Department of Forest Products Technology

Effect of fiber wall chemistry on pulping processes of novel *Eucalyptus* hybrids

Marcelo Coelho dos Santos Muguet Soares

Aalto University

DOCTORAL DISSERTATIONS

Aalto University publication series
DOCTORAL DISSERTATIONS 163/2013

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Doctoral dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the School of Chemical Technology for public examination and debate in Auditorium (Forest Products Building 2) at the Aalto University School of Chemical Technology (Espoo, Finland) on the 15th of November, 2013, at 12 noon.

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Aalto University publication series
DOCTORAL DISSERTATIONS 163/2013

ISBN 978-952-60-5379-0
ISBN 978-952-60-5380-6 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)
http://urn.fi/URN:ISBN:978-952-60-5380-6

Unigrafia Oy
Helsinki 2013

Finland

NORDIC ECOLABEL
441 697
Printed matter

Aalto University

Abstract

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Author
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Name of the doctoral dissertation
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Publisher School of Chemical Technology

Unit Department of Forest Products Technology

Series Aalto University publication series DOCTORAL DISSERTATIONS 163/2013

Field of research Forest Products Chemistry

Manuscript submitted 9 August 2013 **Date of the defence** 15 November 2013

Permission to publish granted (date) 8 October 2013 **Language** English

☐ **Monograph** ☒ **Article dissertation (summary + original articles)**

Abstract

This thesis investigates relevant issues regarding the use of *Eucalyptus* wood: the factors affecting energy consumption during wood defibration, with focus on fiber wall chemistry and the assessment of wood quality from a wide range of novel Brazilian *Eucalyptus* hybrids. The obtained results are reflected to mechanical and traditional chemical processes.

Wood refining experiments were carried out in laboratory scale, with and without chemical pretreatment: alkaline peroxide mechanical pulping (APMP) and thermomechanical pulping (TMP) processes, respectively. The most important finding was the direct influence of the lignin structure on the defibration energy. Especially, the relative contents of the guaiacyl moieties in the wood lignin seem to play a crucial role. The results showed that the higher the amount of guaiacyl structures in the lignin, especially in the middle lamella between the fibers, the higher the specific energy consumption (SEC) in the APMP process. However, for the TMP process the correlation was not as clear. This is most probably due to the fact that in the APMP process the defibration takes place in the middle lamella while in the TMP process other mechanism prevails. However, in the samples with very low amount of guaiacyl structures, SEC decreased substantially also in the TMP process.

A different approach was promoting fiber wall deconstruction via autohydrolysis of wood. The autohydrolysis process changed notably the mechanical properties of the *Eucalyptus* chips, with impressive SEC decrease. Although autohydrolysis was performed under mild temperature (120 ^{o}C), lignin structure was changed. This assumption was based on the characterization of the fiber surfaces via x-ray photoelectron spectroscopy (XPS). Results showed high coverage of the fiber surfaces with lignin, indicating that the defibration of autohydrolyzed *Eucalyptus* wood chips takes place along the middle lamella. This behavior differs from the traditional thermomechanical pulping, where the rupture occurs mostly in the fiber wall (especially in the S1 layer), being similar to chemimechanical processes.

As a final step, traditional kraft pulping was performed, alongside with soda-anthraquinone (NaOH-AQ) pulping, with focus on the surface properties of the produced fibers, analyzed by SEM and XPS. The surface lignin content of NaOH-AQ pulp fibers was lower than that of the kraft counterpart. However, kraft pulp handsheets showed better physical and mechanical properties. XPS data (C2/C3 ratio) strongly suggested, together with the pulp bulk chemical composition that xylan is more abundant on the surface of kraft fibers, probably enhancing their mechanical properties.

Keywords Chemical Pulping, *Eucalyptus* Hybrids, Fiber Wall, Mechanical Pulping, Surface Properties, Wood Deconstruction, Wood Chemistry, Wood Quality

ISBN (printed) 978-952-60-5379-0 **ISBN (pdf)** 978-952-60-5380-6

ISSN-L 1799-4934 **ISSN (printed)** 1799-4934 **ISSN (pdf)** 1799-4942

Location of publisher Helsinki **Location of printing** Helsinki **Year** 2013

Pages 126 **urn** http://urn.fi/URN:ISBN:978-952-60-5380-6

"Nature is a language and every new fact one learns is a new word; but it is not a language taken to pieces and dead in the dictionary, but the language put together into a most significant and universal sense. I wish to learn this language, not that I may know a new grammar, but that I may read the great book which is written in that tongue"

Ralph Waldo Emerson

PREFACE

This study was carried out at the Department of Forest Products Technology at Aalto University, School of Chemical Technology during 2010-2013. The work was performed as a part of the DEFIBRE and E-Wood projects, funded by the Academy of Finland and Aalto University, respectively.

I am thankful to Professor Tapani Vuorinen for giving me the opportunity to work in his group under his supervision, and for giving me the freedom to pursue my own ideas. I am most indebted to Dr. Anna-Stiina Jääskeläinen, for being the responsible person for my coming to Finland, and for all her contribution in this work. I am also most indebted to Dr. Kyösti Ruuttunen, for adopting an orphan Ph.D. student, for being active in enhancing all aspects of this research, and last but not least, for sharing the magical moments on the stage.

I would like to thank PUU professors Sixta, Laine, Rojas and Österberg for providing high-quality courses, which contributed enormously to my formation and this work. Dr. Eero Kontturi is also thanked for the scientific discussions and fun times during work trips.

I will always be indebted to Professor Jorge Colodette, who taught me the basis of pulp and paper research, always believed in my potential and continued being active in advising me and my studies, even after my departure from Viçosa.

Co-authors of the papers, Leena-Sisko Johansson and Fernando Gomes are thanked for their contribution to the research and the resulting publications.

All the colleagues and staff of PUU are highly thanked for creating a smooth atmosphere at work. All the current and old members of Teh Band are highly thanked for the joyful moments we had during rehearsals and gigs (Once in Teh Band, always in Teh Band).

Special thanks go to the Brazilian friends in Finland, Juan, Ander, Tiago, Bruno, Fabrício, who besides making me not forget Portuguese completely, would create that special home atmosphere, sharing the laughs, homesickness, and barbecues. Valeu!

My special gratitude goes to some special people. Michael, Miro, Mao, Michi, Anne, Lotta. You guys know what you all mean to me, and I am very thankful to have met all of you. In addition, Mao, it is hard to explain how grateful I am for all the arrangements you have done since we first had contact until now. Michael, all the time spent together outside work, that 1.m.r. at the gym, serious talks, and “generous” nicknames and greetings every day, will be impossible to replace. Miro, all the moments shared during your stay, epic eurotrips, and all other moments will be remembered forever.

I have to also thank all my friends from home, Vinícius, Bruno Vital, Hélio, Cid, Igor, Yuri, Leandro, Walanem, Gabriel, Vítor, Vicente, …. You gave me the energy to recharge my batteries every single vacation I spent with you, giving me that extra strength to keep up with my life away from home. Valeu galera, tamo junto!!

Finally, I am deeply thankful for having such a great Family. There are no words to describe how thankful I am to my mother, Elizabete, who raised me alone through tough times, giving me the best education, showing me the values to be followed, and always understanding how important every choice I made was, even if it meant to be away from her for such long time. Mãe, eu te amo !!!! I also thank my father, Fábio, for giving me the best 9 years of my life, and for now taking care of me from a VIP spot. Saudades!!! I also thank all my relatives, for always wanting my success and for understanding my absence in very important times.

Espoo, October 7th, 2013

Marcelo Muguet

LIST OF PUBLICATIONS

This thesis is mainly based on the results presented in four publications which are referred as Roman numerals in the text. Some additional unpublished data is also related to the work.

Paper I	Muguet, M.C.S., Colodette, J.L., Jääskeläinen, A.-S. (2012) Alkaline peroxide mechanical pulping of novel Brazilian *Eucalyptus* hybrids. *Bioresources* 7(3), 3823-3836.
Paper II	Muguet, M.C.S., Ruuttunen, K., Jääskeläinen, A.-S., Colodette, J.L., Vuorinen, T. (2013) Thermomechanical pulping of novel Brazilian *Eucalyptus* hybrids. *Holzforschung* 67(5), 489-495.
Paper III	Muguet, M.C.S., Ruuttunen, K., Jääskeläinen, A.-S., Colodette, J.L., Vuorinen, T. (2013) Defibration mechanisms of autohydrolyzed *Eucalyptus* wood chips. *Cellulose* 20(5), 2647-2654.
Paper IV	Muguet, M.C.S., Gomes, F.J.B., Ruuttunen, K., Johansson, L.-S., Jääskeläinen, A.-S., Colodette, J.L., Vuorinen, T. (2013) Pulping-tailored fiber properties from a novel Brazilian *Eucalyptus* hybrid. *Holzforschung*, DOI: 10.1515/hf-2013-0114.

Author's contribution to the appended joint publications:

I, II, III, IV	Marcelo Muguet was responsible for the experimental design, performed the main part of the experimental work, analyzed the corresponding results and wrote the manuscripts.

LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
AH	Autohydrolysis
AHQ	Anthrahydroquinone
AQ	Anthraquinone
APMP	Alkaline peroxide mechanical pulping
CTMP	Chemithermomechanical pulping
DP	Degree of polymerization
DTPA	Diethylene triamine pentaacetic acid
EDTA	Ethylene diamine tetraacetic acid
FTIR	Fourier transform infra-red
G	Guaiacyl lignin
GPC	Gel permeation chromatography
H	*p*-hydroxyphenyl lignin
HPAEC	High performance anion exchange chromatography
M_n	Number-average molar mass
M_w	Weight-average molar mass
PAS	Photoacoustic detection
S	Syringyl lignin
SEC	Specific energy consumption
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
Tg	Glass transition temperature
TMP	Thermomechanical pulping
TRS	Total reduced sulfur
XPS	X-ray photoelectron spectroscopy

TABLE OF CONTENTS

1 INTRODUCTION AND OUTLINE OF THE STUDY

Brazil has a large territorial area (851.5 million ha of land) and has exploited very little of its large biomass production capacity. The forests cover more than half of the Brazilian territory, but only 6.5 million ha (0.8%) is comprised of planted forests (IBGE, 2009). The Brazilian planted forests are dominated by *Eucalyptus* (75%) and *Pinus* (25%) (ABRAF, 2012). *Eucalyptus* is becoming the most important fiber source for papermaking worldwide. The major interest in *Eucalyptus* wood comes from its low production cost in certain regions, mainly because of high forest productivity. In addition, the increased understanding of its application in various paper grades made *Eucalyptus* the preferred fibers worldwide (Magaton et al. 2009).

Around twenty years have passed since the first experiments in genetic mapping and molecular breeding of forest trees. Significant progress has been achieved and the gathered knowledge prompted some short term opportunities for the incorporation of genomic analysis in tree genetics and breeding. The most important program in Brazil is the Genolyptus project (Brazilian Network of *Eucalyptus* Genome Research), a joint governmental and industry partnership initiative. This initiative is based on the generation of a suite of biological and information resources to discover, sequence, map, validate, and understand the underlying variation of genes and genomic regions of economic importance in *Eucalyptus.* This information can be used to optimize growth, wood formation, wood composition and disease resistance (Grattapaglia, 2004, Grattapaglia and Kirst, 2008). The driving principle is that there is ample genetic variation within the genus *Eucalyptus* to allow profound genetic modification of the current planting stock in Brazil, especially in terms of wood properties.

Brazilian breeders are investing on the potential of hybridizing *Eucalyptus globulus* with already established *Eucalyptus* species in Brazil. Due to the fact that *E. globulus* is suited to more temperate climate, this species does not grow particularly fast in Brazil. However, its germplasm supply stands out as a very rich source of genetic variation for all the target wood traits, such as maximum fiber length, adequate wood density and the highest content of carbohydrates among all planted *Eucalyptus* species, as well as the most easily removable lignin.

This thesis investigates relevant issues regarding the use of *Eucalyptus* wood by: verifying the effect of the novel hybrids' wood quality in mechanical and chemical pulping processes, with main focus the chemistry of fiber wall. And additional objective is providing a feedback on the wood behavior of the novel hybrids, which is of great importance to the *Eucalyptus* breeding initiative.

In this study, six novel *Eucalyptus* hybrids derived from the Genolyptus program were used. The initial part (**Papers I** and **II**) deals with mechanical pulping with and without chemical pretreatment: alkaline peroxide mechanical pulping (APMP) and thermomechanical pulping (TMP) processes, respectively. The main focus was on understanding the influence of fiber wall chemistry on the energy consumption during the processes.

An alternative approach was to promote fiber wall deconstruction via autohydrolysis of wood (**Paper III**). The idea behind this part of the work was to study the fundamentals of the defibration mechanisms within a process that can be suitable for current biorefineries.

Finally, traditional kraft pulping was performed, alongside with NaOH-AQ pulping (**Paper IV**). The main reason was to study the behavior of one novel *Eucalyptus* hybrid for chemical pulping process. Furthermore, the focus was on how the wood polymers behave during the processes, in special, the polymers located on the surface of the fibers.

In general, this thesis presents fundamental approach on wood polymers behavior in various pulping systems. The gathered knowledge herein could be useful for different areas, ranging from *Eucalyptus* breeding and wood quality, to uses in pulp mills.

2 BACKGROUND

2.1 Wood ultrastructure and chemistry

Wood has its special place in the history of mankind due to its vast uses, ranging from burning to produce heat, construction, and paper, up to its components being used in nanotechnology applications. Wood can be defined as a natural fibrous composite, formed by semi-crystalline cellulose microfibrils, embedded in a lignin-hemicellulose matrix. Such structure constitutes the wood fibers, which are wood cells that have no longer physiological activity, and have lost their cytoplasm and its organelles. A hierarchical scheme of wood structure is shown in Fig. 1.

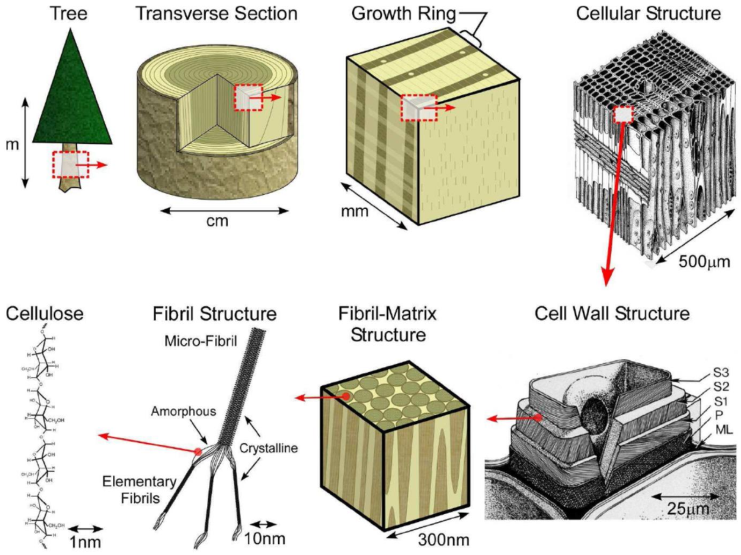


Fig. 1. *Hierarchical structure of wood (Moon, 2008).*

Wood fibers are constituted of the cell wall, which can be simply divided into primary (P) and secondary wall (S). The primary wall is rich in hemicelluloses, pectin, protein and lignin. The secondary wall is divided in three layers: the outer layer (S1), the middle layer (S2) and the inner layer (S3), as illustrated in Fig. 2. The wood cell wall consists mostly of carbohydrates (cellulose and hemicelluloses) and lignin. The middle lamella, comprised mostly of lignin and a small amount of pectin, is located between adjacent cells and its role is to bind the cells together (Alén, 1999a), Cellulose is the structural cell wall component, forming the microfibrils, while hemicelluloses and lignin form a “cement matrix” to glue them, giving rigidity to the cell wall.

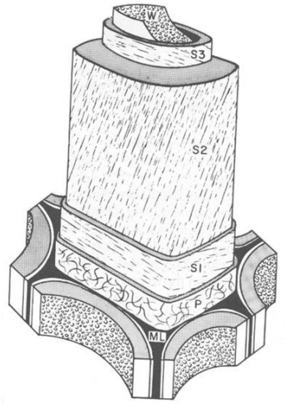


Fig. 2. *Model of fiber wall structure (Côté, 1967).*

2.1.1 Cellulose

Cellulose is the most abundant polymer in the world. It is estimated that about 10^{11} to 10^{12} tons of cellulose are synthesized annually by photosynthesis (Klemm et al. 2002). Cellulose is constituted only of β-D- glucopyranosyl units, linked to each other by 1-4-glycosidic bonds (Fig. 3). With the β-D-link, the every second anhydroglucose unit is twisted, creating a glucose dimer. This dimer is called cellobiose, which is the actual repeating unit of the cellulose polymer. The degree of polymerization (DP) of cellulose varies among species. When cellulose aggregates during the microfibril biosynthesis, crystalline structures are formed, however, some regions stay in disordered form, referred to as amorphous cellulose (Fig. 1 - Fibril structure).

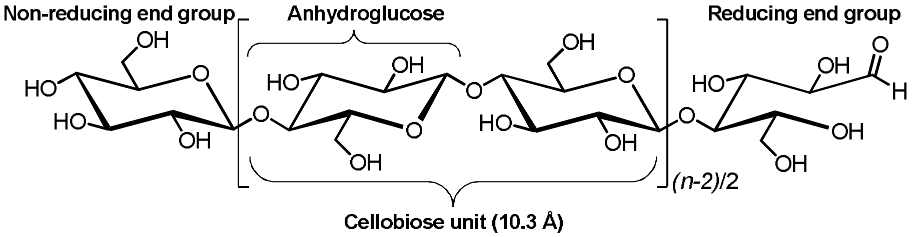


***Fig. 3.** Cellulose structure. The n (DP) refers to the number of anhydroglucose units linked together forming one cellulose chain.*

2.1.2 Hemicelluloses

The main hemicellulose found in *Eucalyptus* wood is xylan. The intrinsic structure of xylan exhibits a (1 → 4) linked β-*D*-xylopyranosyl backbone, with various monomeric side groups or short oligosaccharide chains attached randomly to O-2 and/or O-3 of the xylopyranosyl residues, depending on the species. The structure of xylan in Brazilian *Eucalyptus* (*E. urophylla x E. grandis*) has been previously elucidated (Fig. 4) (Magaton et al. 2008). Xylan present in the aforementioned *Eucalyptus* wood contains one 4-O-methyl-glucuronic acid (MeGlcA) substituent and 5.5 acetyl groups for approximately 10 xylose residues. The xylan is composed of the following structural elements: 51 % unsubstituted, 12% 2-O-acetylated, 20% 3-O-acetylated and 6% 2,3-di-O-acetylated xylose residues and 11% 3-O-acetylated xylose units with α-D-

MeGlcA linked with a glycosidic bond to position O-2. The weight-average molar mass and polydispersity of this xylan were 34.9 kDa and 1.16, respectively (Magaton et al. 2008).

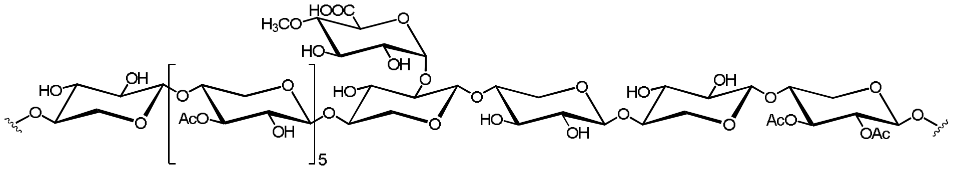


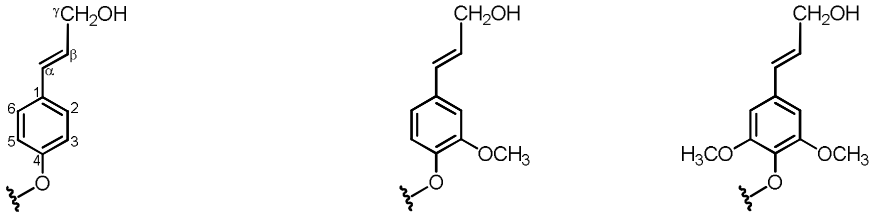
Fig. 4. *Partial chemical structure of Eucalyptus xylan (Adapted from Magaton et al. 2008).*

A minor part of hemicelluloses in *Eucalyptus* wood is comprised by glucomannan. The amount of glucomannan in *Eucalyptus* wood is *ca.* 1-3% (Duarte et al., 2012, Sixta and Rutkowska, 2007, Evtuguin and Pascoal Neto, 2007) and its backbone is comprised of β-D-Glc*p* and β-D-Man*p* structural units of molar ratio 1:1.3 linked by β-(1→4) linkages.

2.1.3 Lignin

Lignins are complex racemic aromatic heteropolymers derived mainly from three hydroxycinnamyl alcohol monomers, differing in their degree of methoxylation: *p*-coumaryl, coniferyl and sinapyl alcohols. These monolignols produce, respectively, *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) phenylpropanoid units when incorporated into the lignin polymer (Boerjan et al. 2003). In *Eucalyptus* species, lignin is comprised mainly of syringyl units, followed by guaiacyl, and show traces of *p*-hydroxyphenyl residues (Rencoret et al. 2008). Syringyl unit shows two methoxyl groups in the position 3 and 5, while guaiacyl structure has only one methoxyl group in the position 3 (Fig. 5).

These structures are located in different regions within the wood. Syringyl lignin is mainly located along the fiber wall's primary and secondary layers, whereas guaiacyl lignin is mostly located in the middle lamella (Musha and Goring, 1975). The validity of this finding was also shown for *Eucalyptus* wood (Watanabe et al. 2004).



p-hydroxyphenyl (H) **Guaiacyl (G)** **Syringyl (S)**

Fig. 5. *Main lignin precursors with varying degree of methoxylation.*

In *Eucalyptus* species, the most important linkages between the lignin monomers are shown in Fig. 6A-F: (A) β-O-4' linkages (most abundant); (B) resinol formed by β- β', α-O-γ', and γ-O-α'; (C) phenylcoumarane structures formed by β-5', α-O-4' linkages; (D) spirodienone structures formed by β-1', α-O-4' linkages; (E) C_α-oxidized β-O-4' linkages and (F) *p*-hydroxycinnamyl alcohol terminal unit.

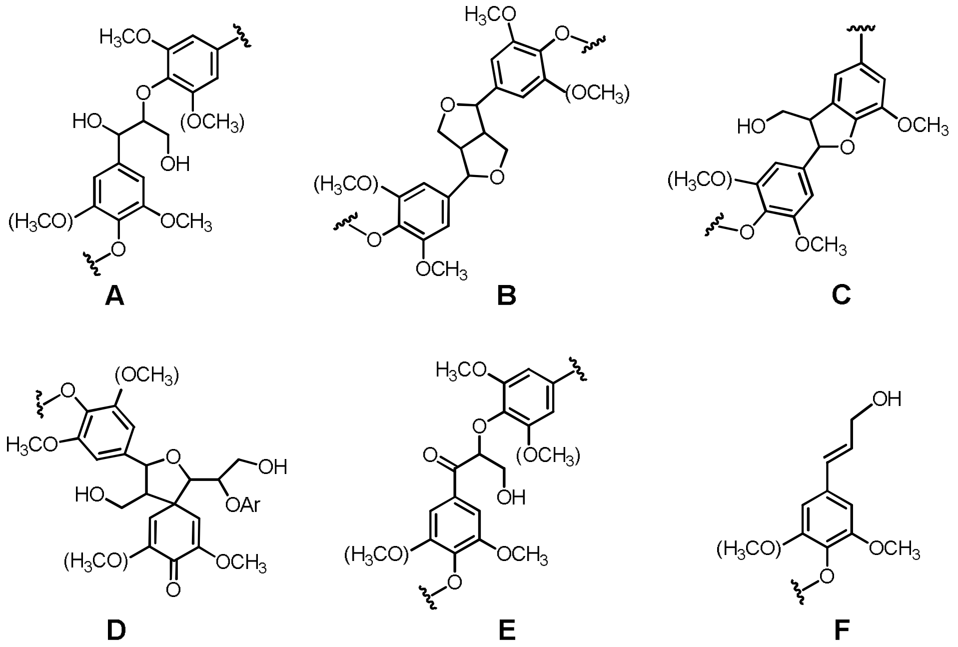


__Fig. 6.__ Lignin main structures observed in Eucalyptus wood (Adapted from Rencoret et al. 2008).

2.2 Wood pretreatments

The concept of value prior to pulping (VPP) is based on utilization of partially or completely extracted hemicelluloses for biofuel production (van Heiningen, 2006). In order to render the process feasible, biomass pretreatment technologies are necessary. These pretreatments (chemical, physical or biological) alter/eliminate structural and compositional constraints to improve hydrolysis rate and increase yield of fermentable sugars from carbohydrates (Carvalheiro et al. 2008). Hemicelluloses surge as an interesting polymer to be removed from wood and further processed.

Various wood pretreatments for the enhancement of hemicelluloses extraction can be found in literature, such as alkaline treatments (NaOH, alkaline peroxide, ammonia fiber explosion, ammonia recycling percolation), acid hydrolysis (concentrated and diluted) as well as hydrothermal (autohydrolysis and steam explosion) (Carvalheiro et al. 2008). Amongst these pretreatments, autohydrolysis is the main technique used for hemicellulose extraction in the pulp industry, especially for dissolving pulp production. Autohydrolysis studies started as early as in the 1940's (Overbeck and Muller, 1942) and this technique consists of the treatment of wood with water at elevated temperatures and pressures (Colodette et al. 2011).

Autohydrolysis is based on the depolymerization of hemicelluloses by hydronium ions (H_3O^+). At first stage, dissociation of water is the only source of hydronium ions. These ions selectively hydrolyze glycosidic bonds, acetyl groups and uronic acids. In a second stage, hydronium ions come from dissociation of acetic acid, acting like a catalyst, and increasing the reaction rate. It has been shown that the contribution of hydronium ions from acetic acid is higher than from water auto-ionization (Heitz et al. 1986). Acids resulting from hydrolysis of acetyl and uronic groups, originally present in hemicelluloses, catalyze hydrolysis of links between hemicelluloses and lignin as well as hydrolysis of carbohydrates. Autohydrolysis products are a mixture of oligosaccharides, monosaccharides, acetic acid, furfural and hydroxymethylfurfural (Carvalheiro et al. 2008).

2.3 Mechanical pulping processes

The purpose of mechanical pulping processes is to separate the fibers from the wood matrix, hopefully in a form suitable for a specific furnishing process (Lönnberg, 2009). Mechanical pulping can be thought to involve two main phases: (1) defibration or fiber separation, where the wood matrix is softened, and the separation of fiber bunches and single fibers begins; (2) fiber development, where the wood fibers start to be disintegrated with the main effects of delamination and internal fibrillation (Fernando and Daniel, 2008, Fernando et al. 2011, Fernando et al. 2012).

High refining energy consumption is a key factor limiting the utilization of wood mechanical pulping (Browne et al. 2001). Chemical pretreatment of wood chips and the application of enzymes have been shown already to reduce energy consumption during refining (Area et al. 1995, Cort and Bohn, 1991, Hart et al. 2009a, Hart et al. 2009b, Xu, 2002, Xu et al. 1996, Xu and Sabourin, 1999). In addition, the energy demand can be decreased by reducing raw materials variability (Dundar et al. 2009) or by changing the spout angle of wood chipper (Hellström et al. 2011). Other factors have been shown to decrease the energy demand, such as decreasing discharge consistency from the primary refiner, on a double-stage refiner (Alami et al. 1997), increasing refining temperature/pressure (Muhíc et al. 2010), and compressing chips prior to refining (Gorski et al. 2010). Earlywood and latewood fractions of wood also have been shown to affect the process energy demand (Lanouette et al. 2010).

This thesis is focused on mechanical processes at high temperatures, such as thermomechanical pulping (TMP) and chemically-pretreated processes such as alkaline peroxide mechanical pulping (APMP).

TMP process involves the refining of fresh-cut wood with no pretreatment at temperatures of 130 ^{o}C or more. However, for *Eucalyptus*, only two processes are suitable for high brightness paper grades and packaging: alkaline peroxide mechanical pulping (APMP) and alkaline sulfite mechanical pulping (CTMP) (Xu and Sabourin, 1999).

The APMP process is an interesting pulping method for *Eucalyptus* woods; being especially suitable for making high-brightness papers, since the wood chips can be fully bleached prior to refining (Cort and Bohn, 1991). Due to its oxidant nature, hydrogen peroxide carboxylates lignin. Furthermore, the easy ionization of the carboxylic acids turns lignin softer, which results in easier defibration. As an example, residual lignin in *Eucalyptus* chemical pulps has been found to be carboxylated in C_α (Ibarra et al. 2007).

The APMP process has several pre-treatment stages prior to the actual defibration. In the first one, chelants, such as DTPA or EDTA are used to remove metals. The removal of metal ions is necessary, especially manganese, which decomposes hydrogen peroxide (Qiu et al. 2003). The process presents high flexibility in processing wood of variable qualities and delivers fibers of higher density, tear, and tensile strength when compared to CTMP fibers (Xu and Sabourin, 1999). The chemical pretreatments are performed in order to alter the properties of the lignin contained in the middle lamella.

2.3.1 Defibration mechanisms

There is a significant amount of data available concerning *Eucalyptus* mechanical pulp production (Area et al. 1995, Area et al. 1998, Area et al. 2007, Area and Kruzolek, 2008, Browne et al. 2001, Cort and Bohn, 1991, Jones and Richardson, 2000, Jones and Richardson, 2001, Ognar and Xu, 1998, Xu et al. 1996, Xu, 2002, Xu and Sabourin, 1999). However, the high amount of energy demand during mechanical pulping is a key limiting factor for the process feasibility (Browne et al. 2001). Therefore, understanding the defibration mechanisms is necessary.

Glass transition temperature (Tg) is a characteristic of viscoelastic behavior of amorphous materials. At temperatures below the transition, the viscoelastic material is stiff and brittle. In the transition region the stiffness decreases and at higher temperatures, the material exhibits rubber-like elasticity (Aklonis et al. 1972). The lignin Tg has a direct influence on the defibration. At temperatures below the lignin Tg, the cell wall can be considered as consisting of largely tangentially oriented lamellae of two zones, each of which has both hard and soft components (Fig. 7). This means that the fibers consist mainly of crystalline cellulose (stiff and 'hard' segments) and the amorphous cellulose and hemicelluloses (as 'soft' segments), which is surrounded by a matrix of 'hard' lignin. Each zone is incompletely softened, and the overall fracture modulus of the wood remains high (Irvine, 1985). That is the case of the TMP process, where the lignin as the main component of the middle lamella, remains hard, whereas the rest of the cell wall is more softened. In this case, the defibration takes place mostly in the segment between the primary wall and the S1 layer of the secondary fiber wall. However, in chemi-mechanical processes, such as CTMP and APMP processes, where wood is treated with chemicals before defibration, the lignin properties are altered in such a way that the softening temperature is lowered. This leads to improved defibration, which takes place mostly in the middle lamella (Franzén, 1986).

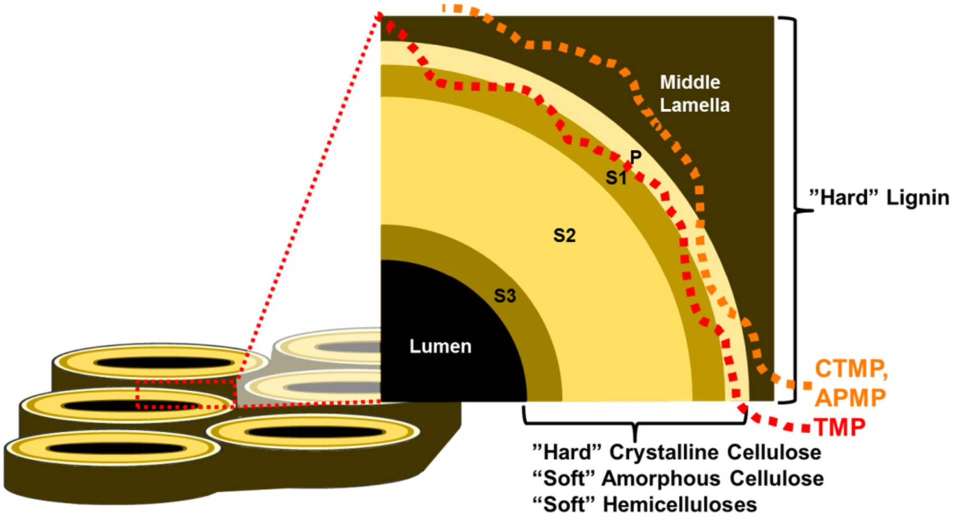


Fig. 7. *Fiber transversal cut model showing the different polymers characteristics, with focus on the rupture point taking place during various mechanical processes. TMP process causes rupture on the primary wall and S1 layer of the secondary wall, whereas CTMP and APMP processes causes rupture mostly in the middle lamella (Adapted from Franzén, 1986).*

2.3 Chemical pulping processes

Chemical pulping is a process where the fibers are isolated from wood with the use of chemicals, often accompanied with high temperature and pressure. Such chemicals aim mainly the lignin located in the middle lamella, however, as wood is a tight-formed composite, the carbohydrates suffer to some extent. There are several types of chemical pulping processes; however, alkaline pulping comprises the majority of the commercial pulp production nowadays. The kraft process accounts for 73.3% of all chemical pulping process and 55.5% of all types of pulps produced globally (FAO, 2011).

2.3.1 Carbohydrate reactions during alkaline chemical pulping

Alkaline chemical pulping aims at the dissolution of lignin present in the middle lamella, in order to isolate the wood fibers. However, due to its high alkali charge coupled with high temperature and pressure, the carbohydrate fraction suffers to some extent. The main carbohydrates reactions under alkaline media are: peeling reactions (primary and secondary), stopping reactions and glycosidic bonds cleavage (Rydholm, 1965).

Peeling reactions

Peeling is the most important reaction taking place in the carbohydrate fraction of wood. It can cause extreme yield losses during pulping process (Alén, 1999b). These reactions take place exclusively in reducing end of carbohydrates, starting at temperatures *ca.* 100 ^{o}C. Primary peeling takes place on natural occurring reducing end groups, whereas secondary peeling is related to reducing end groups formed after random glycosidic bond cleavage, which will be discussed later. Peeling reactions involve five subsequent steps (Fig. 8): Isomerization (A), enediol formation (B), β-alkoxy elimination (C), tautomerization (D) and benzilic acid rearrangement ($E_{a\text{-}g}$ – mechanism described).

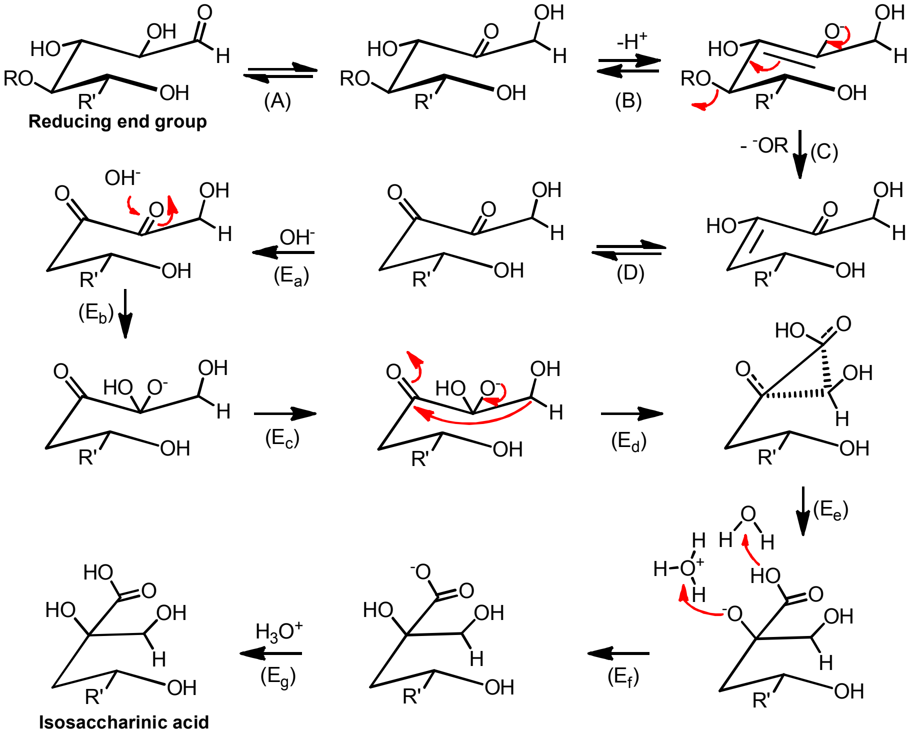


Fig. 8. *Mechanism of cellulose (R'= CH$_2$OH) and hemicellulose (R'= H) peeling reactions (Rydholm, 1965).*

The initial step is the isomerization (A) of a reducing end group to a 2-keto intermediate, followed by β-alkoxy elimination (B-C), leading to a shortened carbohydrate chain with a new reducing end group. The eliminated monosugar is tautomerized (D) to a diketone, which will form (E) either glucoisosaccharinic acid (from cellulose) or xyloisosaccharinic acid (from xylan).

Stopping reactions

Peeling reactions proceed until the introduction of a terminal deoxyaldonic acid group. The presence of the carboxylic acid group prevents the carbohydrate chain against further peeling (Alén, 1999b). The stopping reactions involve four subsequent steps (Fig. 9): enediol formation (A), β-hydroxy elimination (B), tautomerization (C) and benzilic acid rearrangement ($D_{a\text{-}g}$ – mechanism described).

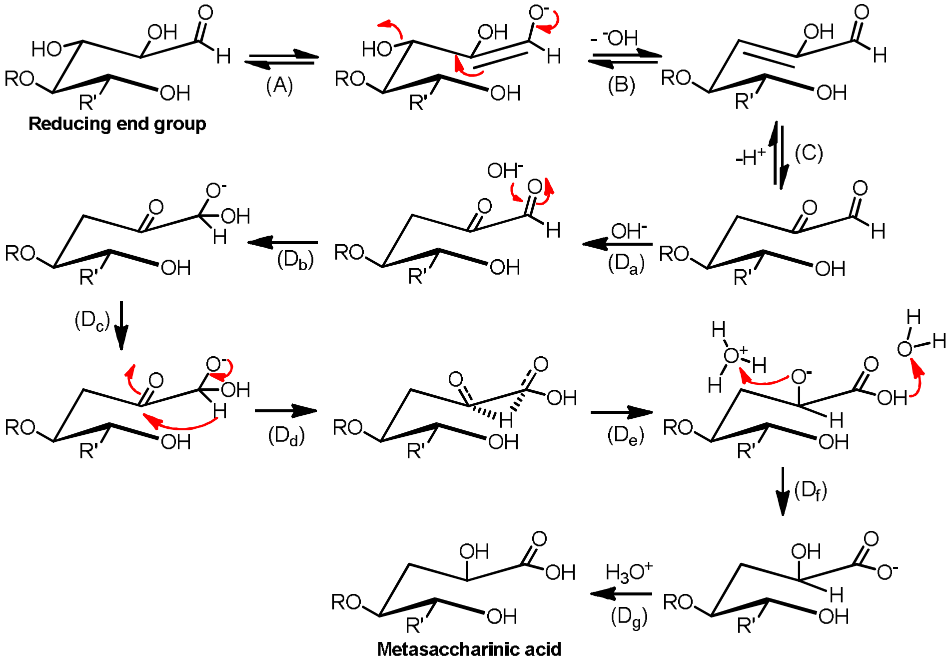


Fig. 9. *Mechanism of cellulose (R'= CH_2OH) and hemicellulose (R'= H) stopping reactions (Franzon and Samuelsson, 1957).*

The reaction is initiated with a β-hydroxy elimination (A-B-C) directly from the reducing end group, without previous isomerization. The diketone is further converted into metasaccharinic acid via benzilic acid rearrangement. Differently from peeling reaction, the formed acid remains attached to the carbohydrate chain.

Glycosidic bond cleavage

Besides primary peeling reactions, alkaline hydrolysis of the glycosidic bond within the carbohydrate chains starts at high temperatures (160-170 °C) in a relatively slow fashion (Alén, 1999b). The reaction involves four subsequent steps (Fig. 10): Inversion of ring conformation (A), C1 attack by ionized hydroxyl groups, forming epoxide (B), opening of epoxide forming a new reducing end group (C-D).

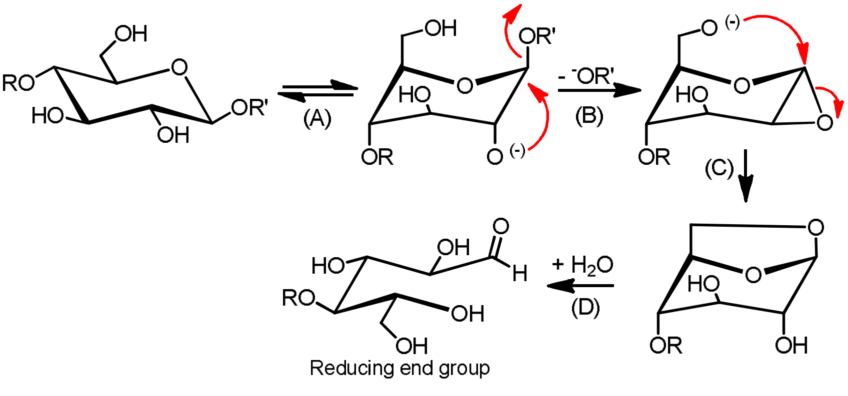


Fig. 10. *Mechanism of glycosidic bond cleavage reactions in cellulose (R= rest of chain on the left; R'= rest of the chain on the right) (Samuelsson et al., 1953).*

Glycosidic bond cleavage takes place randomly in the carbohydrate chains, and has a definite effect on the decrease of molar mass. With the creation of new reducing end groups, peeling reactions start taking place, referred to as secondary peeling reactions.

2.3.2 Hemicelluloses behavior during alkaline chemical pulping

Besides peeling, stopping and glycosidic bond cleavage, other important reactions and other phenomena occur specifically on hemicelluloses, such as deacetylation, hexenuronic acid (HexA) formation, dissolution and resorption onto pulp fibers.

Xylan, the most important hemicellulose in *Eucalyptus* wood, is strongly modified during the chemical pulping process. Firstly, around 50% of xylan is degraded or become soluble in the cooking liquor, by losing part of their molecular weight, due to primary and secondary peeling reactions. Two studies involving this characterization (Magaton et al. 2011, Pinto et al. 2005a) obtained similar results, in which xylan retained almost half of its molecular weight.

Furthermore, xylan has an interesting different behavior during wood delignification, when compared to glucomannan (Wigell et al. 2007). Xylan has a linear yield drop with increasing delignification, while glucomannan show a hyperbolic decay in yield. Although the yield loss of glucomannan is significant during initial delignification, they show to be more stable than xylan when wood is intensively delignified.

Part of the xylan's uronic acid side groups are converted to hexenuronic acid groups (HexA) during alkaline chemical pulping (Fig. 11) (Daniel et al. 2003, Vuorinen et al. 1999, Simão et al. 2005).

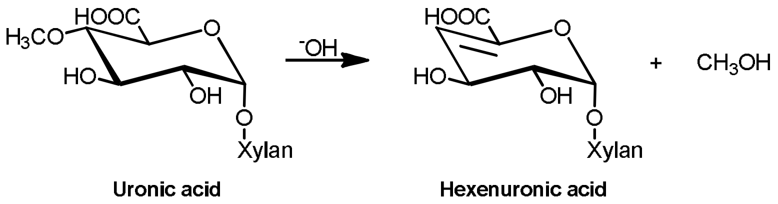


Fig. 11. *Formation of hexenuronic acid during alkaline pulping (Buchert et al., 1995).*

This conversion is thought to have a retarding effect towards alkaline peeling reactions (Jiang et al. 2000), as well as the original uronic acids (Magaton et al. 2009). At high temperatures and strongly alkaline conditions, HexA that was initially formed starts to decompose slowly (Johansson and Samuelson, 1977, Gustavsson and Al-Dajani, 2000). Part of these uronic acids and other substituents, such as acetyl groups are lost as the cooking progresses (Pinto et al. 2005a).

Another point to be raised is that a significant part of xylan is dissolved as a polymer during initial delignification, and during the final part of the cook, this xylan tends to resorb onto the fibers (Aurell, 1963, Aurell, 1965, Danielsson and Lindström, 2005, Danielsson and Lindström, 2009, Hansson and Hartler, 1969, Muguet et al. 2011, Yllner and Enström, 1956, Yllner and Enström, 1957). This phenomenon is affected by many factors, such as hydroxyl ion concentration (pH), ionic strength, temperature and concentration and degree of substitution of xylan.

2.3.3 Kraft *versus* NaOH-AQ pulping

The kraft process is dominant for *Eucalyptus* wood pulping and the resulting fibers are largely used for printing and writing (P&W) and tissue paper grades. Its hegemony in the world is due to the fact that the kraft process produces pulp of high strength, uses any type of biomass and possesses a highly developed chemical recovery technology. The current technology for the recovery of the kraft pulping chemicals, NaOH and Na_2S, with the Tomlinson furnace is very efficient (Bose et al. 2009). However, the ratio between the power and steam production with the current technology is less than desirable. The use of the black liquor gasification technology instead of the Tomlinson furnace would improve this ratio but the presence of sulfur in the black liquor makes the implementation of gasification difficult.

Most modifications of the kraft process have been aimed at improving the yield and the properties of the pulp produced. AQ has been used as an additive in soda and kraft pulping processes due to improved delignification rate and protection of cellulose and hemicelluloses chains against peeling reactions. Anthraquinone acts by oxidizing the reducing end groups in carbohydrates, forming carboxylic acid groups, which stabilize the carbohydrates against peeling reactions. The reduced form of AQ, anthrahydroquinone (AHQ) subsequently depolymerizes lignin, regenerating AQ (Fig. 12) (Sixta, 2006). The benefits of using AQ in *Eucalyptus* kraft pulping have been proven by many authors (Bose et al. 2009, Kanungo et al. 2009, Francis et al. 2008).

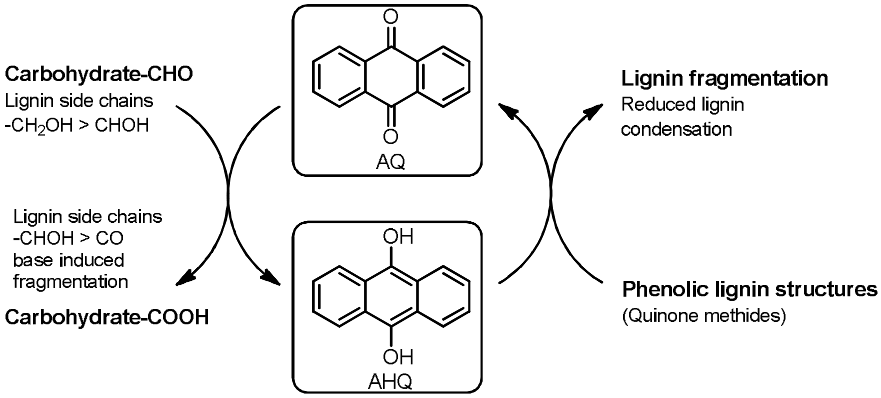


Fig. 12. *General scheme of AQ redox mechanisms (Sixta 2006).*

Emissions of total reduced sulfur compounds (TRS) in a kraft pulp mill have been an environmental concern, due to their corrosive nature and odor at trace concentrations. When generated during pulping, TRS compounds are liberated from the digester together with steam. The formation of these compounds depends on the sulfidity (ratio between Na_2S and total alkali), pulping time and pulping temperature (Andersson and Bergstrom, 1969, Andersson, 1970, Biasca, 1998, Blain, 1998, Chai et al. 1998). Decrease in TRS compounds' emissions has been obtained by reducing pulping sulfidity (Chai et al. 2000, Gomide and Oliveira, 1981, Leduc et al. 2003, Santiago and Pascoal Neto, 2008). Use of low or zero sulfidity with addition of AQ is an alternative to reduce pollutant emission without decreasing delignification efficiency (Silva et al. 2002). For that, NaOH-AQ process surge as an interesting alternative. NaOH-AQ process is similar to Kraft-AQ process, with the exception of not using sulfur compounds (Na_2S). Such process has additional benefits by reducing TRS emission, simplifying the recovery process, and allowing gasification technology to be utilized for chemicals recovery and power generation.

2.4 Effect of hemicelluloses on pulp and paper properties

Hemicelluloses are the second most abundant class of carbohydrates in the fiber besides cellulose. They have lower a DP compared to cellulose, are amorphous and branched. Annergren et al. (1963) stated that the quantity, instead of the chemical nature of hemicellulose seems to determine the paper properties. Molin and Teder (2002) affirmed that pulps with high hemicellulose content have an increased tensile strength, but bonding strength between fibers is not affected. However, other studies state that xylan deposited on kraft pulp fibers increase both the tensile and the bonding strength (Muguet et al. 2011, Schönberg et al. 2001, Sihtola and Blomberg, 1975, Sjöberg et al. 2002).

Some hemicelluloses have ionic carboxylate groups, which increase swelling of fibers. This results in a higher fiber's specific surface with more potentially reactive sites and better flexibility and conformability, increasing the bonding of fibers (Eriksson and Sjöström, 1968, Laine et al. 1997). Dahlman et al. (2003) studied the molecular properties of hemicelluloses located in the inner and surface layers of hardwood and softwood pulps. They concluded that the content and M_w of the hemicelluloses on the surface of the fiber are higher, indicating that these parameters could serve as a predictor of strength and bonding ability of the fibers. Muguet et al. (2011) stated that hemicelluloses can act as a stress-transfer matrix. Kim et al. (1975) suggested that hemicelluloses in fibers allow cellulose fibrils to flow and self-organize in a better way when fibers are dried, and this straightens dislocations and other potential weak spots. Hemicelluloses also diminish energy consumption during pulp beating, leading to economical savings, due to their high hydrophilicity (Muguet et al. 2011). Bhaduri et al. (1995), studying ramie hemicelluloses as a beating additive concluded that the additive helped to reach improved strength properties of the pulp with less energy, thereby reducing the time of the beating operation. Strength properties, such as tensile index, folding endurance and burst index of paper sheets with the additive were also improved significantly.

2.5 Fiber surface properties

Surface properties are of great importance for fiber products, since strength development is partially related to the interface phenomena between fiber surfaces. Fiber surface properties can be analyzed by different methods, *e. g.*, XPS, Raman and FTIR spectroscopy, contact angle measurement, AFM, SEM, TEM, and others. The fiber surface characteristics are important especially for bonding ability, which has great influence on properties of the fiber network. A study characterizing the fiber surface and the inner layer materials from softwood pulps produced by different processes demonstrated significant differences in surface lignin and hemicellulose contents between the pulps investigated (Sjöberg et al. 2002). In particular, the quantity of xylan in the surface layer depended highly on the pulping process, with kraft pulps exhibiting the highest surface content (>30% higher than that of the inner layers of the fibers). High xylan contents in the fiber surface layers of softwood kraft pulps have also been found by several investigators (Dahlman et al. 2003, Kibblewhite and Brookes, 1976, Sjöberg et al. 2002, Sjöberg et al. 2004). Furthermore, the surface lignin content (as defined by the method used) is much higher than the average for unbleached softwood kraft pulp (>2 times higher) (Sjöberg et al. 2002). Sjöberg et al. (2002) evaluated the relationship of surface lignin and hemicellulose contents of kraft pulp fibers taken at different stages during ECF and TCF bleaching. The authors found that the surface layers of fibers revealed greater chemical changes by bleaching operations, when compared to inner layers. Furthermore, a positive correlation between tensile index and the hemicellulose content of the fiber surface was found.

3 EXPERIMENTAL

This chapter describes the material, the main experimental approach and the analytical tools used in this study. More detailed description can be found in Papers I – IV. The colors applied in the schemes (Fig. 14, Fig. 15, Fig. 16, Fig. 17) correspond to the colors used in the respective papers.

3.1 Material

Six different hybrids of Brazilian-grown *Eucalyptus* trees were in focus. These hybrids are from the Brazilian Network of *Eucalyptus* Genome Research – Genolyptus, a nationwide network of laboratories and forestry companies devoted to an integrated molecular breeding approach (Grattapaglia, 2004). The codes were given by the Genolyptus team, and are based on the original species crossing (Table 1).

Table 1. *Code assignment for the novel Eucalyptus hybrids.*

Code	Hybrid name
REF	*E. grandis* x *E. urophylla*
U1xU2	*E. urophylla* x *E. urophylla*
U2xGL1	*E. urophylla x E. globulus*
DGxGL2	*[E. dunnii x E. grandis] x E. globulus*
G1xUGL	*E. grandis x [E. urophylla x E. globulus]*
DGxU2	*[E. dunnii x E. grandis] x E. urophylla*

Wood chipping and chemical characterization was performed at the Pulp and Paper Laboratory, Federal University of Viçosa, Brazil, and the chips were sent to the Department of Forest Products Technology, Aalto University. The chips were stored in polyethylene bags throughout the whole study.

3.2 Methods

The main methods carried out in this thesis were mechanical and chemical pulping processes of *Eucalyptus* wood chips, with further pulp characterization. The detailed principles of these methods are described here. Details of other methods are presented in Papers I-IV and references presented here.

3.2.1 Wood and pulp characterization

Wood density was evaluated according to TAPPI standard method (T258 om-06). The carbohydrate composition was analyzed by HPAEC after acid hydrolysis following the procedure described by Wallis et al. (1996). Klason and acid soluble lignins were measured according to Gomide and Demuner (1986) and Goldschimid (1971), respectively. Total lignin content was defined as the sum of Klason and acid soluble lignin as described by Dence (1992). Lignin syringyl/guaiacyl ratio (S/G) was evaluated according to Lin et al. (1992) and the guaiacyl lignin content was calculated taking into account the S/G values and total lignin content of the wood samples. Total uronic acids and acetyl groups were evaluated according to Scott (1979) and Solar et al. (1987), respectively. Hexenuronic acid content was evaluated according to Vuorinen et al. (1999). Wood characterization results are presented in Table 2.

Table 2. *Chemical and physical characterization of the Eucalyptus hybrids investigated. All percentages are based on dry wood.*

		Abbreviation of *Eucalyptus* hybrids					
Composition, Properties		REF	U1xU2	U2xGL1	DGxGL2	G1xUGL	DGxU2
Carbs (%)	**Glucans**	50.7	48.0	46.8	46.8	46.2	46.6
	Xylans	12.3	12.4	13.7	13.2	13.6	12.9
	Others	2.5	1.7	2.3	1.4	2.1	2.2
Lignin (%)	**Klason**	23.6	26.8	24.3	24.4	25.4	26.2
	A.Sol.	4.3	4.5	5.8	4.5	5.0	4.5
	Total	27.9	31.3	30.1	28.9	30.4	30.7
S/G ratio		2.8	3.0	4.0	3.0	3.1	2.7
Guaiacyl (%)		7.4	8.0	6.1	7.2	7.4	8.3
Acetyl groups (%)		2.0	2.1	2.7	2.6	2.9	2.6
Uronic acids (%)		4.1	3.8	4.1	3.9	4.0	4.1
Density (kg/m^3)		480	504	506	489	500	496

3.2.2 Mechanical processes

Mechanical defibration was carried out on 100 g o.d. chip samples in a wing defibrator (Fig. 13), consisting of four static blades; the refining gap between the blades and the inner refiner wall was ~2.5 mm in Paper I and ~1.0 mm in Papers II and III. Other parameters: *ca.* 750 rpm, at *ca.* 37-43% consistency, 130 °C, and variable refining times. Prior to the refining experiments, three runs with empty refiner (target of 50 Wh pulses) were performed in order to quantify the energy consumed by the refiner itself. This energy value is discounted when calculating the specific energy consumption (S.E.C.) of the wood samples (*Eq. 1*).

Eq. 1 $$S.E.C.(MWh/odt) = \frac{P-((50\ Wh/t_r) \text{ x } t_w)}{m}$$

where:

P = Number of pulses needed for wood sample, Wh
t_r = Average time with empty refiner for 50Wh energy need, min
t_w = Time of wood chips refining, min
m = oven dried mass of wood chips, g

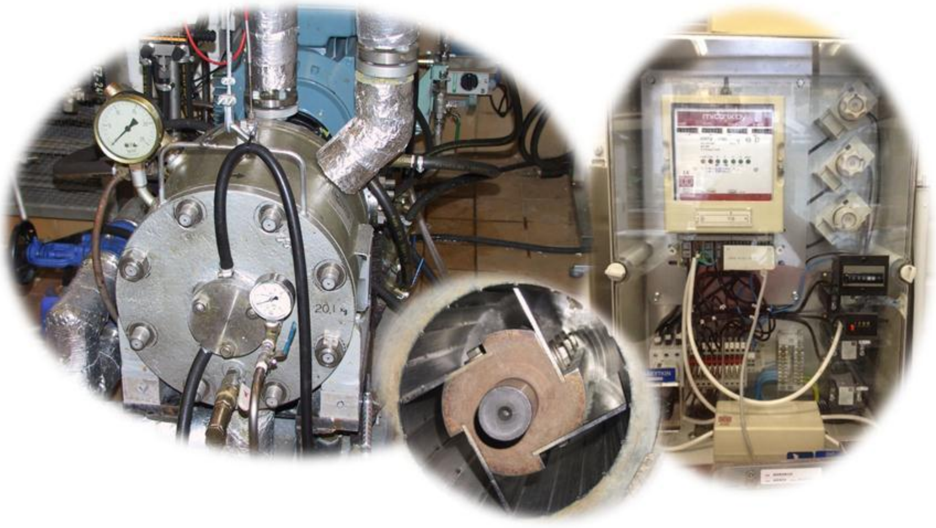


Fig. 13. *Wing defibrator. Left side, a general view; middle, a close up on the inner part, as well as the blades setup; right side, a close up on the energy measuring device.*

The chips were pre-heated with steam inside the refiner for 5 min, and the condensate was released before the refining process started. Pulps were screened with a slot screener of 0.17 mm and tested for Canadian Standard Freeness (ISO 5267-2:2001). In the next section, the pretreatments prior to refining will be discussed.

Alkaline peroxide mechanical pulping (Paper I)

The APMP process was carried out with a pre-vaporization stage of 20 minutes and a double-stage chemical impregnation (Fig. 14). The first impregnation stage consisted of the application of NaOH and DTPA. It was carried out in a press apparatus that works with a compression force of *ca*. 14 MPa. After the chips were squeezed, the chemicals were added and thereafter, the pressure was released, so that the chemicals penetrated the chips. The chelation stage was run at 25 °C, for 20 minutes, with a liquor-to-wood ratio (L/W) of 4:1 l/kg. The liquor was then pressed out of the chips and collected for further analyses. The second impregnation stage consisted of the application of alkaline hydrogen peroxide and stabilizers. It was carried out following the same pressing procedure as of the first stage. The treated chips were transferred in a plastic bag and placed in a warm bath, under 60 °C, for 60 minutes, and an L/W ratio of 4:1 l/kg. The liquor was then pressed out of the chips and collected for further analyses. After pressing, the chips were at *ca.* 43% consistency. Subsequently, the chips were mechanically defibrated.

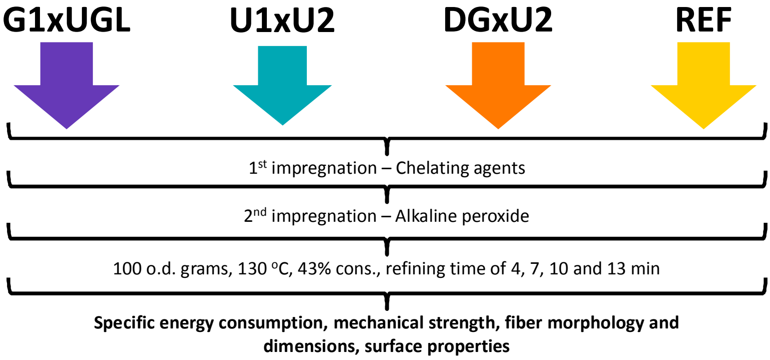


Fig. 14. *Simplified scheme of the APMP experiments (Paper I).*

Thermomechanical pulping (Paper II)

The wood chips were impregnated with deionized water in a rotating digester (Fig. 15). To ensure complete saturation of the chips, 10 bar of pure oxygen was inserted into the digester, for 5 h, at 4 l/kg liquid-to-wood ratio and 25 °C. Then, the chips were removed from the digester and rested for at least 48 h under room temperature and atmospheric pressure. Thereafter, the chips were mechanically defibrated.

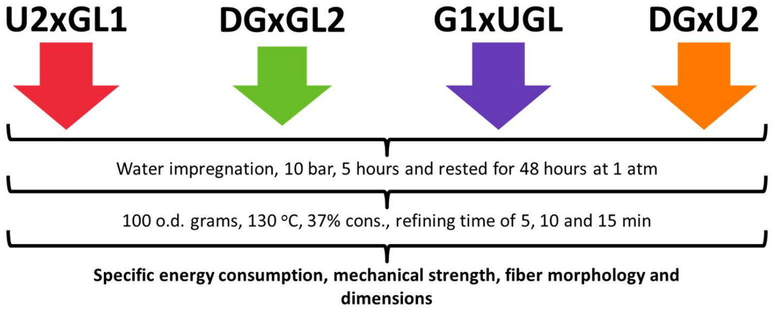


Fig. 15. *Simplified scheme of the TMP experiments (Paper II).*

Autohydrolysis (Paper III)

Autohydrolysis was carried out with 500 o.d. grams of chips in a rotating digester (Fig. 16). The reaction temperature was 120 ^{o}C, and such a low temperature was chosen in order to minimize the changes in the lignin structure. 4 l/kg liquid-to-wood ratio, time-to-temperature was 60 minutes and time-at-temperature varied accordingly to the pre-defined P-factors (200, coded as AH-200 and 800 coded as AH-800). P-factor describes the intensity of the autohydrolysis treatment, being analogous to the H-factor concept used for pulping (Sixta, 2006). After the autohydrolysis stage, the spent liquor was collected and gravimetric yield was determined for the solid material. The reference for this part was the same pulp as in Paper II.

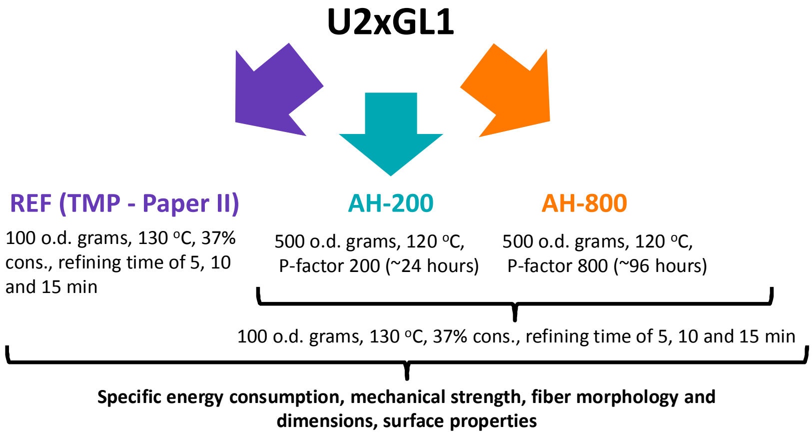


Fig. 16. *Simplified scheme of the autohydrolysis experiments (Paper III).*

3.2.3 Chemical processes (Paper IV)

Kraft and NaOH-AQ processes were chosen for the chemical pulping experiments (Fig. 17). The pulping experiments were carried out in an M&K digester with 2 individual reactors of 10 liters each, equipped with a forced liquor circulation system, electrical heating with temperature and pressure control. The conditions applied in the pulping experiments are presented in Table 3.

Table 3. *Conditions applied in the chemical pulping experiments.*

Parameters	Kraft	NaOH
Akali charge (% on wood)	Variable	Variable
Liquor-to-wood ratio (l/kg)	4:1	4:1
Sulfidity (% on wood)	26	-
Anthraquinone (% on wood)	-	0.05
Maximum temperature (°C)	170	170
Time to temperature (min)	90	90
Time at temperature (min)	50	50

Several cooking experiments were performed using different active alkali charge to establish the delignification curve (kappa number *versus* active alkali). After the determination of the delignification curve, samples of pulp with kappa number 15 were prepared. The kappa number 15 pulp samples were refined in a PFI mill, with four different revolutions levels, aimed at *ca.* 200 ml freeness, according to TAPPI methods (T248 sp-00).

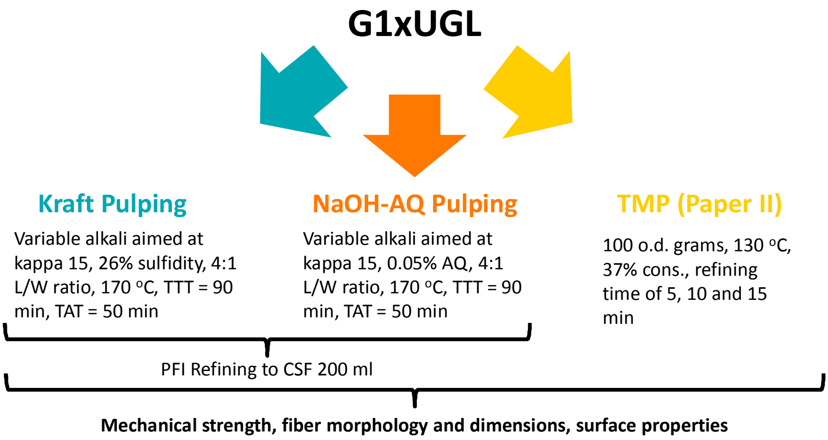


Fig. 17. *Simplified scheme of the chemical pulping experiments (Paper IV).*

2.3.4 X-ray photoelectron spectroscopy (XPS)

The fundamental experiment in XPS involves exposing the sample to a flux of monochromatic x-ray radiation with mean *hv,* and observing the resultant emission of photoelectrons in an image detector (Fig. 18) (Fadley, 1978).

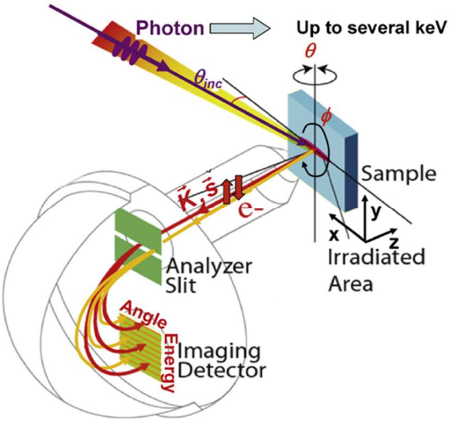


Fig. 18. *Scheme of a typical configuration for XPS experiments (Adapted from Fadley, 2010).*

XPS measurements process can be divided into three steps: (1) penetration of the exciting photon beam into the surface, with some resulting intensity profile (x, y, z) and the coordinates (Fig. 18) and excitation of photoelectrons from each atom in the sample that are located at various depths z (2) transport of the photoelectron from depth z to the surface (3) escape from the surface, which involves refraction and reflection at the surface barrier. Such measurements have been found to reveal a broad array of phenomena that can be used to characterize a given material, in particular the near-surface regions of solids from which most photoelectrons are emitted (Fadley, 2010). The kinetic energies are simply described by *Eq. 2*.

$$\text{Eq. 2} \quad hv = E_b^v(k) + E_{kin}$$

where:
hv = *characteristic energy of the ejected photoelectron*
$E_b^v(k)$ = *binding energy of the* k^{th} *level, as referred to vacuum level*
E_{kin} = *photoelectron kinetic energy*

XPS is a well-known surface characterization technique for wood fiber materials (Johansson and Campbell, 2004, Laine et al. 1994). The core of XPS methods for pulp and paper research lies in carbon analyses (Johansson, 2002). Carbon analyses are of great importance when characterizing fibers surfaces, which will be discussed more specifically further in this thesis.

XPS measurements: A Kratos Analytical AXIS 165 electron spectrometer with a monochromatic A1K$_{\alpha}$ X-ray source was used to analyze the elemental and chemical compositions of the fiber surfaces. The XPS experiments were performed on dry handsheet samples, alongside with a cellulose reference sample. The relative amounts of carbon and oxygen were determined from C1s, O1s signals from low-resolution scans. The high resolution C1s spectra were curve-fitted for further chemical analysis, as described by Johansson et al. (2004).

3.2.4 Other methods

Fiber dimensions

Fiber suspensions of 0.2% were prepared and 1ml was used for each measurement. The measurements were performed with a FiberLab analyzer (Metso Automation, Finland). Fiber length, width, fibrillation index, curl index and amounts of fines are the main results.

Gel permeation chromatography (GPC)

Molar mass distribution of pulps was determined by GPC. The samples were activated by a water – acetone – *N,N*-dimethylacetamide (DMAc) sequence prior to the analyses. The activated samples were dissolved in 90 g/L lithium chloride containing DMAc at room temperature under gentle stirring. The samples were then diluted to 9 g/L LiCl/DMAc, filtered with 0.2 µm syringe filters, and analyzed in a Dionex Ultimate 3000 system with a guard column, four analytical columns (PLgel Mixed-A, 7.5 x 300 mm) and RI-detection (Shodex RI-101). The flow rate and temperature were 0.750 ml/min and 25 °C, respectively. Narrow pullulan standards (343 Da - 2500 kDa, PSS GmbH) were used to calibrate the system. The data were obtained and processed using the Chromeleon software (Dionex, USA).

Handsheets preparation and evaluation

Handsheets were prepared using squared sheet formers according to ISO 5269:1:2005. The sheets were air dried overnight. Subsequently, the sheets were tested for grammage (ISO 536:1995), density (ISO 534:1988), tear strength (ISO 1974:1990, Elmendorf method), tensile index (SCAN-P38) and optical properties (ISO 2470:1999).

Fourier transform infrared spectroscopy with photoacoustic detection (FTIR-PAS)

The spectra were collected using a Bio-Rad FTS 6000 spectrometer (Cambridge, MA) with a MTEC 300 photoacoustic detector (Ames, IA) at a constant mirror velocity of 5 kHz, 1.2 kHz filter, and 8 cm^{-1} resolution. First, a background spectrum with standard carbon black was measured. After collecting the background spectrum, the wood or paper sample was put into a detection cell that was placed into the PAS detector. A minimum of 200 scans were collected and processed using the Win-IR Pro 3.4 software (Digilab, Randolph, MA) Each spectrum taken was normalized to have the same value at 1200 cm^{-1}.

Scanning electron microscopy (SEM)

SEM micrographs were obtained with TM-1000 scanning electron microscope (Hitachi, Japan). The samples were sputtered with gold and the micrographs were taken in secondary electron imaging mode.

4 RESULTS AND DISCUSSION

The most important findings of this thesis are summarized in this chapter. The complete results are presented in the attached Papers I-IV.

4.1 Mechanical pulping processes

In this thesis, three mechanical pulping processes were evaluated: APMP (Paper I), TMP (Paper II) and autohydrolysis followed by TMP – AH-TMP – (Paper III). The main reason was to study the effect of the fiber wall chemistry in chemical, non-chemical and hydrothermal systems, respectively APMP, TMP and AH-TMP. The blades' setup of the wing refiner was changed after Paper I (blades-wall gap ~2.5mm→~1.0mm), which means that comparisons of absolute values of the results between Paper I and Paper II/III may be misleading. For that reason, only trends will be used by means of comparison.

For the APMP experiments, the hybrids G1xUGL, U1xU2, DGxU2 and REF were chosen. Following the APMP results (Paper I), the chosen hybrids for the TMP experiments (Paper II) were U2xGL1, DGxGL2, G1xUGL and DGxU2, due to similarities in chemical composition, except for the lignin structure (S/G ratio). Furthermore, with basis on the TMP results, the hybrid U2xGL1 was chosen for the AH-TMP experiments (Paper III).

4.1.1 Wood refinability

High refining energy consumption is a key factor limiting the utilization of wood mechanical pulping. It is worth noting that the refiner used in this study, based on blades, consumes more energy than pilot scale or industrial disc refiners (Jones and Richardson, 2000, Jones and Richardson, 2001, Xu and Sabourin, 1999). It was assumed that, at least as an approximation, the energy applied with the wing refiner will be proportional to the energy promoting changes to the fibers.

To illustrate the differences in refinability, all the results from all hybrids were plotted together in Fig. 19, revealing high correlation indices for sheet density, tensile index, and tear index with freeness.

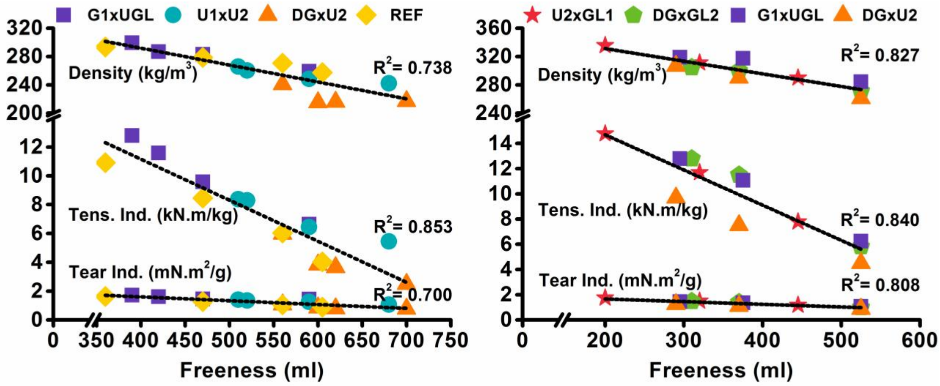


Fig. 19. *Sheet density, tensile index, and tear index vs. freeness for all Eucalyptus hybrids pulp samples. Left: APMP; Right: TMP.*

Both APMP and TMP followed the same trends. This indicated that with more intensive refining, poorly refinable hybrids could achieve similar properties to their refinable counterparts, despite the type of process. However, this would require more energy for the refining process. Some studies have confirmed the fact that differences in wood quality impact negatively on the refining process and pulp quality (Dundar et al. 2009, Jones et al. 2005), but as the hybrids do not show eminent differences among themselves regarding absolute chemical composition, such differences might be related to the wood ultrastructure and/or the fiber wall polymer structure.

4.1.2 Effect of lignin structure

Lignin plays an important role during the defibration of wood. Lignin present in the middle lamella has a higher softening temperature than the whole fiber wall matrix, which contains mainly carbohydrates (Irvine, 1985). In this case, if lignin structure is not altered, the rupture point during the mechanical process is along the fiber wall. That is the case in the TMP process, where the temperature is not high enough to soften the lignin present in the middle lamella. However, when wood is chemically-pretreated prior to refining, lignin structure is altered, so that the fiber wall turns to be stiffer than the lignin matrix, which would result in a rupture point along the middle lamella. This can be exemplified by results found for the G1xUGL hybrid (Table 4). The closer value of APMP fibers to wood fibers surface coverage suggests some rupture taking place along or close to the middle lamella, whereas lower values of TMP suggest a rupture along the fiber wall.

Table 4. *Fiber surface concentration analyzed by XPS of different chemical fractions in early stages of defibration (APMP – 3 minutes, TMP – 5 minutes).*

G1xUGL	Wood fibers	APMP	TMP
Lignin (%)	42.1	30.9	24.1
Carbohydrates (%)	30.8	65.0	73.4

Fiber wall delamination during TMP process could be seen by SEM micrographs of the G1xUGL hybrid (Fig. 20). This is an indication of defibration taking place in the fiber wall in the TMP processes, as previously reported (Fernando and Daniel, 2008, Fernando et al. 2011, Fernando et al. 2012).

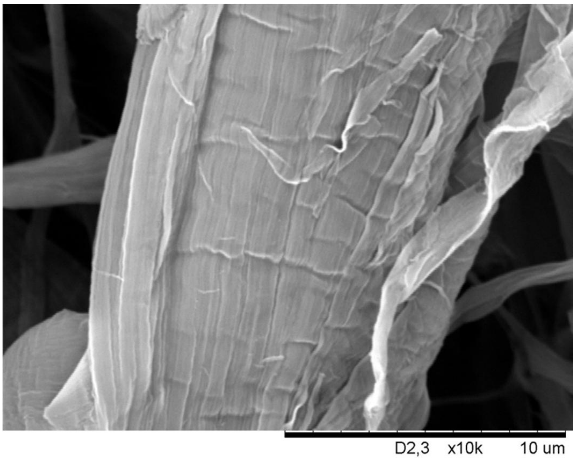


Fig. 20. *Fiber wall delamination during TMP refining of G1xUGL Eucalyptus hybrid.*

In our study, it was noted that guaiacyl units' content had a negative effect on the energy consumption in order to reach certain freeness (450 ml) for the APMP process (Fig. 21). Furthermore, this correlation is due to the fact that the rupture of wood during APMP process takes place where guaiacyl lignin is located (Musha and Goring, 1975, Watanabe et al 2004). However, for the TMP process, lignin was not altered by any pretreatment, thus remained stiff. Hence, no clear trend was seen for guaiacyl content influence, due to the fact that the rupture took place along the fiber wall, which is rich in syringyl lignin. However, at low guaiacyl content (~6.1% for U2xGL1), SEC was substantially lower.

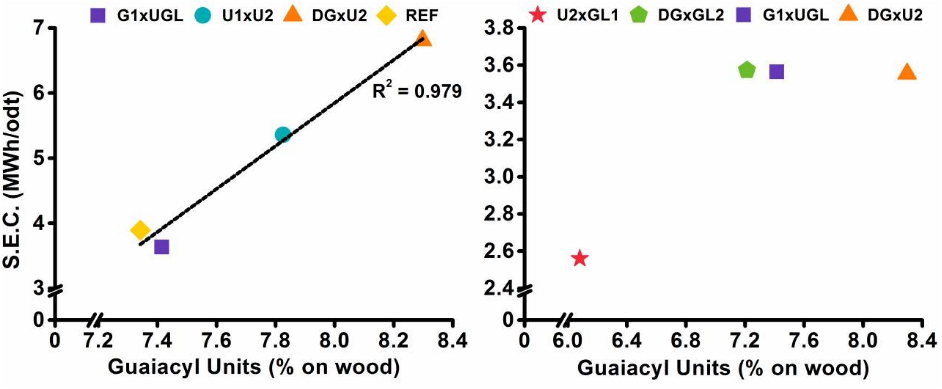


Fig. 21. *Guaiacyl units relationship with energy consumption. Left: APMP; Right: TMP.*

Coincidently, a low S/G ratio (high amounts of guaiacyl lignin) has also been shown to impair chemical pulping processes (del Río et al. 2005, Gomes et al. 2008, González-Vila et al. 1999, Pinto et al. 2005b, Santos et al. 2011).

4.1.3 Effect of fiber wall deconstruction

An alternative approach used in this study was promoting fiber wall deconstruction via autohydrolysis. The hybrid to be used in this section was decided based on the TMP experiments. U2xGL1 had an outstanding performance across the TMP refinings, and was thus chosen for the following experiments.

Autohydrolysis is widely used as a hemicellulose-extracting stage prior to kraft pulping aimed at high-purity cellulose pulps, *e.g.* dissolving pulps. Aiming for minimal structural changes in lignin structure, a strategy of using low temperature (120 °C) treatments was adopted. It is well known that higher P-factors lead to higher hemicellulose removal (Colodette et al. 2011, Liu et al. 2011). In this study the same trend was seen (Table 5) even though the final yield was substantially lower than in other studies with *Eucalyptus* (Colodette et al. 2011, Pedrazzi et al. 2010). This can be an indication of that the P-factor concept should not be an accurate approach when performing the autohydrolysis at low temperatures. Moreover, the low temperature led to extremely long reaction times, e.g. 96 hours for the P-factor 800, which could have possibly enhanced cellulose dissolution reactions.

Table 5. *General chemical composition and yield of untreated and autohydrolyzed Eucalyptus wood chips expressed in % of wood dry weight.*

		REF	**AH-200**	**AH-800**
Carbohydrates	**Glucans**	46.8	46.1	37.5
	Xylans	13.7	8.3	3.3
	Others*	2.3	0.7	0.6
Lignin	**Klason**	24.3	21.2	19.7
	Acid Soluble	5.8	2.5	1.2
	Total	30.1	23.7	20.9
Syringyl/Guaiacyl ratio		4.0	4.0	3.6
Acetyl groups		2.7	ND	ND
Uronic Acids		4.1	1.6	0.4
Yield		-	86.3	67.8

* For AH-200 and AH-800 samples, only mannans were found.

Furthermore, lignin S/G ratio remained constant at P-factor 200, which could indicate that the residual lignin in the chips might still have its original structure. However at P-factor 800 S/G ratio decreased, indicating that lignin structure was altered. Changes in the lignin structure during autohydrolysis have been already shown in recent literature (Leschinsky et al. 2008a, Leschinsky et al. 2008b, Rauhala et al. 2011), such as cleavage of β-O-4 linkages, increase in phenolic groups, as well as decrease of S/G ratio and molar mass. Such changes can have extreme importance when defining the defibration mechanisms of the autohydrolyzed wood chips.

FTIR spectroscopy was applied to investigate the changes in wood structure and composition in more details. Pandey and Pitman (2003), based on extensive literature review, listed the most important peak assignments for FTIR spectra of wood. In Fig. 22, changes due to the severity of the autohydrolysis process are mainly seen in two different peaks: (1) 1738/1734 cm^{-1} for unconjugated C=O in xylans, which is related to dissolution of acetyl groups during autohydrolysis (Garrote et al. 2002), what could also be detected via Solar (1987) method (Table 1) and; (2) 1244 cm^{-1} for xylan and syringyl ring C-O stretch in lignin, which corroborates the high xylan and syringyl lignin losses with increased severity (Table 1).

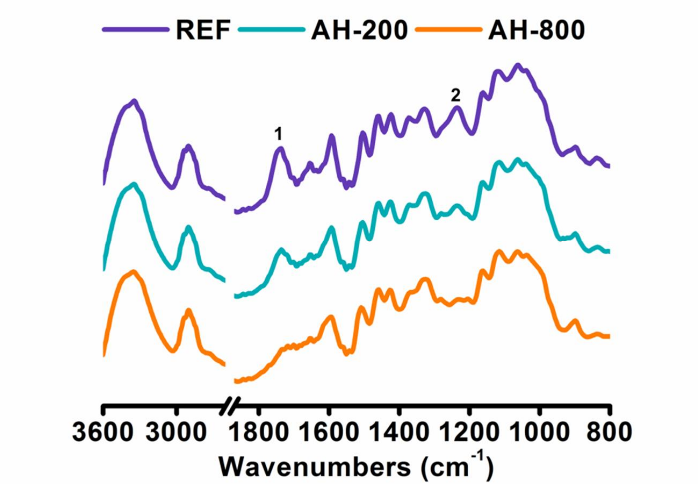


Fig. 22. *FTIR-PAS spectra of untreated and autohydrolyzed Eucalyptus wood chips. (1) 1738/1734 cm^{-1} and; (2) 1244 cm^{-1} peaks.*

XPS experiments were performed in order to reveal the surface properties and helping to understand the defibration phenomena. Wood surface lignin in Fig. 23 resembles the average amount of lignin present in the middle lamella of the wood. The reference pulp showed the lowest surface lignin content among the samples, indicating that the defibration took place inside the fiber wall, more specifically along the S1 layer of the secondary wall, as expected (Franzén, 1986). However, the high surface lignin content of both AH-200 and AH-800 pulps at 5 minutes refining indicate that the defibration took place along the middle lamella. Such behavior is similar to chemimechanical processes, such as APMP and CTMP, where lignin structure is definitely altered. Such results indicate that the strategy of performing the autohydrolysis at low temperatures to avoid lignin structural changes is not successful.

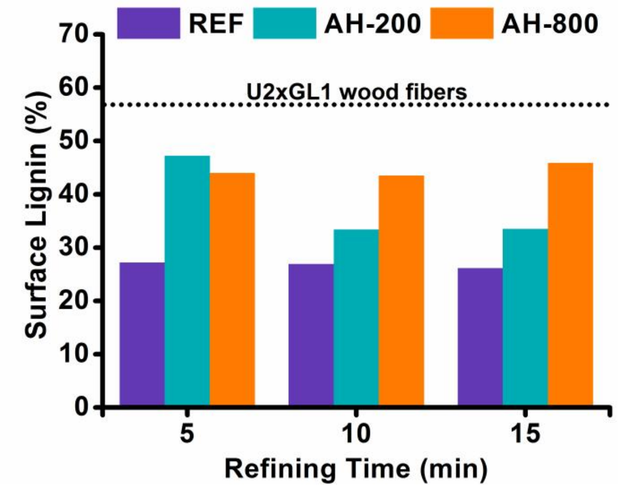


Fig. 23. *Surface lignin content of untreated wood and pulps from the untreated and autohydrolyzed Eucalyptus wood chips.*

The lignin structure alteration was the main reason for an impressive SEC reduction when compared to reference (~80%). However, the fiber wall deconstruction led to a lower strength of the fiber wall itself, especially with the severe P-factor 800 treatment, which could be confirmed by fiber dimensions analysis (Fig. 24). AH-800 pulps displayed the lowest fiber length values. As a consequence, AH-800 pulps had substantially higher amounts of fines in relation to reference or AH-200 pulps, showing the lowest amounts of fines.

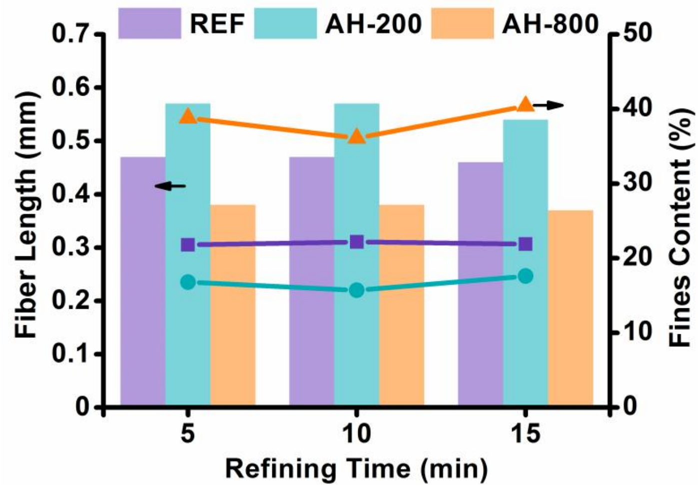


Fig. 24. Length (bar graph) and fines content (line graph) of the fiber samples from the untreated (REF) and autohydrolyzed (AH-200 and AH-800) Eucalyptus wood chips.

The behavior described above can be corroborated by SEM micrographs (Fig. 25). The reference fibers show uneven breaking point (white arrows - left), seeming like fibers resisted to a certain extent the forces inside the refiner, whereas AH-800 fibers (on the right) show a flat breaking point, indicating that the structure of fibers were too weak to withstand the load of refining forces.

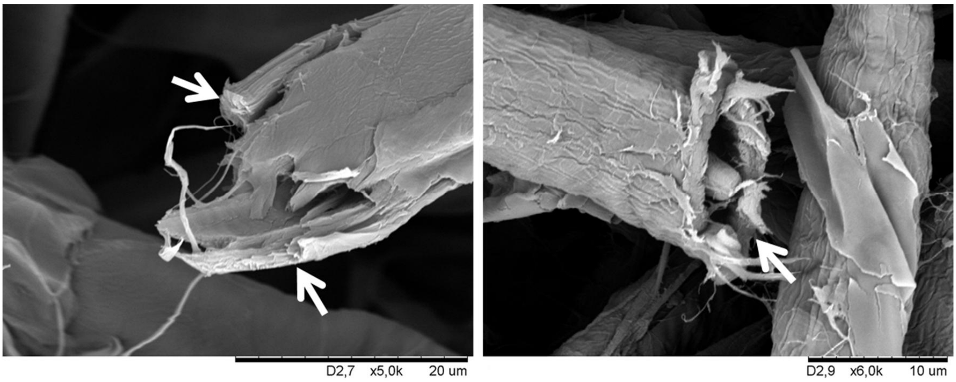


Fig. 25. *SEM micrographs from the 5 minutes refining samples of (Left) Reference, (Right) AH-800. The white arrows point out the types of breaking points of the fibers during the refining process.*

4.2 Chemical processes

Eucalyptus wood in Brazil has been traditionally used for chemical pulping purposes. Kraft pulping has been the dominant process due to the delivery of pulp of high strength, use of any type of biomass, and for possessing a highly developed chemical recovery technology. However, new pulping technologies have surged along the years as possible substitutes, such as the NaOH-AQ process, a sulfur free process that would allow new chemical recovery/power generation technologies, such as gasification.

It has been demonstrated that each technology has a different effect on the pulp fiber properties, especially on the surface properties, which is extremely important for the future uses of these fibers.

4.2.1 Pulping performance

The higher requirement of alkali for NaOH-AQ process (Table 6) shows to be the major disadvantage of NaOH-AQ process when compared to kraft process (Bose et al. 2009). Another major disadvantage is the poorer bleachability of NaOH-AQ pulps when compared to kraft pulp, however this subject was not in the scope of this study.

Table 6. *Kraft and NaOH-AQ cooking results and chemical composition of pulps.*

	Kraft	**NaOH-AQ**
Alkali charge, % NaOH	27.5	29.5
Residual alkali, g/L NaOH	9.6	20.2
Black liquor pH	13.1	13.6
Kappa number	15.0	15.0
Brightness, % ISO	32.7	34.4
Viscosity, dm^3/kg	1144	951
Glucans, %	81.6	86.2
Xylan, %	15.4	10.4
Uronic acids, %	0.7	0.3
HexA, mmol/kg	41.8	21.2
M_w (kDa)	550.2	482.9
M_n (kDa)	106.8	106.0
Polydispersity	5.1	4.6

The higher alkalinity of the NaOH-AQ process led to higher removal of hemicelluloses and degradation of cellulose, which can be confirmed by the carbohydrate composition and molar mass distribution, with focus on the peak of hemicellulose (*ca.* 30 kDa) (Fig. 26).

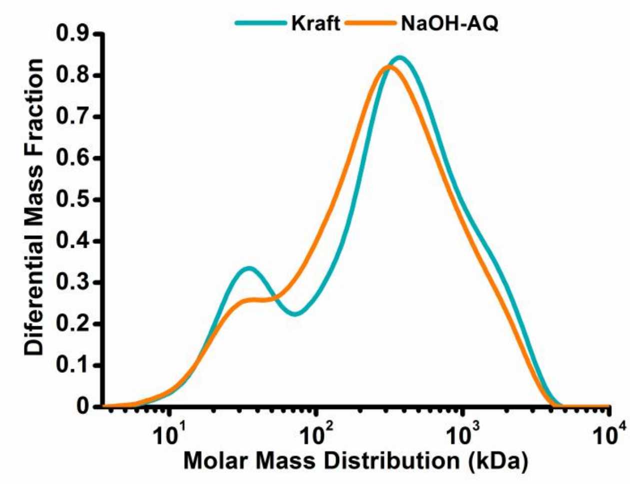


Fig. 26. *Molar mass distribution of kraft and NaOH-AQ pulps.*

During the final part of the cook, xylan tends to resorb onto the fibers (Aurell, 1963, Aurell, 1965, Danielsson and Lindström, 2005, Danielsson and Lindström, 2009, Hansson and Hartler, 1969, Muguet et al. 2011, Yllner and Enström, 1956, Yllner and Enström, 1957). The lower pH of kraft process when compared to NaOH-AQ might have favored xylan resorption, which can explain partly the higher amount of xylan in the kraft pulp.

4.2.2 Surface properties

Surface properties of cellulosic fibers have a significant impact in the properties of fiber products. Moreover, the surface properties govern the interfiber bonding. Both Kraft and NaOH-AQ pulps were submitted to PFI refining, in order to develop strength properties, as well as surface changes.

XPS is a well-known surface characterization technique for wood fiber materials (Johansson and Campbell, 2004, Laine et al. 1994). XPS could be performed under wide or high resolution range (Fig. 27). The wide spectra capture the elemental composition of the fibers, such as carbon and oxygen atoms. However, the bonds from each carbon atom differ. Carbon can be linked to other carbon, as well as oxygen, and that amount varies. To overcome this issue, high resolution spectra (O 1s and C 1s HiRes) can be acquired and carbon species deconvoluted.

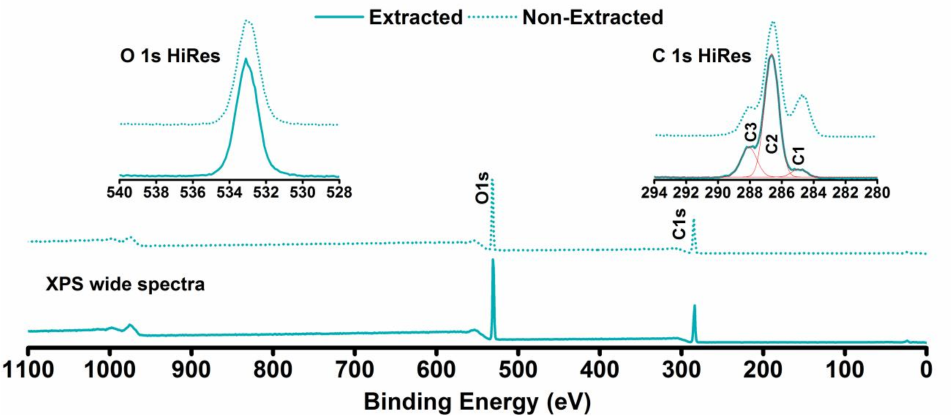


Fig. 27. *Example of XPS wide spectra (Kraft-1000) and O 1s high resolution spectra and C 1s high resolution spectra with calculated carbon components.*

After carbon deconvolution, four different species can be seen: C1, percent carbon with no bonds to oxygen (C-C, C=C); C2, percent carbon atoms with one bond to oxygen (C-O, C-O-C); C3, percent carbon atoms with two bonds to oxygen (C=O, O-C-O); C4, percent carbon atoms with 3 bonds to oxygen (O-C=O) (Zhou et al. 2006). C1 is considered as the non-cellulosic carbon, being present in lignin and extractives. In order to analyze both separately, sample extraction is performed. The importance of extraction, in our case acetone, is clearly seen in Fig. 28: after the extraction, the samples look “cleaner”, with the O/C and CC ratio going towards the direction of cellulose.

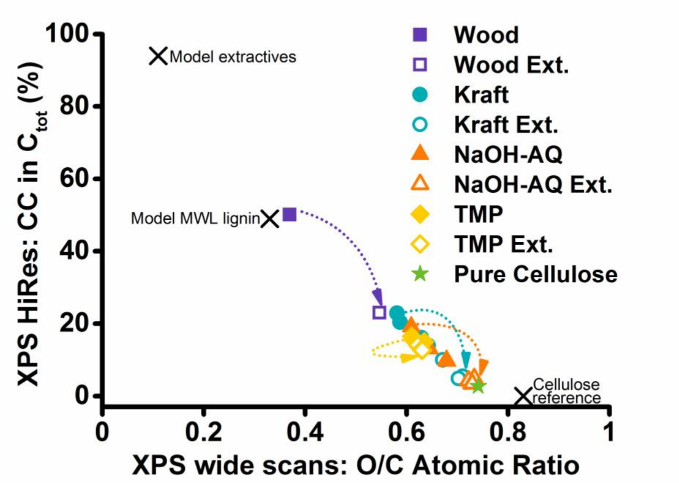


Fig. 28. *Effect of acetone extraction on the CC x O/C relationship. The arrows show the effect of extraction.*

Clearly, when the extraction is performed, the amounts of C1 carbon species decrease, and the reminiscent can be considered to be only lignin-related. Thus, lignin, extractives and carbohydrates contents on the fiber surface can be calculated respectively according to *Eq. 3*, *Eq.* 4 and *Eq.* 5 as described by (Koljonen et al. 2003).

Eq. 3 $$ø_{lignin} = (C1_{ext} - a)\ x\ 100\%/49\%$$

Eq. 4 $$ø_{extractives} = C1_{non\ ext} - C1_{ext}$$

Eq. 5 $$ø_{carbohydrates} = 100\% - ø_{extractives} - ø_{lignin}$$

where:

$C1_{non\ ext}$, relative amount of C1 component of original sample
$C1_{ext}$, relative amount of C1 component of extracted sample
a, value of the lowest relative amount of C1 peak detected
49%, percent of C1 in pure mill wood lignin

Fig. 29 shows the concentration between lignin and carbohydrates calculated after high resolution carbon deconvolution. The decrease in lignin coverage with longer refining (lower freeness values) was expected. Refining exposes the secondary cell wall, which is known to have lower lignin concentration than the primary cell wall in chemical pulp fibers. Similar results have been found earlier for *Eucalyptus* pulp (Fardim and Durán, 2003). NaOH-AQ pulps have lower lignin and higher carbohydrates coverage when compared to the kraft samples.

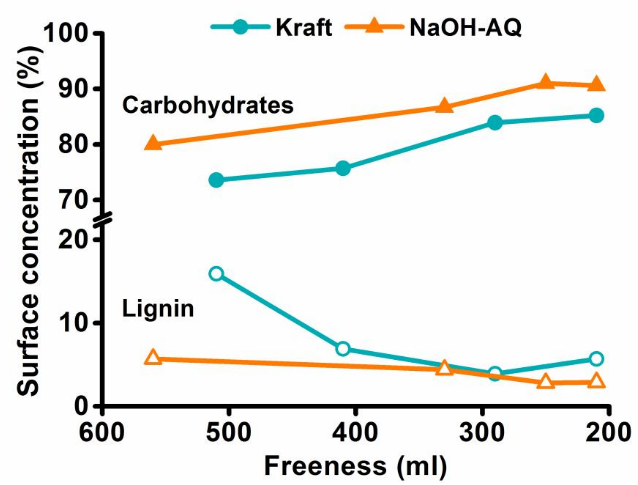
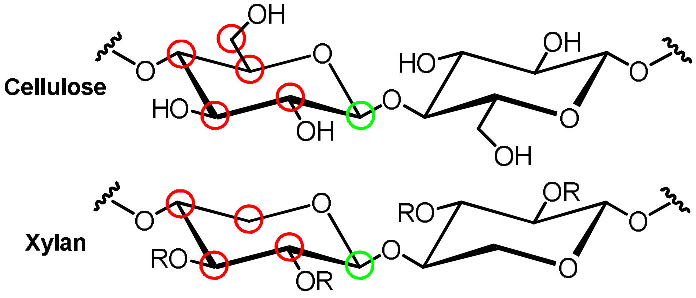


Fig. 29. *Surface concentration of lignin (open symbols) and carbohydrates (solid symbols) from kraft and NaOH-AQ pulp samples. Freeness decreases as refining progresses.*

Furthermore, a novel feature was applied in this study. XPS C2/C3 ratio was calculated in order to characterize the surface of the fibers. The reason is shown in Fig. 30. Nominally, cellulose shows a 5:1 for the C2/C3 ratio, whereas xylan backbone shows a respective ratio to be *ca.* 4:1. However, an experimental ratio of 4.2 for cellulose reference samples is measured. This value has been acquired for years in the XPS laboratory of Aalto's Department of Forest Products Technology, under thousands of experiments. Moreover, it was assumed that the influence of residual lignin, and side groups of xylan would have only a minimum effect on the C2/C3 ratio values.



C2, carbon atoms with one bond to oxygen, C-O, C-O-C
C3, carbon atoms with two bond to oxygen, C=O, O-C-O

Fig. 30. *C2 and C3 carbon atom species in cellulose and xylan molecules.*

The C2/C3 ratios of the extracted pulps shift to slight lower values (4.11 for NaOH-AQ and 4.01 for kraft) from the experimental value of 4.2 measured for pure cellulose. The difference in the C2/C3 ratio between the kraft and NaOH-AQ pulps could be explained by differences in the surface xylan content. In that case, the lower values for kraft pulps suggest that there is more xylan in the carbohydrate fraction of the surface, which is in line with previous studies using surface mechanical peeling (Sjöberg et al. 2002). Furthermore, the higher amount of surface xylan in kraft pulps is in line with the total xylan content (Table 6), and the better tensile strength achieved by the kraft pulp samples when compared to NaOH-AQ pulp.

5 CONCLUDING REMARKS

This thesis investigated relevant issues regarding the use of *Eucalyptus* wood: the factors affecting energy consumption during wood defibration, with focus on fiber wall chemistry and the assessment of wood quality from a wide range of novel Brazilian *Eucalyptus* hybrids. The obtained results were reflected to mechanical and traditional chemical processes.

Firstly, it was demonstrated that lignin structure plays an important role on the energy demand during the wood defibration. Guaiacyl lignin has a definite impact on chemimechanical process (APMP), especially its localization in the middle lamella, where the rupture point of such process takes place. For thermomechanical process (TMP), guaiacyl lignin had a minor influence, due to its low concentration in the fiber wall, where the rupture of TMP processes takes place.

Furthermore, it was demonstrated that promoting fiber wall deconstruction via autohydrolysis, even at low temperatures, changes the lignin structure, which has a definite effect on the defibration phenomena. Rupture point shifts from the fiber wall to the middle lamella. However, the process looked promising for biorefinery applications. The high surface lignin content of the fibers can be positive if using such fibers as reinforcement for green biocomposites. Moreover, the low refining energy consumption during the process can open possibilities for such process as a pretreatment to enhance biomass accessibility in complete hydrolysis and bioethanol production.

Moreover, it was learned how the surface of cellulosic fibers can be tailored, by simply choosing a chemical pulping method. Traditional kraft pulping process leave fibers with higher lignin content, when compared to the NaOH-AQ process. However, kraft process is more selective for xylan, which was shown by the higher bulk and surface content (characterized by a novel approach – XPS C2/C3 ratio), when compared to the NaOH-AQ process. Such properties have a definite effect on the interface phenomena between the fibers.

Finally, it was demonstrated that the recent approach of molecular breeding to increase S/G ratio of lignin, especially under the Genolyptus framework is in the right track. The effect of S/G ratio for chemical process is already known, but for mechanical processes, studies correlating the effect of S/G ratio were lacking. That means that the hybridization approach of *Eucalyptus* wood for chemical processes serves as well for mechanical processes. Moreover, it is clear that the hybrids with *E. globulus* germplasm deliver the best performances in all processes.

Taken together, by understanding the effect and behavior of the wood polymers on several pulping processes, valuable knowledge is gathered for different areas within forest products sector, ranging from *Eucalyptus* breeding technologies and silviculture, to the wood utilization in pulp mills.

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Aalto-DD 163/2013

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ISBN 978-952-60-5379-0
ISBN 978-952-60-5380-6 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934
ISSN 1799-4942 (pdf)

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