Chemical properties of thermally degraded *E. dunnii* and *E. macarthurii*

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AgriSciences at Stellenbosch University
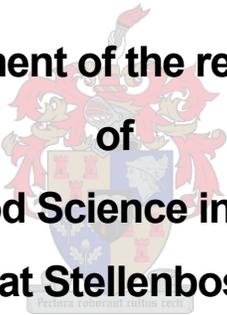
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April 2019

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Declaration

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Summary

Wild fires in South Africa lead to the destruction of an average of 14 000ha of forest plantation annually. In order to reduce the loss of resources the possible recovery of wood after a wildfires was investigated. For this study two eucalyptus species - *Eucalyptus dunnii* and *Eucalyptus macarthurii* were selected, as plantations of these species are located in high risk fire regions.

The main objective of this study was to determine, at which temperature wood degrades to such an extent that it is no longer suitable for the production of pulp and to find out if differences between different species exist. The aim was to determine whether wood that has been exposed to wildfires can still be used.

The change in chemical composition of *E. dunnii* and *E. macarthurii* wood was determined before and after exposure to temperatures ranging from 150°C to 220°C. The cellulose, lignin and extractive content, as well as the molecular weight of cellulose were determined as a function of temperature to determine the change in chemical composition that can be expected after exposure to elevated temperatures.

The acid insoluble lignin content decreased with increasing temperature, while the acid soluble lignin content increased. As a result, the total lignin content was only reduced by 2%, but the composition of the lignin has clearly changed. The ethanol extractive and water extractive content decreased with increasing temperature for both species.

The cellulose content of *E. dunnii* showed a de facto increase due to the decrease of extractive and lignin content. The cellulose content of *E. macarthurii* remained relatively unchanged. The molecular weight of both species decreased after exposure to 150°C and reached a low of 160 000 after exposure to 160°C. However, after exposure to a temperature of 170°C the molecular weight began to increase, which was caused by the disintegration of low molecular weight amorphous cellulose.

In order to utilise wood from fire damaged trees the wood exposed to a temperature of 160°C and higher must be removed to ensure the wood is suitable for pulp production.

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Opsomming

Gevolg van wilde brande word jaarliks 'n gemiddelde van 14000 ha bosplantasie verloor. 'N ondersoek na die moontlike herstel van hout uit brandbeskadigde bome is nodig. Vir hierdie studie is twee eucalyptus spesies - *Eucalyptus dunnii* en *E. macarthurii* is gekies as plantasies van hierdie spesies in hoërisiko-brandstreke.

Die hoofdoel van hierdie studie was om te bepaal, by watter temperatuur hout sodanig degradeer dat dit nie meer geskik is vir die produksie van pulp nie en om uit te vind of daar verskille tussen die verskillende spesies bestaan. Die doel was om te bepaal of hout wat aan veldbrande blootgestel is, nog steeds gebruik kan word.

Die verandering in chemiese samestelling van *E. dunnii* en *E. macarthurii* hout is bepaal voor en na blootstelling aan temperature tussen 150°C tot 220°C. Die sellulose, lignien en ekstrakstofinhoud, sowel as die molekulêre gewig van sellulose, is bepaal as 'n funksie van temperatuur. Dit is gedoen om die verandering in chemiese samestelling te bepaal wat na verwagting na verhoogde temperature verwag kan word.

Die suur-onoplosbare lignieninhoud het met toenemende temperatuur afgeneem, terwyl die suuroplosbare lignieninhoud toegeneem het. As gevolg daarvan is die totale lignieninhoud slegs met 2% verminder, maar die samestelling en lignien het duidelik verander.

Die etanol ekstraksie en water ekstraktiewe inhoud verminder met toenemende temperatuur vir beide spesies.

Sellulose-inhoud van *E. dun*nii het 'n effektiewe verhoging getoon weens die afname in ekstraksie en lignieninhoud. Die sellulose-inhoud van *E. macarthurii* het relatief onveranderd gebly. Die molekulêre gewig van albei spesies het verminder na blootstelling aan 150°C en bereik 'n laagtepunt van 160 000 na blootstelling aan 160°C. Na die blootstelling aan 170°C het die molekulêre gewig egter begin toeneem, wat veroorsaak is deur die disintegrasie van amorfe sellulose met lae molekulêre gewig.

Om hout uit brandbeskadigde bome te gebruik, moet die hout wat blootgestel is aan temperature van 160°C en hoër, verwyder word om te verseker dat die hout geskik is vir pulpproduksie. Vir 'n hoë intensiteitsbrand beteken dit 1 cm hout onder die bas vir *E. macarthurii* en 2 cm vir *E.dunnii* verwyder moet word.

This thesis is dedicated to my family. To my mother and father, for the love and guidance they have given. To my brother for his example of dreaming big and finding my own way in life. Without any doubt I would not have been able to complete this this thesis without there persistent support.

Acknowledgements

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1   Introduction

South African forests are frequently exposed to wild fires caused by lightning, arson, controlled burning of debris, or accidental fires. As a result of these wild fires, an average of 14 000ha of forest plantations is lost annually (Odhiambo et al. 2014). The risk and severity of wildfires is increased by the fact that South Africa has two fire seasons: the dry summer months in the Western Cape and the dry winter months in the rest of the country. Under the wrong circumstances where temperature, humidity and wind conditions are favourable for fire to spread, the result can be catastrophic. In 2007/8 fires raged in Mpumalanga for days, resulting in an estimated loss of 84 000 ha of forest plantation and the most recent fire around Knysna in December 2017 damaged more than 10 000 ha of forest, land and property. The fire damaged area compared to the country's total forest plantation area amounts to around 1%.

Figure 1-1: Jonkershoek plantation after a fire in 2016

The damage resulting to the trees exposed to a wildfire can vary in severity: ranging from only the lower part of the stem being charred, to the entire canopy can be burnt. Figure 1-1 shows an example of trees in the Jonkershoek plantation that were damaged by fire in 2015.

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The extent of fire damage to a tree, or the plantation is difficult to quantify, as the fire temperature, flame height and fire duration can vary significantly between individual trees. The temperature of a typical forest fire can range from 400°C to 1100°C, depending on fuel load, moisture and movement speed with temperatures around 800°C being most commonly reported for forest fires (Dickenson and Johnson 2001). Although the fire temperature can be very high, the inner core of the stem is typically exposed to lower temperatures, due to the low thermal conductivity of wood. This means that the wood beneath the charred layer, might still be clear wood that can be further processed. The cross section of a fire damaged tree can be seen in

Figure 1-2. The bark has been charred, but the wood beneath the bark is not visibly damaged.

Figure 1-2: cross section of a tree stem after fire damage

In South Africa the main wood processing industries are the saw timber, pulp and paper and composite board industries. The largest of these is the pulp & paper industry, which produces R28 billion worth of products each year. The raw material for this industry is mostly provided by around 700 000 ha of South Africa's plantation, of which 450 000 ha are planted with Eucalyptus species (SFSA 2017). Currently fire damaged trees are not commonly harvested for pulp production as the exact properties of the wood after a fire are not known. The properties may adversely affect the pulping process. The total value of wood may not be recoverable from the damaged plantation, but if a usable portion of the wood can still be recovered then the annual loss can be reduced.

Objectives of the study

The inner wood from trees exposed to a forest fire may remain undamaged by the fire, even if the tree died from the damage to the foliage or the cambium cells. Wood harvested from such trees would not be much different from that of wood harvested under normal circumstances, as most of the wood in a living tree is already dead. Problems arise, however, if the heat of the fire was high enough to cause thermal degradation of the wood. The damage caused by fire cannot always be determined by visual inspection, as the internal wood structure may have changed on a molecular level that is not visible. Therefore, it is necessary to determine the extent of thermal degradation through chemical analysis. The chemical composition of wood is very complex and

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exact analysis is expensive and time consuming and it is not feasible to do this repeatedly after each fire for individual trees. It would therefore be of interest to determine the thermal degradation patterns of the individual wood components for different species and create a database, on which the wood processing industry can base a decision, how and if the wood is to be used further.

The objective of this study was to determine, how the chemical properties of *E. dunnii* and *E. macarthurii* wood change due to the exposure to elevated temperatures. The effect of thermal degradation on *E. dunnii* and *E. macarthurii* was determined and the chemical properties, such as alpha cellulose, lignin and extractive content, as well as degree of polymerisation were determined as a function of exposure temperature.

This project is part of a bigger project aiming to determine the potential of using wood from fire damaged trees, with specific interest in the pulp and paper industry.

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2 Background

2.1   The chemical and physical characteristics of wood

The chemical properties of wood vary between species and within species, depending on the growth conditions. Nevertheless, all trees share the same major chemical components, namely cellulose, hemicelluloses, lignin and extractives, which appear in a set range of ratios in all wood.

Cellulose is present in the cell walls in two distinct forms: firstly, in amorphous form, consisting of disorganized cellulose, without distinct orientation and secondly as crystalline cellulose, consisting of cellulose chains that are arranged through hydrogen bonds into supramolecular structures known as crystallites. The surface of these crystallites consists of amorphous cellulose. The ratio of the crystalline to amorphous cellulose is known as the crystallinity index and increases with increasing crystallite size. This increase occurs due the volume of crystalline cellulose increasing faster than the surface area (Kim 2010). The cellulose fibres become more rigid with increasing crystallinity (Gümüskaya et al. 2003)

The chemical properties of crystalline cellulose are different to those of the amorphous cellulose. The first difference is that the amorphous cellulose, like all amorphous polymers, has a transition glass temperature. When the amorphous cellulose is heated above this temperature it becomes more flexible and there can be a change in thermal conductivity.

The glass transition temperature of cellulose is dependent on both the crystallinity index (CI) of the cellulose and the moisture content of the cellulose. The moisture content is defined as the amount of moisture in the wood as a percentage of the wood dry weight. In Figure 2-1 (Szczes´niak et al. 2007) the glass transition temperature can be seen to decrease with increasing moisture content (MC). The glass transition temperature is higher for cellulose with a lower CI. The physical characteristics of the amorphous cellulose change around this temperature and cellulose below the glass transition temperature is more rigid and brittle.

The CI of cellulose in wood is typically above 50% and the MC of sapwood is above 28% for most species and can be as higher than 50% for some species (Tsoumis 2009).

For these reasons it can be deduced that the glass transition state of cellulose is below 0°C for cellulose in the sapwood of the tree and therefore the amorphous cellulose should not experience a change in thermal properties due to the glass transition state during a fire.
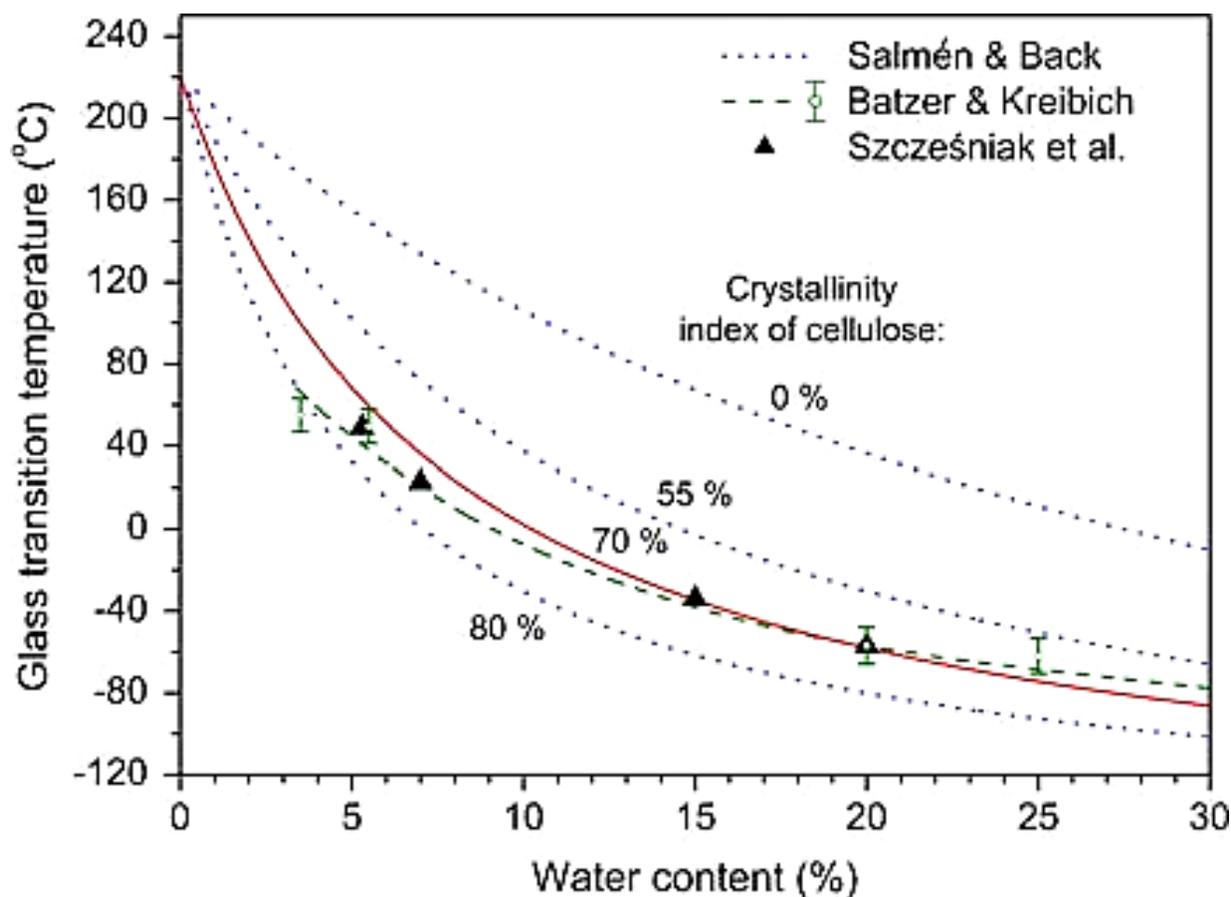
Figure 2-1: The predicted glass transition temperature of cellulose using models by Salme´n and Back (1977) and Baltzer and Kreibich (1981) as a function of time at different crystallinity indices. With experimental data from the study by Szczes´niak et al. (2007).

Crystalline cellulose does not exhibit glass transition, but like most crystals, has a melting point. In 2006 Deguchi et al. showed that crystalline cellulose melts into amorphous cellulose at 320°C. The cellulose did not recrystallize after the temperature decreased again, due to the fact that the cellulose has been degraded. Thermal decomposition of crystalline cellulose occurs at temperatures between 250-350°C.

There is much debate as to the exact orientation of the cellulose molecules in this crystalline structure, but what can be stated with considerable certainty is that the cellulose molecules are orientated either parallel or anti-parallel (Fengel 1989). The supramolecular structures form microfibrils with a width of about 4 nm, which aggregate into fibrils with an average diameter of 16 nm (Fahlén 2005). The cellulose fibrils form the cell walls of the wood cells. Cellulose molecules are uniform chains of cellobiose units, as displayed in Figure 2-2.

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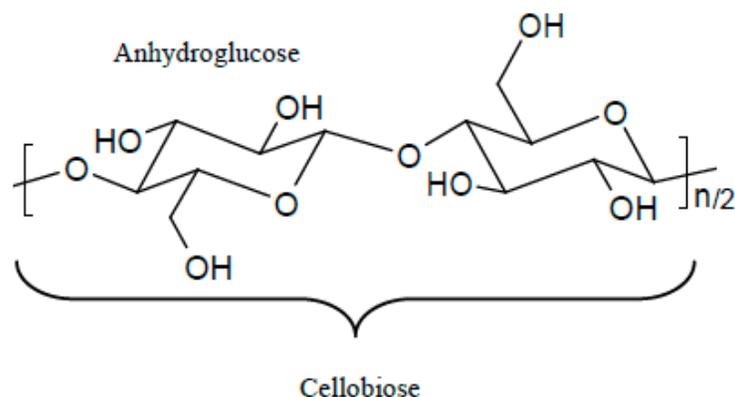
Figure 2-2: consisting of two anhydroglucose units, each of which has a molecular weight of 162.1406 g/mol.

Cellulose molecules do not consist of a fixed number of anhydroclucose units and as a result the molecular weight (MW) of cellulose varies from species to species and within the tree from pith to bark. The MW of a cellulose sample is typically calculated as an average MW of all cellulose molecules within the sample.

Cellulose are not the only polysaccharides in wood. The hemicelluloses are polysaccharides that differ from that of cellulose by various sugar units, lower molecular weight and branching of the molecular chain. The hemicellulose molecules can consist of only one type of sugar or of two or more sugar types. The hemicelluloses can be subdivided into groups by their molecular structure. The resulting subdivisions are the pentoses, hexoses, hexuronic acids and deoxy – hexoses. Unlike the cellulose the hemicelluloses are unwanted in the pulp as they discolour the paper.

The structure of lignin is the most complex of all the wood compounds. The size of lignin molecules varies within the wood itself, ranging in size from monomers and dimers to molecules with a MW of over 16000 (Gralen, 1946). The complexity of lignin molecules is due to the fact that lignin comprises of three distinct monomers namely p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, as shown in Figure 2-3. P-coumaryl alcohol is a minor precursor of both hardwood and softwood lignin, while the dominant precursor of softwood lignin is coniferyl alcohol. Hardwoods have both coniferyl and sinapyl alcohol as a precursor. In addition to the three monomers, lignin differs from the cellulose polymer, because lignin monomers can combine to form more than 90 distinct combinations (Fengel and Wegner 1989).

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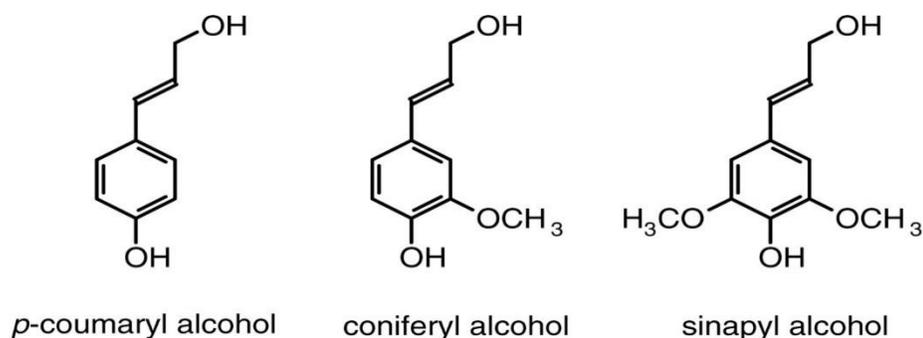
Figure 2-3: The three monolignols of hardwood and softwood lignin

Unlike cellulose and lignin; extractives do not contribute to the structural integrity of the wood and they are present within the cell lumens of the wood. Extractives consist of a variety of compounds including fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin and waxes (Fengel and Wegner 1989). Due to the variation in composition of these compounds for most analytical purposes the extractive content is defined as the number of compounds that are soluble in polar and non-polar solvents.

Cellulose, hemicelluloses and lignin make up the different layers of the cell wall of the wood fibres. The chemical components vary within the layers of the cell walls, as can be seen in Figure 2-4 of a scots pine cell with annotations of the chemical composition of each layer. The cells consist of five layers: the middle lamella, the primary wall and the three secondary walls. The middle lamella and primary cell wall contribute to just over 10% of the wood weight, of which 80% are lignin. The S2 and S3 layers contribute more than 60% to the wood's dry mass and consist of about 50% cellulose, 35% hemicelluloses, and 15% lignin. The S1 layer contributes to just over 20% to the woods dry weight with about 50% lignin. The variation of components within the cell wall layers result in different properties between the layers.

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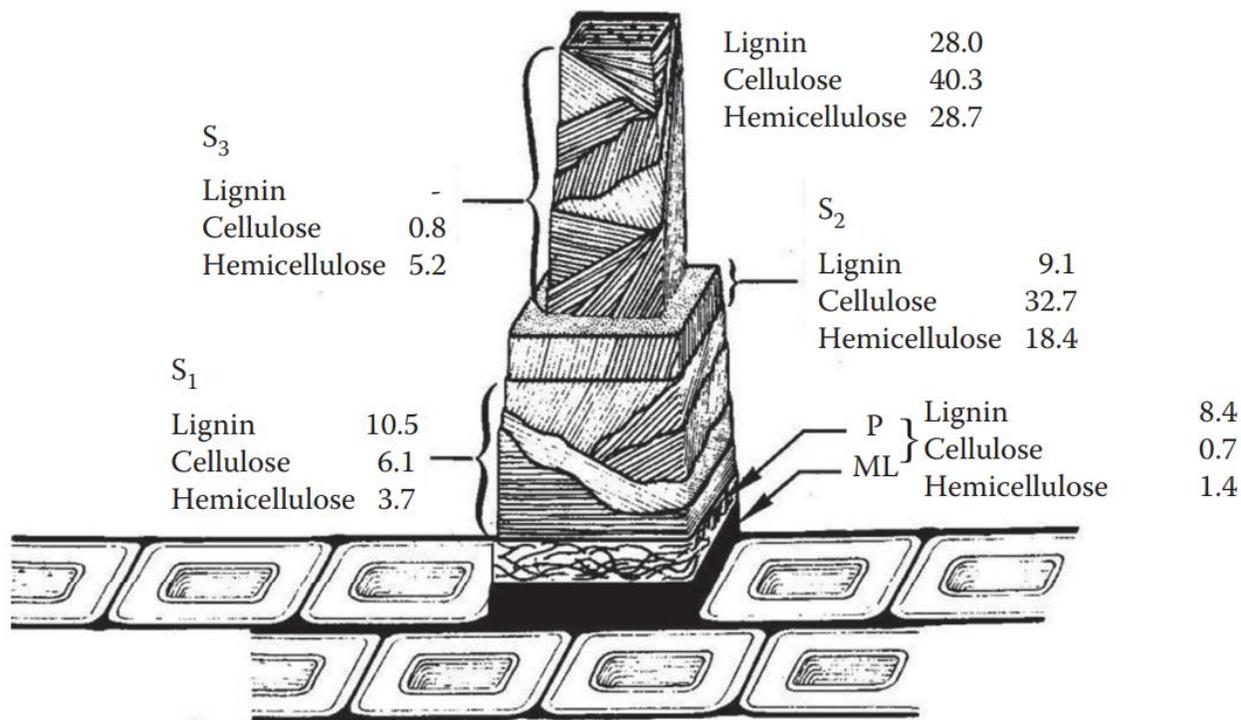
Figure 2-4: Chemical composition of the cell wall of scots pine (Rowell 2005)

Figure 2-4 lists the average percentage of lignin, cellulose and hemicellulose in the different cell wall components, but these values vary between species and between hardwoods and softwoods. Cellulose is the component in wood with the highest concentration, for hardwoods it is generally 38 - 49% of the dry weight. The lignin content for hardwoods ranges from 23% to 30%. The hemicelluloses content is 25 - 35% for hardwoods. The extractive content is only a small fraction of the woods total mass at 0.3 - 11% for hardwoods. Softwoods generally have higher cellulose content between 40 - 45% of the dry weight. The lignin content is only slightly higher than that of hardwoods at 26 - 34%. The hemicelluloses are similar to that of hardwoods at 25-29% and an extractive content of 0.2 – 14.4% (Fengel and Wegner 1989, Rowell 2005, Thomas 1977).

2.2   Structure of the tree stem

There are three parts of a cross section of a tree that can be visually distinguished. These parts are the bark, the wood and the pith (Figure 2-5). The cambium lies between the bark and the wood but can only be seen under a microscope. These layers have different structural

properties within the tree stem. The bark protects the wood from physical attack, such as insects and bacteria, but also fire. The wood is divided into two sections the sapwood consisting of living tissue, primarily responsible for the transport of nutrients and for the mechanical properties of the stem. The heartwood forms the inner portion of the tree stem, consisting of dead cells, which contribute to the mechanical strength of the stem. The heartwood has a higher extractive content than the sapwood, which have antifungal properties and protect the tree stem from degradation from the inside of the tree.

Figure 2-5: Cross section of a tree

The colour of the heartwood is darker, depending on the amount of extractives and the wood species (Dadswell 1972), but it can be difficult to visually distinguish between the sapwood and heartwood. The sapwood has higher moisture content, as it is responsible for the transport of nutrients within the stem. The woody tissue of hardwoods consists primarily of thin and narrow fibres, which largely contributes to the structural properties of the wood. Bigger and shorter vessel elements are responsible for water transport within the stem. The growth of a tree throughout a year results in growth rings and in eucalyptus they are marked by a variation in vessel diameter and prevalence (Tsoumis 2009). Early wood has larger and more vessels than latewood, where they can be absent altogether.

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2.3   Forest fires

Forest fires can be classified into three types. **Ground fires** burn organic material under the surface litter or surface soil and relatively low temperatures and low speed. They can burn unnoticed until combination of dry wind, high air temperatures and low relative humidity cause the fire to surface. **Surface fires** are where the surface material of the ground is burnt depending on the fuel load the intensity of a surface fire can have a low to high intensity. A low intensity fire having temperature below 180°C and the high intensity fires having a temperature of 1000°C Wotton et al. (2012). Surface fires usually burn at a height up to 50 cm. Most fires start out as surface fires and develop into ground fires or **crown fires**, in which the tree branches and leaves have been ignited. The temperature of crown fires can be very intense as the heat of both a surface fire and the crown fire contribute the overall temperature. As a result, crown fires can burn at temperatures as high as 1000°C. The rate of spread of a crown fire depends on the height of the forest crown (Goldammer and Cornelis 2004).

A study by Wotton et al. (2012) investigated the flame structure of a wildfire. Flame structure was characterized as the height from base to tip of the visible flame and temperature variation from base to tip. The effect of different fuel loads and age of the fuel were analysed. The fuel loads were varied by using 2 sites - one dominated with 2 m high shrubs and the other dominated by shrubs no higher than 0.5m. In addition to fuel height the time since the last burn varied from 5 to 20 years.

The flame structure was found to vary widely and rapidly. The flame tip had an average temperature of 300°C irrelevant of the flames height or the fuel present. This is supported by previous studies in laboratory setting (Marcelli 2004). The temperature of the flame increases towards the base, where the maximum temperature is around 1100°C.

The temperature of an experimental wildfire in eucalyptus forest can be seen in Figure 2-6. The fuel at this site was dominated by 2m tall trees and no fire had occurred in over 16 years. The combustion of this plot can be divided into three distinct phases. The first follows ignition and is characterized by tall flames which can last for 27 s. Temperatures can exceed 1000°C during this phase. After this period the head of the fire moves forward. Burning of residual fuels leaves shorter flames that can persist from 37 to 74 s. The duration of this phase is correlated to the fuel load. The final phase is characterized by the smouldering of residual fuels. This phase duration depends on the available fuel load.
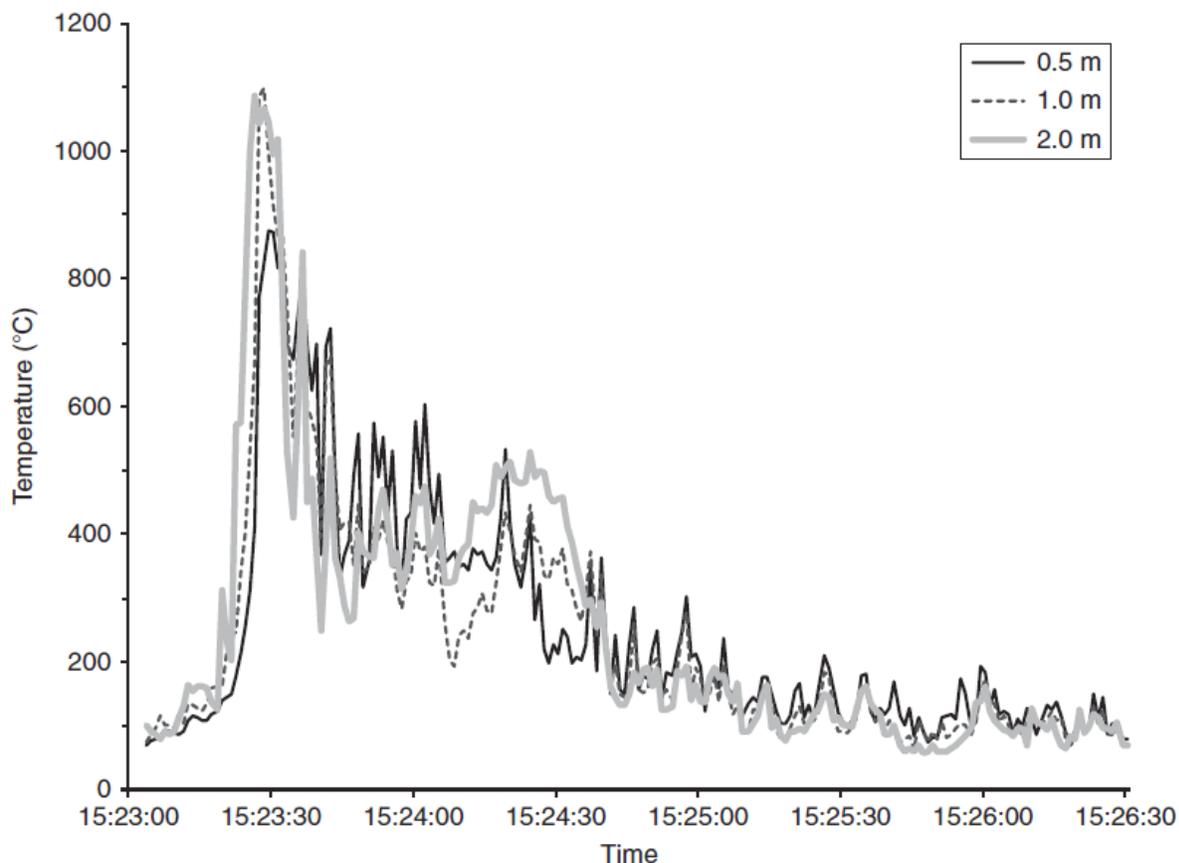
Figure 2-6: A typical temperature trace of a flame at 0.5, 1 and 2m from the ground. From an experimental fire in 16-year-old eucalyptus (Wotton et al. 2012).

Wotton et al. (2012) defined residence time of a fire as the duration that the temperature exceeded 300°C at a position 0.5 m above ground. The average residence time for a dry eucalyptus forest was 37 s. This time did not vary significantly with fuel moisture content, fuel quantity or density.

The duration of the fire may not vary significantly, but fuel load affects the intensity of the fire. In 1993 Miranda et al. studied the air temperature during a wildfire at 1cm, 60cm and 160cm above ground. The tests were carried out at plots that had been exposed to annual controlled burns and on plots where the vegetation had been protected from fire for 15 years. When areas with annual fires were burnt, temperatures as low as 300°C were recorded at 60cm above ground. At another plot with a history of annual fire the tests were done 2 days after rainfall and as a result the temperature only reached 180°C at 60cm above ground. This difference in temperature can be attributed to the increased moisture content of the fuel. On plots where annual fires occur the temperature was never more than 200°C above 160cm, independent of

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rainfall. However, when sites that had not burnt in over 15 years were burnt the temperatures reached 500°C at 60cm above ground.

Various models have been designed in an attempt to predict the spread and intensity of wild fires. A model by Byram (1959) determines fire intensity as measure of energy released per unit area depending on fuel load and moisture content. From the fire intensity it is possible to predict the rise in temperature at a specific height due to wildfire. For equation (1), h is the height above ground and (I) is the fire intensity of the fire in kW/m.

$$T = 3.9(I)^{2/3} \div h \qquad\qquad\qquad (1)$$

2.4 Thermal degradation of wood components

The chemical components of wood degrade at different temperature ranges. The extractives are the least stable of the wood components and begin to evaporate at temperatures between 100°C and 140°C. The thermal degradation of extractives is the least studied of all the major wood components wood, because of the wide variation in composition between species. Because of this wide variation the extractives degrade over a wide temperature range, but the majority of the extractives are volatile and begin to evaporate just above 100°C (Tsoumis 2009).

As the temperature increases the more stable components begin to degrade. At temperatures above 180°C the loss of polysaccharides can become significant. The degradation of the any of the wood components results in mass loss of the sample. Esteves et al. (2007) determined a mass loss of 10% of the woods dry mass after exposure to 200°C for 12h. They determined that as the exposure time increased the mass loss increased. Furthermore, they found that the relationship between exposure time and mass loss was non-linear. This non-linear relationship means that the effect of thermal exposure to temperatures between 150°C and 220°C for a set time cannot simply be estimated from previous studies.

Thermal degradation of wood can be studied with Thermal Gravimetric Analysis (TGA), in which the sample is heated at a constant rate in an inert environment and the mass loss is recorded over time. The derivative of this curve is determined as a function of the temperature. The peaks of the derivative curve represent exothermal peaks where the rate of mass loss is the fastest. Gašparovič et al. (2009) determined TGA curves of a mixture of wood chips from waste wood, as well as isolated cellulose, lignin and hemicelluloses (

Figure 2-7 and

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Figure 2-8). The TGA curve of solid wood shows two peaks, of which the first peak at 289°C can be assigned to hemicelluloses and the second peak at 345°C to cellulose degradation. The temperature ranges over which hemicelluloses, cellulose and lignin decompose overlap each other and the hemicelluloses and amorphous cellulose decomposition peak can appear as a pronounced shoulder rather than a well-defined peak. The lignin peak is not visible in the TGA curve as lignin degrades over a wide temperature range the peak is overshadowed by the cellulose degradation peak.
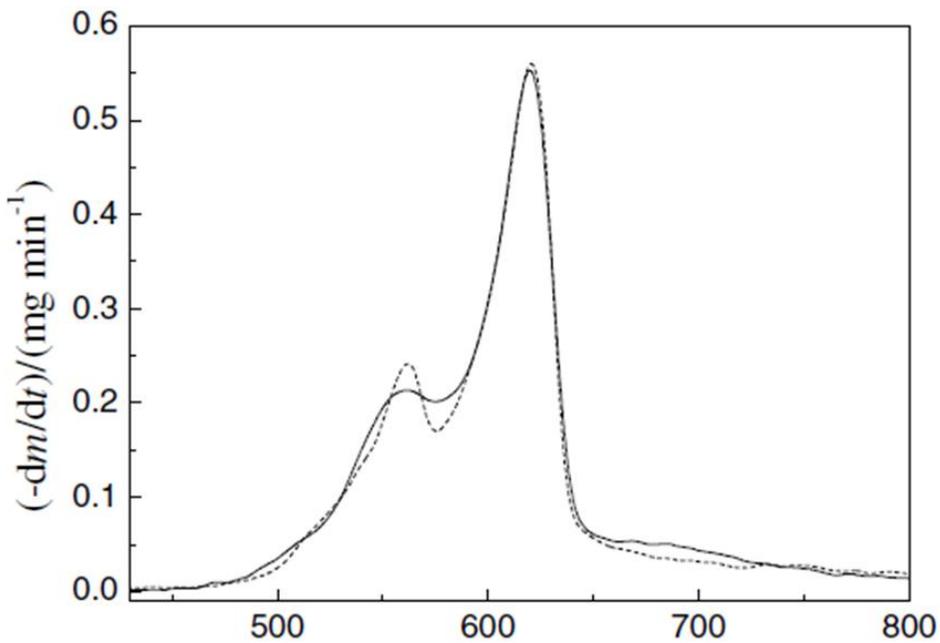
Figure 2-7: Thermal decomposition of wood chips (full line) and sum of hemicelluloses, cellulose and lignin (dashed line) at the heating rate of 5°C /min (Gašparovič et al. 2009).
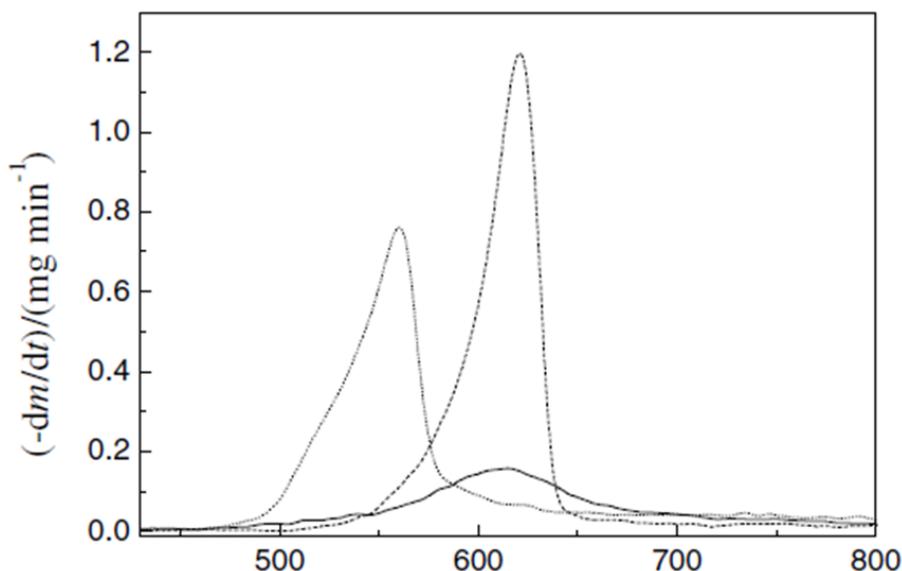
Figure 2-8: Thermal decomposition of hemicelluloses (dotted line), lignin (full line), and cellulose (dashed line) at heating rate of 5°C/min (Gašparovič et al. 2009)

Apart from extractives, hemicelluloses are the least thermally stable components of wood. They consist of low molecular weight sugars, which are less thermally stable than high molecular weight cellulose. The breakdown of hemicelluloses results in the formation of furfural, furan and mucic acid. At the same time the breakdown of acetyl groups results in the formation of acetic acid, which can catalyse further degradation (Bourgois et al. 1989). These degradation products vaporize and exit the wood, resulting in mass loss. Kollmann and Fengel (1965) found that when exposed to elevated temperatures for extended time the hemicelluloses broke down at temperatures as low as 100°C and by 180°C the hemicelluloses content was reduced from 20% to 10% over a 48h exposure. In contrast when wood was exposed to 180°C for 24h the hemicelluloses content increased as a percentage of the woods dry mass from 15% to 18%, although the pentosan fraction hemicellulose showed a clear decrease when exposed to the same treatment (Fengel 1966). This disparity between results shows that the effect of temperature on degradation is time sensitive.

The degradation of **cellulose** involves two processes.

1) The cross linking of cellulose chains, occurring at temperatures above 100°C. The cross linking occurs as water evaporates from the cellulose resulting in the formation of hydrogen bonds between the cellulose molecules. The degradation of cellulose is

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reduced by the presence of water. This reduction in degradation can be assigned to the newly cross-linked cellulose being more crystalline than before the water evaporated. The bonds of crystalline cellulose are less likely to break, which results in the de facto increase of crystalline cellulose (Fengel and Wegner 1989).

2) The depolymerisation of cellulose chains, which results in the formation of levoglucosan from the monomeric unit of the cellulose molecule. The cellulose does not lose mass at temperatures below 300°C, but a reduction in chain length, or in molecular weight (MW) can occur from temperatures as low as 150°C (Shafizadeh 1984), because as the cellulose degrades the cellulose chains are broken into shorter molecules with lower MW. Major (1958) found that when cellulose cotton linters were heated to 170°C for 96 hours, the crystalline regions remained unaffected. However, the MW decreases from 290 000 to around 32 500.

When analysing the thermal degradation of cellulose, it is necessary to distinguish between crystalline and amorphous cellulose regions. The amorphous cellulose is less thermally stable than the crystalline cellulose and the CI can vary between species. Differential thermal analysis (DTA) is an analytical tool whereby a sample in a crucible and an identical reference sample in another crucible are heated simultaneously. The difference in temperature between the sample and reference is plotted against temperature. Phase transformations can be identified as peeks on the graph. The influence of CI on the thermal stability of the cellulose can be seen by comparing the DTA curves of cellulose with different CI indices. In Figure 2-9 the DTA curve of cellulose with a (CI) of 71% had a melting point at 335°C, while cellulose with a lower CI of 53% had a melting point at 312°C. In addition to the lower melting point the amplitude of the peak is higher, which means that more of the cellulose is melting at these temperatures and therefore the lower the CI the less stable the cellulose is at lower temperatures.
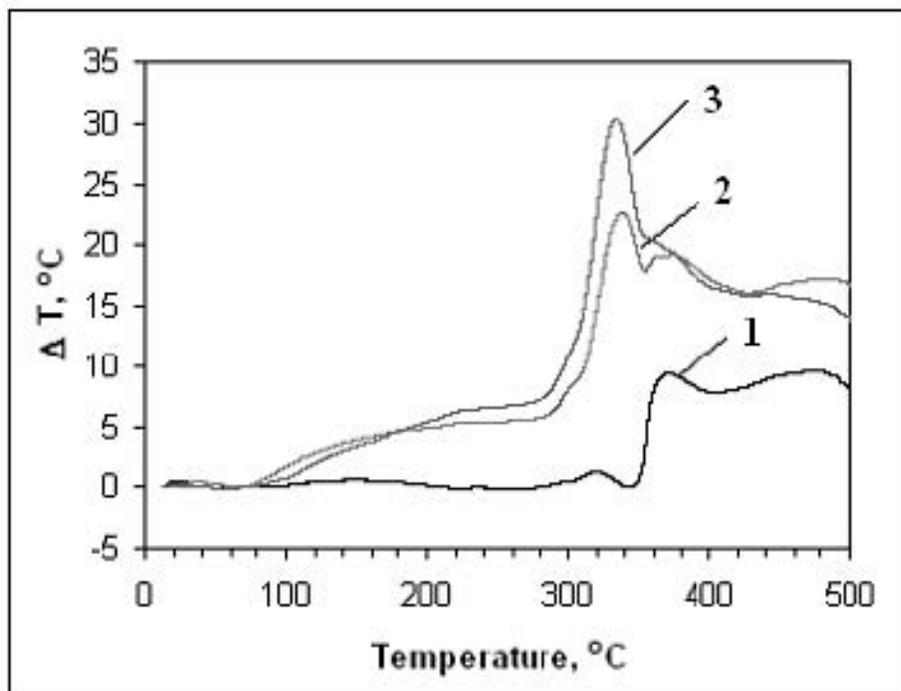
Figure 2-9: DTA curves of cellulose with CI values of (1) 71%, (2) 60% and (3) 53% (Cioluca and Popa 2005)

When comparing the thermal degradation of different tree species, Poletta (2012) found that the thermal stability of wood increased with increasing crystallinity. The crystalline regions begin to degrade between 300°C to 340°C (Kim et al. 2001). Isolated cellulose containing both amorphous and crystalline cellulose, showed substantial weight loss at exposure to 250°C, with 60 wt % loss between 1 and 8 hours of heating. At temperatures above 250°C most of the weight loss occurred within the first hour of heating (Rutherford et al. 2005).

A study on the change of cellulose crystallinity after heat treatment at 180°C, 200°C and 220°C was done by Bhuiyan and Sobue (1999). The study looked into the influence of MC on the re - and de-crystallisation of both isolated cellulose and cellulose in wood. For both cellulose types there was initial increase in crystallinity for all temperatures in the first hour. The increase is caused by the recrystallization of amorphous and semi crystalline regions and the additional degradation of the amorphous. The increase in crystallinity caused by recrystallization is determined by multiplying the crystallinity measured by x-ray diffraction by the ratio of residual and initial mass of the sample. This conversion gives the absolute increase in crystallinity due to recrystallization. The absolute crystallinity increased during the first hour of exposure, but decreased for longer exposure times, due to the de-crystallization and decomposition of the

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cellulose. The re and de-crystallization of cellulose was more significant in wet wood than in isolated cellulose. This may be due to several factors. Firstly, during the isolation of cellulose semi crystalline regions in the cellulose may have been degraded or de-crystallized already and secondly the hemicelluloses present in wood affect the thermal degradation of the cellulose. The hemicelluloses degradation produces acetic acid from the acytal groups and levunic acid in further degradation steps. As a consequence, bonds between hemicellulose and cellulose are broken and the cellulose can form new bonds with other cellulose molecules and crystallize.

A study by Battista (1950) was performed on the hydrolysis of cellulose in hydrochloric acid and the subsequent change of the MW and the degree of crystallinity. The study found that treatment caused an increase in crystallinity and a reduction of the MW of the sample. The increase in crystallinity was attributed to the crystalline regions being more resistant to hydrolysis. The less crystalline cellulose was degraded resulting in a de facto increase in crystallinity. A second factor that contributed to the increase in crystallinity was the crystallization of the non-crystallized cellulose. In addition, the study found that the increased crystallinity resulted in a lower reduction in MW. The reduced MW reduction can be attributed to the crystalline regions being more stable than the amorphous regions and as the crystalline region increases the overall MW degradation decreases.

Degradation of cellulose due to acid hydrolysis is an analogue to how the cellulose degrades due to thermal degradation. No study was found that determines MW and crystallinity as a function of temperature, but some literature has been found characterising the change of the individual characteristics.

Gel permeation chromatography (GPC) is an analytical technique, which can be used to determine the MW distribution of cellulose. The MW distribution is determined by letting cellulose in solution flow down a tube filled with gel beads. The larger molecules move through the gel faster than the smaller cellulose molecules, which results in the typical GPC chromatogram, where the amount of cellulose to pass through the tube is plotted over the flow time. GPC was used by Matsuoka et al. in 2010 to determine the change in MW distribution of isolated cellulose after exposure to a temperature of 240°C for 10 minutes. The peak of the GPC curve did not move but the shape of the curve skewed toward a higher molecular weight distribution, which means that the sample had an increase in its average MW. This increase in average MW was believed to be due to thermal glycosylation between two cellulose molecules in the non-crystalline regions. Thermal glycosylation is a chemical reaction by which the one end of a cellulose molecule can react with another to produce a longer cellulose chain.

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In a follow up study by Matsouka et al. (2011) cellulose was exposed to 240°C, for 60 min and the MW decreased, which was unexpected, considering their previous results. The authors proposed that the initial increase is caused by reactions between two cellulose molecules forming larger molecules. However, as the duration of thermal exposure increases, the cellulose molecules are broken into smaller parts, which cannot recombine because their ends are not reactive due to the degradation. This reduction in reactivity of cellulose by removal of reducing ends is demonstrated by the glycosylation of cellulose with an alcohol. When the alcohol treated cellulose is exposed to elevated temperatures, the MW of the cellulose does not increase indicating that the increase in MW is due to reactions at the ends of the molecules. The authors of the study also investigated the possibility of the discoloration as a result of thermal degradation caused by chemical reactions of functional groups. They exposed untreated cellulose to 280°C for 30 min and found that the samples began to darken in colour. When samples treated with alcohol to remove the functional groups were exposed to 280°C for 30 min the discoloration was far less severe.

The relative stability of amorphous and crystalline cellulose was investigated by Liu et al. in 2012 by determining the mass loss of crystalline and amorphous cellulose. When comparing the mass loss of the two forms of cellulose it can be observed that the amorphous cellulose begins to degrade at 170°C, whereas the crystalline cellulose begins to degrade at 230°C. The mass loss of amorphous cellulose is always greater than that of the mass loss of crystalline cellulose. As the exposure temperature increases the mass loss gradually increases. Substantial mass loss occurs at 250°C to 290°C for amorphous cellulose and at 270°C to 300°C for crystalline cellulose. After 300°C both types of cellulose are significantly degraded (Figure 2-10).
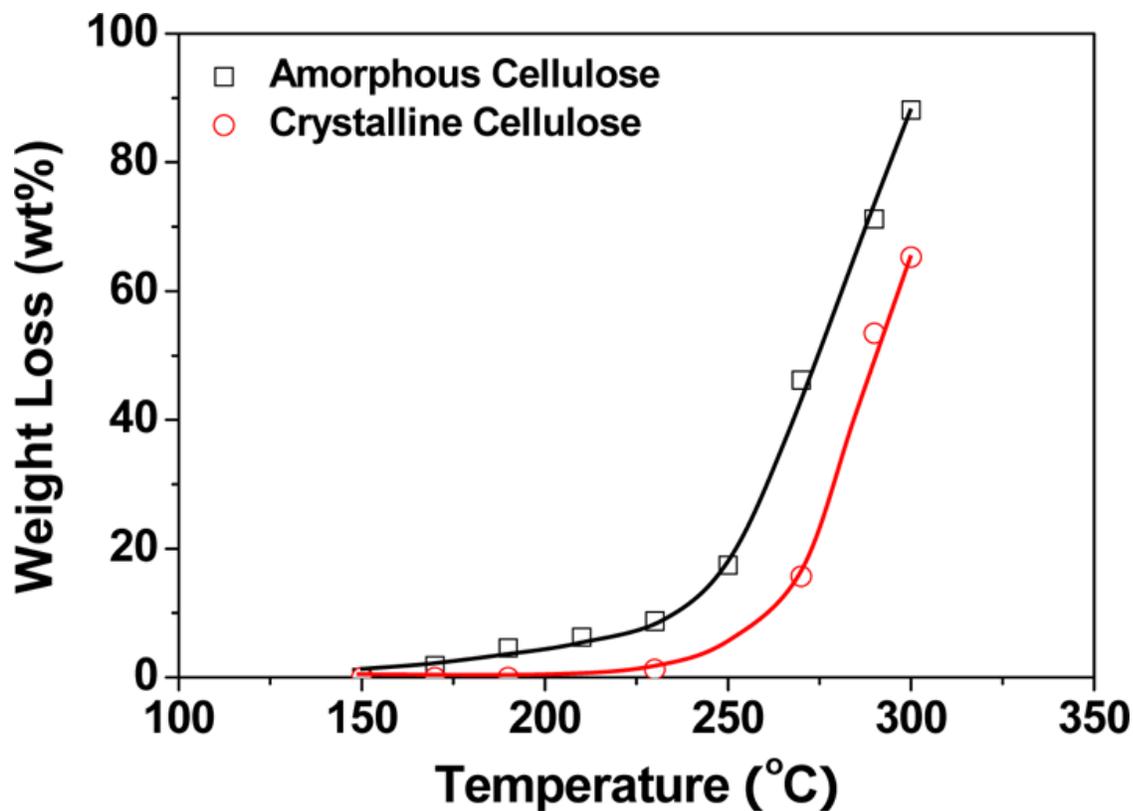
Figure 2-10: Mass loss of amorphous and crystalline cellulose after exposure temperatures ranging from 150°C to 300°C for 30 min (Kim et al. 2001).

The intensity of the x-ray diffraction pattern can be used to determine the change in the amount and size of cellulose crystallites. The relative intensity of the cellulose is a measure of the celluloses crystallinity relative to the untreated celluloses crystallinity. When cotton wood was exposed to various temperatures between 100°C to 360°C both the amorphous and crystalline cellulose degraded rapidly above temperatures of 320°C. There was an initial decrease in relative intensity at temperatures as low as 150°C for both the crystalline and amorphous cellulose. The decrease was however always greater for the amorphous cellulose (Figure 2-11).

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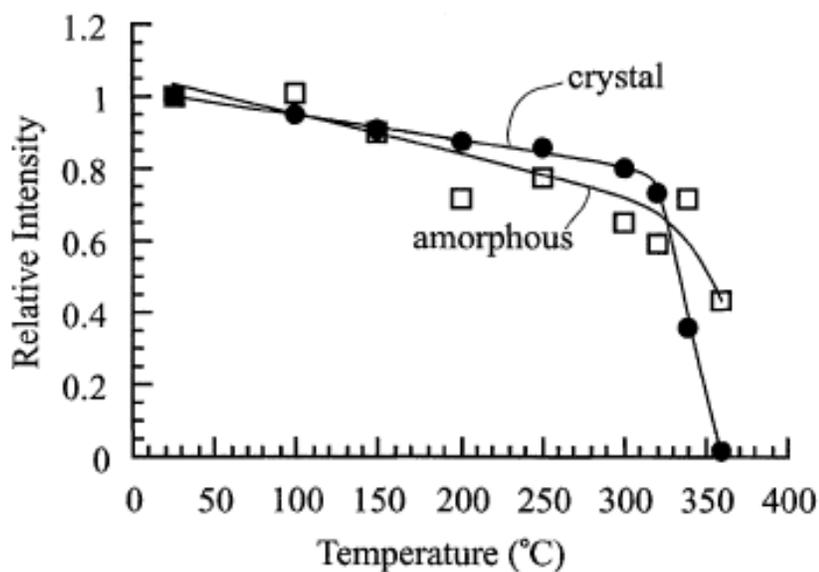
Figure 2-11: change in relative intensity of crystal reflections (circle) and amorphous background (square) during heating of cellulose (Kim et al. 2001).

When investigating how the amount of crystallites and the crystal size of cellulose degrades at 320°C the crystal size was found to degrade at a lower rate than the amount of crystalline cellulose. After 90 min of exposure the crystallinity of the cellulose has decreased by over 90% while the crystal size has only decreased by 40%. In order to understand why the amount of cellulose degrades faster than the crystal size the authors considered 3 different models for the crystallite degradation (Figure 2-12). In the first model (A) the crystallites degrade uniformly from the outside. In the second model (B) degradation occurs along the axis of the fibres, and the smaller crystallites are completely degraded first. In the third model (C) the degradation of an entire crystallite occurs rapidly completely.

With smaller crystallites degrading more easily than larger crystallites, model (A) was rejected as this would result in the amount of cellulose degrading at the same rate as the crystallite size. The authors suggest that the degradation must occur either by mechanism (B) resulting in smaller, less crystalline fibres degrading first or by mechanism (C) where the entire crystallite degrades. There is also the possibility of both (B) and (C) occurring simultaneously.

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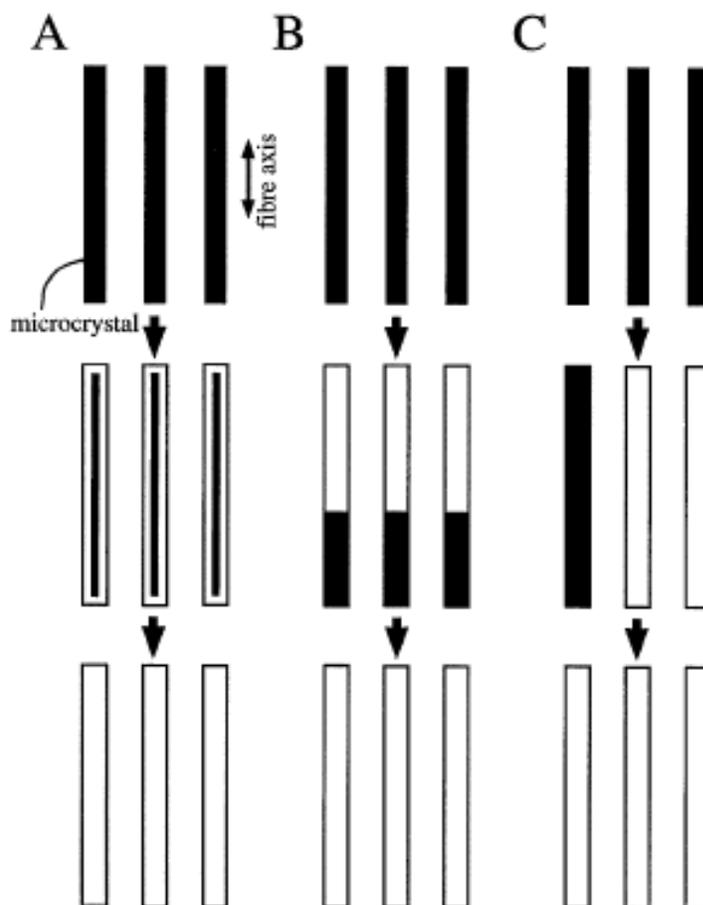
Figure 2-12: Schematic representation of cellulose crystallite degradation (Kim et al. 2001).

In order to understand the degradation of cellulose it is necessary to take into account how the crystallinity, crystal size, MW and mass degrade. If only a single characteristic is taken into account, the determined degradation temperature of cellulose will vary considerably. In addition, the change of the individual properties can influence the others and as a result the degradation pattern may not always be as expected as in the case of the study by Matsuoka et al. (2010) where the MW increased after exposure to 240°C for a short time of 10 minutes. When taking into account the mass loss of the amorphous cellulose at temperatures lower than 300°C, the increase in MW weight when exposed to 240°C may not be solely due to the glycosylation between two cellulose molecules. The reduction in mass may be caused by selective degradation of low molecular weight cellulose.

The large variation in MW and structure of **lignin** leads to a wide temperature range over which lignin degrades. Lignin begins to degrade at temperatures as low as 200°C (Shafizedah and

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DeGroot 1976), but increasing molecule size leads to an increased thermal stability. The thermal stability of lignin can result in a de facto increase of the lignin content expressed as wt % when wood is exposed to moderate temperatures that degrade components with lower thermal stability, such as hemicelluloses, but not the stable parts of the lignin. This can be seen in the results of Kollmann and Fengel (1965) where *Pinus sylvestris* and *Quercus robur* samples were exposed to 180°C for 48h, which resulted in an increase of lignin as % of the woods dry mass from 22% to 41% for *Q. robur* and an increase from 26% to 40% for *P. sylvestris*.

Rutherford et al. (2005) showed that isolated lignin treated at 250°C for 144h retained 80% of its original mass, indicating that little degradation occurs at 250°C and that lignin is relatively stable at this temperature. In order to compare the stability of cellulose and lignin the isolated components from *Eucalyptus spp.* were heated at 300°C for 15 to 90 minutes by Brito and Barrichelo (1979). Table 2-1 lists the residual mass after exposure for 15, 30, 45, 60, 75 and 90 minutes are recorded. Lignin lost 25% of its mass after 15 min and after 90 min the mass decreased by 55%, whereas the cellulose exhibited a mass loss of 70% after 15 min and 99% after 90 min. This clearly indicates that lignin is more thermally stable than cellulose at temperatures below 300ºC.

Tempo (minutos)	% Resíduo	
	Celulose	Lignina
0	100,0	100,0
15	29,9	75,5
30	9,4	67,9
45	1,9	58,9
60	1,1	54,0
75	1,0	46,6
90	1,0	46,5

Table 2-1: residual mass of lignin and cellulose after exposure to 300ºC for times ranging from 15 to 90 min (Brito and Barrichelo 1979)

2.5   Thermal degradation of standing trees

When exposed to elevated temperatures, the thermal degradation of wood in living trees depends on the conditions of exposure, as well as the wood properties. The conditions that influence degradation are temperature and exposure time. The relevant wood properties are the species, presence of water in the wood and the dimensions (Hill 2006).

Wood degrades and loses mass when exposed to elevated temperatures, because the heat causes the evaporation of volatile compounds and water. Furthermore, it causes chemical reactions, which result in the breakdown of large molecules into smaller compounds, which are typically less thermally stable and break down further, until they evaporate or combust.

The resulting degradation is time and temperature dependent and generally the degradation increases with temperature and exposure time. At temperatures above 100°C - 160°C water and volatile components evaporate and below 200°C only non-combustible gasses are produced. These include CO_2, formic acid, acetic acid and glyoxal. From 200°C to 280°C carbon dioxide, formic acid, acetic acid and glyoxal are produced with the addition of CO. At these temperatures the chemical reactions are endothermic and the gaseous products are non-flammable. Active pyrolysis takes place from 280°C to 500°C. The degradation products are combustible and include CH_4, CO, CO_2, H_2, H_2O, tar and residual charcoal. Active pyrolysis is exothermic and leads to secondary reactions among the initial degradation products. Above 500°C, in which the residue consists primarily of charcoal, secondary reactions continue (Beall and Eickcner 1970).

A tree's first line of defence against a forest fire is its bark, which provides a heat insulating barrier. The bark's effectiveness as insulation depends on the thickness, density, the moisture content, height on the tree and structure. The thickness has the largest effect on thermal insulation properties and the thermal resistance increases with thickness. The height above the tree affects the heat resistance due to the bark thickness decreasing with tree height. As a result, the heat resistance decreases towards the top of the tree. This is, however, species dependent as not all species have thinner bark towards the top. Moisture in the bark increases the thermal conductivity, because water is a good thermal conductor (Odhiambo et al. 2014).

Dry wood is a poor heat conductor - a property, which allows the possible use of a significant portion of the stem after a forest fire. A previous study on the thermal conductivity of *E. dunnii* and *E. macarthurii* (Meincken and Mngomezulu, under review) found that after 10 min of exposure to 1000°C the temperature of the wood one centimetre behind the bark rose to 146°C

for *E. macarthurii* and only to 90°C for *E. dunnii.* Two cm behind the bark the temperature rose only 52°C for *E. macarthurii* and 55°C for *E. dunnii.* Temperatures between 60°C and 100°C can result in the death of the cambium (Dickinson and Johnson, 2001), but are not sufficient to cause degradation of the chemical components of wood. However, temperatures exceeding 100°C may lead to the breakdown of parts of the lignin and hemicelluloses, as well as the evaporation of volatile extractives.

2.6   Pulpwood properties

Cellulose is the primary product of the pulp & paper industry and the pulp yield depends on the proportion of cellulose present in the wood that is used. However, the quantity of pulp produced is not the only characteristic of importance.

The chemical composition of the wood is important, and the alpha cellulose content should be close to or above 40% for pulping. A change in the alpha cellulose content will directly influence the pulp yield (Ververis et.al 2003).

The chemical reactions used during the pulping process to separate the cellulose are designed to break down the lignin with minimal damage to cellulose and the volume of chemicals needed to delignify the wood is proportional to the lignin content. A higher proportion of lignin results in higher volumes of chemicals needed, which in return results in higher costs. The extractives are not chemically bound to cellulose like lignin and are easier to remove, but they can still cause production problems, such as difficulty recovering bleaching chemicals and increased chemical consumption during pulping (Hillis 1971).

The MW of cellulose is equally of interest. The average MW of cellulose is a measure of the sum of the MW of all cellulose polymers divided by the number of molecules and the same average MW can be determined for completely different sample compositions - a sample of evenly sized molecules and a mixture of long and short molecules can result in the same average MW.

Goring and Timell (1962) determined the average MW of celluloses from several sources by light-scattering and the results indicated that wood cellulose has an average MW of at least 1,45 – 1,62 million and possibly as high as 2,4 million. A cellulose molecule with a MW of 1,62 million would have a length of 5μm.

The MW of pulp is generally far lower than the values obtained from cellulose depending on the method. The Lower MW of pulp is due to degradation of cellulose during the pulping process. Kraft pulp has a typical average cellulose MW of 160000 and sulphite pulping results in slightly higher average MW of around 200 000 (Lelekakis et al. 2014). A minimum MW of 13 000 is necessary for sufficient mechanical strength. As the MW increases to the range of 32,500 – 65,000 the mechanical strength increases, but for MW above 65,000 the mechanical strength levels off and approaches a constant value (Janes 1968).

3 Materials and methods

3.1 Sample Preparation

Two hardwood species, relevant to the South African pulp industry, were investigated: *Eucalyptus dunnii* and *Eucalyptus macarthurii*. The species were selected by Sappi, as they grow in plantation areas with a high fire risk. In addition, Eucalypts are South Africa's primary hardwood grown mainly for production of pulp and paper products. Samples were provided by Sappi and were obtained from individual trees, from which 2cm thick disks were cut at breast height (1.3m). All trees came from comparable sites, as described in Table 3-1.

Species	District	Compartment	Age @ date of sampling	Estimated SI	SQ	Number of sampled trees
E. macarthurii	Watershed Farm	B21a	7.2	17.4	SQ3	5
E. dunnii	Shafton	E11	9.6	18.9	SQ3	6

Table 3-1: Site characteristics

Disks were transported to Stellenbosch in plastic bags to prevent excess loss of moisture. Four strips from the disks were cut from the sapwood near the bark and cut into 2cm cubes, as graphically displayed in Figure 3-1. The samples were prepared from the sapwood directly behind the bark, as only this wood will be subjected to the high exposure temperatures.

The relative humidity (RH) is the ratio between the partial pressure of water vapour in the room to the equilibrium vapour pressure of water at a given temperature. The cubes were placed in a conditioning room at 65% RH and 20°C for 24 hours. Prior to analysis, the cubes were mixed and 10 random blocks of each species were used for each heat treatment.

39
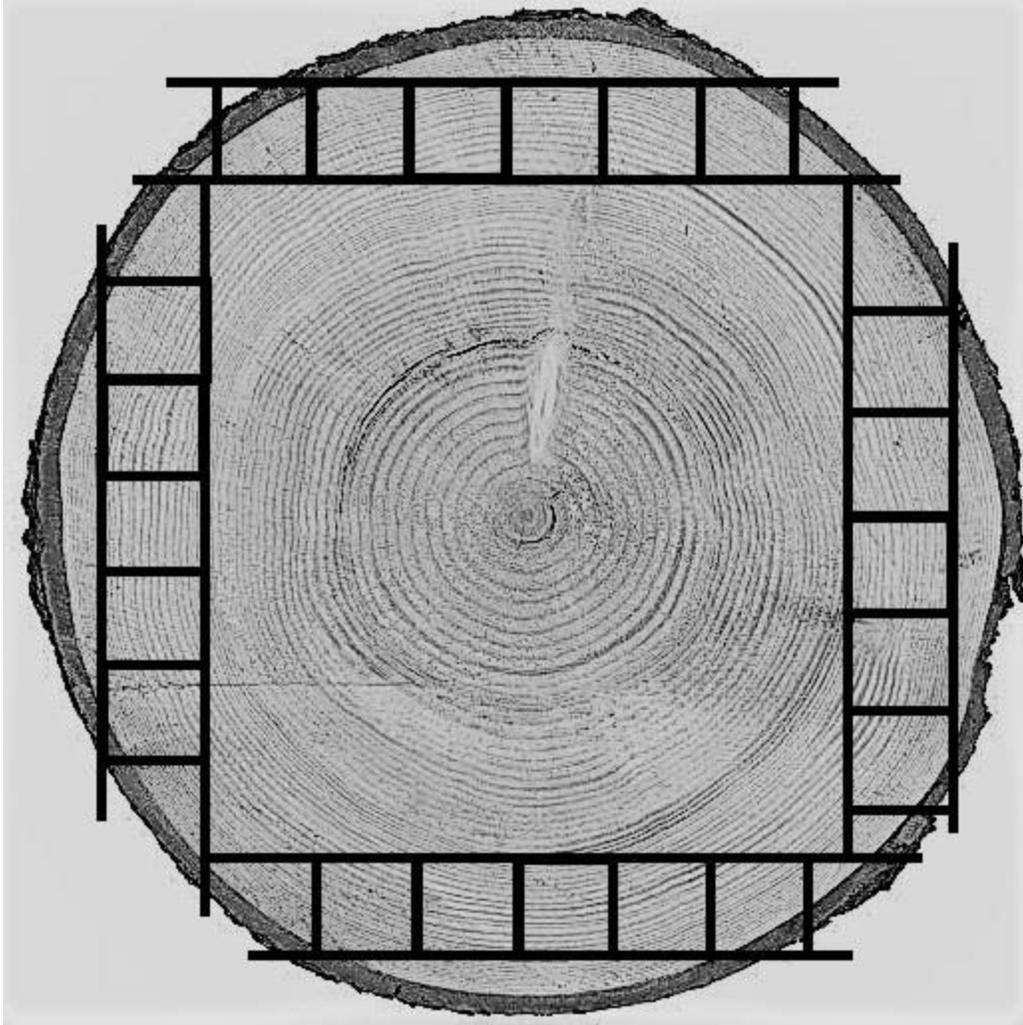
Figure 3-1: Cross section disk with schematic of sample preparation cuts

3.2   Thermal treatment

The residence time of a wildfire was estimated to be 37 s, this duration only accounts for the time the flames exceed 0,5m. Lower flames and smouldering fuels can still persist for several minutes. A time of 10 minutes was chosen as this clearly exceeds typical residence times of a wildfire, as described above. All thermal degradation obtained at this exposure time can be regarded as absolute maximum degradation that can be expected in a standing tree. Ten blocks of about 2 cm^3 were exposed to each temperature for 10 min in a furnace (Scientific Manufacturing, model 909R01), and the temperatures ranged from 150°C to 220°C in 10°C intervals.

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After heat treatment the samples were allowed to cool to room temperature and subsequently milled in a hammer mill to produce particles less than 2mm in size. The particles were then processed in a Retsch ZM 200 mill to reduce the size from 2mm to 0.4 mm. The milled sample was sorted through a 0.4 mm vibratory sieve to produce a homogeneous particle size for chemical analysis. All particles from the same heat treatment were mixed and stored in the conditioning room prior to chemical analysis.

3.3   Determination of chemical components

Extractives

In this study the extractive content is defined as the portion of compounds that are water or ethanol soluble and a can be removed by repeated washing with the solvent every 15min for 6h. This repeated washing is achieved by evaporation of solvent in a round bottom flask and subsequent condensation of solvent in a condenser. The condensed solvent is passed through the sample repeatedly (Hames et al. 2008).

The water extractive content of the sample was measured before the ethanol extractive content. For the water extractive content, the mass of an oven dried round bottom flask was measured. Five gram of wood meal was placed into a cellulose thimble. The thimble was then placed in a soxhlet apparatus, which fills with warm water and then drains the water again at the bottom of the apparatus every10min for 6h. This process of filling and draining the soxhlet apparatus washes the extractives out of the wood, through the thimble and into a round bottom flask. The soxhlet apparatus is filled through condensation of distilled water, which falls down the condenser into the soxhlet apparatus. The setup of the apparatus can be seen in Figure 3-2. The sample and thimble were dried at 100°C. The ethanol extractive content was determined by placing the thimble in a soxhlet apparatus again and then washed with ethanol every 10min for 6h. The extracted content was collected in a flask and weighed, and the extractive content is reported as percentage of the wood's dry mass for both the water and ethanol extractives. The extractive content is reported as an average with standard deviation of three repetitions.

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Figure 3-2: Extractive content determination lab setup

Acid insoluble Lignin (AIL)

The lignin content was determined by means of the Klason method where the carbohydrate and extractive content of wood is degraded through acidic hydrolysis. This method results in a solid portion of the lignin remaining and a portion of the lignin being soluble in the solvent. The solid lignin is referred to as the acid insoluble lignin content (Sluiter et al. 2012).

Three grams of extractive free wood meal were placed into a test tube and 3ml of 72% w/v sulphuric acid was added to the test tube and stirred into the sample. The test tube was then placed in a water bath at 30+/- 5°C and stirred once every 5 minutes for an hour. 84ml of deionized water were added while moving the sample into a sealable screw top jar. The jar was placed in an autoclave at 121°C for one hour. The AIL was then isolated by filtering the soluble portion through a glass crucible. The mass of the glass crucible was previously measured so that the lignin could be measured directly from the thimble after oven drying at 100°C for 24h. For the soluble lignin content determination 50ml of the filtrate were collected and oven dried at

101°C for 12h. The insoluble lignin is reported as a percentage of the wood's dry mass. The AIL content is reported as an average and standard deviation of three repetitions.

Acid soluble Lignin (ASL)

The acid soluble lignin cannot be easily filtered from the solution and is determined through UV Spectroscopy. 3ml of the aliquot collected during the insoluble lignin determination is placed inside an UV spectrometer. The absorbance of the UV light at a wavelength of 240nm is used to calculate the lignin in solution (Sluiter et al. 2012) with the equation 2:

$$ASL = \frac{UVabs \; x \; Vfiltrate \; x \; Dilution}{\varepsilon \; x \; ODWsample \; x \; pathlength} \times 100\% \tag{2}$$

ASL% = acid soluble lignin as % of the wood's extractive free dry weight, UV_{abs} = measured UV absorbance in mol/L, $V_{filtrate}$ = 86.73ml, dilution = (V_{sample} + $V_{solvent}$)/ V_{sample}, ε = Absorptivity of biomass at specific wavelength = 25L·mol^{-1}·cm^{-1}, ODW_{sample} = weight of sample in mg, pathlength = 1cm.

The ASL content is reported as an average and standard deviation of three repetitions.

Cellulose

The alpha cellulose content was determined using the acid chlorite method to isolate the alpha cellulose for molecular weight determination without damaging or severely reducing the MW of the cellulose (Loader et.al. 1997).

One gram of extractive free wood was placed into a sealable flask and 175ml of water, 1.7ml acetic acid and 2ml of 25% sodium chlorite in solution were added successively. The pressure tube was then placed in a steam bath at 75°C for 1h and stirred occasionally and subsequently a second addition of 1.7ml acetic acid and 2ml sodium chlorite were made and the pressure tube was replaced into the steam bath for another hour. A third and fourth addition of 1.7ml acetic acid and 2ml sodium chlorite were made, both followed by an hour in a steam bath. The holo-cellulose was isolated by suction through a glass crucible and washing with cold water and subsequently subjected to 75ml of 10% (w/v) sodium hydroxide at 70°C for 45 min followed by

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67ml of 17% (w/v) sodium hydroxide at room temperature for 45 min. The alpha cellulose was isolated by suction through a glass thimble and washing with hot water. The alpha cellulose content is reported as an average and standard deviation of three repetitions.

3.4 Cellulose molecular weight

The average molecular weight of the isolated alpha cellulose was measured by means of viscometry. The sample preparation and testing were done in accordance with TAPPI standard T 230. A viscometer with standard size "0B" was used in a setup as displayed in Figure 3-3. The relative viscosity of the cellulose solution is determined by allowing a known volume of the solution to drain through thin tube and measuring the time it takes to drain from one marked position to another. The higher the viscosity of the solution the longer the time taken to drain through the tube. When a polymer is dissolved in a solvent the viscosity of the solvent and cellulose should be higher than that of the solvent on its own. The higher the molecular weight of the polymer the greater the increase in viscosity of the solution.

Figure 3-3: Viscometer setup in viscometer temperature jacket

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The relative viscosity is the ratio between the viscosity of the polymer in solution and the viscosity of the solvent calculated with equation 3.

$$relative\ viscosity = \frac{effluxtime\ solution}{effluxtime\ solvent} \quad\quad (3)$$

From the relative viscosity the specific viscosity of the polymer can be calculated by equation 4.

$$specific\ viscosity = relative\ viscosity - 1 \quad\quad (4)$$

The specific viscosity, however, depends on the concentration of the polymer in solvent. In order to characterize the viscosity of the solution due to the dissolved cellulose the reduced viscosity is calculated with equation 5.

$$reduced\ viscosity = \frac{specific\ viscosity}{concentration} \quad\quad (5)$$

The reduced viscosities of a sample with different concentrations are plotted as a function of concentration, as displayed in Figure 3-4. The value of x at y = 0 determined through extrapolation is the intrinsic viscosity of the analysed compound. The intrinsic viscosity is the viscosity of the polymer solution where the solvent concentration is 0. This is a hypothetical viscosity from which the molecular weight of the polymer can be calculated.
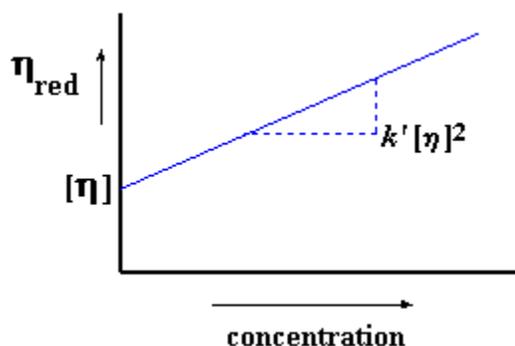

Figure 3-4: Example of reduced viscosity plotted against solvent concentration

The molecular weight of the polymer can be determined from equation 6.

$$intrinsic\ viscosity = K(MW)^a \quad\quad (6)$$

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The two constants K and a are specific to each polymer and a need to be determined experimentally. The values for cellulose were determined to be K = 0.07 cm^3/g and a = 0.7 (Kes and Christen 2013).

For each treated and untreated sample 1.5g of cellulose were oven dried above 60°C for 24h and placed into a sealable glass jar, where it was stirred with a magnetic stirrer after addition of 40ml of distilled water for 2 minutes to disperse the cellulose in the water.

The cellulose must be dissolved in a solvent that is both capable of completely dissolving the cellulose and is suitable for viscometer equipment. Cupriethylenediamine solution has proven to be a compatible solvent and as such 40ml were subsequently added to the jar reducing the concentration of cellulose to solvent to 0.3125% (w/v). The jar was purged with nitrogen gas to remove the oxygen from the jar and reduce oxidation of cupriethylenediamine. The jar was sealed, and the contents were stirred for 15min until all cellulose was dissolved. The nitrogen gas can interfere with the measurements if it gets into the viscometer. For this reason, the jar was degassed by placing it on its side for 5min.

The viscometer was filled with 15ml of cellulose in solution. The viscometer was then placed in a water bath at a 25°C and left for 10min for the solution to reach 25°C. The solution was drawn up the viscometer by means of suction and then pressure was released to allow the liquid to drain down from the first to the second marker on the viscometer. The time taken for the solution to move from the first to the second marker was recorded. This was repeated three times for each solvent concentration and the average was recorded.

For further dilution, the contents of the already measured solution were poured back to the original solution and 10 ml of cupriethylenediamine and 10ml of distilled water were added to reduce the concentration 0.25% (w/v) and the elution time of this concentration was determined. The process of dilution and measuring the elution time of the sample was repeated twice more at the concentrations of 0,2% (w/v) and 0,18% (w/v). For each of these concentrations the relative viscosity was determined from the average elution time. The intrinsic viscosity of the cellulose was determined once for each heat treatment for each wood species.

3.5   Thermogravimetric analysis (TGA)

In addition to the wet chemical analysis, thermogravimetric analysis of alpha cellulose, lignin and wood was performed for both species. Five mg of the dry samples were analysed in a Q500 TGA from TA Instruments. The system was purged with N_2 gas at a flow rate of rate of 50 ml/min. The N_2 purging was done throughout the analysis. The temperature was increased at a rate of 10°C/min from room temperature to 600°C. The output of this test is the mass loss as a function of temperature. The derivative of the TGA curve is used to determine the onset temperature where degradation begins, as well as the temperature where the peak of degradation occurs were derived. One TGA curve was acquired per species/chemical component.

4 Results and Discussion

4.1 Temperature of wood during a forest fire

In order to recover the wood from fire damaged trees it is necessary to know the temperature to which the wood within the tree was exposed. Intense fires can reach a temperature above 1000°C, but with these high temperatures the contact time usually last only a couple of minutes. In a previous study (Meincken and Mngomezulu, under review) the temperature of the wood at 1cm, 2cm and 3cm behind the bark was determined after exposure to 340°C and 470°C. By extrapolating the data an estimate of the temperature at these points can be determined after exposure to 1000°C.

In Figure 4-1 the temperature *E. dunnii* of the wood 1cm behind the bark reached 150°C after 10 min exposure to 1000°C. At 2 cm behind the bark the temperature only increased to 50°C, which is well below the temperature known to degraded wood.
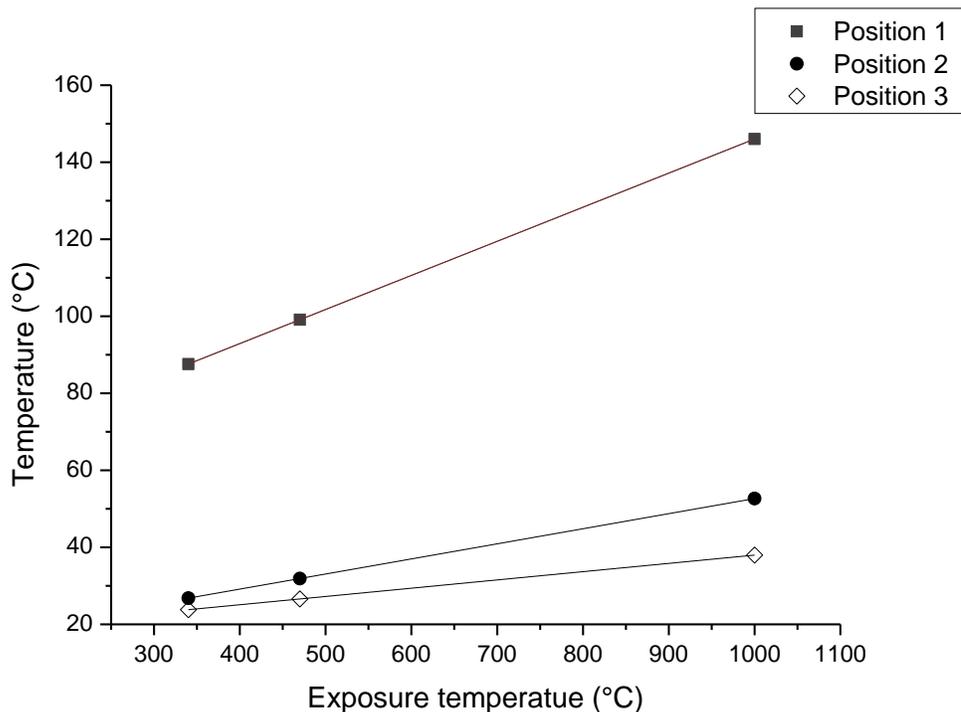
Figure 4-1: Temperature of *E. dunnii* wood within the stem after exposure to elevated temperature for a duration of 10 min. With a line fitted to predict the temperature of the wood after exposure to 1000°C

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In Figure 4-2 the temperature of *E. macarthurii* wood 1cm behind the bark reached 90°C after 10 min exposure to 1000°C. An exposure to 100°C does not degrade wood significantly. It may be sufficient to remove 1cm of wood in order to recover the wood.
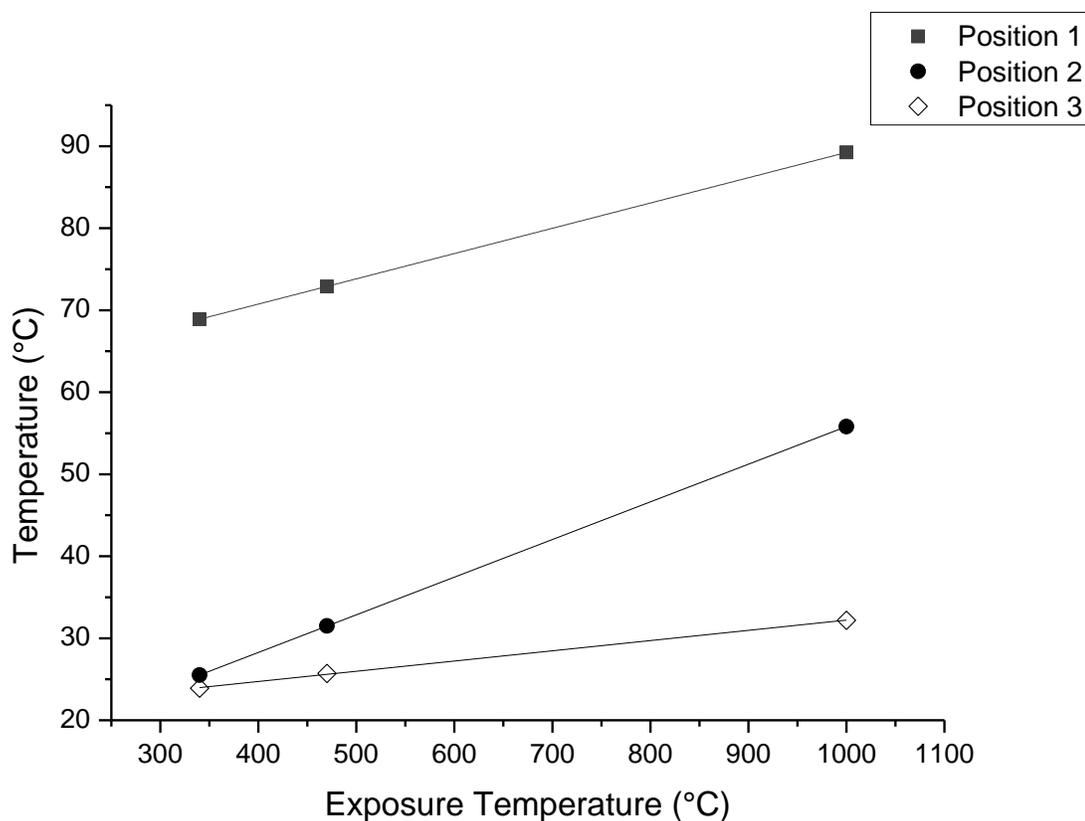
Figure 4-2: Temperature of *E. macarthurii* wood within the stem after exposure to elevated temperature for a duration of 10 min. With a line fitted to predict the temperature of the wood after exposure to 1000°C

4.2   Chemical composition

In Table 4-1 the chemical composition of untreated *E. dunnii* and *E. macarthurii* is presented. The difference in lignin, cellulose and extractive content can influence the rate of degradation of individual wood components and the wood itself. *E. dunnii* has a higher cellulose content than *E. macarthurii*, which may lead to an increased thermal stability of wood when exposed to temperatures below 300°C.

E. dunnii has a lower acid insoluble lignin (ASL) content at 26.3%. Lignin begins to degrade at temperatures below 220°C and thus the higher acid insoluble lignin content of *E. macarthurii* may lead to a lower mass loss of the wood below 220°C. The ASL content *of E. dunnii* is 1.1%

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higher than that of *E. macarthurii* at 2%. The ASL is attributed to lower molecular weight lignin and the degradation products of high molecular weight Acid Insoluble lignin (AIL). The change in ASL is difficult to predict as degraded lower molecular weight lignin should lower the ASL content, but the degradation of AIL produces more ASL. As a result, the ASL may have a de facto increase after thermal degradation depending on the rate, at which the two lignin fractions degrade.

	E. dunnii	E. macarthurii
Water extractives (%)	7,1 ± 0,6	10,5 ± 0,8
Ethanol extractives (%)	0,9 ± 0,08	2,0 ± 0,4
Acid insoluble lignin (%)	26,3 ± 1	29 ± 1
Acid soluble lignin (%)	3,1 ± 1,3	2 ± 0,5
Cellulose (%)	36,4 ± 1	33,4 ± 0,1

Table 4-1: Chemical composition reported as average with standard deviation of *E. dunnii* and *E. macarthurii*

The *E. dunnii* water extractive content at 7.1% is lower than that of the *E. macarthurii* at 9%. Similarly, the ethanol extractive content of *E. dunnii* is at 0.9% lower than that of *E. macarthurii* at 2%. A higher extractive content can lead to increased mass loss at lower temperatures, as the extractives tend to form volatiles at low temperatures. With *E. dunnii* having a lower lignin, lower extractive content and higher cellulose content it can be expected that *E. dunnii* is more thermally stable at temperatures below 220°C.

4.3   Extractives

A decrease in extractive content after exposure to elevated temperatures is expected and the extent can be expected to differ with exposure time.

The water extractive content of *E. macarthurii* decreases after 150°C (Figure 4-3) and reaches a low of 8.5% after exposure to 180°C. At higher temperatures begins to increase again and after exposure to 220°C the water extractive content of *E. macarthurii* is 10%.

E. dunnii shows a similar trend with the water extractive content decreasing from 10% at 150°C to a low of 4% at 190°C. At higher temperatures the water extractive content increases to 7% at 210°C, after which it decreases again.
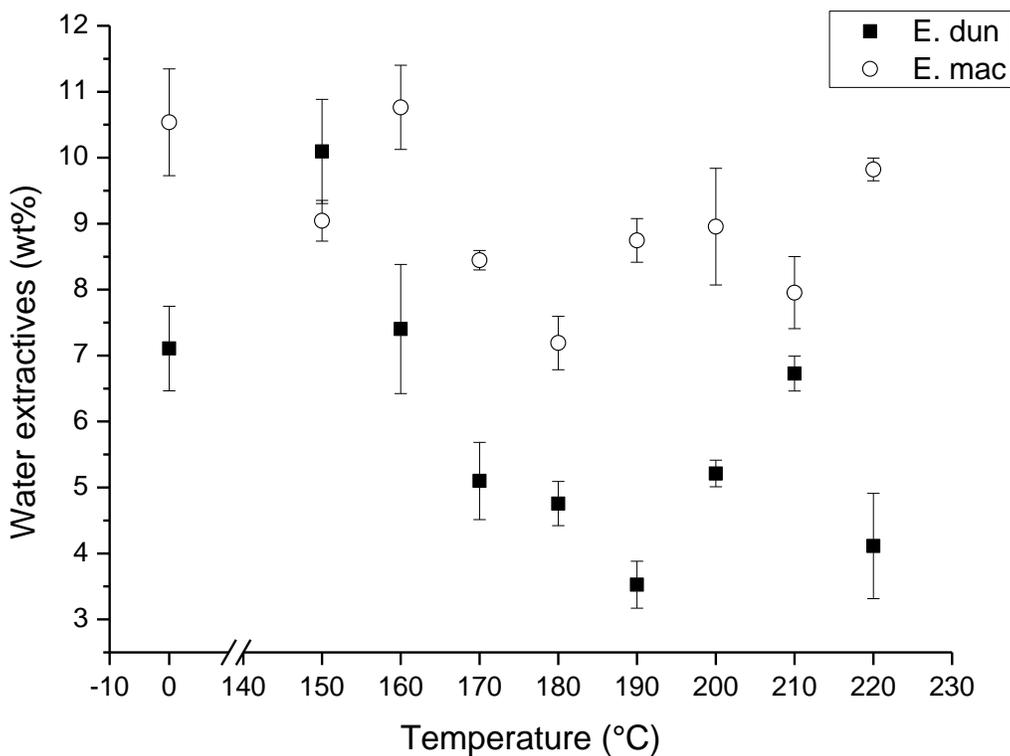
Figure 4-3: Mean water extractive content of *E. macarthurii* and *E. dunnii* after exposure to elevated temperatures and the standard deviation

Figure 4-4 shows that the ethanol extractive content of *E. macarthurii* follows a similar pattern to that of the water extractive content with a decrease from 2% to 1% after exposure to 150°C and a subsequent increase as the temperature increases up to 190°C the extractive content increases again to 2%. At higher temperatures the extractive content decreases sharply down to 0.5%. The ethanol extractive content of *E. dunnii* follows the same trend, although the change is less severe. The extractive content of the untreated *E. dunnii* wood is 0.9% and after exposure

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to 170°C it decreases to just below 0.5%. The ethanol extractive content then increases to above 0.5% after exposure to 190°C and subsequently decreases further after exposure to temperatures higher than 190°C.
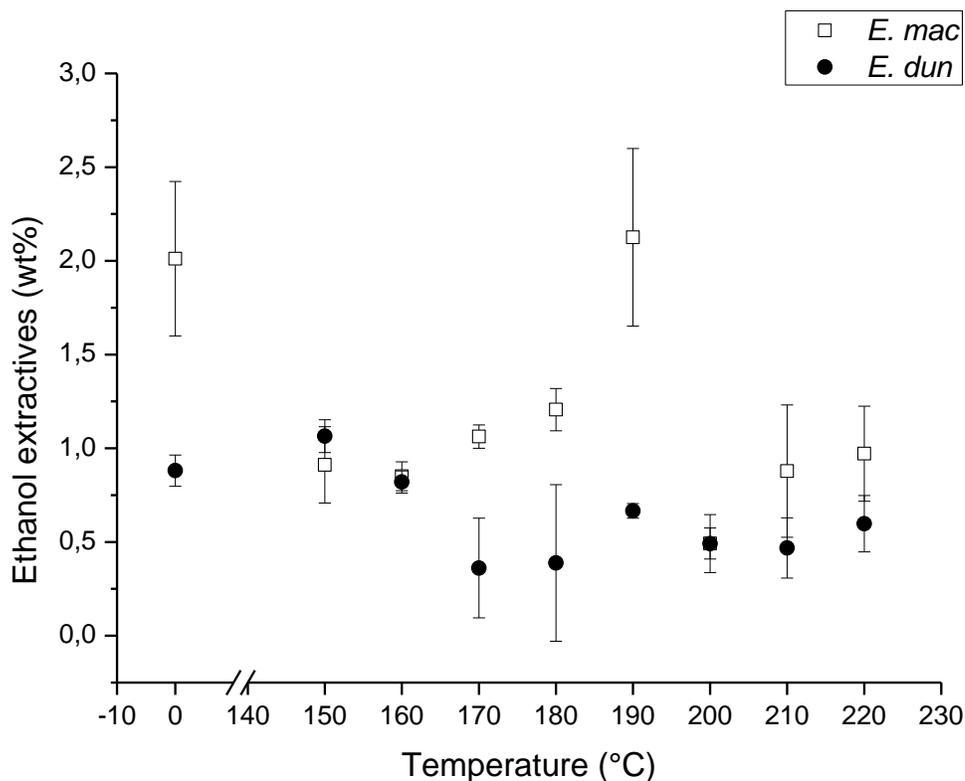

Figure 4-4: Mean ethanol extractive content of *E. macarthurii* and *E. dunnii* after exposure to elevated temperature and the standard deviation

4.4   Acid insoluble lignin content (AIL)

The total lignin content is determined as the sum of the AIL and ASL. The AIL content is represented in Figure 4-5 and the ASL content in Figure 4-6.

The AI lignin content of *E. macarthurii* shows a clear decrease from 29% to 25.5% after exposure to 150°C, after which it increases to 26.5% at 170°C. For higher exposure temperatures the AI lignin content then decreases to around 23%.

The AI lignin of *E. dunnii* follows the same pattern with an initial decrease from 26% to 25% after exposure to 150°C. Subsequently it increases after exposure to 160°C and reaches a peak

of 27% after exposure to 170°C, which is higher than the AIL content of the untreated wood. For higher exposure temperatures the AIL content remains around 21%.

The increase in AI lignin content is not due to an actual increase of the lignin in the wood, but rather due to the relative decrease of other wood components, such as water and ethanol extractives.

The larger decrease of the AIL content of *E. macarthurii* after exposure to 150°C is probably the result of the breakdown of less thermally stable lignin into lower molecular weight AS lignin.
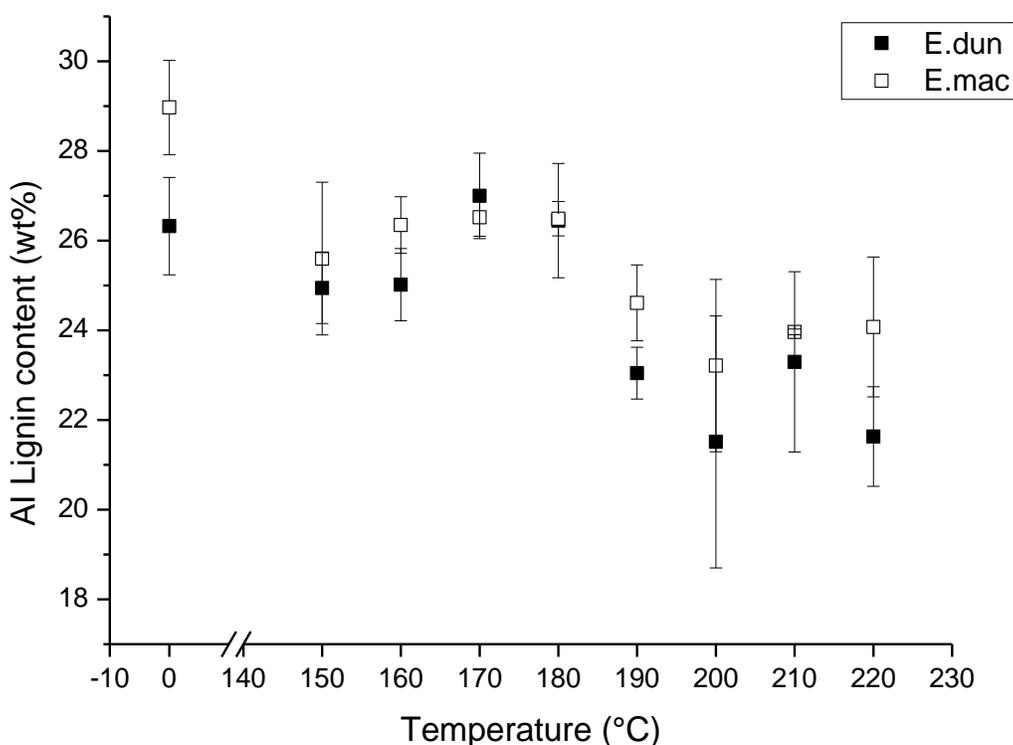

Figure 4-5: Mean acid insoluble lignin content of *E. macarthurii* and *E. dunnii* after exposure to elevated temperatures the standard deviation

4.5   Acid soluble lignin

The ASL content increases for both species with increasing exposure temperature and reaches 9% for *E. macarthurii* and 5.5% for *E. dunnii* at 220°C. The increase in ASL content is probably? due to the degradation of the AI lignin, which results in shorter molecules that lead to a de facto increase in AS lignin. This can be seen by fact that the sum of the untreated AI and AS lignin

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content is not significantly different from the sum of the AI and AS lignin after exposure to 220°C.

The AS lignin in *E. macarthurii* shows a greater increase than that of *E. dunnii* as the AI lignin has a larger decrease after exposure to heat treatment. In addition, there is a greater proportion of AI lignin in *E. macarthurii* and the larger proportion of AI lignin results in more degradation products and thus a greater increase in AS lignin.
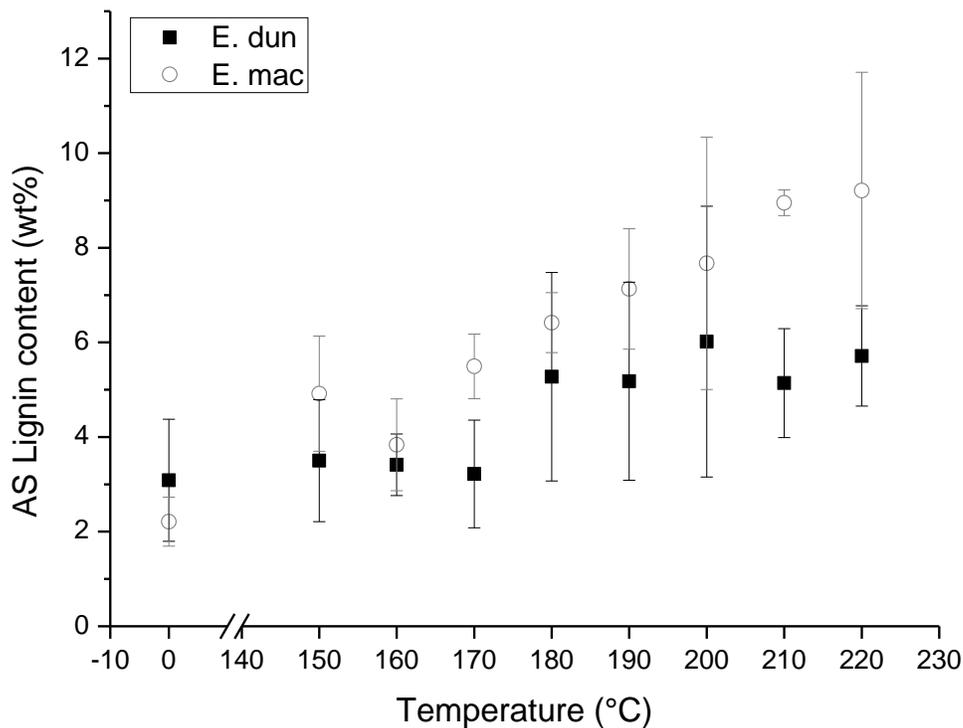

Figure 4-6: Mean acid soluble lignin content of *E. macarthurii* and *E. dunnii* after exposure to elevated temperatures the standard deviation

4.6   Alpha Cellulose

The alpha cellulose content (Figure 4-7) of both *E. dunnii* and *E. macarthurii* remained relatively unchanged up to 160°C. The alpha cellulose content of *E. macarthurii* shows little change in weight percentage to its initial value even after exposure to 220°C. The *E. dunnii* alpha cellulose content, on the other hand increases after 160°C and after exposure to 220°C has increased from 37% to 42%. The relative, proportional increase in alpha cellulose is due the degradation of the other wood components that decrease after exposure to 170°C. One component that

shows a large decrease after exposure to 170°C is the water extractive content (Figure 4-3). The water extractive content of *E. dunnii* decreased more than that of *E. macarthurii*. The *E. macarthurii* alpha cellulose content seems to show no decrease, but this can be the result of the extractives degrading faster than the cellulose. The alpha cellulose of *E. dunnii* increases as the extractive content decreases to such an extent that the cellulose content has a de facto increase.
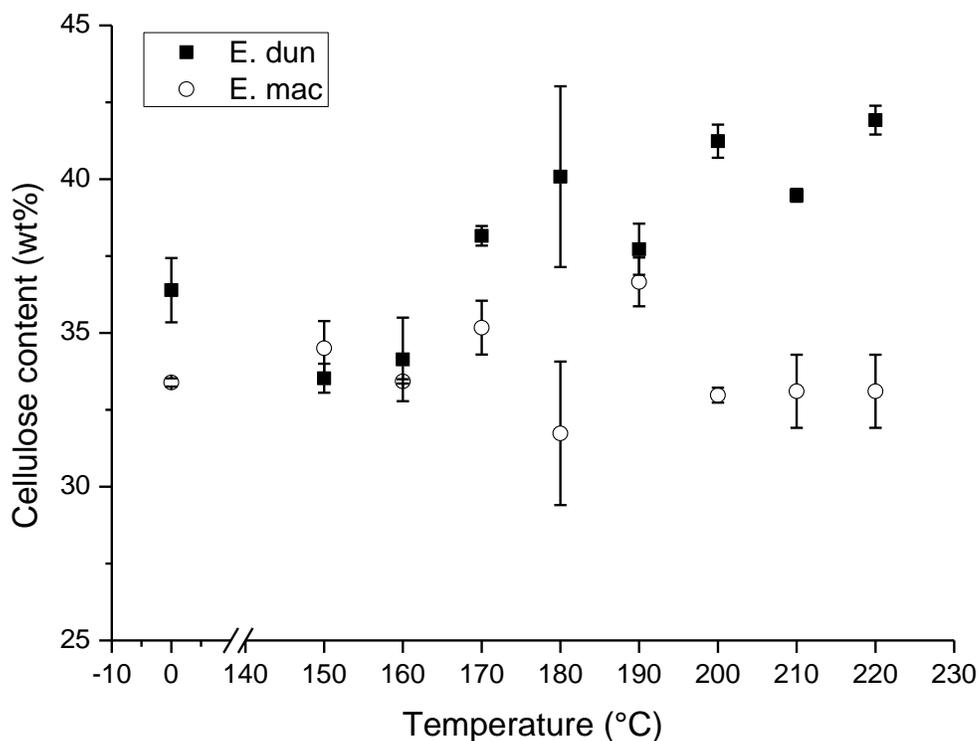

Figure 4-7: Mean alpha cellulose content of *E. macarthurii* and *E. dunnii* after exposure to elevated temperatures the standard deviation

4.7   Summary of chemical analysis

The temperatures in degree Celsius, at which proportion of the analysed chemical components begin to deviate significantly from their original value are listed in Table 4-2. When comparing these results, it can be noted that both species show onset of thermal degradation at temperatures as low as 150°C. However, the extent of degradation does differ.

	E. dunnii	E. macarthurii
Cellulose (increase)	170	NA
Lignin (decrease)	150 and 180	150 and 180
ethanol extractives (decrease)	NA	150
water extractives (decrease)	160	160

Table 4-2: Temperatures (°C) at which the chemical contents of wood deviate from that of untreated wood for *E. dunnii* and *E. macarthurii.*

The hemicellulose content for both *E. dunnii* and *E. macarthurii* were reported as 100% minus the sum of the lignin, cellulose and extractive content. All the components *E. dunnii* of wood are plotted in Figure 4-8. The AIL decreases by 5% while the ASL increases by 2,5% resulting in a net decrease of 2,5%. The ethanol extractive content decreases by 0,3% and the water extractive content decreases by 3%. An increase in cellulose content of 5% may be due to the relative degradation of the extractive and lignin content.
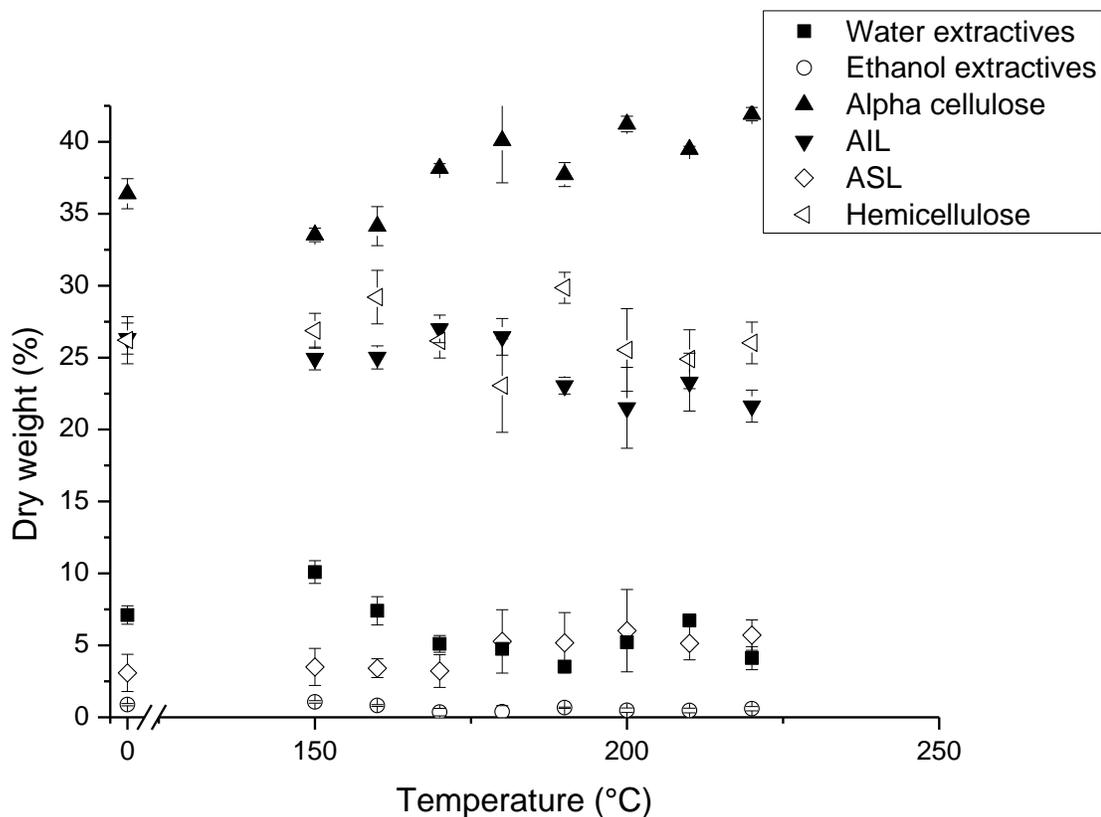
Figure 4-8: The chemical components of *E. dunnii* after exposure to elevated temperatures

Figure 4-9 shows that the AIL of *E. macarthurii* decreases after exposure to 180°C, while the ASL increases, which results in a 1% net increase in lignin content. The water and ethanol extractive content only decrease by 0,5% and 1%, respectively. The hemicellulose and cellulose content of *E. macarthurii* do not change significantly even after exposure to 220°C. The different degradation of cellulose between the two species may be due to difference in degradation of the extractive content and lignin content.
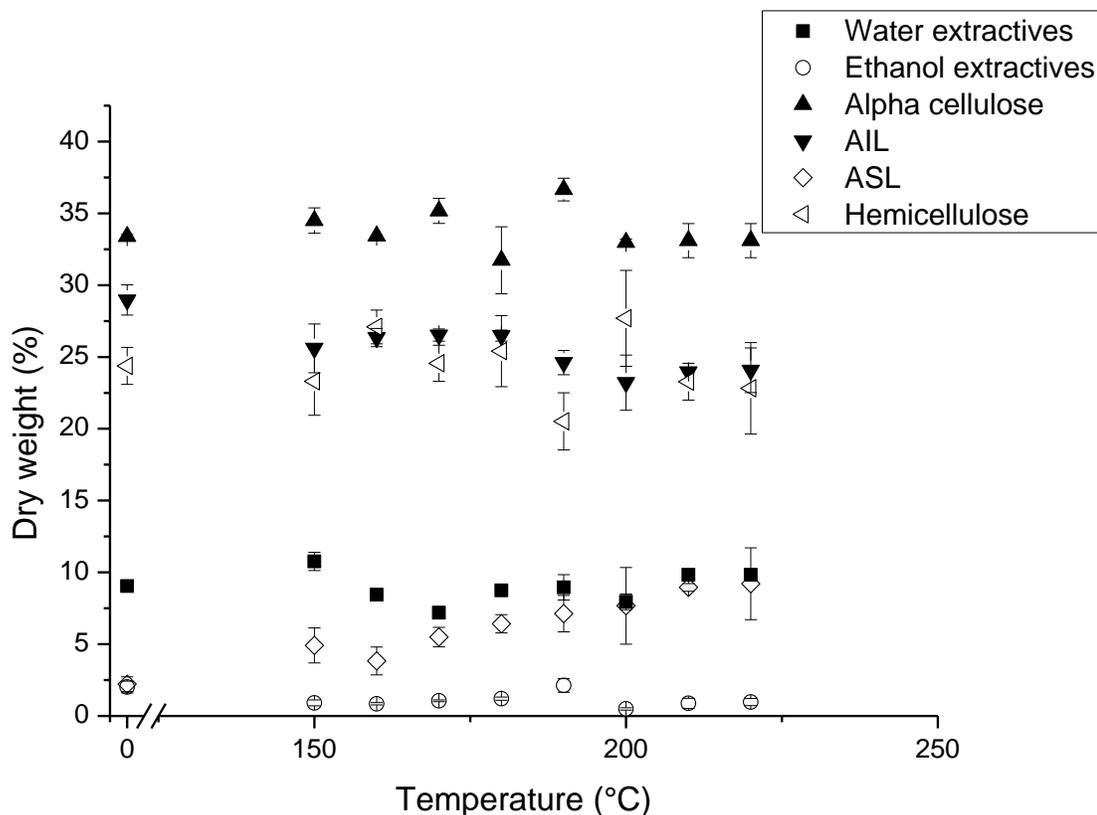
Figure 4-9: The chemical components of *E. macarthurii* after exposure to elevated temperatures

4.8   Thermogravimetric analysis (TGA)

The TGA curves of *E. dunnii* and *E. macarthurii* wood, isolated lignin and isolated cellulose are plotted in Figure 4-10. The isolated cellulose of both species degrades at 350°C and the isolated lignin of both species at 386°C. However, the TGA curves of *E. dunnii* and *E. macarthurii* wood differ. They show two distinct degradation peaks. The first peak can be attributed to the degradation of low molecular weight hemicelluloses. This peak occurs at 278°C for *E. macarthurii* and at 283°C for *E. dunnii*. The second peak can be attributed to the degradation of cellulose and again the peak for *E. macarthurii* is at a lower temperature (338°C) than that of *E. dunnii* (361°C).
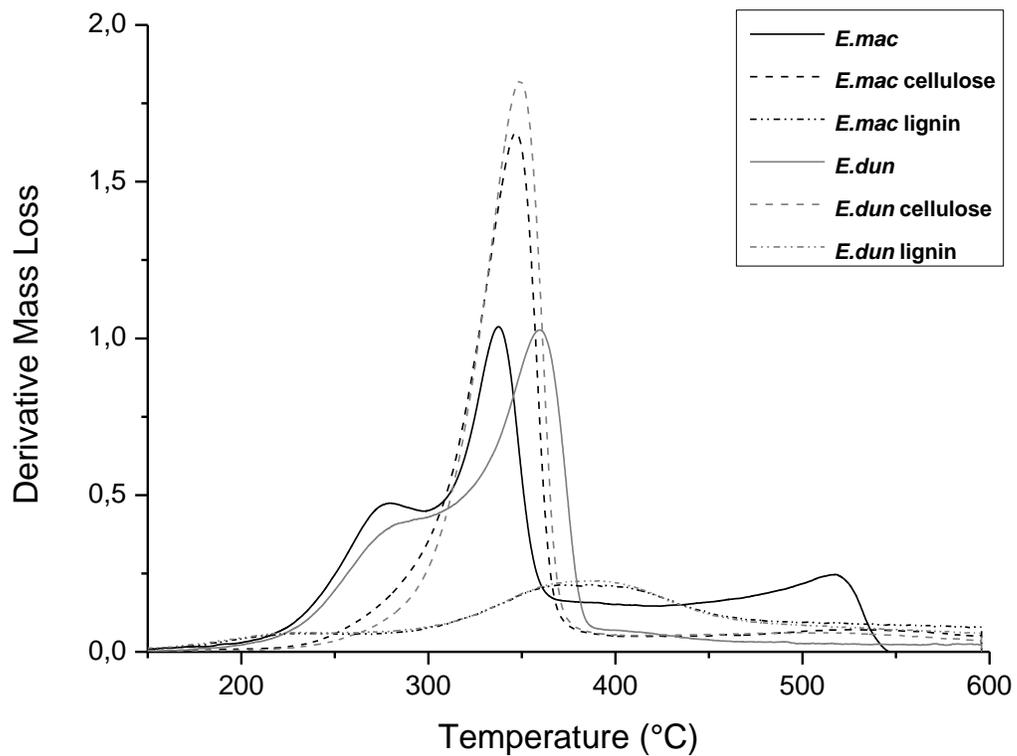
Figure 4-10: Thermogravimetric analysis of *E. dunnii* and *E. macarthurii* wood, isolated lignin and isolated cellulose

In Table 4-3 the degradation temperatures obtained from the TGA curves are summarized, as well the onset temperature, at which the samples begin to degrade. There is little difference between the two species, but *E. dunnii* seems to be somewhat more stable than *E. macarthurii*.

| E. macarthurii | | | | | E. dunnii | | | |
	Onset	Peak 1	Peak 2	Peak 3	Onset	Peak 1	Peak 2	Peak 3
Cellulose	210	348			210	350		
Lignin	150	386			150	386		
Wood	150	278	338	518	170	283	361	

Table 4-3: degradation temperatures (°C) for *E. dunnii* and *E. macarthurii* wood, isolated lignin and isolated cellulose

4.9   Comparison of TGA results and chemical analysis

The TGA curves of alpha cellulose of both species show the same onset of degradation at 210°C and a peak at 348°C for *E. macarthurii* and 350°C for *E. dunnii*.

The increase in alpha cellulose content for *E. dunnii* is probably caused by the degradation of low molecular weight polysaccharides, lignin and extractives, which results in a de facto increase of the weight percentage of alpha cellulose. The fact that the alpha cellulose content does not decrease relative to the other components, means that the overall pulp yield should not decrease after exposure to temperatures below 220°C for less than ten minutes.

The TGA curves of lignin show an onset of degradation at 150°C, which results in a steady decrease with a peak at 386°C for both species. The AI lignin content of *E. macarthurii* and *E. dunnii* begins to decrease at 150°C, but then increases again and reaches a peak at 170°C. The AIL for both species decrease after exposure to temperatures higher than 180°C.

The difference between chemical analysis and the TGA results of isolated lignin for both *E. dunnii* and *E. macarthurii* can be explained by how the lignin degrades relative to the other wood components. The AI lignin initially degrades quickly after exposure to 150°C, as the lower molecular weight lignin degrades. At 170°C the water extractive content of wood decreases by up to 3% for *E. dunnii*. This large decrease in extractive content results in the lignin having a de facto increase after exposure to 170°C. The extractive content continues to decrease until 190°C beyond which it increases again, and the lignin content begins to decrease in response.

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The AS lignin content of both species increases after exposure to 150°C and continues to increase up to 220°C. The AS lignin is the low molecular weight portion of the lignin and an increase of its weight percentage is a result of the molecular weight of the larger lignin molecules being reduced by thermal degradation. The AI lignin content decreases as the MW is reduced and the AS lignin increases as the average MW decreases. The sum of the AI lignin and AS lignin is the total lignin content of the wood, which remains constant even after exposure to 220°C for both *E. macarthurii* and *E. dunnii*.

The TGA curves of untreated *E. macarthurii* and untreated *E. dunnii* wood are different indicating that the thermal degradation of the two species is different. The first difference is the onset of degradation, which begins for *E. macarthurii* at 150°C and for *E. dunnii* at 170°C. The two degradation peaks, assigned to hemicelluloses and cellulose, appear at 278°C and 338°C for *E. macarthurii* and at 283°C and 361°C for *E. dunnii.* In Figure 4-10 *E. macarthurii* has a third degradation peak at 518°C, which may be caused by thermally stable extractives that do not occur in *E. dunnii*.

Overall the TGA curves show that *E. macarthurii* is less thermally stable than *E. dunnii.* This finding is confirmed by the chemical analysis of the untreated wood. *E. macarthurii* has a higher water and ethanol extractive content, as well as lignin content. All of these chemical compounds degrade at temperatures as low as 150°C and as a result *E. macarthurii* wood degrades at a lower temperature. In addition, *E. macarthurii* also has a lower proportion of cellulose that degrades at high temperatures, contributing further to the lower stability of *E. macarthurii* when compared to that of *E. dunnii*.

4.10 Cellulose molecular weight

The molecular weight of cellulose of both species can be seen to decrease after exposure to temperatures as low as 150°C (Figure 4-11). A decrease in MW after exposure to 150°C was also found in a previous study by Shafizadeh (1984). However, contradictory to expectation the MW of both species reaches a low point at 160°C and increases after exposure to170°C.

The lowest MW after thermal exposure was similar for both species at around 155 000 for *E. macarthurii* and 160 000 for *E. dunnii*. These values are close to the average MW of cellulose produced via sulphite pulping, which is typically around 160 000.

The MW of *E. macarthurii* increases again to 235 000 after exposure to 170°C and decreases for higher temperatures, reaching a MW of 220 000 after exposure to 220°C. The MW of *E.*

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dunnii only increases to 173 000 after exposure to 170°C. As the exposure temperature increases The MW of *E. dunnii* continuously increases and reaches a MW of 235 000 after exposure to 220°C, which is just 12 000 less than the MW of cellulose from untreated wood.

A possible explanation for the initial decrease in MW could the scission of cellulose molecules into shorter chains. The scission of cellulose chains continues to occur as the temperature increases, however after 170°C the low MW amorphous cellulose begins to disintegrate, which explains the de-facto increase in average MW after exposure to temperatures above 170°C. The chain scission and disintegration occur simultaneously, but at a varying rate, which explains the different changes in MW after thermal degradation between the two species.

The high initial MW of E. macarthurrii may influence the change in MW. As the larger cellulose chains are cut into smaller parts some of the molecules are still large enough to resist complete disintegration. The amount of lower MW cellulose increases as the high MW cellulose degrades further. The increase in MW of *E. macarthurii* may be caused by the disintegration of lowest MW amorphous cellulose, which disintegrates after exposure to 170°C or higher. After this low MW fraction is degraded the chain scission of the larger MW molecules will have a greater effect and as a result the celluloses average MW decreases.

The gradual increase of *E. dunnii's* MW may be due to a lower initial MW than that of *E. macarthurii*. Lower temperatures are necessary to reduce the MW of *E. dunnii* cellulose before the molecular chains become small enough to degrade completely. This may result in the lowest MW being completely degraded, while higher MW cellulose in the crystalline region degrades at a slower rate, which results in a de facto increase of the MW.

Another possible reason for the increase in MW of the cellulose is that the crystal size influences the degradation temperature of the cellulose. Larger crystals degrade at higher temperatures, which means they resist degradation longer and preserve the MW, while the amorphous cellulose continues to disintegrate. This results in de-facto increase in the cellulose MW, as in the case in *E. dunnii.*

Due to the reduction of MW at 150°C for *E. macarthurii* 1 cm of wood needs to be removed from behind the bark. In the case of *E. dunnii* the wood reaches 150°C 1 cm behind the bark and therefore more than 1 cm needs to be removed. If 2 cm of wood is removed the maximum temperature reached would be around 50°C.

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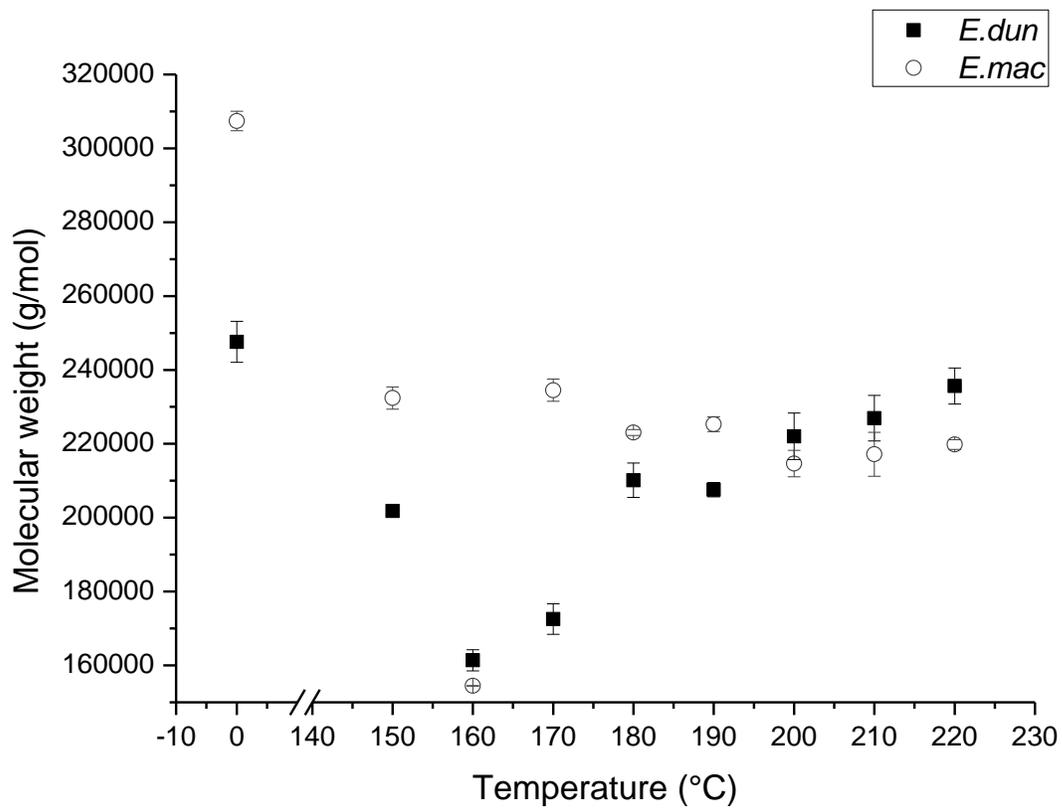
Figure 4-11: Molecular weight of *E. dunnii* and *E. macarthurii* cellulose after heat treatment the standard deviation

4.11 Conclusions

E. macarthurii was generally found to be less thermally stable and showed a larger decrease in cellulose MW and AIL lignin content. However, the differences in thermal degradation observed in this study are not sufficient to recommend *E. dunnii* over *E. macarthurii* for pulp production after thermal degradation.

A decrease in both water and ethanol extractive content could be detected for both species. For *E. macarthurii* the water extractive content decreased from 10.5% to 7.5% of the wood's dry mass. The ethanol extractive content was about 2% lower than the water extractive content and after thermal degradation it decreased to around 0.5%. The extractive content of *E. dunnii* was generally lower than that of *E. macarthurii*. The water extractive content decreased from 7% to 3.5% and the ethanol extractive content decreased from 0.8% to 0.4%. The decrease in extractive content would be beneficial for pulpwood use, as it marginally decreases the amount of chemicals needed for the pulping process.

The total lignin content of *E. macarthurii* remained constant over the temperature range, while the lignin content of *E. dunnii* decreased by 2%. However, when looking at the acid insoluble (AIL) and acid soluble (ASL) lignin content a large change in composition could be observed. The AIL content of *E. dunnii* decreased from 26.5% to 22%, while its ASL content increased from 3 to 5.5%. The AIL of *E. macarthurii* decreased from 29% to 24%, while its ASL increased from 2% to 9%.

After exposure to elevated temperatures up to 220°C the relative mass loss of cellulose was not significant. However, the MW changed significantly even after exposure to fairly low temperatures of around 160°C. The MW of *E. dunnii* was reduced by 35% and that of *E. macarthurii* by 50% after exposure to 160°C.

Pulp produced from the sulphite pulping process typically has a MW of 160 000.The MW of the thermally degraded celluloses was just below 160 000 for both species. If the thermally degraded cellulose were to be pulped, the MW would decrease further as the pulping process also degrades the cellulose to a certain degree. This further degradation may cause the MW to be reduced to such an extent that the properties of pulp are no longer favourable.

In order to recover wood from trees that have been exposed to wild fire, all wood that has been exposed to 160°C or higher should be removed, because the degradation of the cellulose MW is severe from 160°C onwards. The MW of *E. dunnii* is degraded less after exposure to elevated

temperatures and as a result the wood is more suitable for use after exposure to elevated temperatures.

However, a study by Mngomezulu and Meincken (under review) on thermal conductivity of *E. dunnii* and *E. macarthurii* wood found that the bark of *E. macarthurii* insulated the wood better from high temperatures than that of *E. dunnii*. After exposure to 800°C for 10 min the temperature of the wood one cm behind the bark was only raised to 81°C. The bark of *E. dunnii* is less effective at insulating the wood and the temperature of the wood increased to 128°C after exposure to 800°C. For both species the removal of the wood 1cm behind the bark should be sufficient to remove all wood with potential chemical modifications.

However, higher intensity fires can have a temperature as high as 1200°C. If these fires last as long as 10 min the temperature in the wood of *E. macarthurii* would increase to 95°C at a position 1 cm behind the bark and the temperature in the wood of *E. dunnii* can reach 163°C. As a consequence, it is recommended to remove at least 2cm of wood behind the bark in *E. dunnii* trees, if they were exposed to a high intensity fire. Due to the good thermal insulation of the bark, *E. macarthurii* is more suitable for use after a forest fire.

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