PRESSURISED HOT WATER EXTRACTION OF WOOD THREE WOOD SPECIES PRIOR TO PULPING

By

N. MJI

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Date:	**December 2005**
Promoter:	**Prof G.F.R. Gerischer**
Internal Examiner:	**Dr. T. Rypstra**
External Examiner:	**Dr. A. Botha**

DECLARATION

I, the undersigned declare that the work contained in this thesis is my own original work and has not in its entirety or part been submitted at any university for a degree.

SIGNITURE: DATE:
N. MJI

OPSOMMING

Die doel van hierdie studie was om die effek van warm water uitloging van houtspaanders by hoë temperature en onder hoë druk voor alkaliese verpulping te ondersoek. Warm water uitloging van houtspaanders onder druk voor alkaliese verpulping was baie belowend, aangesien dit ekstrakstowwe verwyder het wat andersins verteringschemikalieë sou opgebruik het en ook verbertede verpulpingstoestande meegebring het. Gedurende uitloging het die houtstruktuur verander agv die verwydering van die ekstrakstowwe. Dit het veroorsaak dat die houtstruktuur meer toeganglik geword het, en dit het gelei tot 'n verbeterde diffusie van die kookloog. Die versnelde kookloogdiffusie het 'n verbeterde en meer gelykmatige delignifikasie meegebring.

Warm water uitloging by verhoogde druk is ondersoek vir drie houtsoorte nl. *Eucalyptus grandis*, *Acacia mearnsii* en *Pinus patula*. 'n Twee-uur en 'n een-uur uitlogingstyd van die houtspaanders voorafgaande Kraft en soda-AQ verpulping is ondersoek.Vergelyk met 'n een-uur uitloging is daar gevind dat die twee-uur uitloging van die houtspaanders te drasties was, met 'n gevolg van 'n vermindering in pulpopbrengs, vesellengte en pulpsterkte. Die verlaging in pulpsterkte kon toegeskryf word aan polisaggariedafbreking. Die een-uur uitloging het 'n hoër opbrengs opgelewer as beide die kontrole (nie uitgeloogde houspaanders) en die twee-uur uitgeloogde houtspaanders. Die een-uur uitlogingsperiode het besonder goeie verpulpingsresultate vir die ekstrakstof-ryke *Acacia mearnsii* houtspaanders getoon, met 'n bykomstige verbetering in pulpsterkte eienskappe.

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To my family: with all my love, to my father Tyelinzima Euclid, to my brothers Andile, Vuyo, Thandile, my daughter Sibulele, son Siphosethu and most especially, with all my heart, to my mother Ntobise Sheila who passed away on the 27th March 2000. May her soul rest in peace.

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Chapter 1: Introduction

1.1. Cellulose

In 1938 A. Payen [1] suggested that the cell walls of a large number of plants were constructed of the same substance to which he gave the name cellulose. Pure cellulose is never found in nature; cotton fibre is probably the purest natural cellulose source containing about 5% of other substances after allowance has been made for adsorbed water. More commonly, in wood, plant stalks, leaves and the like, cellulose is associated with substances such as lignin and hemicelluloses. Thus according to the species, wood contains on a dry mass basis between 40 and 55% cellulose, 15 and 35% lignin and 25 and 40% hemicelluloses [1]. There are a number of aspects of cellulose that remain to be fully looked at. Among these, one can mention the structural features of cellulose for which a clear picture has not yet emerged. Though everyone seems to agree on the chemical structure of cellulose, there is still much debate concerning the way in which the cellulose molecules are packed in crystals and how these crystals are assembled into microfibrils, fibres, cell walls or other cellulose morphologies [2]. Cellulose is a linear condensation polymer consisting of D - anhydroglucopyranose units joined together by β - 1,4 - glycosidic bonds, thus it is a 1-4 β - D – glucan [1,3]. It is a homopolymer composed entirely of glucose units ($C_6H_{12}O_6$), a monosaccharide formed through the photosynthesis from atmospheric carbon dioxide [2,3]. When the cellulose molecule is fully extended it takes the form of a flat ribbon with hydroxyl groups protruding laterally and capable of forming inter- and intra- molecular hydrogen bonds. The surface of the ribbon consists mainly of hydrogen atoms linked directly to carbon and is therefore hydrophobic. These two features of the molecular structure of cellulose are responsible for its supramolecular structure and this determines its physical and chemical properties. In the fully extended molecule, adjacent chain units are orientated with their mean planes at an angle of 180^0 to each other [1]. The number of glucose units in the cellulose chain is referred to as the degree of polymerisation (DP) and the average values for the DP of cellulose are between 8000 to 10 000 [4]. The structure of cellulose is shown in **Figure 1.1.**

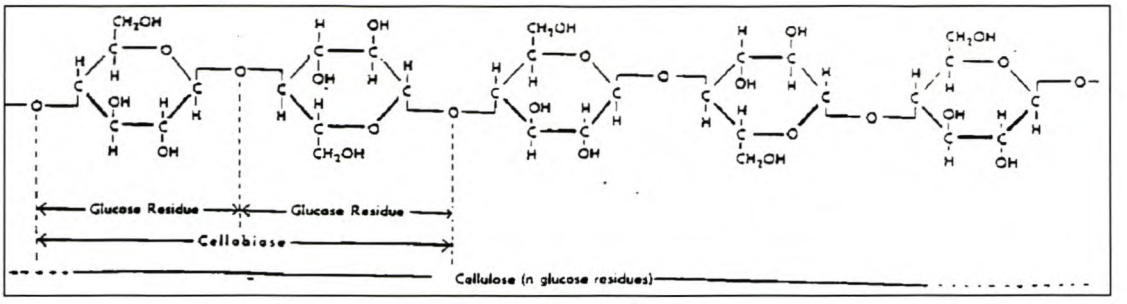

Figure 1.1: Diagram to illustrate the structure of the cellulose molecule

1.2. Hemicelluloses

The name hemicellulose was originally given to all of the polysaccharides of the plant cell wall except cellulose and pectin [1]. More recently the term has been used to describe the non-cellulosic polysaccharides [4]. The hemicelluloses have linear polysaccharide backbones, often but not always homopolymers that are composed of β - 1,4 linked xylose, glucose or mannose units [1]. Hemicelluloses are generally considered to be non-crystalline. This is due to the presence of short side groupings and in some cases branching [5]. The number and composition of the side chain differs greatly between species, tissue and even within the same cell wall at different stages of development [1]. The major hemicellulose found in hardwoods is xylan, it consists of a homo-polymer backbone composed of repeating xylose units with uronic acid derivative side chains. In contrast mannan occurs as the major hemicellulose component of the secondary wall in softwoods. It exists as a glucomannan backbone substituted with acetyl and galactose units [3, 4]. Some common sugars found in hemicelluloses are shown in **Figure 1.2.**

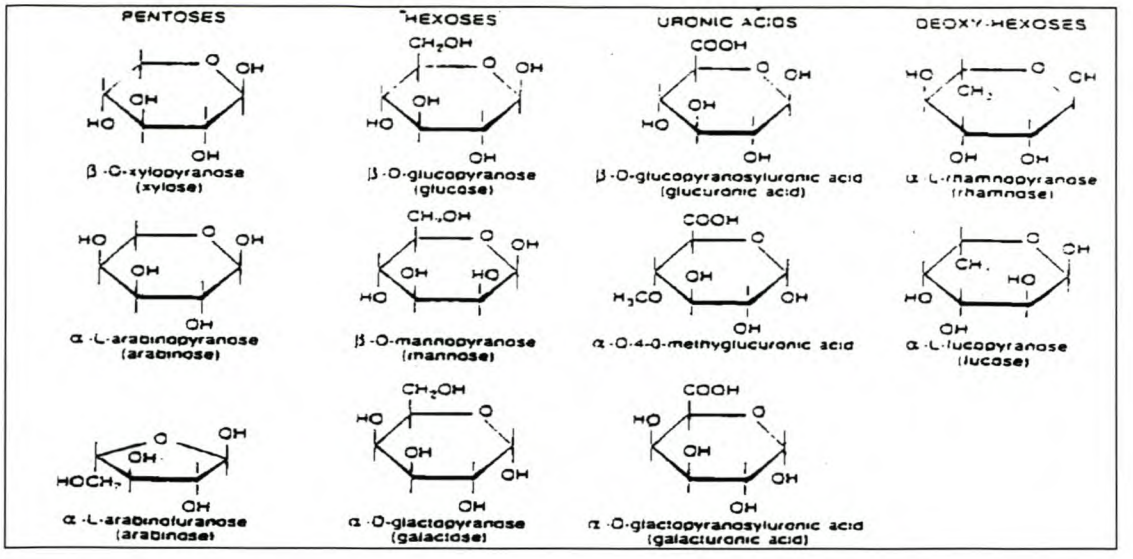

Figure 1.2: Common sugars found in hemicelluloses[8]

1.3. Lignin

The word lignin is derived from the Latin word ``Lignum`` meaning wood. As far as scientists are concerned lignin is a nasty substance to deal with. While polysaccharides are composed of specific carbohydrates linked by glycosidic bonds, lignin structure appears random and unorganized. Lignin is a complex aromatic polymer with molecular mass of about 11 000. It is a polymer that is formed by the three dimensional polymerization of cinnamyl alcohols which are derivatives of phenylpropane [1] (**Figure 1.3**). The aromatic polymer is comprised of a heterogeneous, branched network system with no evident repeating unit (**Figure 1.4**). Lignin occurs in many living plants and grasses, but its composition is not identical in all. Hardwood and softwood lignins are very different in their basic structure. Softwood lignins are comparatively uniform in structure from species to species and hence have been widely studied [5]. Lignins are generally extractable with sulfites, bisulphites, alkalis and acidic alcohols but are modified chemically by such processes. Softwood lignin contents are in the order of 26-32% and hardwood lignin in the range 20-28% The degradation accompanying isolation of soluble lignins has prevented extensive development of their detailed physical picture [6,9].

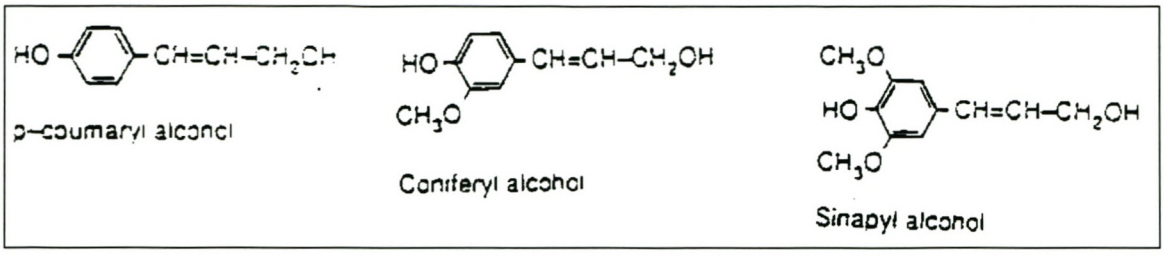

Figure 1.3: The aromatic alcohols that are precursors in the synthesis of lignin

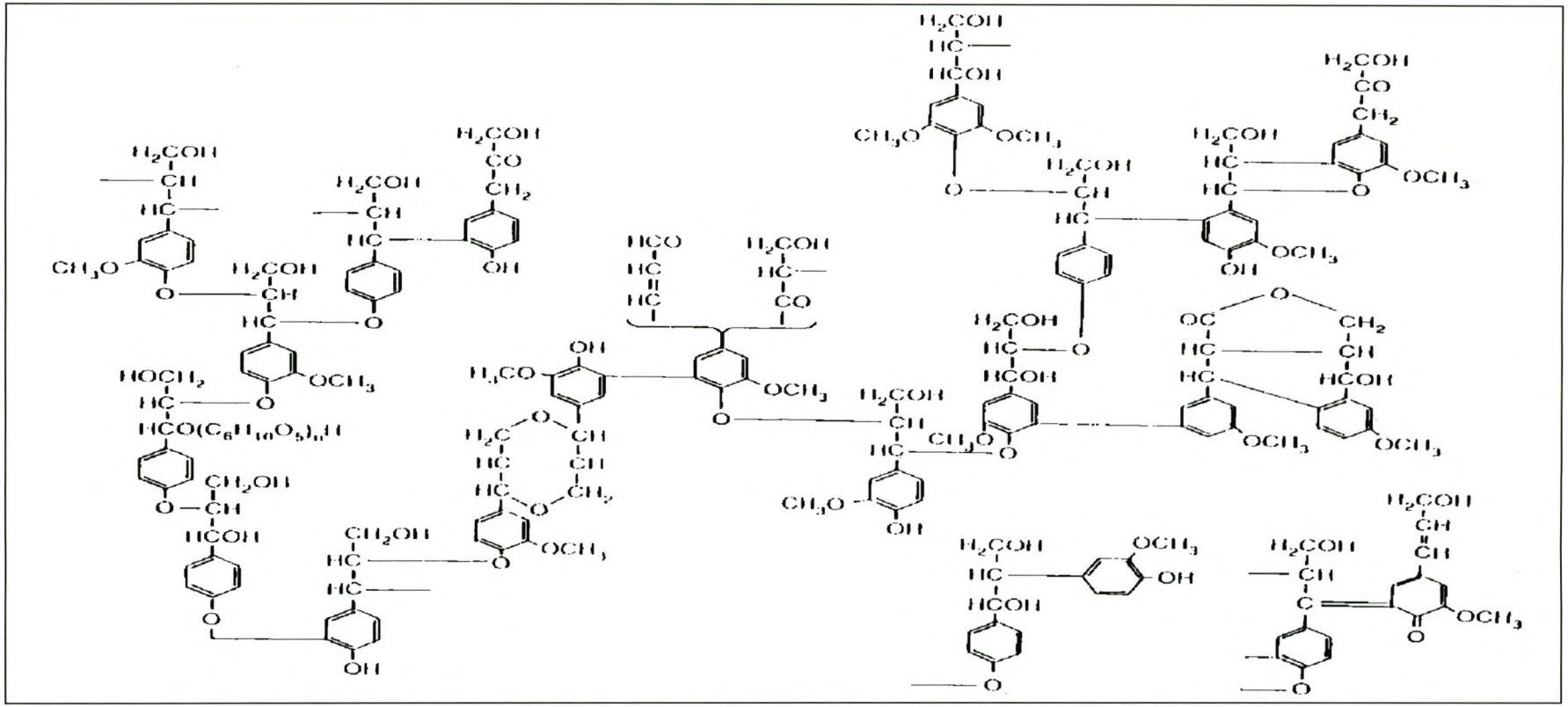

Figure 1.4: Partial structure of spruce lignin as depicted by Freudenberg and Neish (1968)

1.4. Cell wall structure

The cell wall is made up of several layers, namely the middle lamella (M), primary wall (P), outer layer of the secondary wall (S_1), middle layer of the secondary wall (S_2), inner layer of the secondary wall (S_3), helical thickening (HT) and the warty layer (W). These layers differ from one another with respect to their structure such as fibril orientation as well as their chemical composition [7,13].

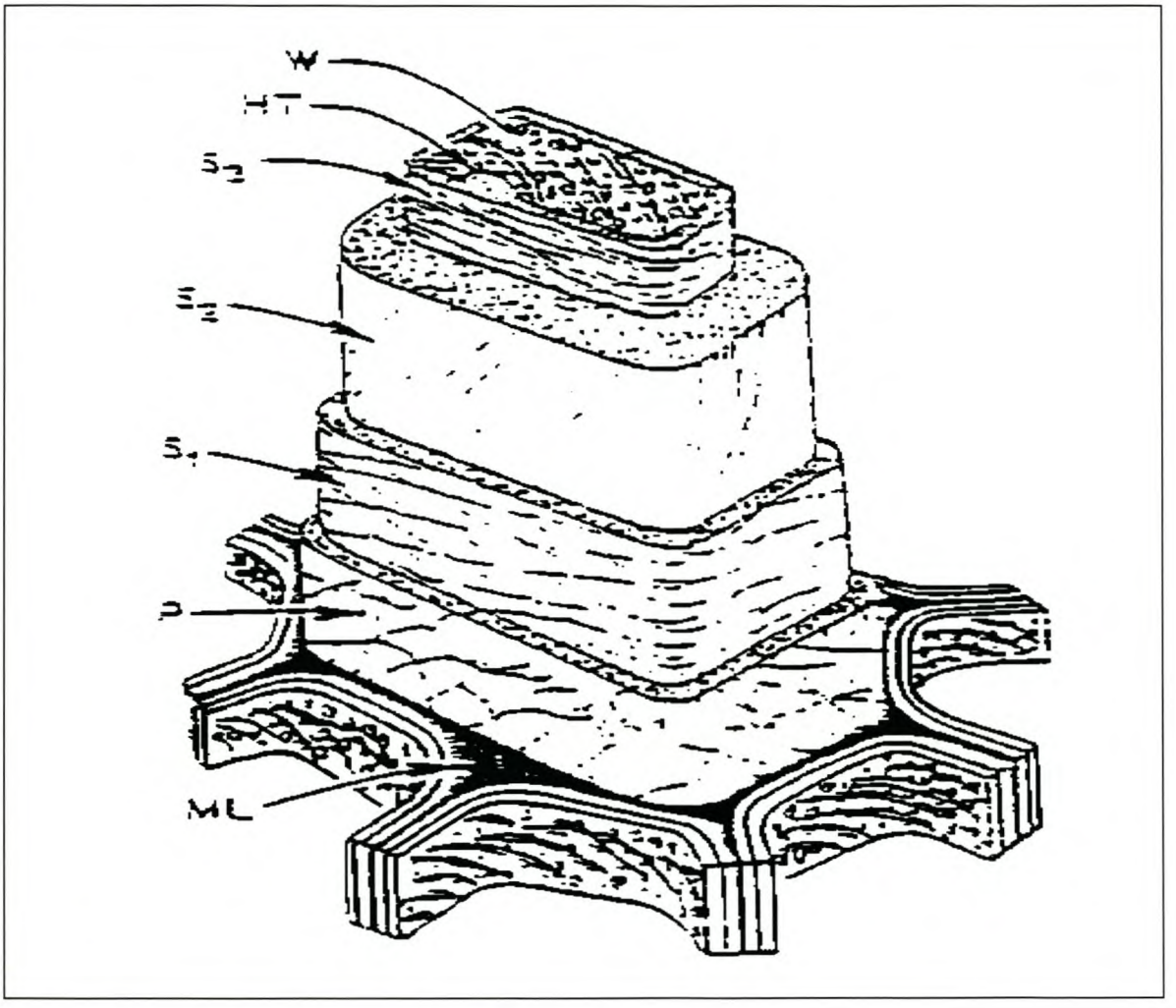

Figure 1.5: Schematic diagram to illustrate the structure of the cell wall[7]

1.5. Cellular structures

Softwoods and hardwoods have different cellular structures. Softwoods have a simple structure and are more uniform in appearance than hardwoods. Softwoods are made up of few cell types with the long, pointed fibrous cells termed tracheids, which provides the support and conducting pathways in wood (**Figure 1.6**). Hardwoods have different cell types with clearly visible conducting cells called vessels [3] (**Figure 1.7**).

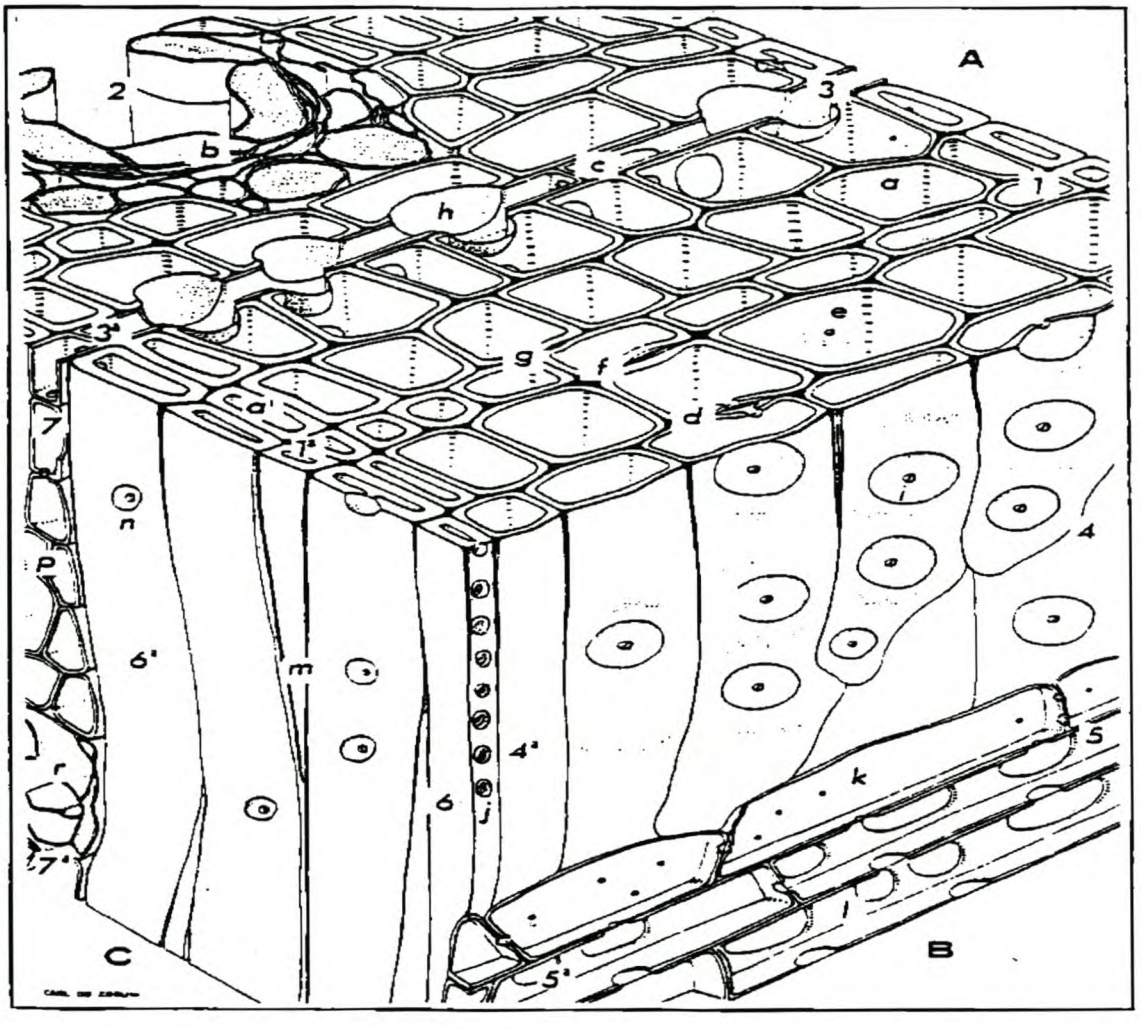

Figure 1.6: The cellular structure of Softwoods

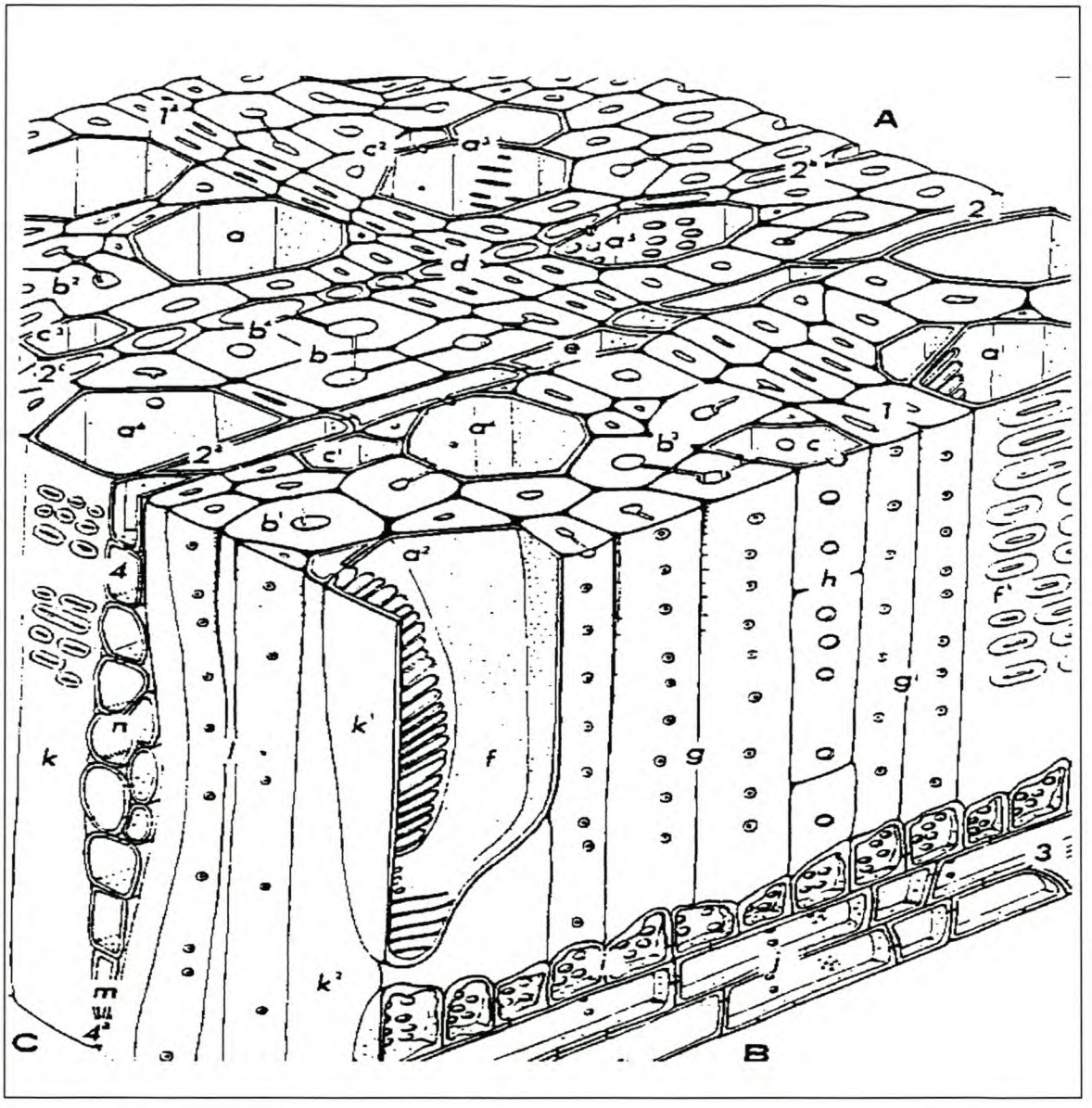

Figure 1.7: The cellular structure of Hardwoods

1.6. Pulp and paper manufacture

The term pulping is used to describe the various processes by which wood is reduced to its component fibres, or to a mixture of fibre and fibre debris. Papermaking, although complex follows basic procedures. Paper is made by spreading a layer of pulp fibres in suspension on the surface of a moving wire mesh or screen so as to form a wet paper web, which after pressing is dried to form paper. There are a number of pulping processes and variations of each. These include mechanical, semi-chemical and chemical pulping. Mechanical pulps require mainly energy for their production and have a high demand for

electrical power consumption. They are obtained in high yields (85-96% of the mass of oven dry wood) and are basically made by two processes namely stone groundwood pulps and refiner mechanical pulps. Stone groundwood pulps are made by pressing roundwood billets against a rotating pulp stone in the presence of water showers. Refiner mechanical pulp is made by placing chips between refiner discs, which separate individual fibres. Semi-chemical mechanical pulps are made by treating wood chips with chemicals at high temperatures so as to remove some lignin and hemicelluloses after which the partially softened chips are defibrerised using a disc refiner. The pulps yields obtained are in the region of 70-85%. The most widely used semi-chemical pulping process is the neutral sulphite semi-chemical (NSSC) procedure. Chemical pulps are prepared by the digestion of wood chips with chemicals at high temperatures (170-180^{0}C) and pressure until much of the lignin has been removed. This process has yields as low as 45-50%. The chemical pulping processes fall into two classes, alkaline pulping of which Kraft is the most important and sulphite pulping. C.F. Dahl developed the Kraft process in 1879. The active chemicals used in the Kraft process are NaOH and Na_2S. The Kraft process has the following main advantages [3]:

1. It has a low alkali demand on wood species including all types of hardwoods and softwoods.
2. It has short cooking times compared with acid pulping.
3. It has a well-established processing of spent liquor.
4. It has excellent pulp strength properties.
5. Pitch problems are less prevalent with this process

Disadvantages of the process include:

1. Odour problems caused by sulphur containing organic compounds.
2. Lower yields than in acid pulping.
3. Unbleached pulps have a dark colour.
4. There are enormous financial costs in the installation of new mills.

1.7. Soda AQ pulping

In the early seventies it was shown that the addition of small quantities of anthraquinone (AQ) to a soda cook increased the rate of delignification so that it is comparable to that of the Kraft method. The AQ added acts as a catalyst promoting the cleavage of the β-aryl ether linkages of the free phenolic lignin units, at the same time the carbohydrates are being protected against end peeling by the oxidation of the reducing end group to a carboxyl. Soda AQ pulps have strengths comparable to that of the Kraft pulps [8].

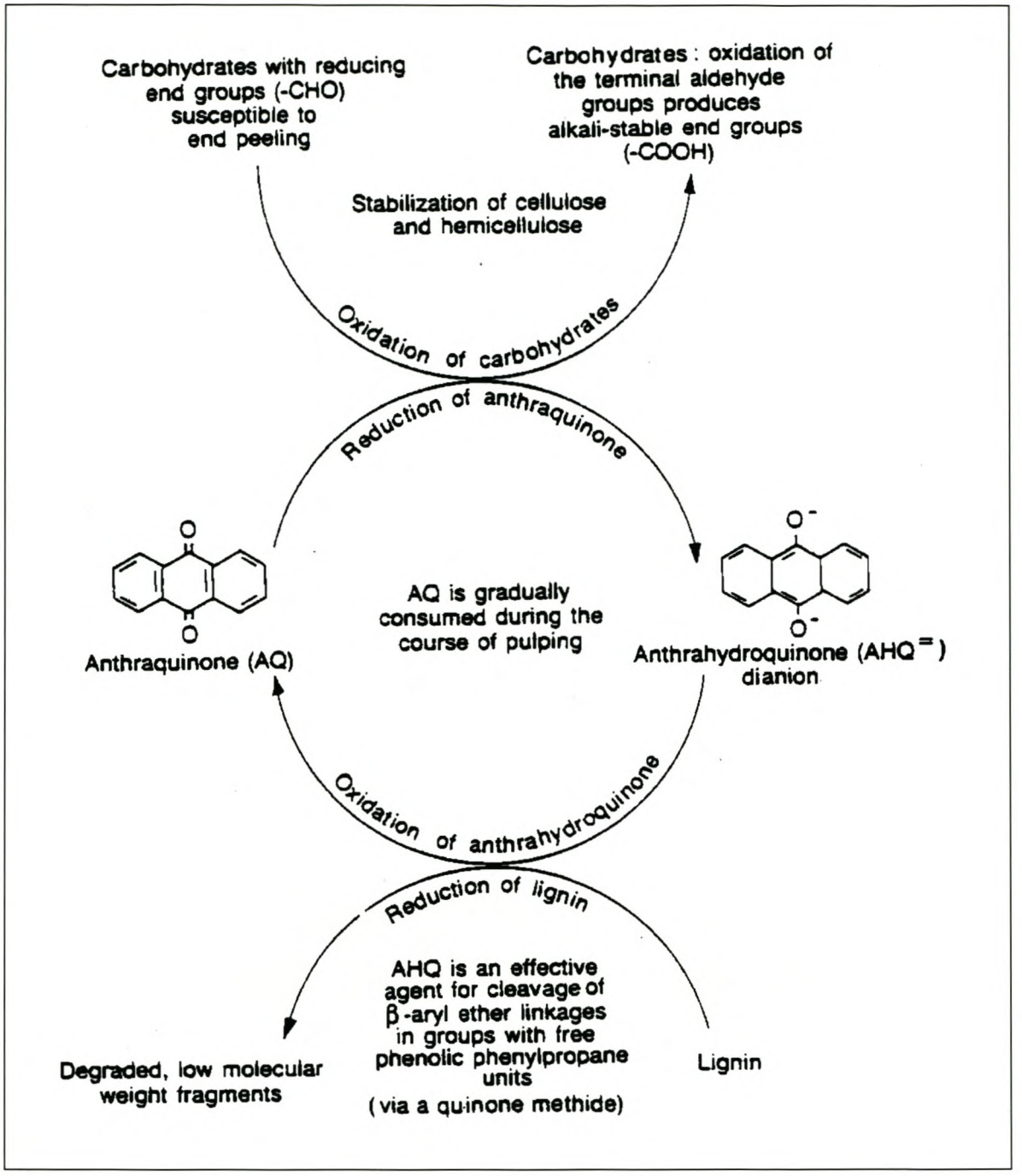

Figure 1.8: Schematic reaction cycle of quinones (e.g. anthraquinone) as cooking additives[8]

1.8. Extractives

Extractive materials in wood are considered non-cell wall constituents and consist of a bewildering number of primary organic non-polymeric compounds that can be extracted from wood with water and neutral organic solvents and/or are volatilized by steam. About 3-10% of dry wood consists of extractives. Softwoods contain 5-8% extractives while hardwoods contain 2-4 %. Extractives include volatile acids, volatile oils, turpentine, pine oil, resin, fatty acid fractions, tannins etc [5]. There is a considerable difference between softwood and hardwood extractives and also between wood species. Resin acids only occur in softwoods and proportions of their distribution vary from species to species. The fatty acid composition also differs between softwoods and hardwoods. Climate has a great influence on the nature of fatty acids found in a wood species. Trees growing in cold regions produce a higher proportion of dienoic and trienoic fatty acids whereas wood species growing in warm climate have higher proportions of saturated and monoenoic fatty acids.

1.8.1. Classification of extractives

1. Volatile oils: these are mainly found in softwoods. They consist of terpenes, which are widespread in nature and are based on the 5-carbon building block. Then there are the monoterpenes, which are fragrant and are based on the 10-carbon molecules. Lastly in this group are turpentine and tropolones.
2. Wood resins are also mainly found in softwoods. They consist of acidic diterpenes, which are 20-carbon molecules, resins of softwood and compounds that are the basis of tall oil.
3. Fats and waxes are minor constituents of extractives. They are less than 0.5%.
4. Tannins are extractives that are found in both softwoods and hardwoods. They comprise compounds that tan leather that include hydrolysable tannins built upon glucose and gallic acid and condensed tannins, which are flavonoid-based.
5. Lignans, which are found in both softwoods and hardwoods. These lignans are optically active lignin dimers.
6. Carbohydrates are typically found as food reserves.

1.8.2. Isolation of extractives

No single solvent is capable of removing all substances that are classed as extractives. Thus for removal of extractives it is necessary to use two or more solvents, for example to extract successively with organic solvent and water. An advantage of successive extraction is the preliminary separation of the extractives into broad groups of similar solubility behavior. The amount of materials volatile with steam is small in most woods. These materials are mostly soluble in organic solvents [10]. If much steam volatile material is present, a separation determination is necessary. Kurth[45] illustrated that extractives are removed in a certain sequence. Owing to the variable composition of extractives, no single sequence of extractions is equally applicable to all woods, therefore, the investigator will need to select the best procedure designed to accomplish his procedure [31,33]. Primary trials may be necessary if the character of the extractives is unknown[10].

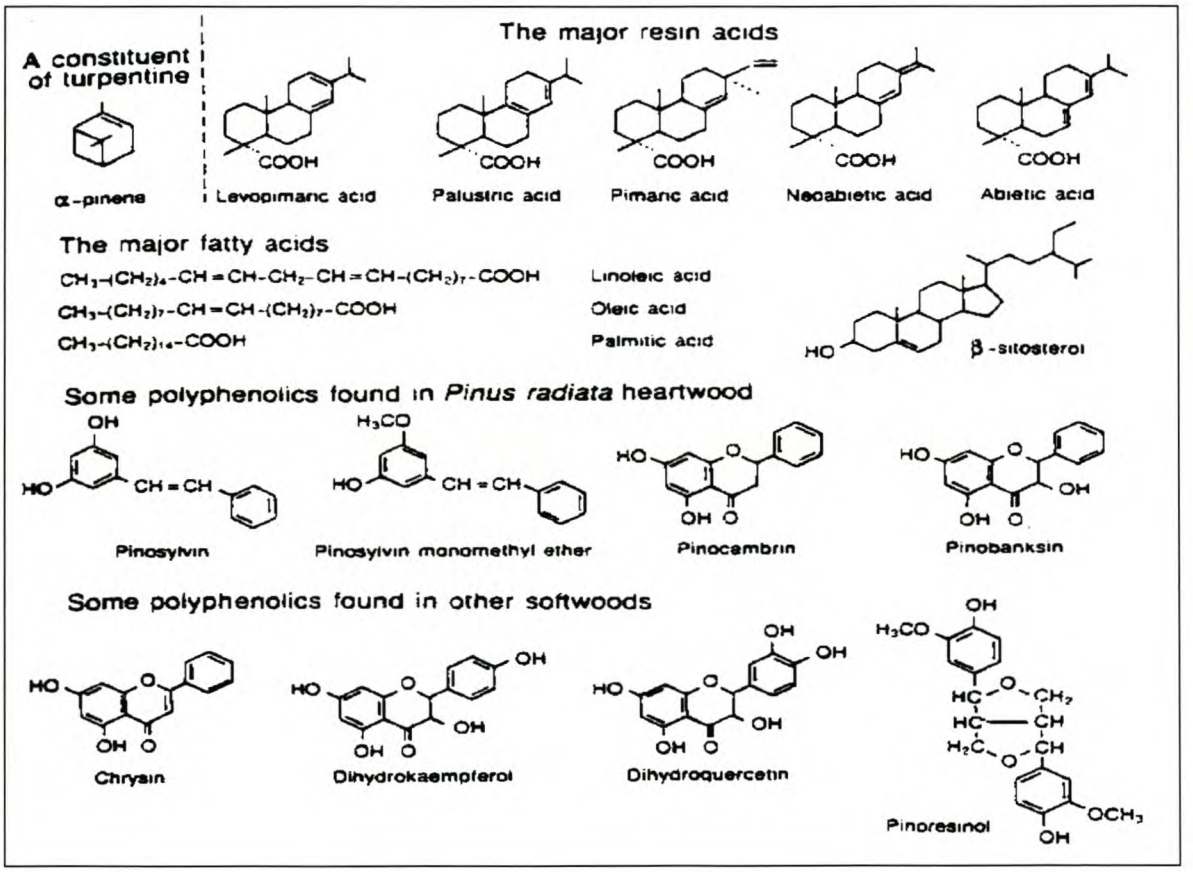

Figure 1.9: Some softwood extractives[8]

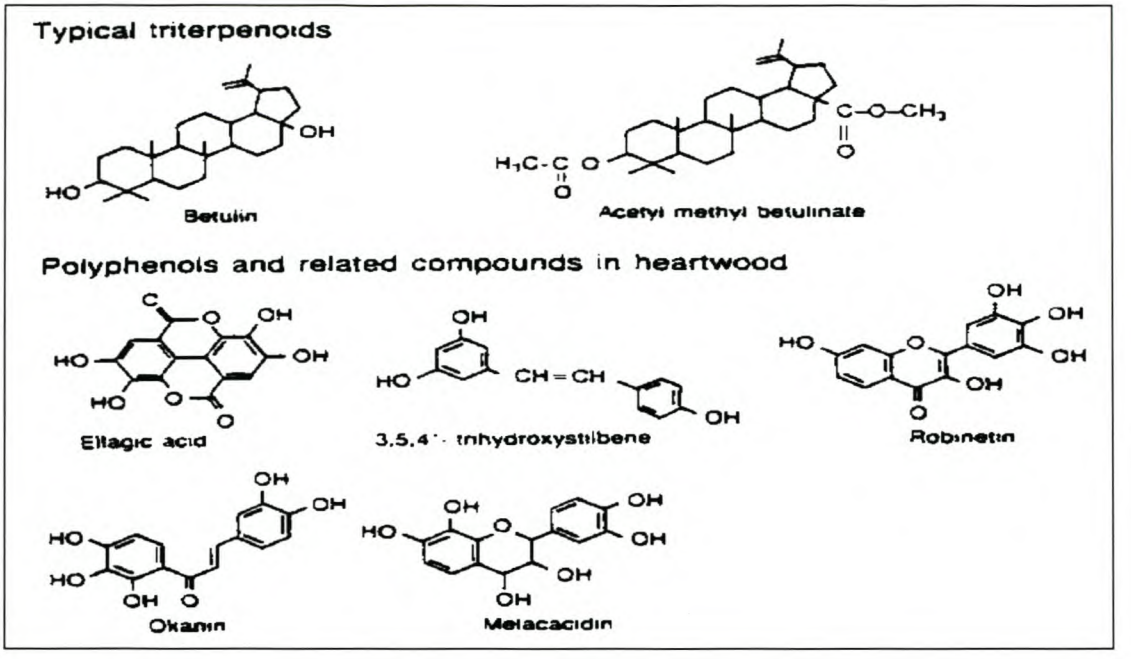

Figure 1.10: Some hardwood extractives[8]

1.8.3. Extractives soluble in water

The water soluble materials in wood include inorganic salts, sugars, polysaccharides, cycloses and cyclitols and some phenolic substances. Some of the materials soluble in water are more or less soluble in many organic solvents. It is also true that material that is soluble in organic solvents may contain a considerable fraction that is also soluble in water. The solubility in water is determined by extraction with cold water, extraction with hot water at approximately 100^0C or by the two treatments successively. If the wood has been previously extracted with an organic solvent the solvent should be removed by drawing air through it or by air-drying it until the solvent has disappeared. Most commercial wood pulps contain 1-2% material that can be extracted with water. The soluble substances include inorganic compounds derived from process water and pulping and bleaching chemicals, together with organic substances from the spent liquor that are not removed in the washing processes. Extraction with hot water removes carbohydrate materials and lignin degradation products from the pulp. The water-soluble components of pulps are complex and greatly variable in composition[10].

1.8.4. Heating of wood in the presence of water

The behavior of wood when heated with water alone is of interest. Bergius and Specht[35] were the first to carry out such experiments. At ordinary temperatures and pressures water does not chemically react with or alter wood. However, at elevated temperatures and pressures water has a very considerable effect upon the various constituents of wood. The action is primarily that of hydrolytic degradation. In many reactions in which water is present its effect has been largely neglected, yet it plays an important part in many industrial applications, including the common mechanical and chemical pulping processes, the Masonite fiberboard process and other well-known processes [21]. Aronovsky and Gortner[35] treated aspen sawdust with water at 170 and 186°C and found that the weight of the sawdust decreased by 25-40%. They found that part of the lignin had been rendered soluble in alcohol after heating under pressure. The material that dissolved in the water consisted of sugars and wood gum (xylan), with the possibility of split products from lignin or of humus. The presence of acetic acid, formic acid, methyl alcohol and furfural was also shown. In view of the ease with which acetic acid is formed from wood by hydrolysis it is probable that the action of hot water is to a large extent hydrolytic. Heating of wood with water under pressure at 130-150°C for two hours caused 12-14% of carbohydrates to dissolve out of spruce and about 26% out of beech. The carbohydrates dissolved were polymeric. Part of the lignin in the residue can be dissolved in alcohol and a second part is soluble in dilute alkali at low temperatures. A part of the lignin is made less soluble in bisulphite by the heating with water. It is possible to dissolve out small amounts of labile lignin-carbohydrate compounds by brief treatment with water under pressure, but it is not possible to cause larger quantities of carbohydrate to go into solution without damaging the lignin. This can be explained on the assumption that lignin is chemically linked to the carbohydrate. When the linkage is broken, the lignin is converted to an easily- soluble form. In the heating of wood with water it has been observed that the quantities of products formed are always larger than would be expected on the basis of the loss in weight of the residue. The basic chemical composition of wood is scarcely affected by the heating under pressure. When wood is treated with water at high temperatures considerable quantities of material go into solution. These extracts have approximately the same composition as the wood. It has

been found that carbon dioxide was formed from wood in the presence of water even at room temperature. It was thus established that gases are evolved when wood is heated. The gasses consisted of 98.6-99.3% carbon dioxide, small amounts of unsaturated hydrocarbons (0.2-0.6%), methane (0.6%) and hydrogen (0.2-0.5%). The process in which wood is treated with steam before mechanical pulping is known as brown mechanical pulping.

1.8.5. Extractives in relation to chemical pulping

Studies by Erdtman[35] in the 1950s showed that the heartwood of *Pinus* species resist sulfite pulping because it contains stilbene pinosylvin, which condenses the lignin during the cooking. Sulfite pulping is also influenced by the presence of resins in wood chips. In Kraft pulping of softwoods, the resin acids and fatty acid esters present consume the active alkali required for delignification and are therefore undesirable. When pulping eucalypts the ellagic acid present in heartwood can form salts that adversely influence the viscosity of the black liquor. In hardwoods rich in polyphenols much of the alkali added for pulping is consumed by the polyphenols. Arbuthnot[34] discussed the relationship between extractive content of a tree and the pulp quality obtained, found that wood quality varied within eucalypts and this was more evident in eucalypt grown on poor sites. He established that a base log of the *eucalyptus* tree contained the highest proportion of extractives and these extractives negatively influenced the screened pulp yield and the kappa number thus leading to poor quality of the pulp obtained from this part of the tree. It has been found that pre-extracted wood chips of *S. sempervirens* resulted in increases in pulp yields when compared to untreated wood chips [35]. In another study, unextracted chips containing 9.4% tannin and about 2.5% nontannin and partially extracted chips containing 1.4% residual extractives were pulped under the same conditions[35]. The pulp from the partially extracted wood chips cooked to a greater degree and contained only 1.9% lignin, whereas that from the unextracted wood chips contained 6.4% lignin[35]. In a study by Dommisse[3], it was found that extraction of wood chips by boiling in water for three hours, resulted in an increase of about 2 % in pulp yield for Soda AQ pulping in micro-digesters. In a study by Burger[39] it was reported that hot water

extracted *Eucalyptus macarthurii* wood chips, resulted in higher yields after alkaline pulping.

1.9 Objective

The objective of this study was to examine the effect of hot water extraction of hardwood (*Eucalyptus grandis* and *Acacia Mearnsii*) and softwood (*Pinus patula*) wood chips at high temperatures and pressure, prior to alkaline chemical pulping (Kraft and Soda AQ). The objective was to investigated the effects of pressurised hot water extraction of wood on pulp yield, paper properties, chemical consumption, residual lignin content, percentage rejects and shive content.

Chapter 2: Soda A.Q – pulping

2.1. Materials and methods

2.1.1. Raw materials

Three different wood species were used in the pulping procedure; they were *Pinus patula*, *Eucalyptus grandis* and *Acacia mearnsii,* which were obtained from the Central Timber Cooperative (CTC) Richards Bay, Kwazulu Natal. The wood was delivered in log form. The logs of the three species were debarked and chipped using a Wigger pilot size chipper. The chips were screened with the 6-8 mm thickness fraction was used for pulping.

2.1.2 Pulping conditions

Prior to pulping the chips were soaked in water at room temperature for 24 hours or until they had a moisture content of 60%. This was done so that active alkali could easily be absorbed into the chips by diffusion. The pulping was done in a 15-liter batch type laboratory digester. The equivalent mass of 1500g dry-mass of wood chips was used for each digestion. A programmable logic controller (PLC) regulated the pulping schedule of the wood chips. The wood chips were pulped in triplicate and the average of all the data obtained was calculated.

For hardwood pulping 14 and 16% sodium hydroxide and 1% anthraquinone charge to 1500g oven dry wood chips was used. The pulping cycle, as shown in **Figure 2.1** was as follows: The temperature was increased from the initial 50 °C to about 155 °C over a period of 90 minutes, followed by a blow-of until the temperature reached about 135 °C. The temperature was then increased and kept for 25 to 30 minutes at the maximum of 170 °C after which blow-down commenced. After the cooking cycle was completed the chips were removed from the digester and black liquor was collected for chemical analysis. The cooked chips were disintegrated to pulp using a high-pressure water nozzle. The fibres were washed through a 10-mesh steel screen and the acceptable pulp was collected on a 150-mesh screen. The digesting schedule for hardwoods is shown in **Figure 2.1**.

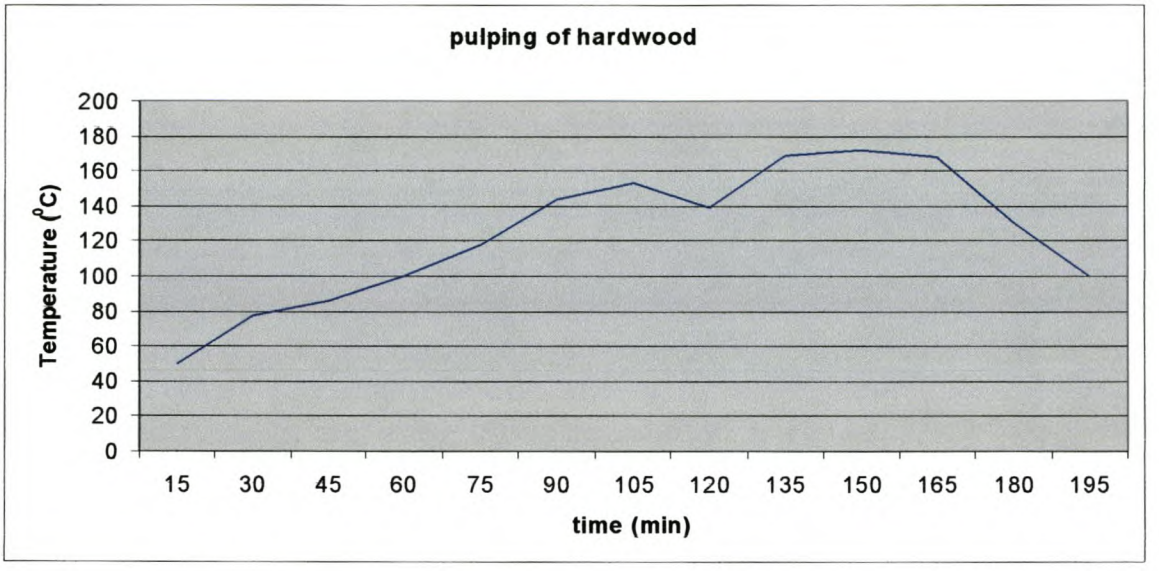

Figure 2.1: Temperature vs. Time graph of a Hardwood cooking cycle

In softwood pulping 16 and 18% sodium hydroxide and 1% anthraquinone to 1500g oven dry wood chips was used. This was made into a solution with water using a 5.4:1 liquid to solid ratio. The pulping cycle, as shown in **Figure 2.2** was as follows: The temperature was increased from the initial 50 °C to about 155 °C over a period of 90 minutes, followed by a blow-of until the temperature reached about 135 °C. The temperature was then increased and kept for 130 minutes at the maximum of 170 °C after which blow-down commenced. The cooked chips were removed from the digester and black liquor was collected for chemical analysis.

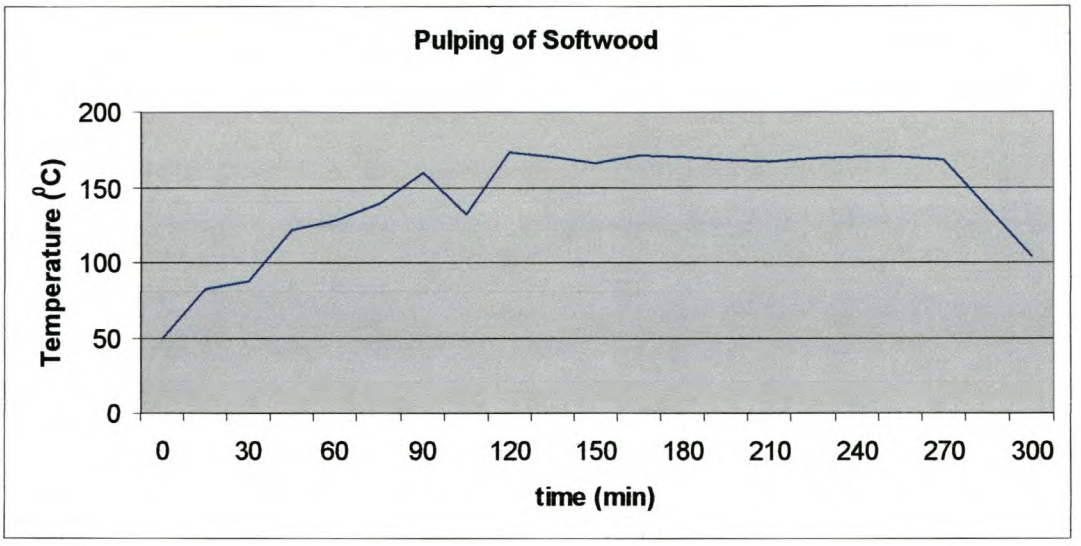

Figure 2.2: Temperature vs. Time graph for Softwood cooking cycle

2.1.3. Pulping effectiveness

Pulp yield, percentage rejects, shive content, chemical consumption, Kappa number, pulp response to beating and freeness of pulp were determined using TAPPI standard test methods.

2.1.3.1 Pulp yield

Pulp yields were measured as the amounts of pulp screened through a 10-mesh screen and retained on the 100-mesh screen after washing. The yields were recorded as the screened yields. It is given as the mean percentage of three pulping cycles.

2.1.3.2. Percentage rejects

Rejects from the pulping cycle were collected and dried for 24 hours in an oven at 105 °C. The dry rejects were then placed in a desiccator containing silica gel for 24 hours before being weighed and the percentage rejects was calculated from the original mass (1500g) of the dry wood chips used for pulping.

2.1.3.3. Chemical consumption

The chemical consumption after each cooking cycle was obtained by determining the residual active alkali (RAA) present in the black liquor as per TAPPI Standard Test Method No T625 om-85. This was done via a potentiometric titration and recording the volume of 0.1M hydrochloric acid required to titrate a treated sample of black liquor to pH 8.3 and calculating the residual active alkali content.

2.1.3.4. Shive content

The shive content was established by screening the obtained pulp in a Packer-type laboratory shive screen. The shives collected were placed in an oven at 105 °C for 24 hours. Shives content was then determined as a percentage of the original dry mass of wood chips.

2.1.3.5. Kappa number

The Kappa number is the amount of lignin left in the pulp after the pulping cycle. The Kappa number was determined using the TAPPI Standard Test Method No T 236 cm-85.

2.1.4. Fibre quality

2.1.4.1. Response to beating

A representative sample of the three digester cooks was prepared for each specie to be beaten. Beating of the pulp was done by taking approximately 800g dry mass of pulp and adding 20 litres of water to obtain a stock consistency of approximately 4%. The pulp was slushed well before adding to a Voith overhead beater. The pulp was then beaten for 1minute per beating cycle for hardwoods and 5 minutes per beating cycle for softwoods.

2.1.4.2. Strength evaluation

Strength tests were performed on handsheets, which were prepared from the beaten stock. The dry handsheets were die cut to the required test specimen sizes and conditioned for 48 hours at 55% relative humidity and 21^0C. 10 handsheets for each beating cycle were

prepared. The grammage of the handsheets ranged between 80 to 100 g/m^2. Die cut paper samples were then tested for tensile, burst and tear strength using TAPPI test methods T404 om-87, T403 om91 and T414 om88 respectively.

2.1.5. Pressurised hot water extraction and pulping

Wood chips were placed in the digester and water was added without the presence of chemicals. Ten litres of water was added to 1500g oven dry wood chips. The chips were pulped using the pulping cycle for hardwoods. According to Figure 2.1 the chips were thus exposed to temperature from 100 to 170^{0}C for two hours. It was anticipated that a two-hour extraction period would be sufficient in order to sufficiently extract the wood chips.

After the pressurised hot water extraction the chips were rinsed with hot water to remove residual extracts. The extracted hardwood chips were pulped in triplicate using 14% and 16% active alkali (AA) and 1% anthraquinone. Softwoods were pulped using 16% and 18% AA and 1% anthraquinone. The lower active alkali charges were selected because degradation was envisioned during the normal active alkali charges for pressurised hot water extracted wood chips. The results were evaluated in the same way as those of the non-extracted wood chips.

2.2 Results and discussion

The results for the screened pulp yield, rejects, shive content, chemical consumption, Kappa number and pulp evaluation of the three species, *Acacia mearnsii*, *Eucalyptus grandis* and *Pinus patula* are given in **Tables 2.1** to **2.11** and **Figures 2.3** to **2.12**.

2.2.1. Pulp yield

From **Table 2.1** and **Figure 2.3** it is seen that for both the hardwood species, there was a drop in screened pulp yield at 16% AA for the pressurised hot water extracted wood chips. This may be due to the fact that hot water extraction at high pressure not only facilitated the removal of extractives, but it also generated acidic conditions as a result of

hydrolysis, causing the wood chips to become softer and more accessible to the pulping liquor, leading to a higher degree of delignification of the raw material with a possible loss of some polysaccharides. The significant drop in the screened yield for the pressurised hot water extracted *Eucalyptus grandis* wood chips pulped with 16% AA as shown in **Table 2.1** could be attributed to the lower extractive content of this species (**Section 2.2.7**). Thus more active alkali was available to break down the polysaccharides. For the 14% AA, it can be seen that an increased pulp yield for the two hardwoods species was obtained for the pressurised hot water extracted wood chips. This can be attributed to the lower chemical charge, which was not too severe on the depolymerisation of the polysaccharides although acid conditions still prevailed. The lower yield at 14% AA for the control also indicates that the chemical charge was not sufficient to achieve complete delignification. For *Pinus patula* using 16% AA, an increase in screened yield for the pressurised hot water extracted chips can be observed in **Figure 2.4**. Again the low screened pulp yield at 16% AA for the control can be attributed to the same reason as discussed above. A decrease in pulp yield at 18% AA of the pressurised hot water extracted pine chips can possibly be explained by the extended pressurised hot water extraction during the 2 hour pressurised hot water extraction period, resulting in losses of polysaccharides.

Table: 2.1. Screened pulp yields

Species	**Screened yield (%) (n=3)**					
	Control			Hot water extracted		
	Active alkali (AA) + 1% AQ			Active alkali (AA) + 1% AQ		
	14%	16%	18%	14%	16%	18%
Acacia mearnsii	31	48	-	37	43	-
Eucalyptus grandis	36	58	-	39	43	-
Pinus patula	-	27	42	-	32	38

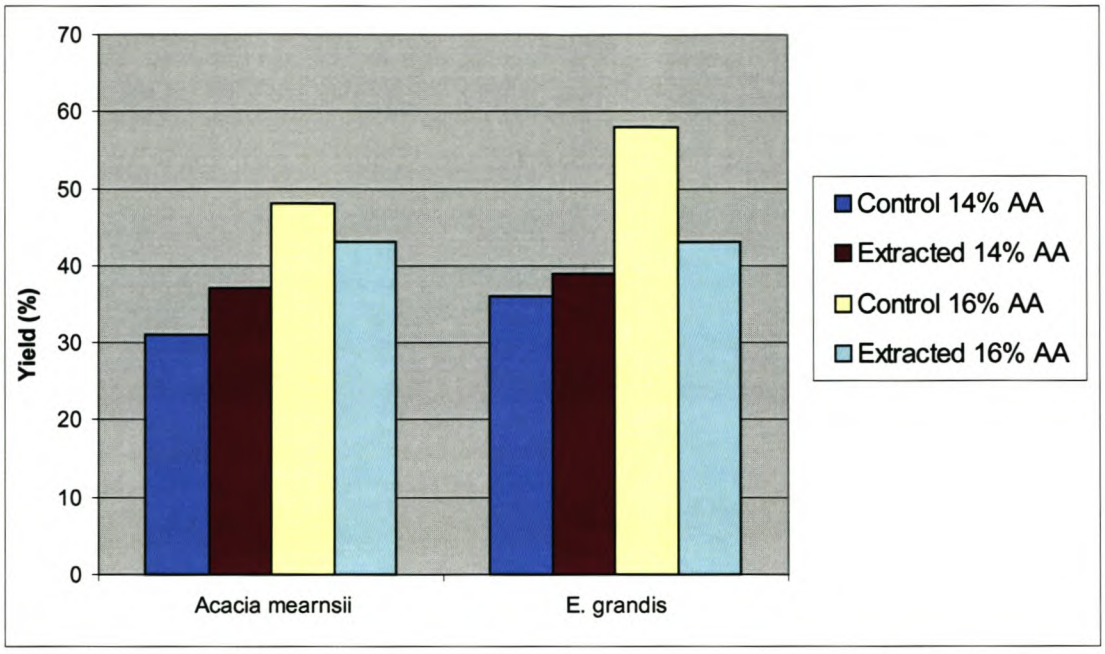

Figure 2.3: ***Acacia mearnsii*** **and** ***Eucalyptus grandis*** **screened pulp yields**

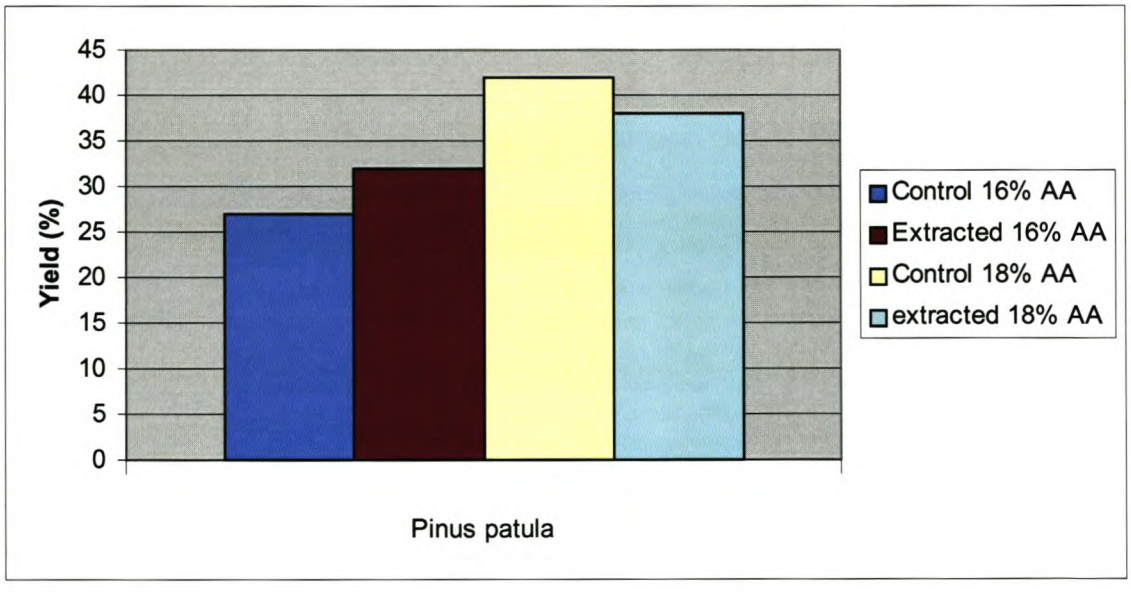

Figure 2.4: ***Pinus patula*** **screened pulp yield**

2.2.2. Percentage rejects

In **Table 2.2** and **Figure 2.5** a substantial decrease in the percentage rejects can be seen for the pressurised hot water extracted hardwood chips as compared to the control for both 14% and 16% AA. This also can be attributed to the higher degree of delignification as described in section 2.2.1. The results obtained for *Acacia mearnsii* indicate an appreciable overall amount of rejects. The larger quantity of extraction material present in the *Acacia mearnsii* wood chips could have been the reason for the lesser delignification as compared to other species even after pressurised hot water extraction. In Figure 2.6, no rejects can be seen for hot water extracted *Pinus patula* and *Eucalyptus grandis.* This is also attributed to the higher degree of delignification as mentioned above. From the results it can be concluded that at the same active alkali, pressurised hot water extraction reduces rejects and increasing the active alkali has the same effect.

Table: 2.2: Percentage rejects

Species	**Rejects (%) (n=3)**					
	Control			Hot water extracted		
	Active alkali (AA) + 1% AQ			Active alkali (AA) + 1% AQ		
	14%	16%	18%	14%	16%	18%
Acacia mearnsii	28.0	10.0	-	10.9	4.1	-
Eucalyptus grandis	14.7	1.7	-	0	0	-
Pinus patula	-	12.6	6.2	-	0	0

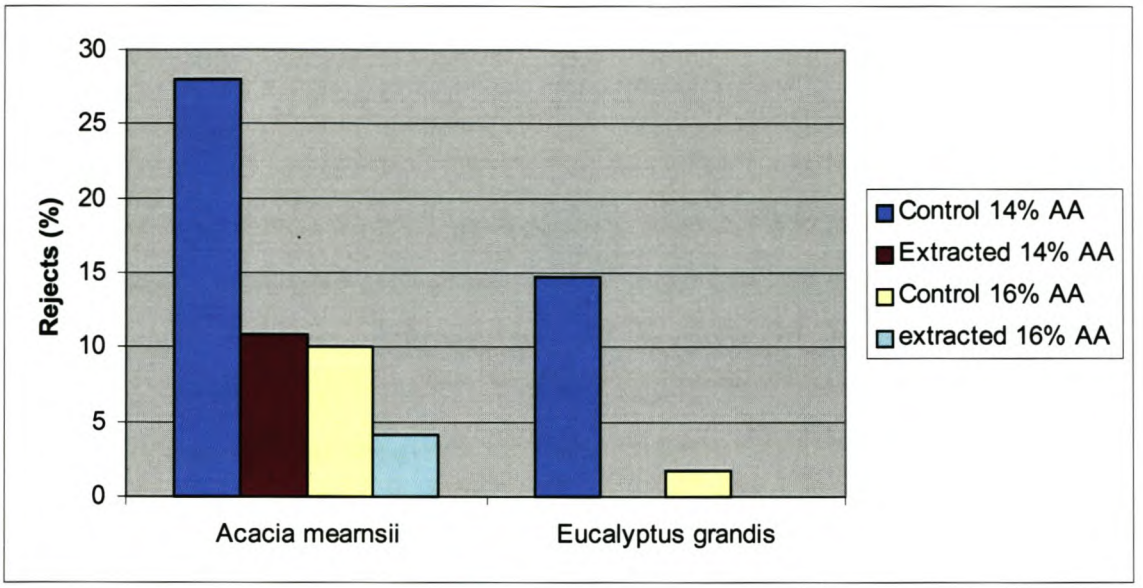

Figure 2.5: Percentage rejects of *Acacia mearnsii* and *Eucalyptus grandis*

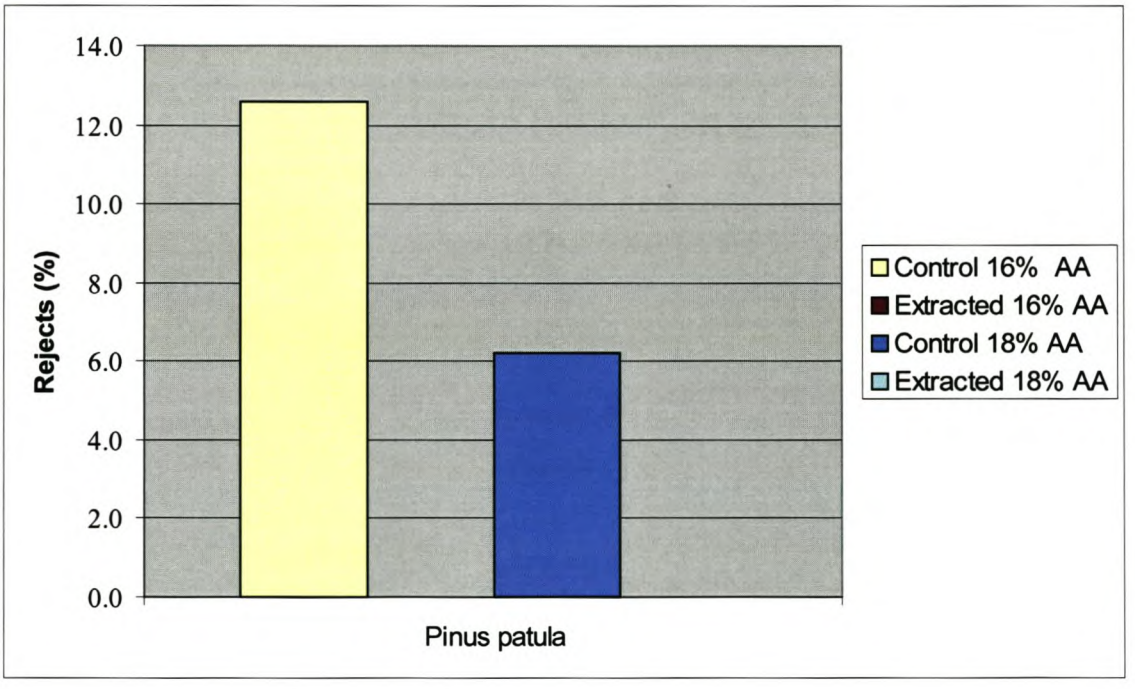

Figure 2.6: Percentage rejects of *Pinus patula*

2.2.3. Shive content

The shive content for the hot water extracted wood chips also was substantially lowered. The results are shown in **Table 2.3** and **Figures 2.7** and **2.8.**

Table 2.3: Shive content after Soda AQ pulping

Species	Shive content (%) (n=3)					
	Control			Hot water extracted		
	Active alkali (AA) + 1% AQ			Active alkali (AA) + 1% AQ		
	14%	16%	18%	14%	16%	18%
Acacia mearnsii	3.2	2.1	-	1.3	0.3	-
Eucalyptus grandis	3.4	1.9	-	0.8	0.1	-
Pinus patula	-	9.1	5.1	-	5.7	3.3

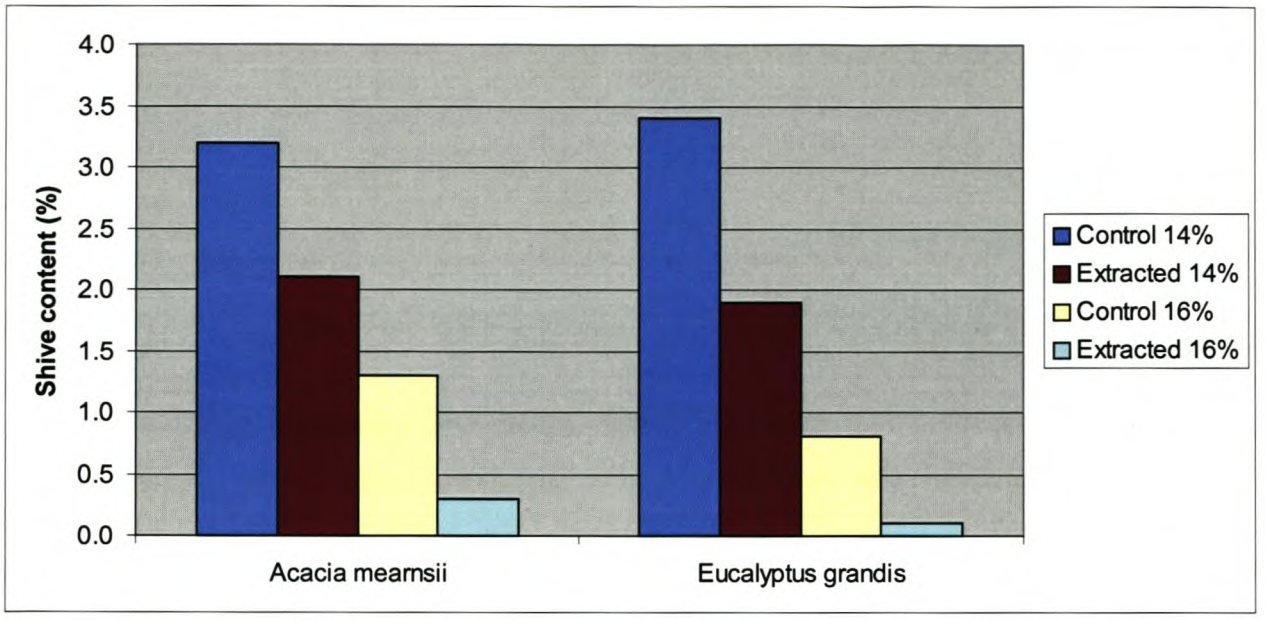

Figure 2.7: Shive content of *Acacia mearnsii* and *Eucalyptus grandis*

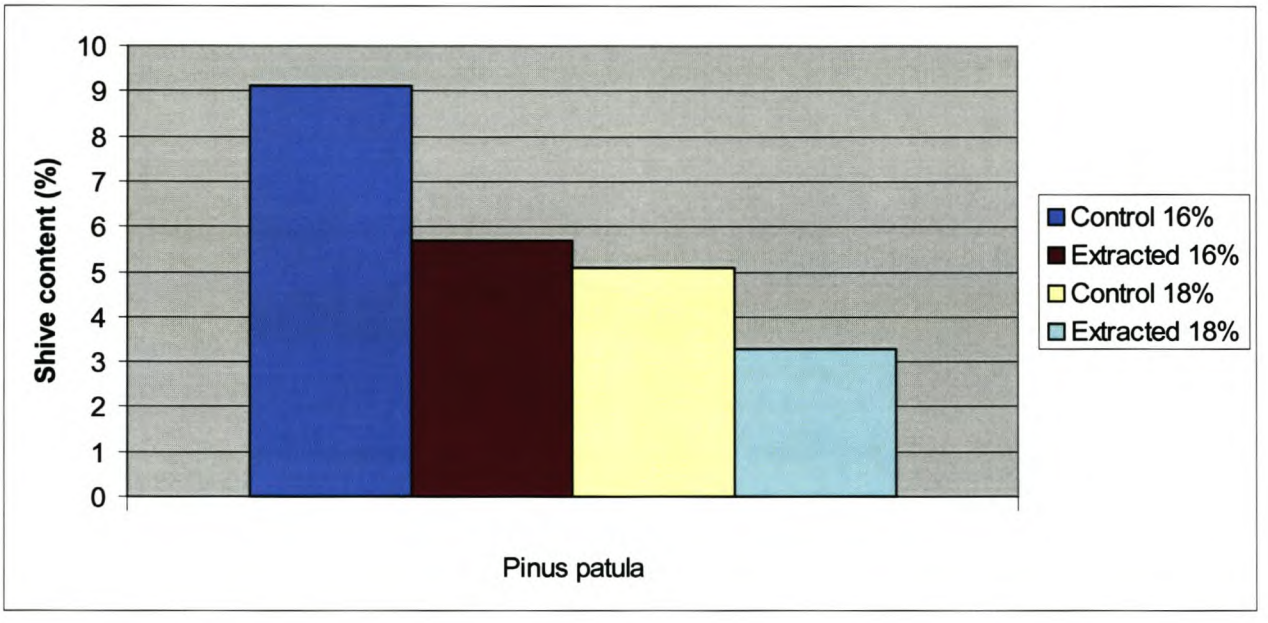

Figure 2.8: Shive content of *Pinus patula*

2.2.4. Consumption of white liquor (RAA)

Hot water extraction enhances the removal of pulping chemical consuming extractives from the wood chips. This in turn was reflected by the lower chemical consumption

during delignification and is expressed in terms of residual active alkali (RAA). The RAA determined for both the control and extracted materials are shown in **Table 2.4.** and **Figures 2.9** and **Figure 2.10.** There was an increase in RAA for the extracted material.

Table 2.4: Chemical consumption (RAA) after Soda AQ pulping

Species	RAA (g/l) (n=3)					
	Control			Hot water extracted		
	Active alkali (AA) + 1% AQ			Active alkali (AA) + 1% AQ		
	14%	16%	18%	14%	16%	18%
Acacia mearnsii	3.2	4.6	-	5.3	7.1	-
Eucalyptus grandis	1.4	2.4	-	4.2	5.9	-
Pinus patula	-	5.7	10.7	-	7.9	11.2

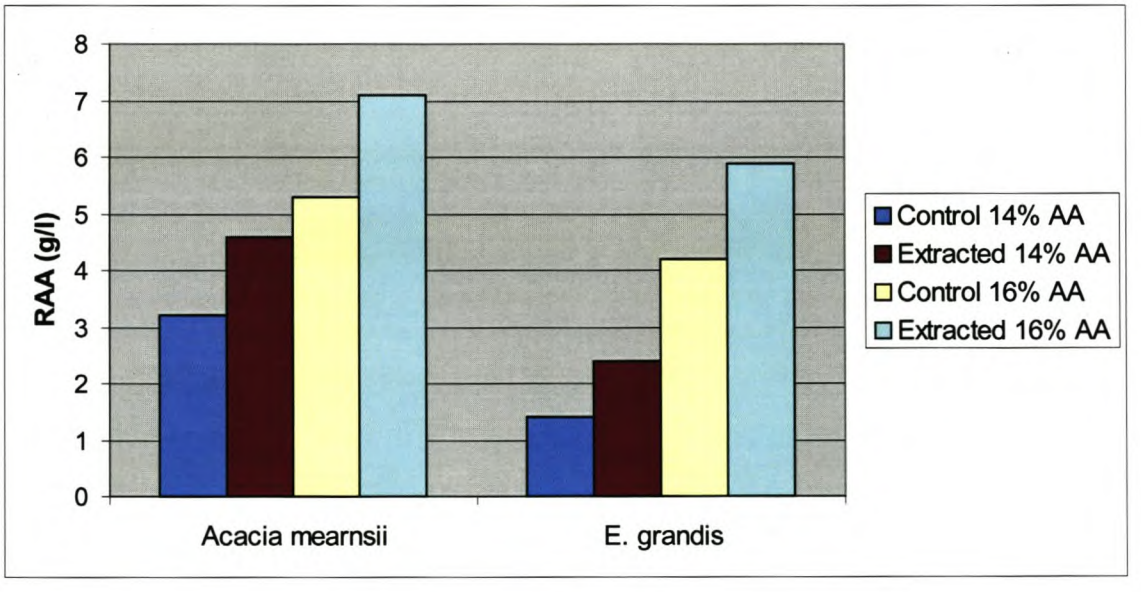

Figure 2.9: RAA of *Acacia mearnsii* and *Eucalyptus grandis* for Soda AQ pulping

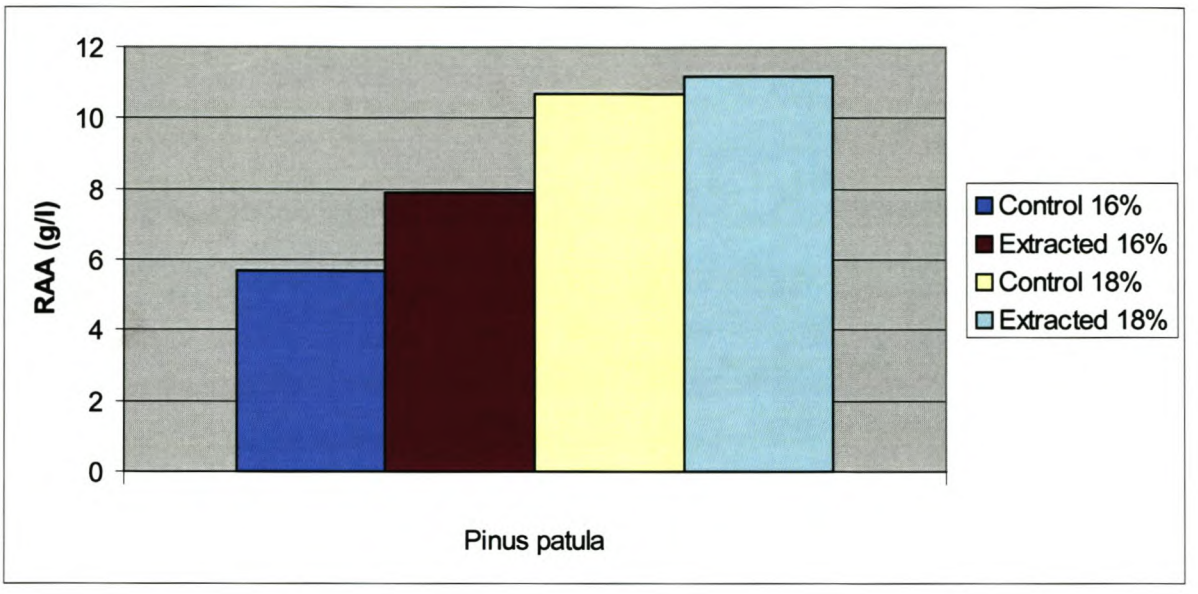

Figure 2.10: RAA of *Pinus patula* for Soda AQ pulping

2.2.5. Kappa number

A significant drop in Kappa number for the three species after pressurised hot water extraction can be seen in **Table 2.5** and **Figures 2.11** and **2.12.** The lower Kappa number of the pulp from the hot water extracted wood chips may have been caused by the better delignification. This was a result of better accessibility of the lignin, after pressurized hot water extraction, by the active alkali. At the same active alkali pressurised hot water extraction resulted in a reduced Kappa number.

Table 2.5: Kappa number

Species	Kappa number (n=3)					
	Control			Hot water extracted		
	Active alkali (AA) + 1% AQ			Active alkali (AA) + 1% AQ		
	14%	16%	18%	14%	16%	18%
Acacia mearnsii	24.0	22.4	-	15.0	8.0	-
Eucalyptus grandis	25.1	23.2	-	12.0	8.3	-
Pinus patula	-	39.8	39.5	-	20.5	15.4

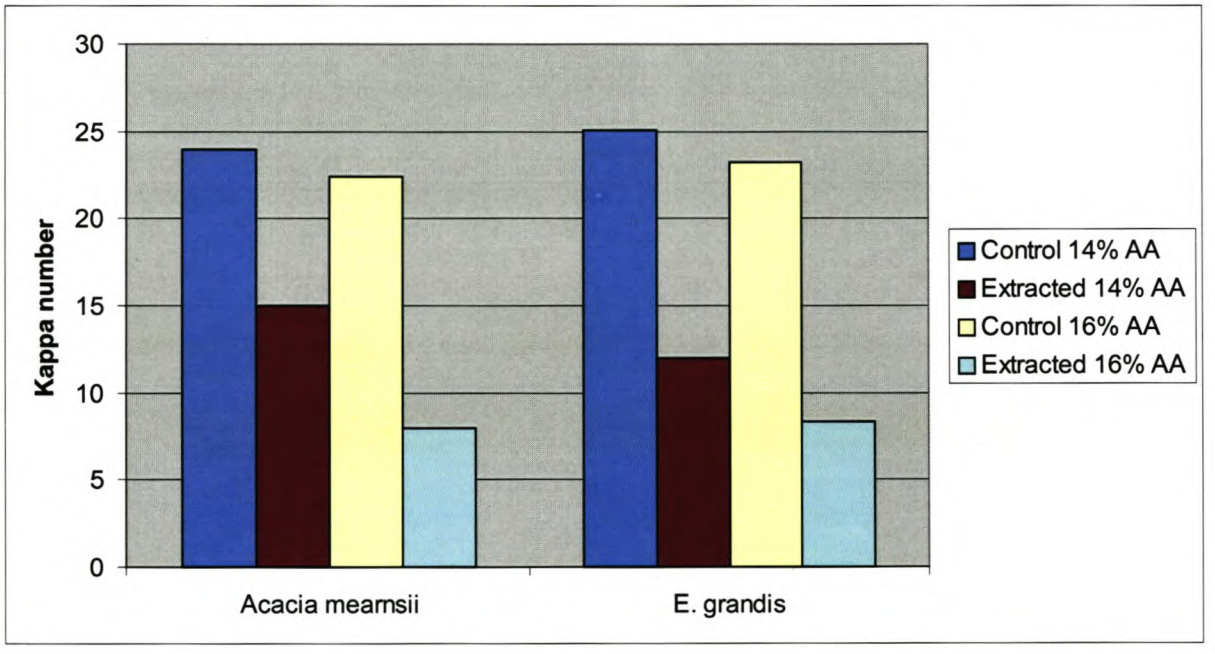

Figure 2.11: Kappa number of *Acacia mearnsii* and *Eucalyptus grandis*

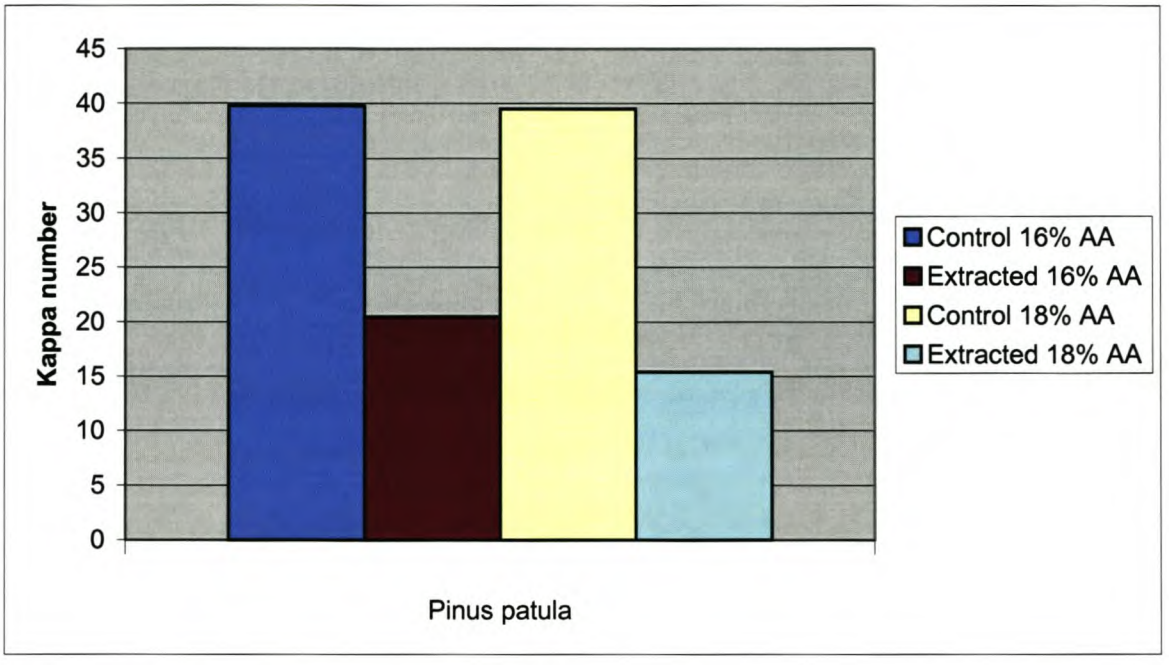

Figure 2.12: Kappa number of *Pinus patula*

2.2.6. Pulp Evaluations and handsheet strength properties

It was decided to only perform evaluations on the pulp obtained from the 16% AA charge for hardwoods as the screened yield was higher and rejects, amount of shives and the obtained Kappa number were lower. The *Pinus patula* pulp from the 18% AA charge was selected for the same reasons. The beating response of the wood pulps is shown in **Tables 2.6** to **2.8** and **Figures 2.13** and **2.14**. The extracted *Acacia mearnsii* pulp showed a slower beating response at the higher beating levels when compared to the control. Extracted *Pinus patula* wood pulp responded faster to beating than the control.

Tables 2.6 to **2.8** and **Figures 2.15** to **2.17** compared the handsheet strength properties of the three wood pulps. When plotted against 38^0SR the handsheet strength values for all three extracted wood species recorded a decrease as shown in **Figures 2.15** to **2.17.** This can be attributed to the depolymerisation and the hydrolytic degradation of the cellulose structure, during the two hour pressurised hot water extraction pre-treatment of the wood chips.

Table 2.6: Beating response and handsheet properties of *Eucalyptus grandis*

Beating time (Min)	°SR (Degrees)		Breaking Length (km)		Tear Index ($mN.m^2/g$)		Burst Index ($kPa.m^2/g$)	
	Control	Hot water extracted	Control	Hot water extracted	Control	Hot water extracted	Control	Hot water extracted
0	20	27	4.4	3.5	5.6	4.6	1.3	1.1
1	33	33	7.0	4.6	9.1	6.1	3.4	1.7
2	42	41	9.5	6.3	9.2	6.3	3.8	2.6
3	51	47	12.0	8.3	10.2	6.7	5.7	3.3

Table 2.7: Beating response and handsheet properties of *Acacia mearnsii*

Beating time (Min)	**°SR (Degrees)**		**Breaking Length (km)**		**Tear Index ($mN.m^2/g$)**		**Burst Index ($kPa.m^2/g$)**	
	Control	Hot water extracted	Control	Hot water extracted	Control	Hot water extracted	Control	Hot water extracted
0	23	24	4.9	1.7	4.3	2.4	1.2	0.4
1	37	39	6.2	4.1	5.2	5.1	1.8	1.6
2	53	46	7.1	6.3	5.9	5.6	2.7	2.1
3	75	60	12.0	6.4	8.2	5.4	5.5	2.4

Table 2.8: Beating response and handsheet properties of *Pinus patula*

Beating time (Min)	°SR (Degrees)		Breaking Length (km)		Tear Index ($mN.m^2/g$)		Burst Index ($kPa.m^2/g$)	
	Control	Hot water extracted	Control	Hot water extracted	Control	Hot water extracted	Control	Hot water extracted
0	13	15	4.5	6.2	11.4	16.6	1.8	3.0
5	19	23	9.7	9.7	20.3	19.8	4.9	5.2
10	25	32	12.4	12.4	21.6	20.3	5.8	5.4
15	33	41	12.7	12.7	21.8	20.4	6.9	5.7
20	44	45	13.5	17.2	20.5	18.9	8.0	6.7
25	53	56	18.9	18.9	24.0	23.3	8.4	6.9

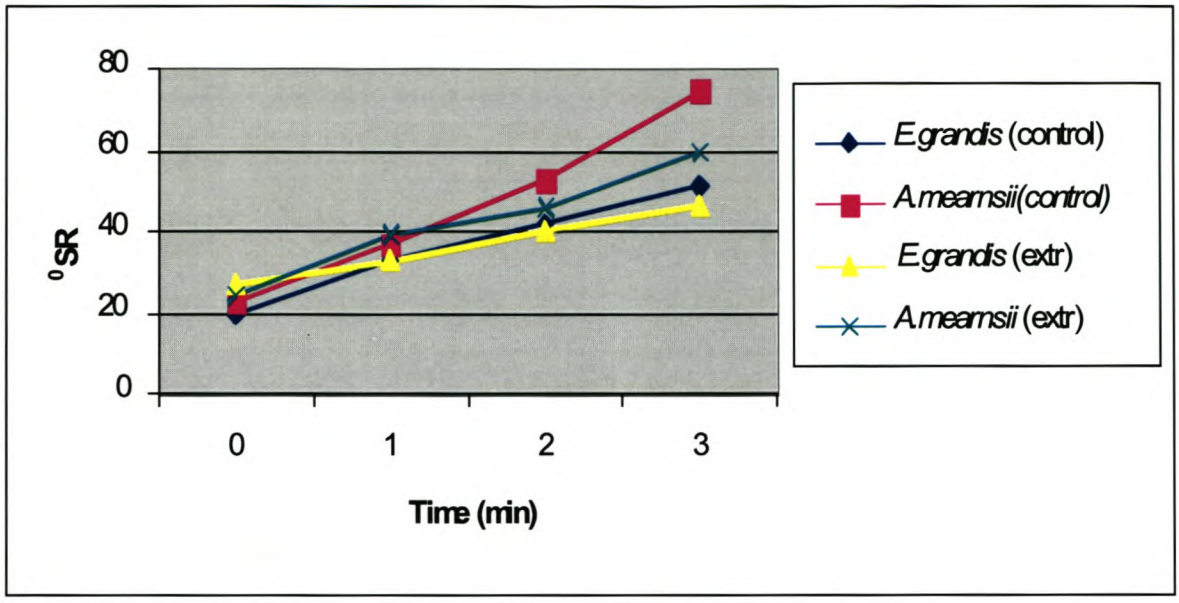

Figure 2.13: Beating response of *Acacia mearnsii* and *Eucalyptus grandis*

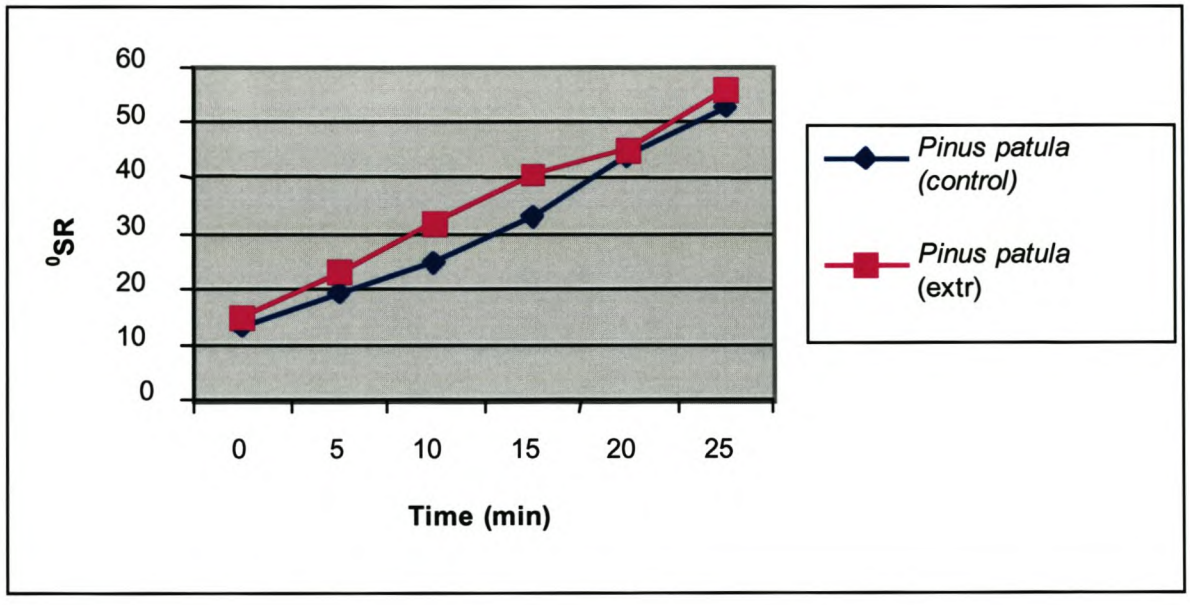

Figure 2.14: Beating response of *Pinus patula*

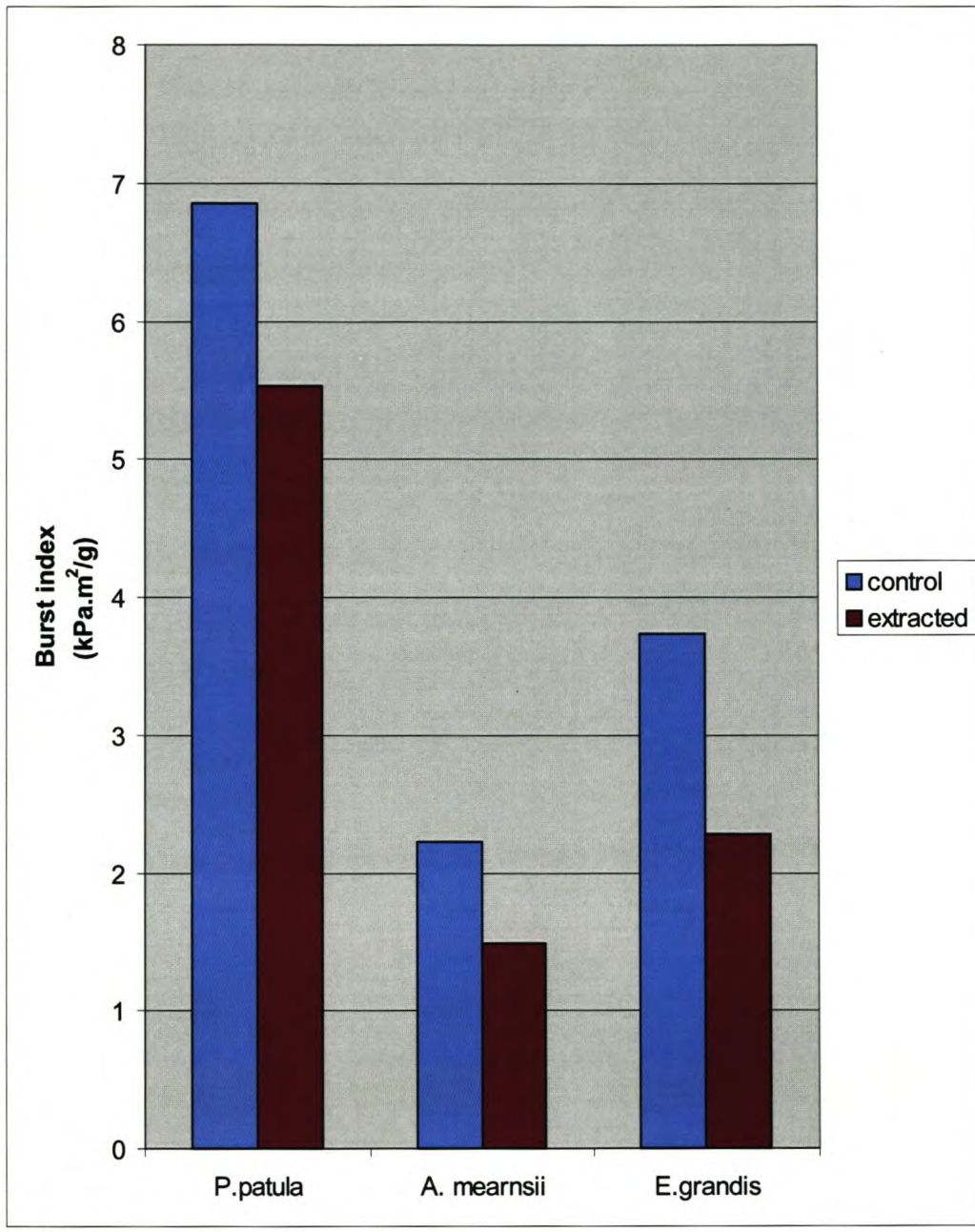

Figure 2.15: Burst index of handsheets made from control and extracted wood pulp at 38 ^{0}SR

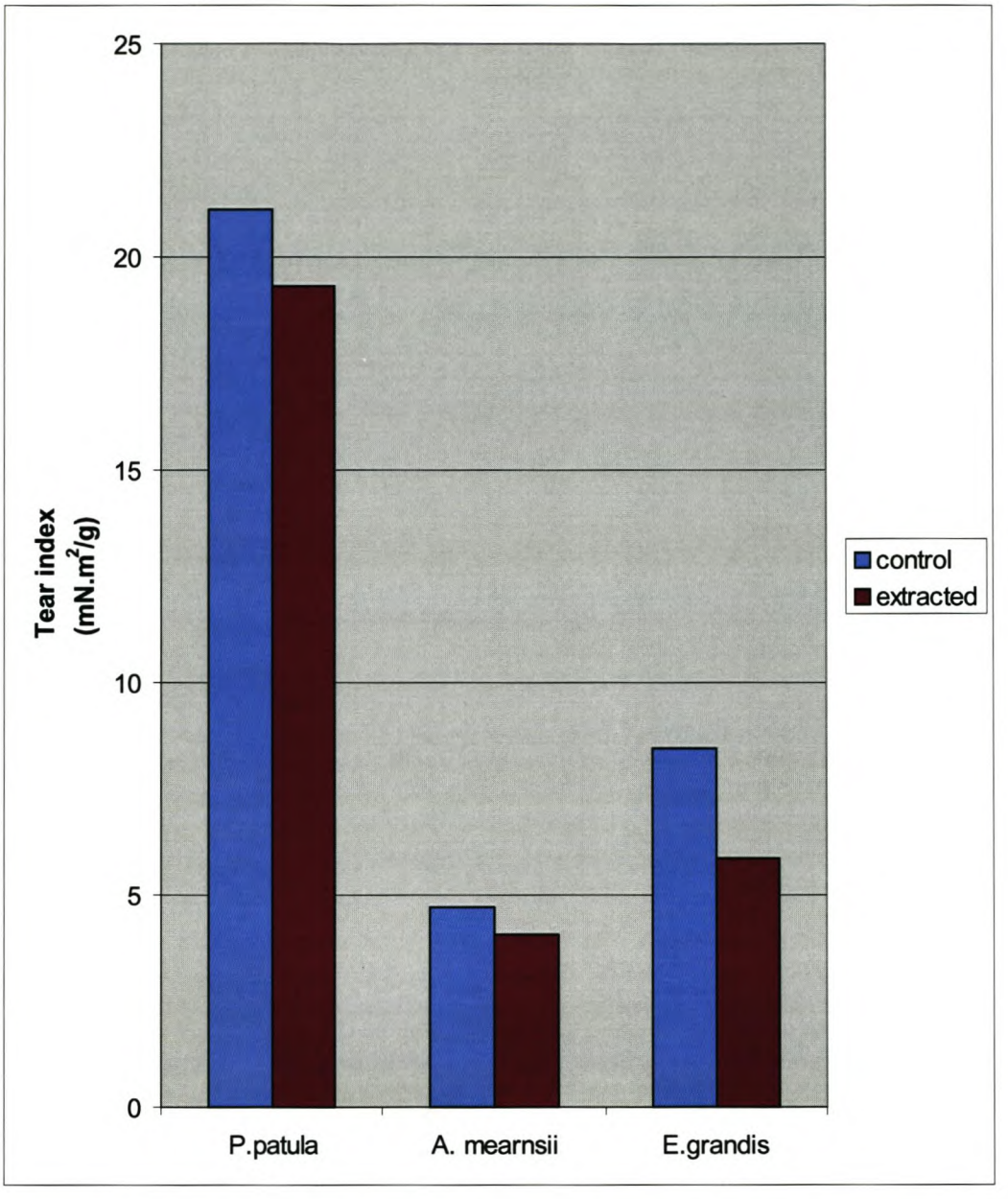

Figure 2.16: Tear index of handsheets made from control and extracted wood pulp at 38 ^{0}SR

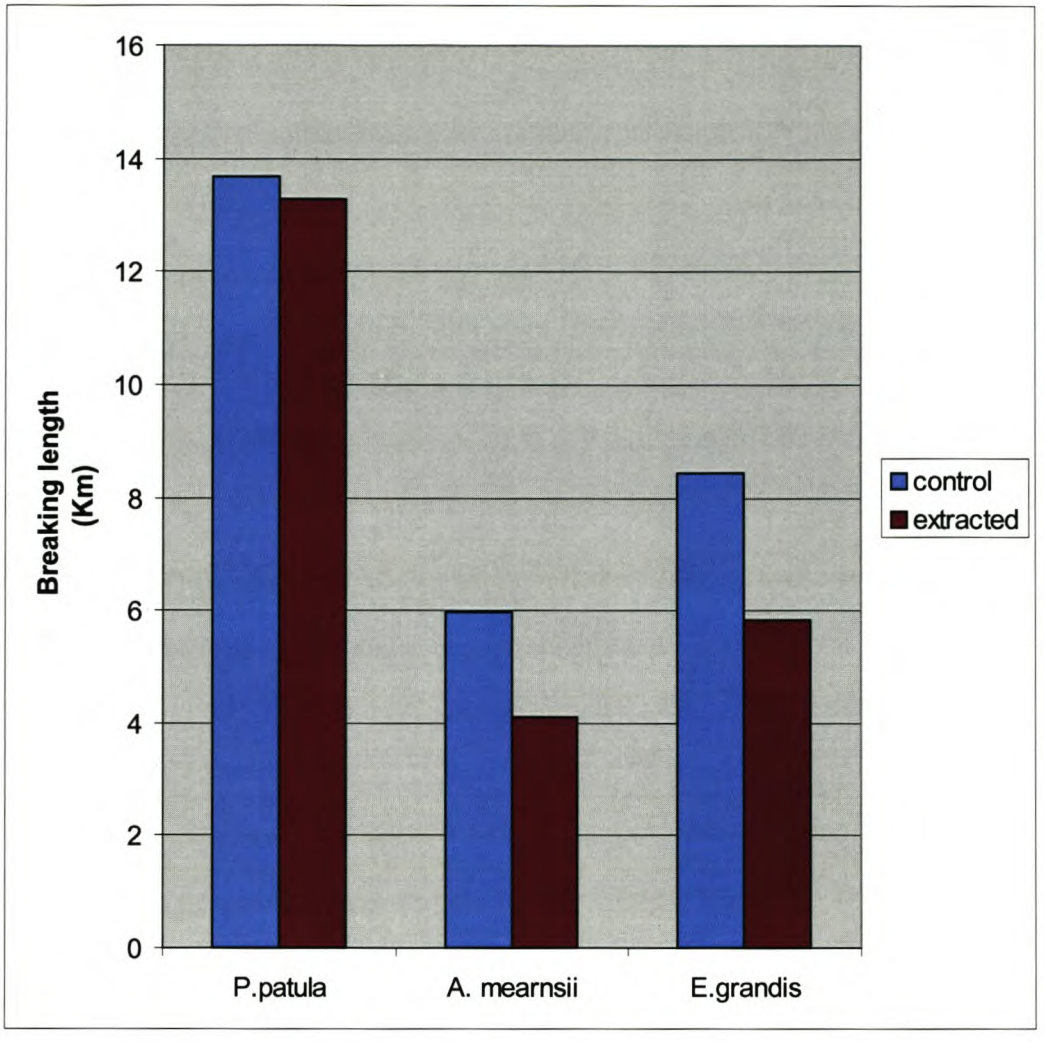

Figure 2.17: Breaking length of handsheets made from control and extracted wood pulp at 38 ^{0}SR

2.2.7. Loss in Mass

The hot water extracted wood chips were oven dried and the total mass loss recorded. Results of the mass loss are shown in **Table 2.9.** It is observed that the pressurised hot water extraction resulted in a substantial loss in mass. This is due to the depolymerisation of cellulose and the removal of extractives. When the extract material was left overnight, dark sawdust like material settled at the bottom of the solution. This may be another reason for the lower mass after extraction. Therefore, mass loss can be accounted for by this material and extractives. It was also observed that of the two hardwood species

Acacia mearnsii had the greater loss in mass. *Pinus patula* also lost a significant amount of mass due to extraction.

Table 2.9: Percentage mass loss after pressurised hot water extraction

	Eucalyptus grandis	*Acacia mearnsii*	*Pinus patula*
Mass loss %	16	28	34

2.3. Conclusion

The two-hour pressurised hot water extraction resulted in lower yields than the controls for each of the three species. Pressurised hot water extraction resulted in less rejects and shives. This indicates better delignification rates for the extracted wood chip material partly due to the degradation of some polysaccharides during the two hour pressurised hot water extraction and partly due to the removal of extractives. The "opening" of the wood structure enhanced the diffusion of cooking liquor and therefore facilitated a more uniform cooking, i.e. less over-cooking of the exterior part of the wood chips and less under-cooking of the centre of the wood chips. The reduction in screened pulp yield after pressurised hot water extraction indicates that the two-hour extraction period was too long causing the degradation of cellulose. The control wood chips of both the hardwoods and the softwood pulped with 16 and 18%AA respectively, obtained screened yields similar to those reported in literature [36,37,38]. More residual active alkali was left in the spent liquor after pulping of the extracted wood chips. It is clear that extractives contained in the wood chips played a significant role in the consumption of the pulping chemicals and by hot water extraction some of these were removed leading to a higher RAA in the spent liquor. It was evident that there was better delignification of the extracted wood chips and, therefore, a reduction in residual lignin content of the hot water extracted wood pulp. This reduction was reflected in the lower Kappa numbers for the hot water extracted wood pulp. The recorded reduction in Kappa number was as much as 35% to 50%. Very little difference in beating response for both the control and pressurised hot water extracted hardwood pulp was evident although there was some difference between *Acacia mearnsii* pulp material at longer beating rates. Pressurised Hot

water extracted *Pinus patula* pulp responded faster than the control pulp. This may be related to the acidic conditions during the pressurised hot water extraction leading to sulfite-like beating characteristics [40]. There was a decrease in handsheet strength properties for the hot water extracted wood chip pulp for all species evaluated, however, *Pinus patula* recorded the least decline in sheet strength. It seems shorter extraction times are required in order to prevent the hydrolytic degradation of cellulose.

Chapter 3: Kraft pulping

3.1. Material and methods

In this chapter the Kraft pulping of the three wood species namely *Acacia mearnsii*, *Eucalyptus grandis* and *Pinus patula* will be discussed. The pulping was performed under similar conditions, which applied to Soda AQ process.

3.1.1. Pulping conditions

For hardwood pulping an active alkali (AA) concentration of 18% sodium hydroxide and 22% sulphidity was used. The liquid to mass ratio was 4.5:1. For softwood pulping an AA of 22% sodium hydroxide and 22% sulphidity was used with a liquid to mass ratio of 5.4:1. The pulping schedule was the same as that used for Soda AQ pulping of hardwood and softwood. After digestion, the wood chips were removed and black liquor collected for chemical analysis. The pulp was washed as previously described in section 2.1.2. The pulping schedules can be seen in **Figure 2.1** and **Figure 2.2**. Pulp yields, percentage rejects, chemical consumption (RAA), shive content, Kappa number, beating response and handsheet strength were determined in the same manner as that of the Soda AQ pulping.

3.2. Results and Discussion

The results for the screened pulp yields, rejects, shive content, chemical consumption (RAA), Kappa number and pulp evaluations for the three species, are given in **Tables 3.1** to **3.11.** and **Figures 3.1** to **3.10**

3.2.1. Pulp yield

Table 3.1 and **Figure 3.1** showed a significant decrease in screened pulp yield for the hot water extracted wood chips. The control screened pulp yield compares well with those reported in literature ranging between 40-50% for bleachable pulps [11,35]. The low screened yield for the pressurised hot water extracted wood chips is attributed to the removal of extractives, which consume active alkali and the possible depolymerisation of

polysaccharides. The low rejects and shive content values shown in **Tables 3.2** and **3.3** and **Figures 3.2** and **Figure 3.3** can be attributed to the same reasons.

Table 3.1:Screened pulp yields for control and hot water extracted wood chips

Species	Screened yield (%)	
	Control	Hot water extracted (2 hours)
Acacia mearnsii	52.0	33.0
Eucalyptus grandis	52.5	42.9
Pinus patula	38.5	32.0

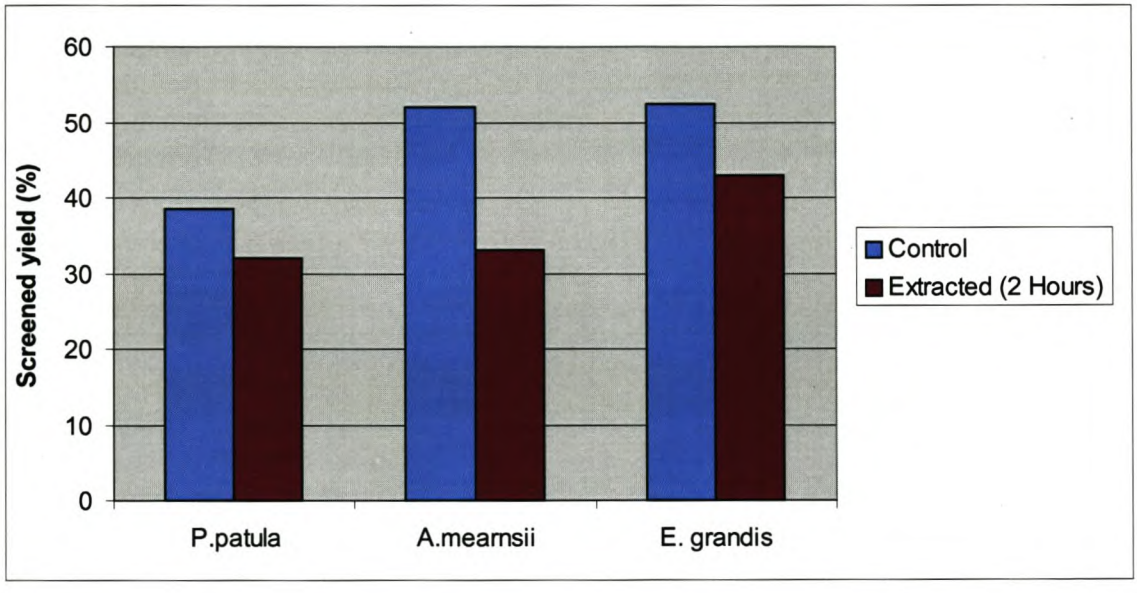

Figure 3.1: Screened yield of control and extracted Kraft wood pulp

3.2.2. Percentage rejects

Table 3.2:Percentage rejects for control and pressurised hot water extracted wood chips

Species	Rejects (%)	
	Control	Hot water extracted (2 hours)
Acacia mearnsii	0.7	0
Eucalyptus grandis	1.5	0
Pinus patula	0	0

3.2.3. Shive content

Table 3.3:Kraft pulp shive content for control and pressurised hot water extracted wood chips

Species	Shive content (%)	
	Control	Hot water extracted (2 hours)
Acacia mearnsii	2.5	0.08
Eucalyptus grandis	0.1	0.10
Pinus patula	2.0	0.17

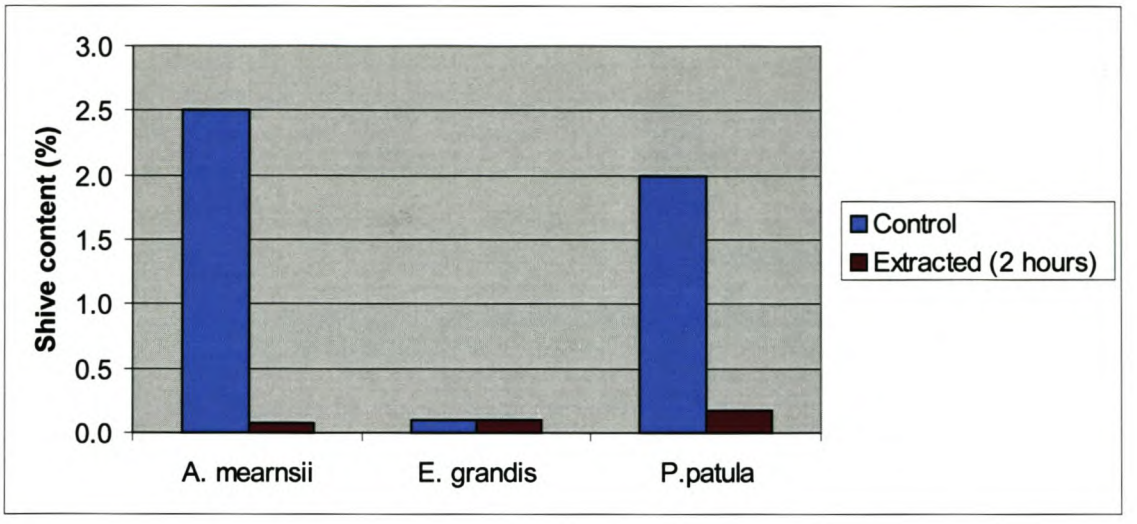

Figure 3.2: Shive content of control and extracted Kraft wood pulp

3.2.4. Consumption of white liquor (RAA)

Table 3.4 and **Figure 3.4** show a drop in RAA for the pressurised hot water extracted wood chips. It thus can be concluded that with pressurised hot water extraction more active alkali is used up during Kraft pulping. This could be due to the opening up of the wood structure leading to better delignification and therefore more consumption of pulping liquor.

Table 3.4: Chemical consumption of control and pressurised hot water extracted wood chips during Kraft pulping

Species	RAA (g/l)	
	Control	Hot water extracted (2 hours)
Acacia mearnsii	16.1	8.6
Eucalyptus grandis	14.8	7.4
Pinus patula	9.6	7.0

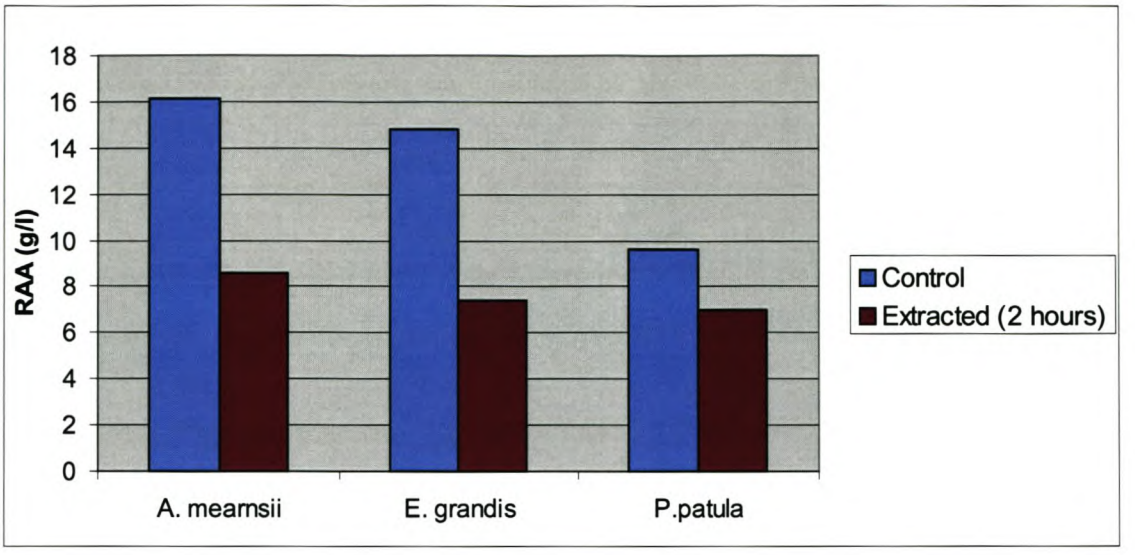

Figure 3.3: Residual active alkali of control and extracted Kraft wood pulp

3.2.5. Kappa number

A sharp drop in the Kappa number is shown in **Table 3.5** and **Figure 3.5.** Pressurised hot water extraction must have loosened the wood structure, which enhanced delignification and explains the reduced residual active alkali in the spent liquor and the dramatic reduction in the Kappa number.

Table 3.5:Kappa number of control and pressurised hot water extracted Kraft wood pulp

Species	Kappa number	
	Control	Hot water extracted (2 hours)
Acacia mearnsii	19.0	8.5
Eucalyptus grandis	19.0	7.6
Pinus patula	37.0	13.8

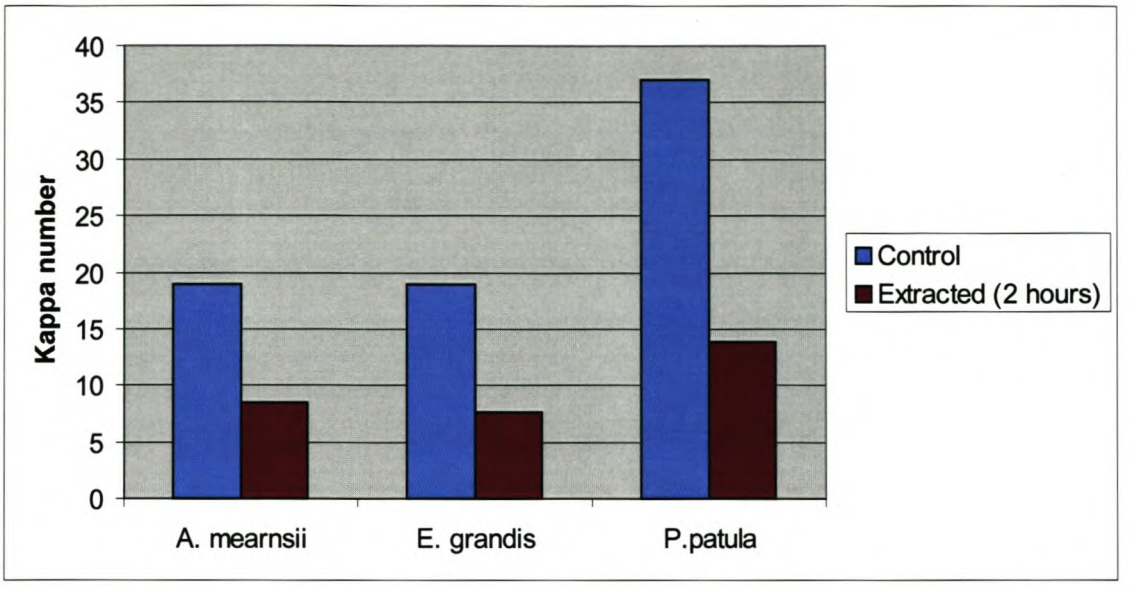

Figure 3.4: Kappa number of control and extracted Kraft wood pulp

3.2.6. Pulp Evaluations

Table 3.6 and **3.7** and **Figure 3.6** show similar responses to beating for both control and pressurised hot water extracted *Acacia mearnsii* and *Eucalyptus grandis* wood chips. **Table 3.8** and **Figure 3.7** on the other hand indicate a slower beating response for the pressurised hot water extracted *Pinus patula* pulp compared to the control sample. This is attributed to the acid conditions during pressurised hot water extraction, which restrict the swelling tendency of fibre and retards beating.

Table 3.6: Beating response and handsheet strength properties of *Eucalyptus grandis* Kraft pulp

Beating time (min)	°SR (Degrees)		Breaking Length (km)		Tear Index ($mN.m^2/g$)		Burst Index ($kPa.m^2/g$)	
	Control	Hot water extracted (2 hours)	Control	Hot water extracted (2 hours)	Control	Hot water extracted (2 hours)	Control	Hot water extracted (2 hours)
0	22	20	4.6	5.1	5.4	4.5	1.5	1.1
1	31	23	10.8	5.3	8.5	5.1	3.3	1.7
2	36	35	10.6	7.3	8.9	5.5	3.9	2.2
3	45	41	13.2	7.6	9.1	6.3	4.7	2.4

Table 3.7: Beating response and handsheet strength properties of *Acacia mearnsii* Kraft pulp

Beating time (min)	°SR (Degrees)		Breaking Length (km)		Tear Index ($mN.m^2/g$)		Burst Index ($kPa.m^2/g$)	
	Control	Hot water extracted (2 hours)	Control	Hot water extracted (2 hours)	Control	Hot water extracted (2 hours)	Control	Hot water extracted (2 hours)
0	24	24	2.3	3.3	4.1	3.1	0.4	0.9
1	28	26	5.2	5.4	4.9	3.9	1.5	1.4
2	34	32	5.4	5.8	6.1	5.3	1.8	1.9
3	38	40	7.1	8.0	7.1	6.0	1.9	2.2

Table 3.8: Beating response and handsheet strength properties of *Pinus patula* Kraft pulp

Beating time (min)	°SR (Degrees)		Breaking Length (km)		Tear Index ($mN.m^2/g$)		Burst Index ($kPa.m^2/g$)	
	Control	Hot water extracted (2 hours)	Control	Hot water extracted (2 hours)	Control	Hot water extracted (2 hours)	Control	Hot water extracted (2 hours)
0	17	14	5.5	5.0	11.1	19.0	2.3	1.8
5	26	19	11.3	10.0	20.6	30.3	5.4	4.3
10	33	23	10.4	10.7	19.5	22.1	5.4	5.3
15	40	26	13.8	12.5	25.9	30.0	6.5	6.2
20	55	29	15.1	11.4	16.5	30.7	6.7	5.5

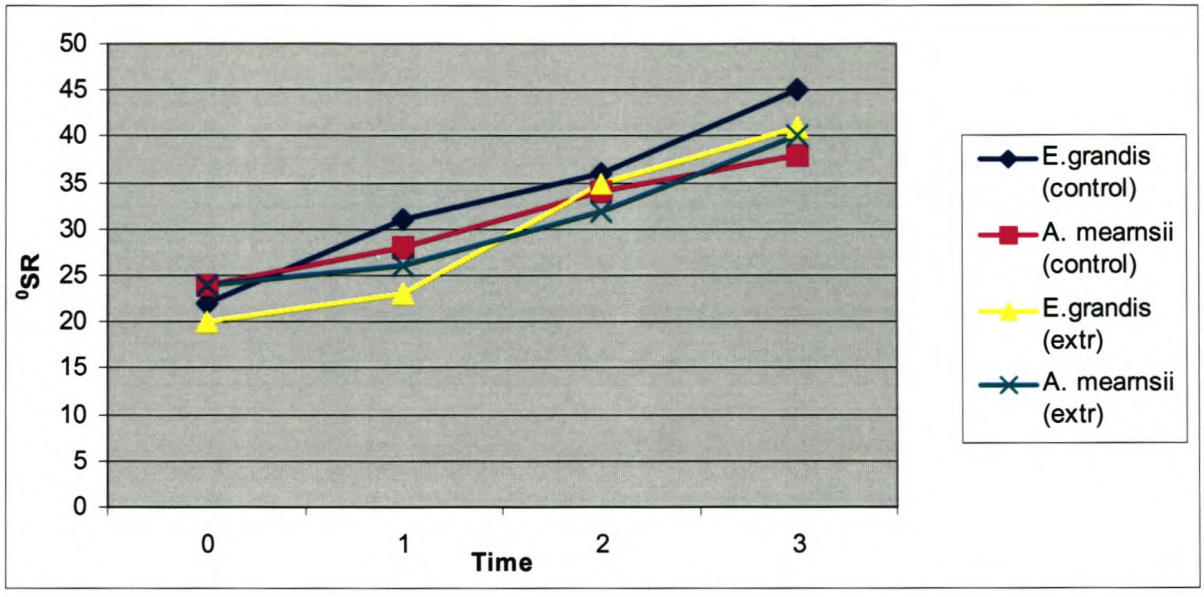

Figure 3.5: Beating response of extracted and non-extracted *Acacia mearnsii* and *E. grandis* Kraft pulp

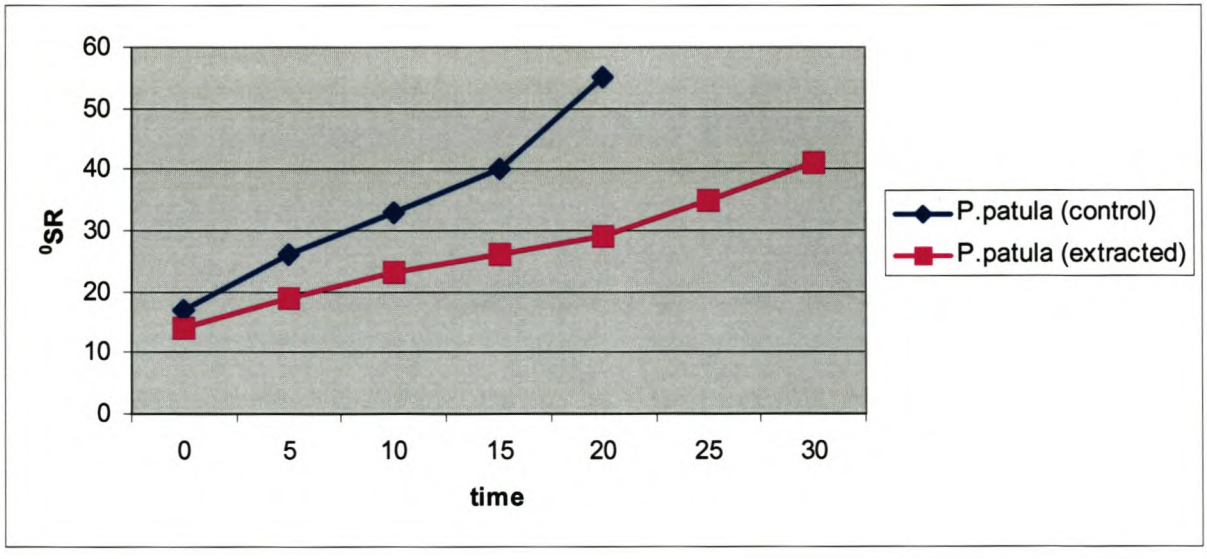

Figure 3.6: Beating response of extracted and non-extracted *P. patula* Kraft pulp

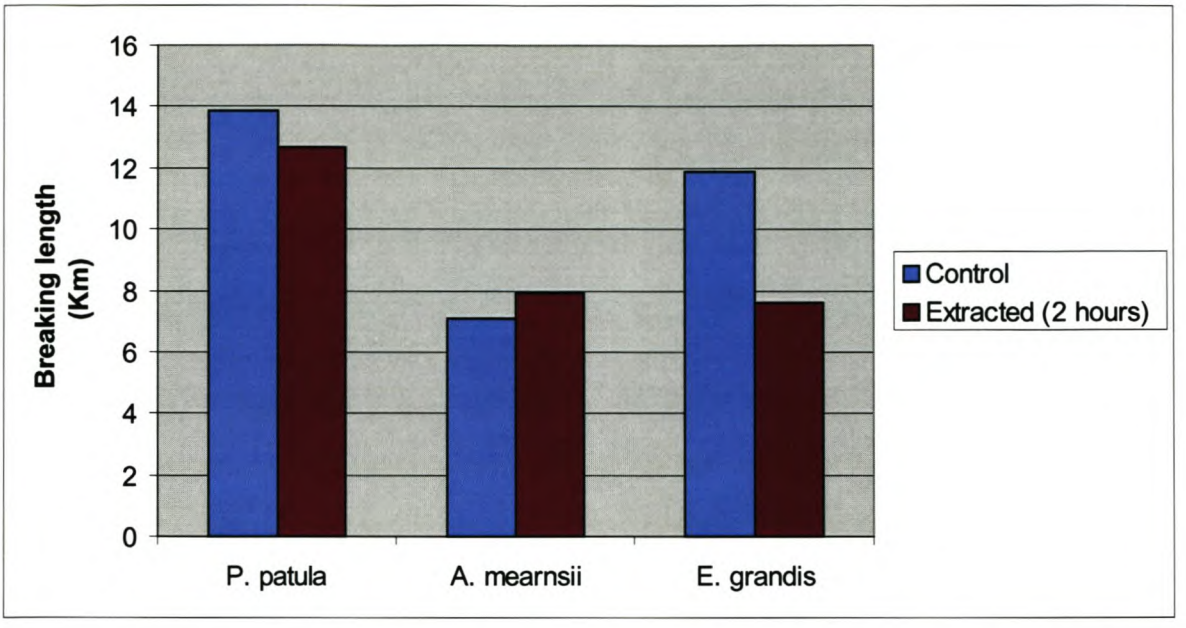

Figure 3.7: Breaking length of handsheets made from control and extracted Kraft wood pulp beaten to 38 °SR

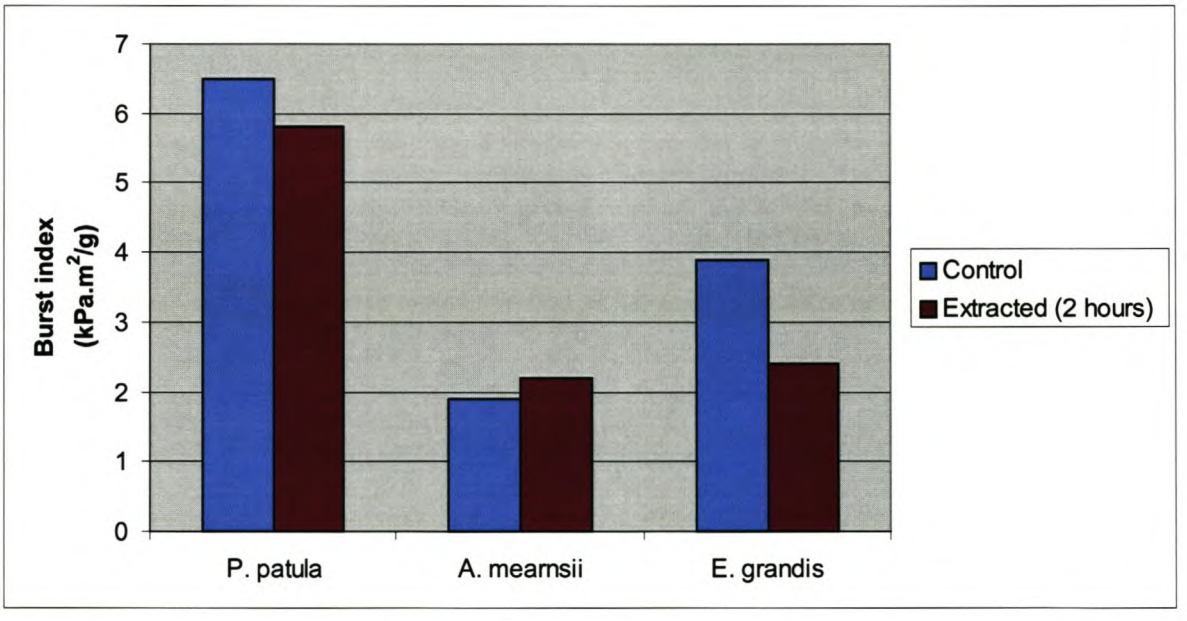

Figure 3.8: Burst index of handsheets made from control and extracted Kraft wood pulp beaten to 38 °SR

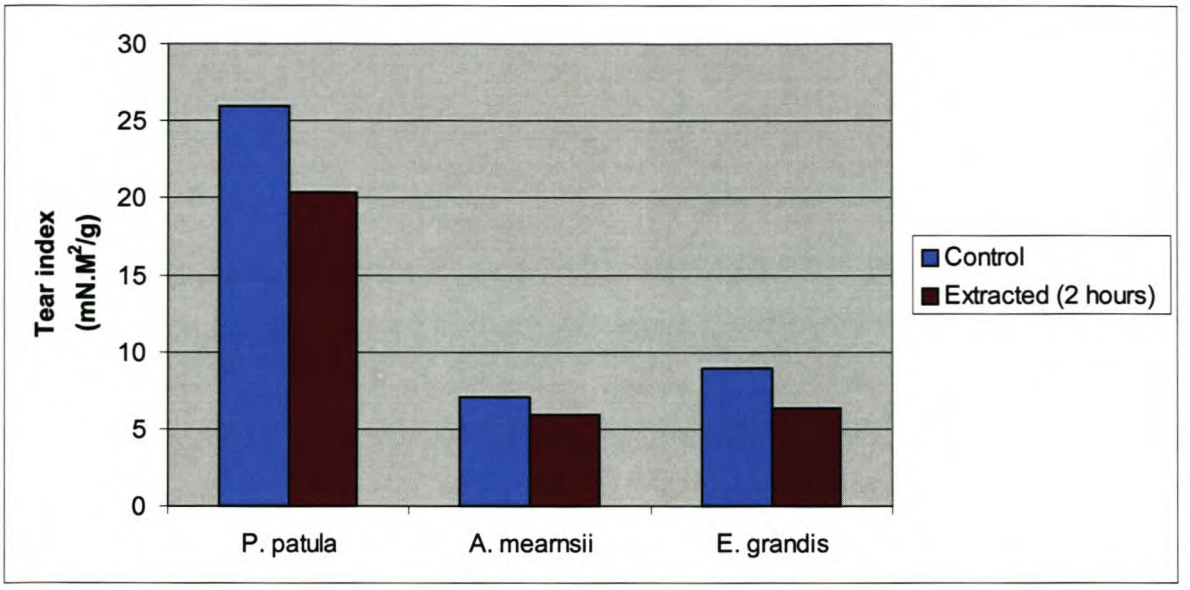

Figure 3.9: Tear index of handsheets made from control and extracted Kraft wood pulp beaten to 38 °SR

3.3. Conclusion

The screened yield for Kraft pulping was calculated in the same manner as that of the Soda AQ process. It is observed that for the Kraft process the pressurised hot water extracted wood chip screened pulp yields decreased for all three wood species. A significant drop in rejects was noticed for *Acacia mearnsii* and also the shive content of *Pinus patula* was noticeably reduced. The extracted wood chips had less residual active alkali in its black liquor as compared to the control wood chips. The Kappa number of *Acacia mearnsii* and *Eucalyptus grandis* was reduced to as low as 8. The reduction in yield is a result of more exposure of lignin to the alkali. This lead to better delignification and as a result the lignin content of the pulp decreased. For the Soda AQ pulping process similar results were obtained. A decrease in all the measured handsheet strengths for pressurised hot water extracted *E. grandis* and *Pinus patula* wood pulp was recorded. This was attributed to increased cellulose degradation. In the case of *Acacia mearnsii* breaking length and burst index increased slightly.

Chapter 4: One hour pressurised hot water extraction

4.1. Introduction

The extraction of wood chips using the hardwood pulping cycle (2 hour extraction) caused extensive degradation of polysaccharides and the extreme extraction conditions resulted in a reduction in screened yield and strength properties of the water extracted wood pulp. It was anticipated that a shorter extraction time would be more beneficial for pulp production efficiency and that the less extreme conditions would be beneficial for pulp yield and paper strength properties. Pressurised hot water extraction for 1-hour was thus considered as an alternative chip pretreatment. Only the Soda A.Q pulping method was used for the evaluation of the shorter extraction period.

4.2 Results and discussion

Screened pulp yield, percentage rejects, shive content, RAA and Kappa number are given in **Tables 4.1** to **4.5** and **Figures 4.1** to **4.5**. The 1-hour results were compared with the 16% active alkali charged control and the results of the 2-hour pressurised hot water extraction. The 1-hour hot water extraction resulted in an increase in screened pulp yield for *Eucalyptus grandis* and *Acacia mearnsii* compared to the 2-hour hot water extraction as shown in **Figure 4.1**. This was attributed to the less extreme extraction conditions, which resulted in lower cellulose degradation. The control samples however produced the highest screened pulp yield except for *Acacia mearnsii*. From **Figure 4.2** it can be seen that for the 1-hour hot water extraction, *Pinus patula* and *Eucalyptus grandis* showed a substantial increase in rejects. The 1-hour pressurised hot water extracted *Acacia mearnsii* on the other hand produced less rejects due to better delignification. Shive content of the extracted wood chips was reduced. The 2-hour hot water extracted *Pinus patula* on the other hand produced more shives than the 1-hour extracted wood chips as shown in **Figure 4.3**. This was attributed to lignin condensation, which resulted in reduced delignification. **Figure 4.4** shows a significant reduction in RAA for 1-hour extracted *Pinus patula*. This is attributed to excessive delignification, which is reflected

by the lower shive content and the reduced Kappa number. From **Figure 4.5** it can be seen that for the hardwoods 1-hour pressurised hot water extracted wood chips produced pulp with a higher Kappa number than the 2-hour pressurised hot water extracted wood chips, but resulted in a lower Kappa number than the control pulp.

Table 4.1: The effect of 1-hour pressurised hot water extraction of wood chips on screened pulp yield compared to control and 2 hour extraction.

Species	Screened yield (%)		
	Hot water extracted (1 hour)	Control	Hot water extracted (2 hours)
Acacia mearnsii	52	48	43
Eucalyptus grandis	51	58	43
Pinus patula	33	42	38

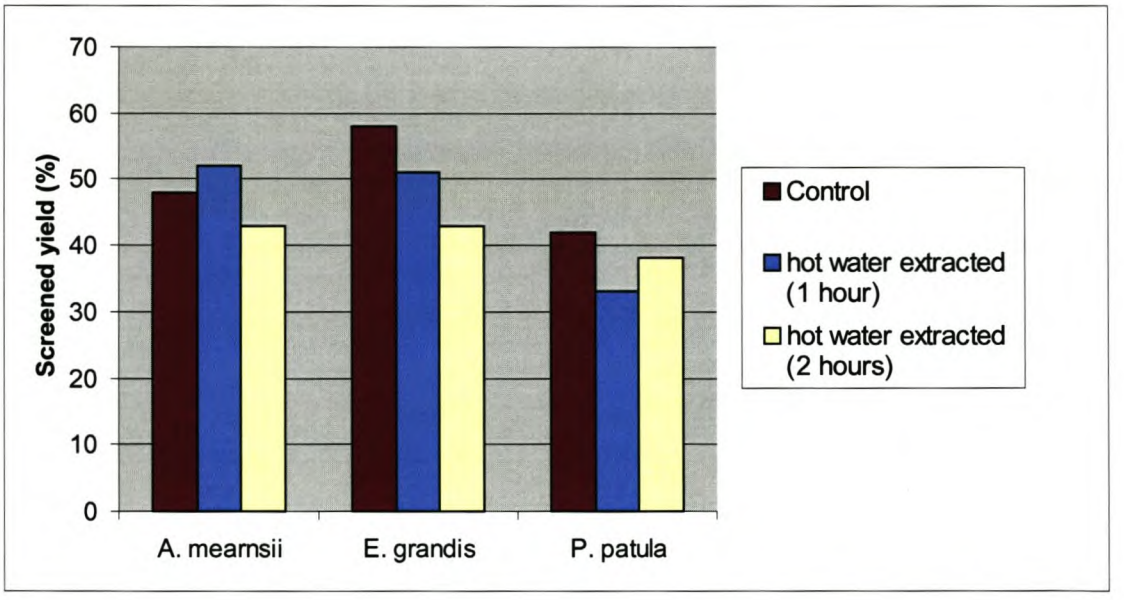

Figure 4.1: Screened pulp yield of 1 hour extracted wood chips compared to control and 2 hour extraction time

extraction the fibre structure was loosened as a result of cellulose degradation. From **Figures 4.7** to **4.10** it can be seen that with increase in beating time 1-hour extracted *Acacia mearnsii* pulp produced higher strength properties than the 2-hour extracted material. This was attributed to the less extreme conditions during the extraction, leading to better delignification and less polysaccharide degradation of the 1-hour extracted wood chips. When interpolated to 38 ^{0}SR the 1-hour extracted wood pulp produced the highest handsheet strength properties as can be seen in **Figures 4.10 to 4.12**.

Table 4.6: Beating response of *Acacia mearnsii* pulp

Beating time (Min)	**^{0}SR (Degrees)**		
	Control	Hot water extracted (1 hour)	Hot water extracted (2 hours)
0	23	23	24
1	37	29	39
2	53	32	46
3	75	37	60

Table 4.7: Breaking length of *Acacia mearnsii* handsheets

Beating time (Min)	**Breaking length (km)**		
	Control	Hot water extracted (1 hour)	Hot water extracted (2 hours)
0	4.9	2.5	1.7
1	6.2	5.7	4.1
2	7.1	6.6	6.3
3	12.0	8.6	6.4

Table 4.8: Tear index of *Acacia mearnsii* handsheets

Beating time (Min)	**Tear index ($mN.m^2/g$)**		
	Control	Hot water extracted (1 hour)	Hot water extracted (2 hours)
0	4.3	3.1	2.4
1	5.2	4.9	5.1
2	5.9	5.4	5.6
3	8.2	7.2	5.4

Table 4.9: Burst index of *Acacia mearnsii* handsheets

Beating time (Min)	**Burst index ($kPa.m^2/g$)**		
	Control	Hot water extracted (1 hour)	Hot water extracted (2 hours)
0	1.2	0.6	0.4
1	1.8	1.7	1.6
2	2.7	2.2	2.1
3	5.5	2.7	2.4

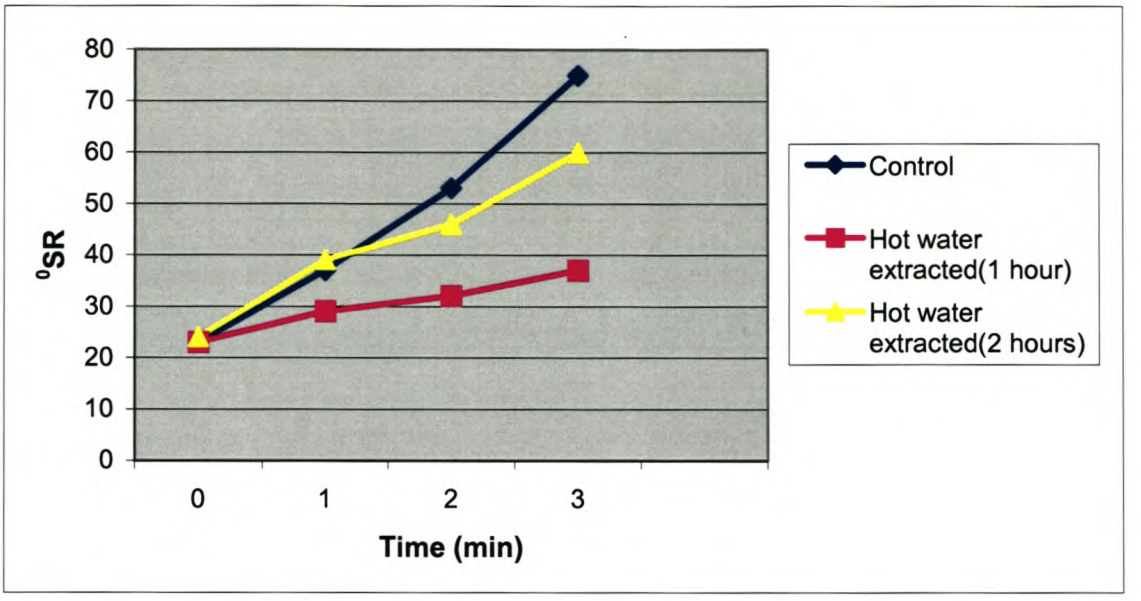

Figure 4.6: Beating response of 1-hour, 2-hours and control *Acacia mearnsii* pulp

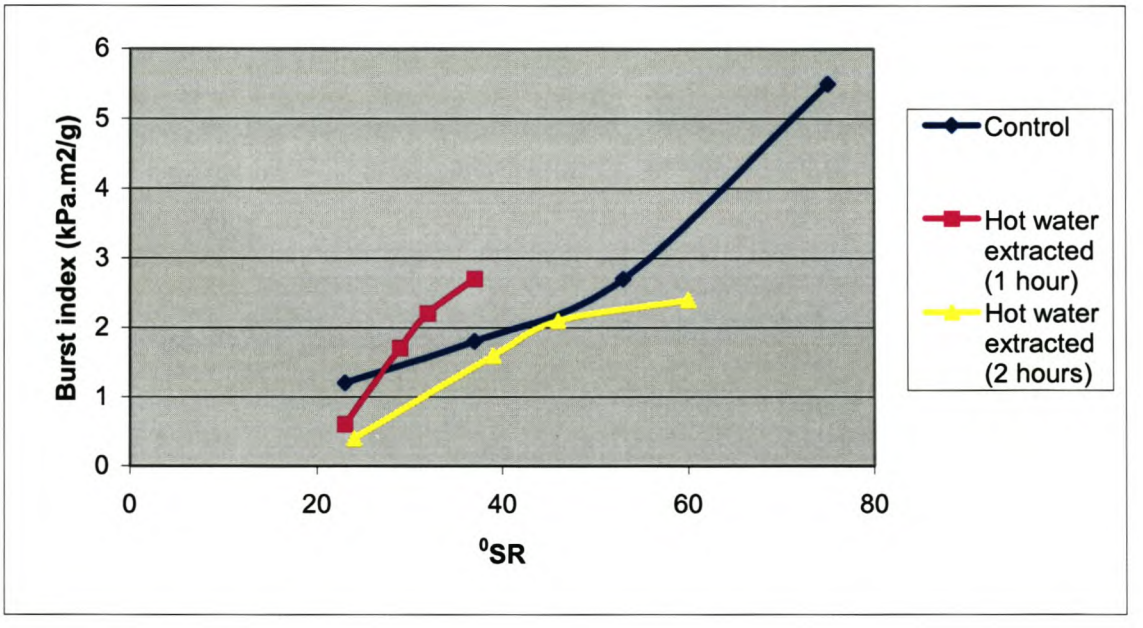

Figure 4.7: Burst index of control, 1 hour extracted and 2 hour extracted wood pulp

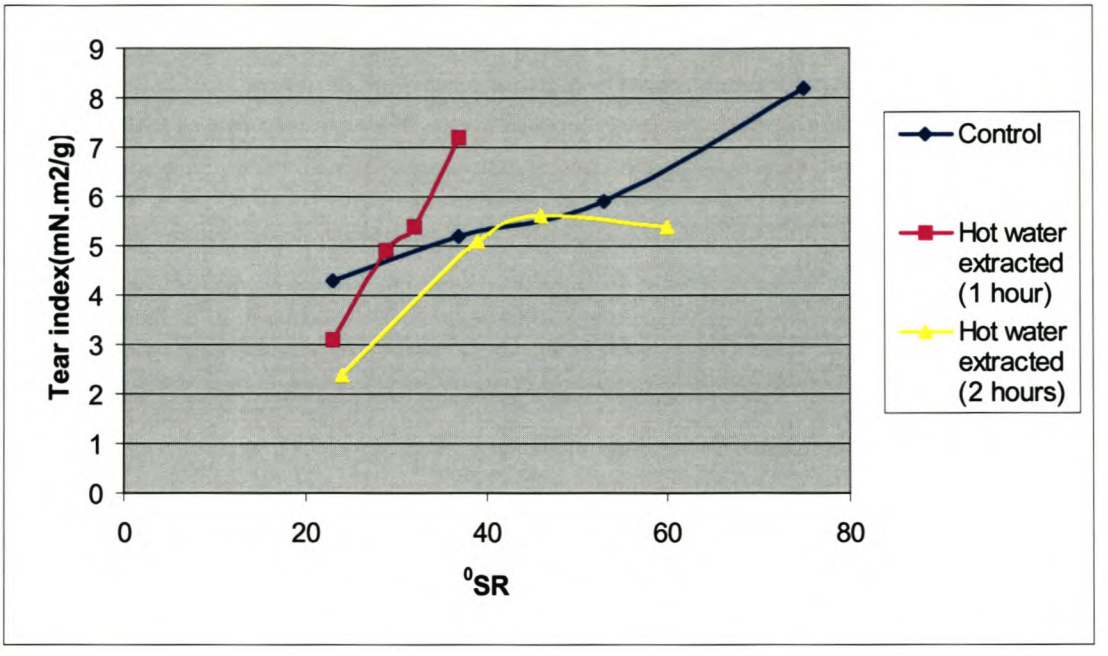

Figure 4.8: Tear index of control, 1 hour extracted and 2 hours extracted wood pulp

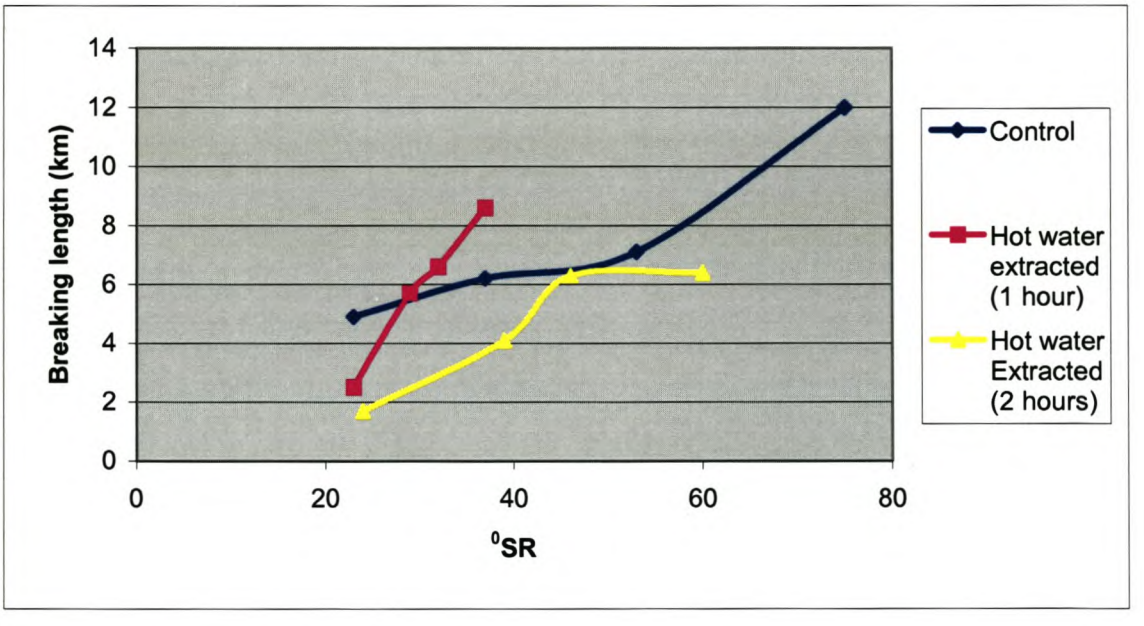

Figure 4.9: Breaking length of control, 1 hour extracted and 2 hours extracted wood pulp

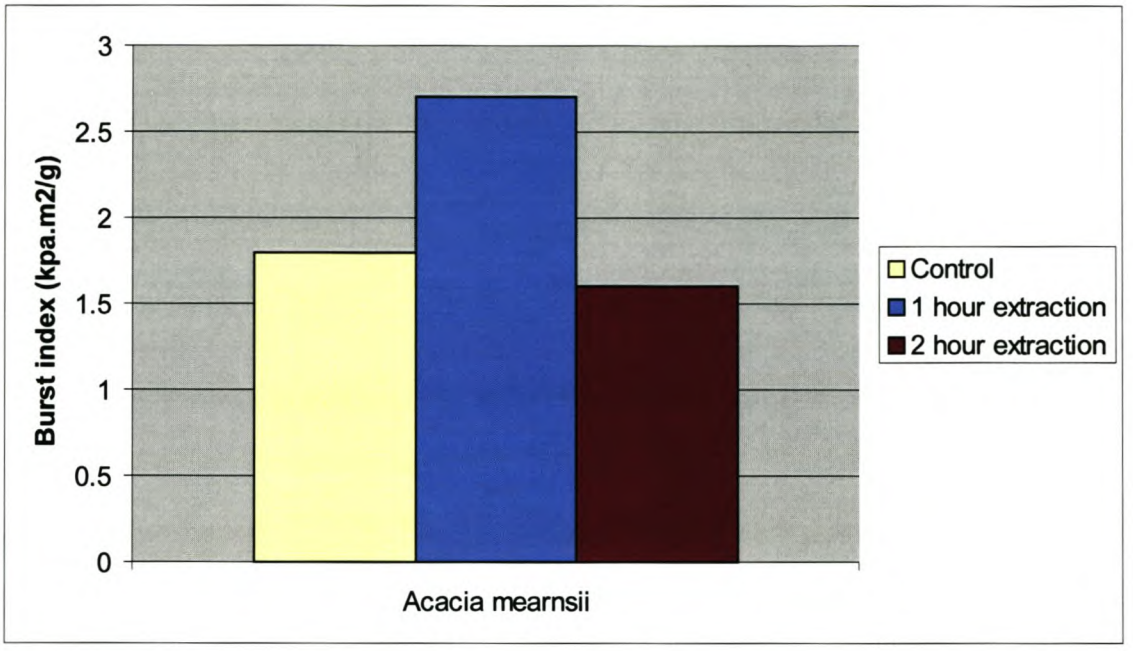

Figure 4.10: Burst index at 38 SR of *Acacia mearnsii* pulp obtained from 1 and 2 hour extracted wood chips compared to control.

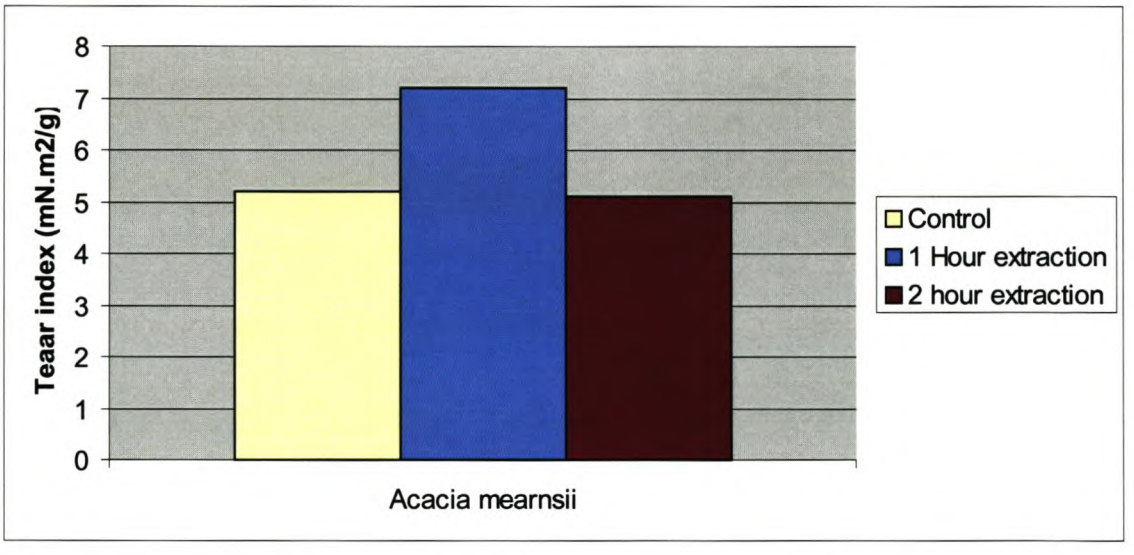

Figure 4.11: Tear index at 38 SR of *Acacia mearnsii* pulp obtained from 1 and 2 hour extracted wood chips compared to control.

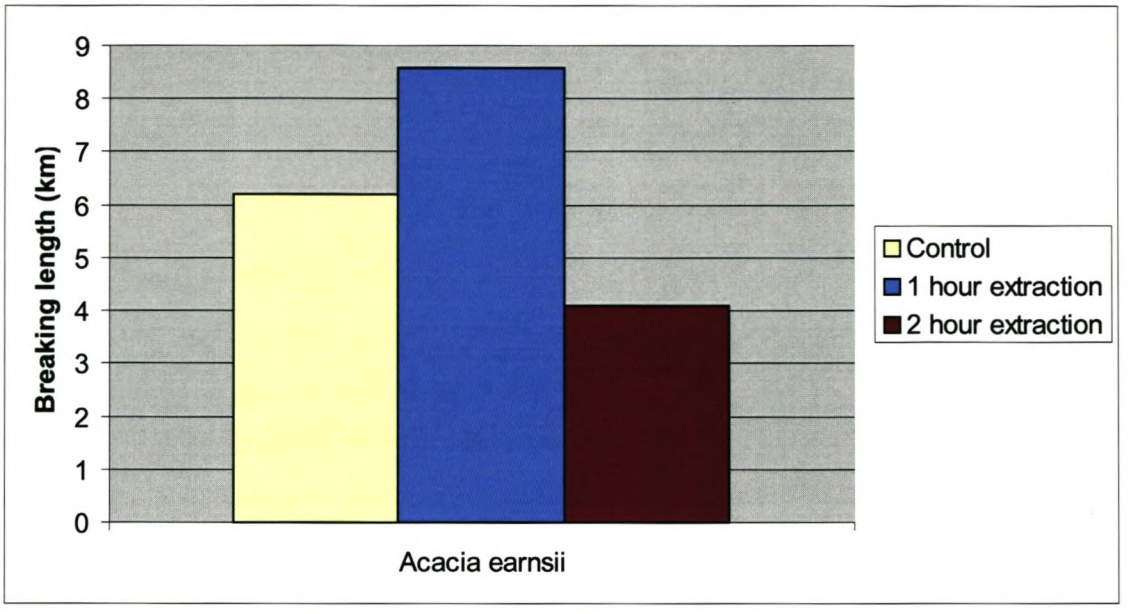

Figure 4.12: Breaking length at 38 SR of *Acacia mearnsii* pulp obtained from 1 and 2 hours extracted wood chips compared to control

4.3. Discussion

The less extreme 1-hour extraction of *Acacia mearnsii* chips produced a slightly higher screened pulp yield than both the control and the 2-hour extracted chips. *Acacia mearnsii* recorded a 4% increase in screened yield for the 1-hour water extracted wood chips compared to the control. The 1-hour water extracted wood chips also showed higher strength properties than the control and 2 hours extracted wood. This can be attributed to the opening of the wood structure during extraction leading to a more uniform cook (less over-cooking of the outside and under-cooking of the centre of the wood chips). The results indicate that the 2-hour extraction period was too severe on the wood chips. The 1-hour extraction of *Acacia mearnsii* seems to eliminate the negative effects of the high wood extractive content. Wood with high extractive contents is hard to pulp and causes pitch problems in the paper making processes. The 1-hour hot water extraction of wood chips before pulping therefore could be beneficial for species with high extractive contents.

Chapter 5: Chemical and physical aspects of hot water extraction of wood chips

5.1. Material and methods

5.1.1. Extraction

As discussed in the previous chapters wood chips of the three species were extracted with water in a laboratory digester. 15000g of wood chips were placed into the digester and 10 litres of water added. The chips were extracted using the pulping cycle for hardwoods. The pressurised hot water extracted chips were rinsed with 2 litres, hot water to remove any excess extracts. The extract including the rinse water was collected in 20 litre containers and 500ml decanted into volumetric flasks for analysis. Non-extracted wood chips were placed in 50 litre drums and were submerged in cold water at room temperature for 48 hours after which a sample of the water was taken. A sample of cold-water extract was also collected in 500ml volumetric flasks for analysis.

5.1.2. Analysis of extract material

To determine the solids content of the extract material, a sample of the 100ml of extract solution was weighed and placed in an oven at 105^0C for 48 hours until all the water had been evaporated. The mass of the solids left in the beaker was recorded and expressed as a percentage of the initial mass of the extract solution. All determinations were done in triplicate. Scanning electron microscopy was performed on the extracted and the control wood chips. The pH a sub sample of the extract solution was measured. Hot water extracted wood chips, extract solutions, the pulp produced, and handsheets prepared from the different pulp samples were photographed for comparison. Slides of extracted and control fibres were made and the fibre length was determined. The handsheet brightness of the 2-hour extracted wood pulp and the control were determined using an Elrepho brightness tester.

5.2.Results

From Table **5.1** it can be seen that the extract solid content of the 2-hour hot water material was considerably higher than that of the cold-water extracted solutions for all three species.

Table 5.1: Solid content of extract solutions

	Cold water extracted mass % (Ambient temp. 48 hours)	Hot water extracted mass % (2 hours)	Hot water extracted mass % (1 hour)
Acacia mearnsii	0.03	5.80	0.90
Eucalyptus grandis	0.07	3.90	0.50
Pinus patula	0.09	3.50	0.60

The pH values for the extract solutions appeared to be in the acid range as shown in **Table 5.2**. This confirms that high-pressure hot water extraction of wood chips takes place under acidic hydrolytic conditions. The acid conditions are attributed to the formation of organic acids from the dissolution of carbohydrates and lignin.

Table 5.2: pH of extract solutions (2 hours)

	pH
A. mearnsii	3.2
E. grandis	3.1
P. patula	3.7

When a solution of the extract material was treated with 2M NaOH a yellow colour appeared, whilst a dark blue colour was observed when the solution was reacted with

ferric chloride. These observations indicated the presence of ellagic and gallic acid[11]. The use of chromatographic techniques would verify the presence of the two acids but this was not possible in this study. Ellagic acid is a non-sintering compound with low water solubility. This acid most probably is complexed with the cell wall material.

The colour difference of the control and the extracted wood pulp handsheets is shown in **Table 5.3.** The reduction in Kappa number (lignin indicator) coincided with an increase in brightness.

Table 5.3: Handsheet Elrepho brightness of control and hot water extracted wood pulp

	Handsheet made from control pulp	Handsheet made from extracted wood chip pulp
A. mearnsii	27.2	56.8
E. grandis	28.1	55.4
P. patula	23.2	51.3

The presence of gallic and ellagic acids, their derivatives and other compounds are mainly responsible for the dark appearance of the extracted wood chips, as seen in **Figure 5.1.** This can be explained by the precipitation of ellagic acid complexes in an acid environment (hydrolysis). During extraction these decomposed gallic and ellagic acids complexes are removed, with the consequence that pulp brightness is improved as can be seen from the results shown in **Table 5.3**.

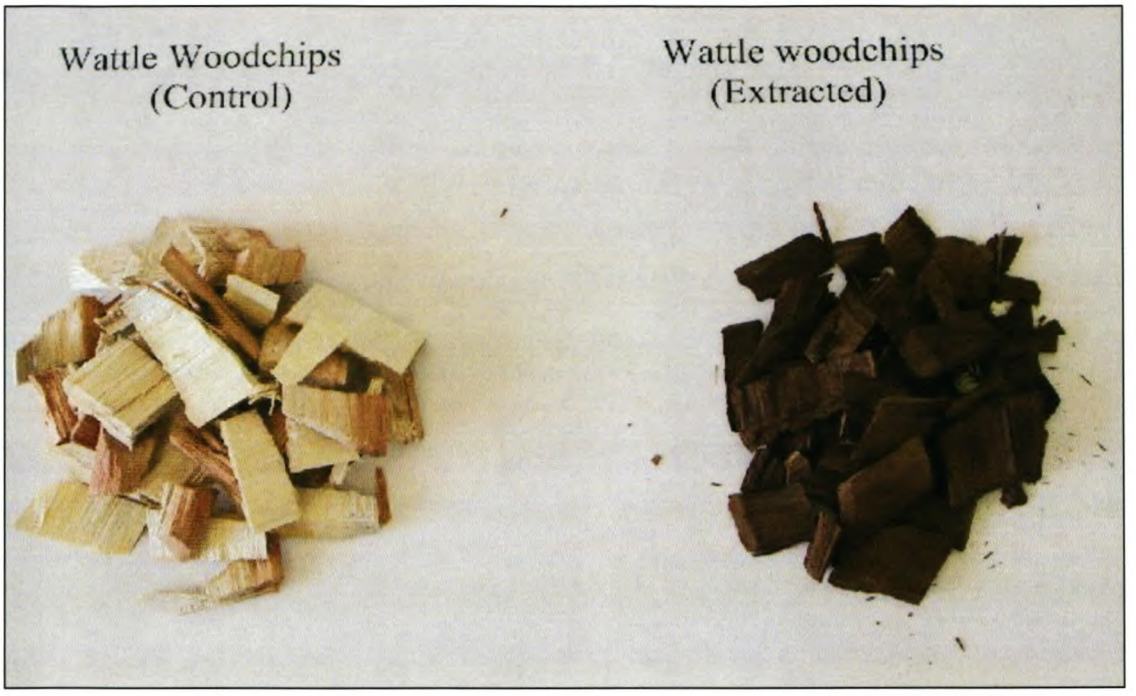

Figure 5.1 Control and extracted (2 hours) *Acacia mearnsii* wood chips

The effect of pressurised hot water extraction on the colour of the extract can be seen in **Figure 5.2.** The cold-water extract was lighter in colour. More and other extracts are removed during pressurised hot water treatment as reflected in its darker colour.

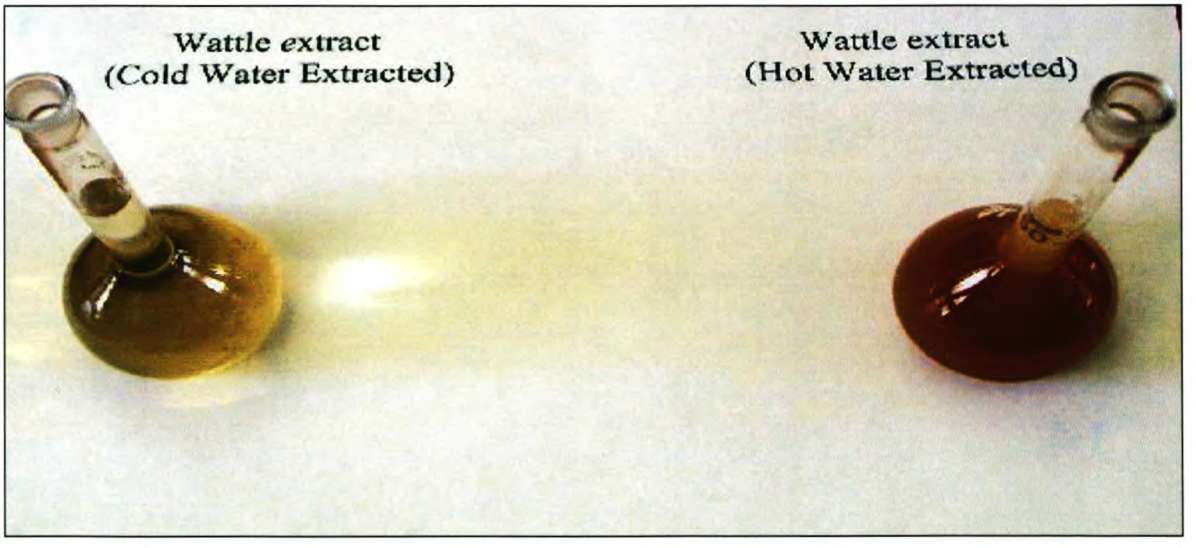

Figure 5.2: Cold and hot water extract (2 hours) of *Acacia mearnsii*

The hot water extracted wood chips produced brighter unbleached pulp as seen in **Figure 5.3**. The brighter colour is attributed to the pressurised hot water extraction and/or the higher degree of delignification.

Figure 5.3: Control and pressurised hot water extracted (2 hours) *Acacia mearnsii* pulp

Handsheets made from hot water extracted wood pulp compared to the control are shown in **Figure 5.4**. The handsheet made from hot water extracted wood pulp is brighter in colour and contains less shives than the control. This lower shive content was attributed to the better delignification of the extracted wood chips.

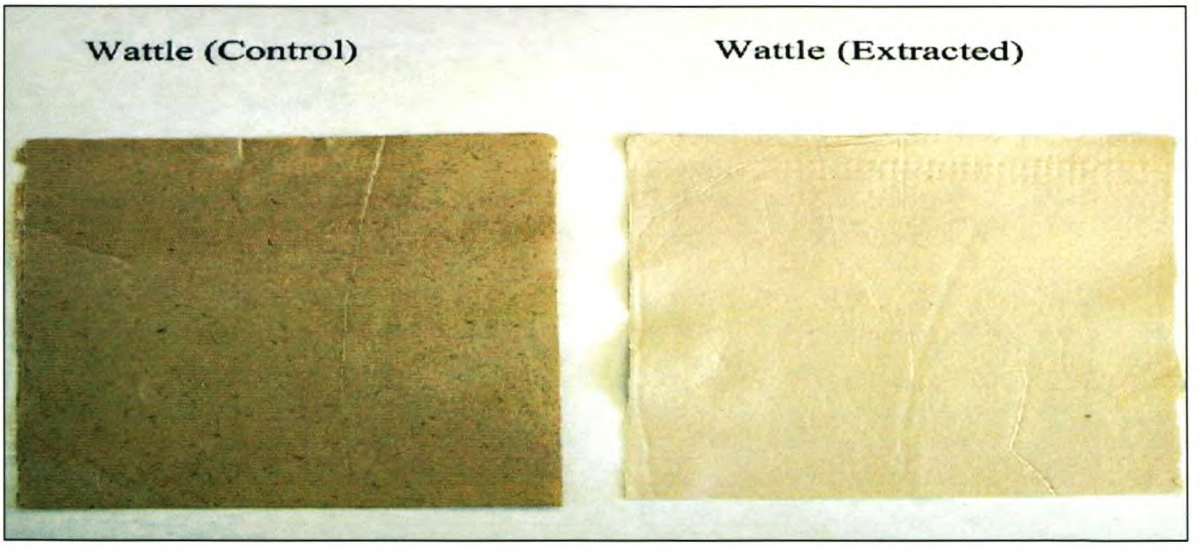

Figure 5.4: Handsheets made from control and hot water extracted (2 hours) *Acacia mearnsii* pulps

5.3. Physical structure of control and extracted wood

A disc of wood was extracted with the wood chips. 2cm cubes were then cut from this disc and a microtome section was cut. The different sections were then scanned using the electron scanning microscope. This was repeated for the control. Scanning electron microscope (SEM) micrographs of the control and an extracted wood chip are shown in **Figures 5.5** to **5.10**. It appears that the internal structure of the pressurised hot water extracted wood chips loosened up leading to a partial collapse of the cell structure. **Figures 5.6** illustrates the softening of the radial section of wood. Lumen and vessels cells, which are clearly seen in the control micrograph, are no longer visible in the hot water extracted wood chip micrograph. This can also be seen in **Figures 5.7** to **5.10** for the cross section and the tangential sections. The cross sectional pores (vessels) of the control can no longer be observed in the hot water extracted material.

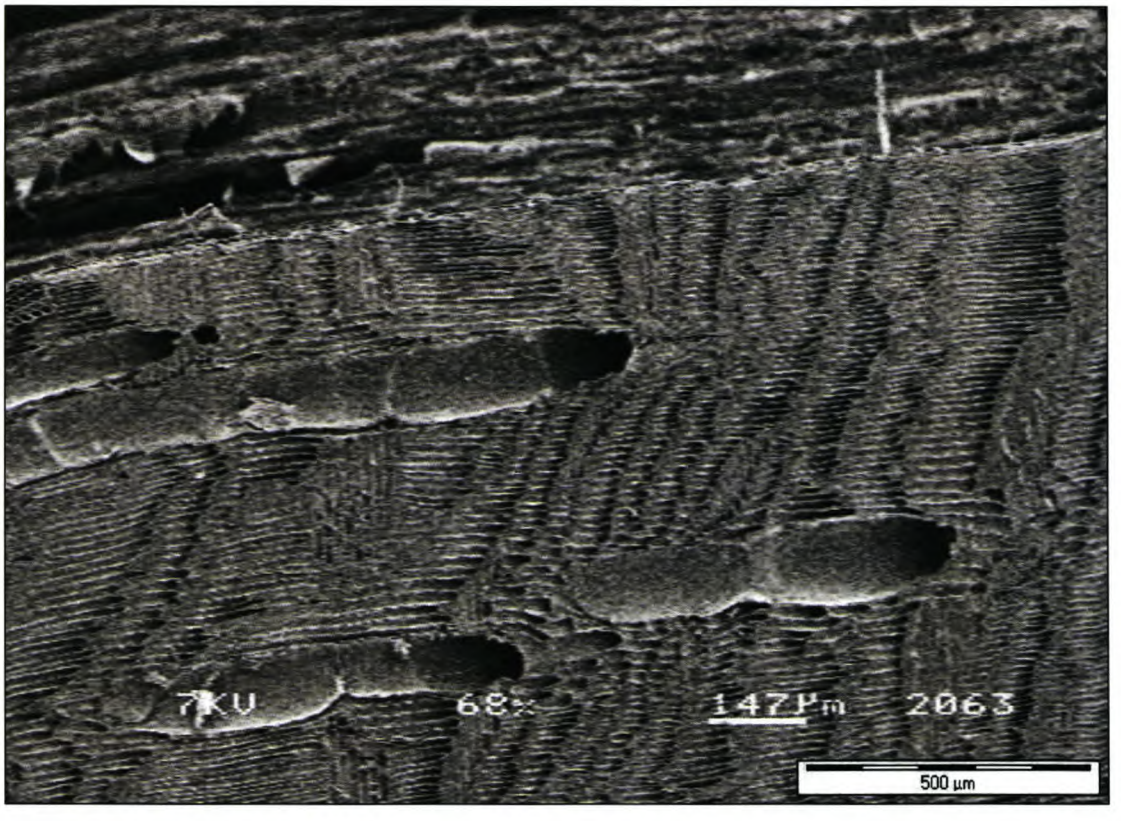

Figure 5.5: Scanning electron micrograph of *E. grandis* radial section (control)

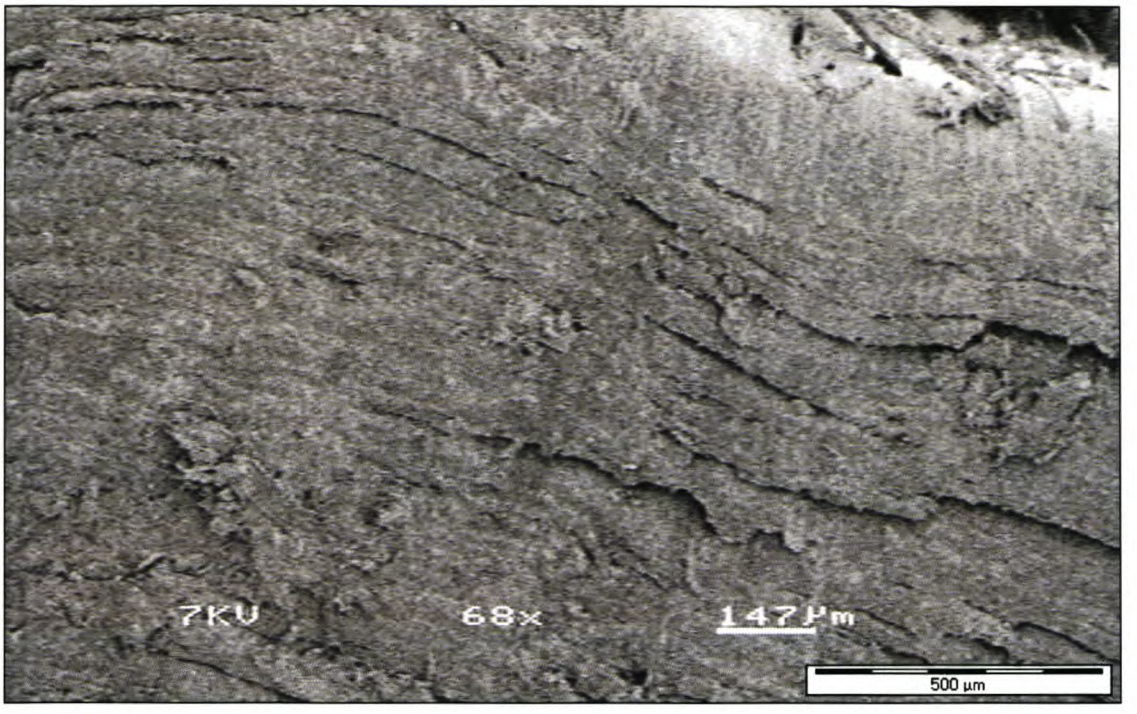

Figure 5.6: Scanning electron micrograph of *E. grandis* radial section (Hot water extracted)

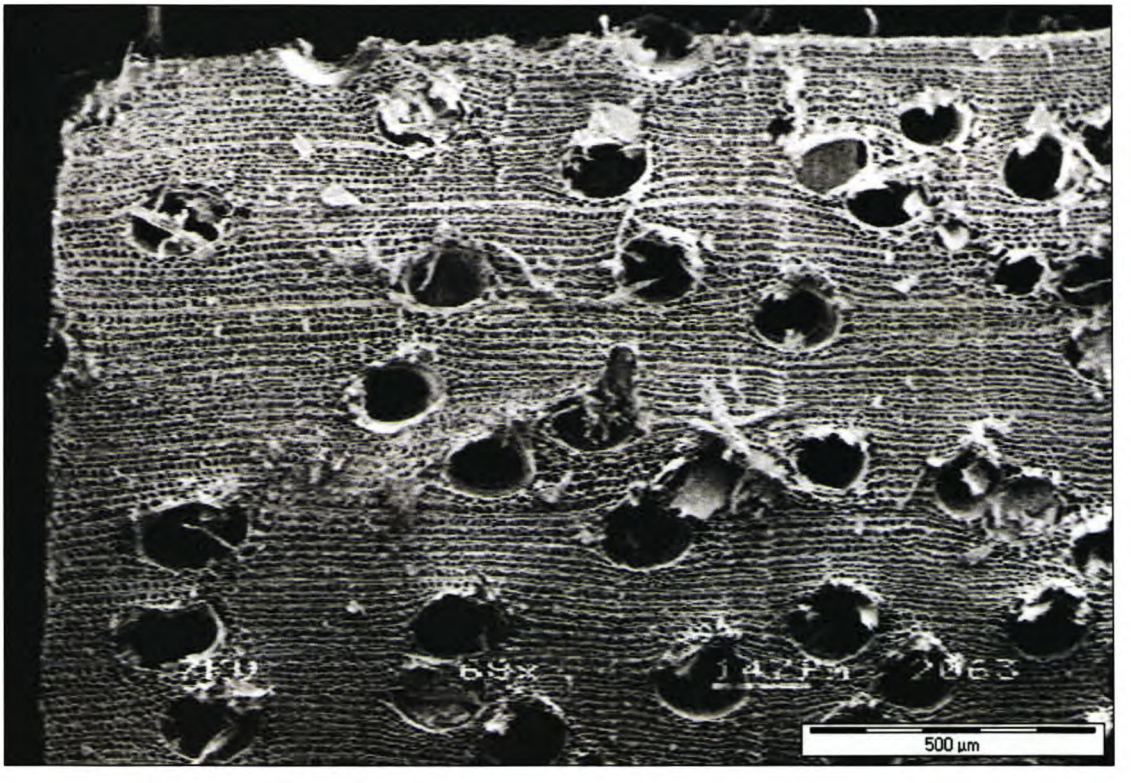

Figure 5.7: Scanning electron micrograph of *E. grandis* cross section (control)

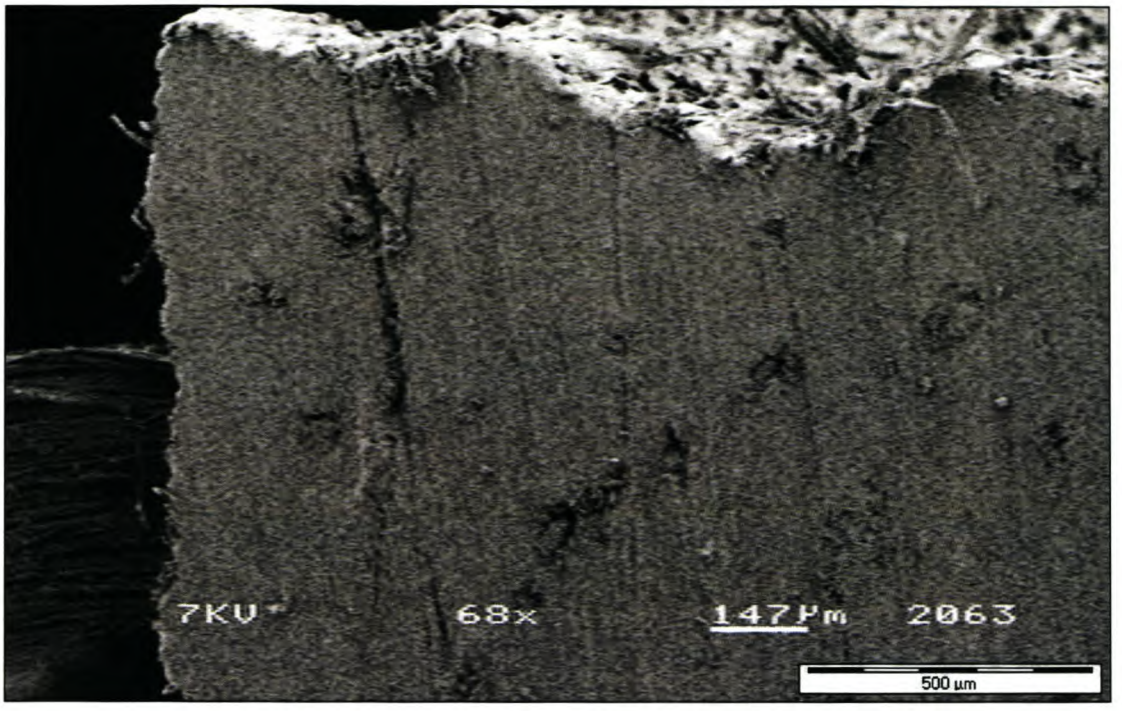

Figure 5.8: Scanning electron micrograph of *E. grandis* cross section (Hot water extracted)

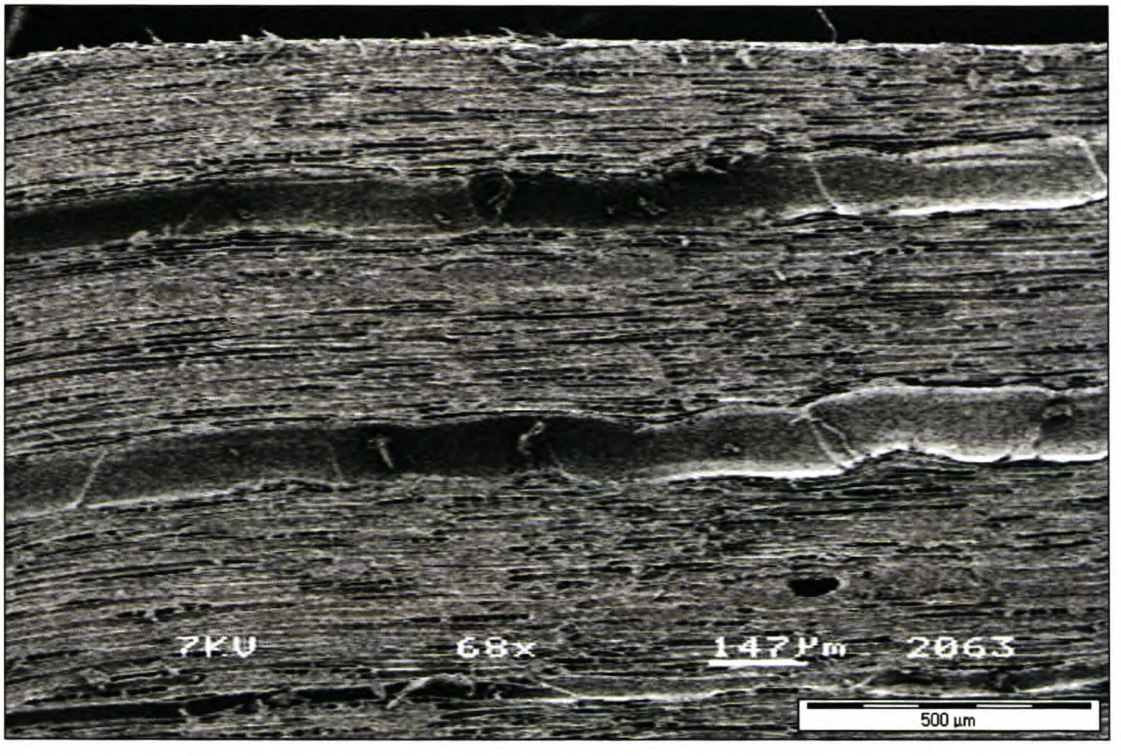

Figure 5.9: Scanning electron micrograph of *E. grandis* tangential section (control)

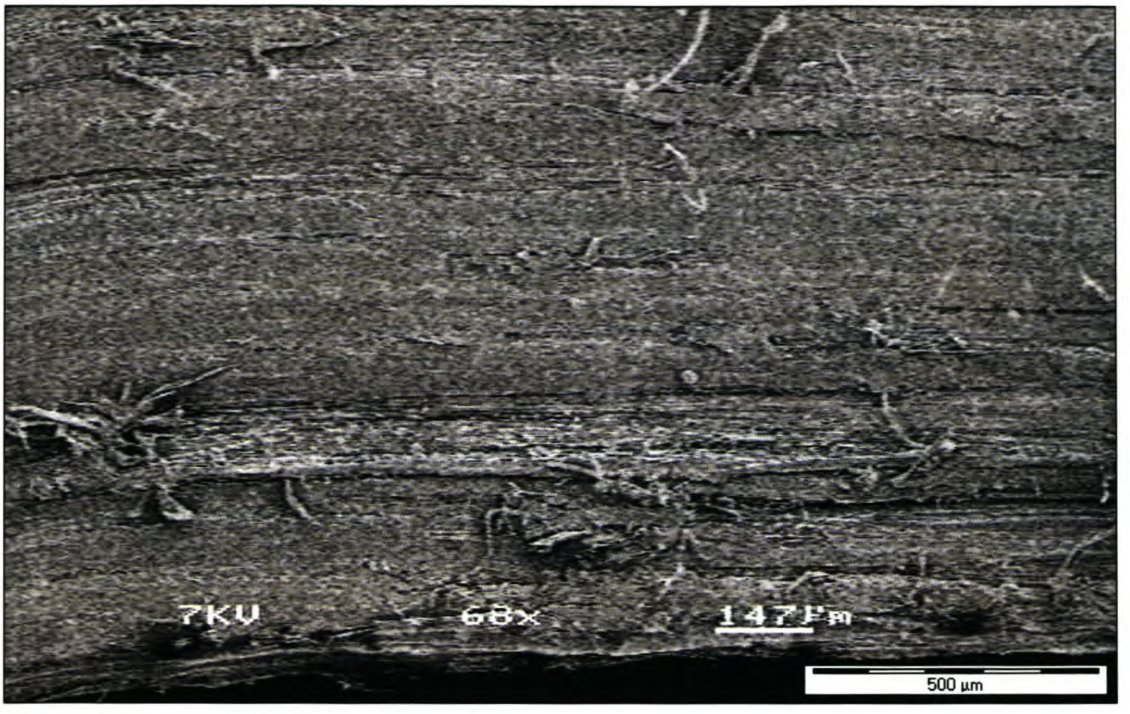

Figure 5.10: Scanning electron micrograph of *E. grandis* tangential section (extracted)

5.4. The effects of pressurised hot water extraction on fibre length

Figures 5.11 to **5.16** show the fibre lengths distribution, measured from pulp, of extracted and control wood. 2 hour extracted wood chips recorded shorter fibre length. This was attributed to cellulose degradation during the hot water treatment. From **Figure 5.11** it can be seen that the control *Pinus patula* fibre length ranged between 2.1 and 2.8 mm while the extracted *Pinus patula* fibre length varied between 2 to 2.5mm. Control *Eucalyptus grandis* fibre length ranged from 1 to 1.4 mm while extracted *Eucalyptus grandis* fibre ranged from 0.8 to 1.15 mm. *Acacia mearnsii* also revealed a drop in fibre length from a range 1.1 to 1.5 mm down to 0.9 to 1.3 mm for the extracted wood chips. These results indicate shortening of the fibre with hot water extraction, which could be attributed to hydrolytic reactions at the glycosidic bonds of carbohydrates[43].

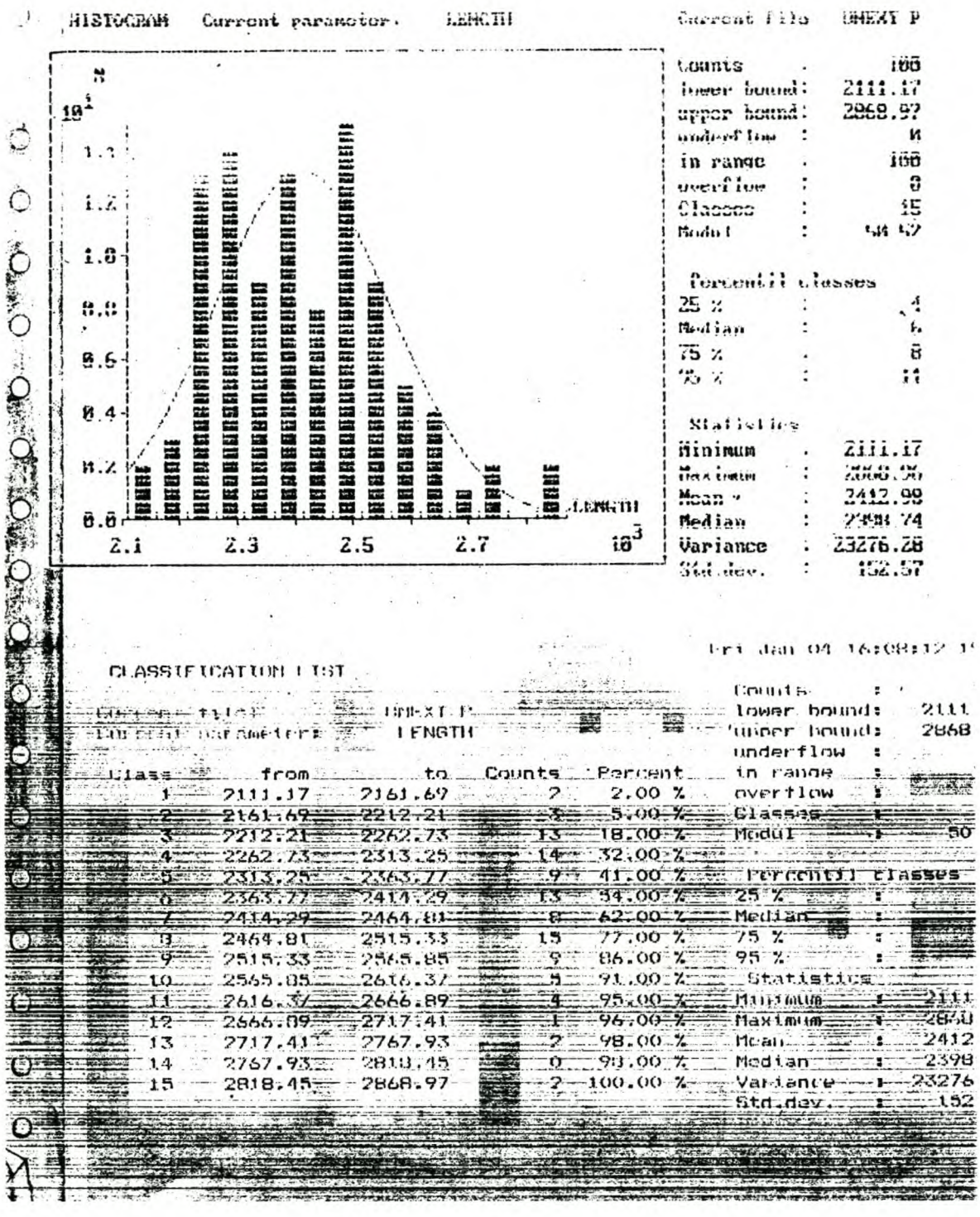

Figure 5.11: Distribution of *Pinus patula* fibre length (Control)

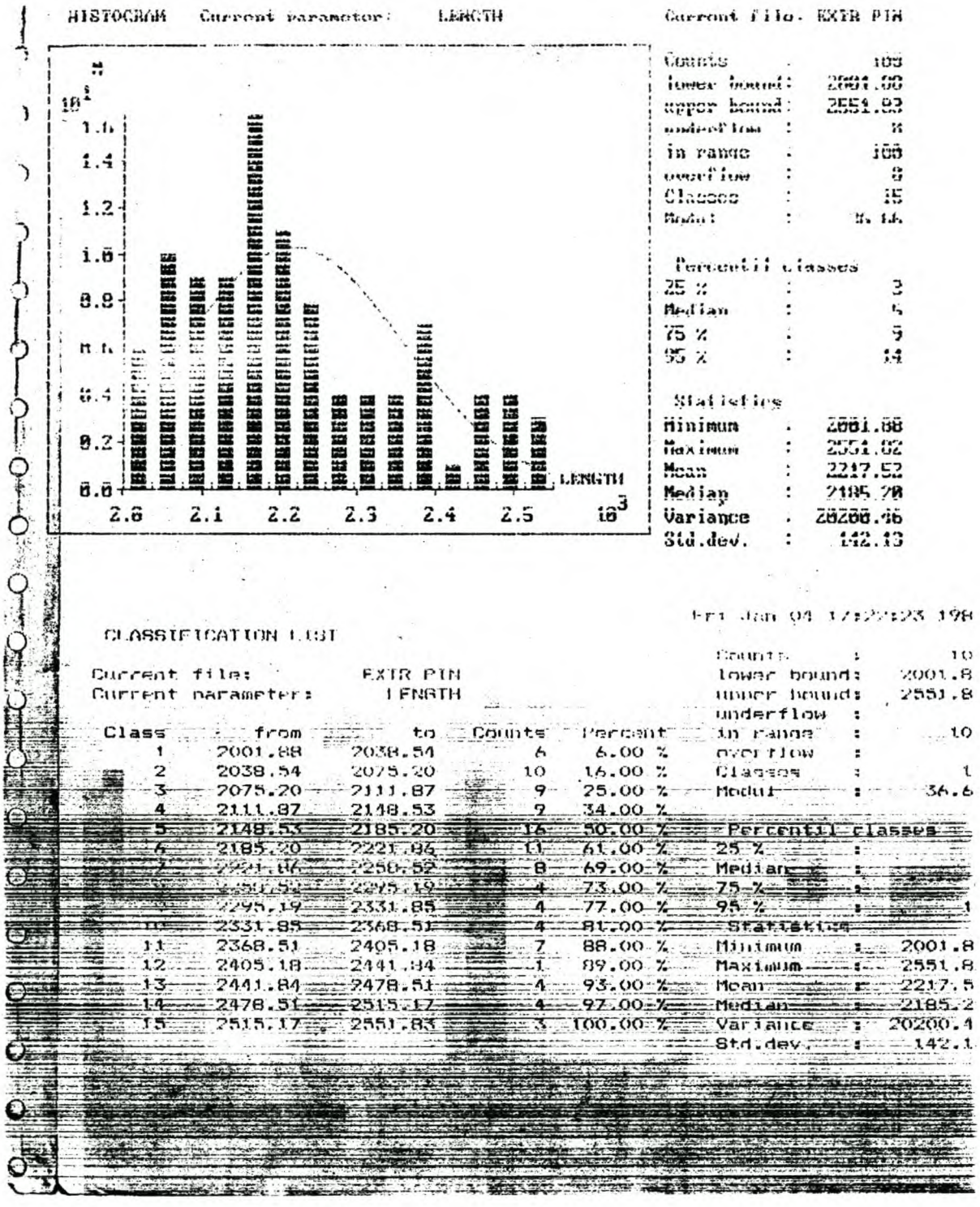

Figure 5.12: Distribution of *Pinus patula* fibre length (Extracted)

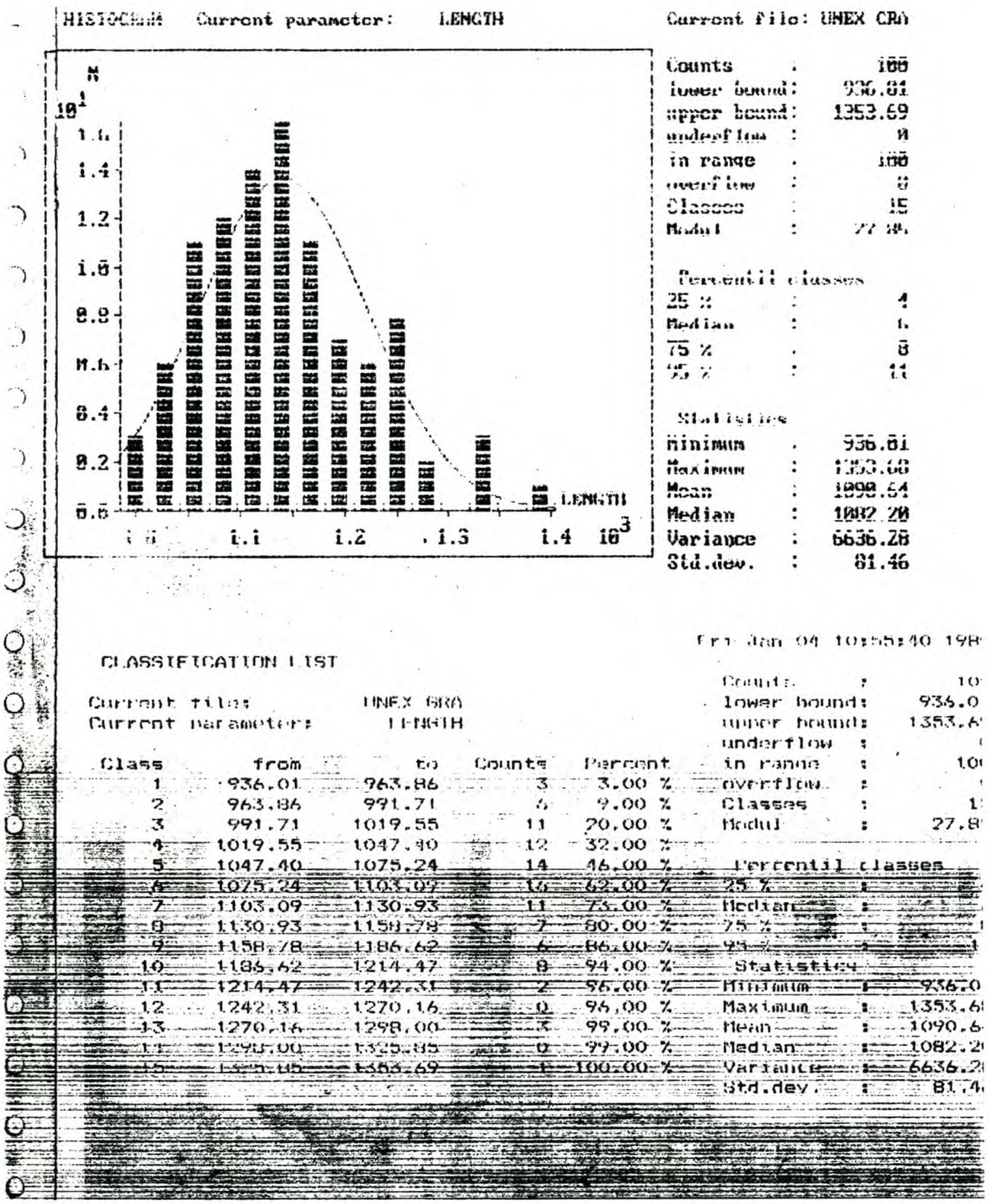

Figure 5.13: Distribution of *Eucalyptus grandis* fibre length (Control)

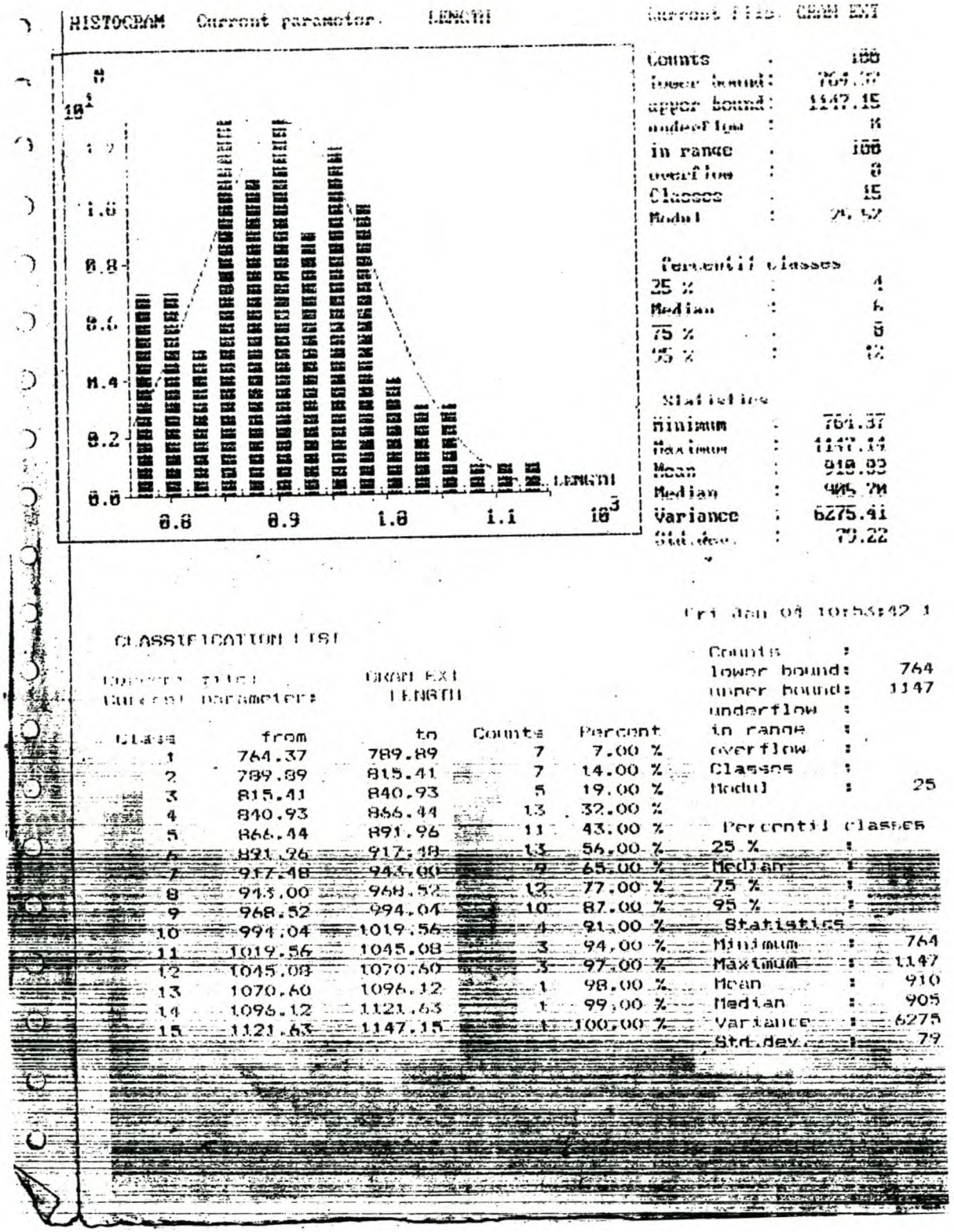

Figure 5.14: Distribution of *Eucalyptus grandis* fibre length (Extracted

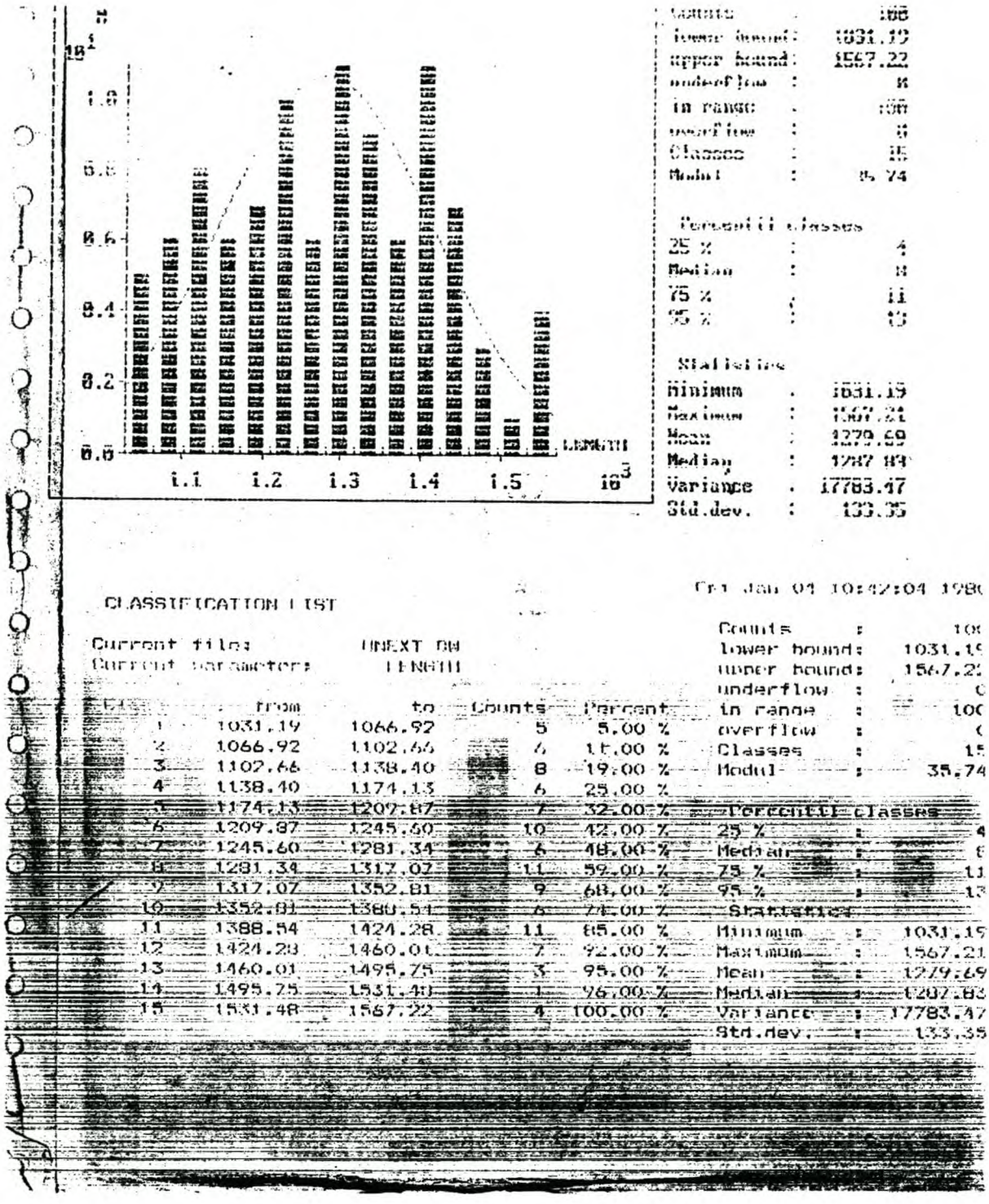

Figure 5.15: Distribution of *Acacia mearnsii* fibre length (Control)

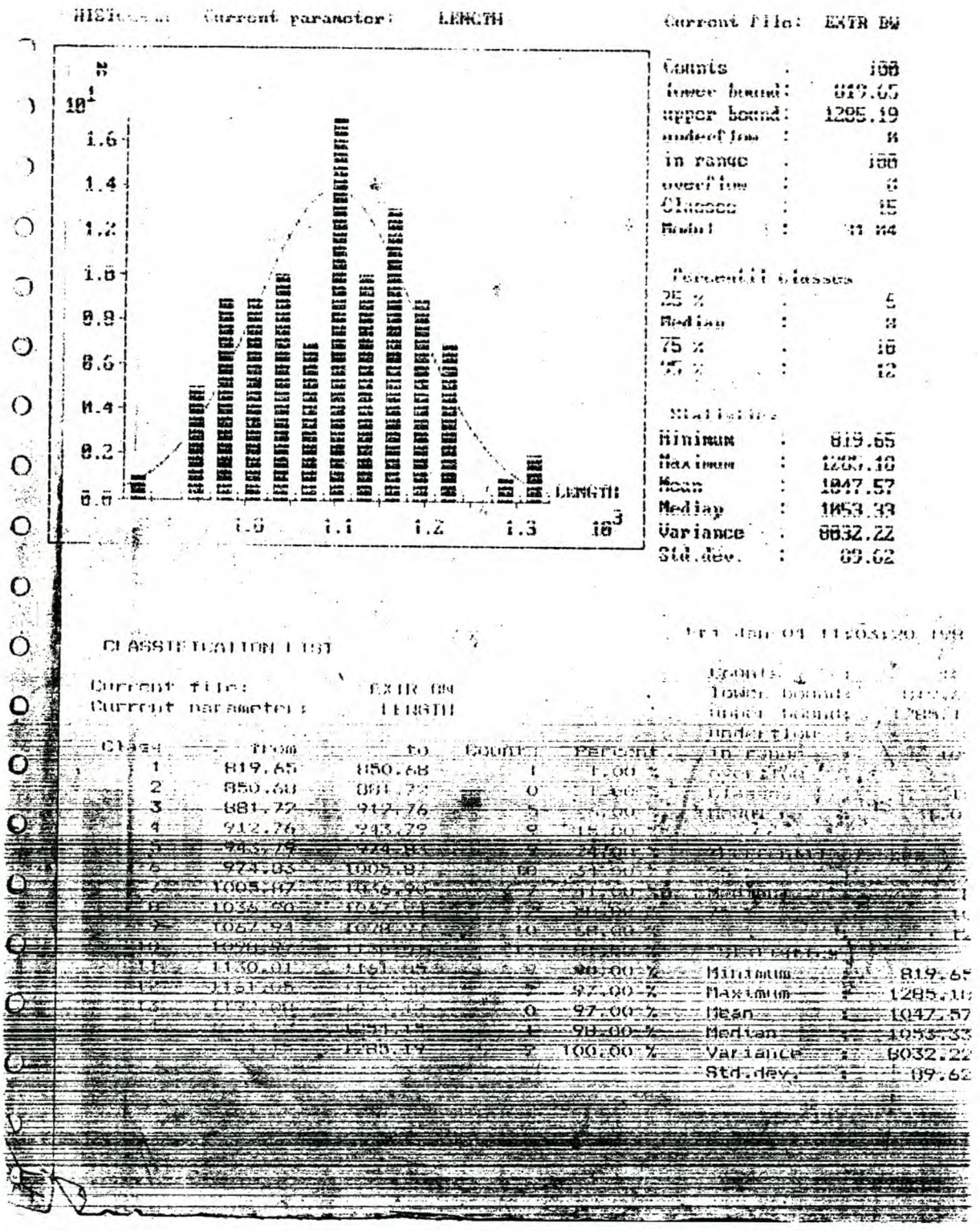

Figure 5.16: Distribution of *Acacia mearnsii* fibre length (Extracted)

Chapter 6: Conclusions

Pressurised hot water extraction of wood chips before alkaline pulping is very promising and has its merits. It removes extractive material that consumes cooking chemicals leading to pulping improvements. During extraction the wood structure is opened, which leads to enhanced diffusion of cooking liquor. This enhanced cooking liquor diffusion leads to better and uniform delignification but also degrades polysaccharides.

Two-hour extraction of wood chips resulted in a significant reduction in screened pulp yield for the three species tested. This reduction was attributed of the extreme conditions of this treatment. The conditions of this treatment resulted in polysaccharide degradation.

One-hour extraction also resulted in a decrease in the screened pulp yield of *Eucalyptus grandis* and *Pinus patula*. On the other hand, the one-hour extracted, extractive rich *Acacia mearnsii* had a higher screened pulp yield

.

Two-hour hot water treatment resulted in significant reductions in Kappa number for the three species tested. This was attributed to the better pulping conditions of the pressurised hot water extracted wood chips than the control chips.

The less extreme one-hour extraction, resulted in an improvement in *Acacia mearnsii* pulp properties but these properties were negatively affected by the two-hour extraction for all three species. This was attributed to the extreme conditions and polysaccharide degradation. The degradation of cellulose was reflected in the shorter fibre lengths of the extracted wood chip fibre compared to the control.

Hot water extraction prior alkaline pulping has been suggested as an alternative to the sulphite process for the production of high alpha cellulose content pulps. Although in general hot water treatment leads to a reduction in pulp yields it has been found to increase the alpha cellulose content[43]. The less extreme, one-hour extraction could be beneficial for the production of high quality alpha cellulose pulps.

One-hour extraction of extractive rich wood species prior to alkaline pulping is recommended and needs to be investigated at a pilot scale.

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