

**Impact of hexenuronic acid on the physical and
chemical properties of *Eucalyptus* clonal pulps during
ECF bleaching**

by

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ABSTRACT

The work described in this dissertation was aimed at obtaining an understanding of the impact of hexenuronic acid (HexA), and its removal during acid hydrolysis (A-stage), on the physical and chemical properties of Kraft pulps produced from commercially important South African *Eucalyptus* hybrid clones which were bleached to 90% ISO brightness using an O/OD₀ED₁ sequence. The clones studied included *E. grandis* x *E. urophylla* (GU) and *E. grandis* x *E. camaldulensis* (GC) which were each sampled from two sites representing extreme differences in site quality. Using the GU clone from the good site, the first phase of the project involved optimising the conditions of the A-stage to ensure maximum removal of HexA but with minimal impact on pulp quality. The optimum conditions found was a temperature of 95°C, a reaction time of 180 minutes and pH 3.5. The second phase of the project involved applying the optimum conditions to the remaining GU clones from the poor site and the GC clones from the good and poor sites in order to determine their response to the A-stage.

The results from the study showed that HexA concentration ranged between 60-70 µmol/g in the unbleached pulps of both clones, and were found to be unreactive during oxygen delignification. Acid hydrolysis however, proved to be effective in the removal of HexA, with the concentration dropping by approximately 98% during acid hydrolysis using a temperature of 125°C, reaction 180 minutes and pH 3.5. Due to the removal of HexA, the Kappa number was reduced by up to 6 units. By correlating the reduction in HexA with the reduction in Kappa number during acid hydrolysis, 10.7 µmol HexA was found to be equivalent to 1 Kappa number unit. Glucose, xylose and lignin remained fairly constant during acid hydrolysis, whilst pulp viscosity was severely affected by the A-stage. The drop in viscosity was found to be more pronounced at temperatures higher than 110°C. One of the major advantages of including the A-stage in the bleaching sequence was the significant savings in bleaching chemicals required to reach 90% ISO brightness. In most instances chlorine dioxide savings greater than 50% were achieved for pulps that were acid hydrolysed prior to bleaching compared to reference pulps that did not undergo acid hydrolysis prior to bleaching. In addition to this, it was found that the pulp yield across pulping and bleaching was unaffected by inclusion of the A-stage in the bleaching sequence, thus offering a distinct advantage for the production of bleached chemical pulps. Most of the physical properties of the pulps were also unaffected by

acid hydrolysis carried out using the optimum conditions. The exception was tensile strength, which showed reduced values for the acid hydrolysed pulps; and brightness reversion, for which no clear-cut relationship could be found with the removal of HexA. Species, site and xylose content were found to influence the amount of HexA formed during Kraft pulping – the GU clones generally contained higher amounts of HexA compared to the GC clones from similar sites, whilst poor sites and higher xylose content (in wood) resulted in higher amounts of HexA in the unbleached pulps.

PREFACE

The experimental work described in this dissertation was carried out at the Forestry and Forest Products (FFP) Research Centre of the Natural Resources and the Environment (NRE) division in the Council for Scientific and Industrial Research (CSIR). The work was carried out during the period January 2004 to August 2006, under the supervision of Dr. Valerie Grzeskowiak (FFP), Mr. Iain Kerr (University of KwaZulu-Natal) and Prof. Philip Turner (University of Napier).

I, the undersigned, hereby declare that, unless specifically indicated to the contrary in the text, the work contained in this dissertation is my own work, and has not been submitted in part, or in whole, to any other tertiary institution.

.....
Jerome E. Andrew

.....
Date

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LIST OF ABBREVIATIONS

A or AH	Acid hydrolysis
AA	Active Alkali
AEC	Anion exchange chromatography
ANOVA	Analysis of variance
CSF	Canadian standard freeness
CV	Co-efficient of variation
DBH	Diameter at breast height
DP	Degree of polymerisation
ECF	Elemental chlorine-free
FTIR	Fourier transform infra-red (spectroscopy)
GS	Good site
HexA	Hexenuronic acid
HPAEC-PAD	High performance anion exchange chromatography – pulsed amperometric detection
IPST	Institute of Paper Science and Technology
ISO	International Organisation for Standardisation
K_γ	Kappa factor
KN	Kappa number
KTH	Royal Institute of Technology
LCC	Lignin-carbohydrate complexes
L:W	Liquor-to-wood ratio
MC	Moisture content
NMR	Nuclear magnetic resonance (spectroscopy)
OB	Oxygen bleached
OD	Oxygen delignified/delignification
PS	Poor site
REJ	Rejects
ROD	Rate of delignification
SD	Standard deviation
SI	Site index
SPY	Screen pulp yield
TAPPI	Technical Association of the Pulp and Paper Industry
TCF	Total chlorine-free
TPY	Total pulp yield

UB	Unbleached
UVRR	Ultra-violet resonance Raman (spectroscopy)
UV-VIS	Ultra-violet visible (spectroscopy)

GLOSSARY

Active alkali	Caustic (NaOH) and sodium sulphide (Na ₂ S) expressed as Na ₂ O in alkaline pulping liquor.
Air dried	Weight of dry wood/pulp/paper in equilibrium with the atmosphere.
Beating/refining	Mechanical treatment of pulp fibres in water to increase surface area, flexibility, and promote bonding when dried.
Black liquor	Liquor that exits the digester with the cooked chips at the end of the Kraft process.
Bleaching	Chemical process used to whiten and purify the pulp by removal of residual lignin and chromophores.
Bleaching sequence	Series of subsequent bleaching stages, typically described by abbreviation. In this project, the bleaching sequence, O/OAD ₀ ED ₁ was used.
Bleach plant	Section of the pulp mill where pulp is bleached.
Brightness	Reflectance or brilliance of paper when measured under a specially calibrated blue light (457nm). Expressed as a percentage. Not necessarily related to color or whiteness.
Bursting strength	Resistance of paper to rupture, as measured by the hydrostatic pressure required to burst it. Burst index is the ratio of the bursting strength (expressed in kPa) and the substance of paper (expressed in g/m ²), determined by standard methods of test.
Clone	Population of trees produced through vegetative reproduction from one individual tree.
Consistency	Percent of oven dry solids, by weight, in pulp or stock solution.
Cooking liquor	Liquor made up of selected chemicals and used for cooking/pulping wood - e.g. cooking liquor in Kraft process consists of NaOH and Na ₂ S.
Cooking/pulping	Reaction of fibrous raw material with chemicals under pressure and temperature to soften and/or remove lignin to separate fibers.
Degree of polymerisation	As applied to cellulose - refers to the average number

	of glucose units in each cellulose molecule of a pulp sample. Usually determined by the viscosity test.
Delignification	Removal of lignin, the material that binds wood fibers together, during the pulping or bleaching process.
Dewater	Removal of water from pulp or from wet web during formation of paper sheet.
Digester	Reaction vessel in which wood chips or other plant materials are cooked with chemicals to separate the fibres by dissolving lignin.
Elemental chlorine free	Pulps bleached using chlorine dioxide rather than elemental chlorine gas as a bleaching agent. This virtually eliminates the discharge of detectable dioxins in the effluent of pulp manufacturing facilities.
Freeness	Defines how quickly or slowly water is drained from the pulp. Freeness is reported in ml CSF and is a measure of the degree of refining or beating.
Hardwoods	Wood from trees of angiosperm class, usually with broad leaves.
Kappa number	Used to define the degree of delignification by giving a measure of the lignin content of pulp.
Kraft pulping	Chemical process in which wood chips are cooked in digesters at high temperature and pressure using aqueous solutions of NaOH and Na ₂ S.
Opacity	Property of paper which minimizes the "show-through" of printing from the backside or the next sheet. The higher the opacity the less likely that the printing on one side will be visible from the other side.
Porosity	Property of paper that allows the permeation of air, an important factor in ink penetration.
Stiffness	Ability of paper or paperboard to resist an applied bending force and to support its own weight while being handled.
Stretch	Maximum tensile strain developed in paper before rupture. The stretch or elongation is expressed as a percentage.
Tear strength	Measure of how likely paper will continue to tear once started. Tear index is the ratio of the tearing strength (expressed in N) and the substance of paper

	(expressed in g/m^2), determined by standard methods of test.
Tensile strength	Measure of how likely paper is to break when pulled at opposite ends. Tensile index is the ratio of the tensile strength (expressed in N/m) and the substance of paper (expressed in g/m^2), determined by standard methods of test.
Total chlorine free	Pulp bleached with a sequence that includes no chlorine or chlorine derivatives.
Yield	Ratio of product output and raw material input, expressed as a percentage.
Zero-span tensile strength	Measure of the tensile strength at the moment of tensile failure of fibres randomly orientated in a sheet. It is used to determine the maximum strength of pulp fibres when beaten/refined.

CHAPTER ONE

INTRODUCTION AND AIMS

Eucalyptus Kraft pulps began to appear on the world markets in the mid 1960s and in less than a decade evolved to become important raw materials for a wide range of printing and writing papers, specialty papers, and tissue papers (Cotterill & Macrae, 1997). Due to the rapid growth in consumption of these papers, increasing demands have been placed on the development of technologies for pulping and bleaching of hardwood eucalypts. The focus of this development has been improved quality, especially in terms of higher brightness levels, but also papermaking properties, decreased effluent emissions and cost-efficient pulp production. In terms of the bleaching process, fundamental research has in the past largely focussed on lignin chemistry. However more recently, intensive investigations have been directed toward carbohydrate chemistry, where various researchers have shown that hemicelluloses influence a variety of important properties throughout the pulping, bleaching, and papermaking process.

Hemicellulose, a complex component of lignocellulose, is a heteropolysaccharide consisting of pentose, hexose and glucuronic acids (Tanczos *et al.*, 2003). The most abundant hemicellulose in hardwoods is O-acetyl-4-O-methylglucuronoxylan, whereas arabino-4-O-methylglucuronoxylan forms a major part of the softwood hemicelluloses (Sjöström, 1981; Teleman *et al.*, 1996b). During Kraft pulping, extensive modification of the hemicelluloses occur as a result of the dissolution of low molecular weight chains, end-initiated depolymerisation reactions (primary peeling), and alkaline hydrolysis of glycosidic bonds, leading to secondary peeling and a decrease in the degree of polymerisation (Sjöström, 1993). In addition, part of the 4-O-methylglucuronic acid side groups, which also undergo alkaline dissolution along with the degradation/dissolution of the xylan chain, are converted to hexenuronic acid (HexA) (Teleman *et al.*, 1995; Buchert *et al.*, 1995; Tanczos *et al.*, 2003). The mechanism of these alkali catalysed reactions was first proposed by Clayton (1963), with Johansson and Samuelson (1977) providing the first evidence to directly support this speculation. Nuclear magnetic resonance (NMR) spectroscopy, which is a well-established method for the characterisation of hexenuronoxylan (which is xylan containing HexA), has played a key role in the elucidation of its pulping and

bleaching chemistry, and together with mass spectroscopy finally confirmed the occurrence of HexA groups during Kraft pulping (Teleman *et al.*, 1995).

The presence of HexA in Kraft pulps has become an active area of research and has been shown to have important implications for the manufacture of bleached chemical pulps. The amount of HexA produced in the pulp has been shown to be influenced by pulping conditions such as temperature, pulping time, ionic charge, hydroxyl ion concentration, sulphidity and liquor-to-wood ratio (Buchert *et al.*, 1995; Gustavsson *et al.*, 1999; Gustavsson & Al-Dajani, 2000; Jiang *et al.*, 2000; Daniel *et al.*, 2003; Pedroso & Carvalho, 2003; Daniel *et al.*, 2004; Simão *et al.*, 2005a, b).

Hexenuronic acid has been found to be unreactive in alkaline oxygen and peroxide bleaching stages (Vuorinen *et al.*, 1996), but due to its unsaturated nature, reacts readily with chlorine dioxide, chlorine, ozone and peracids (Vuorinen *et al.*, 1999). As a consequence, this leads to higher bleaching chemical consumption, increased production costs, and increased effluent emissions (Petit-Breuilh *et al.*, 2004).

Hexenuronic acid is also known to consume permanganate in the Kappa number test (Li & Gellerstedt, 1997), thus distorting the measurement of residual lignin in pulp (Tanczos *et al.*, 2003). Since Kappa measurements are widely used to evaluate the delignification efficiency in pulping and bleaching processes, the presence of these unsaturated constituents affect the results of this analysis and gives erroneously higher measurements for the amounts of residual lignin in the pulp.

Brightness reversion of Kraft pulps have been attributed to the presence of residual lignin, chlorinated extractives and oxidised carbohydrate units. Carboxylic acids and their counter ions have, in the past, also been reported to affect brightness reversion (Sjöström & Eriksson, 1968; Scallan, 1983). More recently, brightness reversion has been shown to be strongly influenced by the presence of HexA (Buchert *et al.*, 1996; Vuorinen *et al.*, 1999).

The intensive chelating ability of HexA results in a strong affinity of Kraft pulps for transition metals ions (Vuorinen *et al.*, 1996), which are known to catalyse the degradation of hydrogen peroxide. As a result, extreme demands are placed on the metal profile adjustment prior to peroxide bleaching. The reaction of HexA with other electrophilic bleaching chemicals such as ozone leads to the formation of oxalic acid (Vuorinen *et al.*, 1999; Elsander *et al.*, 2000), and thus intensifies scaling problems in

bleaching equipment.

Acid hydrolysis studies (Vuorinen *et al.*, 1996; Bergnor-Gidnert *et al.*, 1998; Ratnieks *et al.*, 2001; Furtado *et al.*, 2001) have identified reaction conditions under which HexA can be removed from Kraft pulps without significantly impacting on the pulps physical and chemical properties. Despite this significant body of work done abroad, very little has been done to examine the existence of HexA in pulps produced from South African grown tree species, and their impact on local bleaching operations. It is common practice in South Africa to adopt and run, usually at non-optimal levels, pulp and paper technologies that were developed for northern hemisphere tree species. However, because of the considerable variability of hardwood raw material properties, both morphological and chemical, and their varying response to the heterogeneous nature of wood pulping and the subsequent bleaching process, it is important to understand the response of South African resources to these technologies to ensure superior performance under optimum processing conditions.

The primary focus of this study was therefore to develop an understanding of the impact of HexA, and its removal during acid hydrolysis, on the physical and chemical properties of Kraft pulps, produced from two commercially important South African *Eucalyptus* hybrid clones, and which were bleached to 90% ISO brightness using an elemental chlorine-free bleaching sequence (O/OD₂ED₁). To this end, the aims of the study were to:

- (1) Identify and verify a reliable and cost effective method for the measurement of HexA in *Eucalyptus* pulps;
- (2) Using this method, monitor the level of HexA in pulps through the various stages of the pulping and bleaching process;
- (3) Identify the optimum conditions for the acid hydrolysis stage that results in maximum removal of HexA prior to bleaching but with minimum impact on final pulp quality;
- (4) Determine the impact of acid hydrolysis on pulp bleachability, and on the chemical and physical properties of the bleached pulp;
- (5) Correlate HexA removal to Kappa number reduction.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

The use of wood as papermaking fibres dates back to 1840 AD (Bamber, 1985) and is currently the principal source of cellulosic fibre for pulp and paper manufacture. They provide as much as 93% of the world's virgin fibre requirements, whilst non-wood sources such as bagasse, cereal straws and bamboo provide the remainder (Smook, 1992). *Eucalyptus* species in particular, are grown extensively in many countries and occupy about 80% of the total area covered by hardwoods in South Africa (Malan, 1991). As a result it has become the most important local source of hardwoods in this country (Malan & Gerischer, 1987), and by far, the single most important eucalypt species from a commercial standpoint is *Eucalyptus grandis* (Poynton, 1979). Planted extensively throughout the humid, subtropical and warmer temperate parts of the summer rainfall area, this species is managed on a medium to short term rotation for the production of sawlogs, telephone and transmission poles, mining timber, building and fencing materials. Rapid advances in pulping technologies have also led to the international usage of *Eucalyptus* for the manufacture of paper, and consequently, this hardwood has become an important source of papermaking fibres. This short fibred pulp is ideal for writing and tissue paper because of the high (bleachable) pulp yield, excellent bulk, softness, flexibility, and low bleaching and refining energy requirements (Sidaway, 1988).

The use of clones and hybrid species of trees has become increasingly widespread in South Africa, due to the ever-increasing demands placed on the forestry industry to produce more timber and to improve the quality of the timber they produce. Research has shown that the productivity of forestlands can be greatly improved through sound silvicultural practices or by the use of clones from suitable genotypes, or a combination of the two (Malan, 1993). Hybridisation, which is a crossing of diverse species, has also been shown to be a promising technique in tree breeding to increase yields and adaptability, and to change or improve product quality. Hybrids of *Eucalyptus grandis* and *Eucalyptus camaldulensis* or *Eucalyptus urophylla*, which combines the fast growth rates of the former with the high resistance to drought and

cold of the latter two, are examples of this (Malan, 1993). *Eucalyptus grandis* x *Eucalyptus urophylla* (GU) and *Eucalyptus grandis* x *Eucalyptus camaldulensis* (GC) clones were chosen for this study because they are currently two commercially important hardwood species used by the South African pulp and paper industry.

2.2 WOOD CHEMICAL COMPOSITION

Wood is a carbohydrate composed principally of carbon, hydrogen, and oxygen. As far as the chemical components of wood are concerned, a distinction is made between the main macromolecular cell wall components - cellulose, hemicellulose and lignin, which are present in all woods, and the minor low molecular weight components, extractives and mineral substances, which are generally more related to wood species and varies in the type and amount present. The proportions and chemical composition of lignin and hemicellulose differ in softwoods and hardwoods, while cellulose is a uniform component of all woods.

2.2.1 Cellulose

Cellulose is the main constituent of wood, averaging between 40-50% of the dry wood substance (Haun, 1970). As a linear homopolysaccharide, cellulose is composed of β -D-glucopyranose units, which are linked together by 1:4 glycosidic bonds (Sjöström, 1981). The linear arrangement of the β -linked glucose units in cellulose presents a uniform distribution of hydroxyl groups on the outside of the chain. When two or more cellulose chains make contact, the hydroxyl groups are ideally situated to 'zip' the chains together by forming hydrogen bonds. Zipping many cellulose chains together in this way gives a highly insoluble, rigid and fibrous polymer that is ideal cell wall material (Solomons, 1992). Although there are hydroxyl groups at both ends of the cellulose chain, these groups exhibit different behaviours. The carbon-1 hydroxyl group is an aldehyde hydrate group derived from the ring formation by the intramolecular hemiacetal linkage and has reducing properties, whilst the hydroxyl group at the carbon-4 end of the cellulose chain is an alcoholic hydroxyl with non-reducing properties (Fengel & Wegener, 1984; Kadla & Gilbert, 2000; Smook, 2002).

2.2.2 Hemicellulose

The cellulose and lignin of plant cell walls are closely inter-penetrated by a mixture of polysaccharides called hemicelluloses (McGinnis & Shafizadeh, 1980). Hemicelluloses were originally believed to be intermediates in the biosynthesis of cellulose (Sjöström, 1981). Today it is known, however, that hemicelluloses belong to a group of heterogeneous polysaccharides that are formed through biosynthetic routes different from cellulose. Structurally, the hemicelluloses differ from cellulose in that they are branched and have much lower molecular weights (Sjöström, 1981). Unlike cellulose, which is a homopolysaccharide, hemicelluloses are heteropolysaccharides. These polymers yield, on hydrolysis, the hexose sugars D-glucose, D-mannose, D-galactose and the pentose sugars D-xylose and L-arabinose (Browning, 1970).

A summary of the chemical composition of hardwoods and softwoods is given in **Table 2.1**. In terms of hemicellulose, hardwoods appear to generally contain more hemicellulose than softwoods, with both hardwoods and softwoods containing essentially the same hemicelluloses, but with the type varying much more in softwood than in hardwood species. The hemicelluloses in hardwoods consists mainly of the pentose sugar xylose, while in softwoods it consists mainly of the hexose sugar, mannose. Both hardwoods and softwoods contain small amounts of miscellaneous hemicelluloses consisting largely of the hexose sugar, galactose.

The principal hemicellulose in hardwoods is glucuronoxylan, which is more specifically termed O-acetyl-4-O-methylglucurono- β -xylan. The backbone of this structure consists of β -D-xylopyranose units linked by 1:4 bonds (McGinnis & Shafizadeh, 1980; Teleman *et al.*, 2000). Most of the xylose residues contain an acetyl group on about seven out of ten xylose units, usually located at carbon-2 or carbon-3 (Teleman *et al.*, 2001), but preferentially at carbon-3 (Haun, 1970). The xylose units in the xylan chain additionally carry 1:2 linked 4-O-methyl- α -D-glucuronic acid groups (Tanczos *et al.*, 2003). These average about one uronic acid per ten xylose units (Haun, 1970; Sjöström, 1981; Teleman *et al.*, 2001). The xylosidic bonds between the xylose units are easily hydrolysed by acids, whereas the linkages between the uronic acid groups and xylose are very resistant. Acetyl groups are easily cleaved by alkali, and the acetate formed during Kraft pulping mainly originates from these groups (Sjöström, 1981).

Table 2.1 Chemical Composition of Wood ^a (Haun, 1970).

	Hardwoods (%)	Softwoods (%)
Cellulose	40-50	40-45
Lignin	20-25	25-35
Pectin	1-2	1-2
Starch	Trace	Trace
Hemicellulose	25-35	25-30
Glucuronoxytan	Very large	Small
Glucuronoarabinoxylan	Trace	Small-medium
Glucomannan	Small	Large
Galactoglucomannan	Very small	Small-medium
Arabinogalactan	Small	Very Small ^b
Other galactans	Trace-small	Trace-small

^a Extractive free, ash free basis

^b Certain larch species contain medium to very large quantities

Besides xylan, glucomannans are also present in small amounts in hardwoods (Haun, 1970; Sjöström, 1981), usually between 3 to 5% (McGinnis & Shafizadeh, 1980). This polysaccharide consists of D-glucose and D-mannose in a straight chain linked by 1:4- β – bonds (Haun, 1970; McGinnis & Shafizadeh, 1980; Sjöström, 1981) with the ratio of glucose:mannose varying between 1:2 and 1:1 (McGinnis & Shafizadeh, 1980; Sjöström, 1981). The mannosidic bonds between the mannose units are more rapidly hydrolysed by acid than the corresponding glucosidic bonds, and as a result glucomannan is easily depolymerised under acidic conditions (Sjöström, 1981).

2.2.3 Lignin

Lignin can be described as a three dimensional macromolecule with a high molecular weight (Abreu *et al.*, 1999). It is a complex molecule originating from phenylpropanoid precursors such as coumaryl, coniferyl, and sinapyl alcohol (**Figure 2.2.1**).

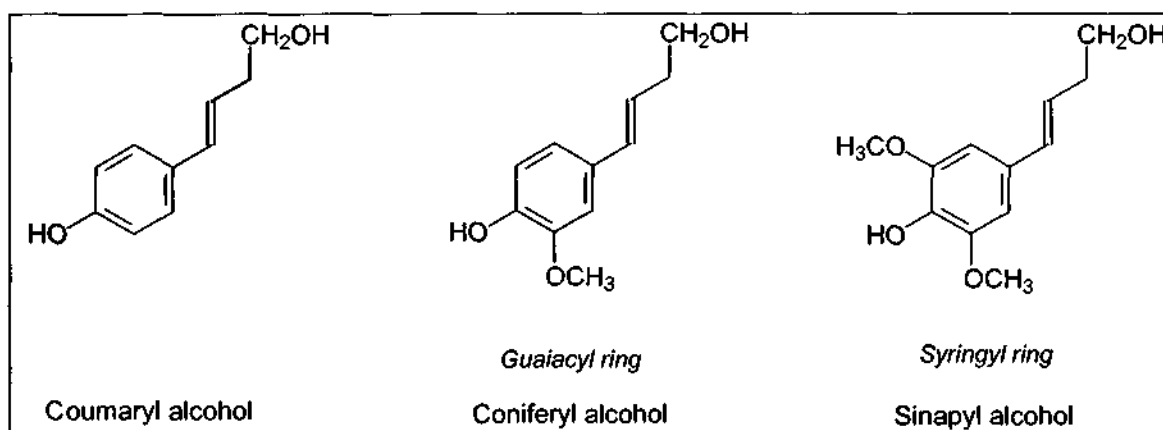


Figure 2.2.1 Phenylpropanoid lignin precursors (Sjöström, 1981; Abreu et al., 1999).

Although composed of carbon, hydrogen and oxygen, lignin is not a carbohydrate. It is essentially phenolic in nature. The precursor alcohols are formed by a series of enzymatic reactions starting with D-glucose formed during photosynthesis, through a series of pathway reactions (shikimic acid and cinnamic acid pathways) (Glasser, 1980). In lignin, the precursors through an enzyme-catalysed dehydrogenative polymerisation reaction results in the formation of a randomly branched and cross-linked structure, for which frequent carbon-to-carbon linkages between phenyl propane units are characteristic (Sarkanen, 1970).

Lignin can be divided into several classes according to their structural elements. The so-called 'guaiacyl' lignin, which occurs in almost all softwoods, is largely a polymerisation product of coniferyl alcohol. The 'guaiacyl-syringyl' lignin, typical of hardwoods, is a co-polymer of coniferyl and sinapyl alcohols, the ratio varying from 4:1 to 1:2 for the two monomeric units (Sjöström, 1981).

In wood, lignin occurs between individual cells and within the cell walls. Between cells, it serves as a binding agent to hold cells together. Within cell walls lignin is very intimately associated with cellulose and serves to impart rigidity to the cell. In the woody tissue of angiosperms, lignin is found in tracheids, fibres, vessels, and parenchyma cells (Abreu et al., 1999). The lignin concentration is high in the middle lamella and low in the secondary wall (Sjöström, 1981). Because of the thickness of the secondary wall however, about 70-80% of the lignin is located here, with measurements indicating that the lignin in the secondary wall of hardwood fibres have a high content of syringyl units whereas larger amounts of guaiacyl units are present in the middle lamella (Sjöström, 1981; Tsutsumi, 1995).

2.3 CELL WALL

It would be impossible to understand the chemical reactions occurring in the pulping process and account for the physical properties of wood without some understanding of the arrangement of cellulose, hemicellulose and lignin in the cell wall. Further to this, the mechanical properties of wood fibres are dependent not only on the chemical composition of the fibres but also on the organisation of their constituents, and the interaction between them.

The cell wall is built up by several layers (**Figure 2.3.1**): the middle lamella (ML), primary wall (P), outer layer of the secondary wall (S1), middle layer of the secondary wall (S2), inner layer of the secondary wall (S3), and the warty layer (W) (Sjöström, 1981).

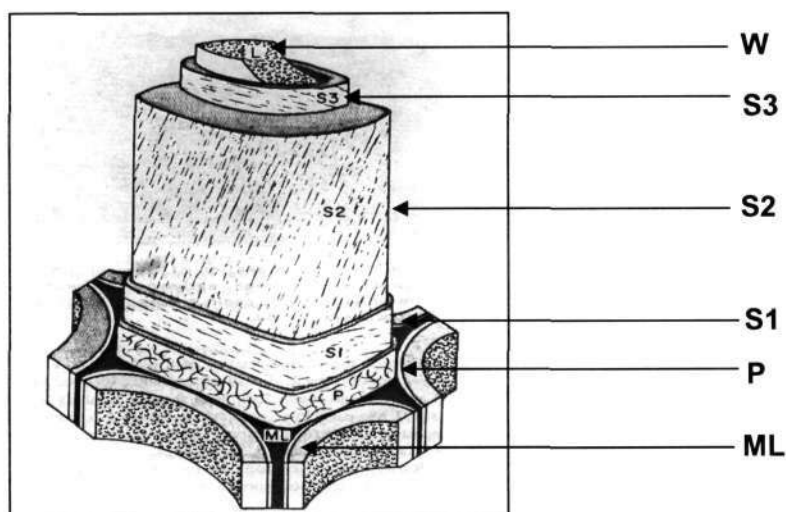


Figure 2.3.1 Schematic of cell wall (Smook, 1992)

The concentric arrangement of the cell wall layers is due to the difference in the chemical composition and by the different orientations of the structural elements. The middle lamella is located between the individual cells and serves to bind or glue the cells together. At early stages of growth it is mainly composed of pectic substances, but it eventually becomes highly lignified (Sjöström, 1981) and is essentially free of cellulose (Fengel & Wegener, 1984). The transition from the middle lamella to the adjacent primary cell wall layer is not very distinct and so are both often referred to as the compound middle lamella. The primary wall is a thin

layer consisting of cellulose, hemicellulose, pectin and protein, and is completely embedded in lignin. Microfibrils, which are bundles of cellulose molecules (Smook, 2002), are arranged in thin crossing layers in the primary wall (Fengel & Wegener, 1984).

The secondary wall consists of three layers, all of which are composed of cellulosic microfibrils embedded in an amorphous matrix of hemicellulose and lignin. The most important layer is the S2 layer which makes up about 80% of the fibre wall (Batchelor *et al.*, 1997; French *et al.*, 2000), and therefore largely determines the fibre properties (Long *et al.*, 2000). The S2 layer consists of helically wound cellulose microfibrils, with the angle of the helix with respect to the fibre axis known as the microfibril angle (Batchelor *et al.*, 1997; French *et al.*, 2000). In the outer layer (S1), the microfibrils form either a Z-helix or S-helix, while the microfibrils in the innermost layer (S3) are orientated in both the Z and S-helix direction (Sjöström, 1981).

2.4 KRAFT PULPING

In an effort to find a substitute for expensive sodium carbonate (soda ash) as makeup for the soda process, it was discovered that the addition of sodium sulphate to the chemical recovery furnace (where it is reduced to sulphide) significantly accelerated delignification, and produced a much stronger pulp. This process was referred to as the Kraft process and was patented in 1884 (Smook, 2002). Today, Kraft pulps dominate the world market place for wood pulps because they are clean, strong and stable in appearance (MacLeod *et al.*, 1995). These qualities make them ideal for the manufacture of high quality printing papers.

In the Kraft pulping process, the wood chips are cooked in digesters at temperatures of about 170°C and in aqueous solutions of sodium hydroxide and sodium sulphide (Kerr, 1970). The objective is to promote lignin fragmentation and subsequent reaction products dissolution, whilst minimising carbohydrate (cellulose and hemicellulose) degradation and/or dissolution (Carvalho *et al.*, 2000). Studies with lignin-model compounds, representing various structural units in lignin, have identified three cleavage reactions that occur during the alkaline fragmentation of lignin during Kraft pulping (Bryce, 1980):

- (1) Cleavage of *a*-aryl ether bonds in phenolic units by way of quinone-methide

intermediates. The additional phenolic groups formed in these reactions increase the solubility of the lignin and make it more susceptible to other degradation reactions.

- (2) Cleavage of β -aryl ether bonds in phenolic units by way of epi-sulphide intermediates. The quinone-methide intermediates react more rapidly with sulphide ions than with hydroxyl ions. This explains the more rapid and extensive degradation of lignin by Kraft pulping liquors than by soda liquors.
- (3) Cleavage of β -aryl ether bonds in non-phenolic units by way of epoxide intermediates. By this reaction, phenolic and glycolic groups are liberated, resulting in complete separation of neighbouring units in the lignin structure and the formation of more stable, lower molecular weight fragments.

The degradation of lignin is also accompanied by condensation reactions that occur simultaneously and which retard lignin dissolution. It has been suggested that the major part of condensation occurs at the unoccupied carbon-5 position of the phenolic units (Sjöström, 1981). The syringyl units of hardwoods cannot, of course, undergo condensation.

The Kraft process is not totally selective for lignin, and the carbohydrates are also degraded. The main reactions of cellulose and hemicellulose that occur in alkali can be summarised as follows (Kocurek, 1996):

- (1) Saponification (hydrolysis of an ester using an alkali to form a salt) of acetyl groups in acetylated hemicelluloses.
- (2) Sequential loss of sugar units from the reducing end of the polysaccharides ('peeling' reaction) until a 'stopping' reaction prevents further loss.
- (3) Random cleavage of the main polysaccharide chain.

The carbohydrate material lost in peeling is converted to various hydroxy acids, which reduce the effective alkali concentration of the cooking liquor. If the peeling reaction was allowed to continue, the whole polysaccharide would eventually be converted to soluble acids. The cessation of peeling may be due to a re-arrangement of the reducing end-group which makes it resistant to peeling (chemical

stopping) or because the reducing end-group has become physically inaccessible to the alkaline reagent (physical stopping).

Because of the alkaline degradation of polysaccharides, Kraft pulping results in considerable carbohydrate losses leading to reduced yield and pulp intrinsic viscosity (Carvalho *et al.*, 2000). The acetyl groups from hardwood xylan are hydrolysed at the very beginning of the Kraft cook (Sjöström, 1981). The reactions of xylan and their retention in Kraft pulps are of considerable interest, since the carbohydrate composition of pulp fibres influences the quality of the paper made from them. The retention of large amounts of xylan in conventional Kraft pulps is probably explained by their comparative stability to alkali, and to the fact that their solubility in the cooking liquor is reduced both by the falling alkalinity during the cook and by the removal of their uronic acids (Kocurek, 1996).

2.5 HEXENURONIC ACID

2.5.1 Formation during Kraft pulping

In the early 1950s, the 4-O-methyl-glucuronic acid unit was found to be the main acidic constituent of xylan in both hardwoods and softwoods (Jiang *et al.*, 2000). This finding led to intensive investigations into the alkaline degradation of 4-O-methyl-glucuronoxylan, (which is xylan containing 4-O-methyl-glucuronic acid groups). In 1963, Clayton hypothesised that 4-O-methyl-glucuronic acid was converted to HexA by the elimination of the 4-O-methoxyl group, after the loss of the hydrogen atom attached to the fifth position of the glucuronic acid residue (**Figure 2.5.1**).

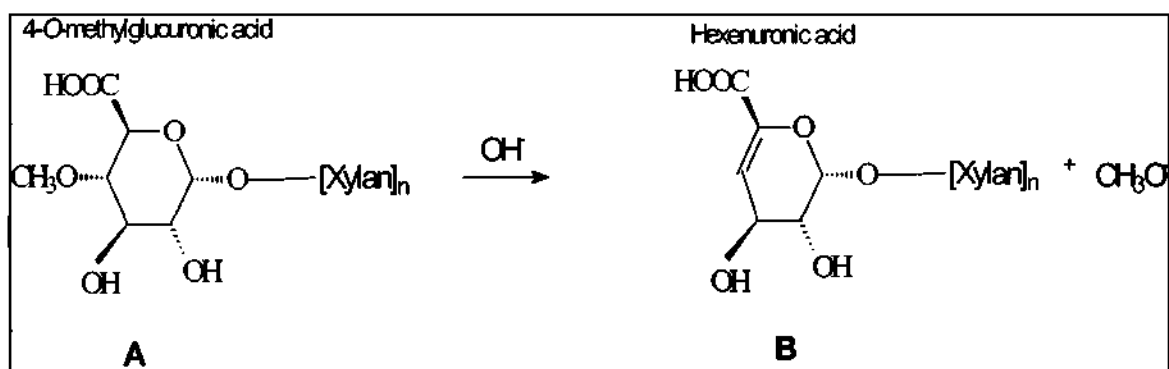


Figure 2.5.1 Conversion of 4-O-methyl-glucuronic acid (A) to hexenuronic acid (B) during Kraft pulping (Clayton, 1963).

Using 2-O-(4-O-methyl- β -D-glucopyranosyluronic acid)-D-xylitol as a model compound for xylan, Johansson and Samuelson (1977) provided the first evidence to support this speculation. They showed that treatment of this compound with sodium hydroxide at elevated temperatures resulted in a 50% yield of 2-O-(4-deoxy- β -L-threo-hex-4-enopyranosyluronic acid)-D-xylitol (hexenuronic acid-D-xylitol), which degraded with time. This experiment showed that epimerisation at carbon-5 of 4-O-methyl- β -D-glucopyranosyluronic acid occurred to give 4-O-methyl- β -L-idopyranosyluronic acid, which is then degraded to HexA (Johansson & Samuelson, 1977). Nuclear magnetic resonance (NMR) spectroscopy, which is a well-established method for the characterisation of hexenuronoxylan, has played a key role in the elucidation of its pulping and bleaching chemistry, and together with mass spectroscopy finally confirmed the occurrence of HexA groups during Kraft pulping (Teleman *et al.*, 1995).

As HexA is formed during Kraft pulping, it is also simultaneously degraded in the alkaline medium of the cooking liquor, or partially eliminated as a result of xylan dissolution (Gustavsson & Al-Dajani, 2000). Alkaline hydrolysis of glycosidic bonds leads to the formation of xylan with a lower degree of polymerisation, which is removed from the pulp by dissolution in the cooking liquor, carrying HexA groups with it (Pedroso & Carvalho, 2003). It therefore appears that the concentration of HexA in unbleached pulps is the result of two competing processes, *i.e.* formation and dissolution/degradation.

During Kraft pulping, the rate of formation and degradation/dissolution of HexA has been shown by many researchers to be influenced by various process parameters.

For softwoods, HexA is essentially formed early in the cook, *i.e.* during the heating up period of the pulping cycle, but then decreases continuously with time (Buchert *et al.*, 1995; Gustavsson & Al-Dajani, 2000). Jiang and co-workers (2003) found, for softwoods, that higher Kappa number pulps generally contained higher amounts of HexA, thus supporting these earlier observations that HexA groups formed during the rise-to-temperature in pulping are partially degraded in the latter phases. Using the results of studies by Ross and Thompson (1965) on the degradation of methoxyl groups, Jiang *et al.* (2000) demonstrated a temperature dependence for the formation of HexA during the heating up period of the pulping cycle. They showed that HexA is not formed in significant amounts at temperatures lower than 130°C. In addition to pulping time and temperature, the rates of dissolution/degradation of HexA, for softwoods, have been shown to increase with increasing hydroxyl ion concentration, hydrogen sulphide ion concentration and ionic strength (Gustavsson & Al-Dajani, 2000).

In investigations into the effects of process variables on the content of HexA in hardwood Kraft pulps, Daniel *et al.* (2003) showed that for *E. globulus* pulps, unlike softwood pulps, HexA content increased with increasing pulping time (degree of delignification). They also showed that at constant Kappa number 14, HexA content decreased when increasing the active alkali from 17-24%, but increased when the active alkali increased in the lower range of 14-17%. In the same study, they found that HexA concentration also increased when increasing sulphidity from 15-28%, decreased when the pulping temperature was increased from 150-170°C or when the liquor-to-wood ratio increased from 4-8.

In other studies, Pedroso & Carvalho (2003) and Simão *et al.* (2005b) showed, for *E. globulus* Kraft pulps, that alkali and temperature were the main factors affecting the amounts of HexA in pulps, whilst sulphidity appeared to be insignificant. Similar to the study by Daniel *et al.* (2003), Pedroso and Carvalho (2003) also found that HexA concentration increased with pulping time. Further to this, they showed that by increasing the temperature from 150-170°C at lower effective alkali (12.8%), HexA content increased, whilst at higher effective alkali (17%), increasing the temperature in the same range, decreased the HexA content. Simão *et al.* (2005a) found similar results, with lowest HexA contents achieved at higher temperatures and higher alkali charges for *E. globulus*.

In addition to the influence of process variables, HexA content also depends on the

species being pulped (Jiang *et al.*, 2000). For example, hardwood pulps contain more HexA groups than softwood pulps similarly cooked (Vuorinen *et al.*, 1999), primarily because hardwoods contain more 4-O-methylglucuronoxylan than softwoods (Sjöström, 1981).

2.5.2 Significance of hexenuronic acid

The presence of HexA groups in pulp result in increased consumption of potassium permanganate in the Kappa number test (Li & Gellerstedt, 1997; Li *et al.*, 2002) due to the well-known fact that permanganate reacts with carbon-carbon double bonds. Since Kappa number measurements are widely used to evaluate the efficiency of delignification in pulping and bleaching processes, the presence of these unsaturated constituents will affect the results of this analysis and give erroneously higher measurements for the amount of residual lignin in the pulp. Studies carried out by Vuorinen and co-workers (1996) to determine the contribution of HexA to Kappa number measurements, found that 10 μ mol of HexA contributed to 1.05 Kappa units. This result was much higher than those reported by Li and Gellerstedt (1997) who quoted values of 0.86 Kappa units.

Hexenuronic acid belongs to a class of compounds that contain enol ether or unsaturated carboxylic acid groups. These functional groups strongly influence the stability and reactivity of HexA, and are the targets of both electrophilic and nucleophilic attack. As a result, chlorine dioxide and other electrophilic bleaching chemicals such as chlorine, ozone, and the peracids, react with the 'ene' functionality of HexA groups (Buchert *et al.*, 1995; Vuorinen *et al.*, 1996; Vuorinen *et al.*, 1999). This means that bleaching chemicals are not consumed during delignification, leading to higher bleaching chemical consumptions, increased production costs, and increased effluent emissions (Petit-Breuilh *et al.*, 2004).

Consumption of other bleaching chemicals such as hydrogen peroxide are affected indirectly because HexA results in a strong affinity of Kraft pulps for certain transition metals which are mainly bound to the uronic acid groups (Vuorinen *et al.*, 1996). These metal ions, with manganese (II) being the most harmful (Vuorinen *et al.*, 1996), are known to catalyse the degradation of hydrogen peroxide during peroxide bleaching. The HexA groups have however, been reported to be unreactive in alkaline oxygen and peroxide bleaching stages (Buchert *et al.*, 1995; Gellerstedt & Li,

1996).

The brightness reversion of Kraft pulps has been attributed to the presence of residual lignin, chlorinated extractives or oxidised carbohydrate units. Carboxylic acids and their counter ions have, in the past, also been reported to affect brightness reversion (Sjöström & Eriksson, 1968; Scallan, 1983). The yellowing tendency of Kraft pulps has been especially shown to be proportional to the uronic acid content (Spinner, 1962), and the removal of HexA in particular, has been shown to improve the brightness stability of these pulps (Vuorinen *et al.*, 1996; Buchert *et al.*, 1997).

2.5.3 Degradation by acid hydrolysis

The presence of HexA in Kraft pulps has never been verified by conventional carbohydrate analysis, but by the use of NMR spectroscopy (Teleman *et al.*, 1995). The most likely reason for this is that the conventional method of analysis of carbohydrates includes an acid hydrolysis step (Wallis *et al.*, 1996; Dahlman *et al.*, 2000). Enol ethers are acid labile, which means that the HexA groups are unstable in acidic conditions (Jiang *et al.*, 2000) and are decarboxylated (Tanczos *et al.*, 2003) and degraded to furan derivatives (Teleman *et al.*, 1996a). Structural analysis of the acidic degradation products of hexenuronoxylan led to the proposed pathway shown in **Figure 2.5.2**.

In their study on the kinetics of the hydrolysis of HexA, Vuorinen and co-workers (1999) found that at a constant pH and temperature, the hydrolysis of HexA groups follows first order kinetics:

$$\Delta [\text{HexA}] = \Delta [\text{HexA}]_{\text{max}} (1 - e^{-kt}) \quad 2-1$$

The hydrolysis rate first increased with decreasing pH but then reached a maximum at pH ~3. It follows, that the reaction rate is proportional to the fraction of free HexA. The pH dependence of the rate constant in this case, is given by the expression:

$$k \sim k_o / (1 + K_a/[\text{H}_3\text{O}^+]) \quad 2-2$$

Where, k_o and K_a denote the rate constant for the free acid and the acid dissociation constant, respectively. Vuorinen and co-workers (1999) also found that the

temperature dependence of the hydrolysis rate constant for a birch Kraft pulp corresponded to an activation energy of 87.6 kJ/mol. The corresponding entropy of activation was -83 kJ/mol. They found that the observed reaction kinetics was very fast in comparison with the hydrolysis of simple pyranosidic linkages (activation energy of 114.5 kJ/mol), and that the high reaction rate therefore led to a high selectivity at relatively low temperatures between 85 and 115°C. Typically, a 90% reduction in the HexA content reduced the viscosity by 50-100 dm³/kg. However, studies carried out on softwood Kraft pulps showed that acidic treatment of the pulps had similar activation energies for both HexA removal and pulp viscosity losses, and these were lower than those previously reported for some hardwood Kraft pulps (Bergnor-Gidnert *et al.*, 1998).

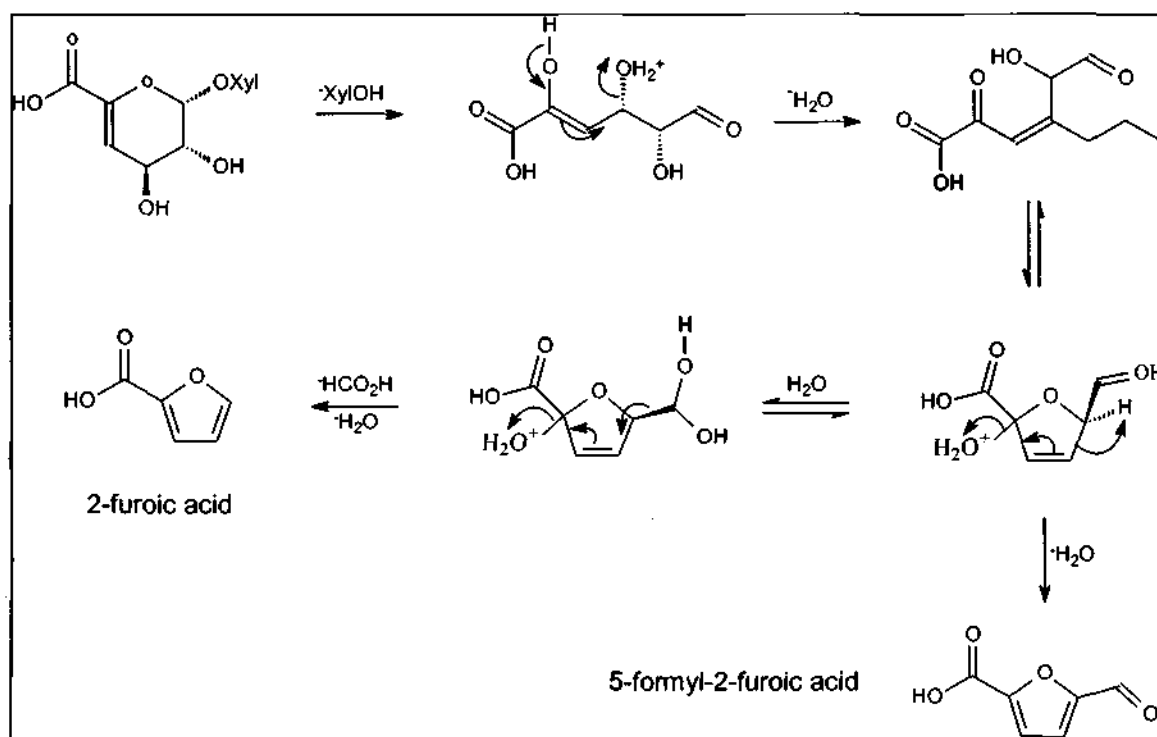


Figure 2.5.2 Proposed reaction pathway for the acid degradation of hexenuronic acid groups attached to xylan, to 2-furoic and formic acids (Teleman *et al.*, 1996a).

The removal of HexA by acid hydrolysis prior to bleaching offers several advantages. One of the major general advantages of acid hydrolysis, and the subsequent removal of HexA, is the reduction of bleaching chemical costs. Vuorinen and co-workers (1996) found that the amount of furan derivatives produced during acid hydrolysis correlated linearly with the decrease in Kappa number of both unbleached and

oxygen bleached softwood and hardwood pulps. They found that depending on the type of pulp, the selective hydrolysis treatment removed 20-60 milli-equivalents HexA per kilogram of pulp and reduced the Kappa number by 2-7 units. This resulted in a 30-40% decrease in chemical consumption during ECF bleaching of birch Kraft pulps.

Furtado, Evtuguin and Gomes (2001) studied the effect of the acid stage on *Eucalyptus globulus* Kraft pulp bleachability and strength during ECF bleaching. In this study, the conditions for the acid pre-treatment of the unbleached pulp were selected to obtain maximum chlorine dioxide savings with minimal losses in yield and viscosity. They found that the acid stage at 90°C and pH 3-3.5 completely satisfied their demands, with savings in chlorine dioxide up to 13–17%, viscosity reductions of 105–115 dm³/kg and yield losses between 2.2–1.9%.

Ratnieks *et al.* (2001) studied the effects of the acid stage to increase bleach pulp production, improve digester Kappa number, and improve acid washing of calcium salts. They used an acid stage at 90°C and pH 3.5 and found that the acid stage reduced the Kappa number by five units with a selectivity of 50 dm³/kg per Kappa number reduction (*i.e.* 250 dm³/kg viscosity loss).

2.5.4 Removal of hexenuronic acid – impact on pulp quality

Acidic treatment of Kraft pulps at elevated temperatures have been reported to give a reduction in the Kappa number due to the removal of HexA (Li & Gellerstedt, 1997; Vuorinen *et al.*, 1999; Jiang *et al.*, 2000; Pedroso & Carvalho, 2003). However, the process is not totally selective and can result in attack on the carbohydrates. This is evident by the loss in pulp viscosity. Viscosity is of great importance in process and quality control, particularly in the bleach plant, because carbohydrate degradation beyond a certain level critically affects pulp strength.

Furtado *et al.* (2001) studied the effect of the acid stage on bleachability and strength and optical properties of ECF bleached *E. globulus* Kraft pulps. They found no clear dependence between pulp brightness reversion and HexA elimination, and only a 1% difference in opacity between an ADEDED and conventional DEDED bleached pulp. The tensile and burst strength of the pulps bleached using the two sequences were virtually equal, with the tear resistance 10% lower in the pulps bleached with the

ADEDED sequence. In the same study, Furtado *et al.* (2001) also studied the effect of the acid stage before and after the oxygen stage in an OADEDED and AODEDED bleaching sequence. In both sequences they found an increase in pulp brightness (2% ISO) and with a decrease in the pulp brightness reversion. The opacity remained unchanged. The addition of the acid stage before and after the oxygen stage had no negative influence on the tear, tensile and burst strengths of the bleached pulp, with the tear strength slightly improving when the acid stage was added after the oxygen stage.

Ratnieks *et al.* (2001) obtained similar results when installing an acid stage in the fibre line for improved eucalyptus pulp production. They found that the pulp quality, measured by the physical strength of the fibres, showed an increase, with tensile strength improving by 10%.

2.5.5 Hexenuronic acid and bleachability

The extent of delignification, measured as Kappa number, and the conditions used in Kraft pulping, affect the chemical composition and structure of unbleached pulps and therefore, their bleachability (Gustavsson *et al.*, 1999; Colodette *et al.*, 2002). As the extent of delignification increases, the composition and structure of the pulp, namely the residual lignin, is strongly modified (Gustavsson *et al.*, 1999). It is therefore not surprising that relationships may be established between bleachability and the chemical structure of lignin. Researchers have thus shown that the decrease in bleaching response is associated with an increase in the degree of condensation of lignin, a lower content of β -O-4 structures and a higher guaiacyl:syringyl ratio (Gustavsson *et al.*, 1999).

However, Daniel and co-workers (2004) showed that for pulps with the same Kappa number, produced by varying the pulping conditions, no clear correlation could be established between bleachability and the content of β -O-4 structures, phenolic hydroxy groups, guaiacyl:syringyl ratios or the degree of condensation of residual lignin. At constant Kappa number, they found that the bleachability increased with a decrease in the residual lignin/HexA content ratio. They also suggested that other chemical structures present in pulps, such as lignin-carbohydrate complexes (LCC) or other unknown unsaturated structures, probably issued from carbohydrates, play a key role in the bleaching response of pulps.

In their quest to determine the role of HexA in pulp bleachability, Jiang and co-workers (2003) suggested that the change in the reactivity of the residual lignin in the pulp could be attributed to the formation of covalent bonds between HexA and lignin, and that these reactions become even more significant during oxygen delignification. Because oxygen is a radical generator (Sjöström, 1981), they proposed that the linkage is formed during a radical coupling reaction (**Figure 2.5.3**). The radical coupling reaction intermediates (III) and HexA radicals (V) could be formed from the extraction of an electron from quinone methide moieties (II) and HexA (IV), respectively. The coupling reaction product (VI) is expected to make both HexA and lignin more resistant towards delignification and bleaching reactions, and therefore explains the lower reactivity.

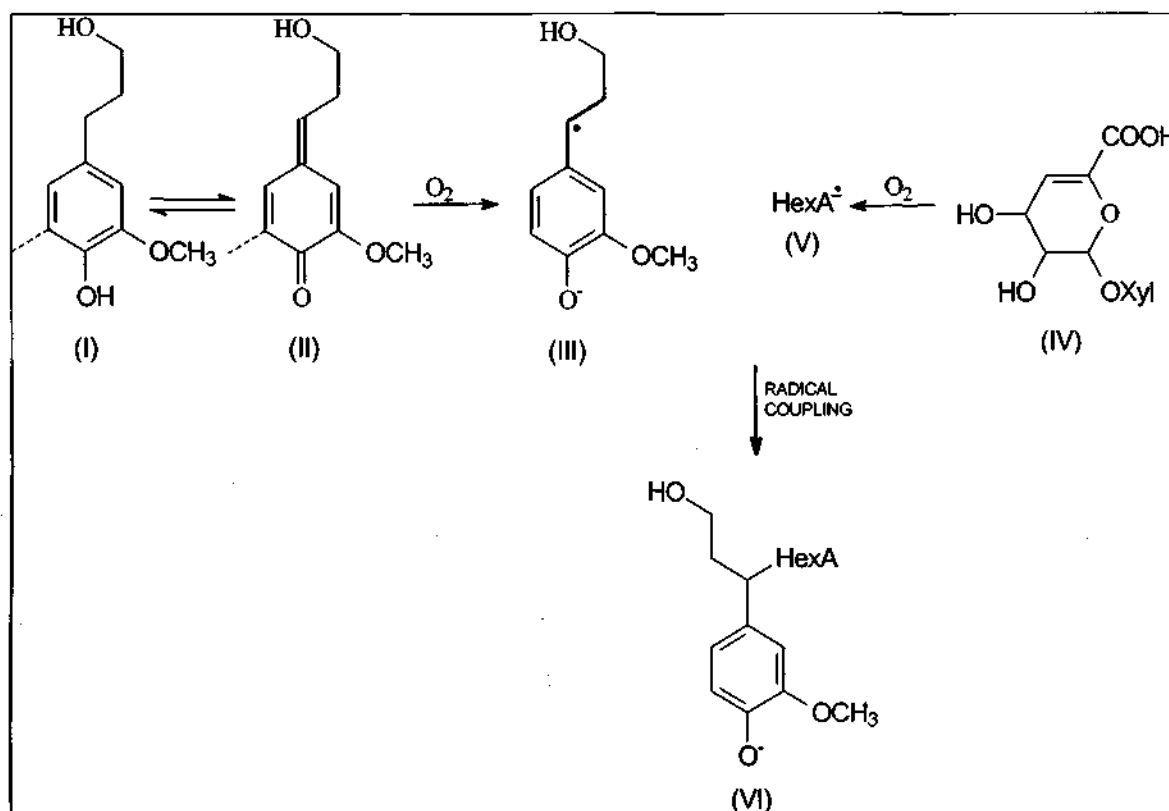


Figure 2.5.3 Proposed reaction pathway for the formation of a covalent bond between lignin (I) and HexA (IV) (Jiang et al., 2003).

2.5.6 Methods for quantification of hexenuronic acid

During the last few years, several methods have been developed to quantify the

HexA content in Kraft pulps. A majority of these methods are based on the hydrolysis of HexA in the pulp followed by the analysis of the degradation products using chromatography and/or ultraviolet spectroscopy.

Vuorinen *et al.* (1996) developed a spectroscopic method based on the selective hydrolysis of HexA with formate buffer solution. The amount of HexA removed was calculated from the absorption maximum at 245nm, which originated from the major hydrolysis product, 2-furancarboxylic acid.

Gellerstedt & Li (1996) described a colorimetric method based on the selective hydrolysis of the glucosidic link between HexA and the xylan chain. This degradation technique involved several treatment steps with mercuric acetate, periodate, sodium arsenite and reaction with thiobarbituric acid to yield a pink product. Quantification was carried out by chromatographic separation and/or UV-VIS spectroscopy, with an absorption maximum at 550nm.

Tenkanen *et al.* (1999) used various cellulolytic and hemicellulolytic enzymes, instead of acids, for the hydrolysis of the pulp polysaccharides. Hexenuronic acid-substituted oligosaccharides in the hydrolysate were then quantified by high performance anion exchange chromatography coupled with pulsed amperometric detection (HPAEC-PAD).

Chai *et al.* (2001) developed a spectroscopic method based on the selective hydrolysis of HexA using a mercuric chloride-sodium acetate mixture as the hydrolysis solution. HexA was measured directly at 260nm. In their method, Chai *et al.* (2001) also described a dual wavelength (260nm and 290nm) spectroscopic technique to eliminate spectral interference resulting from leached lignin in the hydrolysis solution. The method developed by Gellerstedt & Li (1996) was used to calibrate this method.

Jiang *et al.* (2001) used sulphuric acid for the selective hydrolysis of HexA groups to its degradation products, 2-furoic and 5-formyl-2-furoic acid. The degradation products were separated by anion exchange chromatography (AEC) and quantified using suppressed conductivity detection.

Evtuguin *et al.* (2002) developed a method to simultaneously determine both residual lignin and HexA in Kraft pulps by ultraviolet spectroscopy. In this method, the pulps

were dissolved in cadoxen solution and the pulp-cadoxen solutions were scanned in the 205-500nm range. The method developed by Vuorinen *et al.* (1996) was used as a reference.

Saariaho *et al.* (2003) used ultraviolet resonance Raman (UVR) spectroscopy for the determination of lignin and HexA. UVR spectra were collected at wavelengths of 244 and 257nm and the data were calibrated using the partial least squares regression method to obtain good predictability.

Hoang *et al.* (2005) developed a Fourier transform infra-red (FTIR) spectroscopic method for determining HexA content and Kappa number of high yield Kraft pulps. In this method, pulp handsheets were scanned in the transmission mode in the wavenumber range 4000-800cm⁻¹. Based on the transmission spectra, and using a multivariate analysis, the Kappa number and HexA content of the pulps were predicted. The procedure proposed by Chai *et al.* (2001) was used to calibrate this method.

Jääskeläinen *et al.* (2005) developed a method to determine lignin and HexA content of bleached hardwood Kraft pulps. The method was based on UVR spectroscopy. The lignin content of the pulps were determined from the aromatic band heights of the UVR spectra, and HexA content was simultaneously determined from the UVR band heights of unsaturated C=O and C=C structures. The method developed by Vuorinen *et al.* (1996) was used to calibrate this method.

2.6 PULP BLEACHING

2.6.1 Introduction

The main objective of bleaching is to increase the brightness of the pulp and to make it suitable for the manufacture of printing and tissue grade papers, by the removal or modification of some of the constituents of the unbleached pulp, including lignin and its degradation products, resins, metal ions and non-cellulosic carbohydrate components (Singh, 1979). This objective is usually achieved through a continuous sequence of process stages utilising different chemicals in each stage. **Table 2.2** summarises the chemicals used in pulp bleaching, together with their functions, advantages, and disadvantages.

Table 2.2 Functions, advantages and disadvantages of bleaching chemicals (Reeve, 1996a).

Stage	Symbol	Function	Advantages	Disadvantages
Chlorine	C	Oxidise and chlorinate lignin	Effective, economical delignification; good particle removal	Organochlorine formation; highly corrosive
Hypochlorite	H	Oxidise, decolourise, and solubilise lignin	Easy to make and use; low cost	Can cause loss of pulp strength; chloroform formation
Chlorine dioxide	D	Oxidise, decolourise, and solubilise lignin	high brightness without loss of pulp strength; good particle bleaching	On-site production; high cost; some organochlorine formation; highly corrosive
Oxygen	O	Oxidise and solubilise lignin	Low chemical cost; provides chloride-free effluent for recovery	Significant capital equipment when used in large amounts; potential loss of pulp strength
Hydrogen Peroxide	P	Oxidise and decolourise lignin	Easy to use; low capital cost	High chemical cost; poor particle bleaching; potential loss of pulp strength
Ozone	Z	Oxidise, decolourise, and solubilise lignin	Effective; provides chloride-free effluent for recovery	On-site production; high cost; poor particle bleaching and pulp strength
Hydrosulphite ^a	Y	Reduce and decolourise lignin in high yield pulps	Easy to use; low capital costs	Decompose readily; limited brightness gain
Xylanase	X	Catalyse xylan hydrolysis and aid in lignin removal	Easy to use; low capital cost	Limited effectiveness; high cost
Sodium hydroxide	E	Hydrolyse chlorolignin and solubilise lignin	Effective; economical	Darkens pulp
EDTA or DTPA	Q	Removal of metal ions	Improves peroxide selectivity and efficiency	High cost

^a Usually applied to mechanical pulps

Initially, the use of chlorine as a bleaching agent was widespread. However during the 1970s, the negative effects of chlorine on the environment was recognised, and a new social awareness of ecology and the environment resulted in the appearance of new laws regulating processes generating pollution. This awareness, supported by

these laws, placed ever-increasing pressure on industry and obliged it to make changes, adaptations and/or improvements to its processes in order to attain procedures that were more environmentally friendly, *i.e.* have a lower environmental impact. Efforts were therefore focused on the reduction of the volume of these effluents, or their total elimination through recycling back to the boilers. These attempts, however, were met with failure owing to the corrosive effects of chlorine on the process equipment (Pedrola *et al.*, 2004).

The compelling need for reducing or eliminating the formation of organochlorine compounds during the bleaching process thus led to the partial or total replacement of chlorine by chlorine dioxide, a more widespread use of oxygen delignification and a greater consumption of hydrogen peroxide. This gave rise to the appearance of elemental chlorine-free (ECF) and total chlorine-free (TCF) bleaching sequences. ECF pulp bleached with chlorine dioxide continues to grow and now dominates the world bleached chemical pulp market. Over the last decade, field studies, research and chemical analysis have demonstrated that treated wastewater from well-managed pulp and paper mills using ECF bleaching sequences with chlorine dioxide, is virtually free of dioxin and persistent bio-accumulative toxic substances (Pryke, 2003). Market data has also showed that ECF production grew by 17% alone in 2001, holding the highest worldwide market share for bleached chemical pulp, at greater than 75%, or more than 63 million tonnes (Pryke, 2003).

Some typical ECF bleaching sequences include, D₀ED₁ED₂ (e.g. Fuhrmann *et al.*, 1996; Daniel *et al.*, 2004), D(EO) (e.g. Froass *et al.*, 1996) and OD₀ED₁ED₂ (e.g. Jiang *et al.*, 2003), to name a few. In this present study, an O/OAD₀ED₁ bleaching sequence was used. The chemistry of each stage of this sequence is discussed in more detail below, excluding the acid hydrolysis stage which was discussed previously in section 2.5.3.

2.6.2 Oxygen delignification

The Kappa number after pulping that gives the minimum production costs depends on the final brightness target, the bleaching sequence, and the relative costs of wood and bleaching chemicals (Nordén & Boman, 1996). One of the challenges therefore, is to reduce the Kappa number of the unbleached pulp as far as possible without

compromising pulp strength properties. One option is to extend delignification during pulping. However, the negative effects associated with this are reduced pulp yield, reduced digester throughput, increased loading of the chemical recovery system, and in some cases, impaired pulp quality. Another alternative is to reduce the Kappa number through extended delignification in the oxygen stage. When the oxygen delignification process is effective, there is no need to go to very low Kappa numbers during pulping and optimum Kappa numbers range between 20-25 and 16-18 for unbleached softwood and hardwood pulps, respectively. The Kappa number can then be further reduced to 10-12 for softwoods and 10-8 for hardwoods during oxygen delignification (Pikka *et al.*, 1996). As a result of these low Kappa numbers, it is possible to produce bleached pulp at a low chemical cost and environmental impact, and still maintain good pulp properties.

Oxygen delignification has therefore become increasingly important in pulp bleaching technologies for the 21st Century and has developed rapidly since the early 1980s, when serious concern was voiced about energy consumption, pollution control and bleach plant effluent discharges (Li *et al.*, 1996). There are various oxygen delignification systems available today, usually single reactor systems, but more and more often, a two stage system is selected in order to maximise the delignification potential of oxygen. The first stage represents a quicker initial delignification, and the latter, a slower residual delignification which allows approximately 10% more delignification than single reactor systems (Pikka *et al.*, 1996). One of the most important factors in oxygen delignification is the mixing of oxygen gas into the pulp. The objective of mixing is to achieve a homogenic fibre-liquid-oxygen foam in the reactor (Pikka *et al.*, 1996). The solubility of oxygen in the liquid depends, among other things, on the size of the oxygen bubble and the partial pressure of oxygen. In the case of two-stage oxygen delignification systems, the pressure of the first stage is high which does not allow the bubble to grow in size. In this way, it is possible to get the oxygen efficiently into the liquid and further into the fibre (Pikka *et al.*, 1996).

In general, oxygen delignification is a heterogeneous process involving lignin in the fibre wall, oxygen and chemical charge (Nguyen & Liang, 2002), with the latter two, together with temperature and reaction time being identified as the key process variables (Zou *et al.*, 2000). Molecular oxygen, in its normal or electronically stable form, has two unpaired electrons and it may be reduced to water in four stages (**Figure 2.6.1**) by one electron transfer that gives rise to hydroperoxy radicals or superoxide anions (I), hydrogen peroxide or peroxide dianions (II), and hydroxyl

radicals or hydroxide ions (III) (Sjöström, 1981).

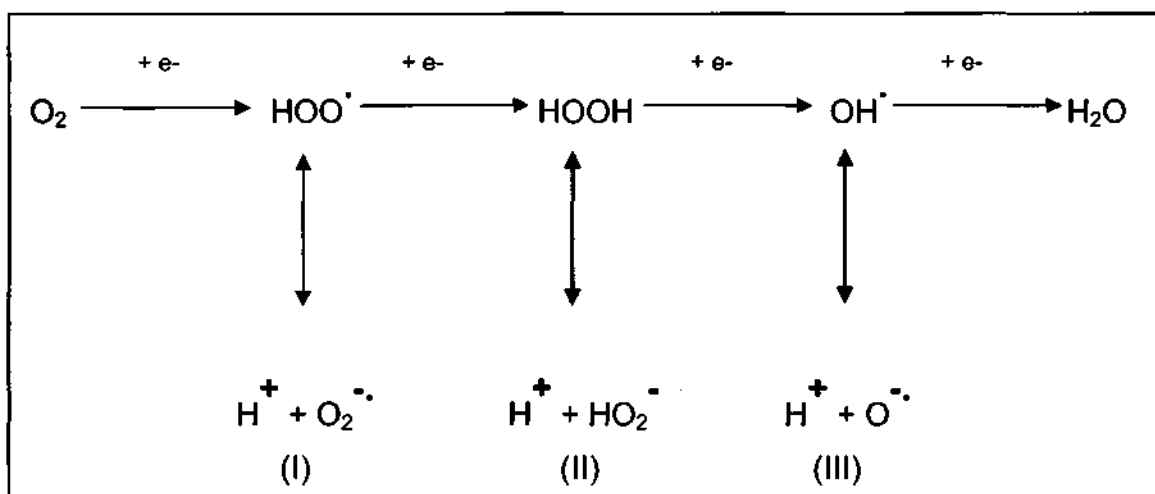


Figure 2.6.1 Reduction of oxygen by a one electron transfer mechanism (Sjöström, 1981).

Oxygen has a strong tendency to react with organic substances derived from both lignin and carbohydrates, and radical chain reactions are initiated (Singh & Dillner, 1979). **Figure 2.6.2** shows likely initiation, propagation, and termination steps.

Oxygen in its normal state is a weak oxidising agent, so it is necessary to promote its reaction either by raising the temperature or by providing a reactive substrate. In oxygen bleaching, the substrate is activated by providing alkaline conditions to ionise free phenolic hydroxyl groups in the residual lignin (McDonough, 1996).

It has been suggested that radicals generated by electron abstraction from phenolate ions in lignin, gives rise to resonance-stabilised phenoxy radicals (Lorås, 1980; Sjöström, 1981) and this is the primary reaction of oxygen with lignin under alkaline conditions (Singh & Dillner, 1979). The phenoxy radical is a resonance hybrid of structures in which the odd electron resides at the phenolic oxygen or at one of the several different carbon atoms in the aromatic ring or at the β -carbon atom of the side chain. All of these positions are therefore potential sites for further reaction (**Figure 2.6.3**).

INITIATION	$RO^\cdot + O_2 \rightarrow RO^\cdot + O_2^\cdot$	(1)
	$RH + O_2 \rightarrow R^\cdot + HO_2^\cdot$	(2)
PROPAGATION	$R^\cdot + O_2 \rightarrow RO_2^\cdot$	(3)
	$RO_2^\cdot + RH \rightarrow RO_2H + R^\cdot$	(4)
TERMINATION	$RO^\cdot + R^\cdot \rightarrow ROR$	(5)

Figure 2.6.2 Steps in the mechanism of oxygen bleaching (McDonough, 1996).

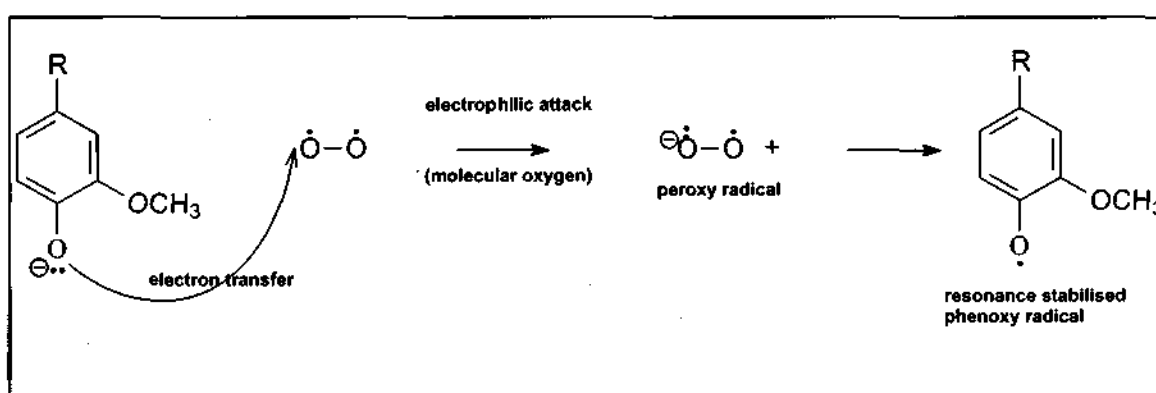


Figure 2.6.3 Initial attack of oxygen on phenolic nuclei (Sjöström, 1981; Singh & Dillner, 1979).

Oxygen bleaching is usually carried out in alkaline medium, as the alkali promotes the solubility of lignin and neutralises the acidic products formed from lignin and carbohydrates (Li *et al.*, 1996). If enough alkali is used, the Kappa number will continue to drop as a function of time (Li *et al.*, 1996). However, the degree of delignification is limited to 50-55% because of the poor selectivity of the process (Agarwal *et al.*, 1999), which also results in attack of the carbohydrates (Lorås, 1980; Sjöström, 1981). Reactions that degrade cellulose can be divided into two categories (McDonough, 1996): (1) random chain cleavage, which may occur at any point along the chain, and (2) endwise peeling, in which units on the chain are attacked and successively removed.

Degradation of cellulose and other wood polysaccharides during oxygen bleaching is often accompanied by a loss in pulp yield and viscosity. This degradation appears to be due to oxygen initiated free radical chain reactions whose rates are strongly influenced by the presence of hydrogen peroxide and transition metal ions (Singh & Dillner, 1979). One approach for dealing with transition metals is to remove them by acid washing before the oxygen stage, or by addition of a protector that inhibits carbohydrate degradation. The protector or inhibitor of greatest commercial importance is the magnesium ion, whose discovery provided a great impetus for the development of oxygen bleaching (McDonough, 1996).

2.6.3 Chlorine dioxide bleaching

The pulp bleaching process in industry requires important technical and economic consideration, particularly for the early delignification stages. Formation of chlorinated organic compounds during bleaching of chemical pulps has been an environmental issue for several years. Although environmental concerns are beginning to introduce new chemical bleaching alternatives, the trend nowadays in producing bleached pulp, is towards bleaching technologies that are free of elemental chlorine.

In the early 1940s, large-scale chlorine dioxide manufacturing and chlorine dioxide bleaching was first practiced (Reeve, 1991). This led to the development in the 1950s of the CEDED five-stage bleaching sequence that allowed production of very high brightness pulp with minimal loss in pulp strength. However, a CEDED sequence typically produces between 4-6kg of organically bound chlorine per metric tonne of pulp (Joncourt *et al.*, 2000). Substitution of element chlorine (Cl_2) with chlorine dioxide (ClO_2) was found to reduce the formation of chlorinated organic matter by as much as 80% (Joncourt *et al.*, 2000). Thus chlorine dioxide has become, and still is, the most widely used reactant in bleaching (Barroca *et al.*, 2000). Its characteristics, and in particular, its high selectivity, ensure a good level of delignification while preserving the physical and chemical properties of the pulp (Barroca *et al.*, 2000).

Chlorine dioxide is an oxidant that accepts five electrons per molecule when reduced to chloride through a series of steps involving several intermediates. Hypochlorous acid (HClO) and chlorine (Cl_2) are among the intermediates, and their presence can

lead to the formation of chlorinated organic matter (Pryke, 2000). Another undesirable by-product is the chlorate ion (ClO_3^-), which is not reactive and so its formation means a loss of bleaching efficiency (Reeve, 1996b).

Figure 2.6.4 illustrates the changes in oxidation states and reaction pathways of the reactive intermediates during chlorine dioxide bleaching of pulp (Reeve, 1996b). Chlorine dioxide (ClO_2) reacts with the pulp, transferring in the process one electron to produce chlorite ions (ClO_2^-) by reaction {1}. The chlorite ions thus produced does not react directly with the pulp. Chlorine dioxide also reacts with the pulp to form hypochlorous acid (HOCl) {2}, which is in part converted to chlorine (Cl_2) by hydrolysis {3}. Hypochlorous acid and chlorine react with the pulp to produce chloride ions (Cl^-) and chlorinated organic matter {4-7}. Chlorine reacts with chlorite to regenerate chlorine dioxide {10}, while hypochlorous acid reacts with chlorite to form chlorate ions (ClO_3^-) {8}. Under acidic conditions, chlorite decomposes to chlorine dioxide and chloride ions {9}.

Based on model compound studies, the two principle types of reactions that occur when chlorine dioxide is used as a delignifying agent can be classified as oxidation and aromatic chlorine substitution (Dence, 1996). Chlorine dioxide is an electrophile and as such preferentially attacks electron-rich lignin sites typified by phenolic rings, non-phenolic rings, and ring-conjugated ethylenic groups. Although the free phenolic structures are oxidised faster, chlorine dioxide also destroys the non-phenolic phenyl propane units and the double bonds present in the pulp chromophores. After cleavage of the benzene ring, various di-carboxylic acids are formed, such as oxalic, muconic, maleic and fumaric acids, in addition to products substituted with chlorine. As a result of depolymerisation and formation of carboxyl groups, the modified lignin is dissolved during the chlorine dioxide treatment and during the sodium hydroxide extraction stage that usually follows (Sjöström, 1981).

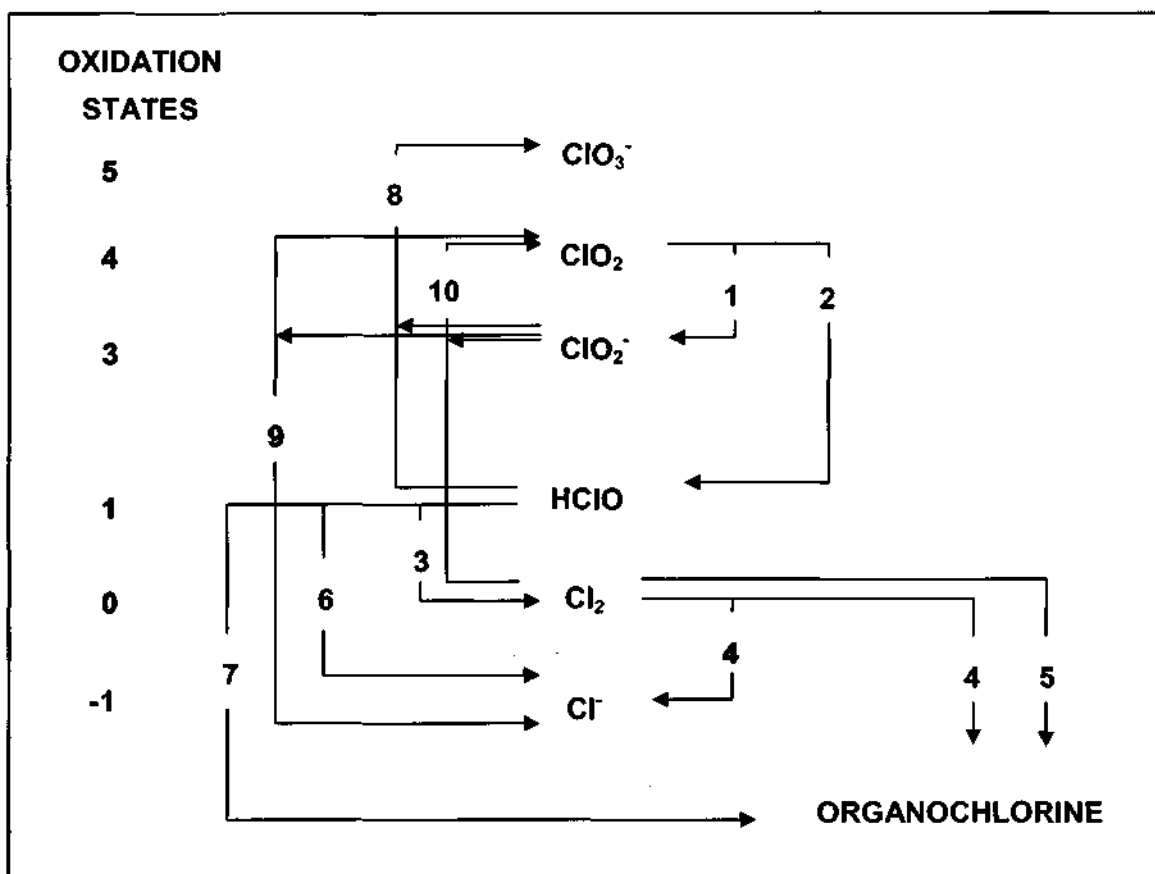


Figure 2.6.4 Reactions of chlorine dioxide with pulp during delignification and bleaching (Reeve, 1996b).

2.6.4 Alkaline extraction

Alkali has been used in the past to achieve several objectives in the bleaching process. In the first application cited, alkali was used to provide an optimum reaction pH for hypochlorite and simultaneously to provide conditions under which the reaction products could be hydrolysed and solubilised (Berry, 1996). However, it was later recognised that chlorine is more effective under acidic conditions, and so the oxidation step, chlorination, and the hydrolysis/solubilisation step, extraction, were separated. This led to the development of multiple-stage bleaching processes such as CEH and CEDED, where the oxidation and hydrolysis steps are separated (Berry, 1996).

The chemistry of alkaline extraction is very complex, and the following reactions are assumed to occur during the alkaline extraction of the chlorinated and/or oxidised pulp (Singh & Atkinson, 1979):

- (1) Solubilisation and removal of a major portion of the chlorinated lignin.
- (2) Removal of hemicellulose from the fibre.
- (3) Saponification of fatty acids and resin acids present in the pulp.
- (4) Degradation of the chain length of the polysaccharide component of the fibre.

For the producers of bleached Kraft pulps, the role of extraction is to remove the lignin made potentially soluble by the previous acidic oxidising stage, and to reactivate the pulp to further oxidation. Directly after pulping, the combination of a single acid oxidising stage and an extraction stage can remove as much as 90% of the remaining lignin (Berry, 1996). The alkali serves to neutralise acid carryover from the first stage; to hydrolyse chlorine bound to the pulp, which creates new phenolic groups; and to neutralise phenolic and other acidic groups in the pulp, which leads to ionisation and increased water solubility of lignin fragments (Reeve, 1996b).

Several hypotheses exist to explain the role of extraction in the reactivation of the pulp (Berry, 1996) - one hypothesis is that oxidation cannot continue further because of chemical deactivation of the remaining lignin in the pulp. Acidic oxidation leads to the modification of the molecular structure of lignin and creation of blocking groups that prevent further oxidation. These however, can be broken down under alkaline conditions. The role of alkaline extraction, according to this hypothesis, is to generate new active groups on the remaining lignin structure that allows reaction with the oxidising agent in the next stage.

Besides lignin, other pulp components such as cellulose and hemicellulose are also affected by the alkaline extraction stage. Available evidence indicates that some of the main reactions of wood pulp polysaccharides during alkaline extraction include dissolution/solubilisation, endwise degradation, stabilisation reactions, alkaline hydrolysis of glycosidic bonds, and xylan retake (Singh & Atkinson, 1979).

CHAPTER THREE

MATERIALS AND METHODS

3.1 FIELD SAMPLING

The material used in this study consisted of two *Eucalyptus* hybrid clones, *E. grandis* x *E. urophylla* (GU A380) and *E. grandis* x *E. camaldulensis* (GC G438). Each clone was sampled from two sites representing extreme differences in site quality. Site index (SI) gives an indication of site quality – a higher site index value corresponds to a favourable site for tree growth, and as a result, faster growing trees. The site quality was determined by assessing tree growth (height, mean annual increment and diameter at breast height) at five years and calculating a site index based on this data. Ten trees per compartment were felled and a 3m bottom billet was taken from each tree. The key characteristics of the compartments sampled for this study are listed in Table 3.1.

Table 3.1 Site characteristics.

Species	GU A380	GU A380	GC G438	GC G438
Site index	26.6	17.8	28.5	19.0
Site description	Good	Poor	Good	Poor
Plantation	Kwambo	Palmridge	Mavuya	Palmridge
Region	Zululand (south), KZN	Zululand (north), KZN	Zululand (south), KZN	Zululand (north), KZN
Age (years)	9	9	7	7
Mean DBH ^a (cm)	20.8	16.9	18.9	11.0
SD ^b DBH	2.2	1.4	1.5	1.1
Mean total height (m)	30.0	20.4	27.4	19.4
SD ^b total height	1.5	0.9	0.9	0.9

^a Diameter at breast height of trees at time of sampling
^b Standard Deviation

3.2 OVERVIEW OF EXPERIMENTAL DESIGN

Figure 3.2.1 describes an overview of the experimental design used in the study. After sampling, the ten billets from each compartment were chipped and combined into one sample before being pulped in a laboratory rotating digester, using the Kraft process. Multiple pulping experiments, using the same conditions, were carried out for each sample to ensure that there was sufficient unbleached pulp for the subsequent acid hydrolysis and bleaching experiments. The multiple cooks were screened to remove shives and combined into one composite sample, representative of the unbleached pulp for a particular clone and site. The screened unbleached pulps were then subjected to a dual oxygen delignification stage. Multiple oxygen delignification experiments, using the same conditions, were also carried out on each sample to ensure that there was sufficient oxygen delignified pulp for the subsequent acid hydrolysis and bleaching experiments. These pulps were also combined to produce a composite sample representative of the oxygen delignified pulp for a particular clone and site.

In order to determine the optimum conditions for maximum removal of HexA, but at the same time, with minimum impact on pulp quality, a single clone (GU) from the good site was chosen and subjected to acid hydrolysis in which the reaction conditions were varied. Selected acid hydrolysed pulps, containing varying amounts of HexA, were then chosen and individually bleached using an elemental chlorine-free sequence (D_0ED_1) to achieve a target brightness of 90% ISO. Oxygen delignified pulps that were not acid hydrolysed were also subjected to the same bleaching sequence and were used as controls in the study. Based on the response of the GU clone from the good site to the acid hydrolysis process, and on the quality of the resulting pulp after bleaching, the optimum conditions for acid hydrolysis were established. The optimum conditions were then applied to the remaining clones and sites.

Chemical analyses were carried out at the various stages in the process of converting the raw material to fully bleached pulp. The two major constituent monosaccharides of hardwoods (glucose and xylose) were determined in the wood in order to establish a baseline for these sugars. Viscosity, hemicellulose and HexA were measured in the unbleached, oxygen delignified, acid hydrolysed, and fully bleached pulps. Lignin content and Kappa number was measured up until, and including, the acid hydrolysis stage.

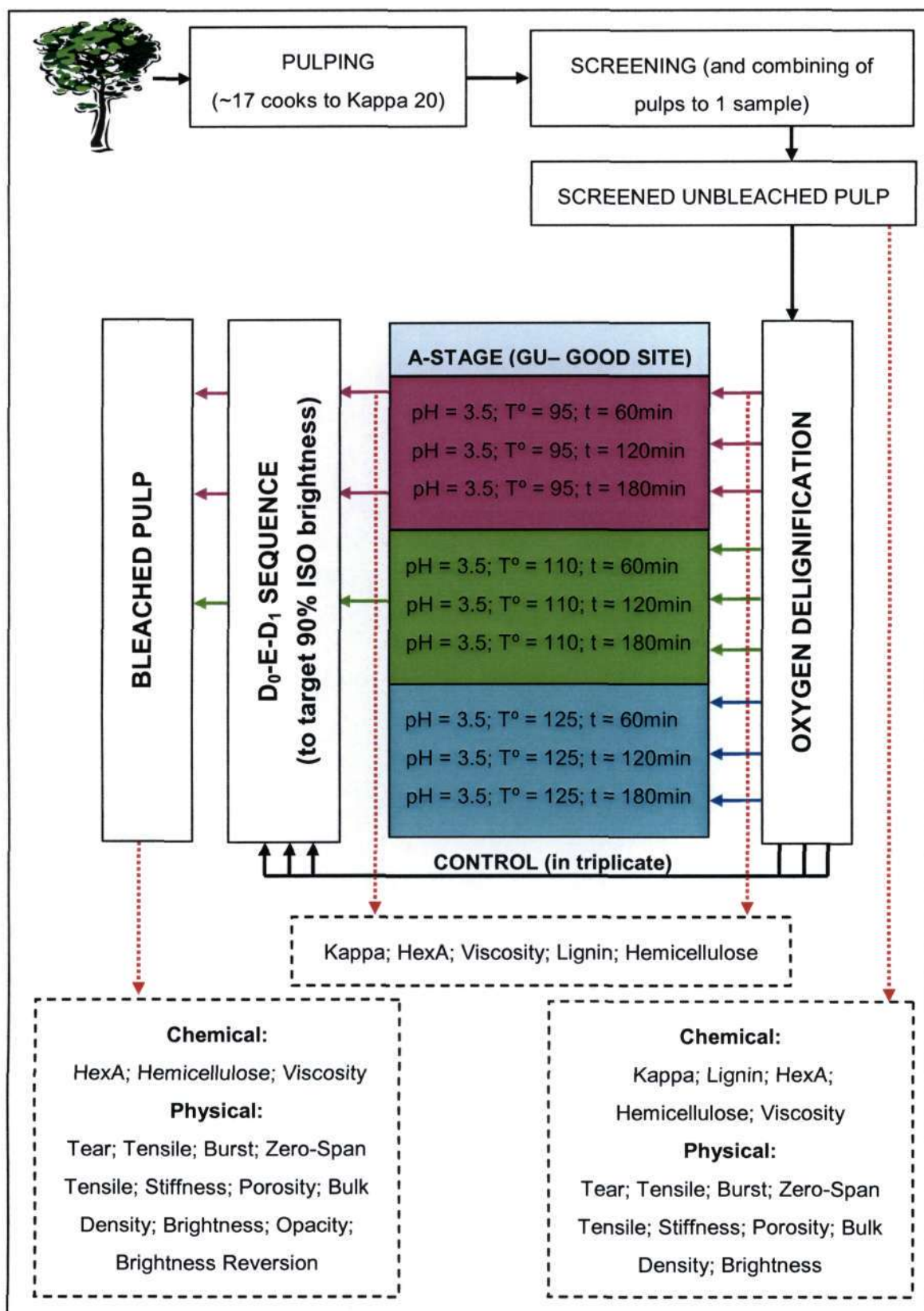


Figure 3.2.1 Flow diagram showing overview of experimental design.

In order to assess the papermaking potential of the pulps, the unbleached and fully bleached pulps were beaten in a PFI mill at three levels of refining (beating) and handsheets were prepared from the resulting pulps. An unbeaten pulp was used as a control. Brightness, sheet density, burst, tear, tensile, and zero-span tensile strength, stiffness and air resistance were measured on the handsheets produced from the unbleached and fully bleached pulps. In addition to the aforementioned properties, the fully bleached pulps were tested for brightness reversion and opacity.

3.3 KRAFT PULPING

The ten billets sampled of each clone from each site were chipped at the Sappi Saiccor dissolving pulp mill in Umkomaas, south of Durban. The chips were screened to remove knots and bark, and any over and under-sized chips. The screened chips were allowed to air-dry on custom built chip drying racks at the CSIR's Forestry and Forest Products Research Centre. The drying period was approximately three weeks which proved to be sufficient for the chips to reach equilibrium moisture with the atmosphere. The moisture content of the chips was determined by drying a representative sample of each clone from each site in an oven set at $105 \pm 2^{\circ}\text{C}$, to constant mass.

Pulping was carried out in electrically heated rotating digesters using the Kraft process. Eight hundred grams oven-dried equivalent chips per cook were pulped using the conditions summarised in **Table 3.2**. The pulping time required to achieve the target Kappa number of 20 (± 2) was obtained by determining the rate of delignification (ROD) of each clone from the different sites. The material used in the ROD study was obtained from an earlier sampling trip (Tsanwani, 2004a, b).

During pulping, the moisture content of the chips was taken into account in order to maintain a constant liquor-to-wood ratio of 4.5:1. The cooked chips were washed with tap water, under high pressure and through a 10-mesh (1.7mm) screen onto a 200-mesh ($75\mu\text{m}$) screen to separate the fibres from the rejects. Screenings remaining on the 10-mesh screen were considered as rejects. The pulp remaining on the 200-mesh screen was placed into a cotton bag with a drawstring and dewatered by spin drying for 10 minutes in a DEFY Twinmaid 920 top-loader washing machine. After dewatering, the pulp was removed from the cotton bag,

transferred to a tared plastic bag and weighed. The moisture content of the pulps was determined according to the TAPPI standard method T550 om-93 (Tappi, 1996a). The rejects remaining on the 10-mesh screen were oven-dried at $105 \pm 2^\circ\text{C}$ to constant mass. The screened pulp and rejects were measured and expressed as a percentage of their oven-dry mass over the oven dry mass of chips pulped, to give the percent screened pulp yield (%SPY) and percent rejects (%REJ).

Table 3.2 Standard conditions used for Kraft pulping.

Sulphidity (Na_2S)	25%
Mass of chips (oven dried equivalent)	800g
Active alkali (as Na_2O)/OD chips	18%
Liquor-to-wood ratio	4.5:1
Pulping cycle	
Time from ambient to maximum temperature (170°C)	90 minutes
Time at maximum temperature	varied
Target Kappa number	18-22
Degassing temperatures	120 and 140°C
Duration of blowdown to ambient pressure	20 minutes

The amount of cooking liquor used in each pulping experiment was dependant on the percent active alkali (AA) charge on oven-dried wood and was calculated using **Equation 3-1**.

$$\text{Liquor volume (ml)} = \left(\frac{\%AA}{100} \times \text{OD chips (g)} \right) \times \left(\frac{1000\text{ml/L}}{\text{Active Alkalinity (g/L)}} \right) \quad (3-1)$$

The active alkali of the cooking liquor was obtained by standardisation using the procedure described in **Appendix 2**. The amount of water used in each pulping experiment was dependant on the moisture content (MC) of the chips and on the liquor-to-wood ratio (L:W), and was calculated according to **Equation 3-2**.

$$\text{Vol. of water (ml)} = (L:W \times OD \text{ chips}) - (\text{liquor vol.} + MC \text{ of chips}) \quad (3-2)$$

Degassing, to remove gases not condensable in water, was carried out at 120°C and 140°C during the cook. Aliquots of black liquor (spent liquor) were taken at the end of each cook and were analysed for AA consumption according to the TAPPI standard method T625 cm-85 (Tappi, 1996b). The Kappa number of the pulps (uncorrected for HexA) was measured according to the TAPPI standard method T236 cm-85 (Tappi, 1996c).

Approximately seventeen replicate pulping experiments to a target Kappa number of 20 (± 2) were carried out for each clone from each site, using the predicted pulping times obtained from the ROD study. During screening of the pulps on a Somerville screen to remove shives, the pulps of each clone were combined into one pulp sample after a subsample had been taken for re-measurement of Kappa number (corrected for shive content and uncorrected for HexA). The calculation of the amount of bleaching chemicals used in the subsequent bleaching stages was based on the Kappa number result of the shive-free pulp.

3.4 PULP BLEACHING

The unbleached pulps were subjected to extended delignification (oxygen delignification) followed by a four stage bleaching sequence, AD₀ED₁, as described in **Table 3.3**. In the case of the control pulps, the A-stage was omitted, and the oxygen delignified pulps were subjected to a three stage, D₀ED₁ sequence.

Table 3.3 Symbolic notation and sequence used in bleaching experiments.

	Designation	Description
STAGE 1	O/O	Dual oxygen delignification – reaction with molecular oxygen at high pressure in alkaline medium
STAGE 2	A or AH	Acid hydrolysis – reaction in acidic medium with hydrochloric acid
STAGE 3	D ₀	1 st Chlorine dioxide addition – reaction with chlorine dioxide in acidic medium
STAGE 4	E	Alkaline extraction – dissolution of reaction products with sodium hydroxide
STAGE 5	D ₁	2 nd Chlorine dioxide addition – reaction with chlorine dioxide in acidic medium

3.4.1 Oxygen delignification

Medium consistency oxygen delignification was carried out in electrically heated rotating digesters employing a dual-stage process. Concern was initially expressed over the efficiency of the rotating digester to simulate medium consistency oxygen delignification. This was addressed in a separate study that compared the rotating digester to a quantum reactor at the Sappi Technology Centre (Govender, 2006). The results from this study showed that the rotating digester compared favourably to the quantum reactor and was suitable for simulation of medium consistency oxygen delignification in the laboratory. Other researchers have also reported the use of similar equipment (rotating autoclaves) for medium consistency oxygen delignification (Marcoccia *et al.*, 1996; Yang *et al.*, 2003; Leroy *et al.*, 2004; Tran, 2004).

During oxygen delignification, 350g oven-dried equivalent pulp was oxygen bleached using the conditions summarised in **Table 3.4**. The amount of sodium hydroxide required was calculated based on a Kappa factor of 0.125 using **Equation 3-3**. Magnesium sulphate (heptahydrate) was used as a cellulose protector and the amount required was calculated based on Mg, using **Equation 3-4**. Both chemicals were calculated on an oven dry pulp basis.

$$NaOH \text{ dosage (\%)} = Kappa \text{ number of unbleached pulp} \times Kappa \text{ factor} \quad 3-3$$

$$\text{Mg (\%)} = \frac{\text{Molecular mass of MgSO}_4 \cdot 7\text{H}_2\text{O}}{\text{Molecular mass of Mg}} \times \% \text{ Dosage}$$

3-4

Table 3.4 Conditions for two-stage oxygen delignification.

	1 st Oxygen Stage	2 nd Oxygen Stage
Temperature (°C)	87	98
Reaction time (min)	30	60
Oxygen pressure (kPa)	700	700
Consistency (%)	10	10
Kappa factor	0.125	0.125
MgSO ₄ dosage (%Mg)	0.1	0.1

The chemicals were dissolved in hot deionised water and mixed with the pulp at 10% consistency. The pulp was added to a preheated digester and purged three times with medical grade oxygen. The oxygen pressure was thereafter maintained at 700kPa for both stages. The temperature of the first stage was held constant at 87°C for 30 minutes. It was then ramped up to 98°C in the second stage, and was held constant at this temperature for a further 60 minutes.

Upon completion of the oxygen delignification stage, the pulp was removed from the digester and washed under vacuum on a Büchner flask and funnel using deionised water. Prior to washing, an aliquot of the undiluted filtrate was taken for pH measurement. The washed pulp was dewatered by spin drying for 10 minutes. The moisture content (Tappi, 1996a) and Kappa number uncorrected for HexA (Tappi, 1996c), was then measured on the pulp. The pulp yield was expressed as a percentage of the oven-dried mass of oxygen delignified pulp over the oven-dried mass of brown pulp initially used.

3.4.2 Acid hydrolysis

In order to determine the acid hydrolysis conditions that resulted in maximum removal of HexA but with minimum impact on pulp quality, a range of conditions in which the temperature and reaction time was varied, was applied to the GU clone

from the good site (**Table 3.5**). The acid hydrolysis procedure was carried out in triplicate for each temperature and reaction time, and the pH was kept constant at 3.5 for all experiments. Once the optimum set of conditions was determined, these conditions were applied to the remaining clones from the different sites.

A solution of hydrochloric acid was used to lower the pH of the pulp to 3.5. The acid hydrolysis step was carried out at 10% pulp consistency in the rotating digesters that were used for pulping. The digesters were acid washed with 1% hydrochloric acid solution prior to use.

Upon completion of the acid hydrolysis step, the pulp was removed from the digester and transferred to a Büchner funnel attached to a Büchner flask. An undiluted aliquot of the filtrate was taken for pH measurement prior to washing the pulp with deionised water. The washed pulp was dewatered by spin drying for 10 minutes. The moisture content (Tappi 1996a) and Kappa number uncorrected for HexA (Tappi, 1996c) was then measured on the pulp. The pulp yield was expressed as a percentage of the oven-dried mass of the acid hydrolysed pulp over the oven-dried mass of oxygen delignified pulp initially used.

Table 3.5 Acid hydrolysis conditions applied to GU clone from good site to determine the optimum conditions for HexA removal.

pH	Temp (°C)	Reaction time (min)	No. of Replicates
3.5	95	60	3
3.5	95	120	3
3.5	95	180	3
3.5	110	60	3
3.5	110	120	3
3.5	110	180	3
3.5	125	60	3
3.5	125	120	3
3.5	125	180	3

3.4.3 Chlorine dioxide (D₀ and D₁ stages)

The chlorine dioxide dosage was split over two D-stages, D₀ (70%) and D₁ (30%). The conditions used in both stages are summarised in **Table 3.6**.

Table 3.6 Conditions for chlorine dioxide bleaching.

Pulp consistency (%)	8
ClO ₂ dosage (%)	K _f x Kappa no. after A or O ₂ stage
Reaction time (min)	120
Temperature (°C)	70
Pressure	Ambient
K _f – Kappa factor	

Chlorine dioxide bleaching was carried out in plastic bags in a thermostatted water-bath set at 70°C. The reaction time was 120 minutes for both stages. The chlorine dioxide solution was obtained from the Sappi Saiccor mill, and the concentration was determined according to the standardisation procedure described in **Appendix 3**. The chlorine dioxide dosage was calculated from the Kappa factor (K_f), which was varied to achieve the target brightness of 90% ISO, as well as from the Kappa number after acid hydrolysis or oxygen delignification. The dosage was calculated using **Equations 3-5 to 3-7**.

$$\% \text{ ClO}_2 \text{ dosage (as active chlorine)} = \text{Kappa No.} \times K_f \quad 3-5$$

$$\text{Mass of ClO}_2 \text{ (g)} = \frac{\% \text{ ClO}_2 \text{ (as active chlorine)}}{100\%} \times \text{mass of pulp (g)} \quad 3-6$$

$$\text{Vol. of ClO}_2 \text{ to add (ml)} = \frac{\text{Mass of ClO}_2 \times 1000\text{ml}}{\text{Conc. of ClO}_2} \quad 3-7$$

Bleaching was carried out at 8% consistency, and the volume of deionised water required was calculated using **Equation 3-8**.

$$\text{Vol. of water (ml)} = \text{vol. at 8\% cons.} - \text{mass of pulp} - \text{vol. of ClO}_2$$

3-8

At the end of the reaction period, the pulp was transferred to a Büchner funnel attached to a Büchner flask. The pulp was washed under vacuum with deionised water. Prior to washing, an undiluted aliquot of the filtrate was taken for pH and chlorine dioxide consumption measurement. The washed pulp was dewatered by spin drying for 10 minutes, and the pulp moisture content was determined using the TAPPI standard method T550 om-93 (Tappi, 1996a). The pulp yield was expressed as a percentage of the oven-dried mass of the bleached pulp over the oven-dried mass of the pulp initially used. The chlorine dioxide consumption, expressed as the percent total active chlorine (%TAC) was determined according to the procedure described in **Appendix 3**.

3.4.4 Alkaline extraction

The alkaline extraction stage was carried out using the conditions summarised in **Table 3.7**.

Table 3.7 Conditions for alkaline extraction.

Pulp consistency (%)	8
NaOH dosage (%)	1.5
Reaction time (min)	60
Temperature (°C)	70
Pressure	Ambient

Alkaline extraction was also carried out at 8% pulp consistency, and the sodium hydroxide dosage was 1.5% based on an oven dry pulp basis. The extraction was carried out in plastic bags in a thermostatted water-bath set at 70°C for a reaction period of 60 minutes. On completion of the reaction, the pulp was transferred to a Büchner funnel attached to a Büchner flask. An undiluted aliquot of the filtrate was taken for pH measurement prior to washing the pulp under vacuum with deionised water. The washed pulp was dewatered by spin drying for 10 minutes, and the pulp

moisture content was determined using the TAPPI standard method T550 om-93 (Tappi, 1996a). The pulp yield was expressed as a percentage of the oven-dry mass of the bleached pulp over the original oven-dry mass of the pulp used in the alkaline extraction stage.

3.5 CHEMICAL PROPERTIES OF WOOD AND PULP

A representative sample of chips of each clone was randomly taken in triplicate. The chips were examined to ensure that they were free of bark, knots, tension and compression wood. The conversion of the wood chips into sawdust for chemical analysis involved a three-step procedure in which the chips were first passed through a hammer-mill, and then a Wiley-mill, before finally being screened into the different particle size fractions using a vibratory screener. According to the TAPPI standard method T257 cm-85 (Tappi, 1996d), only sawdust that passed through the 40 mesh (0.40mm) screen was used in the chemical analysis.

The relative amounts of the two major constituent monosaccharides of hardwoods (glucose and xylose) were determined by acid hydrolysis of the wood or pulp (TAPPI T249 cm-85) (Tappi, 1996e) followed by separation using High Performance Anion Exchange Chromatography (HPAEC) coupled with Pulsed Amperometric Detection (PAD). A full description of this method is given in **Appendix 4**. Lignin in pulp was determined using a modification of the TAPPI standard method T249 cm-85 (Tappi, 1996e), in which the hydrolysate from the acid hydrolysis step used in the determination of the monosaccharides, was quantitatively filtered under vacuum through a 0.45 μ m filter paper. The material remaining on the filter paper was defined as Klason lignin. The pulp viscosity was determined at the Sappi Saiccor mill using a modification of the TAPPI standard method T206 05-63 (Tappi, 1971). A full description of this method is given in **Appendix 5**.

Hexenuronic acid in pulp was determined using the method developed by Chai *et al.* (2001) at the Institute of Paper Science and Technology (IPST). A summary of this procedure is as follows: Approximately 0.05g of air dried pulp handsheets with known moisture content were accurately weighed and placed into 20ml vials. Ten millilitres of hydrolysis solution, consisting of 0.6% mercuric chloride and 0.7% sodium acetate, was added to each vial containing the pulp sample. The vials were sealed and the fibres were dispersed in the hydrolysis solution by handshaking. The vials were then

placed in a waterbath set at 60°C for a reaction time of 30 minutes. At the end of the reaction period, the vials were cooled to room temperature and the hydrolysis solution was filtered using a plastic syringe and 0.45µm syringe filter. Ultraviolet absorption measurements were made in matched 10mm path length silica cells using a UV-VIS diode array spectrophotometer scanning from 200 to 400nm at a scan rate of 100nm/min. An absorption maximum occurs at 260nm which corresponds to the UV absorption of HexA.

Calibration was done using a standard pulp sample obtained from the Royal Institute of Technology (KTH) in Sweden. The concentration of HexA in the standard pulp was 59µmol/g and was determined at the KTH laboratories using the method developed by Gellerstedt & Li (1996). This method involved a selective hydrolysis step with mercuric acetate, and quantification of HexA was carried out using HPLC separation and measurement of the absorbance of the coloured product formed at 549nm.

Six standards with concentration 0.01; 0.02; 0.04; 0.06; 0.08 and 0.10mol/L HexA were prepared by weighing out appropriate amounts of the standard pulp sample and subjecting it to the procedure described above. The absorbance for each standard was recorded and a calibration curve was constructed, from which the molar absorptivity was calculated. Possible interference due to leaching of lignin during hydrolysis was corrected for by subtracting 1.2 times the absorbance at 290nm from the absorbance at 260nm (Chai *et al.*, 2001). Using a modification of Beer's Law (Equation 3-9), the concentration of HexA in pulp was calculated.

$$A_{260} - (1.2 \times A_{290}) = \epsilon bc \quad 3-9$$

where,

A_{260} and A_{290} = absorbance at 260nm and 290nm, respectively

ϵ = molar absorptivity, L/cm/mol

b = path length, cm

c = concentration of HexA, mol/L

(WARNING: Mercuric chloride is classified as extremely toxic. It poses serious risk of poisoning by inhalation, swallowing or skin contact. There is also the danger of

cumulative effects resulting from prolonged exposure. It is imperative that personal protective equipment such as safety goggles, gloves and dustcoats be worn at all times when working with it. A comprehensive material safety data sheet for mercuric chloride can be obtained from <http://www.jtbaker.com>. Mercuric chloride is also dangerous to the environment and disposal must be made according to official regulations. In this project, the mercuric chloride waste was collected in two-litre glass bottles, and when sufficient waste chemicals were accumulated, they were disposed off via Enviroserve, which is one of the approved hazardous chemical waste service providers for the CSIR).

3.6 PHYSICAL PROPERTIES OF PULP

The physical properties of the pulp were assessed by preparing and testing handsheets. Pulps were beaten in a PFI mill at 10% consistency for 1000, 3000 and 5000 revolutions. Unbeaten pulps (0 revolutions) were used as controls. The freeness of the pulps at each level of beating was determined according to the Canadian Standard Freeness (CSF) method using the TAPPI standard method T227 om-94 (Tappi, 1996f). Handsheets with a basis weight of 60g/m² were prepared on a Rapid Köthen sheet-forming machine using a combination of the TAPPI standard method T205 sp-96 (Tappi, 1996g) and the ISO standard method ISO 5269-1 (ISO, 1998). This procedure involved one pressing and heated drying of the handsheets.

Twelve handsheets per level of beating were prepared and allowed to condition in an atmosphere controlled at 23 ± 1°C and 50 ± 2% relative humidity for at least 24 hours. The conditioned handsheets were then tested for the properties listed in **Table 3.8**.

Table 3.8 Measured properties, methods and equipment.

Measured Property	Test Method	Equipment
Grammage	Tappi T220 sp-96 (Tappi, 1996h)	Analytical balance
Sheet Density	Tappi T220 sp-96 (Tappi, 1996h)	L&W micrometer
Burst index	Tappi T403 om-91 (Tappi, 1996i)	L&W burst-o-matic
Tear index	Tappi T414 om-88 (Tappi, 1996j)	Messmer Büchel digi-tear
Tensile index	Tappi T494 om-88 (Tappi, 1996k)	Regmed DI-21 tensile tester
Zero-span tensile index	Tappi T231 cm-96 (Tappi, 1996l)	Regmed DI-21 tensile tester
Bending resistance (stiffness)	ISO 2493 (ISO, 1992)	L&W SE016 stiffness tester
Air resistance (porosity)	Tappi T460 om-96 (Tappi, 1996m)	Elof Hansson gurley meter
Brightness reversion	Tappi T260 om-91 (Tappi, 1996n)	Elrepho reflectance meter
Diffuse opacity	Tappi T519 om-96 (Tappi, 1996o)	Elrepho reflectance meter

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 KRAFT PULPING

Besides the influence of process variables such as liquor-to-wood ratio, active alkali concentration, sulphidity, pulping time, and temperature on the rate of delignification (ROD) of wood (Kerr, 1970), other variables such as species, origin, age, and growing environment are also known to play an important role (Clarke *et al.*, 1998). The first step in this study was therefore to determine the ROD of the clones from the different sites, using a specified set of pulping conditions. This was achieved by subjecting each clone from each site to 4 different pulping times (10, 25, 50 and 90 minutes) at maximum temperature, whilst keeping the other conditions constant. From this the approximate pulping time at maximum temperature required for each clone to reach a target Kappa number of 20 (± 2) was obtained. The resulting pulp properties (**Table 4.1**) were tested for significant differences using analysis of variance (ANOVA) and Duncan multiple range tests at a 95% confidence level. As expected, site quality had a significant impact on the ROD, with both clones from the poor sites requiring longer pulping times to reach the target Kappa number. Due to the longer pulping times required by these clones, active alkali consumptions were significantly higher, whilst rejects were lower. For the GU clones, screen pulp yield was significantly higher on the good site compared to the poor site. An opposite trend was found for the GC clones, with the clones from the poor site showing a significantly higher screen pulp yield.

Table 4.1 Pulp properties at Kappa number 20 for GU and GC clones from good and poor sites.

	GU(poor site)	GU(good site)	GC(poor site)	GC(good site)
Site index	17.8	26.6	19.0	28.5
Pulping time at 170°C	50min	25min	90min	35min
Number of cooks	17	17	15	16
%SPY (std dev.)	47.5 (0.36)	50.9 (0.37)	50.8 (0.87)	49.4 (0.60)
%REJ (std dev.)	0.7 (0.23)	2.6 (0.75)	0.1 (0.07)	1.5 (0.80)
%AA consumption (std dev.)	96.8 (0.10)	96.2 (0.16)	99.4 (0.11)	91.8 (0.80)
SPY – screened pulp yield; REJ – rejects; AA – active alkali; std dev. – standard deviation				

4.2 OXYGEN DELIGNIFICATION

The unbleached pulps of each clone from the different sites were then subjected to a dual oxygen delignification stage. The Kappa numbers before and after oxygen delignification, together with the pulp yields after oxygen delignification, are presented in **Table 4.2**. The GU clone from the good site was chosen to optimise the conditions of the A-stage, and as a result, a large number of oxygen delignification trials were carried out using this clone to ensure that there was sufficient material available for the subsequent optimisation studies.

The results in **Table 4.2** shows that the GU clone from the good and poor sites achieved approximately 44% and 48% delignification respectively, whilst the GC clone achieved a similar degree of delignification for both sites (52%). According to Pikka *et al.* (1996) and Yang *et al.* (2003), with two-stage oxygen delignification it is possible to achieve a degree of delignification exceeding 45% without compromising the physical characteristics of the pulp. Pikka *et al.* (1996) reported Kappa reductions between 45-55% for hardwoods using two-stage oxygen delignification. A similar degree of delignification using two-stage oxygen delignification has been reported by other researchers (Li *et al.*, 1996; Leroy *et al.*, 2004; Tran 2004). In terms of pulp yield, the GU and GC clones from the poor sites showed 0.5% and 1.1% lower pulp yield respectively, after oxygen delignification, compared to their corresponding clones from the good sites.

Table 4.2 Results of oxygen delignification.

Clone	No. of Trials	KN (UB)	KN (OD)	Std Dev. (KN OD)	%CV (KN OD)	%PY (OD)	Std Dev. (PY OD)	% CV (PY OD)
GU (GS)	24	20.13	11.25	0.24	2.17	97.71	1.64	1.67
GU (PS)	13	21.72	11.24	0.39	3.50	97.21	0.36	0.37
GC (GS)	7	20.12	9.60	0.25	2.58	99.04	0.70	0.70
GC (PS)	13	19.36	9.23	0.23	2.54	97.94	0.42	0.43

KN – Kappa number; UB – unbleached pulp; OD – oxygen delignified pulp;
PY – pulp yield; CV – coefficient of variation; GS – Good Site; PS – Poor site

4.3 ACID HYDROLYSIS

4.3.1 Defining the acid hydrolysis conditions

As part of a preliminary investigation, the oxygen delignified pulp of the GU clone from the good site was acid hydrolysed at three temperatures (95, 110 and 125°C), and at a fixed pH of 3.5 and reaction time of 180 minutes. This was done in order to understand the response of the material to the acid hydrolysis procedure by determining the upper temperature limit that resulted in maximum removal of HexA. The acid hydrolysed pulps, together with the unbleached and oxygen bleached pulps were sent to KTH for HexA analysis, as the method for measurement of HexA was not standardised at the CSIR at that time. The procedure used for the analysis at KTH was according to Gellerstedt & Li (1996), and the results of this analysis are listed in **Table 4.3**.

Table 4.3 Preliminary HexA results from KTH for acid hydrolysed pulps of GU clone from good site. The standard deviation is given in brackets.

Pulp Type	pH	Temperature (°C)	Reaction Time (min)	HexA (µmol/g)
Unbleached	--	--	--	56.0 (1.67)
Oxygen delignified	--	--	--	52.9 (0.52)
Acid hydrolysed	3.5	95	180	23.3 (0.38)
Acid hydrolysed	3.5	110	180	6.30 (0.64)
Acid hydrolysed	3.5	125	180	1.80 (0.62)

The oxygen delignified pulps showed a slight reduction in HexA content compared to the unbleached pulps (3.1 $\mu\text{mol/g}$). This is consistent with studies carried out by various researchers who showed that HexA are unreactive during oxygen delignification, and therefore the concentration should essentially remain unchanged after oxygen delignification (Buchert *et al.* 1995; Gellerstedt & Li, 1996; Vuorinen *et al.*, 1999; Süess *et al.*, 2005a). During acid hydrolysis at a temperature of 95°C, there was a 58% reduction in the HexA content, and this reduction was further increased to 88% at a temperature of 110°C. At 125°C essentially all of the HexA were removed, with 3.2% (1.80 $\mu\text{mol/g}$) remaining in the pulp.

Based on these results, the conditions for the A-stage employed in this study are listed in **Table 4.4**. These conditions were again only applied to the GU clone from the good site to determine the optimum conditions that resulted in maximum removal of HexA and with minimum impact on pulp quality. Each set of conditions was run in triplicate. Once the optimum conditions were established, they were applied to the remaining clones from the different sites in order to understand their response to these conditions.

Table 4.4 Conditions for acid hydrolysis stage applied to GU clone from the good site.

pH	Temperature (°C)	Reaction Time (min)
3.5	95	60, 120, 180
3.5	110	60, 120, 180
3.5	125	60, 120, 180

4.3.2 Measurement of hexenuronic acid

Several methods have been developed over the years for the quantification of HexA in Kraft pulps (Vuorinen *et al.*, 1996; Gellerstedt & Li, 1996; Tenkanen *et al.*, 1999; Jiang *et al.*, 2001; Chai *et al.*, 2001; Evtuguin *et al.*, 2002; Saariaho *et al.*, 2003; Jääskeläinen *et al.*, 2005; Hoang *et al.*, 2005). The choice of method to be used in this study therefore depended on several factors such as the availability of equipment, cost of chemicals, simplicity of the procedure, and speed of analysis. Initially it was decided to use the method developed by Gellerstedt & Li (1996) at

KTH. This method is a colorimetric method based on the selective hydrolysis of the glucosidic link between HexA and the xylan chain. This degradation technique involves several treatment steps with mercuric acetate, periodate, sodium arsenite and reaction with thiobarbituric acid to yield a pink product. Quantification is carried out by chromatographic separation and/or visible spectroscopy, with an absorption maximum at 549nm.

However, Chai *et al.* (2001) from IPST described a simple and more rapid technique that is also based on the selective hydrolysis of HexA, but using a mercuric chloride-sodium acetate solution. The amount of HexA, in this method, is directly determined by UV absorbance of the hydrolysis solution at 260nm. Chai *et al.* (2001) used the KTH method proposed by Gellerstedt & Li (1996) to calibrate their method. Due to the relative simplicity of this method and availability of equipment, it was decided to use the method developed at IPST for HexA determination. The IPST method is well documented in literature where various researchers have made use of the method in their studies (e.g. Pedroso & Carvalho, 2003; Petit-Breuilh *et al.*, 2004; Shin *et al.*, 2005). The method was also used as a reference to calibrate a Fourier transform infra-red (FTIR) method (Hoang *et al.*, 2005) for the quantification of HexA.

For the purpose of an inter-laboratory study, five pulp samples representing varying concentrations of HexA were prepared according to **Table 4.5**. These pulps were sent, in triplicate, to IPST to be analysed using the method proposed by Chai *et al.* (2001), and they were also analysed at the CSIR using the same method.

Table 4.5 Samples prepared for inter-laboratory study.

Sample	pH	Temperature (°C)	Reaction Time (min)
Unbleached	--	--	--
Oxygen bleached	--	--	--
Acid hydrolysed	3.5	95	180
Acid hydrolysed	3.5	110	180
Acid hydrolysed	3.5	125	180

Similar to Chai *et al.* (2001), a standard unbleached pulp sample with known HexA content was obtained from KTH to calibrate the method at the CSIR. **Figure 4.3.1**

shows the calibration curve that was obtained. The curve follows Beer's Law very well, and the value obtained for the molar absorptivity of the hydrolysis products in the hydrolysis solution was 4.54×10^3 L/cm/mol. Chai *et al.* (2001) quoted a similar value of 4.25×10^3 L/cm/mol.

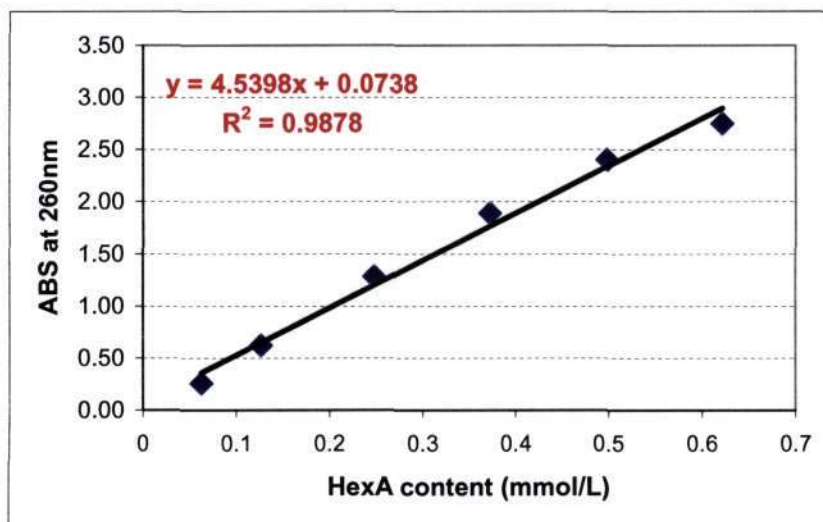


Figure 4.3.1 Calibration curve produced at the CSIR using standard pulp from KTH.

The inter-laboratory samples were also sent to KTH, as an independent laboratory, to analyse the samples using the KTH method (Gellerstedt & Li, 1996). The results of the inter-laboratory study between CSIR, KTH and IPST are depicted in **Figures 4.3.2 – 4.3.4**, and show good correlation between laboratories using the same method (IPST & CSIR) and also between laboratories using different methods (CSIR & KTH and IPST & KTH).

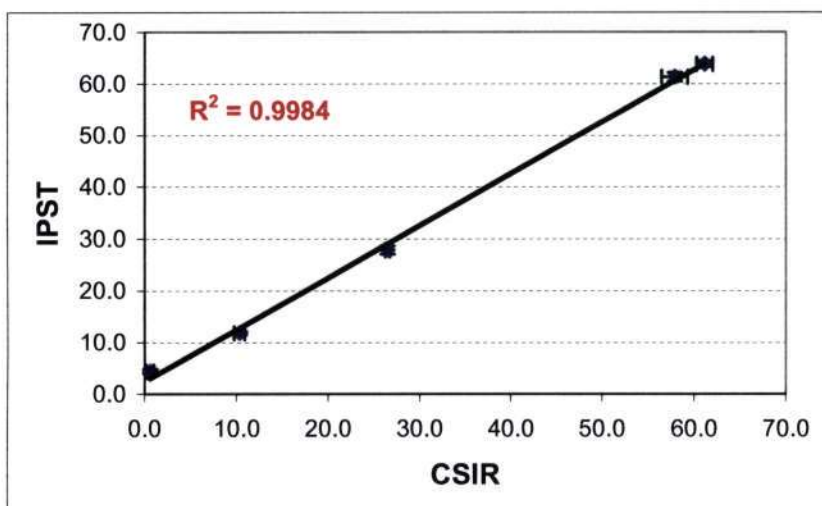


Figure 4.3.2 Correlation of inter-laboratory results between IPST and CSIR using the same method, as described by Chai et al. (2001). The unit of measurement is $\mu\text{mol/g}$ and each point represents the mean of three measurements, with the whiskers as the standard deviation.

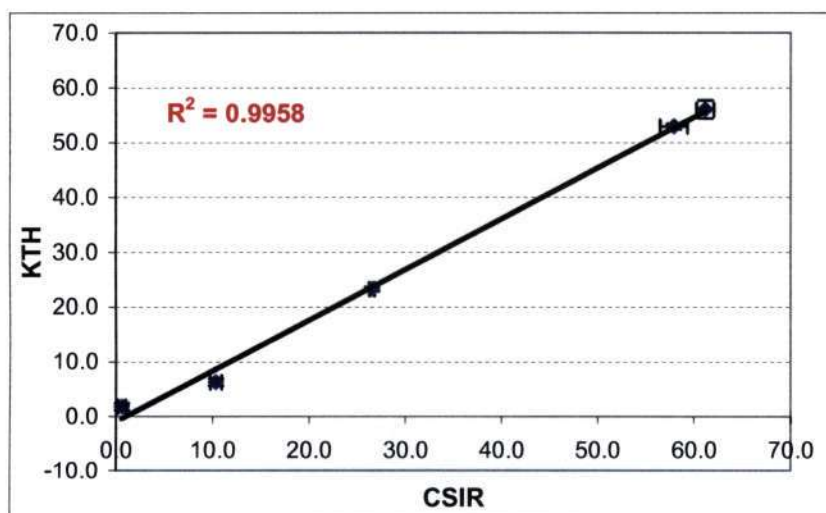


Figure 4.3.3 Correlation of inter-laboratory results between CSIR, using the method described by Chai et al. (2001), and KTH, using the method described by Gellerstedt & Li (1996). The unit of measurement is $\mu\text{mol/g}$ and each point represents the mean of three measurements, with the whiskers as the standard deviation.

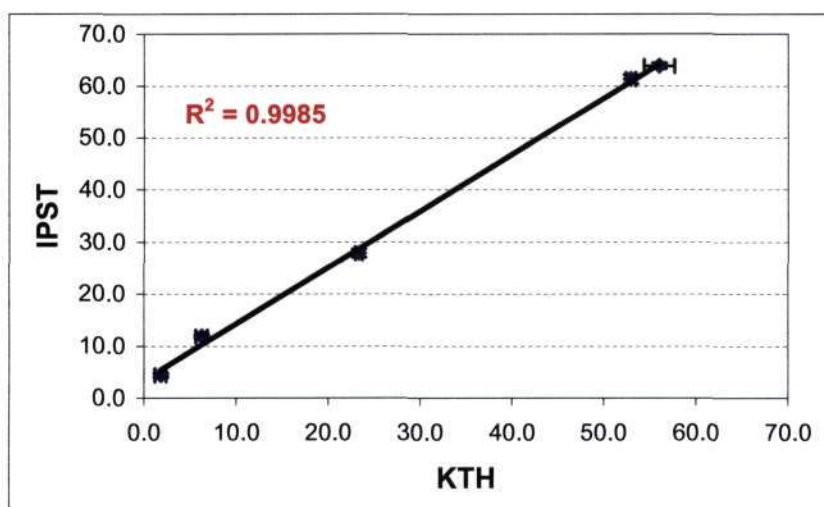


Figure 4.3.4 Correlation of inter-laboratory results between IPST, using the method described by Chai *et al.* (2001), and KTH, using the method described by Gellerstedt & Li (1996). The unit of measurement is $\mu\text{mol/g}$ and each point represents the mean of three measurements, with the whiskers as the standard deviation.

4.3.3 Optimisation of A-stage conditions using GU clone from good site

Using the conditions defined in **Table 4.4**, the oxygen delignified pulp of the GU clone from the good site was subjected to acid hydrolysis in which the temperature and reaction times were varied. The objective of this part of the study was to determine the conditions of the A-stage that resulted in maximum removal of HexA but with minimum impact on pulp quality. Once the optimum conditions were determined, they were applied to the remaining GU clone from the poor site and the GC clones from the good and poor sites.

4.3.3.1 Effect of A-stage on hexenuronic acid content of pulp

The HexA content decreased during acid hydrolysis, as the temperature and reaction time of the A-stage was increased (**Figure 4.3.5**). The unbleached and oxygen delignified pulps showed no significant difference in HexA content due to its un-reactivity during oxygen delignification (Buchert *et al.*, 1995; Gellerstedt & Li, 1996; Vuorinen *et al.*, 1999; Shin *et al.*, 2005; Süess *et al.*, 2005a, b). At 95°C there was a

significant drop in the concentration of HexA with increasing reaction time, and this decreasing trend continued until 110°C-120min, where approximately 95% of HexA was removed. Beyond this point, increasing the temperature and reaction time had little effect on the concentration of HexA in the pulp. Using a temperature of 110°C, but with a shorter reaction time of 60 minutes for acid hydrolysis, Vuorinen *et al.* (1999) reported approximately 90% reduction in HexA concentration. In this present study, under the same conditions used by Vuorinen *et al.* (1999), a reduction of 88% was achieved.

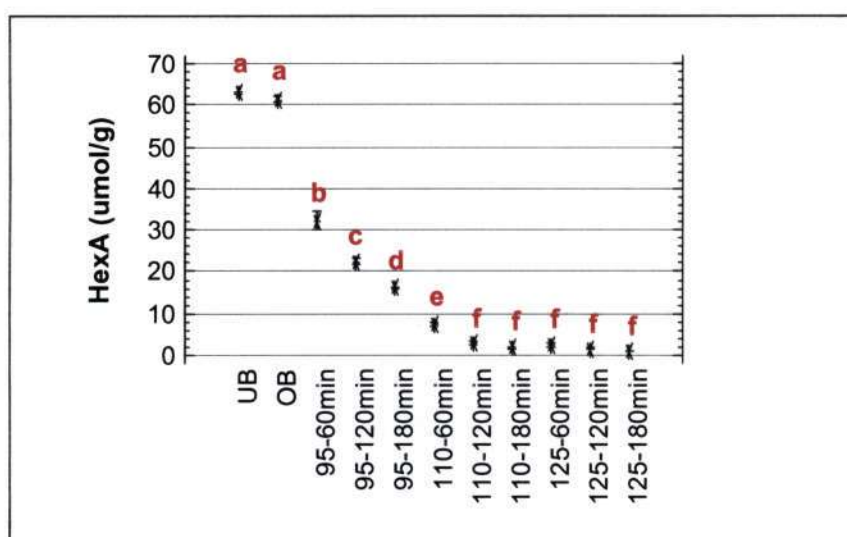


Figure 4.3.5 Effect of acid hydrolysis on hexenuronic acid (HexA) content of pulp of GU clone from good site. Each point represents the mean HexA content of 3 individual acid hydrolysis experiments, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels. (UB – unbleached, OB – oxygen bleached).

4.3.3.2 Effect of A-stage on Kappa number of pulp

An increase in temperature and reaction time during acid hydrolysis significantly reduced the Kappa number of the oxygen delignified pulp (**Figure 4.3.6**). At 125°C-180min, the Kappa number was reduced by 6.5 units, from 11.3 to 4.8. The reason for this decrease was due largely to the removal of HexA which is known to consume potassium permanganate in the Kappa number test (Li & Gellerstedt, 1997; Li *et al.*, 2002).

From **Figure 4.3.5** above, it was found that the reduction in the concentration of HexA during acid hydrolysis reached a maximum at 110°C-120min, beyond which there was no further decrease. The Kappa number on the other hand, continued to drop significantly beyond this point. A possible explanation for this is the removal of lignin during acid hydrolysis resulting in the Kappa number of the pulp continuing to decrease.

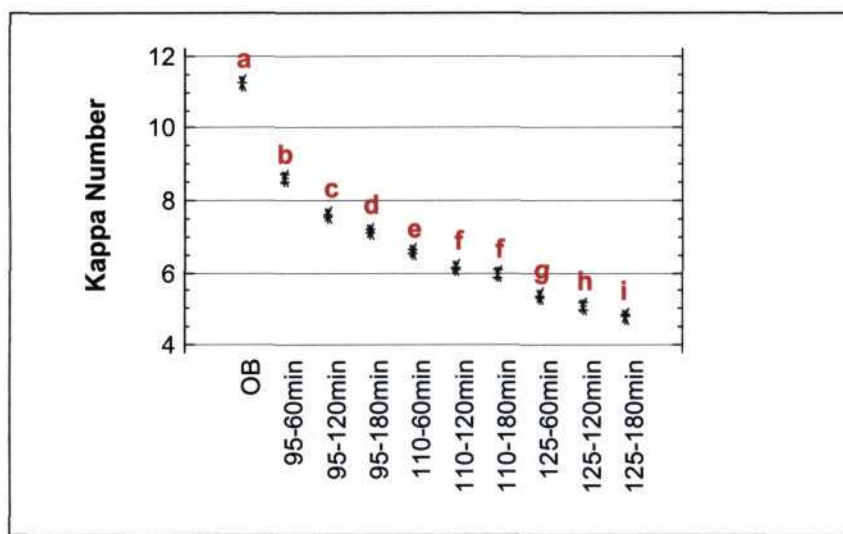


Figure 4.3.6 Effect of acid hydrolysis on Kappa number of pulp of GU clone from good site. Each point represents the mean Kappa number of 3 individual acid hydrolysis experiments, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels. (OB – oxygen bleached).

4.3.3.3 Effect of A-stage on chemical composition of pulp

As expected, the concentration of lignin dropped significantly after oxygen delignification (**Figure 4.3.7**). During acid hydrolysis at 95°C-60min, a further loss in lignin was observed (~0.4%), which was probably as a result of the partial degradation and condensation of lignin in the acidic medium (Furtado *et al.*, 2001). Beyond this point however, the lignin content appeared to remain fairly constant during acid hydrolysis even with further increase in temperature and reaction time of the A-stage. This is important because it showed that the decrease in Kappa number during acid hydrolysis was due largely to the decrease in the concentration of HexA

and not to the removal of lignin.

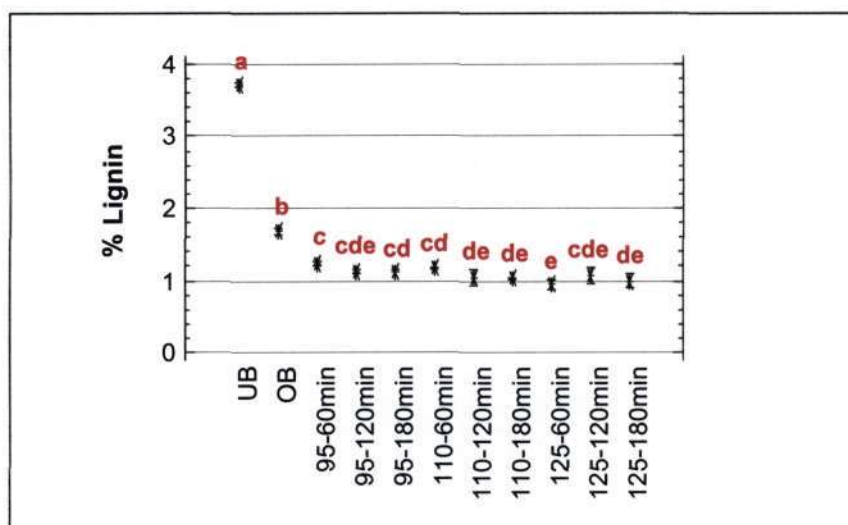


Figure 4.3.7 Effect of acid hydrolysis on the lignin content of pulp of GU clone from good site. Each point represents the mean lignin content of 3 individual acid hydrolysis experiments, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels. (UB – unbleached, OB – oxygen bleached).

The glucose and xylose content, expressed as a percentage in wood, is illustrated in **Figure 4.3.8**. After pulping, the glucose content dropped to approximately 37% in the unbleached pulp, and remained fairly constant at this value during oxygen delignification and acid hydrolysis. The xylose content after pulping dropped to approximately 6%, and also appeared to stabilise around this value during oxygen delignification and acid hydrolysis. Both glucose and xylose content of the pulps hydrolysed at 125°C-180min showed no significant differences to the unbleached pulps. This is also important because it showed that oxygen delignification was selective for lignin with minimal or no impact on the carbohydrates. More importantly however, it showed that the acid hydrolysis procedure also had little or no impact on the carbohydrate content.

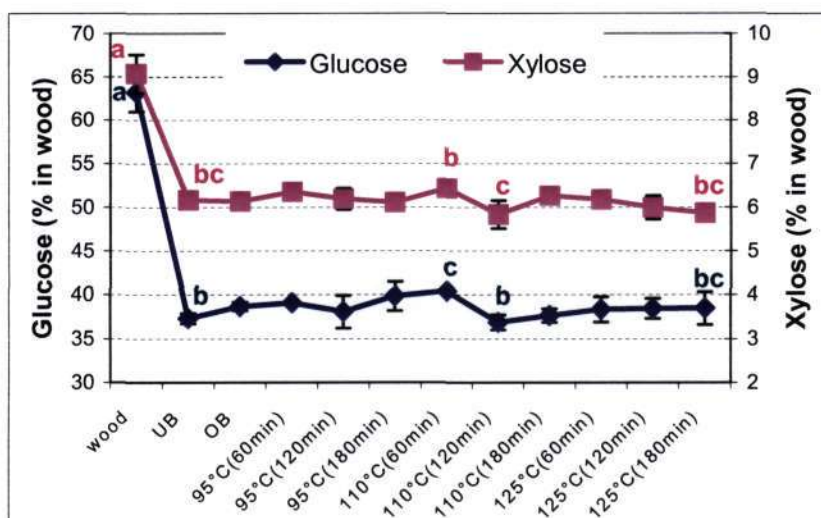


Figure 4.3.8 Effect of acid hydrolysis on glucose and xylose content of pulp of GU clone from good site. Each point represents the mean glucose or xylose content of 3 individual acid hydrolysis experiments, with the whiskers as the standard deviation. Common letters indicate no significant differences amongst the means, at 95% confidence levels, and are only applicable within a specific colour. (UB – unbleached, OB – oxygen bleached).

4.3.3.4 Effect of A-stage on pulp viscosity

Acid hydrolysis affected the cellulose degree of polymerisation (DP), as shown by the reduction in viscosity with increasing temperature and reaction time of the A-stage (**Figure 4.3.9**). The decrease was found to be more pronounced at higher temperatures, with the viscosity reduction exceeding 50% at 125°C compared to the pulps hydrolysed at 95°C. Similar findings were reported by Petit-Breuilh *et al.* (2004) using severe A-stage conditions. For the pulps hydrolysed at 95°C and 110°C, the viscosity was significantly lower compared to the oxygen delignified and unbleached pulps, but appeared to have stabilised at these temperatures. At 125°C, further losses in viscosity occurred with increasing reaction time, and were significantly lower than the viscosity at 95°C and 110°C.

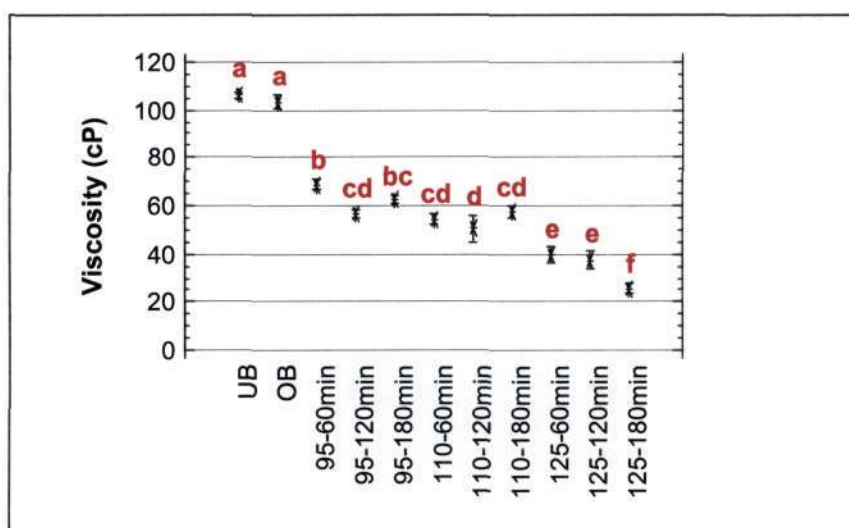


Figure 4.3.9 Effect of acid hydrolysis on the viscosity of pulp of GU clone from good site. Each point represents the mean viscosity of 3 individual acid hydrolysis experiments, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels. (UB – unbleached, OB – oxygen bleached).

4.3.3.5 Effect of A-stage on yield

Pulp yield after acid hydrolysis decreased steadily as the temperature and reaction times of the A-stage increased (**Figure 4.3.10**). Overall, there was approximately 2% decrease in yield as the temperature was increased from 95°C to 125°C. Similar to the reduction in viscosity shown in **Figure 4.3.9**, the drop in yield was more pronounced at the higher temperature, with the pulps hydrolysed at 95°C and 110°C showing no significant difference in yield.

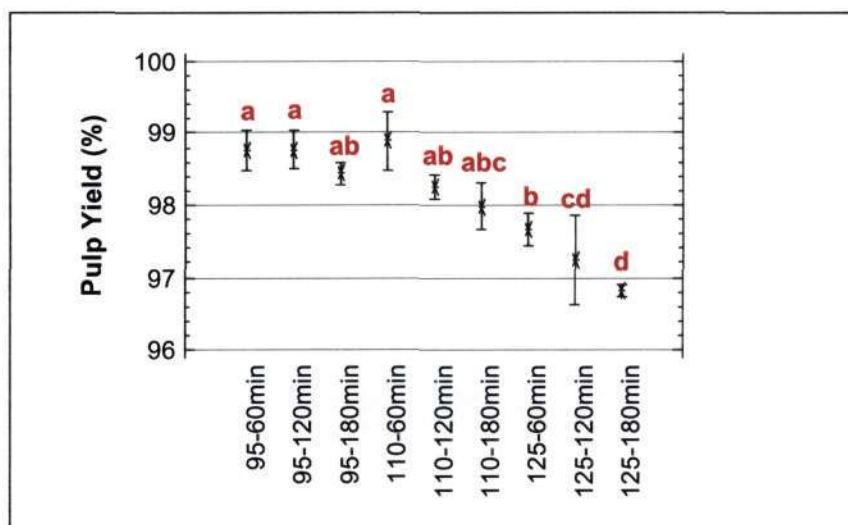


Figure 4.3.10 Pulp yield after acid hydrolysis. Each point represents the mean pulp yield of 3 individual acid hydrolysis experiments, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels.

4.3.4 Correlating Kappa number to hexenuronic acid content

In correlating the Kappa number drop to the removal of HexA, the Kappa number reduction after acid hydrolysis was compared to the HexA reduction after acid hydrolysis. The contribution of HexA to Kappa number was found to range between 9.4 and 11.6 μmol HexA per Kappa number unit, depending on the acid hydrolysis conditions (**Table 4.6**). This finding is consistent with studies by others on the contribution of HexA to Kappa number, where it was shown that approximately 10 μmol of HexA contributed to 1 Kappa unit (Vuorinen *et al.*, 1996; Li & Gellerstedt, 1997; Chai *et al.*, 2001; Pedroso & Carvalho, 2003; Petit-Breuilh *et al.*, 2004). This consistency also points favourably to the accuracy of the method used for the determination of HexA at the CSIR.

Figure 4.3.11 gives a graphical representation of the data shown in **Table 4.6**, and shows the strong correlation between the reduction in HexA and Kappa number after acid hydrolysis ($R^2 = 0.9579$).

Table 4.6 Contribution of hexenuronic acid to Kappa number.

Pulp	Kappa	Kappa Reduction	HexA ($\mu\text{mol/g}$)	HexA Reduction	HexA _{red} /Kappa _{red}
Oxygen bleached	11.25	--	61.17	--	--
95°C – 60min	8.64	2.61	32.27	28.90	11.1
95°C – 120min	7.60	3.65	22.25	38.92	10.7
95°C – 180min	7.16	4.09	16.13	45.04	11.0
110°C – 60min	6.60	4.65	7.25	53.95	11.6
110°C – 120min	6.12	5.13	3.15	58.02	11.3
110°C – 180min	5.99	5.26	1.87	59.30	11.3
125°C – 60min	5.33	5.92	2.48	58.69	9.9
125°C – 120min	5.08	6.17	1.75	59.42	9.6
125°C – 180min	4.82	6.43	1.02	60.15	9.4

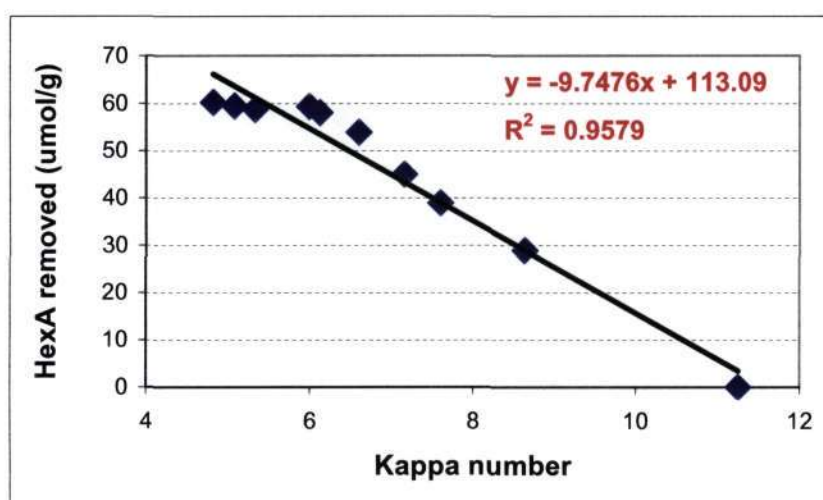


Figure 4.3.11 Correlation between reduction in hexenuronic acid (HexA) concentration and Kappa number after acid hydrolysis.

4.4 DETERMINATION OF OPTIMUM A-STAGE CONDITIONS

The parameters used to decide on the optimum conditions for the A-stage were the conditions that resulted in (1) maximum removal of HexA, (2) maximum pulp yield after bleaching, (3) minimum bleaching chemical consumption, and (4) minimum impact on pulp quality. In order to determine the optimum conditions, three acid hydrolysed pulps of the GU clone from the good site, containing varying

concentrations of HexA, were selected and fully bleached to 90% ISO brightness using a D₀ED₁ sequence. These samples are listed in **Table 4.7**. The oxygen delignified pulps that were not subjected to acid hydrolysis, and which contained maximum amounts of HexA, were also bleached to 90% ISO brightness. These pulps were used as controls in the study. The pulps hydrolysed at 110°C-120min were chosen as the upper limit because any further increase in temperature and/or reaction time of the A-stage did not result in a further significant reduction in the concentration of HexA in the pulps (see **Figure 4.3.5**).

Table 4.7 Selected acid hydrolysed pulps containing varying amounts of HexA that were bleached to 90% ISO brightness using D₀ED₁ sequence.

Pulp Type	pH	Temp (°C)	Reaction Time (min)	HexA (μmol/g)
Oxygen delignified (control)	--	--	--	61.2
Acid hydrolysed	3.5	95	60	32.3
Acid hydrolysed	3.5	95	180	16.1
Acid hydrolysed	3.5	110	120	3.2

4.4.1 Total active chlorine consumption

Compared to the control pulps that did not undergo acid hydrolysis, the total active chlorine (TAC) consumption decreased significantly for the acid hydrolysed pulps, as the conditions of the A-stage increased (**Figure 4.4.1**). According to **Table 4.7**, the control pulps contained maximum HexA, and the concentration decreased significantly as the temperature and/or the reaction time of the A-stage increased.

Hexenuronic acid belongs to a class of compounds that contain enol ether or unsaturated carboxylic acid groups, which are the targets of both electrophilic and nucleophilic attack. As a result, chlorine dioxide, together with other electrophilic bleaching chemicals, react with HexA groups (Buchert *et al.*, 1995; Vuorinen *et al.*, 1996; Vuorinen *et al.*, 1999; Jiang *et al.*, 2005). Because of the presence of HexA, bleaching chemicals such as chlorine dioxide are partially consumed during their reaction with HexA and are therefore not consumed during delignification, resulting in increased consumption of these chemicals. **Figure 4.4.1** shows that the inclusion of

the A-stage prior to bleaching effectively removed HexA thereby resulting in significant chemical savings up to 44% at 110°C-120min. Vuorinen *et al.* (1999) reported chemical savings up to 35% using less severe conditions for the A-stage (110°C, 60min, pH 3.5), whilst Furtado *et al.* (2001) reported savings up to 25% using even milder conditions (90°C, 120min, pH 3.5).

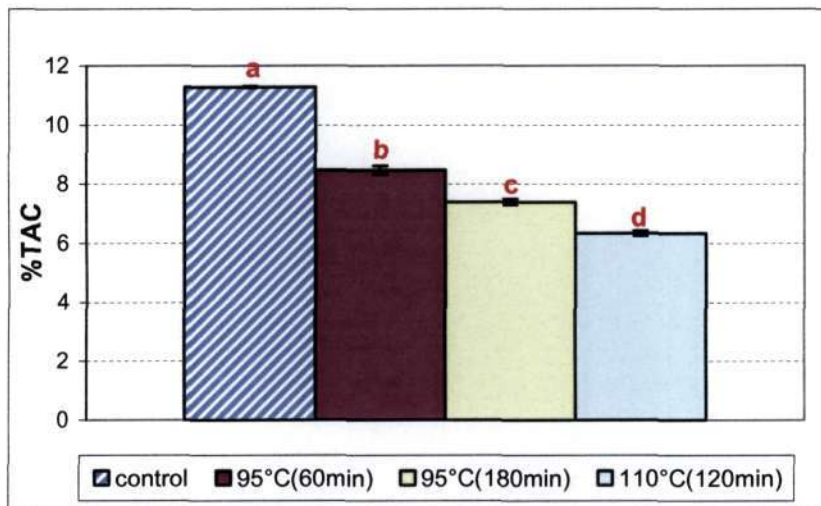


Figure 4.4.1 Mean total active chlorine (TAC) consumption required to reach 90% ISO brightness for the GU clone from the good site. The error bars denote the standard deviation, with common letters indicating no significant differences amongst the means, at 95% confidence levels.

4.4.2 Chemical composition of bleached pulps

The glucose and xylose content of the bleached pulps, expressed as a percentage in wood, is shown in **Figure 4.4.2**. Compared to the control pulps, the inclusion of the A-stage in the bleaching sequence had no significant impact on the glucose content. Xylose however, appeared to be more sensitive to acid hydrolysis. The xylose content of the bleached pulps that were acid hydrolysed prior to bleaching was significantly lower compared to the control pulps. Amongst the acid hydrolysed pulps, xylose content was found to be similar.

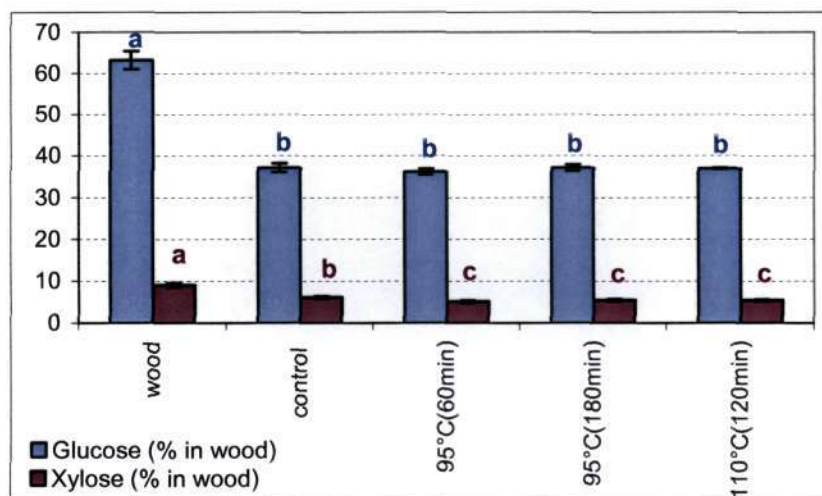


Figure 4.4.2 Glucose and xylose content of fully bleached control and acid hydrolysed pulps. The error bars denote the standard deviation, with common letters indicating no significant differences amongst the means at 95% confidence levels, and are only applicable within a specific colour.

4.4.3 Viscosity of bleached pulp

The acid hydrolysed pulps that were bleached showed a significantly lower final viscosity compared to the control pulps that did not undergo acid hydrolysis prior to bleaching (**Figure 4.4.3**). The temperature of the A-stage appeared to play an important role in the reduction of viscosity. The pulps hydrolysed for 60 and 180 minutes at 95°C showed no significant differences in viscosity, whilst the pulps hydrolysed at 110°C were significantly lower.

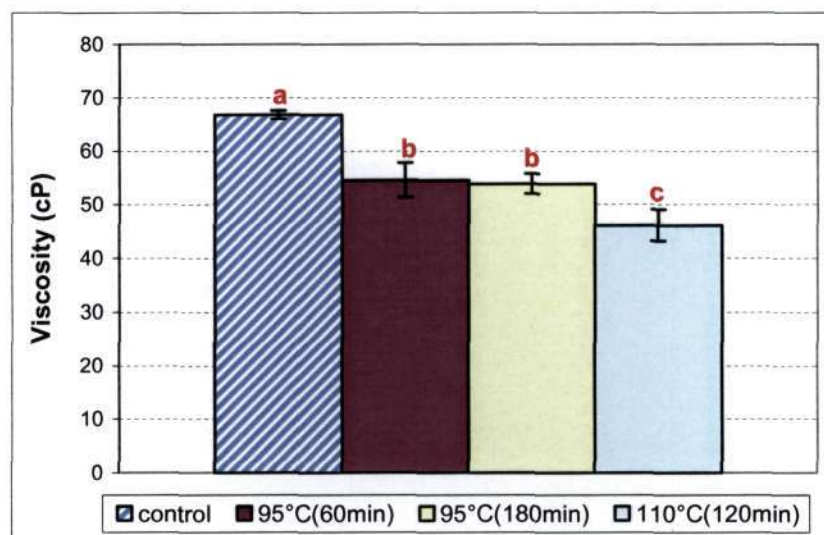


Figure 4.4.3 Mean Viscosity of bleached pulps of GU clone from good site that were acid hydrolysed prior to bleaching. The error bars denote the standard deviation, with common letters indicating no significant differences amongst the means, at 95% confidence levels.

4.4.4 Pulp yield across bleaching

The pulp yield after the 1st chlorine dioxide (D_0), alkaline extraction (E) and 2nd chlorine dioxide (D_1) stages are depicted in **Figure 4.4.4**. The control pulps that did not undergo acid hydrolysis prior to bleaching showed the lowest pulp yield in the D_0 -stage. The yield of the remaining acid hydrolysed pulps in this stage increased as the conditions of the A-stage increased. During the E-stage this order was reversed. The control pulps now showed the highest pulp yield, followed by the acid hydrolysed pulps, for which the pulp yields decreased as the temperature and reaction times of the A-stage increased. In the D_1 -stage, the pulp yields were all similar, within 1% of each other.

Across the D_0ED_1 bleaching sequence, no significant difference in pulp yield was found for the acid hydrolysed and the control pulps (**Figure 4.4.5**). The pulps hydrolysed at 95°C-180min and 110°C-120min did however, show slightly improved pulp yields compared to the control pulps. Similar results were reported by Vuorinen *et al.* (1999) who also found increased pulp yields across the D_0ED_1 bleaching sequence for pulps hydrolysed at 110°C(60min), compared to reference pulps that

did not undergo acid hydrolysis prior to bleaching.

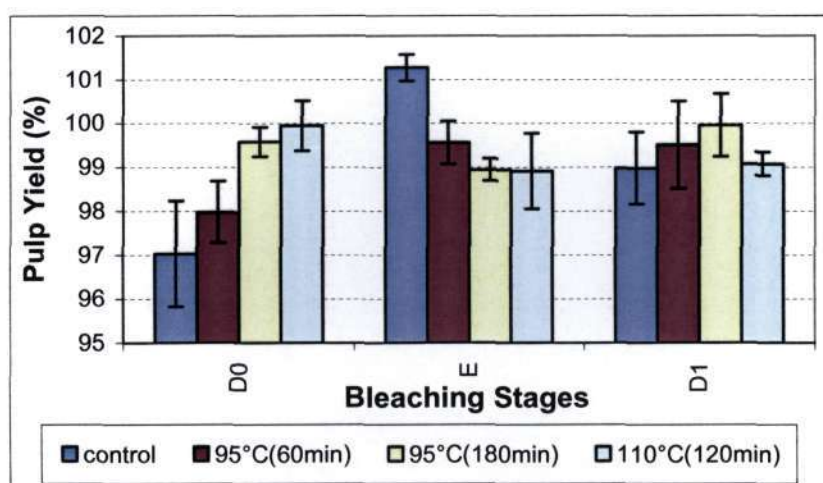


Figure 4.4.4 Pulp yield after 1st chlorine dioxide (D₀), alkaline extraction (E) and 2nd chlorine dioxide (D₁) stages for GU clone from good site. The error bars denote the standard deviation.

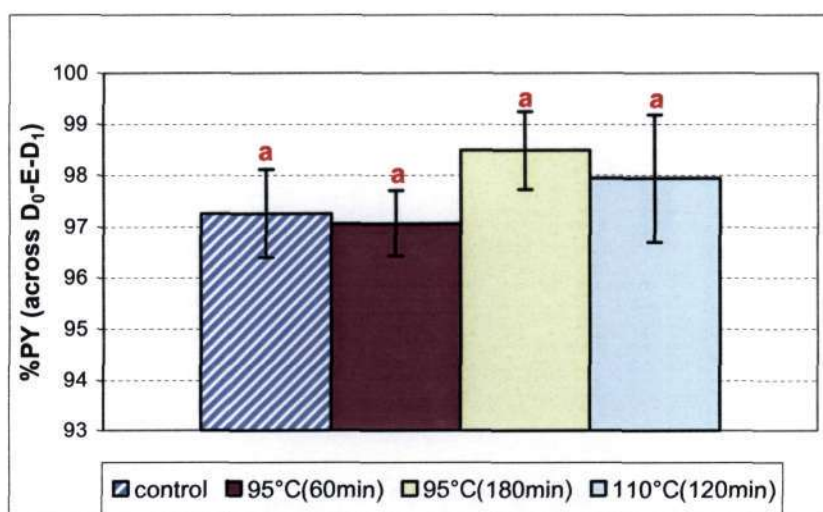


Figure 4.4.5 Pulp yield across the D₀ED₁ bleaching sequence for acid hydrolysed and control pulps of the GU clone from good site. The error bars denote the standard deviation, with common letters indicating no significant differences amongst the means, at 95% confidence levels.

The total pulp yield across pulping and bleaching is depicted in **Figure 4.4.6**. The

oxygen delignified control pulps were subjected to a three stage D_0ED_1 bleaching sequence, whilst the acid hydrolysed pulps were subjected to a four stage AD_0ED_1 sequence. From **Figure 4.4.6**, the total pulp yields across pulping and bleaching ranged between 47.7% and 48.4%, and were not significantly different from each other. This means that the inclusion of the A-stage in the bleaching sequence has no significant impact on the total pulp yield across pulping and bleaching compared to the control pulps that did not undergo acid hydrolysis prior to bleaching.

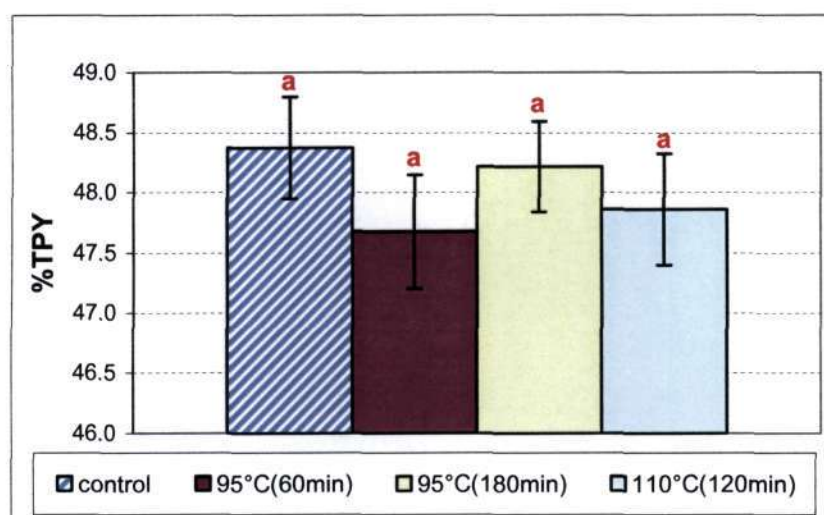


Figure 4.4.6 Mean total pulp yield across pulping and bleaching for acid hydrolysed and control pulps of GU clone from good site. The error bars denote the standard deviation, with common letters indicating no significant differences amongst the means, at 95% confidence levels.

4.4.5 Pulp quality

The removal of HexA by acid hydrolysis prior to bleaching offers several advantages. One of the major general advantages of acid hydrolysis, and the subsequent removal of HexA, is the reduction of chemical costs. Because of this, much of the research has been directed towards improving bleachability by manipulating the concentration of HexA in unbleached pulps during pulping (Buchert *et al.*, 1995; Gustavsson & Al-Dajani, 2000; Jiang *et al.*, 2003; Daniel *et al.*, 2003; Pedroso & Carvalho, 2003; Simão *et al.*, 2005a, b). As a consequence, only a few researchers have studied the impact of acid hydrolysis used in the removal of HexA, on the strength properties of

hardwoods (Vuorinen *et al.*, 1999; Ratnieks *et al.*, 2001; Furtado *et al.*, 2001) and softwoods (Bergnor-Gidnert *et al.*, 1998). Even so, in all of these studies, the broad spectrum of the pulp properties were not covered as in the case of this present study, but only focused on a few of the more important strength properties such as tear, tensile and zero-span tensile. Further to this, because there is no standard testing protocol for measuring effects on the physical properties of pulps, different researchers describe such effects differently (e.g. tear at constant freeness, or tear at constant sheet density, or tear at constant zero-span tensile, etc.). It therefore made it difficult to compare results of this part of the study to those of other researchers, but where possible, comparisons were made.

In the present study, the pulp strength properties of the fully bleached pulps that underwent acid hydrolysis prior to bleaching were plotted as a function of freeness. The values of the specific properties were interpolated at a constant freeness value of 400CSF from the respective property-freeness curves. One-way analysis of variance (ANOVA) and Duncan multiple range tests were then used to test for significant differences, at 95% confidence levels, amongst the means of each property at constant freeness. For all properties, whisker plots showing the means and standard errors were generated. In each plot, each point represents the mean of 3 measurements with the standard error as the whiskers. In addition, the means were represented by letters with the same letters indicating no significant differences amongst the means. The control pulps that were not subjected to acid hydrolysis but also bleached to 90% ISO brightness, together with the unbleached pulps, were also included in the comparisons.

4.4.5.1 Burst index

Burst index increased for all pulps as freeness decreased (**Figure 4.4.7**). Overall, the unbleached pulps showed the highest burst strength across all levels of freeness. The control and acid hydrolysed pulps showed similar burst strengths across all levels of freeness, with the pulps hydrolysed at 95°C-180min showing slightly higher burst strengths at low levels of freeness compared to the remaining acid hydrolysed pulps.

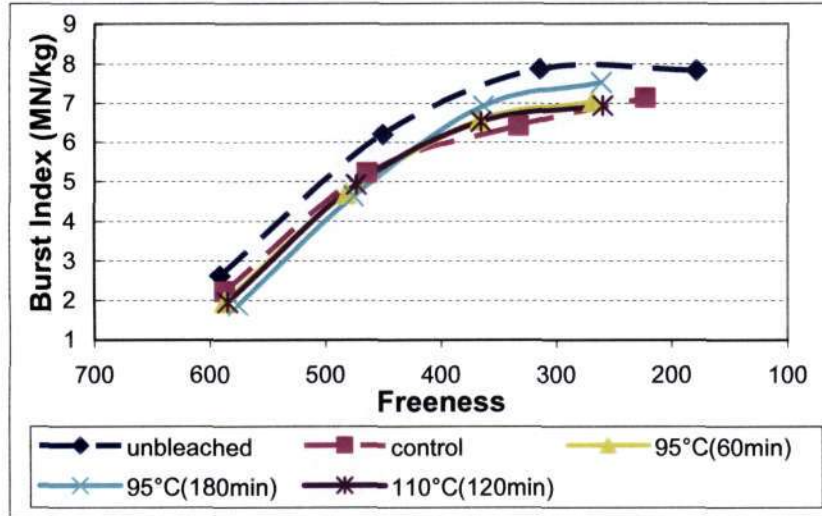


Figure 4.4.7 Relationship between burst index and freeness for acid hydrolysed pulps that were bleached to 90% ISO brightness. Control pulps that were not acid hydrolysed but bleached to 90% ISO brightness, together with the unbleached pulps, are also depicted for comparison purposes.

At constant freeness (400CSF) (**Figure 4.4.8**), the A-stage was found to have no impact on burst, as the control and acid hydrolysed pulps showed no significant differences in burst strength. The acid hydrolysed pulps did however, show an increasing trend as the reaction time was increased at 95°C. At 110°C burst decreased slightly. Similar results were reported by Furtado *et al.* (2001) who found that acid hydrolysis had no impact on burst compared to reference pulps that did not undergo hydrolysis prior to bleaching.

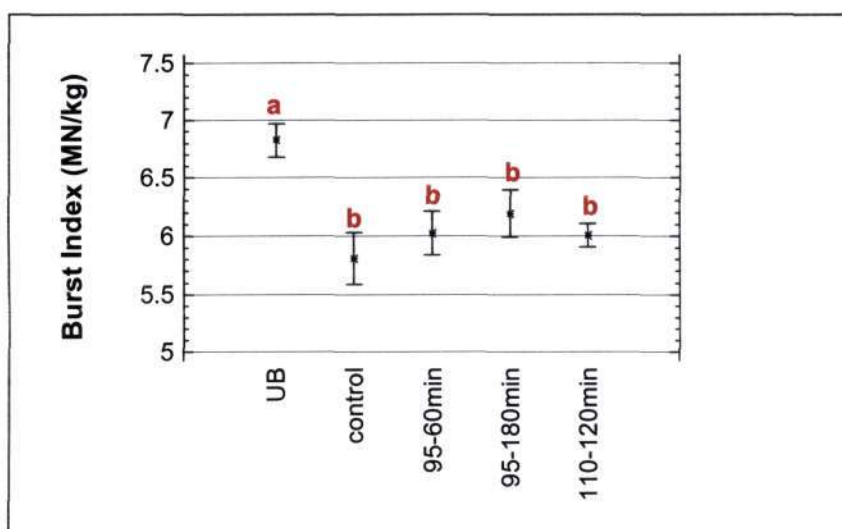


Figure 4.4.8 Burst Index at constant freeness (400CSF). Each point represents the mean burst index of 3 measurements, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels.

4.4.5.2 Tear index

The tear index initially increased as freeness decreased, but then decreased at lower freeness as the pulps were beaten further (**Figure 4.4.9**). At maximum, tear strength decreased as the temperature and reaction time of the A-stage increased. The pulps hydrolysed at 110°C-120min showed the lowest tear strength and were also lower than the unbleached and control pulps. The unbeaten acid hydrolysed pulps initially showed lower tear strengths compared to the control pulps, but then increased to higher tear strengths upon beating as the freeness decreased, except for the pulps hydrolysed at 110°C-120min.

At constant freeness (400CSF) (**Figure 4.4.10**), the A-stage applied at a lower temperature (95°C) was found to have no significant impact on the tear strength compared to the control pulps. A reaction time of 60min at 95°C slightly improved tear, whilst at 180min, at the same temperature, tear decreased slightly. At a higher temperature (110°C) tear was found to decrease significantly compared to the control pulps and the pulps hydrolysed at 95°C-60min. Reduced tear strengths for pulps hydrolysed at 110°C-60min were also reported by Vuorinen *et al.* (1999), whilst Furtado *et al.* (2001) reported slight improvements in tear strength for pulps

hydrolysed using milder conditions (90°C-120min), compared to pulps that did not undergo hydrolysis prior to bleaching.

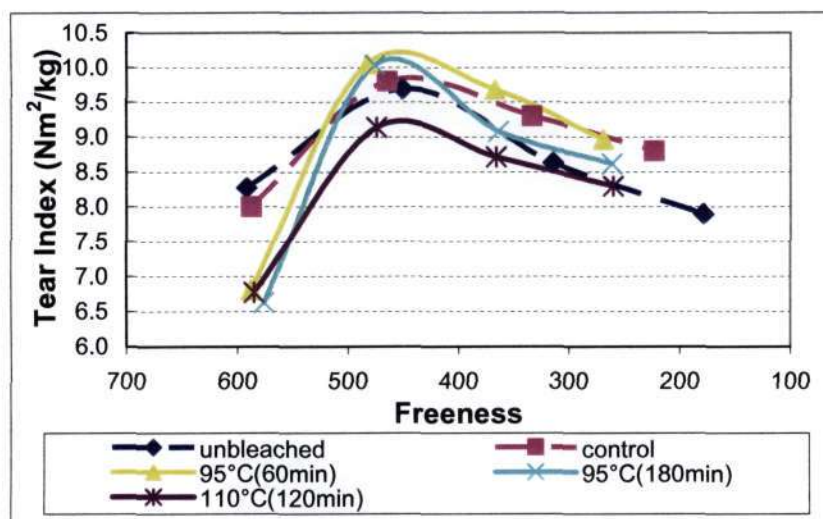


Figure 4.4.9 Relationship between tear index and freeness for acid hydrolysed pulps that were bleached to 90% ISO brightness. Control pulps that were not acid hydrolysed but bleached to 90% ISO brightness, together with the unbleached pulps, are also depicted for comparison purposes.

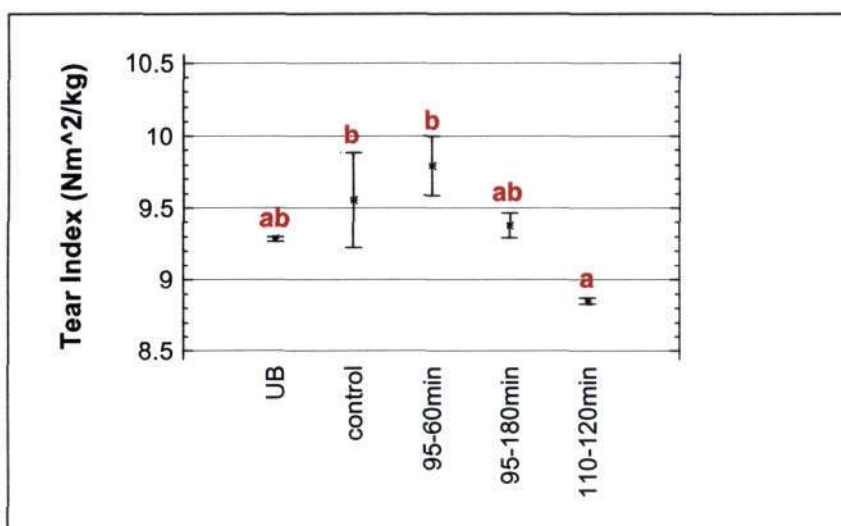


Figure 4.4. 10 Tear index at constant freeness (400CSF). Each point represents the mean tear index of 3 measurements, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels.

4.4.5.3 Tensile index

Tensile index increased for all pulps as freeness decreased (**Figure 4.4.11**). Overall, the unbleached pulps showed the highest tensile strength across all levels of freeness. The control and acid hydrolysed pulps showed similar tensile strengths across all levels of freeness, with the pulps hydrolysed at 95°C-180min increasing slightly at low freeness, compared to the remaining acid hydrolysed pulps.

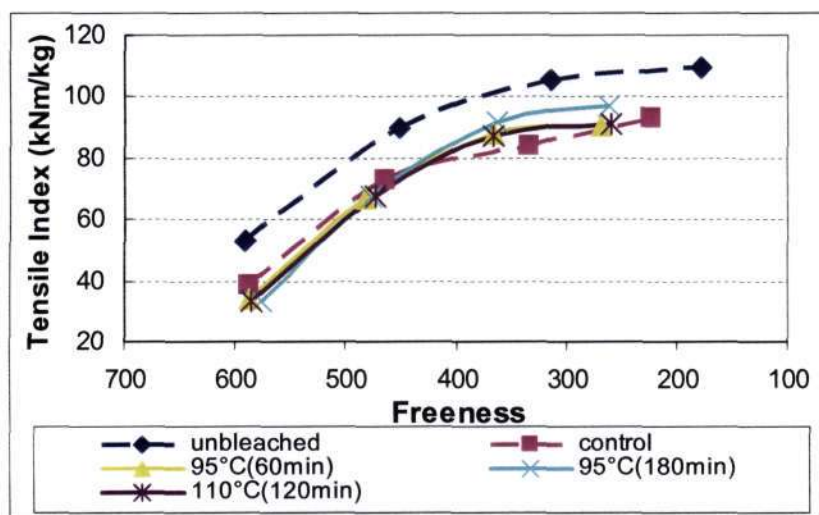


Figure 4.4.11 Relationship between tensile index and freeness for acid hydrolysed pulps that were bleached to 90% ISO brightness. Control pulps that were not acid hydrolysed but bleached to 90% ISO brightness, together with the unbleached pulps, are also depicted for comparison purposes.

At constant freeness (400CSF) (**Figure 4.4.12**), the A-stage was found to have no significant impact on the tensile strength of the bleached pulps. The acid hydrolysed pulps did however show an increasing trend in tensile strength as the conditions of the A-stage increased. At 110°C-120min tensile strength decreased slightly, but was still slightly higher than the control pulps. Vuorinen *et al.* (1999) found that tensile index, compared at constant sheet density, was unaffected by the A-stage, whilst improved tensile strength were reported by Furtado *et al.* (2001) for pulps acid hydrolysed prior to bleaching, compared to pulps that did not undergo hydrolysis prior to bleaching.

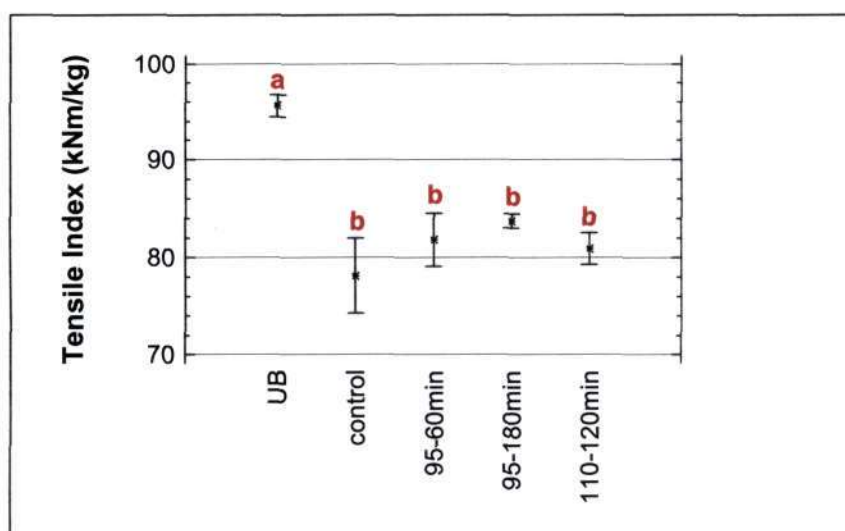


Figure 4.4.12 Tensile index at constant freeness (400CSF). Each point represents the mean tensile index of 3 measurements, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels.

4.4.5.4 Zero-span tensile index

Similar to tensile strength, the unbleached pulp showed the highest zero-span tensile strength across all levels of freeness (**Figure 4.4.13**). This was followed by the 110°C-120min acid hydrolysed pulps. For the pulps hydrolysed at 95°C, the 180min pulps showed slightly higher zero-span tensile strengths at high freeness compared to the 60min pulps. At low freeness, both pulps reached similar values. The control pulps initially showed higher zero-span tensile at high freeness compared to the pulps hydrolysed at 95°C, but decreased at low freeness upon further beating.

At constant freeness (400CSF) (**Figure 4.4.14**), the A-stage carried out at 95°C (60min & 180min) was found to have no impact on zero-span tensile strength, as no significant differences were found between the control pulps and the pulps hydrolysed at 95°C. At 110°C-120min however, zero-span tensile improved significantly and reached similar levels as the unbleached pulps.

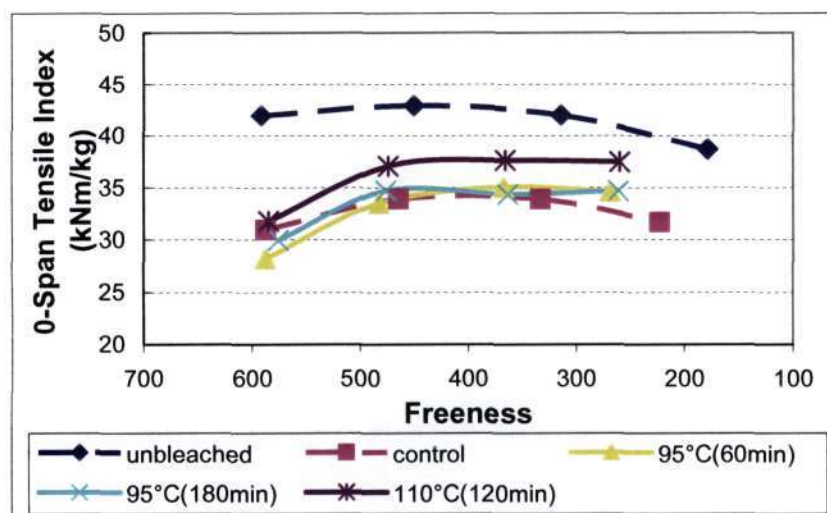


Figure 4.4.13 Relationship between zero-span (0-span) tensile index and freeness for acid hydrolysed pulps that were bleached to 90% ISO brightness. Control pulps that were not acid hydrolysed but bleached to 90% ISO brightness, together with the unbleached pulps, are also depicted for comparison purposes.

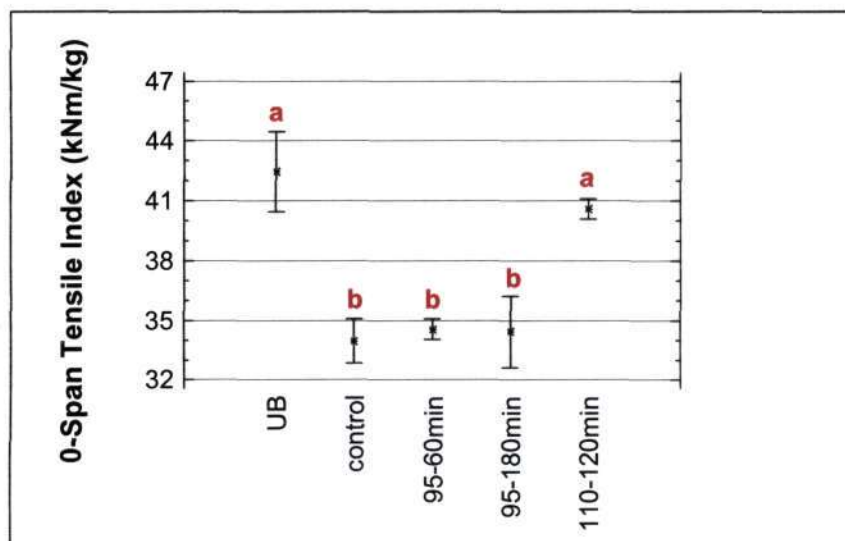


Figure 4.4.14 Zero-span (0-span) tensile index at constant freeness (400CSF). Each point represents the mean 0-span tensile index of 3 measurements, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels.

4.4.5.5 Stretch

Stretch increased for all pulps as freeness decreased (**Figure 4.4.15**). Unlike burst, tensile and zero-span tensile strength, the unbleached pulp showed the lowest stretch across all levels of freeness, but reached similar values, at low freeness, to the control pulps and the pulps hydrolysed at 95°C-180min and 110°C-120min. Amongst the acid hydrolysed pulps, the 95°C-60min pulp showed the highest stretch across all levels of freeness. The 95°C-180min and 110°C-120min pulps showed similar values of stretch to the control pulps and were slightly lower than the pulps hydrolysed at 95°C-60min.

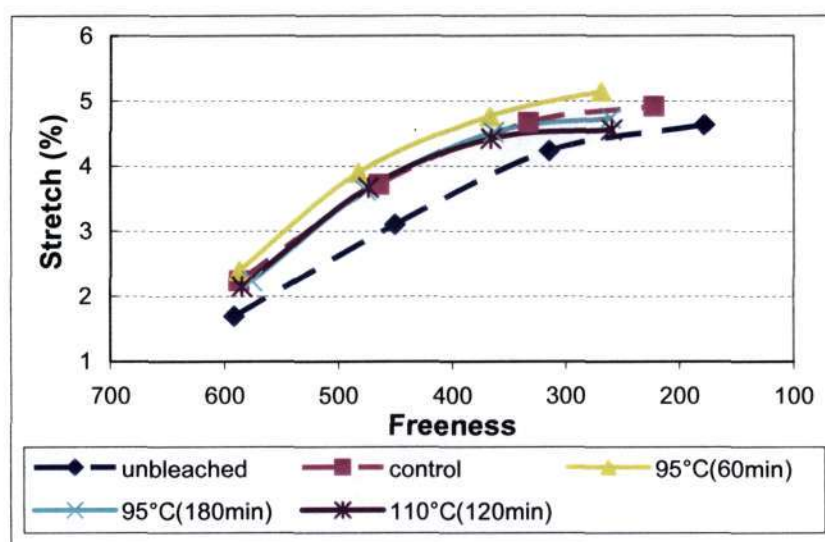


Figure 4.4.15 Relationship between stretch and freeness for acid hydrolysed pulps that were bleached to 90% ISO brightness. Control pulps that were not acid hydrolysed but bleached to 90% ISO brightness, together with the unbleached pulps, are also depicted for comparison purposes.

At constant freeness (400CSF) (**Figure 4.4.16**), application of the A-stage at 95°C-60min significantly improved stretch of the bleached pulps. However, further increase in the temperature and/or the reaction time of the A-stage lowered stretch to similar levels as the control pulps. The unbleached pulps showed the lowest stretch, and were significantly lower than the control and acid hydrolysed pulps.

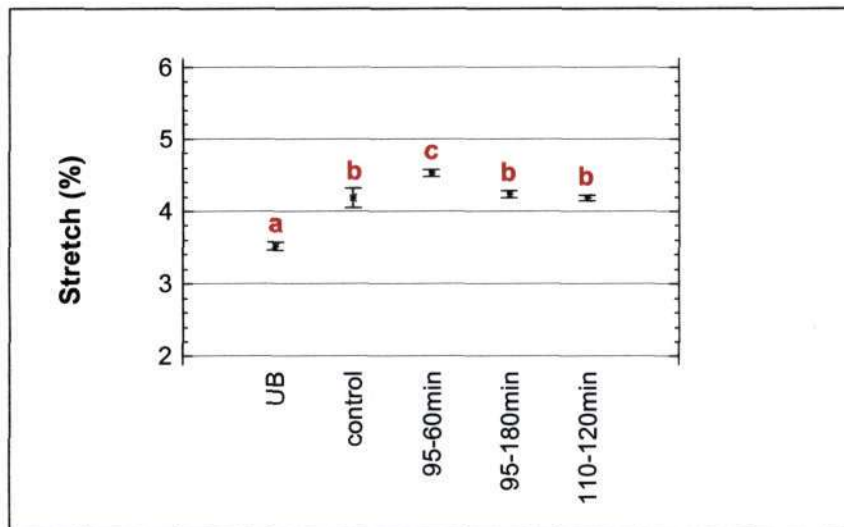


Figure 4.4.16 Stretch at constant freeness (400CSF). Each point represents the mean stretch of 3 measurements with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels.

4.4.5.6 Stiffness

Stiffness of the unbleached pulp decreased as freeness decreased (**Figure 4.4.17**). The bleached pulps initially increased with beating, but then decreased at lower freeness as the pulps were beaten further. At maximum, the acid hydrolysed pulps showed higher values of stiffness compared to the control pulps.

At constant freeness (400CSF) (**Figure 4.4.18**), the A-stage was found to improve stiffness of the bleached pulps compared to the control pulps that did not undergo acid hydrolysis prior to bleaching. At 95°C-180min and 110°C-120min, the improvement was significant.

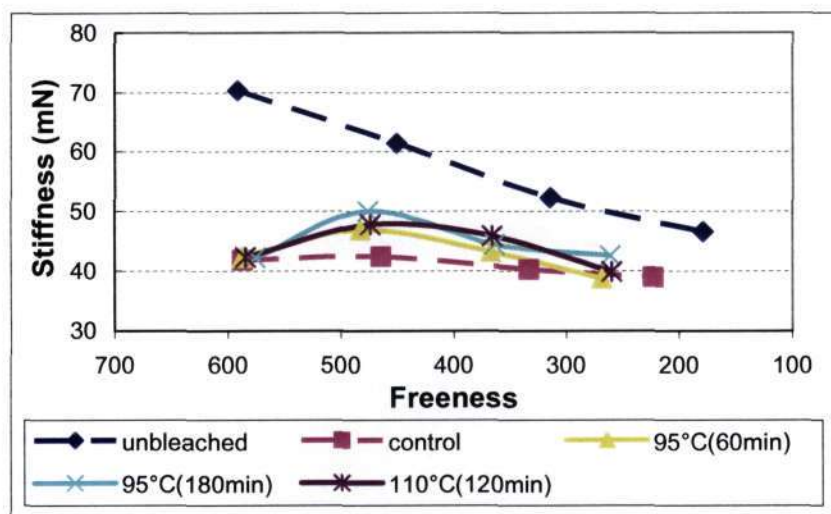


Figure 4.4.17 Relationship between stiffness and freeness for acid hydrolysed pulps that were bleached to 90% ISO brightness. Control pulps that were not acid hydrolysed but bleached to 90% ISO brightness, together with the unbleached pulps are also depicted for comparison purposes.

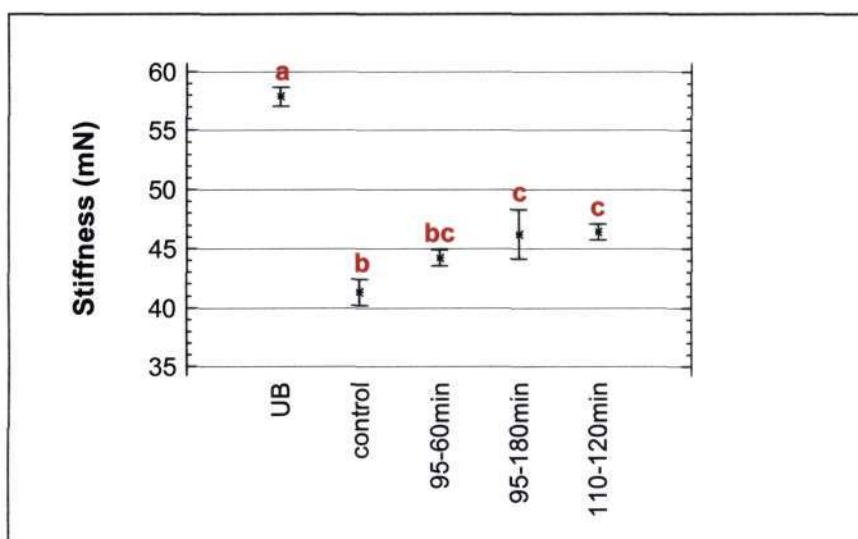


Figure 4.4.18 Stiffness at constant freeness (400CSF). Each point represents the mean stiffness of 3 measurements, with the whiskers as the standard error. Common letters indicate no significant difference amongst the means, at 95% confidence levels.

4.4.5.7 Sheet density

Sheet density showed the same general trend for all pulps of increasing with decreasing freeness (Figure 4.4.19). The unbleached pulps showed the lowest sheet density at high freeness, but reached similar levels as the control pulps at low freeness. At high freeness, the pulps hydrolysed at 95°C (60 and 180min) showed a slightly lower sheet density compared to the control pulps, whilst the pulps hydrolysed at 110°C-120min showed a similar sheet density to the control pulps. At low freeness, the acid hydrolysed pulps all showed similar sheet densities and were slightly higher than the control pulps.

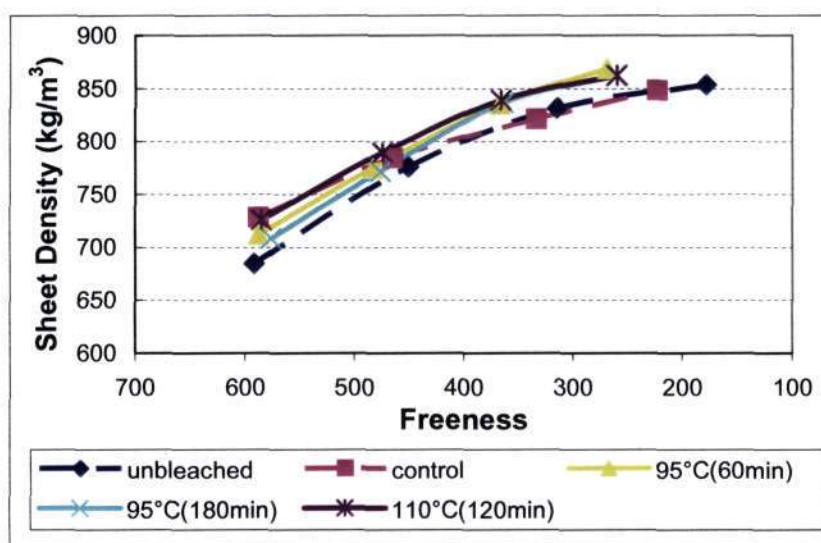


Figure 4.4.19 Relationship between sheet density and freeness for acid hydrolysed pulps that were bleached to 90% ISO brightness. Control pulps that were not acid hydrolysed but bleached to 90% ISO brightness, together with the unbleached pulps, are also depicted for comparison purposes.

At constant freeness (400CSF) (Figure 4.4.20), the A-stage was found to have no impact on sheet density of the bleached pulps. There was however, an increasing trend in sheet density as the temperature and reaction time of the A-stage increased. The unbleached pulps were significantly lower than the pulp hydrolysed at 110°C-120min, but showed similar sheet densities to the control pulps and the pulps hydrolysed at 95°C.

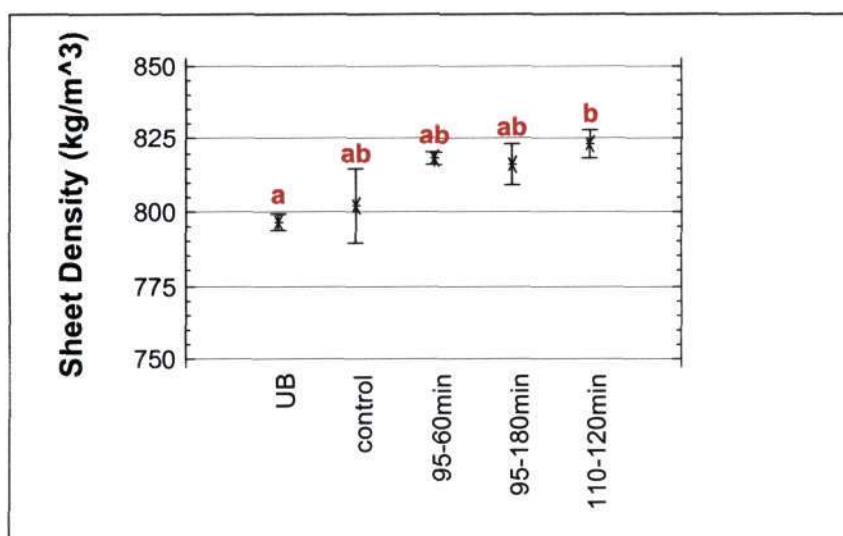


Figure 4.4.20 Sheet density at constant freeness (400CSF). Each point represents the mean sheet density of 3 measurements, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels.

4.4.5.8 Opacity

Opacity decreased for all pulps as freeness decreased (**Figure 4.4.21**). Amongst the acid hydrolysed pulps, opacity was slightly lower for the pulps hydrolysed at 95°C-60min compared to the remaining acid hydrolysed pulps. The control pulps showed similar opacity to the acid hydrolysed pulps at high freeness, but decreased at a slower rate at lower freeness compared to the acid hydrolysed pulps.

At constant freeness (400CSF) (**Figure 4.4.22**), application of the A-stage at 95°C-60min significantly lowered the opacity of the bleached pulps. However, as the temperature and reaction time of the A-stage increased, opacity increased to similar levels as the control pulps.

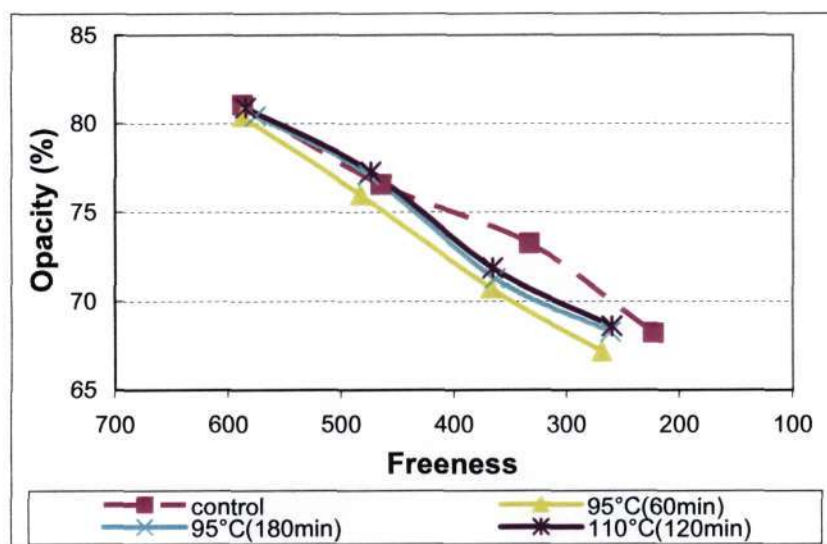


Figure 4.4.21 Relationship between opacity and freeness for acid hydrolysed pulps that were bleached to 90% ISO brightness. Control pulps that were not acid hydrolysis but bleached to 90% ISO brightness are also depicted for comparison purposes.

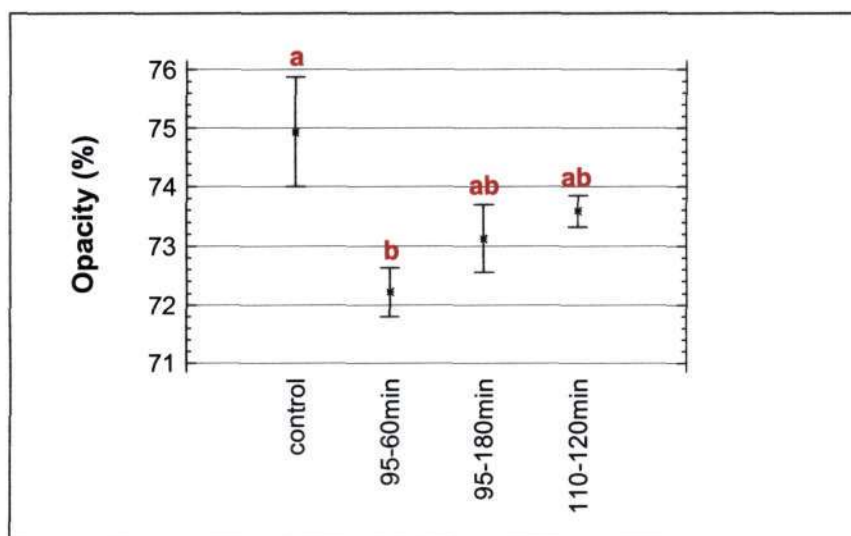


Figure 4.4.22 Opacity at constant freeness (400CSF). Each point represents the mean opacity of 3 measurements, with the whiskers as the standard error. Common letters indicate no significant difference amongst the means, at 95% confidence levels.

4.4.5.9 Air resistance

The air resistance increased gradually at high freeness and then increased rapidly upon further beating, as freeness decreased (**Figure 4.4.23**). All pulps showed similar air resistance values at high freeness but differed at lower freeness. At lower freeness, air resistance of the unbleached and controls pulps was higher compared to the acid hydrolysed pulps.

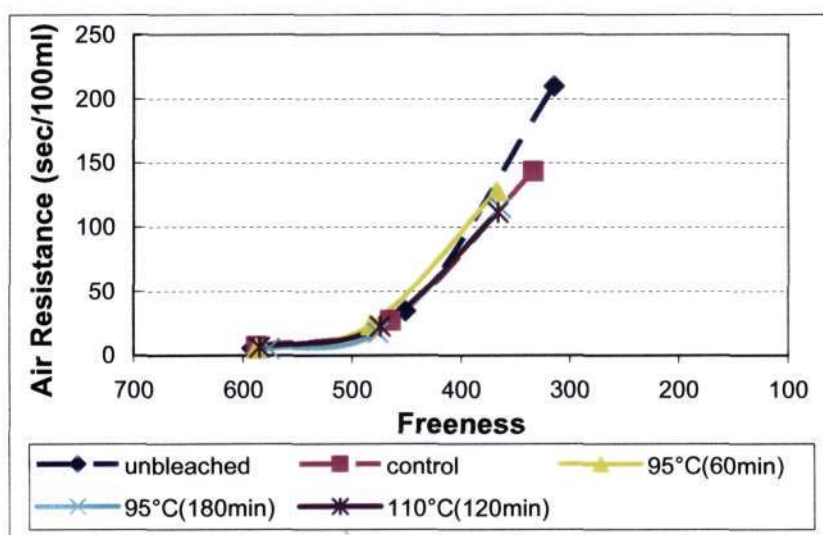


Figure 4.4.23 Relationship between air resistance and freeness for acid hydrolysed pulps that were bleached to 90% ISO brightness. Control pulps that were not acid hydrolysed but bleached to 90% ISO brightness, together with the unbleached pulps, are also depicted for comparison purposes.

At constant freeness (400CSF) (**Figure 4.4.24**), application of the A-stage at 95°C-60min significantly increased the air resistance compared to the control pulps. However, further increase in the temperature or reaction time of the A-stage decreased air resistance to similar levels as the control pulps.

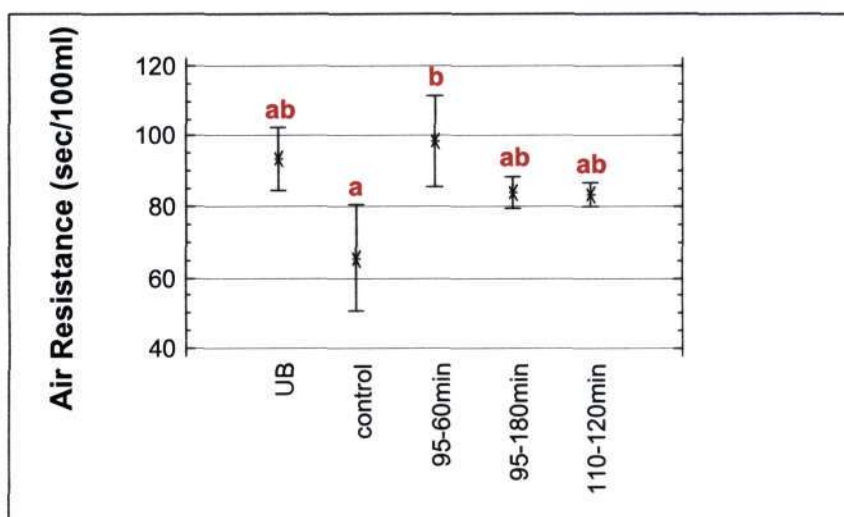


Figure 4.4.24 Air resistance at constant freeness (400CSF). Each point represents the mean air resistance of 3 measurements, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels.

4.4.5.10 Brightness reversion

The brightness reversion of the fully bleached pulps decreased significantly for the pulps that were acid hydrolysed prior to bleaching (**Figure 4.4.25**). Because HexA has come to hold a prominent position amongst the different theories regarding the causes of brightness reversion (Buchert *et al.*, 1996; Vuorinen *et al.*, 1999; Sevastyanova, *et al.*, 2006), a first response in explaining this decrease would be the removal of HexA during acid hydrolysis thus resulting in improved brightness stability.

However, the pulps illustrated in **Figure 4.4.25** (besides the controls) were acid hydrolysed to remove HexA prior to being fully bleached using a D₀ED₁ sequence. Any remaining HexA in the pulps after acid hydrolysis was further removed during the D₀ and D₁ stages due to its reaction with chlorine dioxide (Buchert *et al.*, 1995; Vuorinen *et al.*, 1996; Vuorinen *et al.*, 1999; Jiang *et al.*, 2005). This was seen in this study by the higher amounts of chlorine dioxide required to bleach pulps containing HexA to 90% ISO brightness (**Figures 4.3.5 and 4.4.1**). Therefore the bleached acid hydrolysed and control pulps were essentially free of HexA, and the reduction in HexA content after acid hydrolysis could not be used to explain the reduction in brightness reversion in the bleached pulps.

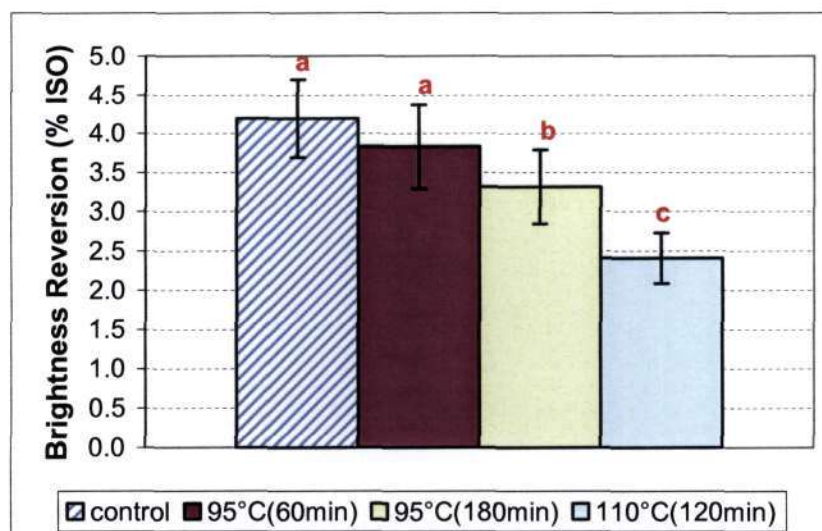


Figure 4.4.25 Mean brightness reversion of bleached pulps for GU clone from good site that were acid hydrolysed prior to bleaching. The error bars denote the standard deviation, with common letters indicating no significant difference amongst the means, at 95% confidence levels.

Similar conclusions were reached by Süess *et al.* (2004). In an attempt to understand the role of HexA in reversion, they subjected pulps already bleached using a D₀EopD₁P sequence to a further acid treatment for 2 hours at 95°C and pH<3 in order to remove any residual HexA. Their study showed that reversion was identical, with or without the acid hydrolysis treatment. Furtado *et al.* (2001) also found no clear dependence between pulp brightness reversion and HexA elimination in the A-stage.

In this present study, HexA was measured in the fully bleached pulps in order to confirm their absence. As expected, none were detected. The accuracy of the method at low concentration of HexA was tested against a standard fully bleached pulp sample obtained from KTH. The concentration of HexA in this standard pulp, measured using the KTH method (Gellerstedt & Li, 1996), was given as 8.6 µmol/g. Measurements carried out using the IPST method (Chai *et al.*, 2001) in this study, yielded an average result of 8.9 µmol/g.

According to Süess *et al.* (2004), a possible explanation for the observed decrease in brightness reversion could lie in the bleaching sequence used. Chlorine dioxide as a delignifying agent results in the formation of quinoid structures which have been

proposed as comprising the coloured products formed during the initial stages of reversion (Heitner, 1996). From **Figure 4.4.1**, due to the increased removal of HexA as the conditions of the A-stage increased, the amount of chlorine dioxide required to reach the target brightness decreased. Therefore pulps requiring lesser amounts of chlorine dioxide produced lesser amounts of quinoid structures, resulting in the observed decrease in brightness reversion.

In general, other possibilities to consider when examining brightness reversion in pulps include, the wood species and the pulping and bleaching process (Heitner 1996); the washing efficiency, oxidised carbohydrates and chromophores generated by condensation reactions (Süess *et al.*, 2004); and chlorinated extractives and the formation of metal ion complexes (Sevastyanova, *et al.*, 2006). It was also found that reversion may occur if bleaching chemicals become exhausted part way through the bleaching stage (Tessier & Savoie, 2002).

4.4.6 Optimum acid hydrolysis conditions

Table 4.8 summarises the results obtained for the three acid hydrolysed pulps (95°C–60min; 95°C–180min; and 110°C–120min), together with the control pulps, that were selected and bleached to 90% ISO brightness. Each result is the mean of three measurements. The means are also represented by letters, with common letters indicating no significant difference amongst the means, at 95% confidence levels.

The three acid hydrolysis treatments significantly reduced the HexA concentration of the oxygen delignified pulp. Reductions of 48%, 74% and 95% were achieved for the 95°C-60min, 95°C-180min and 110°C-120min acid treatments, respectively. As a result of the reduction in HexA concentration, Kappa number decreased significantly, whilst the chlorine dioxide consumption during bleaching to reach a target brightness of 90% ISO, also decreased significantly across the three treatments. Total pulp yield across pulping and bleaching, and pulp properties such as burst, tensile, zero-span tensile, stretch, stiffness, air resistance and sheet density were either unaffected by the acid treatments or showed improvement after the acid treatments. Final bleached pulp viscosity and tear strength was negatively impacted by the acid treatments, with the 110°C-120min acid treatment having the greatest impact.

Table 4.8 Summary of pulp results obtained for the GU clone from the good site that was subjected to acid hydrolysis and then bleached to 90% ISO brightness. Each value is the mean of 3 measurements. Common letters in brackets indicate no significant difference amongst the means for a particular property, at 95% confidence levels.

Property	Control	95°C (60min)	95°C (180min)	110°C (120min)
HexA content ($\mu\text{mol/g}$)	61(A)*	32 (B)	16 (C)	3 (D)
Kappa number	11.3 (A)*	8.7 (B)	7.2 (C)	6.2 (D)
TPY across pulping and bleaching (%)	48.4 (A)	47.7 (A)	48.2 (A)	47.9 (A)
TAC consumption (%)	11.3 (A)	8.5 (B)	7.4 (C)	6.3 (D)
Viscosity (cP)	67 (A)	55 (B)	54 (B)	46 (C)
Glucose (% in wood)	37.1 (A)	36.2 (A)	37.1 (A)	37.0 (A)
Xylose (% in wood)	6.1 (A)	5.1 (B)	5.4 (B)	5.5 (B)
Burst index at 400CSF (MN/kg)	5.8 (A)	6.0 (A)	6.2 (A)	6.0 (A)
Tear index at 400CSF (Nm^2/kg)	9.6 (A)	9.8 (A)	9.4 (AB)	8.9 (B)
Tensile index at 400CSF (kNm/kg)	78 (A)	82 (A)	84 (A)	81 (A)
0-span tensile index at 400CSF (kNm/kg)	34 (A)	35 (A)	34 (A)	41 (B)
Stretch at 400CSF (%)	4.2 (A)	4.5 (B)	4.2 (A)	4.2 (A)
Stiffness at 400CSF (mN)	41 (A)	44 (AB)	46 (B)	46 (B)
Air resistance at 400CSF (sec/100ml)	66 (A)	99 (B)	84 (AB)	84 (AB)
Sheet density at 400CSF (kg/m^3)	802 (A)	818 (A)	816 (A)	823 (A)
Opacity at 400CSF (%)	74.9 (A)	72.2 (B)	73.1 (AB)	73.6 (AB)
Brightness reversion (% ISO)	4.2 (A)	3.8 (A)	3.3 (B)	2.4 (C)

*Control pulps were not acid hydrolysis and so the value indicated is for the oxygen delignified pulps.

In deciding on the optimum set of conditions for acid hydrolysis, a compromise between the efficiency of HexA removal, the resulting pulp quality after acid hydrolysis, and practical considerations for implementation of the A-stage in industry, was required. The choice for the optimum set of conditions was therefore between 95°C-180min and 110°C-120min, mainly because of the lower HexA concentration, and as a result, the higher Kappa number reduction and lower bleaching chemical consumption to reach 90% ISO brightness. However, because of the higher operating temperature (and pressure) required, and the lower tear strength and viscosity obtained for the pulps hydrolysed at 110°C-120min, the 95°C-180min acid hydrolysis conditions appeared to be the more attractive option.

The remaining clones were acid hydrolysed prior to bleaching using the optimum conditions: temperature 95°C; reaction time 180min, and pH 3.5.

4.5 INFLUENCE OF SPECIES AND SITE ON HEXENURONIC ACID CONTENT

The HexA content of the unbleached and oxygen bleached pulps of the GU and GC clones from the different sites are depicted in **Figure 4.5.1**. Site quality was found to significantly influence the levels of HexA in the unbleached pulps, with both clones from the good sites showing significantly lower HexA concentrations compared to their respective clones from the poor sites. Average HexA content for the unbleached pulps of the GU clones from the poor and good sites were 71.6 and 62.8 $\mu\text{mol/g}$, respectively, whilst the GC clones showed concentrations of 68.8 and 60.9 $\mu\text{mol/g}$ for the poor and good sites, respectively. The difference in HexA content amongst the clones from similar sites was also significant.

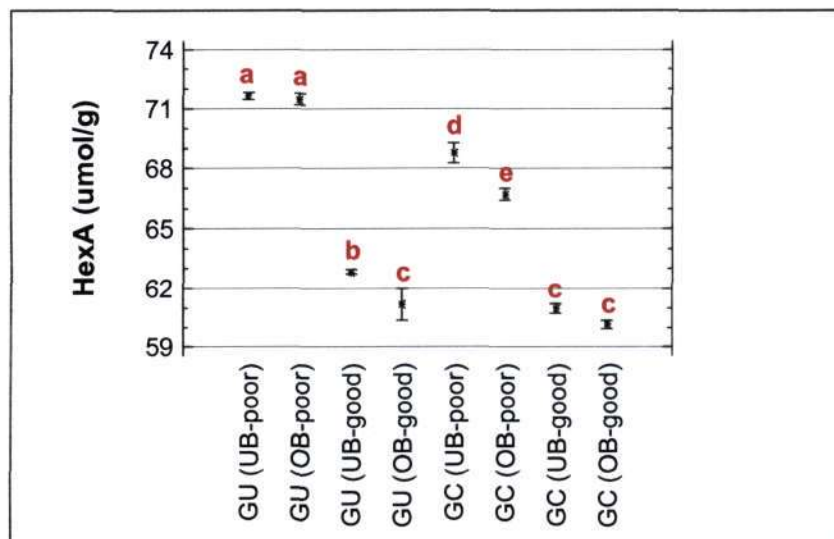


Figure 4.5.1 Hexenuronic acid (HexA) content in unbleached (UB) and oxygen bleached (OB) pulps of GU and GC clones from good and poor sites. Each point represents the mean HexA content of 3 measurements, with the whiskers as the standard error. Common letters indicate no significant differences amongst the means, at 95% confidence levels.

Similar levels of HexA for hardwoods in the range 50-70 $\mu\text{mol/g}$ were previously reported in unbleached, *E. globulus* pulps (Evtuguin *et al.*, 2002; Daniel *et al.*, 2003; Pedroso & Carvalho, 2003; Daniel *et al.*, 2004); birch pulps (Gellerstedt & Li, 1996; Li & Gellerstedt, 1997; Chai *et al.*, 2001); maple pulps (Chai *et al.*, 2001); sweetgum pulps (Chai *et al.*, 2001); and aspen pulps (Shin *et al.*, 2005).

Using the correlation of HexA contribution to Kappa number obtained in **Table 4.6** (section 4.3.4), the levels of HexA found in the unbleached pulps could potentially contribute between 5-6 'Kappa units' to the Kappa number of the unbleached pulps, measured using the conventional Tappi standard method (Tappi, 1996c).

After oxygen delignification, the GU clone from the good site and the GC clone from the poor site showed lower levels of HexA compared to their corresponding unbleached pulps. The GU clone from the poor site and the GC clone from the good site however, showed no differences between unbleached and oxygen delignified pulps. HexA are known to be unreactive during oxygen delignification and so the levels found in the unbleached pulp should essentially remain unchanged during oxygen delignification (Buchert *et al.* 1995; Gellerstedt & Li, 1996; Vuorinen *et al.*, 1999; Suess *et al.*, 2005a).

The xylose content in wood was determined for each clone from the different sites and then correlated with the amount of HexA formed. **Figure 4.5.2** shows the relationship between xylose content of wood and HexA formed in the unbleached pulps after Kraft pulping. This strong correlation is consistent with the proposed mechanism of HexA formation - the xylose units in the xylan chain carry 1:2 linked methyl-glucuronic acid groups (Tanczos *et al.*, 2003), which average about one uronic acid per ten xylose units (Haun, 1970; Sjöström, 1981; Teleman *et al.*, 2001). It follows that a higher xylose content will result in a higher methyl-glucuronic acid content. During Kraft pulping, methyl-glucuronic acid is converted to HexA (Clayton, 1963; Johansson & Samuelson, 1977; Teleman *et al.*, 1995), and thus the amount of HexA formed should be related to the amount of methyl-glucuronic acid attached to the xylan chain, which it turn, should be related to the amount of xylose present in the wood. Vuorinen *et al.* (1999) also reported higher HexA content in hardwood pulps compared to softwood pulps similarly cooked, primarily because hardwoods contain more methyl-glucuronoxylan than softwoods (Sjöström, 1981).

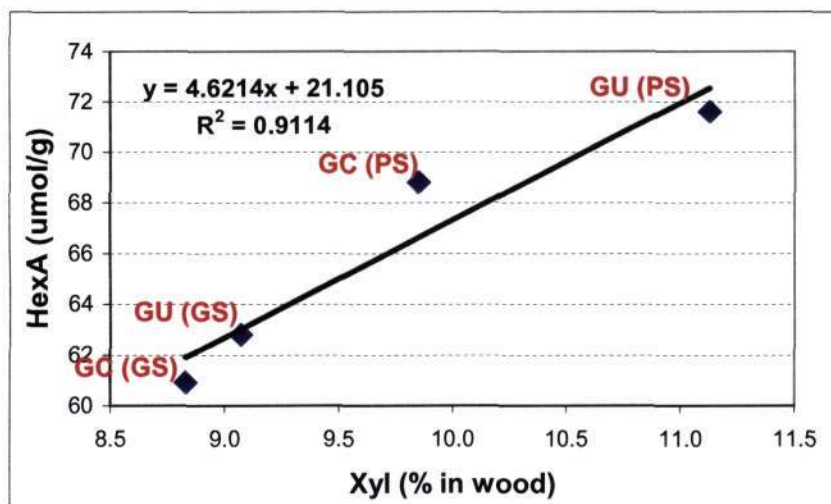


Figure 4.5.2 Correlation between xylose content of wood and hexenuronic acid (HexA) content of unbleached pulp. (GS=good site and PS=poor site).

4.6 ACID HYDROLYSIS OF CLONES USING OPTIMUM CONDITIONS

Using the GU clone from the good site, the optimum A-stage conditions were found to be a temperature of 95°C, reaction time of 180 minutes, and pH 3.5. This set of conditions was applied to the remaining GU clone from the poor site and the GC clones from both poor and good sites. This part of the work focused on the impact of the A-stage, using the optimum conditions, on the physical and chemical properties of the GU and GC clones from the different sites.

4.6.1 Effect of optimum A-stage on hexenuronic acid content of pulps

Hexenuronic acid reduction in pulps of the GU and GC clones after acid hydrolysis, using the optimum conditions, is shown in **Figure 4.6.1**. The GU clone from the good site showed a reduction of 74%, with HexA content dropping from 61.2 to 16.1 μmol/g in the pulp after acid hydrolysis. The pulps of the same clone from the poor site showed a reduction of 63%, dropping from 71.5 to 26.7 μmol/g. The GC clones exhibited a similar trend to the GU clones, in that the pulps of the GC clone from the good site showed a higher HexA reduction after acid hydrolysis compared to the poor site. On the good site, HexA content of pulps dropped from 60.2 to 13.4 μmol/g (78%

reduction), whilst on the poor site, the HexA reduction in pulps was 66%, dropping from 66.7 to 22.8 $\mu\text{mol/g}$.

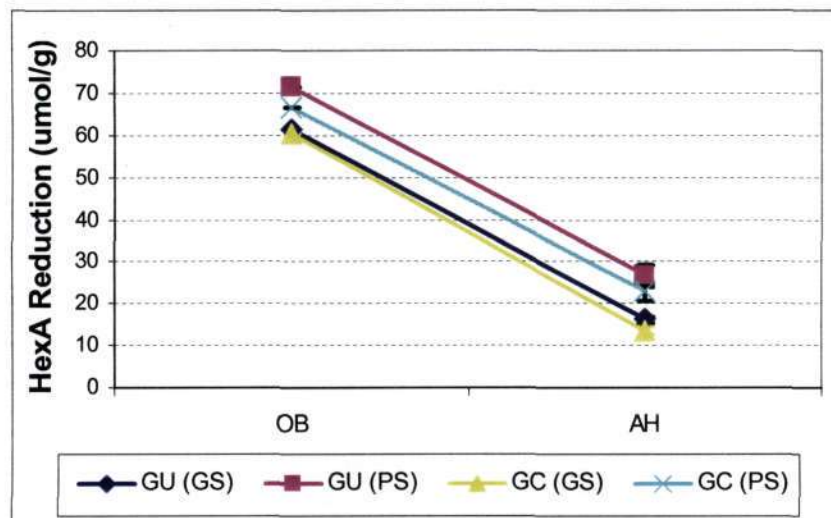


Figure 4.6.1 Hexenuronic acid (HexA) reduction after acid hydrolysis (AH) using optimum conditions (95°C; 180min; pH 3.5) for GU and GC clones from good (GS) and poor (PS) sites. Each point is the mean of 3 acid hydrolysis experiments with the whiskers as the standard deviation. (OB = oxygen bleached pulp).

4.6.2 Effect of optimum A-stage on Kappa number of pulps

Both clones from both sites showed a reduction in Kappa number of 4 units after acid hydrolysis (**Figure 4.6.2**). The Kappa number of pulps of the GU clones dropped from approximately 11 to 7, whilst the Kappa number of pulps of the GC clones dropped from approximately 9 to 5, after acid hydrolysis.

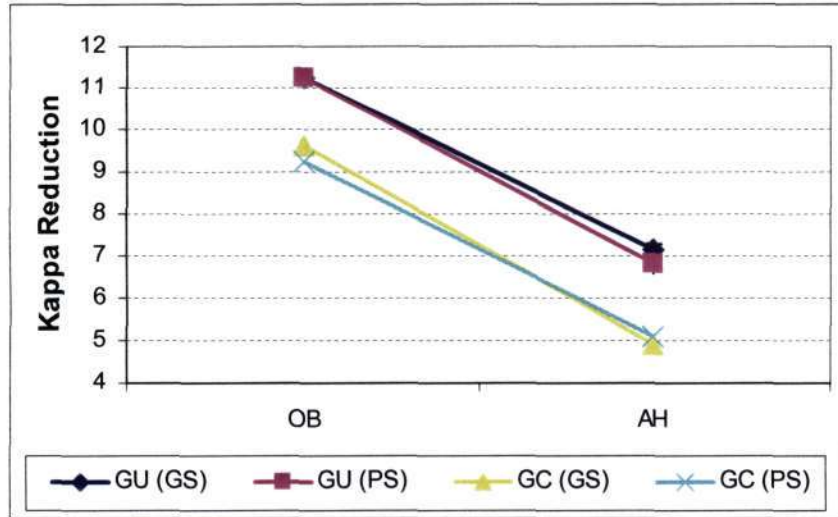


Figure 4.6.2 Kappa number reduction after acid hydrolysis using optimum conditions (95°C; 180min; pH 3.5) for GU and GC clones from good (GS) and poor (PS) sites. Each point is the mean of 3 acid hydrolysis experiments with the whiskers as the standard deviation.

From section 4.3.4 (**Table 4.6**), it was found that between 9.4 and 11.6 μ mol HexA contributed to 1.0 Kappa unit. The correlation was obtained by subjecting the GU clone from the good site to a series of acid hydrolysis experiments in which the temperature and reaction times were varied. This correlation was tested using the remaining clones in the study. **Table 4.9** shows the difference in Kappa number and HexA before and after the A-stage. By correlating the reduction in HexA with the reduction in Kappa number, it was again found that between 10.0 and 11.0 μ mol HexA contributed to 1.0 Kappa unit, thereby confirming the earlier findings in this study, and of others (Vuorinen *et al.*, 1996; Li & Gellerstedt, 1997; Chai *et al.*, 2001; Pedroso & Carvalho, 2003; Petit-Breuilh *et al.*, 2004).

Table 4.9 Correlation of Kappa number reduction (ΔKN) with HexA reduction ($\Delta HexA$) after acid hydrolysis for GU and GC clones from good and poor sites. (OD = oxygen delignified pulp; A = acid hydrolysis stage).

Sample	KN (OD)	KN (post A)	ΔKN	HexA (OD)	HexA (post A)	$\Delta HexA$	$\Delta HexA/\Delta KN$
GU (good)	11.3	7.2	4.1	61.2	16.1	45.1	11.0
GU (poor)	11.2	6.8	4.4	71.5	26.7	44.8	10.2
GC (good)	9.6	4.9	4.7	60.2	13.4	46.8	10.0
GC (poor)	9.2	5.1	4.1	66.7	22.8	43.9	10.7

4.6.3 Effect of optimum A-stage on chemical composition of pulps

The effect of the A-stage on the lignin content of the oxygen delignified pulps of both clones is shown in **Figure 4.6.3**. The lignin concentration appeared fairly constant after acid hydrolysis for both clones, except the GU clone from the good site, for which the acid hydrolysed pulps showed a significantly lower lignin content compared to its corresponding oxygen delignified pulps. This was discussed in section 4.3.3.3 and could be the result of partial degradation and condensation of lignin in the acidic medium.

The glucose content of the acid hydrolysed pulps, expressed as a percentage in wood, is illustrated in **Figure 4.6.4**. Besides the GC clone from the poor site, the A-stage was found to have no significant impact on the glucose content of the acid hydrolysed pulps.

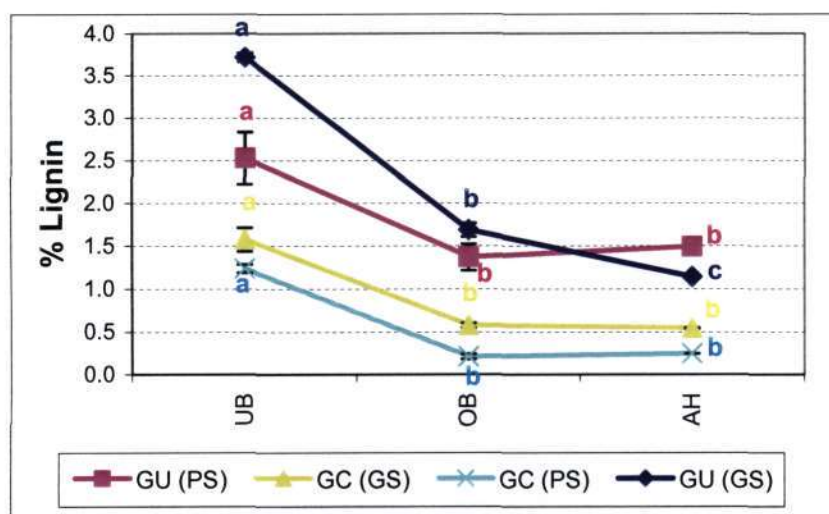


Figure 4.6.3 Lignin content of unbleached (UB), oxygen bleached (OB) and acid hydrolysed (AH) pulps of GU and GC clones from good (GS) and poor (PS) sites. Hydrolysis was carried out using the optimum conditions (95°C; 180min; pH 3.5). Each point represents the mean lignin content of 3 measurements, with the whiskers as the standard deviation. Common letters indicate no significant differences amongst the means at 95% confidence levels, and are only applicable within a specific colour.

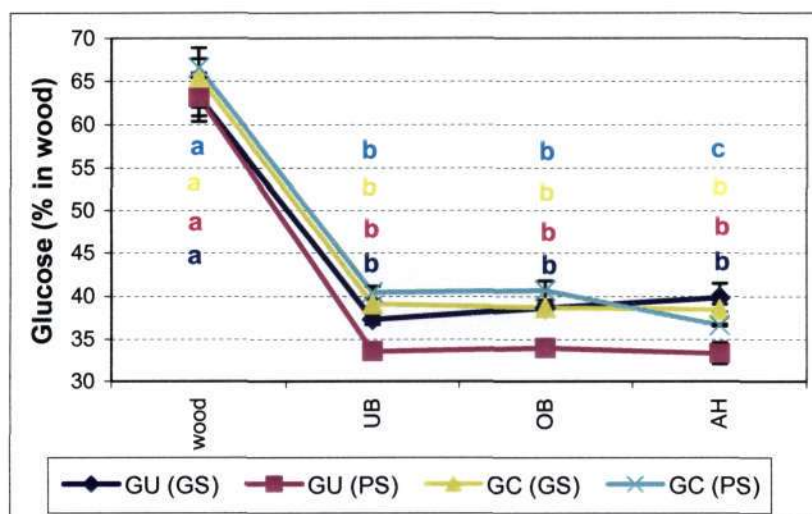


Figure 4.6.4 Glucose content of unbleached (UB), oxygen bleached (OB) and acid hydrolysed (AH) pulps of GU and GC clones from good (GS) and poor (PS) sites. Hydrolysis was carried out using the optimum conditions (95°C; 180min; pH 3.5). Each point represents the mean glucose content of 3 measurements, with the whiskers as the standard deviation. Common letters indicate no significant differences amongst the means at 95% confidence levels, and are only applicable within a specific colour.

The xylose content of the acid hydrolysed pulps, expressed as a percentage in wood, is illustrated in **Figure 4.6.5**. Here again, the A-stage was found to have no significant impact on xylose. However for the GC clone from the poor site, the oxygen delignification and acid hydrolysis stages both individually reduced the xylose content. As a result, the combined effect was a significantly lower xylose content in the acid hydrolysed pulps compared to the unbleached pulps.

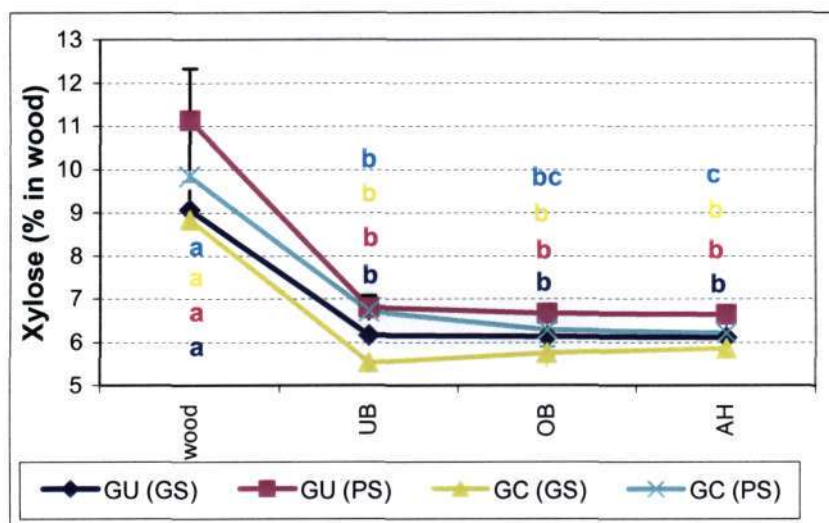


Figure 4.6.5 Xylose content of unbleached (UB), oxygen bleached (OB) and acid hydrolysed (AH) pulps of GU and GC clones from good (GS) and poor (PS) sites. Hydrolysis was carried out using the optimum conditions (95°C; 180min; pH 3.5). Each point represents the mean xylose content of 3 measurements, with the whiskers as the standard deviation. Common letters indicate no significant difference amongst the means at 95% confidence levels, and are only applicable within a specific colour.

4.6.4 Effect of optimum A-stage on viscosity of pulps

The pulp viscosity of the GU and GC clones from both sites, before and after acid hydrolysis, is showed in **Figure 4.6.6**. The drop in viscosity after hydrolysis was more pronounced for the GU clones compared to the GC clones. However, the viscosity of the GU clones was still approximately 50% higher than that of the GC clones after hydrolysis. The GU clone from the good site showed a reduction in viscosity of 40%, with the viscosity dropping from 103.3 to 62.5cP. The reduction in viscosity for the same clone from the poor site was much smaller (27%), dropping

from 84.7 to 61.7cP after hydrolysis. The GC clones showed similar changes in pulp viscosity for both sites with the good site dropping from 38.2 to 31.5cP and the poor site dropping from 37.1 to 32.1cP after acid hydrolysis.

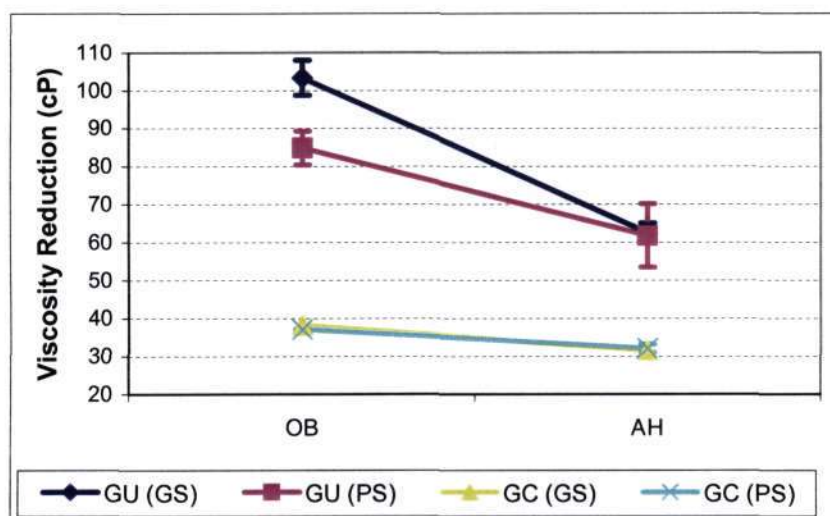


Figure 4.6.6 Pulp viscosity reduction of oxygen bleached (OB) pulps after acid hydrolysis (AH) using optimum conditions (95°C; 180min; pH 3.5) for GU and GC clones from good (GS) and poor (PS) sites. Each point is the mean of 3 acid hydrolysis experiments with the whiskers as the standard deviation.

4.6.5 Effect of optimum A-stage on pulp yields

The pulp yield of the GU and GC clones after acid hydrolysis is shown in **Figure 4.6.7**. No significant differences in pulp yield after acid hydrolysis were found between the GU clones from the good sites (98.4%) and poor sites (96.8%). The A-stage however, was found to have a significant impact on the pulp yield of the GC clone from the poor site. This clone showed a significantly lower pulp yield (5.5%) after acid hydrolysis compared to the same clone from the good site. The reduced pulp yield could, to some extent, be related to the loss in glucose and xylose observed in **Figures 4.6.4** and **4.6.5**, but will require further investigation, as the yield loss is significant.

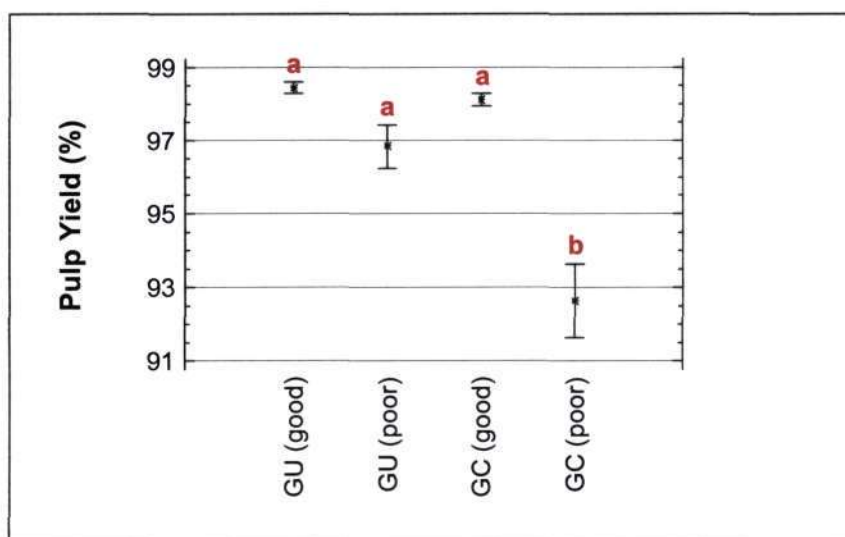


Figure 4.6.7 Pulp yield after acid hydrolysis using optimum conditions (95°C; 180min; pH 3.5) for GU and GC clones from good and poor sites. Each point represents the mean pulp yield of 3 individual acid hydrolysis experiments, with the whisker as the standard error. Common letters indicate no significant difference amongst the means, at 95% confidence levels.

4.7 BLEACHING OF ACID HYDROLYSED PULPS

The pulps of the GU and GC clones from the different sites that were acid hydrolysed using the optimum conditions (95°C; 180min; pH 3.5) were then bleached to 90% ISO brightness using the D₀ED₁ sequence. Pulps of both clones from the different sites that were not acid hydrolysed were also subjected to the same bleaching sequence and were used as controls in the study. The comparison between the fully bleached control pulps and acid hydrolysed pulps in terms of TAC consumption, chemical composition, viscosity and pulp yield is summarised in **Table 4.10**. For the strength properties of these pulps, the comparisons were made at a constant freeness value of 400CSF, and are also shown in **Table 4.10**. The individual property-freeness curves for each clone from the different sites can be found in **Appendix 1**.

In all instances, the addition of the A-stage in the bleaching sequence significantly reduced the TAC consumption compared to the control pulps. For the GU clones from the good and poor sites, the savings in chlorine dioxide were 35% and 48%, respectively. For the GC clones, the chlorine dioxide consumption was more than halved, with the good and poor sites showing savings up to 61% and 55%,

respectively.

The glucose and xylose content of the fully bleached acid hydrolysed pulps of the GC clones from both sites was found to be significantly higher than their corresponding control pulps. The GU clone from the good site showed similar glucose levels between the fully bleached acid hydrolysed and control pulps, whilst xylose in the acid hydrolysed pulps of this clone was significantly lower after bleaching. Similar to the GC clones, the GU clone from the poor site showed higher glucose for the acid hydrolysed pulps compared to the control pulps, whilst xylose was found to be similar for both the bleached acid hydrolysed and control pulps.

Viscosity of the bleached acid hydrolysed pulps of the GU clones from both sites showed significantly lower values compared to their respective control pulps. The GC clones from both sites showed similar viscosities between their respective acid hydrolysed and control pulps.

Despite some differences in pulp yield between the acid hydrolysed and control pulps in the individual bleaching stages, the total pulp yield of the GU and GC clones across pulping and bleaching were unaffected by the inclusion of the A-stage in the bleaching sequence. In fact, the GC clone from the good site showed a significant improvement in bleached pulp yield (~2%) for the pulps that were acid hydrolysed prior to bleaching compared to control pulps that did not undergo acid hydrolysis prior to bleaching.

The acid hydrolysis treatment of the GU clone from the poor site and the GC clones from the good and poor sites, using the optimum conditions, were found to significantly affect certain strength properties. Because the conditions of the A-stage were optimised using the GU clone from the good site, the strength properties of this clone were not negatively impacted on by the A-stage under the optimum conditions 95°C, 180min, pH 3.5. Burst strengths of the remaining clones were unaffected by the A-stage, except for the GC clone from the poor site, for which burst was negatively impacted. Tear strength, air resistance, sheet density and opacity were unaffected by the A-stage for these clones, whilst zero-span tensile strength improved significantly for the acid hydrolysed pulps compared to the control pulps. Stiffness also showed improvements in some instances for the pulps that were acid hydrolysed prior to bleaching. Tensile strength and stretch were the only properties that were negatively affected, with the acid hydrolysed pulps showing significantly

lower values, compared to the control pulps that did not undergo acid hydrolysis prior to bleaching.

The brightness reversion of the bleached pulps of the GU clone from the good site decreased significantly for the acid hydrolysed pulps compared to the control pulps. However, the same clone from the poor site showed similar reversions for both the acid hydrolysed and control pulps. This confirmed the fact, also discussed in the optimisation study (section 4.4.5.10), that no clear dependence between pulp brightness reversion and HexA elimination in the A-stage could be found. This fact was further highlighted by the results obtained for the GC clones. Both sites showed significantly increased reversions for the acid hydrolysed pulps compared to their respective control pulps. This finding however, also contradicted the previous explanation offered in the optimisation study. It was stated that the decrease in brightness reversion in pulps that were hydrolysed prior to bleaching could be related to decreased amounts of quinoid structures formed in the bleached pulps as a result of the lower amounts of chlorine dioxide used for bleaching. Based on the results obtained for the GC clones, this is obviously not the sole reason, as the acid hydrolysed pulps consumed lower amounts of chlorine dioxide to reach 90% ISO brightness due to the removal of HexA and therefore, according to the explanation given above, should have resulted in lower amounts of quinoid structures been formed, thus leading to improved brightness stability.

Table 4.10 Summary of the effect of acid hydrolysis (AH) on bleached pulp properties of GU and GC clones from good and poor sites. Properties of pulps that were acid hydrolysed prior to bleaching, using the optimum conditions (95°C-180min), were compared to their respective control pulps that did not undergo acid hydrolysis prior to bleaching. The common letters in brackets indicate that there is no significant difference amongst the means values at a 95% confidence level, and are only applicable within a given property.

Property	GU (GOOD SITE)		GU (POOR SITE)		GC (GOOD SITE)		GC (POOR SITE)	
	CONTROL	AH	CONTROL	AH	CONTROL	AH	CONTROL	AH
TAC consumption (%)	11.3(A)	7.4(B)	13.2(C)	6.8(D)	12.0(E)	4.7(F)	11.6(G)	5.2(H)
Glucose (% in wood)	37.1(A)	37.1(AB)	34.2(C)	35.5(D)	36.0(BD)	40.5(E)	35.3(D)	38.6(F)
Xylose (% in wood)	6.1(A)	5.4(B)	6.8(C)	6.9(C)	5.4(B)	6.0(A)	6.1(A)	6.8(C)
Viscosity (cP)	66.8(A)	53.9(B)	67.0(A)	48.5(C)	28.0(D)	24.9(D)	29.2(D)	25.4(D)
PY across pulping and bleaching (%)	48.4(A)	48.2(A)	44.3(BC)	44.0(C)	45.4(BC)	47.3(D)	45.6(B)	45.4(BC)
Burst index at 400CSF (MN/kg)	5.8(AB)	6.2(A)	5.0(CD)	4.9(D)	5.4(BC)	5.2(CD)	5.4(BC)	4.9(D)
Tear index at 400CSF (Nm ² /kg)	9.6(A)	9.4(AB)	7.8(C)	7.6(C)	10.2(D)	9.9(AD)	8.9(BE)	8.5(E)
Tensile index at 400CSF (kNm/kg)	78.1(AB)	83.8(B)	70.0(CD)	62.5(E)	78.5(AB)	69.1(CD)	74.6(AC)	66.6(DE)
0-span tensile index at 400CSF (kNm/kg)	33.9(AB)	34.4(B)	27.7(C)	32.8(ABD)	31.1(AD)	40.9(E)	29.8(CD)	37.8(E)
Stretch at 400CSF (%)	4.2(A)	4.2(A)	4.0(AE)	3.4(BD)	3.9(CE)	3.5(BD)	3.7(BC)	3.3(D)
Stiffness at 400CSF (mN)	41.3(A)	46.2(AB)	41.0(A)	48.2(BD)	55.3(C)	58.0(C)	56.5(C)	53.1(DC)
Air resistance at 400CSF (sec/100ml)	65.5(AB)	83.9(A)	65.2(AB)	43.6(BC)	28.2(CD)	13.0(D)	19.1(D)	16.0(D)
Sheet density at 400CSF (kg/m ³)	802(AB)	816(A)	800(ABC)	780BCD)	766(D)	757(D)	776(CD)	780(BCD)
Opacity at 400CSF (%)	74.9(AB)	73.1(B)	74.9(AB)	76.6(AC)	77.5(C)	77.9(C)	77.4(C)	78.3(C)
Brightness reversion (%ISO)	4.2(A)	3.3(B)	3.0(BC)	2.9(CD)	2.2(E)	2.6(D)	1.9(E)	2.8(CD)

CHAPTER FIVE

CONCLUSIONS

5.1 SUMMARY OF RESULTS

The primary focus of this study was to develop an understanding of the impact of HexA, and its removal during acid hydrolysis, on the bleachability of eucalypt Kraft pulps. In order to achieve this, two commercially important South Africa grown *Eucalyptus* hybrid clones, *E. grandis* x *E. urophylla* (GU) and *E. grandis* x *E. camaldulensis* (GC) were selected for the study. Each clone was sampled from two sites representing extreme differences in site quality.

The clones were pulped to a constant Kappa number of 20 (± 2) (uncorrected for HexA) using the Kraft process. The pulping time required to reach Kappa 20 was determined from a preliminary study on the rate of delignification (ROD) of each clone from the different sites. The results from this study showed that both species and site quality had a significant impact on the ROD under the specified pulping conditions. A significantly shorter pulping time at maximum temperature (170°C) was required for both clones from the good site to reach the target Kappa number, compared to the poor sites.

Extended delignification of the unbleached pulps of each clone from the different sites was carried out using a medium consistency dual oxygen delignification stage. Oxygen delignification resulted in 44% and 48% delignification for the GU clone from the good and poor sites, respectively, whilst the GC clones achieved a similar degree of delignification for both sites (52%). Pulp yield after oxygen delignification was lower on the poor sites compared to the good sites for both clones (0.5% for the GU clone and 1.1% for the GC clone).

Before commencement of the acid hydrolysis studies, the first step in the project was to identify a suitable method for the quantification of HexA. A UV/VIS spectroscopic method developed at the Institute of Paper Science and Technology (IPST) in USA was adopted in this study. The method proved to be inexpensive, uncomplicated and less time consuming, compared to other methods reviewed. The accuracy of the

method was verified by participation in a proficiency testing scheme (inter-laboratory study) with IPST, and a second research organisation, the Royal Institute of Technology (KTH), who have also developed their own method for the quantification of HexA. The results from the proficiency testing showed good correlations between laboratories using the same method (CSIR & IPST), and also between laboratories using different methods (CSIR & KTH and IPST & KTH). Correlation co-efficients greater than 0.99 were achieved in all instances.

As part of a preliminary investigation to determine the conditions (temperature and reaction time) of the A-stage that resulted in maximum removal of HexA, the oxygen delignified pulp of the GU clone from the good site was subjected to acid hydrolysis at three temperatures, 95, 110 and 125°C. The reaction time and pH was kept constant at 180min and 3.5. The results from this investigation showed that a temperature of 125°C and reaction time of 180min was sufficient to remove up to 97% of HexA from the pulp.

Knowing the upper temperature limit and reaction time required to remove the majority of HexA from the pulp, further investigations were carried out to optimise the conditions of the A-stage. The objective here was to ensure maximum removal of HexA but with minimal impact on the physical and chemical properties of the pulp. Here again, the GU clone from the good site was used, and was subjected to three temperatures (95, 110 and 125°C) and three reaction times (60, 120 and 180min). The pH was kept constant at 3.5 for all experiments. The effect of the A-stage under these conditions on HexA removal, Kappa number reduction, lignin and carbohydrate content, pulp viscosity and pulp yield, were investigated.

The results from this part of the study showed that HexA was unreactive during oxygen delignification, and in most instances the levels of HexA found in the oxygen delignified pulps were similar to the unbleached pulps. During acid hydrolysis however, the HexA concentration decreased significantly in the pulp as the temperature and reaction time of the A-stage increased. A temperature of 110°C and reaction time of 120min removed approximately 95% of HexA, and any further increase in temperature and/or reaction time beyond this point had no significant impact on the residual amount of HexA in the pulp. Due to the removal of HexA during acid hydrolysis, the Kappa number decreased significantly as the temperature and reaction time of the A-stage increased. At 110°C-120min, the Kappa number was reduced by up to 5 units.

Measurement of the lignin content during acid hydrolysis, at each temperature and reaction time, showed that the concentration of lignin in the pulp was reduced by approximately 0.4% at 95°C-60min, after-which it remained fairly constant, even with further increase in temperature and reaction times during acid hydrolysis. Therefore the decrease in Kappa number during acid hydrolysis was attributed largely to the decrease in the concentration of HexA and not to the loss of lignin.

From the removal of HexA during acid hydrolysis and the accompanying reduction in Kappa number, the contribution of HexA to Kappa number was determined by correlating the reduction in HexA after acid hydrolysis to the reduction in Kappa number after acid hydrolysis. The results showed that between 9.4 and 11.6 μ mol HexA contributed to 1 Kappa unit – a finding that was consistent with the findings of many researchers. Analysis of the HexA content of the unbleached pulps of both clones gave values between 60-70 μ mol/g. This means that a pulp produced to Kappa number 20 (measured using the conventional Tappi standard method, T236 cm-85), essentially equates to a true Kappa number of 13-14, after correction for HexA.

The two major monosaccharides in hardwoods (glucose and xylose) were found to be more resistant to acid hydrolysis than lignin. After pulping, the glucose and xylose content of the unbleached pulps remained unchanged during acid hydrolysis across all temperatures used.

Acid hydrolysis however, significantly decreased the viscosity of the pulp. At 95°C-120min the viscosity was reduced by 45%, but stabilised at this level during acid hydrolysis at 95°C and 110°C. At a higher temperature (125°C) it was further reduced and was significantly lower than the pulp viscosity at 95°C and 110°C.

At lower temperatures of the A-stage (95°C and 110°C), pulp yield was unaffected by acid hydrolysis. At 125°C, it was reduced by as much as 2%.

From the acid hydrolysed pulps, three pulps: 95°C-60min, 95°C-180min and 110°C-120min, which contained varying amounts of HexA, were selected and bleached to 90% ISO brightness using a D₀ED₁ bleaching sequence. The 110°C-120min A-stage conditions were chosen as the upper limit because it was found that a further increase in temperature and reaction time beyond this point did not significantly reduce the concentration of HexA further. An oxygen delignified pulp that was not

acid hydrolysed, and which contained maximum HexA, was also bleached to 90% ISO brightness. This pulp was used as a control in the study and allowed comparisons to be made between the bleached acid hydrolysed pulps and bleached control pulps. Pulp properties investigated were total active chlorine (TAC) consumption to reach 90% brightness, chemical composition of the bleached pulps, viscosity of the bleached pulps, pulp yield after each stage of bleaching, and total pulp yield across pulping and bleaching. Physical properties measured on the bleached pulps were burst, tear, tensile, zero-span tensile, stretch, stiffness, sheet density, air resistance, opacity, and brightness reversion. Each property, besides brightness reversion, was compared at constant freeness (400CSF) to the control pulps that did not undergo acid hydrolysis prior to bleaching.

It was found that pulp bleachability, expressed as the amount of bleaching chemical (in this case chlorine dioxide) required to reach 90% brightness, improved significantly as the temperature and reaction times of the A-stage increased. This was due primarily to the removal of HexA, thus requiring lesser amounts of chlorine dioxide to reach the target brightness. The %TAC was reduced by 25%, 35%, and 44% for the 95°C-60min, 95°C-180min, and 110°C-120min acid hydrolysed pulps, respectively.

Compared to the bleached control pulps, the glucose contents of the bleached acid hydrolysed pulps were unaffected by the A-stage, whilst xylose contents were found to be approximately 1% lower for the pulps that were acid hydrolysed prior to bleaching.

Viscosity of the bleached pulps was affected by inclusion of the A-stage in the bleaching sequence. Compared to the control pulps that did not undergo acid hydrolysis prior to bleaching, the pulps hydrolysed at 95°C(60 and 180min) prior to bleaching both showed approximately 20% lower viscosity, whilst the viscosity of the pulps hydrolysed at 110°C-120min prior to bleaching was reduced by approximately 30%.

Measurement of pulp yield after each bleaching stage in the D₀ED₁ sequence showed that in the D₀-stage the control pulps had lower pulp yields compared to the acid hydrolysed pulps. In the E-stage, pulp yield was higher for the control pulps, whilst in the D₁-stage, similar pulp yields were obtained for the control and acid hydrolysed pulps. Despite the variation of yield in the individual bleaching stages,

across the D₀ED₁ sequence no significant differences in pulp yield were found between the acid hydrolysed and control pulps. More importantly, it was found that across pulping and bleaching, inclusion of the A-stage in the bleaching sequence had no significant impact on the total pulp yield.

Acid hydrolysis was also found to have no significant impact on most of the physical properties of the bleached pulps. Properties such as burst, tensile, zero-span tensile, stretch, stiffness, air resistance and sheet density were either unaffected by the acid treatments, or in some cases, showed improvements after the acid treatments. The exceptions were opacity and tear strength. Opacity was found to be significantly lower for the pulps hydrolysed at 95°C-60min compared to the control pulps, but increased to the same level as the control pulps for the 95°C-180min and 110°C-120min acid hydrolysed pulps. Tear on the other hand, was unaffected by acid hydrolysis carried out at the lower temperature of 95°C(60 and 180min), but decreased significantly in the pulps hydrolysed at 110°C-120min.

Brightness reversion was found to decrease significantly as the temperature and reaction time of the A-stage increased. The control pulps showed the highest reversion. The decreasing concentration of HexA in the pulps, as the temperature and reaction time of the A-stage increased, could not be linked to the improvement in brightness stability because HexA measurements on the bleached pulps, both control and acid hydrolysed, showed that none were present. This was mainly due to its reaction with chlorine dioxide, which resulted in increased consumptions of bleaching chemicals. A possible explanation for this observation was that the use of chlorine dioxide in bleaching results in the formation of quinoid structures in the pulp which have been linked to the formation of coloured products during the initial stages of delignification. Due to the increased removal of HexA as the conditions of the A-stage increased, the amount of chlorine dioxide required to reach the target brightness decreased. Therefore pulps requiring lesser amounts of chlorine dioxide are expected to produce lesser amounts of quinoid structures, resulting in the decrease in brightness reversion that was observed.

In deciding on the most suitable conditions for the A-stage, a compromise between efficiency of HexA removal, the resulting quality of the bleached pulps, and practical considerations for full scale industrial implementation of the A-stage, was required. Based on these requirements, the optimum conditions were considered to be a temperature of 95°C, reaction time of 180min, and pH 3.5. These conditions were

applied to the remaining GU clone from the poor site and the GC clones from the poor and good sites. Here again, the response of the different clones to the A-stage, using the optimum conditions, were investigated.

Acid hydrolysis using the optimum conditions reduced the HexA content of the GC clones from the good and poor sites by 78% and 66%, respectively. Under the same conditions of the A-stage, the GU clones showed HexA reductions of 74% and 63% for the good and poor sites, respectively. Kappa number reductions for both clones from both sites were similar, between 4-5 units. Measurement of the lignin content of the pulps before and after hydrolysis showed that lignin was not removed during acid hydrolysis. The relationship between HexA and Kappa number that was determined in the optimisation study was tested using the GU clone from the poor site and the GC clones from both the good and poor sites. A similar result was found – between 10-11 μ mol HexA contributed to 1 Kappa number unit.

The glucose and xylose content of the GU and GC clones was found to be unaffected by the A-stage, using the optimum conditions. The exception was the GC clone from the poor site, which showed lower glucose and xylose in the acid hydrolysed pulps compared to the unbleached pulps.

Acid hydrolysis using the optimum conditions, significantly lowered viscosity of both clones. The viscosity of the GU clones from the good and poor sites was reduced by approximately 40% and 27%, respectively. The GC clones from the good and poor sites showed lower viscosity reductions of approximately 18% and 13%, respectively. Although the viscosity reductions were lower for the GC clones compared to the GU clones, the viscosity of the GU clones after hydrolysis were approximately twice the viscosity of the GC clones after hydrolysis.

Pulp yields after acid hydrolysis, using the optimum conditions, were found to be similar for the GU clones from the good site (98.4%) and poor site (96.8%). The GC clone from the good site also showed similar pulp yields to the GU clones (98.1%). For the GC clone from the poor site, acid hydrolysis was found to have a significant impact on the pulp yield (92.6%). This significantly lower pulp yield could, to some degree, be attributed to the loss of glucose and xylose that was experienced during acid hydrolysis, but will require further investigation.

As in the case of the optimisation studies, both clones that were acid hydrolysed

using the optimum conditions, were then bleached to 90% ISO brightness. Oxygen delignified pulps of each clone that were not acid hydrolysed prior to bleaching were used as controls. Bleached pulp properties investigated were the same as in the optimisation study.

Similar to the results obtained in the optimisation study, bleachability was significantly improved for all pulps that were acid hydrolysed prior to bleaching. Savings in chlorine dioxide ranged between 35% and 61% for these pulps compared to the control pulps that did not undergo acid hydrolysis prior to bleaching.

In most instances, the levels of glucose and xylose were found to be higher in the pulps that were acid hydrolysed prior to bleaching. The viscosity of the fully bleached pulps of the GU clones was significantly affected by including the A-stage in the bleaching sequence, but acid hydrolysis was found to have no impact on pulp viscosity of the GC clones.

Despite some variation in pulp yield after each bleaching stage, the total pulp yields across pulping and bleaching for both clones were unaffected by the A-stage. In fact, the GC clone from the good site showed approximately 2% improvement in pulp yield for the pulps that were acid hydrolysed prior to bleaching.

Comparison of the strength properties at constant freeness showed that the pulps that were acid hydrolysed prior to bleaching were, in most instances, unaffected by including the A-stage in the bleaching sequence, despite the significantly lower viscosity. The exceptions were tensile strength and stretch. For the GC clones, brightness reversion was found to be significantly higher for the pulps that were acid hydrolysed prior to bleaching compared to the control pulps. These results were contrary to those obtained for the GU clones where acid hydrolysis was found to have a positive effect on brightness reversion.

5.2 CONCLUSIONS

- A simple and rapid method was identified for the quantification of HexA in Kraft pulps. The accuracy of the method was verified by inter-laboratory studies with IPST and KTH.
- Acid hydrolysis was found to be effective in the removal of HexA. At 110°C-

120min, approximately 95% reduction in HexA concentration was achieved.

- Due to the removal of HexA during acid hydrolysis, the Kappa number also decreased. At 110°C-120min, the Kappa number was reduced by 5 units.
- Between 10-11µmol HexA was found to contribute to 1 Kappa number unit.
- The concentration of HexA in GU and GC clones ranged between 60-70µmol/g.
- Species, site and xylose content was found to affect the amount of HexA formed in Kraft pulps – GU clones generally contained more HexA than GC clones from the same sites, whilst poor sites and high xylose contents resulted in a higher concentration of HexA in pulps, for the given set of pulping conditions used in this study.
- In most instances, lignin, glucose and xylose content of the pulp was unaffected by acid hydrolysis.
- Viscosity was severely affected by acid hydrolysis, but generally this had no impact on strength properties. The exceptions were tear and tensile strengths which were found to be lower in some instances.
- The best conditions for efficient removal of HexA with minimal impact on pulp quality were found to be 95°C, 3 hours reaction time and pH 3.5.
- In terms of brightness reversion, no clear-cut relationship between reversion and HexA concentration could be found.
- Significant chlorine dioxide savings, in some instances greater than 50%, were obtained for all pulps that were acid hydrolysed prior to being bleached to 90% ISO brightness using a D₀ED₁ sequence.
- Total pulp yield across pulping and bleaching was unaffected by including an acid hydrolysis stage in the bleaching sequence.

5.3 RECOMMENDATIONS

The study showed that Kraft pulps produced from *Eucalyptus* clones contain significant amounts of HexA. The presence of HexA was shown to contribute to the Kappa number of the pulp, measured using the conventional Tappi standard method. In industry, this has serious implications for the control of pulping and bleaching processes which make use of online Kappa number analysers to monitor the process. These online sensors, in most instances, are calibrated against the standard method that is used to measure Kappa number. It is therefore

recommended that the HexA content be measured in the pulp. This can be done using the IPST method that was validated in this study, which was found to be a simple and rapid technique. Measurement of the HexA content will allow the Kappa number reading to be adjusted by using the Kappa-to-HexA factor determined in this study.

The reasons for brightness reversion of bleached pulps appear to be complex, and quite possibly, inter-related. In this study, HexA failed to account for the reversion of pulps bleached using the sequences O/OD₀ED₁ and O/OAD₀ED₁. This was mainly because they were removed during bleaching either by acid hydrolysis or by reaction with chlorine dioxide. As a result, the reasons for reversion still need to be addressed in a separate study, and in greater detail.

This study showed that significant chemical savings are possible when an acid hydrolysis stage is included in the bleaching sequence. In most instances, pulp yields and other properties were unaffected by acid hydrolysis. It therefore appears that the acid hydrolysis stage offers distinct advantages for the production of bleached hardwood Kraft pulps, and the economical feasibility of implementing such a stage in the current bleaching sequences used in industry, should be investigated. It should however be noted, that there is a negative impact on pulp viscosity in applying the acid stage.

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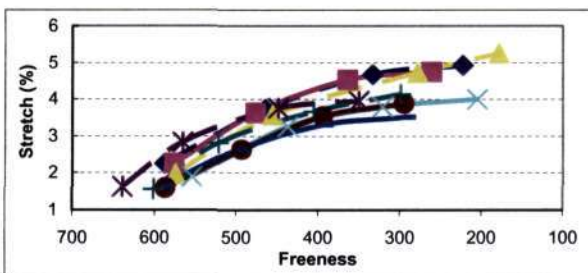
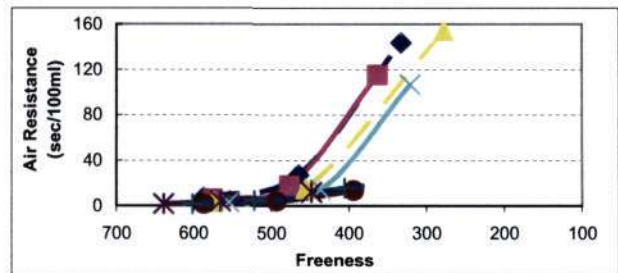
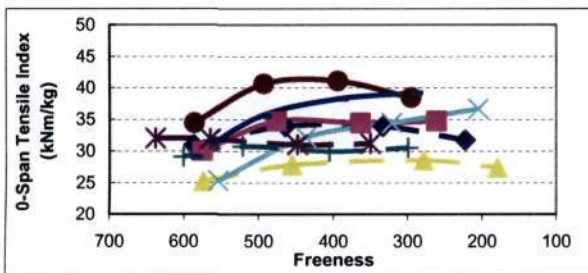
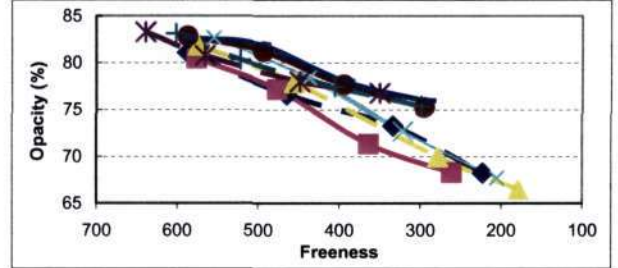
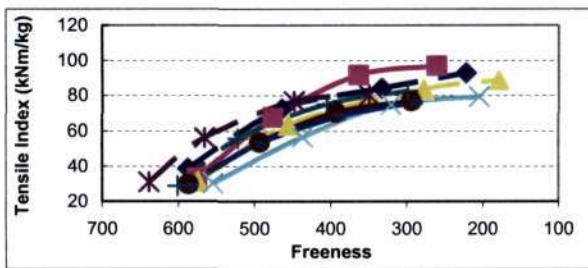
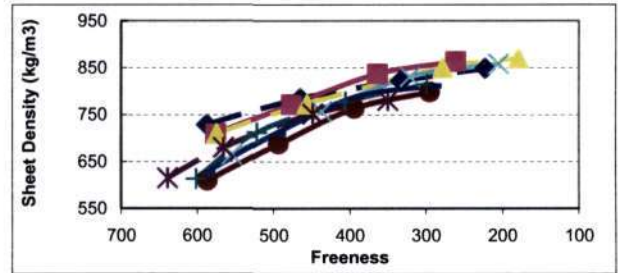
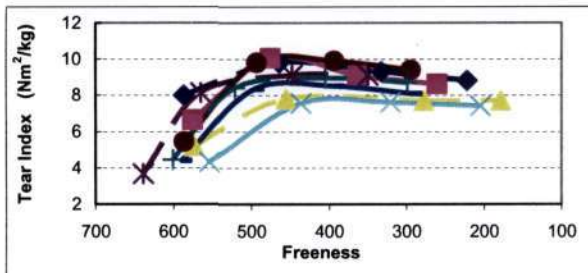
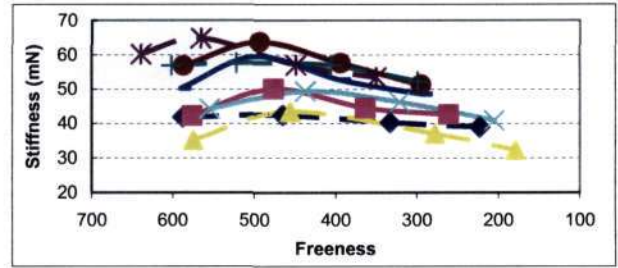
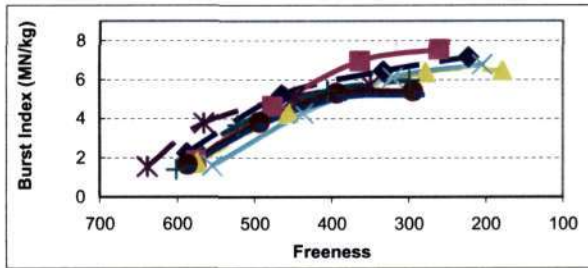
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APPENDIX 1



Legend used:

- ◆— GU (good site) – control
- ▲— GU (poor site) – control
- *— GC (good site) – control
- +— GC (poor site) – control
- GU (good site) – acid hydrolysed
- x— GU (poor site) – acid hydrolysed
- GC (good site) – acid hydrolysed
- GC (poor site) – acid hydrolysed

APPENDIX 2

2.1 Total alkalinity

10.0 (\pm 0.1)ml of well agitated cooking liquor was pipetted into a 250ml Erlenmeyer flask containing 100ml of deionised water. A small amount (3–4 drops) of phenolphthalein indicator was added, and the solution was titrated with 1.0N hydrochloric acid until colourless (Reading A). To the same solution, few drops of methyl orange were added and the solution was titrated further until it turned red (Reading B). The total alkalinity (as Na₂O, g/L) was calculated as follows:

$$\text{Total Alkalinity} = B \times 3.1$$

2.2 Active alkalinity and Sulphidity

10.0 (\pm 0.1)ml of well agitated cooking liquor was pipetted into a 250ml Erlenmeyer flask containing 100ml deionised water and 50ml of 10% barium chloride (BaCl₂). The solution was mixed well and titrated with 1.0N hydrochloric acid until colourless, using phenolphthalein as indicator (Reading C). To the same solution, 5ml of formaldehyde was added and the solution was again titrated to colourless (Reading D). The active alkalinity (as g/L Na₂O) and sulphidity (as g/L Na₂O) was calculated as follows:

$$\text{Active Alkalinity} = (B - [(A - C) \times 2]) \times 3.1$$

$$\text{Sulphidity} = (D - C) \times 6.2$$

$$\% \text{ Sulphidity} = \frac{\text{Sulphidity}}{\text{Active Alkalinity}} \times 100\%$$

APPENDIX 3

3.1 Standardisation of chlorine dioxide

5.0 (\pm 0.01)ml of chlorine dioxide (ClO_2) was pipetted into a 250ml Erlenmeyer flask containing 50ml of deionised water, 20ml of 1.0N potassium iodide (KI) and 10ml of 4.0N sulphuric acid (H_2SO_4). The solution was titrated with 0.2N sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$). Towards the end of the titration, when the solution turns straw-yellow, a few drops starch solution was added and the solution was titrated to colourless. The concentration of ClO_2 was calculated as follows:

$$\text{Conc. of } \text{ClO}_2 \text{ (g } \text{Cl}^- \text{ / L)} = \frac{\text{Conc. of thiosulphate} \times \text{Vol. of thiosulphate}}{5\text{ml}} \times 35.5$$

3.2 Chlorine dioxide consumption after bleaching (%TAC)

100ml of filtrate was pipetted into a 250ml Erlenmeyer flask containing 20ml of 1.0N potassium iodide (KI) and 10ml of 4.0N sulphuric acid (H_2SO_4). The solution was titrated with 0.2N sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$). Towards the end of the titration, when the solution turns straw-yellow, a few drops starch solution was added and the solution was titrated to colourless. The consumption of ClO_2 was calculated as follows:

$$\text{Residual level of available chlorine in filtrate (g / L av. Cl}_2\text{)} = V_{\text{thio}} \times N_{\text{thio}} \times 0.3545$$

$$\text{Total filtrate volume (ml)} = \text{mass of pulp at 8\% cons. (g)} - \text{OD mass of pulp (g)}$$

$$\text{Total mass of residual av. chlorine (g)} = \text{total filtrate vol. (L)} \times \text{residual av. chlorine (g / L)}$$

$$\% \text{ residual av. chlorine on OD pulp} = \frac{\text{total mass of residual av. chlorine (g)}}{\text{OD mass of pulp (g)}} \times 100$$

$$\% \text{ Consumption} = \text{ClO}_2 \text{ charge (\%)} - \text{residual av. chlorine on OD pulp (\%)}$$

APPENDIX 4

1. Scope and definition

This method is used to determine the six principal monosaccharides that constitute the carbohydrate composition in wood, wood pulp and final sheet. The constituents determined quantitatively are glucose, mannose, arabinose, xylose, rhamnose and galactose. Concentration of the individual components as low as 0.1% can be determined. This method is applicable to extractive-free wood as well as to wood pulp and final sheet.

2. Apparatus

- 2.1 High Performance Liquid Chromatograph comprising an autosampler, quaternary LC pump, column oven, pulsed amperometric detector, isocratic LC post column pump, Dionex CarboPac PA1 analytical column (with Dionex borate trap and Phenomenex SAX guard cartridge).
- 2.2 Constant temperature water bath, regulated to $30 \pm 3^{\circ}\text{C}$
- 2.3 Autoclave, capable of operation at $103 \pm 7\text{kPa}$ (120°C)
- 2.4 Other apparatus: conical glass test tubes, 15ml; glass stirring rods, beakers, 50ml; graduated cylinders, 100ml; bulb pipettes, 3ml, 10ml, 25ml; volumetric flasks, 100ml, 200ml, 250ml, 1000ml; Schott bottles, 250ml.

3. Reagents

- 3.1 Glucose, mannose, arabinose, xylose, rhamnose and galactose-monosaccharide standards used for calibration.
- 3.2 Fucose - Internal standard, 1.00g/100ml deionised water.
- 3.3 Hydrochloric acid (standardised 1N)
- 3.4 Sodium hydroxide 50% (m/v)

To 400ml deionised water contained in a 1000ml beaker, slowly add 500g of NaOH. Keep the beaker submerged in cold water while continuously stirring the solution until the NaOH is completely dissolved. Allow the solution to cool to room temperature and transfer to a 1000ml volumetric flask. Make up to the mark with deionised water. Allow the solution to stand until the suspended carbonates have settled. Pipette 10ml of the solution and make up to 100ml in a volumetric flask and standardise the diluted solution using standardised 1N HCl. Degas solution for 30 minutes in an ultra-sonic bath.

3.5 Sodium hydroxide (0.350M and 0.200M)

Calculate the volume of the 50% (m/v) NaOH needed to prepare 1000ml of the 0.350M and 0.200M solutions, using the equation below:

$$V_1 = \frac{1000ml \times C_2}{C_1}$$

where,

V_1 = Volume of the 50% (m/v) NaOH solution required, ml

C_1 = Exact concentration (M) of the 50% (m/v) NaOH solution (from standardisation)

C_2 = Concentration of the NaOH solution required (i.e. 0.500, 0.350 or 0.200M)

3.6 130mM sodium acetate in 200mM NaOH

Weigh out 14.97 ± 0.01 g AR grade sodium acetate trihydrate and make up to 1000ml in a volumetric flask with 200mM NaOH. Degas solution for 30 min in ultrasonic bath.

3.7 120mM Sodium Acetate in 200mM NaOH

Weigh out 13.82 ± 0.01 g AR grade sodium acetate trihydrate and make up to 1000ml in a volumetric flask with 200mM NaOH. Degas solution for 30min in ultrasonic bath.

3.8 Sulphuric acid (72% (m/m) or 24N)

To 250ml deionised water in a 1000ml volumetric flask, slowly add 665ml of

concentrated sulphuric acid 98% (m/m) (sp. gr 1.84). Allow to cool and make up to the mark with deionised water. Mix well. Standardise the solution using the standardised sodium hydroxide – the concentration of the sulphuric acid should be $24N \pm 0.1N$.

4. Analytical procedure

4.1 Preparation of wood pulp sample - Wet pulp should be dried overnight at $105 \pm 3^{\circ}\text{C}$.

4.2 Preparation of wood sample - Preparation of sawdust is carried out in accordance with 'The Preparation of Wood for Chemical Analysis'. Prepare 6 - 8g of extractive free wood.

4.3 Preparation of final sheet sample - Final sheet should be scraped with a sharp knife to separate fibres.

4.4 Analysis of wood, pulp and final sheet samples

4.4.1 Allow sawdust, pulp or final sheet sample to reach moisture equilibrium in the atmosphere near the balance.

4.4.2 In order to achieve a constant mass of cellulose in the sample for HPLC analysis, the following masses should be weighed:

Extractive-free wood: 0.35 g (50% cellulose, 8% moisture)

Pulp: 0.2 g oven-dry (90% cellulose, 60% moisture)

Final Sheet: 0.16 g (98% cellulose, 7% moisture)

Masses should be $\pm 0.01\text{g}$ to the nearest 0.1mg and transferred into 15ml glass test tubes.

4.4.3 At the same time weigh another 2.0 g specimen for moisture determination.

4.4.4 To the specimen in the test tube, add exactly 3 ml of 72% (m/m) H_2SO_4 with a bulb pipette. Stir the contents of the tube with a stirring rod to dissolve the sample.

4.4.5 Place tube in a $30 \pm 3^{\circ}\text{C}$ water bath for 1 hour. Stir occasionally. Wash the contents of the tube quantitatively into a 250ml Schott bottle with 84ml of deionised water. If any specimen solution is lost during the hydrolysis and transfer steps, terminate the analysis, weigh out a new specimen, and repeat the analysis.

4.4.6 Place the Schott bottle with specimen solution in an autoclave set at $103 \pm 7\text{kPa}$ and 120°C for 1 hour. Ensure that the cap of the Schott bottle is only

- partially tightened.
- 4.4.7 Cool the hydrolysate to room temperature and allow the lignin to settle. Filter quantitatively under vacuum through a 0.45 μ m filter paper, finally using deionised water to transfer and wash the precipitate and to rinse the Schott bottle.
- 4.4.8 Transfer the filtrate quantitatively into a 200ml volumetric flask and dilute to the mark with deionised water. Mix well.
- 4.4.9 Transfer about 50ml into a plastic bag, seal and place in the freezer for a minimum of 24 hours.
- 4.4.10 Thaw sample and pipette exactly 2 x 50 μ L of sample and 400 μ L deionised water using a fixed volume pipette into the autosampler vial and place in the autosampler tray, recording the position and identity.
- 4.4.11 When all the samples for the batch are in the tray, place the vial containing the internal standard in a convenient position in the tray.
- 4.4.12 Before running the samples and standards, program the autosampler offline to add 20 μ L of internal standard solution (1mg/ml fucose) from the designated internal standard vial (suggested vial: 100) and mix for 3 cycles.
- 4.4.13 Program the HPLC for analysis –Use Totalchrom software.
- 4.4.14 Conditions for HPLC analysis are set as follows:
- (a) Filtered deionised water for 6.5min (equilibration)
 - (b) Injection (5 μ L)
 - (c) Filtered deionised water for 6min (separation)
 - (d) Ramp to 130mM or 120mM sodium acetate in 200mM NaOH for 1min.
 - (e) 130mM or 120mM sodium acetate in 200mM NaOH for 3 min (acetate loading step)
 - (f) Ramp to filtered deionised water for 1min
- Flow rate for steps (a), (c) – (f) is 1 ml/min.
- (g) Post-column addition of 350mM NaOH at a flow rate of 0.5ml/min.
- 4.4.15 Peak areas from the sample chromatograms are converted into percent composition for each carbohydrate by comparison of peak area ratio of each carbohydrate / internal standard to a calibration of peak area ratio of each carbohydrate / internal standard vs. concentration for each carbohydrate standard.
- 4.4.16 Report the percentages of each carbohydrate to the nearest 0.1%.
- 4.4.17 The maximum concentration expected for 150 mg cellulose/ hemicellulose in the samples is as follows:

	Hardwoods		Softwoods	
	g/100ml	mg/ml	g/100ml	mg/ml
Glucose	0.0850	0.850	0.085	0.850
Xylose	0.0220	0.220	0.010	0.100
Galactose	0.0010	0.010	0.0025	0.025
Arabinose	0.0005	0.005	0.0015	0.015
Rhamnose	0.0005	0.005	0.0015	0.015
Mannose	0.0030	0.030	0.0100	0.100

4.5 Preparation of standards for HPLC analysis

4.5.1 Dry all sugars to constant mass. (This converts glucose to the anhydrous form). DO NOT OVERDRY – if sugar discolours discard.

The stock solutions must be concentrated enough for convenient storage but not so concentrated that excessive dilution is required (leading to dilution errors). Because of the very low concentration of some of the sugars (0.005g/100ml), two dilutions are presently carried out so that the primary solution is not so dilute that weighing errors occur. To ensure accurate dilutions (evident from the calibration line), standard volume pipettes and volumetric flasks of large enough size (min 10ml pipette) must be used.

4.5.2 Prepare stock solutions of each monosaccharide standard by weighing the following dry masses $\pm 0.01\text{g}$ to the nearest 0.1mg and transferring each mass quantitatively into a separate 100ml volumetric flask and making up to the mark with deionised water:

Glucose:	1.00g
Xylose:	0.25g
Mannose:	0.30g
Galactose:	0.20g
Arabinose:	0.10g
Rhamnose:	0.15g (not generally included)

4.5.3 Primary stock mix: Pipette 10ml each of arabinose and galactose stocks into a 100ml volumetric flask 'A'. (Pipette 10ml rhamnose standard into flask 'A' if required). Mix and make up to volume with deionised water. Pipette 10ml each of the glucose, xylose, and mannose stocks and 10ml from volumetric flask A into another 100ml volumetric flask 'B'. Mix and make up to volume with deionised water.

4.5.4 Pipette 10ml of the primary stock mix into a 100ml volumetric flask and make

up to the mark with deionised water. This is the **100% standard**.

- 4.5.5 The working standards are prepared from the 100% standard as follows using bulb pipettes:

10% standard: pipette 10ml of the 100% standard (4.5.4) into a 100ml volumetric flask, and make up to the mark with deionised water.

25% standard: pipette 25ml of the 100% standard into a 100ml volumetric flask, and make up to the mark with deionised water.

50% standard: pipette 50ml* of the 100% standard into a 100ml volumetric flask, and make up to the mark with deionised water.

* 2 x 25ml - using the same 25ml pipette.

This will give 100ml each of the diluted standards and 15ml of the 100% standard. If the full set of standards is used each time this is sufficient for 30 standards.

- 4.5.6 The exact concentration of each of the components in each standard is calculated using the exact masses weighed.

- 4.5.7 The standards are stored in sealed plastic bags and placed in the freezer for a minimum of 24 hours before analysis.

- 4.5.8 After thawing the standards, pipette exactly 2 x 50 μ L of standard and 400 μ L deionised water using a fixed volume pipette into the autosampler vial, and place in the autosampler tray, recording the position and identity.

- 4.5.9 The procedure for analysing the standards using HPLC is the same as for the samples i.e. steps 4.4.13 – 4.4.16.

- 4.5.10 Full set of standards should be run after every 10 –12 samples.

- 4.5.11 When calculating the amount of carbohydrates from the sugar concentration, a factor of 0.9 for glucose (divisor from cellulose) should be used to account for the water of hydrolysis to hexoses, and a factor of 0.88 for the pentoses.

5. References

- 5.1 TAPPI Test Methods (1996-1997), test method no. T249 cm-85.
- 5.2 Wright, P.J., and Wallis, A.F.A. 1996. *Rapid determination of carbohydrates in Hardwoods*. Holzforschung. Walter de Gruyter, Berlin. **50**: 518-524.
- 5.3 Wallis, A.F.A., Wearne, R.H., Wright, P.J. 1996. *Chemical analysis of polysaccharides in plantation eucalypt woods and pulps*. Appita Journal. **49(4)**: 258-262.

APPENDIX 5

5.1 Viscosity of pulp

The moisture content of the pulp was determined by drying approximately 5g of pulp in an oven set at 125-135°C for 1 hour. From the value obtained, exactly 1g OD equivalent of pulp was weighed out into a 100ml amber glass bottle. To this was added 15ml of 1N sodium hydroxide (NaOH), thoroughly wetting the pulp. Thereafter 85ml of cuprammonium solution was added, together with stainless steel pieces (enough to close the air gap in the bottle). The bottle was stoppered and placed in a mechanical shaker for 45 minutes. At the end of the 45 minute period, the bottle was transferred to a thermostat controlled water bath set at 20 ±1°C, for 1 hour. At the end of the 1 hour period, the solution was sucked up into the Ostwald viscometer. The viscometer was enclosed in a water jacket through which water at 20 ±1°C was continuously being passed. The time taken for the liquid level to pass from the upper to the lower mark on the viscometer was measured using a stopwatch. The viscosity of the pulp was calculated as follows:

$$TAPPI\ Viscosity\ (cP) = \frac{time\ (sec) \times viscometer\ coefficient}{1.56}$$

The viscometer coefficient was obtained from the calibration of the viscometer using standard viscosity oil.