002	:	A	F	150.1	If $T - SP < 0.2\text{ }^{\circ}\text{C}$ during the ramp stage, or	
	:	=	Q	4.1	$T - SP < 0\text{ }^{\circ}\text{C}$ during the constant temperature	
	:	=	Q	4.2	stage, all three banks of heating elements are	
	:	=	Q	4.3	switched on.	
	:					
	:					
	:	BE				

FB200

Programmed by P. Lombard.

NAME :

SETUPL1

```

:      L      KF      +0
:      T      FY      64
:      L      KF      +0
:      T      FY      64
:
:      L      KF      +0
:      T      FY      64
:      L      KF      +0
:      T      FY      64
:      L      KF      +0
:      T      FY      64
:
:      L      KF      +0
:      T      FY      64
:      L      KF      +0
:      T      FY      64
:      L      KF      +0
:      T      FY      64
:
:      L      KF      +0
:      T      FY      64
:      L      KF      +0
:      T      FY      64
:      L      KF      +0
:      T      FY      64
:
:      L      KF      +0
:      T      FY      64
:      L      KF      +0
:      T      FY      64
:      L      KF      +0
:      T      FY      64
:
:      L      KH      EE4D
:      L      KH      EA7F
:
:      TNB          14
```



```

:
:      L      KH      0080
:      T      -REC_BYTE
:
:      L      KH      0000
:      T      -SND_BYTE
:
:      L      KH      0000
:      T      FW       64
:      T      FW       66
:      T      FW       68
:      T      FW       70
:      T      FW       72
:      T      FW       74
:      T      FW       76
: --
:
:      BE

```

```

NAME :      FB201
      LI-RX

```

Programmed by P. Lombard.

```

:      C      DB      10
:
:      A      -LI_R_BSY
:      BEC
:
:      AN     -LI_R_BSY
:      S      -LI_R_BSY
:
:      L      -LI_COMMS
:      SLW          1
:      T      -LI_COMMS
:
:      AN     F        81.3
:      JC     =M001
:
:      L      KH      0001
:      T      -LI_COMMS
:

```

M001 : \*\*\*

```

                                FB202                Programmed by P. Lombard.
NAME :    LI-TX

      :    C      DB      10
      :
      :    A      -LI_S_BSY
      :    BEC
      :
      :    AN      -LI_S_BSY
      :    S      -LI_S_BSY
      :
      : -    ***
```

## Turbolink program

In addition to the PLC input and output data, the following internal tags are used:

Digital:

Tag name	Description
----------	-------------

FLAG1

FLAG2

Analogue

Tag name	Description
----------	-------------

RAMP                                      Ramp time (min)

COOKTEMP                                Constant cooking temperature (°C)

RAMP(S)                                  Ramp time (s)

RAMPRATE	Rate of temperature setpoint ramping ( $^{\circ}\text{C} \times 10/\text{s}$ )
RAMPPAST0	Ramp time completed in previous cycle (hrs)
COOLPAST0	Cooling stage time completed in previous cycle (hrs)
C/HPAST	Constant temperature stage time completed in previous cycle (hrs)
HFACTOR0	H-factor in previous cycle
COOKTIME	Cooking time (min)
COOK(S)	Cooking time (s)
RAMPLEFTS	Ramp time left (s)
TIC1	Digester temperature ( $^{\circ}\text{C}$ )
TIC1-K	Digester temperature (K)
Y	$N/T$ in H-factor equation
X	$M - Y$ in H-factor equation
A	$e^X$ in H-factor equation
RAMPPASTH	Ramp time completed (hrs)
C/HTARGETS	Constant temperature stage target time (s)
C/HPASTH	Constant temperature stage time left (hrs)
COOLLEFTS	Cooling stage time left (s)
COOLPASTH	Cooling stage time completed (hrs)
SETPOINT	Temperature setpoint ( $^{\circ}\text{C}$ )
M	H-factor constant
N	H-factor constant
PURGE2	Purge time (s)
SAMPLE	Sampling time (s)
PI1	Digester pressure (bar)
DT	Time increment (hrs)

The following parameters are entered through the mimic screens:

Analogue:

RAMP	Duration of the ramping stage (min).
COOKTIME	Duration of the cooking at constant temperature stage (min).
COOKTEMP	Cooking temperature ( $^{\circ}\text{C}$ ).
OPTHFACT	This is switched on if the cook is ended when a certain H-factor is reached, instead of after a specified time.
TARGETH	H-factor at which the cook is ended, if H-factor control is used.
PURGE2	Time for which the venting solenoid is opened when the temperature reaches $110^{\circ}\text{C}$ (s).
SAMPLE	Time for which sampling solenoid is opened when the temperature reaches $90^{\circ}\text{C}$ during the cooling down stage (s).

M	H-factor constant (described in appendix C).
N	H-factor constant (K, described in appendix C).
Digital:	
START	Switch to start the process.
RESET	Switch used to reset all the parameters used in the control process in order to start a new cook. It can also be used as an emergency stop.
MANUAL	Switched on to enable the operator to manually operate the pump and drain, wash water and isolation valves.
DRAIN	Opens and closes the drain valve.
ISOLATE	Opens and closes the isolation valve.
WASH	Opens and closes the wash water valve.
PUMP	Switches pump on and off.
SAMPLE - -	Switched on to enable sampling of the liquor at any stage during a cook.

Program name: DIGESTER

Program		Description
AN	RESET	If the RESET switch is off, go to label 2.
JC	2	
		<u>Resetting:</u>
L	RAMP	The ramp time entered by the operator is loaded and converted to seconds.
*K	60.0000	
T	RAMP(S)	The ramp time in seconds is converted to a fixed point number for use in the PLC program.
L	RAMP(S)	
/K	10.0000	
+K	3000.0000	
T	RAMPTIMED	The cook time entered by the operator is loaded and converted to seconds.
L	COOKTIME	
*K	60.0000	The cook time in seconds is converted to a fixed point number for use in the PLC program.
T	COOK(S)	
L	COOK(S)	
/K	10.0000	
+K	3000.0000	
T	COOKTIMED	

L	COOKTEMP	The cook temperature in °C entered by the operator is loaded and
*K	10.0000	multiplied by 10. This is done since the PLC can't process values
T	COOK10	with decimal points.
L	COOK10	The ramp rate is calculated by taking the difference between the
-K	400.0000	cooking temperature (x10) and 40 °C x10, and dividing by the
		ramp time.
/	RAMP(S)	
T	RAMPRATE	
LK	0.0000	Set RAMPPAST0 to 0
T	RAMPPAST0	
LK	0.0000	Set COOLPAST0 to 0
T	COOLPAST0	
LK	0.0000	Set C/HPAST0 to 0
T	C/HPAST0	
LK	0.0000	Set HFACTOR0 to 0
T	HFACTOR0	
LK	0.0000	Set the H-factor = 0 for the start of a new cook.
T	HFACTOR	
A	RESET	START, RAMPING and COOKING are reset if these were on
R	START	when the RESET switch was switched on.
R	RAMPING	
R	COOKING	
LBL	2	<u>End of resetting</u>
A	COOLING	START is reset when cooling starts.
R	START	
L	PURGE2	The purge time entered by the operator is loaded and converted to a
+K	2000.0000	fixed point value for use in the PLC program.
T	PURGE2D	
L	SAMPLE	The sampling time entered by the operator is loaded and converted
+K	2000.0000	to a fixed point value for use in the PLC program.
T	SAMPLED	
L	RAMPLEFTD	The fixed point value for the ramp time left from the PLC is
-K	3000.0000	converted to seconds.
*K	3000.0000	
T	RAMPLEFTS	
L	RAMP(S)	The setpoint for the ramp stage is calculated by subtracting the
-	RAMPLEFTS	ramp time left from the total ramp time, multiplying by the

*	RAMPRATE	ramprate, and adding to $40\text{ }^{\circ}\text{C} \times 10$ , since ramping starts at $40\text{ }^{\circ}\text{C}$ .
+K	400.0000	
T	SP10	
L	TEMPHEX	The temperature signal from the PLC is loaded and multiplied by
*K	1.4600	$(300-0) \times 10 / (2562-514) = 1.46$ . This is since the range of the
T	TIC10	thermocouple is $0-300\text{ }^{\circ}\text{C}$ , and is represented by a fixed point number, with 514 representing $0\text{ }^{\circ}\text{C}$ , and 2562 representing $300\text{ }^{\circ}\text{C}$ . The obtained value is transferred to TIC10.
L	PRESSHEX	The pressure signal from the PLC is loaded and multiplied by
K	0.7800	$(16-0) \times 100 / (2562-514) = 0.78$ . The pressure indicator's range is
/K	100.0000	$0 - 16$ bar. The value is multiplied by 100 to incorporate more
T	PI1	significant numbers in the calculation. After multiplying, the value is divided by 100 to obtain the reading in bar and transferred to PI1.
L	TIC10	TIC10 is divided by 10 to obtain the temperature reading in $^{\circ}\text{C}$ .
/K	10.0000	
T	TIC1	
L	TIC1	The temperature reading is converted from $^{\circ}\text{C}$ to K.
+K	273.1500	
T	TIC-K	
L	N	The X and Y values in the H-factor calculation
/	TIC-K	are calculated ( $X = M - Y$ and $H\text{-factor} = \int e^X dt$ .)
T	Y	
L	M	
-	Y	
T	X	
L	X	If X is negative, FLAG1 = 1.
LK	0.0000	
<	FLAG1	
A	FLAG1	If X is negative, go to label 7.
JC	7	
L	X	If $X = 0$ , FLAG2 = 1.
LK	0.0000	
=	FLAG2	
A	FLAG2	If $X = 0$ , go to label 8.
JC	8	
LK	2.7183	If $X > 0$ (X not 0 or negative), $A = e^X$ is calculated.
PWR	X	
T	A	

JU	9	
LBL	7	When using the power function in Turbolink, the exponent
LK	0.0000	has to be positive. Therefore, if $X < 0$ , $A = 1/(e^{-X})$ is
-	X	calculated, since $-X$ will be positive ( $X$ is negative) and
T	X	$1/(e^{-X}) = e^X$
LK	2.7183	
PWR	X	
T	A	
LK	1.0000	
/	A	
T	A	
JU	9	
LBL	8	If $X = 0$ , $A = e^0 = 1$ .
LK	1.0000	
T	A -	
LBL	9	
A	RAMPING	If ramping is in progress, go to label 20.
JC	20	
A	COOKING	If constant temperature stage is in progress, go to label 10.
JC	10	
A	COOLING	If cooling stage is in progress, go to label 11.
JC	11	
LK	0.0000	If the cook is not ramping, in constant temperature stage or
T	DT	cooling, the H-factor is not calculated, thus dt is set equal to 0.
JU	12	
LBL	20	If ramping is in progress, the ramp time elapsed (hrs) is calculated
L	RAMP(S)	by subtracting the ramp time left (s) from the total ramp time (s)
-	RAMPLEFTS	and dividing by 3600. This value is transferred to RAMPPASTH.
/K	3600.0000	
T	RAMPPASTH	
L	RAMPPASTH	To calculate dt in the H-factor equation, the ramp time elapsed in
-	RAMPPAST0	the previous cycle is subtracted from RAMPPASTH.
T	DT	
JU	12	
LBL	10	
L	C/HLEFT	The fixed point value of the time left at constant temperature from
-K	3000.0000	the PLC is converted to seconds.
*K	10.0000	
T	C/HLEFTS	
L	C/HTRGTD	The fixed point constant temperature stage target time value is

-K	3000.0000	converted to seconds.
*K	10.0000	
T	C/HTARGETS	
L	C/HTARGETS	The time at constant temperature elapsed (hrs) is calculated by
-	C/HLEFTS	subtracting the time left (s) from the target time (s) and dividing
/K	3600.0000	by 3600. This value is transferred to C/HPAST.
T	C/HPAST	
L	C/HPAST	The value of dt in the constant temperature stage is calculated
-	C/HPAST0	similarly to dt in the ramp stage.
T	DT	
JU	12	
LBL	11	
L	COOLLEFTD	The fixed point value for the time left in the cooling stage is
-K	3000.0000	converted to seconds.
*K	10.0000	
T	COOLLEFTS	
L	COOLTRGT	The cooling stage time elapsed (hrs) is calculated by subtracting
-	COOLLEFTS	the time left (s) from the target time (s), and dividing by 3600.
/K	3600.0000	this value is transferred to COOLPASTH.
T	COOLPASTH	
L	COOLPASTH	The value of dt in the cooling stage is calculated similarly to
-	COOLPAST0	dt in the ramp stage.
T	DT	
LBL	12	
L	DT	The applicable value for dt is multiplied by A to find the H-factor
*	A	for the time increment dt. This is added to the cumulative H-factor
+	HFACTOR0	of the previous cycle to obtain the current cumulative H-factor.
T	HFACTOR	
LBL	13	
L	HFACTOR	The current H-factor is loaded into HFACTOR0 for the next cycle.
T	HFACTOR0	
L	RAMPPASTH	RAMPPASTH is loaded into RAMPPAST0 for the next cycle.
T	RAMPPAST0	
L	C/HPASTH	C/HPASTH is loaded into C/HPAST0 for the next cycle.
T	C/HPAST0	
L	COOLPASTH	COOLPASTH is loaded into COOLPAST0 for the next cycle.
T	COOLPAST0	
A	RAMPING	If ramping is in progress, go to label 3
JC	3	
A	COOKING	If constant temperature stage is in progress, go to label 4



JC	4	
LK	0.0000	The setpoint is set to zero if neither the ramping or constant temperature stages are in progress.
T	SETPOINT	
JU	5	
LBL	3	If ramping is in progress, the calculated setpoint SP10 for the ramp stage in °C x 10 is divided by 10 and loaded into SETPOINT.
L	SP10	
/K	10.0000	
T	SETPOINT	
JU	5	
LBL	4	If the constant temperature stage is in progress, the cooking temperature value entered by the operator is loaded into SETPOINT
L	COOKTEMP	
T	SETPOINT	
LBL	5	
A	RAMPING	
JC	14 -	
LK	0.0000	If ramping is not in progress, RAMPPAST0 is set equal to 0.
T	RAMPPAST0	
LBL	14	
A	COOKING	
JC	15	
LK	0.0000	If the constant temperature stage is not in progress, C/HPAST0 is set equal to 0.
T	C/HPAST0	
LBL	15	
A	COOLING	
JC	16	
LK	0.0000	If cooling is not in progress, COOLPAST0 is set equal to 0.
T	COOLPAST0	
LBL	16	
END		

The following digital and analogue values are displayed on a mimic screen in Turbolink;

Digital:

PUMP1	Pump status
HEATBOT	Bottom heater bank status
HEATMID	Middle heater bank status
HEATTOP	Top heater bank status
VI	Wash water valve status

V2	Isolation valve status
V3	Drain valve status
V4	Sampling valve status
V5	Venting valve status
V6	Cooling jacket valve status
RAMPING	On when ramp stage is in progress
COOKING	On when constant temperature stage is in progress
COOLING	On when cooling stage is in progress
END	On when cook is completed
BATTFAIL	On in case of battery failure

#### Analogue:

TIC1	--	Digester temperature (°C)
SETPOINT		Temperature setpoint (°C)
PI1		Digester pressure (bar)
HFACTOR		Current H-factor

## **Appendix D:**

### **Mondi Kraft Laboratory Standard Methods**

The following Laboratory Standard Methods are presented:

- Determination of Cooking Liquor Active Alkali Test (NB What is described as active alkali (AA) in this test method is in fact total alkali (TA) as described by Tappi Test Method T 624 cm-00 [50].
- Determination of Sulfite Percentage
- Determination of Black Liquor Active Alkali (NB What is described as active alkali (AA) in this test method is in fact total alkali (TA) as described by Tappi Test Method T 624 cm-00 [50].
- Determination of Hypo Number of Pulp

--

## QUALITY ASSURANCE

### Laboratory Standard Method

#### DETERMINATION OF COOKING LIQUOR ACTIVE ALKALI TEST

##### 1. PURPOSE

The purpose of this work Instruction is to lay out the method for active alkali analyses.

##### 2. SCOPE

This work Instruction applies to active alkali analyses performed in the Wet Laboratory.

##### 3. PROCEDURE

Use a clean container for sampling. Open the sampling valve for a few seconds to drain the liquor which remained in the pipe during the previous sampling. Collect a sample, enough to carry out the test.

##### 4. APPARATUS

- 4.1. pH Meter (Calibrated)
- 4.2. Beaker 250 mls.
- 4.3. Buret 50 mls.
- 4.4. Pipet 10 mls.

##### 5. REAGENTS: Hydrochloric Acid 1.0 N.

##### 6. METHOD

- 6.1. Transfer 10 mls of the cooking liquor sample into a 250 mls beaker, containing 50 mls of the deionised water and mix well.
- 6.2. Titrate under Hydrochloric acid 1.0 N to pH 4.00

##### 7. CALCULATION

$$AA \text{ ( g/l Na}_2\text{O)} = \left( \frac{T_{\text{ration}}}{10} + \frac{a}{2} \right) \times 31$$

See Work Instruction WIPI.005

##### 8. RECORDS: Record the result in the Digester/Copeland Process Data Sheet.

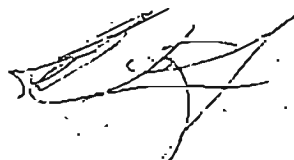
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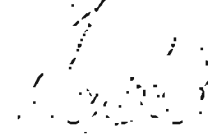
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## QUALITY ASSURANCE

### Laboratory Standard Method

#### DETERMINATION OF SULPHITE PERCENTAGE

1. PURPOSE

The purpose of this work Instruction is to lay out the method for sulphite percentage analysis.

2. SCOPE

This work Instruction applies to sulphite percentage analyses performed in the Wet Laboratory.

3. PROCEDURE

See Work Instruction WIPI.004.

4. APPARATUS

- 4.1. Measuring cylinder 25 mls.
- 4.2. Pipet 25 and 10 mls.
- 4.3. Conical Flask 250 mls.
- 4.4. Volumetric flask 250 mls.

5. REAGENTS

- 5.1. Iodine solution 0.10 N.
- 5.2. Sodium Thiosulphate 0.10 N.
- 5.3. Sulphuric Acid 4.0 N.
- 5.4. Starch Indicator 2.0%.
- 5.5. Buret 50 mls.

6. METHOD

- 6.1. Pipet 10 mls of cooking liquor sample.
- 6.2. Transfer into a volumetric flask 250 mls and make it up to the mark with deionised water. Mix well.
- 6.3. Transfer by pipet 25 mls of the Iodine solution 0.10 N into a 250 mls conical flask containing 100 mls of the deionised water.

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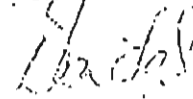
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## QUALITY ASSURANCE

### Laboratory Standard Method

- 6.4. Add 10 mls of the cooking liquor from the volumetric flask, 250 mls and 20 mls of Sulphuric Acid 4 N.
- 6.5. Titrate under Sodium Thiosulphate 0.10 N to a light yellow colour. Add starch indicator.
- 6.6. Continue titrating until the colour changes from blue to clear.

#### 7. CALCULATION

$$a = 2.5 (25 \times A - T \times B)$$

A = Normality of  $I_2$  solution.

T = Titre mls (Sodium Thiosulphate).

B = Normality of Sodium Thiosulphate.

$$\% \text{ Sulphite (m/m Na}_2\text{O)} = \frac{31 \times a \times 100}{AA}$$

AA = Active alkali (See Work Instruction WIPI.004).

#### 8. RECORDS

Record the results in the Digester/Copeland Process Data Sheet.

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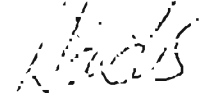
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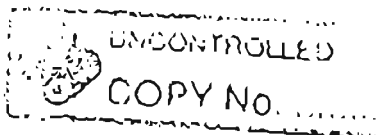


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## QUALITY ASSURANCE

### Laboratory Standard Method

#### DETERMINATION OF BLACK LIQUOR ACTIVE ALKALI

1. PURPOSE

The purpose of this work instruction is to lay down a method for determining the active alkali in extracted black liquor.

2. SCOPE

This work instruction applies to active alkali analysis performed in the Wet Laboratory.

3. PROCEDURE

Use a clean sampling container. Open the sampling valve for few seconds to drain the liquor which remained in the pipe after the previous sampling. Collect a sample enough to carry out the test.

4. APPARATUS

- 4.1. Volumetric flask 250 ml.
- 4.2. Pipet 100 ml.
- 4.3. Plastic beaker 250 ml.
- 4.4. pH meter.

5. REAGENTS

- 5.1. Barium chloride 0.10 N.
- 5.2. Deionised water.
- 5.3. Hydrochloric acid 1.0 N.

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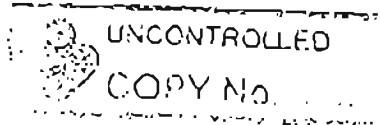
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## QUALITY ASSURANCE

### Laboratory Standard Method

#### 6. METHOD

- 6.1. Pipet 100 mls of the black liquor sample into a 250 mls volumetric flask.
- 6.2. Add 100 mls of barium chloride 0.10 N solution by using a pipet.
- 6.3. Add deionised water and make up a total volume of 250 mls. Mix.
- 6.4. Let it stand until the sediment settles at the bottom.
- 6.5. Pipet 100 mls of the solution, without disturbing the sediment, into a 250 ml beaker.
- 6.6. Titrate under hydrochloric 1.0 N to pH 4.0 (pH meter) and note the titration volume at that point.

#### 7. CALCULATION

$$A.A. = \text{Titration} \times 0,775$$

$$\frac{\text{Titration}}{40} \times 31$$

#### 8. RECORD

Record the test results in the Digester/Copeland progress Data Sheet.

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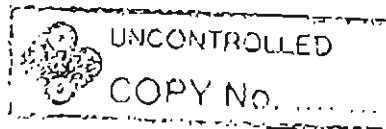
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WIP1.003

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OF 4

## TOTAL QUALITY MANAGEMENT

### Laboratory Standard Method

#### DETERMINATION OF HYPO NUMBER OF PULP

##### 1. PURPOSE

The purpose of this work instruction is to lay out the method for Hypo No. of Pulp determination.

##### 2. SCOPE

This work instruction applies to Hypo. No. of pulp analysis performed in the Wel Laboratory.

##### 3. PROCEDURE

Take a sample ex the slurry press from the conveyor belt approximately 3 to 5 grams oven dry. Put the sample into a plastic bag and take it to the laboratory.

##### 4. APPARATUS

- 4.1. Filtering apparatus (Mavis Consistency Apparatus).
- 4.2. Emerson speed dryer.
- 4.3. Press and felts.
- 4.4. Wiley-Mill.
- 4.5. Filter paper 15 cm No. 541.
- 4.6. Measuring cylinder 500 mls.
- 4.7. Pipets 10 and 25 mls.
- 4.8. Magnetic stirrer and the follower.
- 4.9. Buret, stand and clamp.
- 4.10. Stopwatch (Calibrated) and Griffen Filler.
- 4.11. Flat bottom flask 1 000 mls with a ground joint 24/29.
- 4.12. Bellow 50 mls.
- 4.13. Separating Funnel 50 or 100 mls with a ground joint to fit 24/29 flat bottom flask.

##### 5. REAGENTS

- 5.1. Hydrochloric Acid 4.0 Molar
- 5.2. Potassium Iodide 1.5 Molar
- 5.3. Sodium Thiosulphate 0.20 N
- 5.4. Starch Indicator 2.0 %
- 5.5. Deionised water.
- 5.6. Sodium Hypochlorite  $\pm$  0.40 N.

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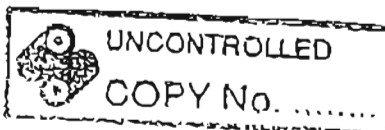
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## TOTAL QUALITY MANAGEMENT

### Laboratory Standard Method

#### 6. METHOD

- 6.1. Mix the pulp with de-ionised water, filter using filtering apparatus.
- 6.2. Put the suspension between two dry felts and press in the press to remove excess of water.
- 6.3. Remove the pad from the felts and dry it on the Emerson speed dryer.
- 6.4. Tear the pad into small pieces by hand and start the Willey Mill.
- 6.5. Hold the filter paper underneath the disintegrator to receive the discharge and put the pieces of the pad to disintegrate.
- 6.6. Disintegrate until enough sample is obtained and stop the Wiley Mill.
- 6.7. Dry the disintegrated sample in the Emerson speed dryer. Whilst waiting, clean the Wiley Mill.
- 6.8. When the sample is dry weigh out  $0.5 \pm 0.0005$  gram.
- 6.9. Measure 365 mls of de-ionised water and transfer with water into a 1 000 mls flat bottom flask the weighed sample.
- 6.10 Put the flat bottom flask on the magnetic stirrer and the magnetic follower into a flat bottom flask.

NOTE: The time for the comprehensive test is 11 minutes in total.

- 6.11 Add 10 mls of 4 M hydrochloric acid and stir for one minute exactly (limer).
- 6.12 Discontinue stirring, then add 25 mls of sodium hypochlorite solution, keeping the tip of the pipet on the surface of the liquid without disturbing the suspension. Start the stop clock when the pipet is half full.
- 6.13 Immediately place the separating funnel with the stop cock closed and start stirring gently.
- 6.14 Add 10 mls of the potassium iodide solution 1.5 M and connect the bellow on top of the funnel.
- 6.15 After exactly 10 minutes force the potassium iodide solution into the flask by pressurising the funnel and opening the stop cock. Close the stop cock immediately.

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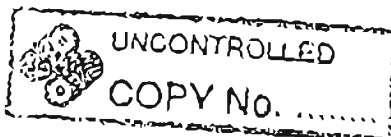
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## TOTAL QUALITY MANAGEMENT

### Laboratory Standard Method

- 6.16 Shake the flask by hand for 10 - 15 seconds and remove the funnel.
- 6.17 Rinse the tip of the flask with water into the pulp suspension.
- 6.18 Titrate the suspension under 0.20 N sodium thiosulphate using starch as Indicator - colour change sky blue to clear.
- 6.19 Make a blank determination following the same procedure omitting the test specimen

N.B. Repeat a test with a smaller test specimen if the titration takes less than 20mls.

#### 7. CALCULATION

$$\text{Hypo No.} = \frac{0.03546 (V_0 - V) \times N \times 1000 \times F}{W}$$

- IF  $V_0$  = Blank titration
- $V$  = Titration of test specimen
- $N$  = Normality of thiosulphate solution
- $W$  = Weight of test specimen, g oven-dry
- $F$  = Factor for correction to 50% chlorine consumption

N.B. Where 0.03546 = Weight of chlorine in grams, equivalent to 1 cm<sup>3</sup> of the sodium thiosulphate.

To obtain the factor "F" calculate at first the chlorine consumption "P" in percent, then read "F" from the table:

$$P\% = \frac{V_0 - V}{V_0} \times 100$$

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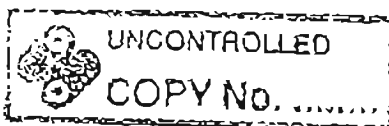
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## TOTAL QUALITY MANAGEMENT

### Laboratory Standard Method

F										
0		0,941	0,942	0,943	0,944	0,945	0,947	0,948	0,949	0,950
10	0,951	0,952	0,953	0,954	0,956	0,957	0,958	0,959	0,960	0,962
20	0,963	0,964	0,965	0,967	0,968	0,969	0,970	0,971	0,973	0,974
30	0,975	0,976	0,978	0,979	0,980	0,981	0,983	0,984	0,985	0,986
40	0,987	0,989	0,990	0,991	0,992	0,994	0,995	0,996	0,997	0,999
50	1,000	1,001	1,003	1,004	1,005	1,006	1,008	1,009	1,010	1,011
60	1,012									
P%	+0	1	2	3	4	5	6	7	8	9

#### 8. RECORDS

Record the test result in the Copeland/Digester Process Data Sheet.

DATE:

REV. No:

AUTHORITY

CHECKED BY:

23/06/98

1

*[Signature]*

## Appendix E:

### Digester charge sample calculations

These sample calculations are presented for a cook done at the standard mill conditions as used at Mondi Kraft, Piet Retief, namely:

TA charge:	9.5 % as $\text{Na}_2\text{O}$ on O.D. wood mass
AQ dosage:	0.1 % on O.D. wood mass
Softwood %:	41 % on O.D. wood basis

The calculations are done for the following given variables:

O.D. wood charge to digester:	1000 g
Liquor to wood ratio:	5:1
Softwood moisture content:	14.5 %
Hardwood moisture content:	14.3 %
Cooking liquor strength:	121.0 g $\text{Na}_2\text{O}$ /L
AQ dispersion strength:	0.419 g AQ/L

Calculations:

O.D. softwood required	$= 1000 \text{ g} \times (41/100)$
	$= 410 \text{ g}$

O.D. hardwood required	$= 1000 \text{ g} \times [(100-41)/100]$
	$= 59 \text{ g}$

Moist softwood required	$= 410 \text{ g} \times [100/(100-14.5)]$
	$= 479.5 \text{ g}$

Moist hardwood required	$= 590 \text{ g} \times [100/(100-14.3)]$
	$= 688.4 \text{ g}$

Total alkali required	$= 1000 \text{ g} \times (9.5/100)$
	$= 95 \text{ g as } \text{Na}_2\text{O}$

Volume of cooking liquor required	$= 95 \text{ g } \text{Na}_2\text{O} / (121.0 \text{ g } \text{Na}_2\text{O} / \text{L})$
	$= 0.785 \text{ L}$
	$= 785 \text{ mL}$

$$\begin{aligned}\text{AQ required} &= 1000 \text{ g} \times (0.1/100) \\ &= 1 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Volume of AQ dispersion required} &= 1 \text{ g AQ} / (0.419 \text{ g AQ/mL}) \\ &= 2.39 \text{ mL} \\ &\approx 2.4 \text{ mL}\end{aligned}$$

$$\begin{aligned}\text{Water required} &= 1000 \text{ g L} (5/1) \\ &= 5000 \text{ g} \\ &\approx 5000 \text{ mL (assume density of water} = 1 \text{ kg/L)}\end{aligned}$$

$$\begin{aligned}\text{Total moisture in wood} &= \text{Moisture in softwood} + \text{moisture in hardwood} \\ &= (479.5 \text{ g} - 410 \text{ g}) + (688.4 \text{ g} - 590 \text{ g}) \\ &= 167.9 \text{ g} \\ &\approx 168 \text{ mL (assume density of water} \approx 1 \text{ kg/L)}\end{aligned}$$

$$\begin{aligned}\text{Volume of water added} &= \text{Water required} - \text{cooking liquor} - \text{moisture in wood} - \text{AQ} \\ &\quad \text{dispersion} \\ &= 5000 \text{ mL} - 785 \text{ mL} - 168 \text{ mL} - 2 \text{ mL} \\ &= 4045 \text{ mL}\end{aligned}$$

## Appendix F:

### Hypo number testing method reproducibility

The repeatability of the Hypo number testing method (Tappi Test Method T 253 wd-98 [50]) is quoted as being 2.6 % for Hypo numbers between 10 and 20. However when this method was used to determine the Hypo number of a pulp sample from the Piet Retief mill, the repeatability was found to be 4.66 % for six determinations (see table F-1). The testing method was slightly modified, as suggested by Arbuthnot [53]. Instead of using a positive pressure in the separating funnel to force the potassium iodide solution into the reaction flask to terminate the reaction, a vacuum was created in the reaction flask before any chemicals were added. This vacuum was used to suck all the reagents into the flask through the separating funnel, with distilled water being used to rinse the funnel after each chemical had been added.

To investigate the reproducibility, six Hypo number determinations were done on a pulp sample from the Piet Retief mill, according to the modified method. The results for these determinations, as well as those done by the original method, and their relative reproducibilities are shown in Table F-1:

	Original method	Modified method
1	17.0	17.5
2	16.8	17.5
3	17.8	17.3
4	18.3	17.4
5	16.6	17.7
6	17.1	17.6
Average	17.5	17.3
Standard deviation	0.650	0.141
Repeatability (%)	4.66 %	1.00 %

Table F-1: Reproducibility data for Hypo number determinations done on a pulp sample from Piet Retief by means of the original and modified Tappi Test Method T 253 wd-98.

The modified method clearly improves the repeatability, from 4.66 % to 1.00 %, which is less than the value of 2.6 % quoted for Hypo numbers between 10 and 20 [50].

## Appendix G:

### Raw data

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Cook no	Wood species	Cooking temp (°C)	Ramp time (min)	Cooking time (min)	TA charge (% Na2O)	AQ dosage (%)	Liquor/wood ratio	Refined yield (%)	Hypo no	Initial pH	Black liquor pH	Black liquor AA
1A	50/50 Vol.	179	60	0	9.5	0.1	5	91.5	24.1	10.41	no sample	-
1B	50/50 Vol.	179	60	13	9.5	0.1	5	87.8	23.7	10.40	7.85	5.58
1C	50/50 Vol.	179	60	40	9.5	0.1	5	83.6	22.6	10.40	7.23	3.76
1D	50/50 Vol.	179	60	50	9.5	0.1	5	82.1	21.8	10.40	7.49	3.41
1E	50/50 Vol.	179	60	60	9.5	0.1	5	80.1	21.0	10.41	7.80	3.53
1F	50/50 Vol.	179	60	80	9.5	0.1	5	77.2	20.3	10.40	7.52	3.45
1G	50/50 Vol.	179	60	100	9.5	0.1	5	75.3	19.0	10.41	7.65	3.80
1H	50/50 Vol.	179	60	120	9.5	0.1	5	73.0	18.1	10.41	7.59	3.55
1I	50/50 Vol.	179	60	150	9.5	0.1	5	71.6	17.7	10.40	7.51	3.19

Table G-1: Raw data for cooks done with different cooking times at constant temperature.

Cook no	Wood species	Cooking temp (°C)	Ramp time (min)	Cooking time (min)	TA charge (% Na2O)	AQ dosage (%)	Liquor/wood ratio	Refined yield (%)	Hypo no	Initial pH	Black liquor pH	Black liquor AA
2A	50/50 Vol.	179	60	120	1	0.1	5	93.0	30.1	10.17	3.39	0.00
2B	50/50 Vol.	179	60	120	4	0.1	5	89.2	28.5	10.32	5.01	2.40
2C	50/50 Vol.	179	60	120	7	0.1	5	82.1	22.7	10.40	6.55	2.64
2D	50/50 Vol.	179	60	120	12.5	0.1	5	67.2	15.8	10.41	7.87	6.02
2E	50/50 Vol.	179	60	120	16	0.1	5	64.0	14.3	10.41	8.98	6.93

Table G-2: Raw data for cooks done at different TA charges.

Cook no	Wood species	Cooking temp (°C)	Ramp time (min)	Cooking time (min)	TA charge (% Na <sub>2</sub> O)	AQ dosage (%)	Liquor/wood ratio	Refined yield (%)	Hypo no	Initial pH	Black liquor pH	Black liquor AA
3A	50/50 Vol.	169	60	120	9.5	0.1	5	82.0	21.0	10.41	7.51	3.33
3B	50/50 Vol.	174	60	120	9.5	0.1	5	76.8	19.2	10.41	-	-
3C	50/50 Vol.	184	60	120	9.5	0.1	5	69.3	17.5	10.40	-	-
3D	50/50 Vol.	189	60	120	9.5	0.1	5	67.3	17.1	10.40	7.12	3.46

Table G-3: Raw data for cooks done at different cooking temperatures.

Cook no	Wood species	Cooking temp (°C)	Ramp time (min)	Cooking time (min)	TA charge (% Na <sub>2</sub> O)	AQ dosage (%)	Liquor/wood ratio	Refined yield (%)	Hypo no	Initial pH	Black liquor pH	Black liquor AA
4A	0 % SW	179	60	120	9.5	0.1	5	68.3	17.1	10.41	7.27	3.70
4B	15 % SW	179	60	120	9.5	0.1	5	70.3	17.5	10.42	-	-
4C	30% SW	179	60	120	9.5	0.1	5	71.8	17.8	10.41	-	-
4D	50 % SW	179	60	120	9.5	0.1	5	74.0	18.4	10.41	-	-
4E	75 % SW	179	60	120	9.5	0.1	5	75.7	19.0	10.40	-	-
4F	100 % SW	179	60	120	9.5	0.1	5	77.1	19.6	10.41	8.07	2.95

Table G-4: Raw data for cooks using different chip compositions.

Cook no	Wood species	Cooking temp (°C)	Ramp time (min)	Cooking time (min)	TA charge (% Na <sub>2</sub> O)	AQ dosage (%)	Liquor/wood ratio	Refined yield (%)	Hypo no
5A	HW	179	60	120	9.5	0	5	66.5	17.4
5B	HW	179	60	120	9.5	0.05	5	67.3	17.2
5C	HW	179	60	120	9.5	0.2	5	64.8	16.9
5D	HW	179	60	120	9.5	0.5	5	63.6	17.0
5E	SW	179	60	120	9.5	0	5	73.1	22.8
5F	SW	179	60	120	9.5	0.05	5	69.7	20.2
5G	SW	179	60	120	9.5	0.2	5	69.2	18.6
5H	SW	179	60	120	9.5	0.5	5	67.7	17.1
5I	50/50 Vol.	179	60	120	9.5	0	5	67.7	20.2
5J	50/50 Vol.	179	60	120	9.5	0.05	5	70	19.3
5K	50/50 Vol.	179	60	120	9.5	0.2	5	69.6	17.8
5L	50/50 Vol.	179	60	120	9.5	0.5	5	65.5	16.9

Table G-5: Raw data for cooks done with different AQ dosages.

Cook no	Wood species	Cooking temp (°C)	Ramp time (min)	Cooking time (min)	AA charge (% Na <sub>2</sub> O)	AQ dosage (%)	Liquor/wood ratio	Unrefined yield (%)	Hypo no
6A	50/50 Vol.	179	60	120	9.5	0.1	5	77.1	17.8
6B	50/50 Vol.	179	60	120	9.5	0.1	5	77.4	18.0
6C	50/50 Vol.	179	60	120	9.5	0.1	5	76.5	18.0
6D	50/50 Vol.	179	60	120	9.5	0.1	5	77.7	18.1
Standard deviation:								0.505	0.126
Repeatability (%):								0.900	0.860

Table G-6: Reproducibility data.

Cook no	Wood species	Cooking temp (°C)	Ramp time (min)	Cooking time (min)	TA charge (% Na <sub>2</sub> O)	AQ dosage (%)	Liquor/wood ratio	Refined yield (%)	Hypo no
HW169	HW	169	60	120	9.5	0.1	5	73.7	19.2
HW159	HW	159	60	120	9.5	0.1	5	81.8	22.5
HW8.5	HW	179	60	120	8.5	0.1	5	70.1	18.1
HW7.5	HW	179	60	120	7.5	0.1	5	72.1	20.1
SW189	SW	189	60	120	9.5	0.1	5	74.3	19.2
SW189B	SW	189	60	120	10.5	0.1	5	72.1	19.0
SW10.5	SW	179	60	120	10.5	0.1	5		
SW11.5	SW	179	60	120	11.5	0.1	5	71.4	17.8
SW12	SW	179	60	120	12.0	0.1	5	68.9	17.6
SW11.5B	SW	189	60	120	11.5	0.1	5	69.8	17.6

Table G-7: Raw data for hardwood and softwood cooks at different temperatures and TA charges.

Cook no	Wood species	Cooking temp (°C)	Ramp time (min)	Cooking time (min)	TA charge (% Na <sub>2</sub> O)	AQ dosage (%)	Liquor/wood ratio	Refined yield (%)	Hypo no
Caustic	50/50 Vol.	179	60	120	9.5	0.1	5	71.4	17.3

Table G-8: Raw data for alkaline sulphite cook.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	100	210	400	1000	100	210	400	1000	100	210	400	1000
	2.03	1.94	1.92	1.94	349	402	440	488	373	325	349	272
	1.98	1.91	1.98	1.90	383	424	471	481	354	344	291	267
	1.98	1.94	1.95	1.93	389	419	430	518	368	320	291	213
	1.95	1.95	1.93	1.90	334	386	483	548	397	339	330	277
	2.00	1.90	1.98	1.92	352	443	508	432	387	387	320	248
	1.98	1.98	1.99	1.94	334	429	490	520	392	354	349	218
					370	384	494	499				
	Freeness (CSF)				356	432	482	468				
	540	442	288	35	353	418	494	446				
					388	369	479	496				

Table G-9: Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 14.3.

	Stretch (%)				Tensile strength (kN/m)			
PFI revs (x0.1)	100	210	400	1000	100	210	400	1000
	2.19	2.96	2.88	2.99	5.088	6.203	7.383	7.342
	2.60	2.89	2.63	2.46	5.877	6.203	7.863	5.722
	2.37	2.74	2.74	3.46	5.258	5.576	6.561	7.342
	2.24	2.79	3.24	3.21	6.007	6.520	6.756	7.033
	2.19	2.43	3.12	2.89	4.990	5.006	6.878	7.277
	2.22	2.87	2.82	3.29	5.771	6.081	7.823	6.585

Table G-9 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 14.3.

	O.D Mass (g)					Burst strength (kPa)				
PFI revs (x0.1)	400	500	700	1000	1500	400	500	700	1000	1500
	1.71	1.78	1.81	1.83	1.85	284	298	339	380	373
	1.70	1.73	1.77	1.84	1.78	274	326	331	377	341
	1.71	1.73	1.80	1.84	1.71	258	315	379	417	346
	1.68	1.73	1.78	1.84	1.7	287	272	354	378	317
	1.69	1.76	1.77	1.86	1.9	285	323	368	404	335
	1.69	1.76	1.80	1.87	1.84	294	318	318	417	376
						299	307	357	412	367
	Freeness (CSF)					306	319	352	388	367
	451	330	210	103	80	266	297	378	413	316
						288	315	348	417	349

Table G-10: Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 18.1.

	Tear strength (mN)					Stretch (%)				
PFI revs (x0.1)	400	500	700	1000	1500	400	500	700	1000	1500
	363	344	253	209	184	2.73	2.87	2.90	2.80	2.05
	238	257	248	238	189	2.37	2.64	2.94	2.89	3.27
	248	248	253	257	204	2.40	2.41	2.06	2.70	3.17
	238	253	248	223	174	2.35	2.66	2.65	3.11	2.79
	349	238	228	272	213	2.65	2.45	2.88	2.82	3.47
	243	267	223	213	218	2.55	2.75	2.52	2.86	3.32

Table G-10 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 18.1.

	Tensile strength (kN/m)				
PFI revs (x0.1)	400	500	700	1000	1500
	3.883	4.819	5.714	5.869	5.339598
	4.868	4.762	5.372	6.113	4.932873
	4.493	4.917	4.754	5.641	5.97465
	3.948	4.754	4.534	6.610	4.273698
	4.876	4.135	5.845	5.698	5.6661
	4.998	5.063	5.161	6.170	4.965411

Table G-10 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood, Hypo number = 18.1.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	400	500	600	1000	400	500	600	1000	400	500	600	1000
	1.89	1.92	1.88	1.77	290	337	312	327	291	335	253	218
	1.94	1.90	1.86	1.77	300	278	331	380	315	306	315	184
	1.87	1.90	1.90	1.76	280	302	310	356	344	306	277	199
	1.94	1.89	1.92	1.77	315	289	300	322	296	325	359	-
	1.87	1.91	1.90	1.76	290	296	329	327	282	291	265	-
	1.86	1.91	1.93	1.77	297	318	324	336	296	277	-	-
					277	331	365	326				
	Freeness (CSF)				297	315	296	318				
	472	382	310	112	282	287	300	375				
					271	289	310	318				

Table G-11: Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 20.3.

	Stretch (%)				Tensile strength (kN/m)			
PFI revs (x0.1)	400	500	600	1000	400	500	600	1000
	2.37	2.48	2.46	2.91	4.208	4.672	4.615	5.031
	2.42	2.56	2.39	2.53	4.200	5.193	5.315	5.315
	2.56	2.56	2.60	2.71	4.819	5.250	5.600	5.120
	2.35	2.33	2.65	2.69	3.744	4.681	5.983	4.998
	2.43	2.52	2.49	2.77	4.737	4.306	5.364	5.674
	2.44	2.30	2.71	2.47	4.558	4.493	4.892	5.340

Table G-11 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 20.3.



	O.D Mass (g)					Burst strength (kPa)				
PFI revs (x0.1)	400	500	600	700	1000	400	500	600	700	1000
	1.91	1.91	1.90	1.91	1.81	257	233	242	270	275
	1.99	1.93	1.91	1.86	1.85	241	259	297	272	347
	1.99	1.89	1.90	1.88	1.82	268	267	261	260	323
	2.03	1.90	1.90	1.88	1.84	258	269	269	275	313
	2.03	1.91	1.90	1.89	1.80	256	284	263	298	315
	2.01	1.92	1.91	1.89	1.81	233	267	282	287	319
						263	266	278	239	306
	Freeness (CSF)					260	279	299	327	315
	450	340	305	260	125	225	270	259	287	346
						272	236	291	285	309

Table G-12: Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 21.8.

	Tear strength (mN)					Stretch (%)				
PFI revs (x0.1)	400	500	600	700	1000	400	500	600	700	1000
	315	272	248	272	218	2.21	2.38	2.62	2.67	2.56
	315	301	286	253	199	2.33	2.23	2.20	2.63	2.29
	315	-	257	233	213	2.17	2.47	2.56	2.75	2.63
	286	-	267	277	213	2.30	2.42	2.45	3.22	2.55
	282	272	282	277	204	2.33	2.58	2.50	2.70	2.35
	320	286	277	243	204	2.26	2.50	2.53	2.56	2.82

Table G-12 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 21.8.

	Tensile strength (kN/m)				
PFI revs (x0.1)	400	500	600	700	1000
	4.249	4.298	4.737	4.469	4.960
	4.111	4.770	4.347	4.412	5.047
	4.265	4.119	4.835	4.624	5.185
	4.770	4.347	4.493	4.982	5.185
	4.298	4.591	4.917	4.542	4.884
	3.956	4.184	4.860	4.982	4.786

Table G-12 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 21.8.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	400	500	600	1000	400	500	600	1000	400	500	600	1000
	1.90	1.69	1.76	1.93	231	215	245	271	277	209	214	272
	1.87	1.68	1.80	1.98	250	218	245	292	296	243	219	200
	1.90	1.70	1.77	1.90	195	216	302	310	282	209	200	238
	1.90	1.69	1.75	1.93	229	219	225	313	301	219	195	214
	1.89	1.70	1.73	1.87	214	208	225	311	301	253	234	185
	1.87	1.67	1.71	1.92	218	201	239	310	287	243	180	195
					183	211	215	247				
					189	199	244	305				
	Freeness (CSF)											
	424	340	286	110	229	235	229	289				
					218	204	223	313				

Table G-13: Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 22.7.

	Stretch (%)				Tensile strength (kN/m)			
PFI revs (x0.1)	400	500	600	1000	400	500	600	1000
	2.46	2.47	2.74	2.71	3.967	3.747	3.592	5.033
	2.35	2.40	2.19	2.91	4.105	3.307	3.332	4.813
	2.09	2.47	2.83	2.66	3.494	3.486	4.260	5.684
	2.56	2.06	2.53	2.53	4.528	3.543	4.056	5.074
	2.12	1.97	2.53	2.26	4.463	2.957	4.015	4.422
	1.69	2.26	2.65	2.62	3.446	4.024	3.494	5.554

Table G-13 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood; Hypo number = 22.7.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	400	700	1000	1500	400	700	1000	1500	400	700	1000	1500
	1.96	2.01	1.98	1.95	294	316	362	391	313	315	267	265
	1.96	2.00	1.98	1.94	299	333	362	413	313	317	291	235
	1.95	2.01	1.97	1.94	265	324	345	355	298	288	269	244
	1.94	1.99	1.97	1.92	252	296	302	339	341	286	279	271
	1.97	2.01	1.97	1.95	254	285	322	379	336	299	270	276
	1.96	2.02	1.98	1.95	311	313	364	385	326	310	292	258
					305	329	325	364				
	Freeness (CSF)				314	331	356	351				
	501	381	269	178	289	336	346	371				
					275	331	356	379				

Table G-14: Raw handsheet data for simultaneously pulped hardwood and softwood; softwood percentage = 15 %.

	Tensile strength (kN/m)			
PFI revs (x0.1)	400	700	1000	1500
	5.023	5.846	5.984	6.359
	4.859	5.126	5.624	6.054
	4.659	5.468	6.235	5.826
	5.426	5.326	6.001	5.648
	5.516	5.754	5.452	6.198
	5.734	5.739	5.324	5.729

Table G-14 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood; softwood percentage = 15 %.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	400	700	1000	1500	400	700	1000	1500	400	700	1000	1500
	1.96	1.96	1.90	1.90	270	300	316	337	287	325	229	234
	1.95	1.95	1.90	1.90	273	347	316	350	306	329	339	315
	1.94	1.97	1.91	1.94	264	308	345	377	267	315	287	229
	1.97	1.95	1.91	1.92	276	315	328	333	358	325	320	348
	1.96	1.99	1.91	1.98	244	311	337	369	287	267	253	229
	1.94	1.93	1.90	1.91	297	294	311	355	296	277	267	272
					245	310	339	341				
					283	295	321	357				
					256	267	321	341				
					298	307	352	373				

Table G-15: Raw handsheet data for simultaneously pulped hardwood and softwood; softwood percentage = 30 %.

	Stretch (%)				Tensile strength (kN/m)			
PFI revs (x0.1)	400	700	1000	1500	400	700	1000	1500
	2.69	2.91	3.18	3.19	4.855	5.561	5.398	5.398
	2.41	3.01	3.32	3.47	4.625	5.602	6.198	5.602
	2.47	2.97	3.24	3.45	5.195	5.612	5.412	6.904
	2.52	3.21	3.13	3.39	6.429	5.859	6.470	7.501
	2.15	3.01	2.64	3.21	4.855	5.330	5.154	6.592
	2.58	2.99	2.97	3.42	5.968	5.493	5.602	5.642

Table G-15 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood; softwood percentage = 30 %.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	400	700	1000	1500	400	700	1000	1500	400	700	1000	1500
	1.96	1.99	1.94	1.89	258	307	314	318	362	371	357	290
	1.97	1.93	1.95	1.89	286	292	339	340	376	386	295	300
	1.99	1.94	1.94	1.90	280	274	320	304	374	324	390	271
	1.99	1.98	1.95	1.88	260	293	342	317	376	348	357	314
	1.96	1.93	1.96	1.91	280	288	293	348	343	386	286	381
	2.01	1.97	1.92	1.93	269	304	311	363	414	338	333	314
					300	285	340	333				
	Freeness (CSF)				254	299	330	350				
	574	529	400	334	282	279	339	328				
					293	266	339	347				

Table G-16: Raw handsheet data for simultaneously pulped hardwood and softwood; softwood percentage = 50 %.

	Stretch (%)				Tensile strength (kN/m)			
PFI revs (x0.1)	400	700	1000	1500	400	700	1000	1500
	2.43	2.49	2.58	2.86	5.195	4.218	4.801	5.886
	2.18	2.57	2.86	2.75	4.964	5.574	5.384	5.724
	2.42	2.69	2.79	2.65	4.381	5.384	4.964	4.774
	2.59	2.90	2.58	2.92	3.919	4.177	5.642	6.076
	2.29	2.43	2.56	2.85	4.910	4.313	4.815	5.466
	2.28	2.83	2.39	2.98	5.018	4.625	5.412	5.452

Table G-16 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood; softwood percentage = 50 %.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	400	700	1000	1500	400	700	1000	1500	400	700	1000	1500
	1.95	1.99	1.98	2.03	241	265	263	344	389	358	365	361
	1.94	1.98	1.96	2.01	215	254	295	352	381	367	361	352
	1.94	1.98	1.95	2.05	236	295	301	285	361	359	349	334
	1.94	1.99	1.94	2.03	264	287	293	295	380	386	331	319
	1.95	1.99	1.96	2.05	281	279	278	279	347	394	345	342
	1.93	1.97	1.95	2.03	275	261	257	308	357	372	341	325
					263	261	261	302				
	Freeness (CSF)				279	264	254	312				
	621	586	521	401	251	276	283	295				
					246	294	281	338				

Table G-17: Raw handsheet data for simultaneously pulped hardwood and softwood; softwood percentage = 75 %.

	Tensile strength (kN/m)			
PFI revs (x0.1)	400	700	1000	1500
	3.956	5.171	4.756	5.697
	4.101	4.256	4.879	4.957
	4.657	4.156	4.779	5.002
	4.756	4.527	4.116	4.865
	4.582	4.698	4.653	5.670
	4.562	4.751	4.815	5.147

Table G-17 (cont.): Raw handsheet data for simultaneously pulped hardwood and softwood; softwood percentage = 75 %.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	400	500	600	1000	400	500	600	1000	400	500	600	1000
	2.20	2.10	2.13	2.08	420	412	420	463	395	330	324	324
	2.22	2.08	2.11	2.03	399	359	404	479	363	369	330	285
	2.22	2.10	2.18	2.04	363	396	363	469	356	363	311	278
	2.16	2.06	2.13	2.10	404	371	442	439	395	317	317	259
	2.21	2.13	2.09	2.09	399	408	411	487	408	356	330	278
	2.13	2.13	2.10	2.08	429	393	365	486	369	337	337	272
					402	427	451	447				
	Freeness (CSF)				420	430	393	475				
	450	350	310	110	366	396	417	456				
					395	429	373	460				

Table G-18: Raw handsheet data for a hardwood/softwood mixture pulped with 0.5 % AQ; Hypo number = 16.9.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	1000	1500	2500	2600	1000	1500	2500	2600	1000	1500	2500	2600
	1.95	1.76	1.94	1.84	365	335	285	334	272	245	145	135
	1.90	1.78	1.94	1.81	315	304	381	317	286	265	179	135
	1.91	1.91	1.99	1.56	340	327	408	249	291	245	154	174
	1.95	1.82	1.95	1.94	361	343	363	314	325	206	204	125
	1.96	1.85	1.85	1.83	329	351	402	280	272	209	189	218
	1.91	1.79	1.85	1.55	389	312	333	341	252	-	164	174
					361	358	298	301				
	Freeness (CSF)				316	328	336	424				
	411	160	40	20	424	-	339	298				
					288	-	389	348				

Table G-19: Raw handsheet data for softwood pulp; Hypo number = 17.8.

	Stretch (%)				Tensile strength (kN/m)			
PFI revs (x0.1)	1000	1500	2500	2600	1000	1500	2500	2600
	2.03	1.55	2.02	2.22	4.009	4.326	4.656	5.283
	2.88	2.47	2.77	1.65	4.428	4.560	4.982	4.086
	2.23	1.89	2.86	2.18	4.103	4.169	5.096	5.421
	1.61	2.81	1.62	2.13	4.265	4.336	4.819	4.389
	2.68	2.40	1.90	2.01	4.599	4.756	4.265	3.940
	2.62	2.36	2.58	1.95	4.583	4.697	4.705	5.348

Table G-19 (cont.): Raw handsheet data for softwood pulp; Hypo number = 17.8.



	O.D Mass (g)						Burst strength (kPa)					
PFI revs (x0.1)	100	200	300	600	1000	1100	100	200	300	600	1000	1100
	1.78	1.93	1.73	1.89	1.94	1.76	192	250	258	345	467	433
	1.80	1.95	1.76	1.88	1.88	1.74	186	276	239	419	487	404
	1.82	1.96	1.74	1.93	1.92	1.78	169	256	284	355	487	406
	1.81	1.99	1.77	1.92	1.94	1.81	176	256	286	434	498	421
	1.82	1.97	1.76	1.91	1.90	1.76	188	243	282	420	461	429
	1.80	1.95	1.69	1.98	1.89	1.77	186	236	222	411	476	414
	Freeness (CSF)						186	241	207	405	477	437
	492	371	278	107	40	38	211	276	278	431	496	422
							206	241	264	389	478	417
							192	249	288	419	476	284

Table G-20: Raw handsheet data for hardwood pulp; Hypo number = 18.1.

	Tear strength (mN)						Stretch (%)					
PFI revs (x0.1)	100	200	300	600	1000	1100	100	200	300	600	1000	1100
	301	306	272	267	223	249	2.21	2.38	2.62	2.67	2.56	3.62
	325	392	282	252	252	238	2.33	2.23	2.20	2.63	2.29	2.22
	277	296	248	248	267	250	2.17	2.47	2.56	2.75	2.63	2.57
	291	267	257	228	238	209	2.30	2.42	2.45	3.22	2.55	3.26
	262	277	252	-	267	197	2.33	2.58	2.50	2.70	2.35	3.01
	219	311	286	-	223	216	2.26	2.50	2.53	2.56	2.82	2.54

Table G-20 (cont.): Raw handsheet data for hardwood pulp; Hypo number = 18.1.

	Tensile strength (kN/m)					
PFI revs (x0.1)	100	200	300	600	1000	1100
	3.598	4.982	4.461	6.365	6.770	4.379
	3.541	4.900	3.956	5.714	6.316	5.323
	3.362	4.737	4.379	6.903	6.531	4.990
	3.793	4.444	4.493	5.714	6.400	5.373
	3.834	4.672	4.477	4.892	6.871	5.446
	4.298	4.086	3.956	6.740	5.836	-

Table G-20 (cont.): Raw handsheet data for hardwood pulp; Hypo number = 18.1.

	O.D Mass (g)					Burst strength (kPa)				
PFI revs (x0.1)	400	600	800	1000	1500	400	600	800	1000	1500
	1.96	1.63	1.89	1.87	1.88	306	279	378	419	381
	2.15	1.69	1.93	1.90	1.89	305	287	407	404	392
	2.11	1.71	1.90	1.89	1.90	410	290	399	379	350
	2.21	1.69	1.87	1.89	1.87	300	294	343	411	343
	2.12	1.64	1.91	1.91	1.89	398	295	374	398	365
	1.99	1.67	1.89	1.91	1.88	374	306	380	422	381
						346	305	372	416	381
	Freeness (CSF)					300	310	394	433	366
	380	190	109	83	64	322	284	405	398	376
						348	322	391	391	371

Table G-21: Raw handsheet data for a mixture of separately pulped hardwood (Hypo no = 18.1) and softwood (Hypo no = 17.8) pulp.

	Tear strength (mN)					Stretch (%)				
PFI revs (x0.1)	400	600	800	1000	1500	400	600	800	1000	1500
	449	233	233	238	216	2.46	2.47	2.74	2.71	2.51
	416	243	233	270	234	2.35	2.40	2.19	2.91	2.67
	335	282	257	220	227	2.09	2.47	2.83	2.66	2.43
	335	277	252	223	197	2.56	2.06	2.53	2.53	2.35
	344	262	252	257	192	2.12	1.97	2.53	2.26	2.65
	430	243	243	244	191	1.69	2.26	2.65	2.62	2.43

Table G-21 (cont.): Raw handsheet data for a mixture of separately pulped hardwood (Hypo no = 18.1) and softwood (Hypo no = 17.8) pulp.

	Tensile strength (kN/m)				
PFI revs (x0.1)	400	600	800	1000	1500
	6.186	4.746	4.803	6.61	5.621
	5.747	5.161	5.999	6.04	5.231
	5.405	4.908	5.902	6.471	5.224
	5.324	3.435	5.592	5.608	5.123
	5.478	5.039	5.234	5.845	5.462
	5.079	4.689	5.576	6.984	5.623

Table G-21 (cont.): Raw handsheet data for a mixture of separately pulped hardwood (Hypo no = 18.1) and softwood (Hypo no = 17.8) pulp.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	180	200	260	400	180	200	260	400	180	200	260	400
	1.98	2.13	2.07	2.03	250	342	397	428	304	324	304	317
	1.96	2.09	2.06	2.05	266	311	318	386	259	343	330	265
	1.99	2.12	2.07	2.05	263	334	317	321	298	324	369	265
	1.97	2.07	2.09	2.04	291	363	349	431	395	304	324	291
	1.95	2.10	2.09	2.05	298	355	377	421	259	337	317	304
	1.99	2.15	2.11	2.06	300	224	347	389	304	285	317	278
	Freeness (CSF)				287	335	405	397				
	405	370	330	195	279	344	299	416				
					250	344	344	404				
					272	346	341	394				

Table G-22: Raw handsheet data hardwood pulp; Hypo number = 17.1.

	Tensile strength (kN/m)			
PFI revs (x0.1)	180	200	260	400
	5.102	6.003	5.623	6.602
	4.856	6.234	5.468	5.987
	4.965	5.812	5.996	5.879
	5.236	5.489	6.125	6.259
	5.492	5.268	6.014	6.351
	5.374	5.602	5.862	6.120

Table G-22 (cont.): Raw handsheet data for hardwood pulp; Hypo number = 17.1.

	O.D Mass (g)				Burst strength (kPa)				Tear strength (mN)			
PFI revs (x0.1)	400	600	800	1200	400	600	800	1200	400	600	800	1200
	1.99	2.06	2.05	2.04	362	371	414	450	447	458	519	397
	2.04	2.05	2.06	2.02	362	371	389	401	434	439	458	359
	2.08	2.02	2.04	2.04	372	382	395	409	425	425	430	411
	2.07	2.06	2.04	2.02	355	351	425	426	439	444	382	449
	2.06	2.01	2.04	2.04	325	366	400	436	444	439	408	467
	2.09	2.02	2.04	2.05	356	362	389	427	494	449	439	406
					346	351	387	427				
	Freeness (CSF)				353	356	405	401				
	511	470	397	288	361	348	413	416				
					343	361	413	413				

Table G-23: Raw handsheet data for ASSC-AQ pulp from a hardwood/softwood mixture; Hypo number = 17.3.

	Stretch (%)				Tensile strength (kN/m)			
PFI revs (x0.1)	400	600	800	1200	400	600	800	1200
	2.43	2.64	3.33	3.41	5.155	5.914	6.716	6.295
	2.84	2.68	3.40	3.28	6.892	6.186	7.177	7.245
	2.11	2.40	3.09	3.19	5.196	4.613	7.068	6.132
	2.40	2.70	2.92	2.68	5.440	6.024	5.644	5.644
	2.91	2.71	2.84	3.12	6.132	5.969	7.733	7.516
	2.64	2.88	3.01	2.89	6.227	5.752	6.526	5.698

Table G-23 (cont.): Raw handsheet data for ASSC-AQ pulp from a hardwood/softwood mixture; Hypo number = 17.3.

## Appendix H:

### Regression techniques

The aim of linear regression is to find the straight line which best fits a range of x and y values, where x is an independent variable, and y is a dependant variable. The equation for a straight line is:

$$y = mx + b$$

where m and b are constants. These constants are calculated as follows for n sets of variables x and y, according to Perry [54]:

$$m = n(\sum xy)(\sum x)(\sum y) / [n(\sum(x^2)) - (\sum x)^2]$$

$$b = [(\sum y)(\sum(x^2)) - (\sum x)(\sum xy)] / [n(\sum(x^2)) - (\sum x)^2]$$

The degree of correlation of the obtained equation is measured by  $r^2$ , which is calculated as follows [54]:

$$r^2 = \{ \sum (x_{\text{actual}} - x_{\text{average}}) * (y_{\text{actual}} - y_{\text{average}}) \}^2 / [ \sum (x_{\text{actual}} - x_{\text{average}})^2 * \sum (y_{\text{actual}} - y_{\text{average}})^2 ]$$

where:  $y_{\text{actual}}$  = actual y values  
 $y_{\text{average}}$  = average of actual y values

The value of  $r^2$  varies between 0 and 1, with a value close to 1 indicating a good fit [54].

Regression can also be applied to find a power function that best fits a set of data. In this case the resulting function will be in the form:

$$y = bm^x$$

where b and m are constants. To determine these constants, the natural logarithm of both sides of the equation is taken:

$$\ln y = \ln (bm^x)$$

Simplifying this equation gives the following:

$$\ln y = x \ln m + \ln b$$

This equation is that of a straight line, with  $\ln y$  being the dependant variable,  $x$  the independent variable and  $\ln m$  and  $\ln b$  constants. Linear regression is used determine the values of  $\ln m$  and  $\ln b$ , and subsequently  $m$  and  $b$ . The value of  $r^2$  is determined as previously discussed.

Similarly, a logarithmic function of the following format can be fitted:

$$y = m \ln x + b$$

In this instance,  $\ln x$  is the independent variable and  $y$  is the dependant variable.

In the development of the economic model (appendix I), for each set of data points all three types of curves were fitted, with the curve with the highest value for  $r^2$  being used.

## Appendix I:

### Graphical representations

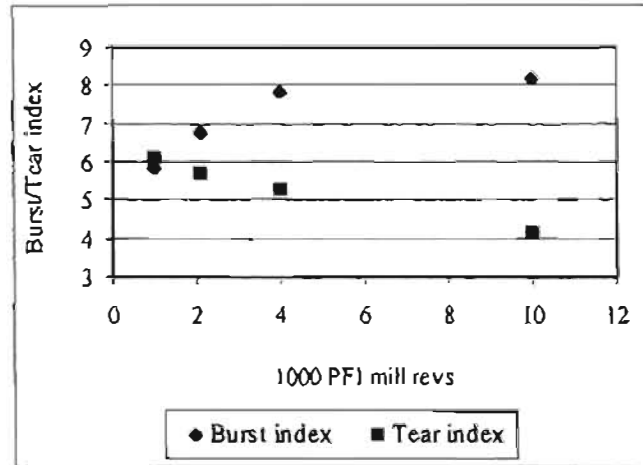


Fig. I-1: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus PFI mill revolutions for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 14.3.

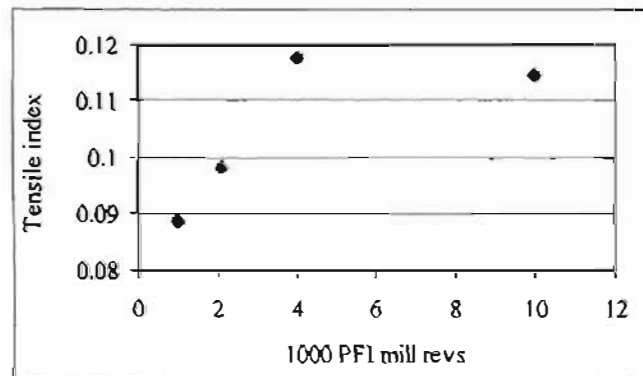


Fig. I-2: Tensile index (Nm/g) versus PFI mill revolutions for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 14.3.



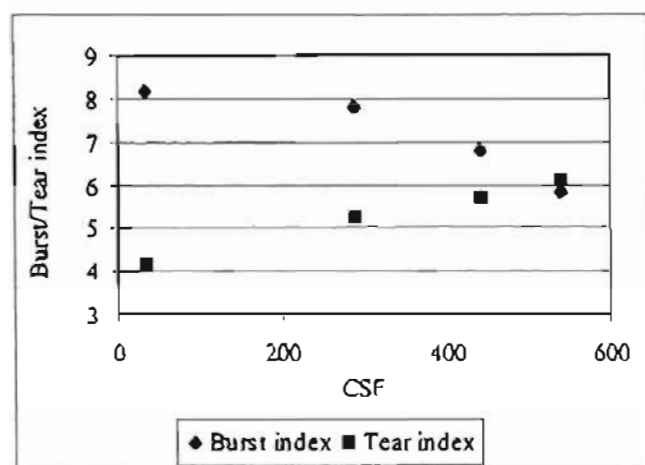


Fig. I-3: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 14.3.

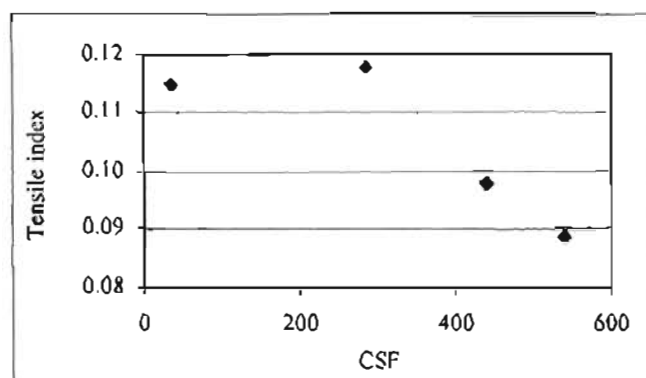


Fig. I-4: Tensile index (Nm/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 14.3.

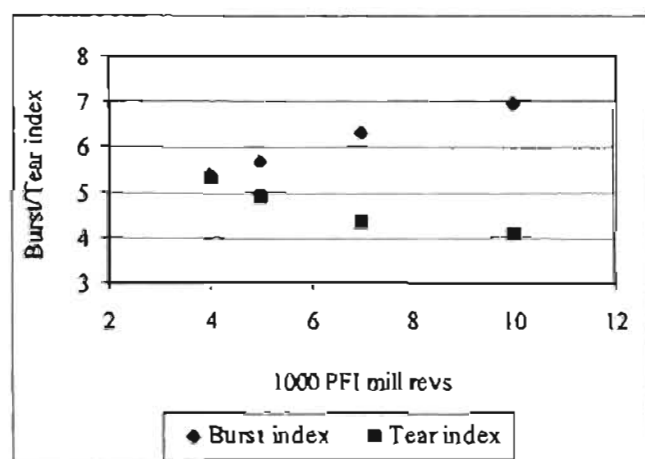


Fig. I-5: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus PFI mill revolutions for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 18.1.

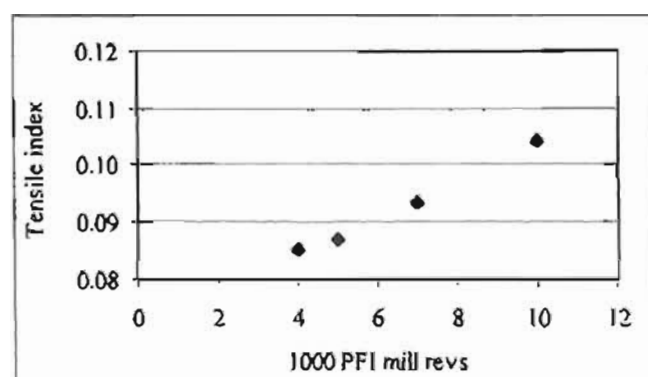


Fig. I-6: Tensile index (Nm/g) versus PFI mill revolutions for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 18.1.

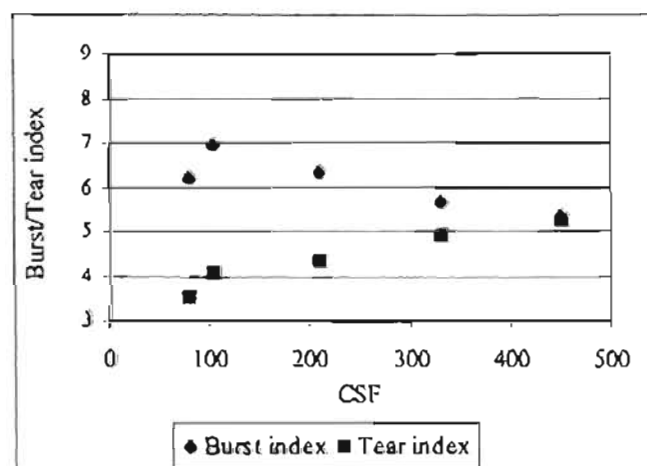


Fig. I-7: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 18.1.

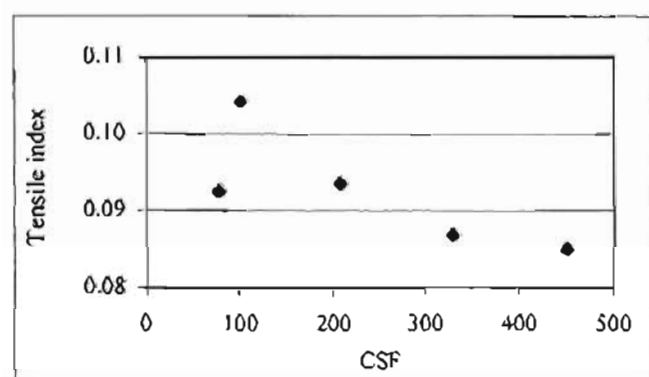


Fig. I-8: Tensile index (Nm/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 18.1.

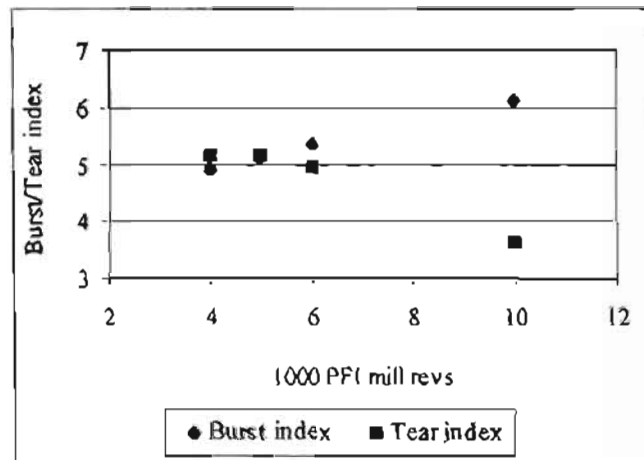


Fig. 1-9: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus PFI mill revolutions for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 20.3.

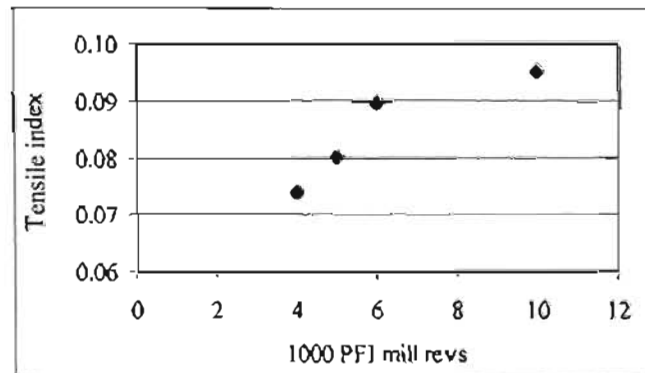


Fig. 1-10: Tensile index (Nm/g) versus PFI mill revolutions for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 20.3.

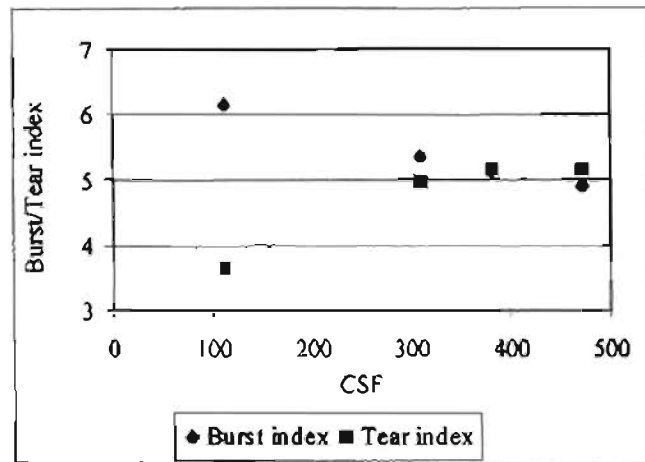


Fig. 1-11: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 20.3.

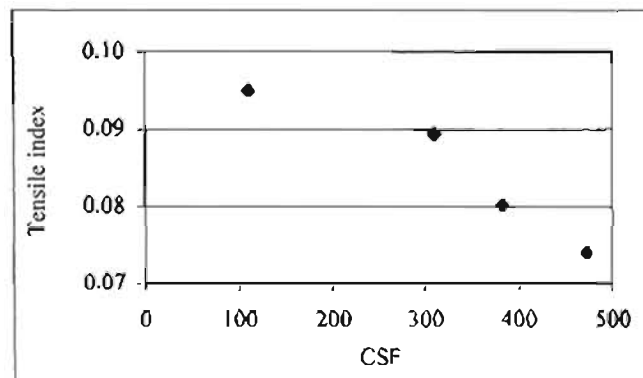


Fig. 1-12: Tensile index (Nm/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 20.3.

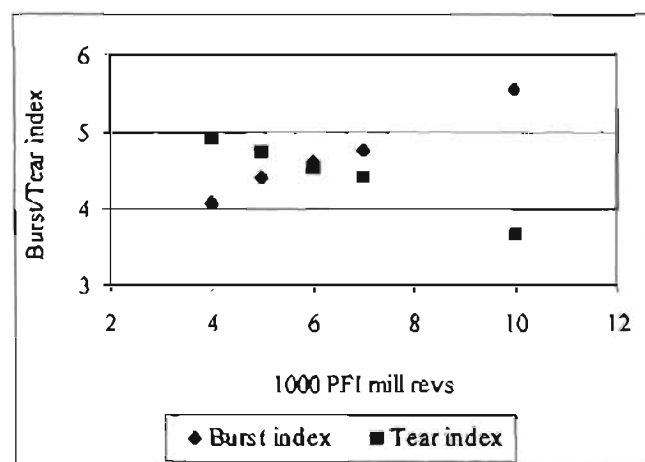


Fig. 1-13: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus PFI mill revolutions for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 21.8.

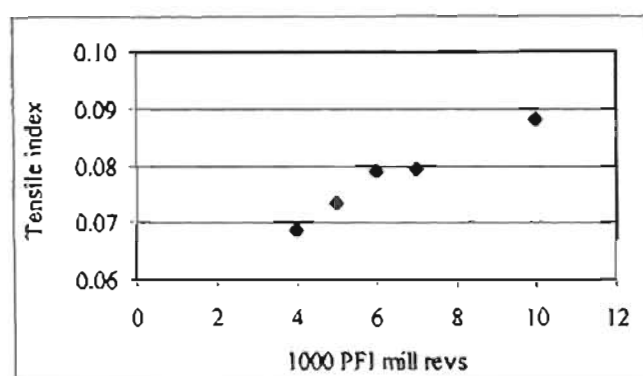


Fig. I-14: Tensile index (Nm/g) versus PFI mill revolutions for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 21.8.

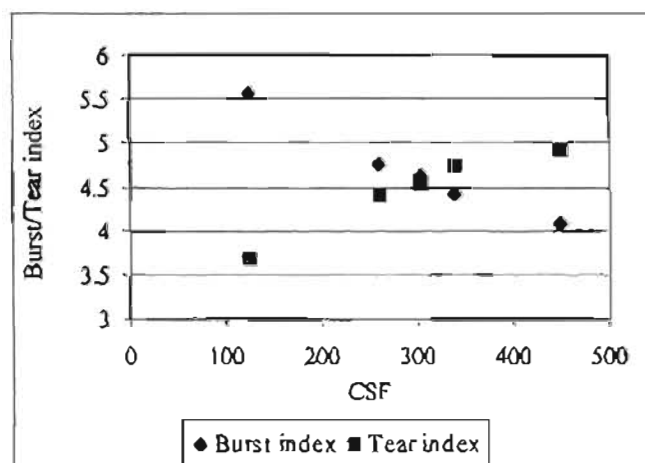


Fig. I-15: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 21.8.

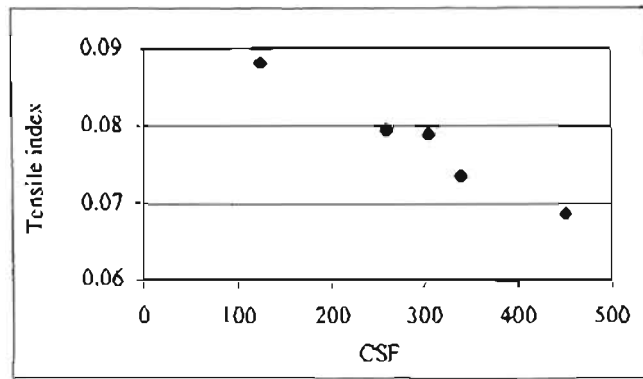


Fig. I-16: Tensile index (Nm/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 21.8.

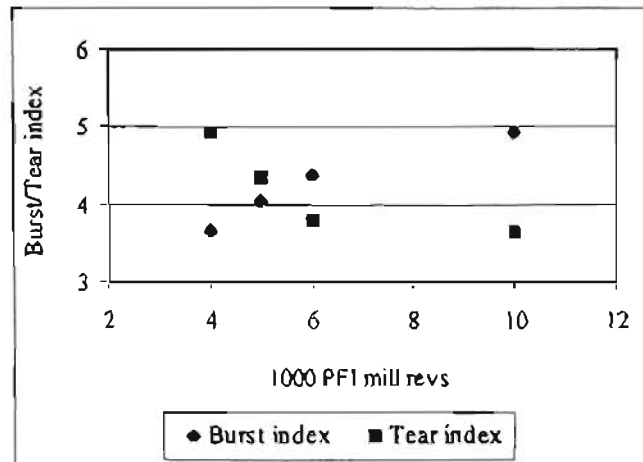


Fig. I-17: Burst index (kPa.m²/g) and Tear index (mN.m²/g) versus PFI mill revolutions for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 22.7.

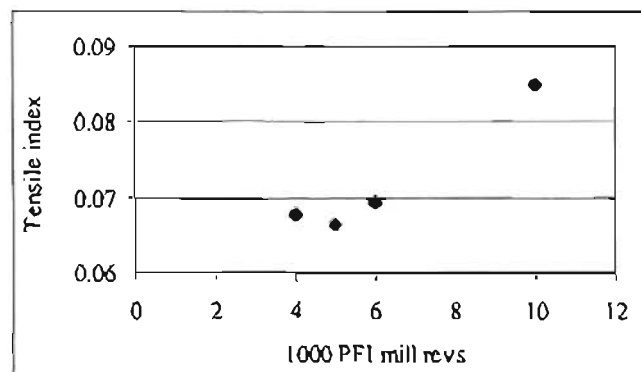


Fig. I-18: Tensile index (Nm/g) versus PFI mill revolutions for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 22.7.

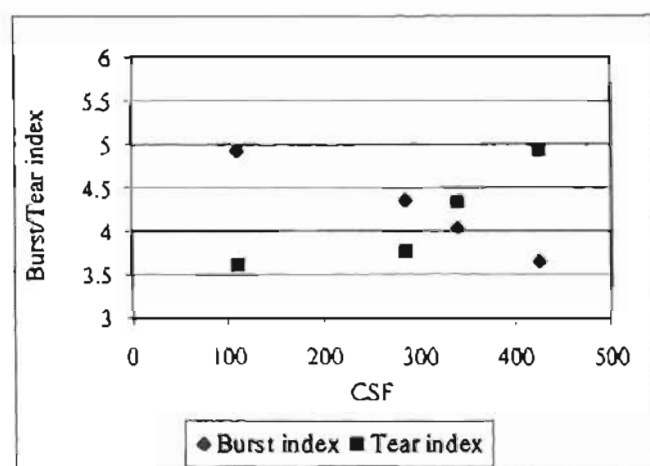


Fig. I-19: Burst index (kPa.m<sup>3</sup>/g) and Tear index (mN.m<sup>3</sup>/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 22.7.

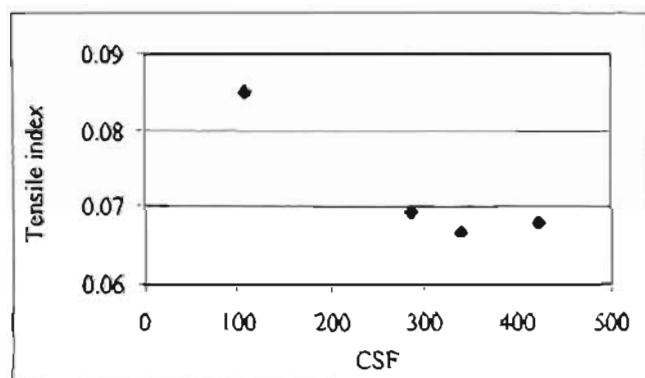


Fig. I-20: Tensile index (Nm/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, Hypo number = 22.7.

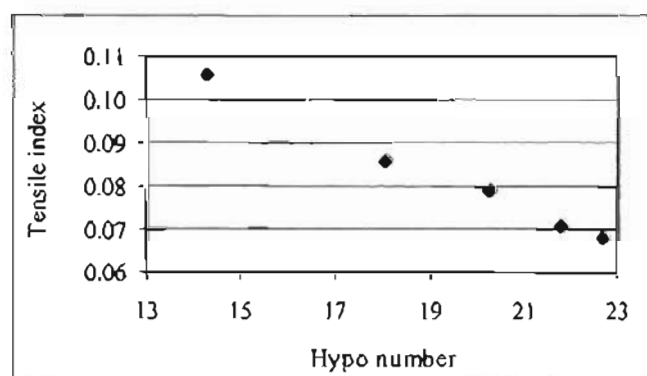


Fig. I-21: Tensile index (Nm/g) versus Hypo number for a simultaneously pulped mixture of hardwood and softwood, softwood percentage = 41 %.

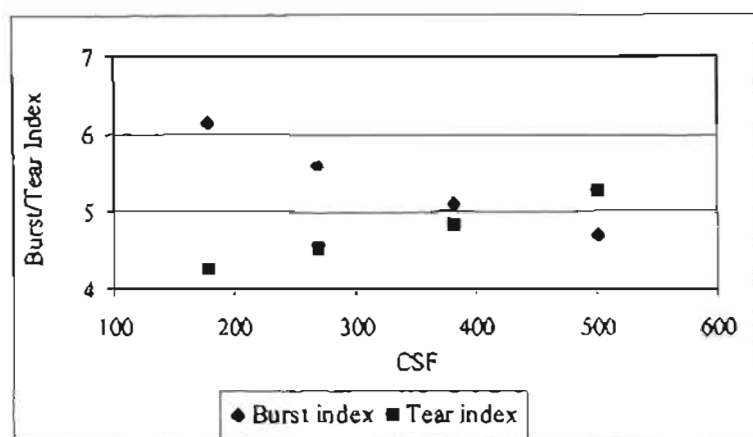


Fig. I-22: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, softwood percentage = 15 %.

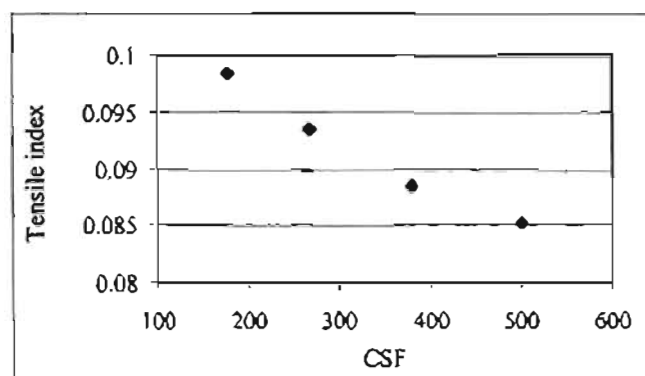


Fig. I-23: Tensile index (Nm/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, softwood percentage = 15 %.

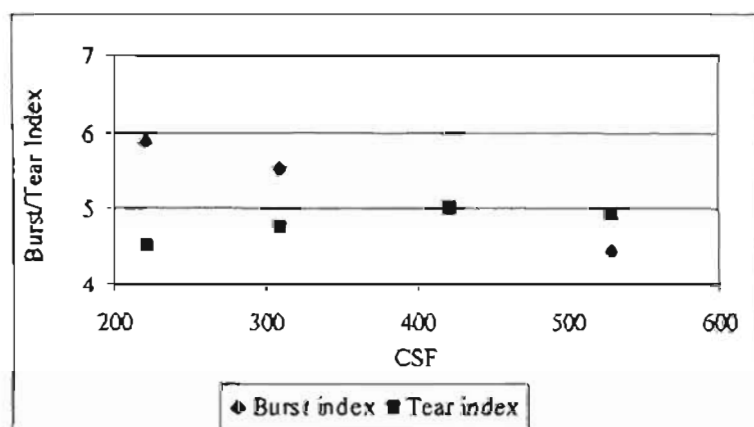


Fig. I-24: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, softwood percentage = 30 %.



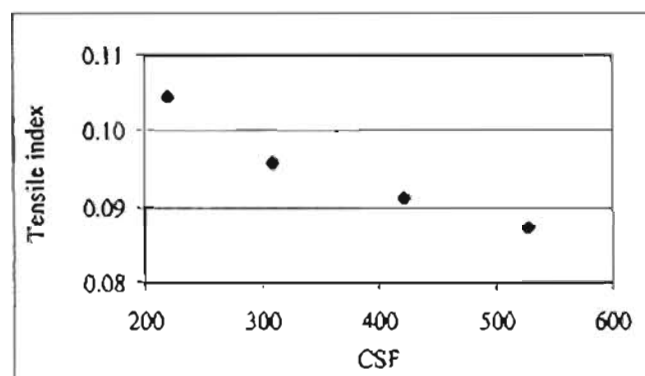


Fig. I-25: Tensile index (Nm/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, softwood percentage = 30 %.

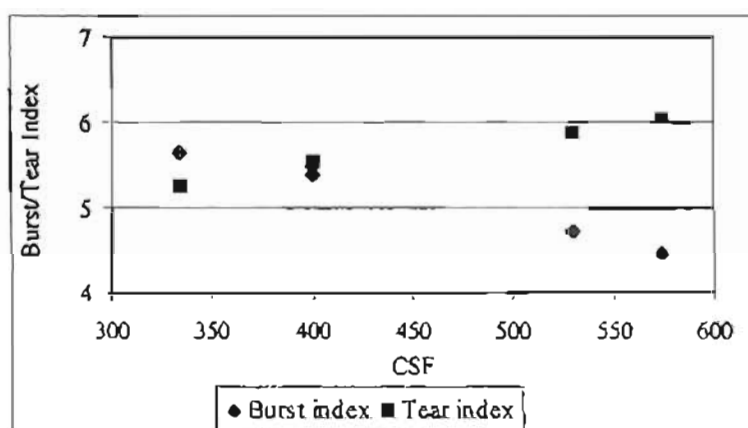


Fig. I-26: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, softwood percentage = 50 %.

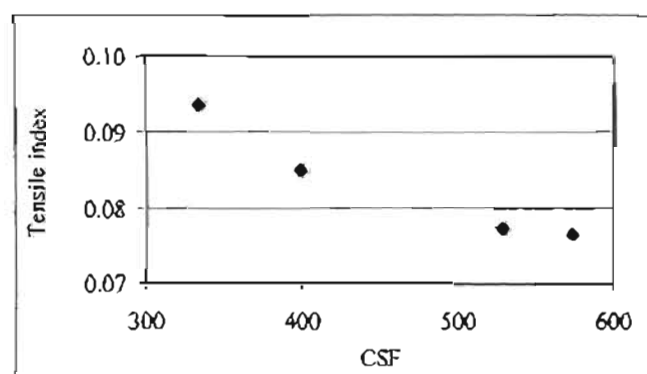


Fig. I-27: Tensile index (Nm/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, softwood percentage = 50 %.

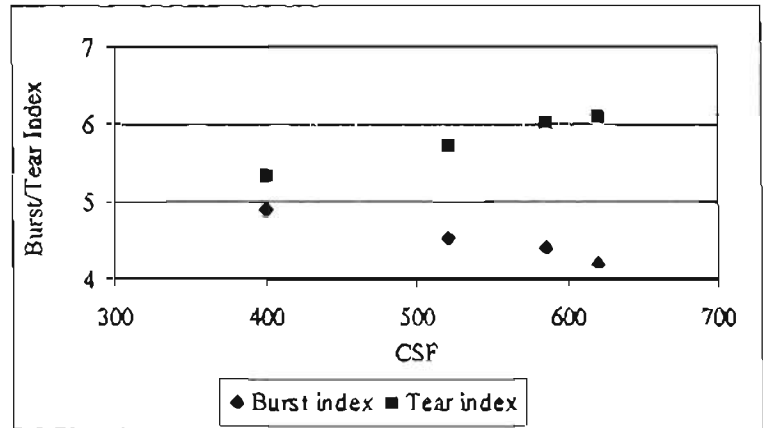


Fig. I-28: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, softwood percentage = 75 %.

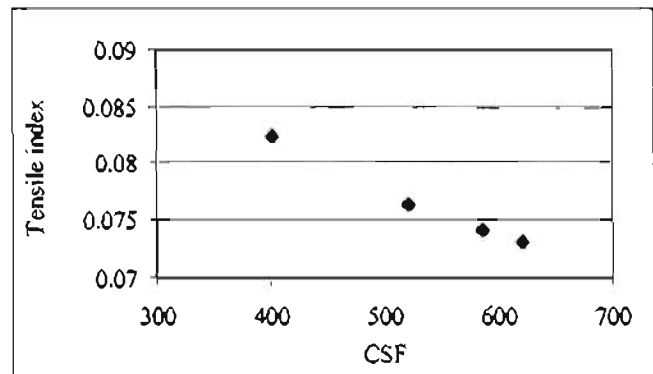


Fig. I-29: Tensile index (Nm/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood, softwood percentage = 75 %.

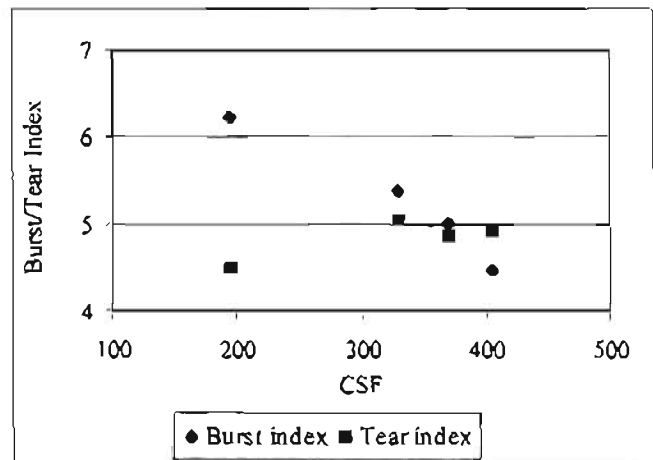


Fig. I-30: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus CSF for hardwood pulp, Hypo number = 17.1.

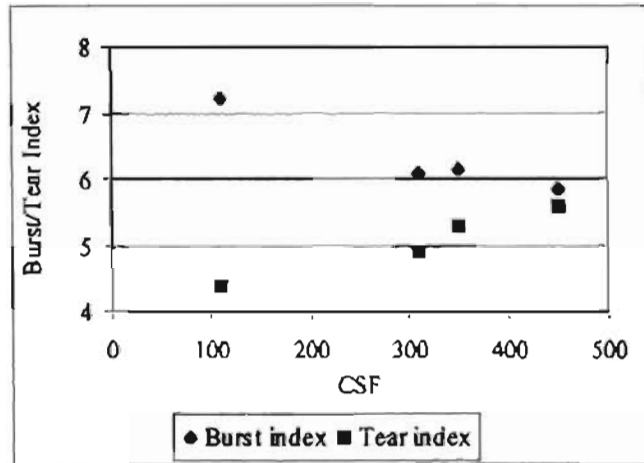


Fig. I-31: Burst index (kPa.m<sup>2</sup>/g) and Tear index (mN.m<sup>2</sup>/g) versus CSF for a simultaneously pulped mixture of hardwood and softwood using an AQ dosage of 0.5 %, Hypo number = 16.9.

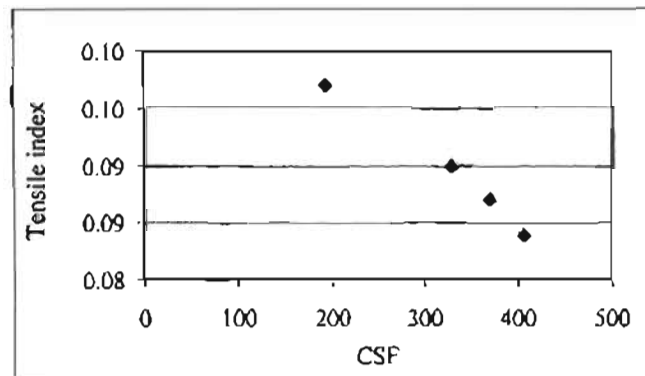


Fig. I-32: Tensile index (Nm/g) versus CSF for hardwood pulp, Hypo number = 17.1.

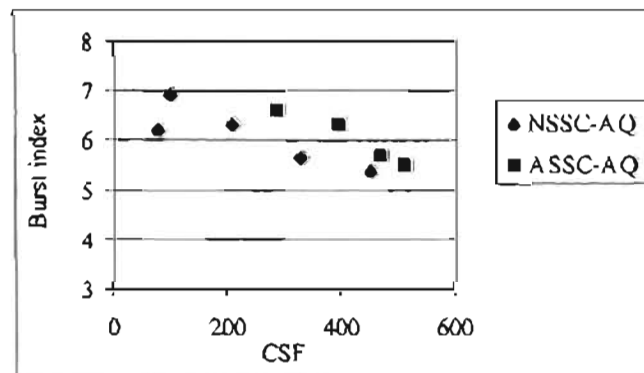


Fig. I-33: Burst index (kPa.m<sup>2</sup>/g) versus CSF for ASSC-AQ pulp (Hypo no = 17.3) and NSSC-AQ pulp (Hypo no = 18.1).

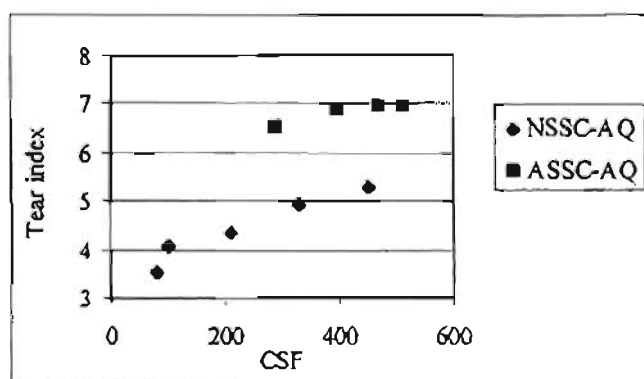


Fig. I-34: Tear index (mN.m<sup>2</sup>/g) versus CSF for ASSC-AQ pulp (Hypo no = 17.3) and NSSC-AQ pulp (Hypo no = 18.1).

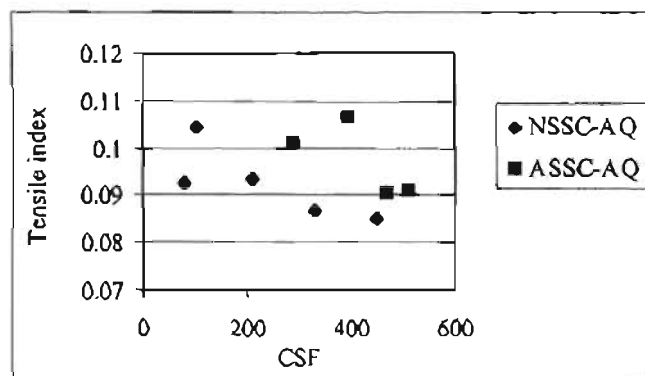


Fig. I-35: Tensile index (Nm/g) versus CSF for ASSC-AQ pulp (Hypo no = 17.3) and NSSC-AQ pulp (Hypo no = 18.1).

## Appendix J:

### Development of economic model

For the development of an economic model, linear and logarithmic regression (appendix H) was applied to the data collected during this project (appendix G).

The following equations were obtained:

$$\text{Burst index (kPa.m}^2\text{/g)} = -0.382 \times (\text{Hypo number}) + 12.6 \quad r^2 = 0.990 \quad \dots(\text{eq J-1})$$

$$\text{Tear index (mN.m}^2\text{/g)} = -0.101 \times (\text{Hypo number}) + 7.03 \quad r^2 = 0.945 \quad \dots(\text{eq J-2})$$

$$\text{Tensile index (Nm/g)} = -0.00435 \times (\text{Hypo number}) + 0.166 \quad r^2 = 0.990 \quad \dots(\text{eq J-3})$$

$$\text{Refined yield (\%)} = 87.84 \times 0.9800^{\text{TA charge}} \quad r^2 = 0.982 \quad \dots(\text{eq J-4})$$

$$\text{Hypo number} = 25.2 \times 0.9646^{\text{TA charge}} \quad r^2 = 0.964 \quad \dots(\text{eq J-5})$$

where TA charge is in % as Na<sub>2</sub>O on O.D. wood

To relate the chemical cost to the TA charge, the contribution of Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> to the TA charge had to be determined. Since the TA charge is expressed as Na<sub>2</sub>O, and since the Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> are mixed in a ratio of 10:1, the following expression is derived for a 1 kg O.D. wood charge:

$$a \times (M_{\text{Na}_2\text{O}}/M_{\text{Na}_2\text{CO}_3}) + 10a \times (M_{\text{Na}_2\text{O}}/M_{\text{Na}_2\text{SO}_3}) = (\text{TA charge}/100) \times 1000$$

where:  $a$  = contribution of Na<sub>2</sub>CO<sub>3</sub> to the TA charge (g Na<sub>2</sub>CO<sub>3</sub>)

$M_{\text{Na}_2\text{O}}$  = molecular mass of Na<sub>2</sub>O (g/mole)

$M_{\text{Na}_2\text{CO}_3}$  = molecular mass of Na<sub>2</sub>CO<sub>3</sub> (g/mole)

$M_{\text{Na}_2\text{SO}_3}$  = molecular mass of Na<sub>2</sub>SO<sub>3</sub> (g/mole)

Substituting the molecular masses of Na<sub>2</sub>O, Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> and simplifying leads to the following equation:

$$a = 1.817 \times \text{TA charge}$$

Since the ratio of Na<sub>2</sub>SO<sub>3</sub> to Na<sub>2</sub>CO<sub>3</sub> is 10:1, and remembering that  $a$  is the contribution of Na<sub>2</sub>CO<sub>3</sub> to the TA charge, the following equations are obtained:

g Na<sub>2</sub>SO<sub>3</sub> per 1kg of O.D. wood = 18.17xTA charge

g Na<sub>2</sub>CO<sub>3</sub> per 1kg of O.D. wood = 1.82xTA charge

Introducing the chemical costs of Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> as variables, the chemical costs as a function of the TA charge can be calculated as follows:

$$\text{Na}_2\text{SO}_3 \text{ (R/ton O.D. wood)} = R_{\text{Na}_2\text{SO}_3} \times (100/\text{purity}_{\text{SO}_3}) \times 18.17 \times \text{TA charge}/1000 \quad \dots(\text{eq J-6})$$

$$\text{Na}_2\text{CO}_3 \text{ (R/ton O.D. wood)} = R_{\text{Na}_2\text{CO}_3} \times (100/\text{purity}_{\text{CO}_3}) \times 1.82 \times \text{TA charge}/1000 \quad \dots(\text{eq J-7})$$

Where  $R_{\text{Na}_2\text{SO}_3}$  and  $R_{\text{Na}_2\text{CO}_3}$  are the costs of sodium sulphite and sodium carbonate in Rands per ton, and  $\text{purity}_{\text{SO}_3}$  and  $\text{purity}_{\text{CO}_3}$  are the purities Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> respectively, expressed as mass percentages. The chemical costs are regarded as confidential and are not reported in this thesis. Purity for Na<sub>2</sub>SO<sub>3</sub> is around 94% according to the chemical data sheet, whilst the purity of Na<sub>2</sub>CO<sub>3</sub> was determined as 98% by Cassant [19]. These values were used in the economic assessment calculations.

To obtain the Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> costs per ton of pulp produced, equations J-6 and J-7 were divided by the refined yield. The following equations resulted:

$$\text{Na}_2\text{SO}_3 \text{ (R/ton O.D. pulp)} = R_{\text{Na}_2\text{SO}_3} \times (100/\text{purity}_{\text{SO}_3}) \times 18.17 \times \text{TA charge}/(1000 \times \text{yield}) \quad \dots(\text{eq J-8})$$

$$\text{Na}_2\text{CO}_3 \text{ (R/ton O.D. pulp)} = R_{\text{Na}_2\text{CO}_3} \times (100/\text{purity}_{\text{CO}_3}) \times 1.82 \times \text{TA charge}/(1000 \times \text{yield}) \quad \dots(\text{eq J-9})$$

Substituting a TA charge value in equations J-1 to J-5, J-8 and J-9 will give the expected strength properties, Hypo number, refined yield and chemical costs of Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> associated with that particular TA charge.

Equations were also developed to determine the effect of the TA charge on the total raw material costs. The total raw material costs included the costs of hardwood chips, softwood chips, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and AQ. Other costs associated with pulp production, i.e. steam, electricity, etc. were not taken into account.

For the wood chips, the following equations give the costs per oven dry ton of pulp produced:

$$\text{HW} = [(\text{HW}\%/100) \times R_{\text{HW}} \times 100/(100-\text{MC})] \times (100/\text{yield}\%)$$

$$\text{SW} = [(\text{SW}\%/100) \times R_{\text{SW}} \times 100/(100-\text{MC})] \times (100/\text{yield}\%)$$

Where HW% and SW% are the hardwood and softwood percentages of the chip charge,  $R_{HW}$  and  $R_{SW}$  are the costs of hardwood and softwood chips in Rands per ton and MC is the moisture content. The moisture content values for the chips vary, and an average value of 40% was assumed for both hardwood and softwood. The wood chip prices are confidential and are not reported.

For the AQ dosage, the following equation was developed for a ton of oven dry pulp produced:

$$AQ = [(AQ\%/100) \times R_{AQ} \times (100/disp\%)(100/yield\%)$$

Where AQ% is the AQ dosage,  $R_{AQ}$  is the cost of AQ dispersion in Rands per ton and disp% is the strength of the AQ dispersion in g AQ/g dispersion. The dispersion strength was determined as 37.3 g AQ/ g dispersion. The cost of AQ dispersion is confidential and is not reported.

## Appendix K:

### Replicate SEM photographs

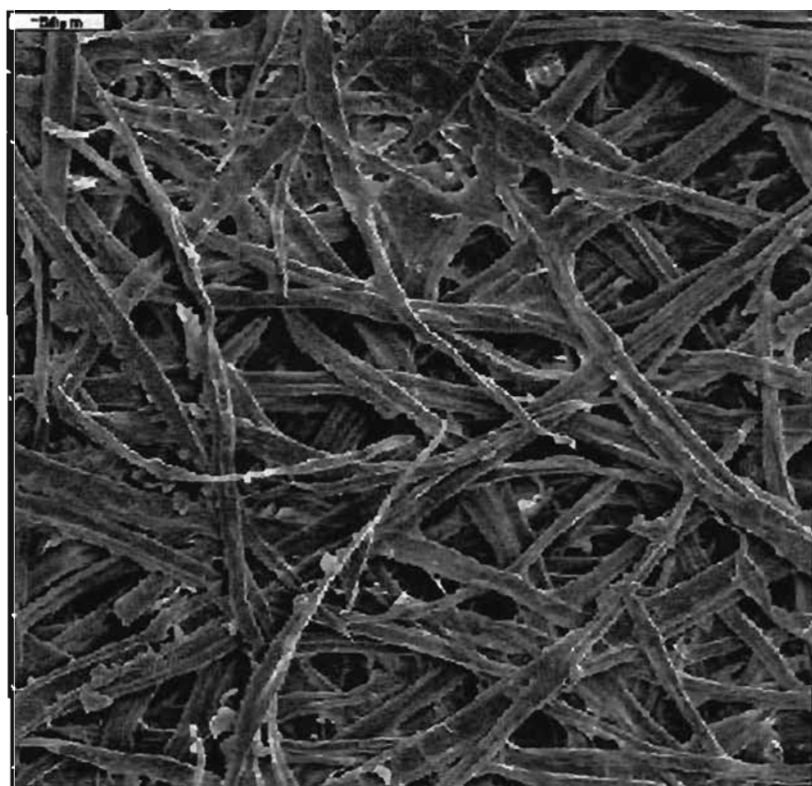


Fig. K-1: SEM image of a handsheet of hardwood pulp, Hypo number 18.1; 2 000 PF1 mill revolutions; 371 CSF (white bar = 50  $\mu\text{m}$ ).



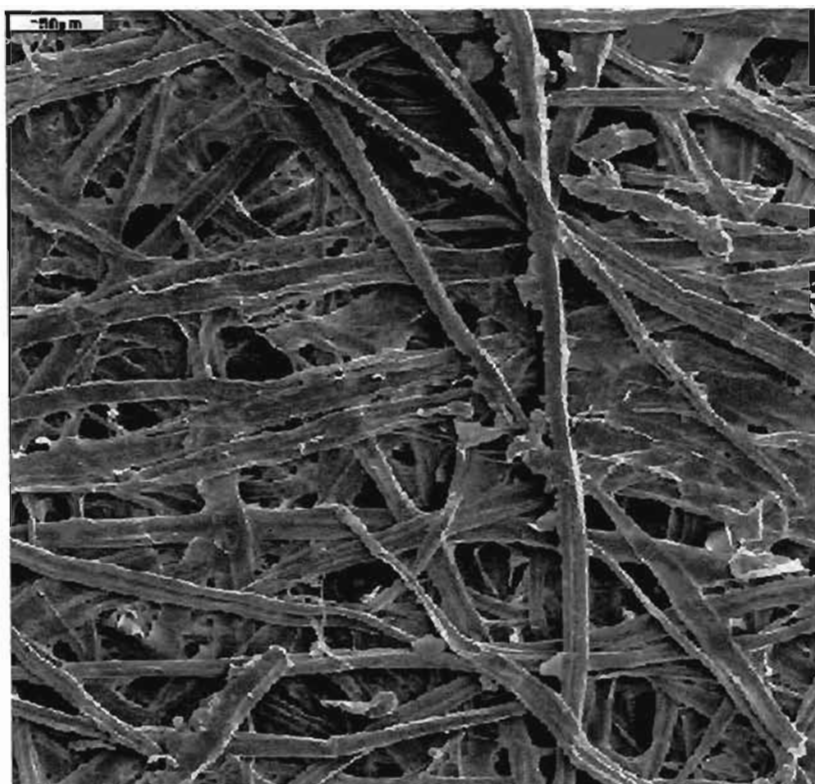


Fig. K-2: SEM image of a handsheet of hardwood pulp; Hypo number 18.1; 2 000 PFI mill revolutions; 371 CSF (white bar = 50  $\mu\text{m}$ ).

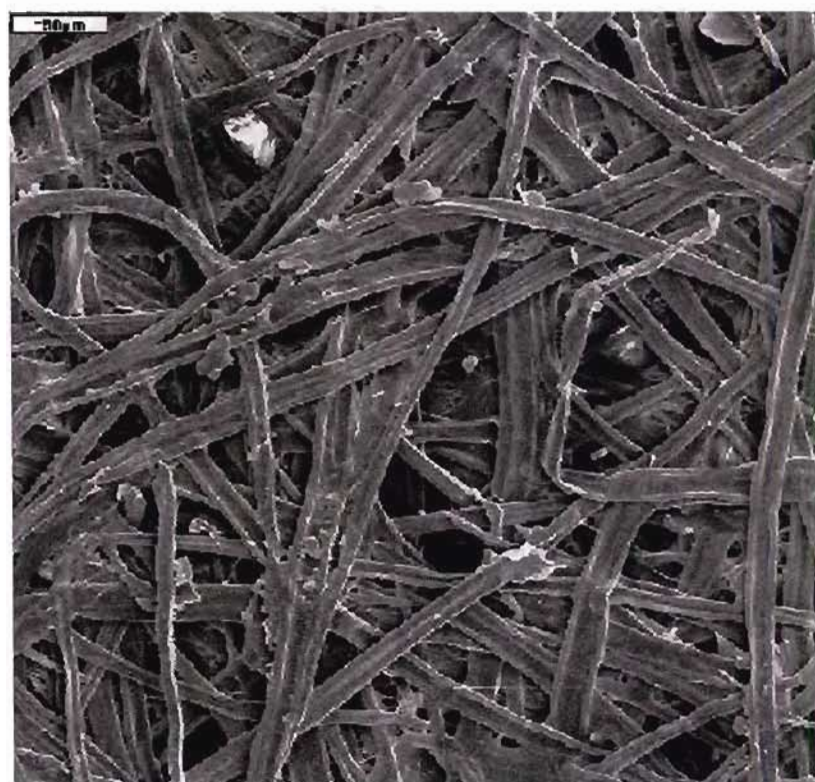


Fig. K-3: SEM image of a handsheet of hardwood pulp; Hypo number 18.1; 2 000 PFI mill revolutions; 371 CSF (white bar = 50  $\mu\text{m}$ ).

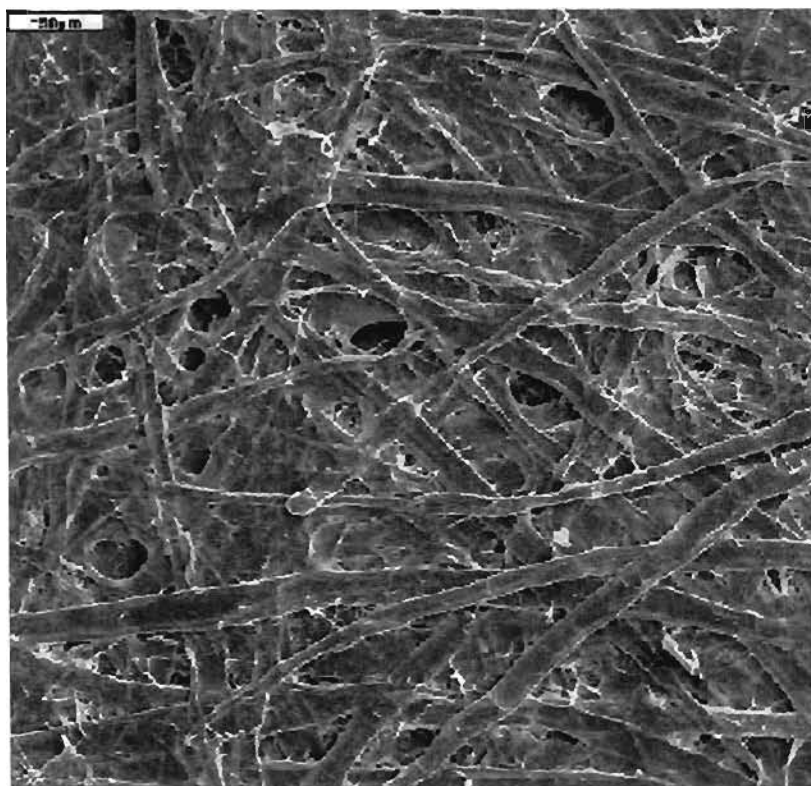


Fig. K-4: SEM image of a handsheet of hardwood pulp; Hypo number 18.1; 11 000 PFI mill revolutions; 38 CSF (white bar = 50  $\mu$ m).

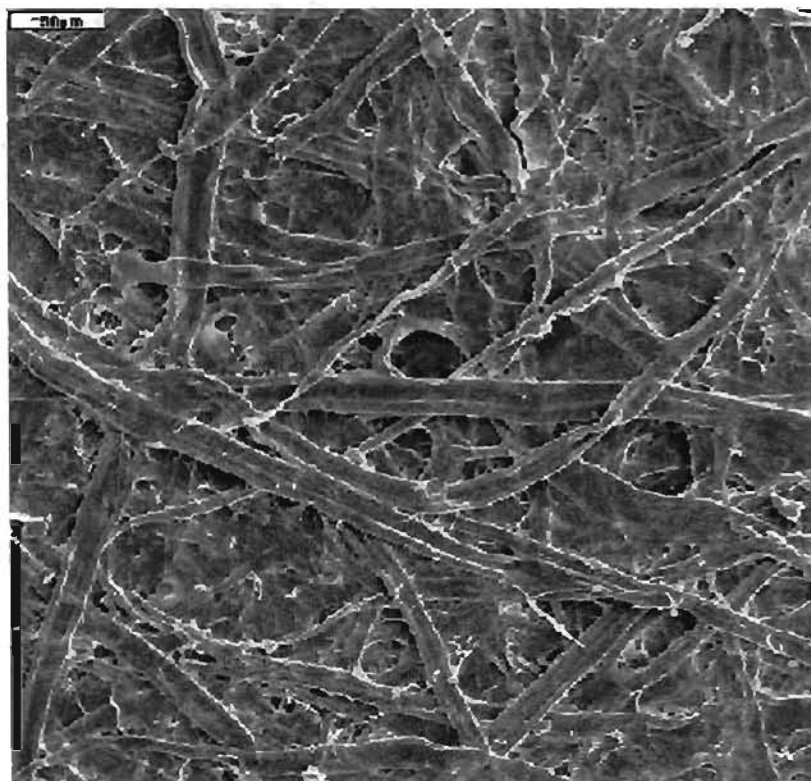


Fig. K-5: SEM image of a handsheet of hardwood pulp; Hypo number 18.1; 11 000 PFI mill revolutions; 38 CSF (white bar = 50  $\mu$ m).



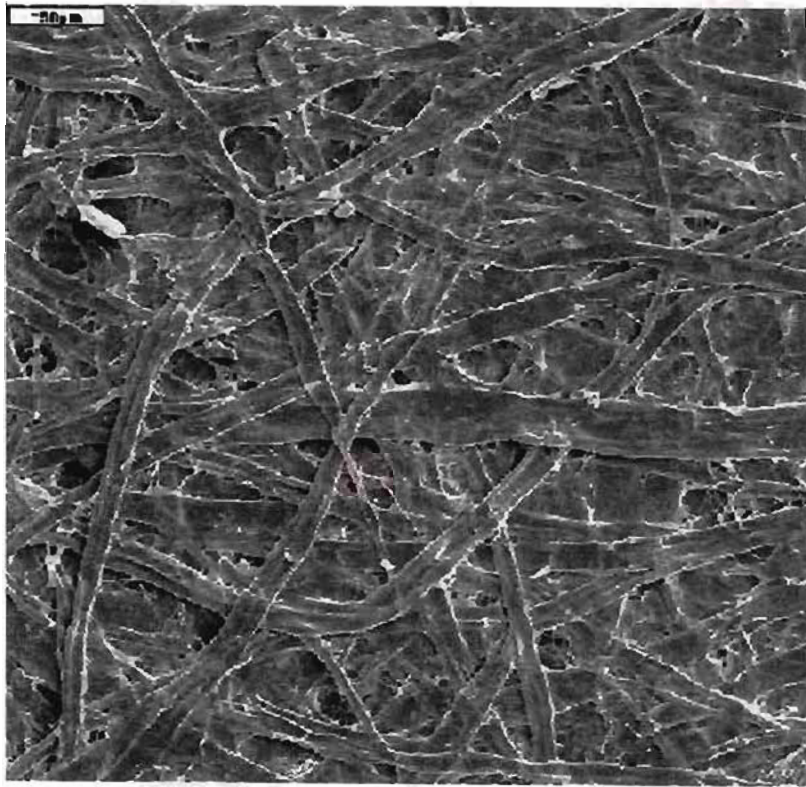


Fig. K-6: SEM image of a handsheet of hardwood pulp; Hypo number 18.1; 11 000 PFI mill revolutions; 38 CSF (white bar = 50  $\mu\text{m}$ ).



Fig. K-7: SEM image of a handsheet of softwood pulp; Hypo number 17.8; 10 000 PFI mill revolutions; 411 CSF (white bar = 50  $\mu\text{m}$ ).



Fig. K-8: SEM image of a handsheet of softwood pulp, Hypo number 17.8; 10 000 PFI mill revolutions; 411 CSF (white bar = 50  $\mu\text{m}$ ).

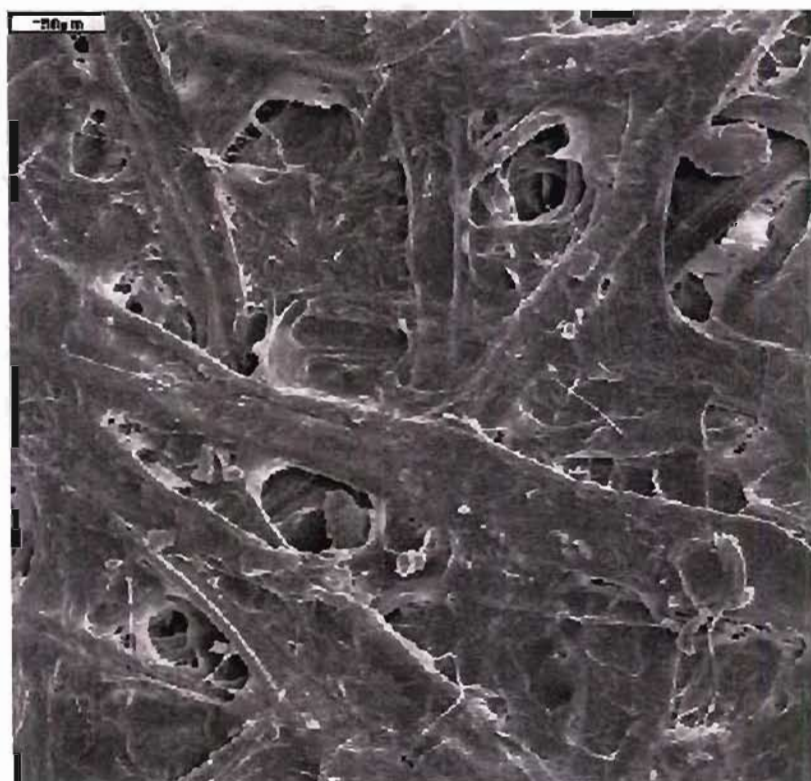


Fig. K-9: SEM image of a handsheet of softwood pulp; Hypo number 17.8; 10 000 PFI mill revolutions; 411 CSF (white bar = 50  $\mu\text{m}$ ).





Fig. K-10: SEM image of a handsheet of softwood pulp; Hypo number 17.8; 25 000 PFI mill revolutions; 40 CSF (white bar = 50  $\mu\text{m}$ ).



Fig. K-11: SEM image of a handsheet of softwood pulp; Hypo number 17.8; 25 000 PFI mill revolutions; 40 CSF (white bar = 50  $\mu\text{m}$ ).



Fig. K-12: SEM image of a handsheet of softwood pulp; Hypo number 17.8; 25 000 PFI mill revolutions; 40 CSF (white bar = 50  $\mu\text{m}$ ).

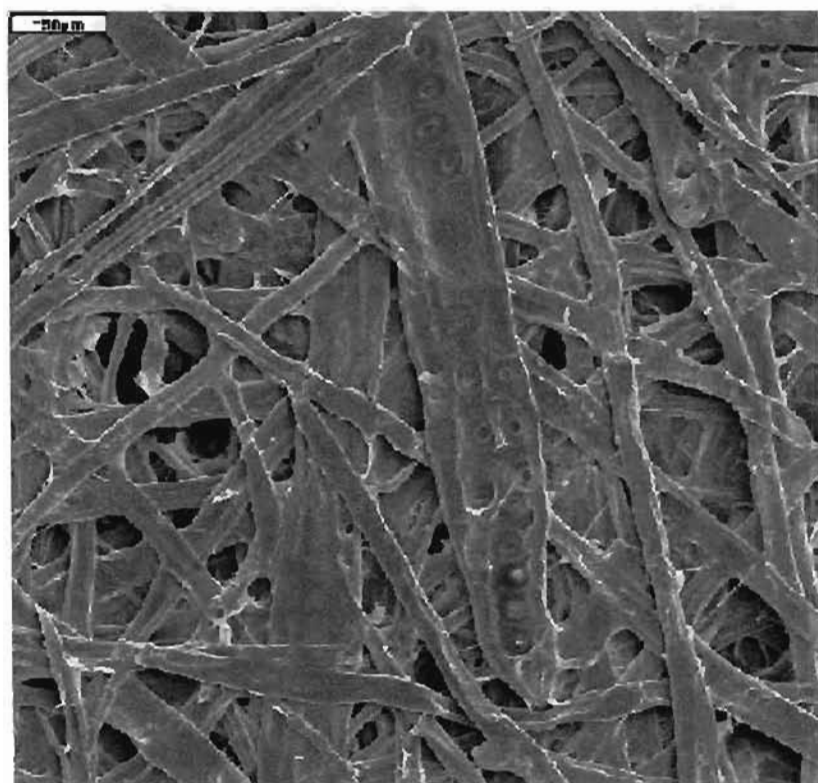


Fig. K-13: SEM image of a handsheet of a simultaneously pulped mixture of hardwood and softwood; Hypo number 18.1; 4 000 PFI mill revolutions; 451 CSF (white bar = 50  $\mu\text{m}$ ).



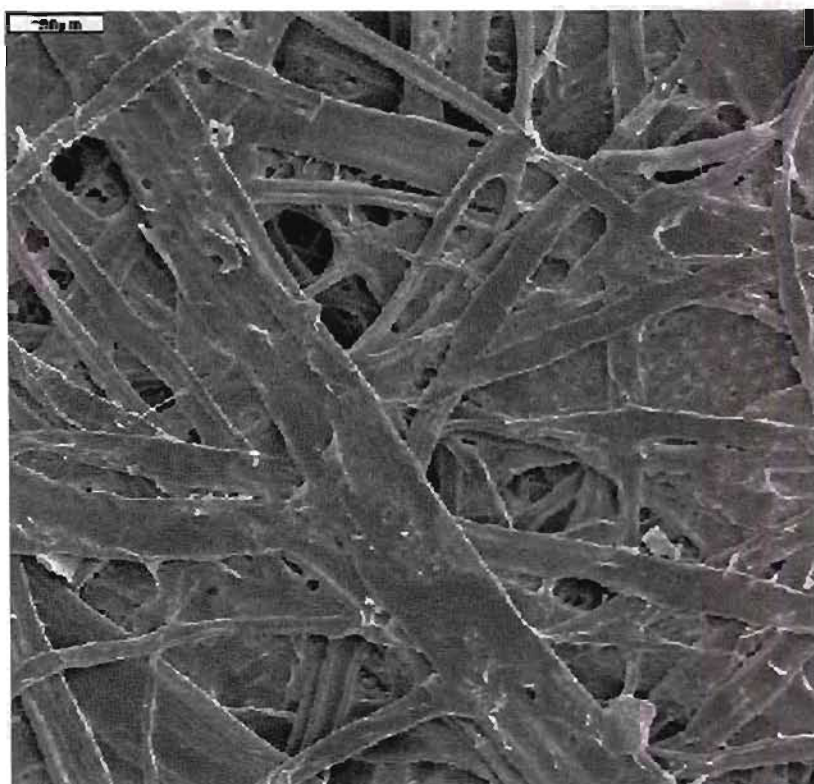


Fig. K-14: SEM image of a handsheet of a simultaneously pulped mixture of hardwood and softwood; Hypo number 18.1; 4 000 PFI mill revolutions; 451 CSF (white bar = 50  $\mu\text{m}$ ).



Fig. K-15: SEM image of a handsheet of a simultaneously pulped mixture of hardwood and softwood; Hypo number 18.1; 4 000 PFI mill revolutions; 451 CSF (white bar = 50  $\mu\text{m}$ ).

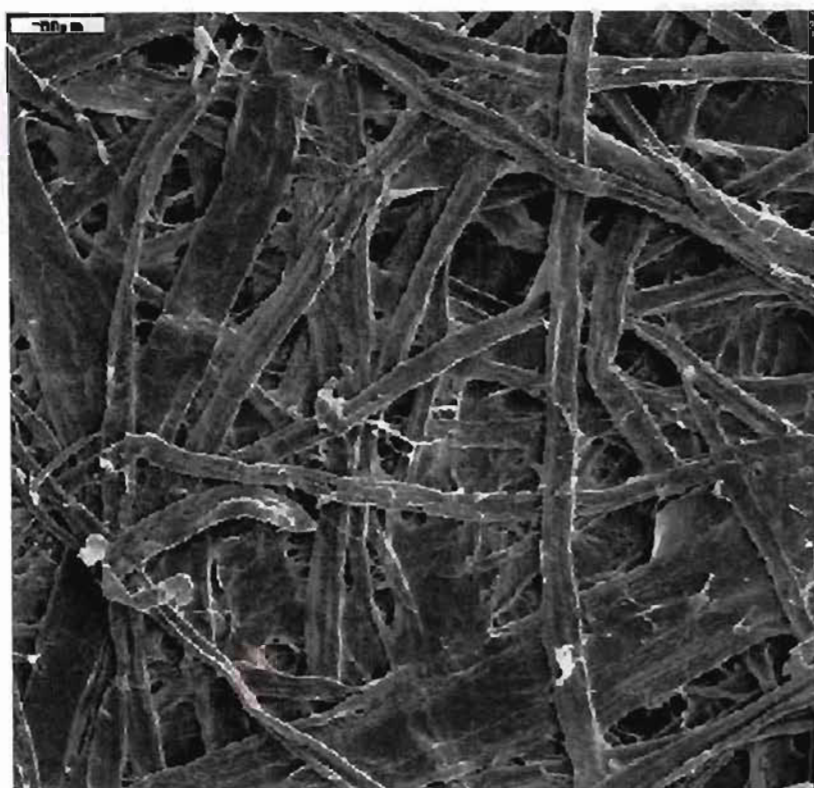


Fig. K-16: SEM image of a handsheet of a mixture of separately pulped hardwood (Hypo number 18.1) and softwood (Hypo number 17.8); 4 000 PFI mill revolutions; 380 CSF (white bar = 50  $\mu$ m).

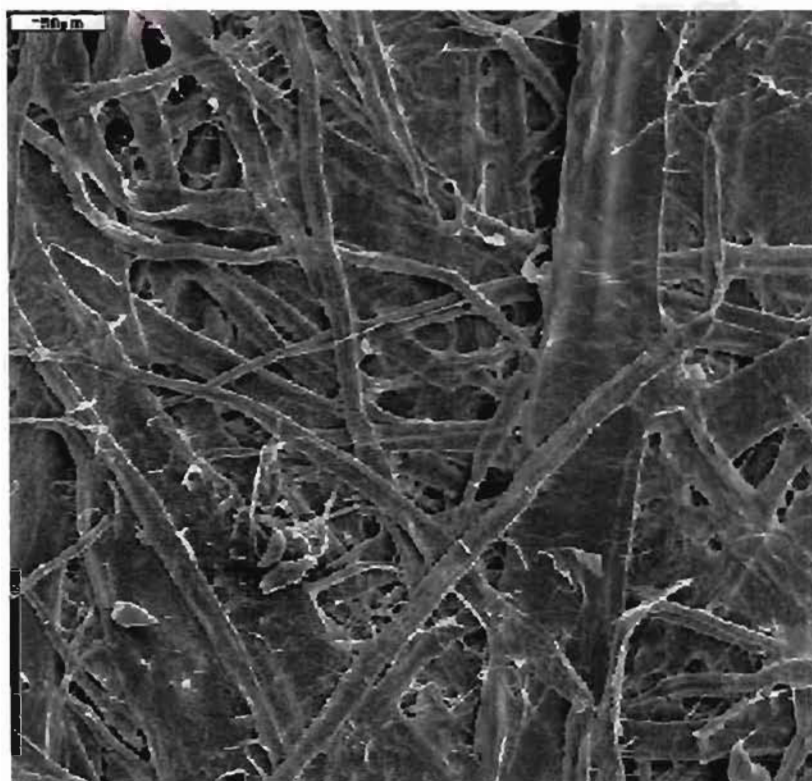


Fig. K-17: SEM image of a handsheet of a mixture of separately pulped hardwood (Hypo number 18.1) and softwood (Hypo number 17.8); 4 000 PFI mill revolutions; 380 CSF .



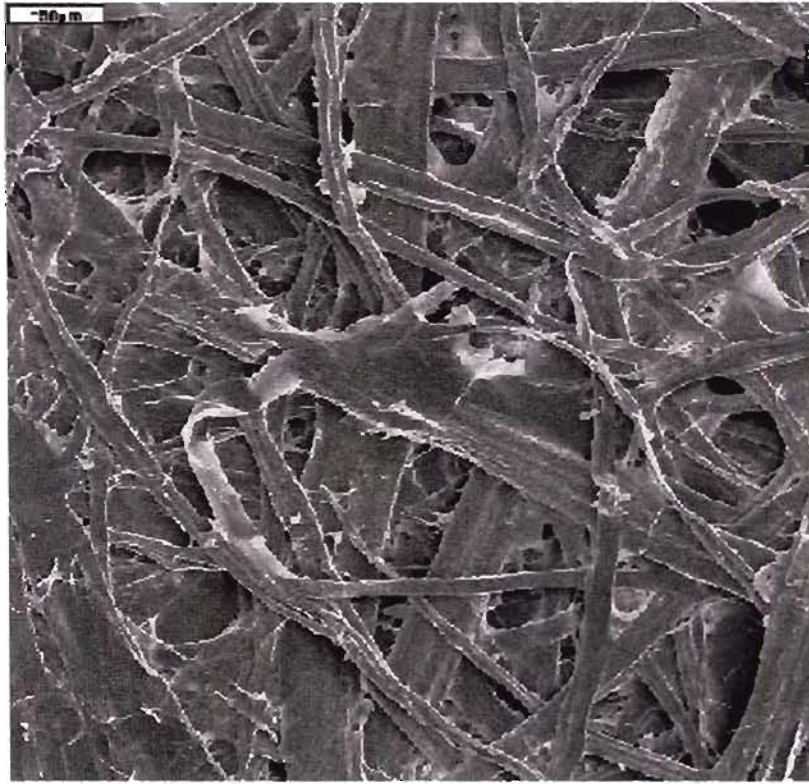


Fig. K-18: SEM image of a handsheet of a mixture of separately pulped hardwood (Hypo number 18.1) and softwood (Hypo number 17.8); 4 000 PFI mill revolutions; 380 CSF (white bar = 50  $\mu$ m).

## Appendix L:

### Calculated data

PFI revs (x 0.1)	100	210	400	1000
Grammage (g/m <sup>2</sup> )	62.00	60.44	61.12	59.97
Bursting strength (kPa)	360.8	410.6	477.1	489.6
Burst index (kPa.m <sup>2</sup> /g)	5.819	6.793	7.806	8.163
Tearing strength (mN)	378.5	344.8	321.7	249.2
Tear index (mN.m <sup>2</sup> /g)	6.105	5.705	5.263	4.155
Tensile strength (kN/m)	5.499	5.932	7.211	6.884
Tensile index (Nm/g)	0.089	0.098	0.118	0.115
Breaking length (km)	9.05	10.01	12.03	11.71
Stretch (%)	2.30	2.78	2.91	3.05
Freeness (CSF)	540	442	288	35

Table L-1: Calculated pulp strength properties for simultaneously pulped hardwood and softwood; Hypo number = 14.3.

PFI revs (x 0.1)	400	500	700	1000	1500
Grammage (g/m <sup>2</sup> )	52.95	54.56	55.81	57.63	56.07
Bursting strength (kPa)	284.1	309.0	352.4	400.3	348.7
Burst index (kPa.m <sup>2</sup> /g)	5.365	5.663	6.314	6.946	6.219
Tearing strength (mN)	279.8	267.8	242.2	235.3	197
Tear index (mN.m <sup>2</sup> /g)	5.285	4.909	4.339	4.083	3.513
Tensile strength (kN/m)	4.511	4.742	5.230	6.017	5.192
Tensile index (Nm/g)	0.0852	0.0869	0.0937	0.1044	0.0926
Breaking length (km)	8.69	8.86	9.56	10.65	9.44
Stretch (%)	2.508	2.630	2.658	2.863	3.012
Freeness (CSF)	451	330	210	103	80

Table L-2: Calculated pulp strength properties for simultaneously pulped hardwood and softwood; Hypo number = 18.1.

PFI revs (x 0.1)	400	500	600	1000
Grammage (g/m <sup>2</sup> )	59.14	59.45	59.25	55.14
Bursting strength (kPa)	289.9	304.2	317.7	338.5
Burst index (kPa.m <sup>2</sup> /g)	4.902	5.117	5.362	6.139
Tearing strength (mN)	304.0	306.7	293.8	200.3
Tear index (mN.m <sup>2</sup> /g)	5.140	5.158	4.959	3.633
Tensile strength (kN/m)	4.378	4.766	5.295	5.246
Tensile index (Nm/g)	0.0740	0.0802	0.0894	0.0952
Breaking length (km)	7.55	8.18	9.12	9.71
Stretch (%)	2.428	2.458	2.550	2.680
Freeness (CSF)	472	382	310	112

Table L-3: Calculated pulp strength properties for simultaneously pulped hardwood and softwood; Hypo number = 20.3.

PFI revs (x 0.1)	400	500	600	700	1000
Grammage (g/m <sup>2</sup> )	62.21	59.61	59.40	58.83	56.85
Bursting strength (kPa)	253.3	263.0	274.1	280.0	316.8
Burst index (kPa.m <sup>2</sup> /g)	4.072	4.412	4.614	4.759	5.572
Tearing strength (mN)	305.5	282.8	269.5	259.2	208.5
Tear index (mN.m <sup>2</sup> /g)	4.911	4.743	4.537	4.405	3.667
Tensile strength (kN/m)	4.275	4.385	4.698	4.669	5.008
Tensile index (Nm/g)	0.0687	0.0736	0.0791	0.0794	0.0881
Breaking length (km)	7.01	7.50	8.07	8.09	8.98
Stretch (%)	2.267	2.430	2.477	2.755	2.533
Freeness (CSF)	450	340	305	260	125

Table L-4: Calculated pulp strength properties for simultaneously pulped hardwood and softwood; Hypo number = 21.8.

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PFI revs (x 0.1)	400	500	600	1000
Grammage (g/m <sup>2</sup> )	58.93	52.69	54.72	59.97
Bursting strength (kPa)	215.6	212.6	239.2	296.1
Burst index (kPa.m <sup>2</sup> /g)	3.658	4.035	4.371	4.937
Tearing strength (mN)	290.7	229.3	207.0	217.3
Tear index (mN.m <sup>2</sup> /g)	4.932	4.352	3.783	3.624
Tensile strength (kN/m)	4.001	3.511	3.792	5.097
Tensile index (Nm/g)	0.0679	0.0666	0.0693	0.0850
Breaking length (km)	6.92	6.80	7.07	8.67
Stretch (%)	2.212	2.272	2.578	2.615
Freeness (CSF)	424	340	286	110

Table L-5: Calculated pulp strength properties for simultaneously pulped hardwood and softwood; Hypo number = 22.7.

PFI revs (x 0.1)	400	700	1000	1500
Grammage (g/m <sup>2</sup> )	61.07	62.63	61.64	60.60
Bursting strength (kPa)	285.8	319.4	344.0	372.7
Burst index (kPa.m <sup>2</sup> /g)	4.680	5.100	5.581	6.150
Tearing strength (mN)	321.2	302.5	278.0	258.2
Tear index (mN.m <sup>2</sup> /g)	5.259	4.830	4.510	4.260
Tensile strength (kN/m)	5.203	5.543	5.770	5.969
Tensile index (Nm/g)	0.0852	0.0885	0.0936	0.0985
Breaking length (km)	8.69	9.03	9.55	10.05
Freeness (CSF)	501	381	269	178

Table L-6: Calculated pulp strength properties for simultaneously pulped hardwood and softwood; softwood percentage = 15 %.

PFI revs (x 0.1)	400	700	1000	1500
Grammage (g/m <sup>2</sup> )	60.96	61.12	59.45	60.08
Bursting strength (kPa)	270.6	305.4	328.6	353.3
Burst index (kPa.m <sup>2</sup> /g)	4.439	4.997	5.527	5.881
Tearing strength (mN)	300.2	306.3	282.5	271.2
Tear index (mN.m <sup>2</sup> /g)	4.924	5.012	4.752	4.514
Tensile strength (kN/m)	5.321	5.576	5.706	6.273
Tensile index (Nm/g)	0.0873	0.0912	0.0960	0.1044
Breaking length (km)	8.90	9.31	9.79	10.65
Stretch (%)	2.470	3.017	3.080	3.355
Freeness (CSF)	529	422	310	221

Table L-7: Calculated pulp strength properties for simultaneously pulped hardwood and softwood; softwood percentage = 30 %.

PFI revs (x 0.1)	400	700	1000	1500
Grammage (g/m <sup>2</sup> )	61.80	61.07	60.65	59.30
Bursting strength (kPa)	276.2	288.7	326.7	334.8
Burst index (kPa.m <sup>2</sup> /g)	4.470	4.728	5.387	5.646
Tearing strength (mN)	374.2	358.8	336.3	311.7
Tear index (mN.m <sup>2</sup> /g)	6.055	5.876	5.545	5.256
Tensile strength (kN/m)	4.731	4.715	5.170	5.563
Tensile index (Nm/g)	0.0766	0.0772	0.0852	0.0938
Breaking length (km)	7.81	7.88	8.69	9.57
Stretch (%)	2.365	2.652	2.627	2.835
Freeness (CSF)	574	529	400	334

Table L-8: Calculated pulp strength properties for simultaneously pulped hardwood and softwood; softwood percentage = 50 %.

PFI revs (x 0.1)	400	700	1000	1500
Grammage (g/m <sup>2</sup> )	60.60	61.90	61.07	63.46
Bursting strength (kPa)	255.1	273.6	276.6	311.0
Burst index (kPa.m <sup>2</sup> /g)	4.210	4.420	4.529	4.901
Tearing strength (mN)	369.2	372.7	348.7	338.8
Tear index (mN.m <sup>2</sup> /g)	6.092	6.021	5.710	5.339
Tensile strength (kN/m)	4.436	4.593	4.666	5.223
Tensile index (Nm/g)	0.0732	0.0742	0.0764	0.0823
Breaking length (km)	7.47	7.57	7.79	8.40
Freeness (CSF)	621	586	521	401

Table L-9: Calculated pulp strength properties for simultaneously pulped hardwood and softwood; softwood percentage = 75 %.

PFI revs (x 0.1)	180	200	260	400
Grammage (g/m <sup>2</sup> )	61.59	65.85	64.97	63.88
Bursting strength (kPa)	275.6	329.8	349.4	398.7
Burst index (kPa.m <sup>2</sup> /g)	4.475	5.008	5.378	6.242
Tearing strength (mN)	303.2	319.5	326.8	286.7
Tear index (mN.m <sup>2</sup> /g)	4.923	4.852	5.031	4.488
Tensile strength (kN/m)	5.171	5.735	5.848	6.200
Tensile index (Nm/g)	0.0840	0.0871	0.0900	0.0971
Breaking length (km)	8.56	8.88	9.18	9.90
Freeness (CSF)	405	370	330	195

Table L-10: Calculated pulp strength properties for hardwood pulp; Hypo number = 17.1.

PFI revs (x 0.1)	400	500	600	1000
Grammage (g/m <sup>2</sup> )	68.35	65.54	66.27	64.6
Bursting strength (kPa)	399.7	402.1	403.9	466.1
Burst index (kPa.m <sup>2</sup> /g)	5.848	6.135	6.095	7.215
Tearing strength (mN)	381.0	345.3	324.8	282.7
Tear index (mN.m <sup>2</sup> /g)	5.574	5.269	4.902	4.375
Freeness (CSF)	450	350	310	110

Table L-11: Calculated pulp strength properties for simultaneously pulped hardwood and softwood with an AQ dosage of 0.5 %; Hypo number = 16.9.

PFI revs (x 0.1)	1000	1500	2500	2600
Grammage (g/m <sup>2</sup> )	60.23	56.75	59.92	54.77
Bursting strength (kPa)	348.8	332.3	353.4	320.6
Burst index (kPa.m <sup>2</sup> /g)	5.791	5.855	5.898	5.853
Tearing strength (mN)	283.0	234.0	172.5	160.2
Tear index (mN.m <sup>2</sup> /g)	4.698	4.123	2.879	2.924
Tensile strength (kN/m)	4.331	4.474	4.754	4.745
Tensile index (Nm/g)	0.0719	0.0788	0.0793	0.0866
Breaking length (km)	7.33	8.04	8.09	8.84
Stretch (%)	2.342	2.247	2.292	2.023
Freeness (CSF)	411	160	40	20

Table L-12: Calculated pulp strength properties for softwood pulp; Hypo number = 17.8.

PFI revs (x 0.1)	100	200	300	600	1000	1100
Grammage (g/m <sup>2</sup> )	56.33	61.12	54.36	59.87	59.66	55.24
Bursting strength (kPa)	189.2	252.4	260.8	402.8	480.3	406.7
Burst index (kPa.m <sup>2</sup> /g)	3.359	4.130	4.798	6.728	8.050	7.362
Tearing strength (mN)	279.2	308.2	266.2	248.8	245.0	226.5
Tear index (mN.m <sup>2</sup> /g)	4.956	5.042	4.897	4.155	4.106	4.100
Tensile strength (kN/m)	3.738	4.637	4.287	6.055	6.454	5.102
Tensile index (Nm/g)	0.0663	0.0759	0.0789	0.1011	0.1082	0.0924
Breaking length (km)	6.77	7.74	8.04	10.32	11.03	9.42
Stretch (%)	2.267	2.430	2.477	2.755	2.533	2.870
Freeness (CSF)	492	371	278	107	40	38

Table L-13: Calculated pulp strength properties for hardwood pulp; Hypo number = 18.1.

PFI revs (x 0.1)	400	600	800	1000	1500
Grammage (g/m <sup>2</sup> )	65.23	52.17	59.25	59.14	58.83
Bursting strength (kPa)	340.9	297.2	384.3	407.1	370.6
Burst index (kPa.m <sup>2</sup> /g)	5.226	5.697	6.486	6.883	6.299
Tearing strength (mN)	384.8	256.7	245.0	242.0	209.5
Tear index (mN.m <sup>2</sup> /g)	5.900	4.920	4.135	4.092	3.561
Tensile strength (kN/m)	5.537	4.663	5.518	6.260	5.381
Tensile index (Nm/g)	0.0849	0.0894	0.0931	0.1058	0.0915
Breaking length (km)	8.66	9.12	9.50	10.80	9.33
Stretch (%)	2.212	2.272	2.578	2.615	2.507
Freeness (CSF)	380	190	109	83	64

Table L-14: Calculated pulp strength properties for a mixture of separately pulped softwood (Hypo no = 17.8) and hardwood (Hypo no = 18.1) pulp.

PFI revs (x 0.1)	400	600	800	1200
Grammage (g/m <sup>2</sup> )	64.14	63.56	63.82	63.51
Bursting strength (kPa)	353.5	361.9	403	420.6
Burst index (kPa.m <sup>2</sup> /g)	5.511	5.694	6.315	6.623
Tearing strength (mN)	447.2	442.3	439.3	414.8
Tear index (mN.m <sup>2</sup> /g)	6.972	6.959	6.884	6.532
Tensile strength (kN/m)	5.840	5.743	6.811	6.422
Tensile index (Nm/g)	0.0911	0.0904	0.1067	0.1011
Breaking length (km)	9.29	9.22	10.88	10.31
Stretch (%)	2.555	2.668	3.098	3.095
Freeness (CSF)	511	470	397	288

Table L-15: Calculated pulp strength properties for ASSC-AQ pulp from a mixture of hardwood and softwood; Hypo number = 17.3.