Mestrado Integrado em Engenharia Química

Delignification and hemicellulose dissolution/degradation in Kraft cooking of Scots pine and Blue gum

Tese de Mestrado

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Resumo

O processo Kraft é o método de produção de pasta de papel a partir de madeira mais utilizado actualmente. Desde a sua invenção (1879, por Carl Dahl), diversas melhorias foram implementadas neste processo. Contudo, apesar da intensa pesquisa que vem sendo levada a cabo ao longo dos anos, as reacções químicas que ocorrem durante o cozimento da madeira, envolvendo a lenhina e os carbohidratos, não se encontram ainda totalmente compreendidas. Assim, como parte integrante dessa vasta pesquisa, esta tese visa o estudo da degradação/dissolução de alguns dos contituintes da madeira (mais concretamente, lenhina e hemiceluloses) durante o cozimento Kraft.

Além de uma comparação entre os cozimentos do alburno e do cerne de madeira da espécie *Pinus silvestris* (madeira resinosa), foi estabelecida também uma comparação entre o cozimento deste tipo de madeira e o da espécie *Eucalyptus globulus* (madeira folhosa). Nesse sentido, diversos cozimentos de "farinha de madeira" das espécies referidas foram realizados, utilizando diferentes concentrações de iões OH^- e HS^-, bem como uma elevada relação licor/madeira (200:1). Seguidamente, os carbohidratos foram analisados recorrendo a Cromatografia Líquida de Alta Performance ("High Performance Liquid Chromatography"), e a lenhina foi submetida a uma análise gravimétrica.

Durante o cozimento Kraft do alburno e do cerne da espécie *Pinus silvestris*, em condições tais que a resistência à transferência de massa possa ser considerada ausente, a lenhina, o glucomanano e o xilano mostram comportamentos praticamente coincidentes. Também nestas condições, a taxa de deslenhificação para a espécie *Eucalyptus globulus* pode atingir valores cerca de 5,6 vezes mais elevados do que os da taxa de deslenhificação no caso da espécie *Pinus silvestris*. Para ambas as espécies, independentemente da concentração de iões no licor, verifica-se uma diminuição acentuada da quantidade de glucomanano no início do cozimento. No entanto, na parte final do mesmo, a quantidade de glucomanano na espécie resinosa é ainda cerca de 20 % do valor inicial, enquanto na espécie folhosa praticamente todo o glucomanano é degradado. Em relação à quantidade de xilano, verifica-se, para ambas as espécies de madeira, um decrescimento mais acentuado quando a concentração de iões OH^- é aumentada. Também para ambas as espécies, um aumento na concentração de iões HS^- tem um ligeiro efeito negativo no decrescimento da quantidade de xilano durante o cozimento. Além disso, a existência de uma relação próxima da linearidade entre a variação das quantidades de xilano e lenhina, verificada durante o cozimento de ambas as espécies de madeira, sugere a existência de interacções entre estes dois componentes. Por outro lado, a existência de uma quantidade considerável de xilano na parte final do cozimento de ambas as espécies sugere a existência de interacções entre esta hemicelulose e a celulose.

Palavras-chave: Kraft pulping, Delignification, Hemicellulose degradation, Softwood, Hardwood

Abstract

The Kraft pulping process is the most common method for producing pulp from wood. Since its invention (1879, by Carl Dahl), it has been through many improvements. However, despite the extensive research that has been done so far, the chemical reactions involving lignin and the carbohydrates, in the Kraft cooking stage, are still not completely understood. This thesis is part of that vast research and it regards delignification and hemicellulose dissolution/degradation during Kraft cooking.

A comparison was established between Scots pine sapwood and heartwood, as well as between Scots pine and Blue gum. In order to do so, wood meal of both wood types was cooked over a wide range of concentrations of hydroxide and hydrosulphide ions and a high liquor-to-wood ratio (200:1) was used. Thereafter, the carbohydrates were analysed using High Performance Liquid Chromatography and lignin was analysed gravimetrically.

During Kraft cooking of both Scots pine sapwood and heartwood, lignin, glucomannan and xylan show an almost coincident behaviour when resistance to mass transfer phenomena is practically absent. Furthermore, in such conditions, the rate of delignification of Blue gum can be approximately 5.6 times higher than the delignification rate of Scots pine. A rapid initial decrease in the content of glucomannan is observed for both wood species. However, in the final part of the cook, there is still approximately 20 % of the initial amount of glucomannan for Scots pine, whereas, for Blue gum, almost all glucomannan is degraded, regardless of the concentrations of hydroxide and hydrosulphide ions. Xylan content decreases with an increase in the concentration of hydroxide ions, for both Blue gum and Scots pine. Moreover, an increase in the concentration of hydrosulphide ions seems to have a slightly negative effect on the content of xylan during Kraft cooking, for both wood species. Furthermore, an approximately linear relation between xylan and lignin contents, verified during cooking of Scots pine and Blue gum, suggests the existence of interactions between these two components in both wood species. On the other hand, the considerable amount of xylan that remains at the end of the cook also suggests the existence of interactions between xylan and cellulose in both wood species.

Keywords: Kraft pulping, Delignification, Hemicellulose degradation, Softwood, Hardwood

Contents

1. Introduction

1.1. Background

Paper pulp is a fibrous material obtained from manufacturing processes involving chemical and/or mechanical treatment of different types of plant material (especially woody plants).

Although paper pulp is mainly used for the production of paper and paperboard, and demand keeps growing, its use in the textile, food and pharmaceutical industries is considerably increasing [Sixta 2006]. Furthermore, the pulp production technology, which has its origin in the 19th century, has still a high potential of further innovations regarding not only improvements in pulp industry itself but also development of processes for production of alternative fuels integrated in the concept of biorefinery.

Among all existing pulp production processes, the Kraft process is the most common one used today, since it accepts a wider variety of wood types and provides high quality pulps. However, despite the fact that this process was invented in 1879 by Carl Dahl, it is still far from being completely understood. The loss of considerable amounts of carbohydrates (especially hemicelluloses), when removing lignin from wood in Kraft pulping, is an obstacle concerning the production of pulps with even higher quality. Thus, comprehension of the Kraft pulping stage is important and necessary.

1.2. Objectives of this thesis

The Kraft pulping process represents a huge step in the technological evolution of pulp and paper industry. Nevertheless, there are still a large number of questions associated to this process that need to be answered. A considerable part of those questions are connected to the Kraft cooking stage, which performance depends on a considerable number of variables, such as the wood species used, temperature and the concentrations of the active chemicals.

This thesis is part of a vast work that has been and will continue to be developed with the aim of improving the performance of the Kraft cooking stage by increasing the knowledge of the underlying mechanisms responsible for delignification and carbohydrate dissolution/degradation that occur during this stage. Thus, the main objective of this thesis is to establish a comparison between Scots pine (*Pinus silvestris*) heartwood and sapwood, as well as between Scots pine and Blue gum (*Eucalyptus globulus*), regarding their delignification and hemicellulose dissolution/degradation. This has been accomplished by performing numerous Kraft cooking experiments over different concentrations of active chemicals and different temperatures.

2. Literature

2.1. Pulp production processes

For many years, linen and cotton rags (waste from the textile industry) were the basic fibre sources for the production of paper. However, the increasing demand for this product during the first half of the 19th century caused a necessity for the development of new paper production processes using a more abundant material – wood – which is mainly constituted by carbohydrates (i.e., cellulose and hemicelluloses) and lignin. Thus, even though pulp can be produced from materials such as cereals (e. g., corn, wheat, rice), bamboo, sugarcane bagasse, cotton, etc., wood provides approximately 90 % of the worldwide pulp production today [Sixta 2006].

When producing pulp from wood the main aim is to liberate the cellulosic fibres from each other. To achieve this, there are two major processes of producing pulp – mechanical and chemical processes.

In mechanical processes, wood is pre-treated with steam, before its separation into fibrous material by abrasive refining or grinding, and further treated by screening, washing, bleaching and purification operations [Sixta 2006].

On the other hand, chemical processes rely on the use of chemical reactants, at elevated temperature, to degrade and solubilise lignin, in order to obtain a fibrous material mainly composed by cellulose and hemicelluloses (chemical pulp).

There are three main chemical processes for pulp production – Soda process, Sulphite process and Kraft process.

The Soda process was the first chemical pulping process, whose name results from the fact that it uses caustic soda as the cooking agent. However, due to the high consumptions of soda, methods of recovering this cooking agent from the spent cooking liquors (such as evaporation, combustion of the waste liquor and recausticizing of the sodium carbonate formed) were developed. Nevertheless, sodium carbonate had to be added to the causticizing unit, in order to compensate for the losses, and since its preparation from sodium sulphate was considerably expensive, sodium sulphate was later directly introduced in a soda pulping recovery system in replace of sodium carbonate. This change was responsible for the production of a stronger pulp, so-called “kraft” (the German word for “strong”) pulp, and for the consequent conversion of many Soda pulping mills into Kraft pulping mills [Sixta 2006].

The Sulphite process was developed around the acid calcium bisulphite process and today it can be divided into different types of pulping processes (acid bisulphite, bisulphite, neutral sulphite, alkaline sulphite, multistage sulphite and anthraquinone-catalyzed sulphite pulping). It was the dominating process for the first 50 years of chemical pulp production, due to the high brightness and high bleachability of the sulphite pulps. However, the development of a reductive recovery boiler for the regeneration of the Kraft cooking liquor and the introduction of chlorine as a selective bleaching agent made Kraft pulping the preferred process, since it provides better energy economy, better paper strength properties and it is less sensitive towards different types of wood [Sixta 2006].

2.1.1. Kraft pulping mill

Since its invention in 1879 by Carl Dahl, the Kraft process has been through many improvements, in order to solve its initial problems associated with dark pulp and bleaching difficulties, and today it has become the most common pulping process used.

In a Kraft pulping mill, after being stored and sorted, the wood logs are chopped into wood chips. In the conventional Kraft process, the wood chips are then fed to a digester, where they are impregnated with white liquor, which mainly contains sodium hydroxide and sodium hydrosulphide. However, most part of the Kraft pulping mills that exist today use a mixture of white liquor and black liquor (see below in this section). At elevated temperatures (150-170°C), the active chemicals (i.e. hydroxide and hydrosulphide ions) react with lignin and the carbohydrates (mainly glucomannans and xylans). As a result of this, the cellulose fibres can be easily separated from each other originating a dark pulp. The outlet stream of the digester contains the previously mentioned pulp and the so-called black liquor, whose colour results from its high lignin content. Thus, this mixture is separated in a washing stage, using water as the separation agent. Thereafter, the black liquor is transferred to the recovery cycle, where it is converted into white liquor and energy, and the pulp is oxygen delignified. Due to its colour, the brightness of the pulp is increased in a multistep bleaching stage, where the residual lignin is removed, and further commercialized as pulp or converted into paper.

The recovery cycle of the Kraft process represents its main advantage. In the recovery process, part of the water contained in the black liquor that comes from the washing stage is evaporated and the resulting concentrated black liquor is burned in a recovery boiler, thus providing energy. The melted inorganic components are then dissolved in white liquor of low concentration, forming the green liquor, which is further causticized in order to be converted into white liquor for the pulping stage.

The following figure shows a general schematic representation of a Kraft pulping mill.

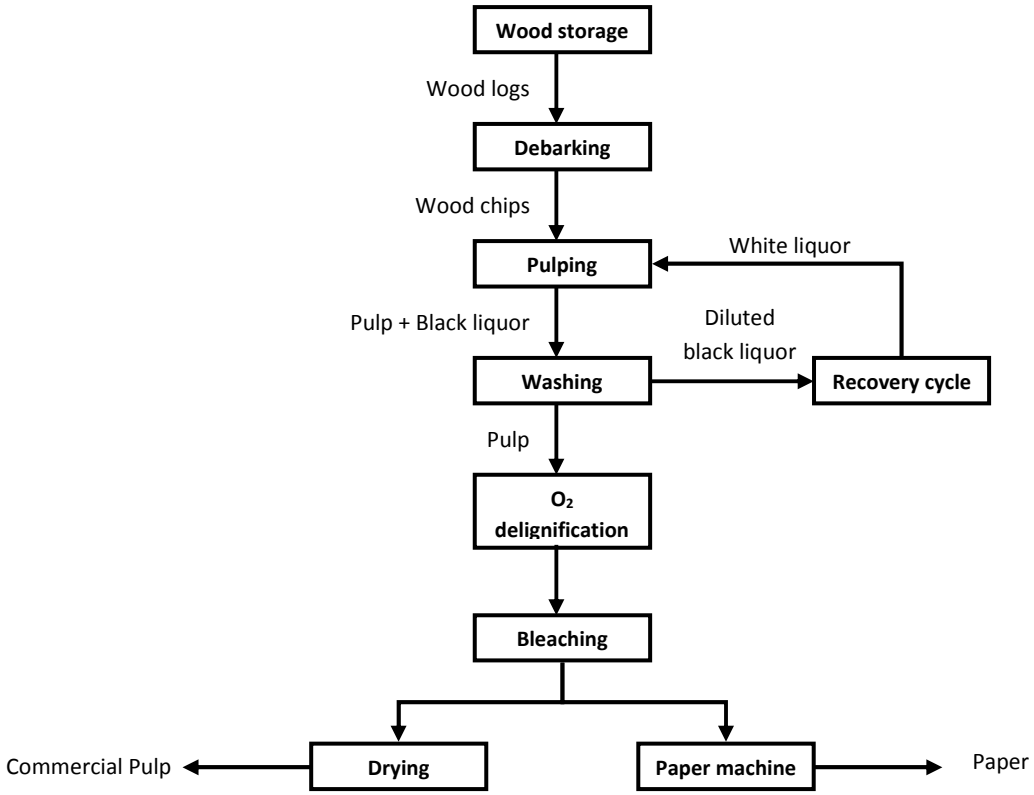


Figure 2.1 – General scheme of a Kraft pulping mill.

2.1.2. Kraft cooking stage

In the Kraft process, the cooking stage is an extremely complex and relevant operation, which is characterized by the occurrence of chemical reactions and mass transfer phenomena.

Thus, when cooking wood, it is necessary to achieve a good impregnation of the white liquor into the wood chips, which is driven by penetration (pressure gradients) and by diffusion (concentration gradients). Penetration can be natural or forced. The first one occurs due to capillary force phenomena and the second one results from an externally applied pressure. On the other hand, when the void areas of the wood chips are filled with liquor, diffusion phenomena take place through the water layer of the cell wall [Sixta 2006]. The existence of diffusion phenomena is extremely important, since this is the main transport mechanism of the active chemicals to the reaction sites while those are being consumed during the chemical reactions.

In a general way, the active chemicals contained in the white liquor (i.e., hydroxide and hydrosulphide ions) are transferred from the bulk to the surface of the chips and from there to the reaction site, where the reactions and dissolution of the wood components take place. Thereafter, the dissolved wood components (mainly lignin and some carbohydrates) are transported from the reaction site to the surface and finally to the bulk. The selectivity of this process has three phases as it is shown in the following figure [Gellerstedt 2004].

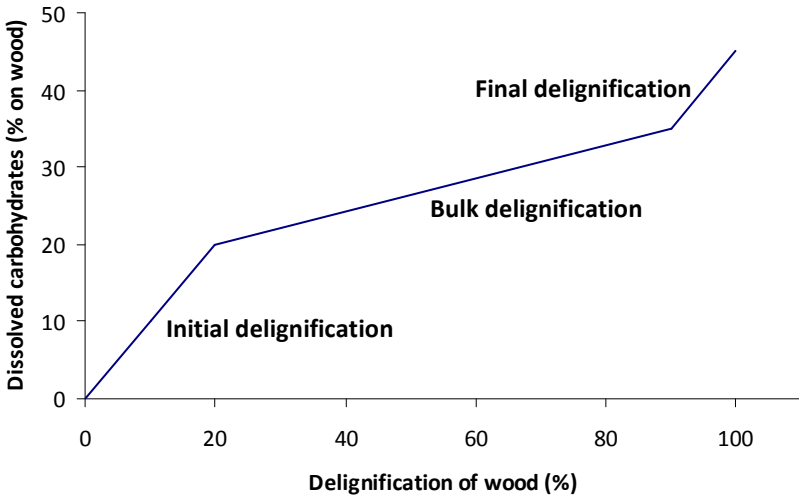


Figure 2.2 – Selectivity during dissolution of carbohydrates and lignin in Kraft pulping.

The initial phase proceeds with an extraction of lignin and carbohydrates until around 20 % of both types of wood components are dissolved. At this moment, a significant kinetic change occurs and a selective dissolution towards lignin takes place until approximately 90 % of all lignin is dissolved (bulk delignification). Finally, during the last phase (final delignification), the difficult removal of the residual lignin from the wood involves the loss of a large portion of carbohydrates, due to the fact that most of the hemicelluloses are degraded and dissolved in the alkaline liquor. Therefore, the cooking stage is normally interrupted at the transition point between the end of the bulk phase and the beginning of the final phase, in order to preserve the yield and the quality of the pulp [Gellerstedt 2004].

2.2. Wood – Raw material for pulp production

2.2.1. Wood types

Wood species can be divided in two major types: softwoods (coniferous woods) and hardwoods (deciduous woods). The main differences between these two types includes the structure of their wood and cell elements, as well as the chemical composition.

Softwoods are basically composed of both earlywood tracheids (with transport functions) and latewood tracheids (that provide mechanical strength), with a length-to-width ratio higher than 100:1, which makes this fibre cells extremely suitable for papermaking. Parenchyma cells are also present in softwoods, but their unfavourable length-to-width ratio (3:1) reduces their suitability to the production of paper [Sixta 2006].

On the other hand, hardwoods, with a more diversified structure than softwoods, are characterized by the presence of libriform fibres with 1 mm length and 10 to 40 µm width, depending on the wood species. Moreover, hardwoods contain vessels (specialized in water conduction) and a higher content of parenchyma cells, in comparison to softwoods [Sixta 2006].

The following table shows some examples of common softwood and hardwood species used for pulping and papermaking [Henriksson et al. 2004].

Table 2.1 – Examples of wood species used for pulping and papermaking.

Wood type	Species	Latin name
Softwoods	Norway spruce	*Picea abies*
	Scots pine	*Pinus silvetris*
	Douglas-fir	*Pseudotsuga menziesii*
Hardwoods	Silver birch	*Betula verrucosa*
	Blue gum	*Eucalyptus globulus*
	Quacking aspen	*Populus tremuloides*

2.2.2. Wood parts

When observing a transversal section of a wood stem, two zones can be distinguished. The central part is called heartwood and the outer part is called sapwood, as shown in the following figure.

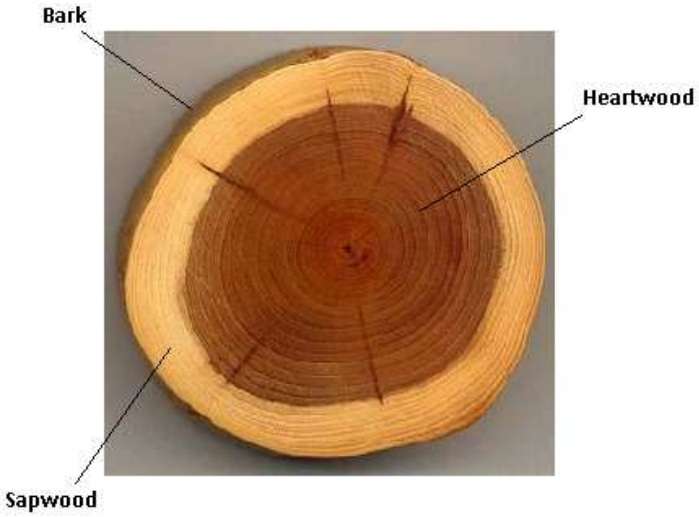


Figure 2.3 – Parts of wood in a Yew stem.

Heartwood is often darker than sapwood, due to its higher content of extractives. Thus, in comparison to sapwood, heartwood may show an increased stability, a slight increased density and a reduced permeability, which make it more difficult to dry and to impregnate with chemical preservatives in processes such as timber production. In addition, heartwood cells are all dead, unlike sapwood, which contains both living and dead cells [Miller 1999].

The bark has a low content of fibres and consequently, in a pulping process, this part has to be removed. Otherwise, it would be responsible for problems such as a yield decrease, equipment damage or the presence of dirt on pulp and paper [Brännvall 2004].

2.2.3. Wood components

As it was previously mentioned, wood is mainly composed of lignin and carbohydrates (i.e., cellulose and hemicelluloses). The following sections provide literature information about the structure of these components (as well as wood extractives) and their behaviour during the Kraft pulping stage.

2.2.3.1. Lignin

Lignin is a complex hydrophobic polymer that binds wood fibres together and provides protection against microbial degradation of wood. The fact that lignin is always associated with the carbohydrates makes it impossible to determine its molecular weight. Lignin is polymerized from three main monomers (monolignols) – p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Figure 1.2).

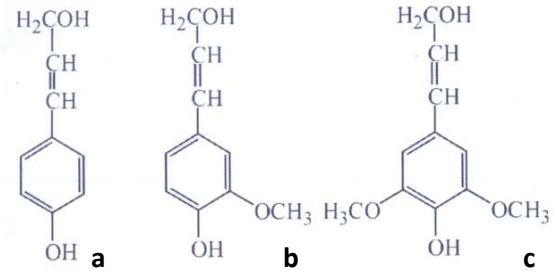


Figure 2.4 – Monolignols – a) p-coumaryl alcohol; b) coniferyl alcohol; c) sinapyl alcohol

There are different bonds between these monolignols. However, the so-called β-O-4 linkage is the most important one from the pulp production point of view, since it is involved in the cleavage reactions in Kraft pulping [Henriksson 2004], which are promoted by the presence of hydroxide and hydrosulphide ions. Furthermore, it is known that the presence of hydrosulphide ions is responsible for an increase in the extent of fragmentation of the phenolic β-O-4 structures, whereas hydroxide ions alone provide a lower rate and efficiency of delignification [Gellerstedt 2004].

Moreover, the variations in lignin composition and amount verified in the existing wood species, result in different delignification rates during Kraft cooking. In general, softwood lignin (about 25 to 31 % in wood) practically consists of coniferyl alcohol, whereas hardwood lignin (about 16 to 24 % in wood) contains from approximately equal amounts of both coniferyl and sinapyl alcohols to three times higher quantities of the second one [Henriksson 2004]. In addition, Chang & Sarkanen (1973) also stated the existence of a higher content of syringylpropane units in hardwood lignin than in softwood lignin. Thus, according to their study, this difference explains the reason why delignification is faster in hardwood than in softwood.

2.2.3.2. Cellulose

Cellulose is the most abundant organic compound in nature also representing 40 to 50 % of the total components that constitute wood. It is a linear polymer, with a degree of polymerisation that may reach 10000 [Sjöström 1993], and it is composed of β-D-glucose units, which are connected by 1→4-glucosidic linkages. Furthermore, cellulose chains can be ordered (crystalline) or unordered (amorphous) [Lennholm and Blomqvist 2004].

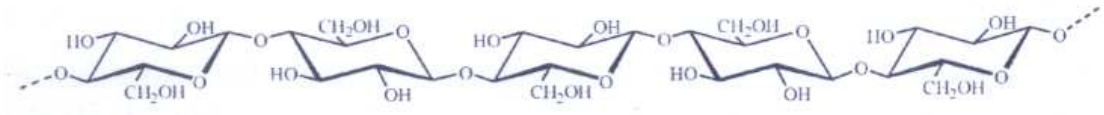


Figure 2.5 – Molecular structure of a segment of a cellulose chain.

Even though the reducing end-groups of this polysaccharide are susceptible to rearrangements that lead to the so-called peeling (see section 2.2.3.3), the high degree of polymerisation of cellulose and its crystalline structured regions make it a very stable compound and provide a high resistance to degradation during Kraft cooking [Lennholm and Blomqvist 2004].

2.2.3.3. Hemicelluloses

Hemicelluloses are polysaccharides that can be found in the matrix between cellulose fibrils in the cell wall. The following table contains the principal hemicelluloses and their dry weight amount range for both softwood and hardwood [Teleman 2004].

Table 2.2 – Main hemicelluloses in softwood and hardwood.

Wood type	Hemicellulose	Amount (% dry weight)
Softwood	(Galacto)glucomannan	15-23
	Arabinoglucuronoxylan	7-15
Hardwood	Glucuronoxylan	15-35
	Glucomannan	2-5

- **Softwood and hardwood glucomannans**

As shown in the Table 2.1, in softwoods, the main hemicellulose is (galacto)glucomannan. The backbone of this compound consists of glucose and mannose bound by 1→4 linkages. Depending on the content of galactose units, which are linked with 1→6 linkages to mannose residues, (galacto)glucomannan can be divided in two forms: galactoglucomannan, with a ratio of galactose to glucose to mannose units of 1:1:3-4; and glucomannan, with a ratio of galactose to glucose to mannose of 0.1:1:3-4. Therefore, the difference between these two forms is the fact that galactoglucomannan has a higher content of galactose units than glucomannan [Teleman 2004]. Furthermore, the degree of polymerisation of (galacto)glucomannan is approximately 100 [Sjöström 1993].

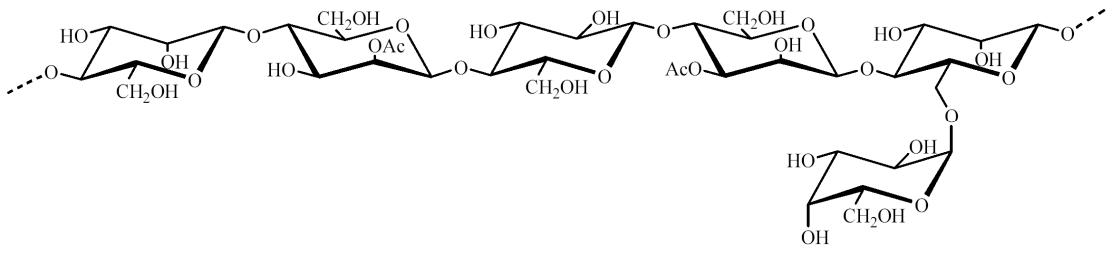


Figure 2.6 – Structural formula for softwood galactoglucomannan.

On the other hand, hardwood glucomannans consist only of glucose and mannose units, linked by β-(1,4)-glucosidic bonds, with a glucose to mannose ratio that varies from 1:1 to 1:2. Thus, hardwood glucomannans have a simpler structure than softwood glucomannans and a degree of polymerisation of approximately 60-70 [Teleman 2004].

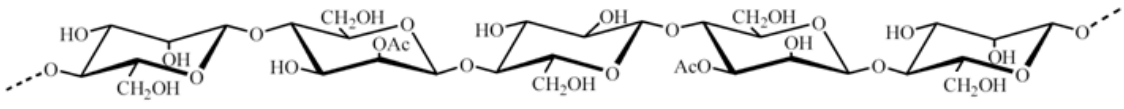


Figure 2.7 – Structural formula for hardwood glucomannan.

- **Softwood and hardwood xylans**

Softwood xylans (arabinoglucuronoxylans) have a backbone that consists of xylose units linked by 1→4 bonds. These hemicelluloses are characterized by the lack of acetyl groups. However, arabinose units are present at every 8-9 xylose unit, at C-3, and 4-O-methylglucoronic acid (MeGlcA) is linked to C-2 at every 5-6 xylose unit [Teleman 2004]. In addition, the degree of polymerisation of arabinoglucuronoxylan is approximately 100 [Sjöström 1993].

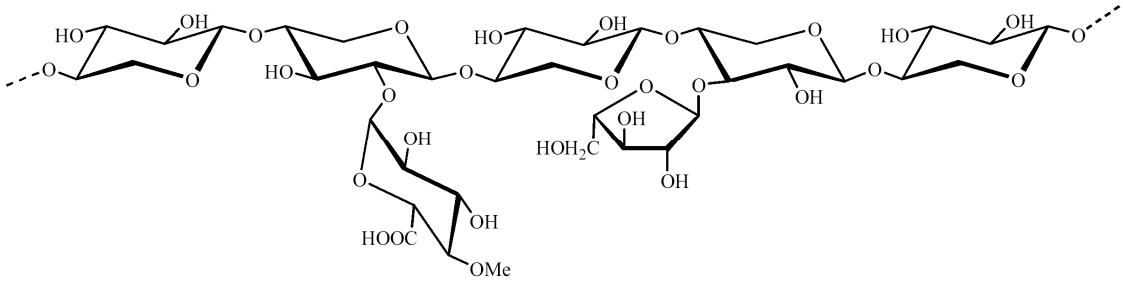


Figure 2.8 – Structural formula for softwood arabinoglucuronoxylan.

On the other hand, in hardwood, glucuronoxylan is the main hemicellulose component. Its backbone is also constituted by xylose units and 4-O-methylglucuronic acid is also present. However, no arabinose is found in this component and the MeGlcA units are irregularly distributed. Moreover, many of the OH-groups at C2 and C3 of the xylose units are substituted by O-acetyl groups. The degree of polymerisation of this hemicellulose is also around 100 [Teleman 2004].

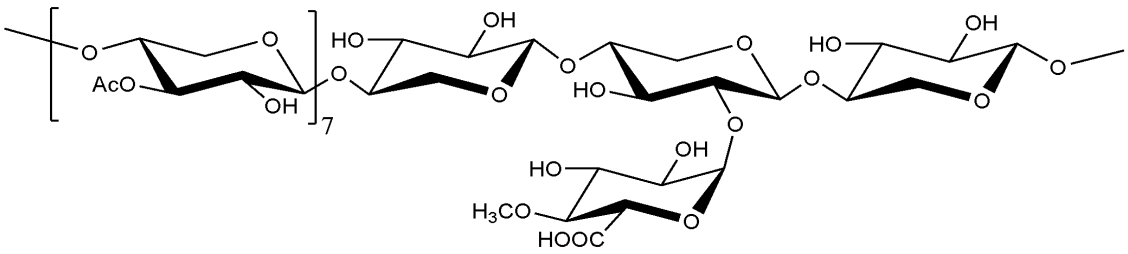


Figure 2.9 – Structural formula for hardwood glucuronoxylan.

During Kraft cooking, at temperatures around 100 °C, the reducing end-groups in the chain of carbohydrates are attacked by hydroxide ions, in the so-called peeling reaction, whose rate, however, does not depend on the alkali concentration. This reaction is responsible for chewing off unit by unit of the carbohydrate chain until a stopping reaction occurs, due to the conversion of the end unit into a more alkali stable structure. Nevertheless, when temperature

passes 130 °C, alkaline hydrolysis takes place and breaks the carbohydrate chain at a random linkage. Thus, another reducing end-group is created and secondary peeling can start [Brännvall 2004].

Although all carbohydrates are affected by peeling reactions, some are more affected than others. In fact, due to its high degree of polymerisation, cellulose is the most resistant carbohydrate. Concerning the hemicelluloses, peeling reactions have a lower efficiency in xylans than in glucomannans, due to the presence of substituents (arabinose and MeGlA in softwood xylan and MeGlA in hardwood xylan) that provide a stabilisation of the xylan chain [Gellerstedt 2004]. Thus, xylans have more tendency to dissolve in alkaline environment, whereas glucomannans tend to dissolve at temperatures below 100 °C and to be affected by peeling reactions at temperatures between 100 °C and 130 °C. Thereafter, the remaining glucomannan is rather resistant to alkali [Brännvall 2004].

The existence of interactions between the different components of wood, which may have influence on the behaviour of those components during Kraft pulping, has also been reported in several studies. In a study of degradation/dissolution of softwood hemicelluloses during alkaline cooking, Wigell *et al.* (2007) suggests the existence of a close interaction between glucomannan and cellulose. Furthermore, the simultaneous degradation/dissolution of lignin and xylan verified in the same study implies the existence of the so-called lignin-carbohydrate complexes (LCCs). In agreement with this, Lawoko (2005) suggests the existence of a closer interaction of glucomannan with cellulose and xylan with lignin. Nevertheless, despite all indications, the influence of these interactions is still a matter of discussion.

2.2.3.4. Wood extractives

In addition to the previously mentioned components, wood also contains the so-called extractives, whose name derives from the fact that they can be extracted from wood with organic solvents or hot water. Wood of trees from temperate zones may contain 2 to 5 % of extractives, whereas tropical and subtropical woods can contain up to 20 % of these compounds [Sixta 2006]. Thus, depending on the several wood species, extractives can improve the stability and durability of wood, since they may affect its chemical, biological, physical and optical properties to different extents.

The content of extractives can also affect delignification during Kraft pulping. According to a study of pulping yield and delignification kinetics of heartwood and sapwood of Maritime pine by Esteves *et al.* (2005), the higher amount of extractives in the heartwood of this tree leads to the obtention of lower yields.

3. Materials and Methods

This chapter contains a description of the materials and methods used for the experiments with both *Pinus silvestris* (softwood) heartwood and *Eucalyptus globulus* (hardwood).

All data regarding Scots pine sapwood were obtained from Bogren (2006).

3.1. Experimental procedure overview

The following figure shows a general schematic representation of the various steps that constituted the experimental procedure.

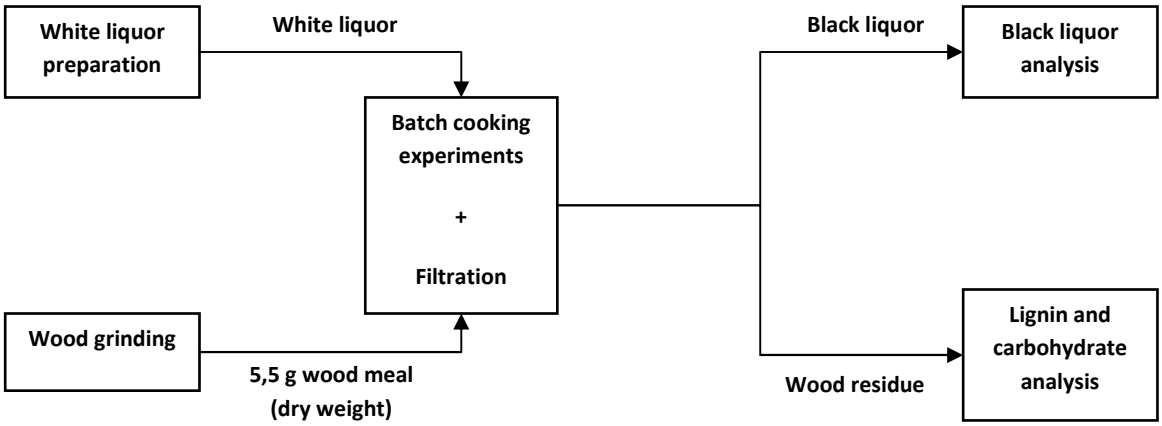


Figure 3.1 – Steps that constitute the experimental procedure.

Sections 3.1.1 and 3.1.2 contain a more detailed description of the materials and methods used during the experiments.

3.1.1. Batch Kraft cooking

The main aim of this thesis is to perform a kinetics study of Kraft pulping by establishing a comparison between sapwood and heartwood of *Pinus silvestris* (Scots pine) as well as between the referred softwood specie and *Eucalyptus globulus* (Blue gum). For that matter, Scots pine heartwood, from a log grown in southwest Sweden, and Blue gum wood chips, from Uruguay, were ground into wood meal (particles smaller than 1 mm) in a Wiley mill (Figure 3.2). The purpose of using wood meal in the cooking experiments instead of wood chips was to minimize the mass transfer resistance for the active chemicals (i.e., hydroxide and hydrosulphide ions contained in the white liquor) to be transported into the reaction site (in wood), so that the dominant step could be the pulping kinetic reactions. In order to ensure uniform moisture content, the meal of both wood species was stored under room conditions before pulping.

Figure 3.2 – Wiley mill used for grinding both Scots pine heartwood and Blue gum.

The batch cooking experiments were carried out in autoclaves rotated in a polyethylene glycol (PEG) bath previously heated to 170 °C and were performed with a high liquor-to-wood ratio of 200:1 (1100 g of liquor to 5.5 g dry weight of wood meal) in order to maintain the active chemicals concentration roughly constant during pulping[1]. Furthermore, all the autoclaves were evacuated for 5 minutes and further pressurized with nitrogen to a 5 bar pressure for additional 5 minutes, in order to guarantee an oxygen-free environment during pulping and good impregnation of the liquor into the wood meal. The applied pressure was released before the autoclaves were placed in the PEG bath.

For each white liquor concentration, six autoclaves were used, in order to obtain results for six different times. The preparation of the different white liquors used in the experiments was accomplished by mixing sodium sulphide nonahydrate ($Na_2S \cdot 9H_2O$), sodium hydroxide (NaOH) and sodium hydrosulphide hydrate (NaHS – 68%), in order to obtain the desired active chemicals concentrations (see section 3.1.1.1). The following table presents the cooking operating conditions corresponding to Scots pine sapwood data selected for this thesis, as well as the operating cooking conditions used for both Scots pine heartwood and Blue gum.

[1] The normal liquor-to-wood ratio used in pulp and paper industry is 3.5/4:1. This ratio provides uniform contact between the liquor and the wood chips, lower heating demands in the digester and favourable solid concentration for the Kraft process recovery cycle.

Table 3.1 – Active chemicals concentrations and cooking times used for digestion of Scots pine (sapwood[2] and heartwood) and Blue gum.

Wood type		Temperature (°C)	$[OH^-]$ (mol/kg_{liquor})	$[HS^-]$ (mol/kg_{liquor})	Time (min)
Scots pine	Sapwood	168	0.10	0.25	5, 10, 20, 30, 60, 90, 120, 180
			0.25	0.10	
			0.25	0.50	
			0.75	0.25	25, 40, 60, 90, 120
	Heartwood	168	0.10	0.25	10, 20, 30, 60, 90, 180
			0.25	0.10	
			0.25	0.50	10, 20, 30, 40, 60, 90
			0.75	0.25	
Blue gum		168	0.10	0.25	5, 10, 20, 30, 40, 60
			0.25	0.10	
			0.25	0.50	
			0.75	0.25	
		154	0.10	0.25	10, 20, 30, 60, 90, 120
			0.25	0.10	
			0.25	0.50	
			0.75	0.25	

Once the desired cooking time was reached, each autoclave was removed from the PEG bath and placed in a cold water tank for 15 minutes. After being cooled down, the content of each autoclave was filtrated with a glass filter, whose dry weight had been previously measured. A sample of each filtrate (black liquor) was then collected for further confirmation of the active chemicals concentrations (see section 3.1.1.2) and the wood residue that resulted from digestion was washed with water. Thereafter, the filters (whose weight had been previously measured) containing the wood residue were dried in the oven, overnight, at a 105 °C temperature. After determining the weight of the different wood residues (in order to calculate the yield), these were stored in small bags for further lignin and carbohydrate analysis.

[2] The selected sapwood data corresponding to a hydroxide and hydrosulphide ion concentrations of 0.75 and 0.25 mol/kg_{liquor}, respectively, does not include data for times out of the 25 to 120 minutes interval. Such fact happens because that data was obtained from cooking experiments in which a different Scots pine log was used.

The following figure shows the general steps that constituted the cooking experiments.

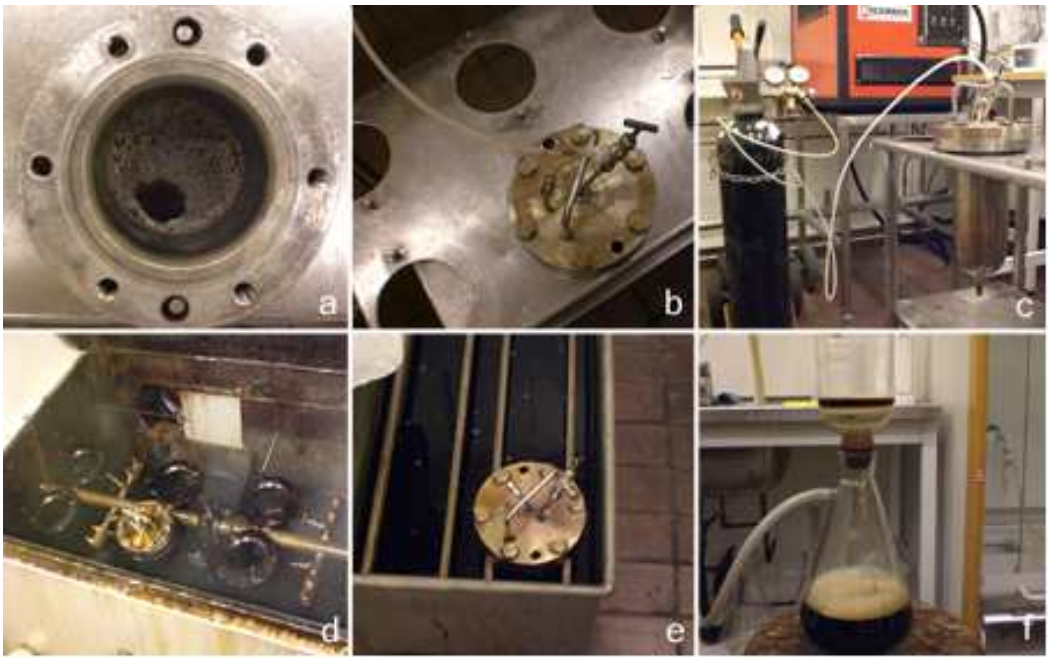


Figure 3.3 – Cooking experiments steps: a) autoclave containing white liquor and wood meal; b) autoclave evacuation; c) autoclave pressurization with N_2; d) autoclave placed in the PEG bath; e) autoclave placed in the cold water tank; f) filtration of the content of an autoclave.

3.1.1.1. White liquor preparation

When preparing white liquor, the sodium sulphide added is almost completely hydrolysed to sodium hydroxide and sodium hydrosulphide, according to the following reaction equation:

$$Na_2S + H_2O \rightarrow NaOH + NaHS$$

Thus, the preparation of the different white liquors used in the cooking experiments depended on which of the active chemicals concentration was desired to be higher:

- **$[OH^-] > [HS^-]$**

According to the desired hydrosulphide ions concentration, an estimate of the necessary mass of Na_2S for a primary liquor preparation was determined using equation 3.1:

$$m_{Na_2S\cdot 9H_2O} = N_a \times m_{liq,d} \times \left[HS^-\right]_{liq,d} \times M_{Na_2S\cdot 9H_2O} \qquad (3.1)$$

Thus, $Na_2S\cdot 9H_2O$ (in approximately 20 g excess to the calculated value) and water were transferred to a plastic container. After total dissolution, approximately 8 g of this primary liquor were titrated with a hydrochloric acid 1M solution and the concentrations of the active chemicals in the liquor were determined as follows:

$$\left[OH^-\right]_{liq} = \frac{\left[HCl\right] \times V_{HCl,OH^-}}{m_{liq,t}} \tag{3.2}$$

$$\left[HS^-\right]_{liq} = \frac{\left[HCl\right] \times V_{HCl,HS^-}}{m_{liq,t}} \tag{3.3}$$

The necessary quantities of both NaOH and the previously mentioned liquor for the preparation of the desired cooking liquor were calculated according to the following system of equations:

$$\begin{cases} m_{liq} = \dfrac{\left[HS^-\right]_{liq,d} \times m_{liq,d}}{\left[HS^-\right]_{liq}} & (3.4) \\ m_{NaOH} = M_{NaOH} \times m_{liq,d} \times \left(\left[OH^-\right]_{liq,d} - \dfrac{\left[OH^-\right]_{liq} \times \left[HS^-\right]_{liq,d}}{\left[HS^-\right]_{liq}} \right) & (3.5) \end{cases}$$

For each autoclave, the calculated quantities of both NaOH and primary liquor were mixed in a container and water was added until a weight value of 1100 g was reached.

- **$[OH^-] < [HS^-]$**

According to the desired hydroxide ions concentration, an estimate of the necessary mass of $Na_2S{\cdot}9H_2O$ for a primary liquor preparation was determined using equation 3.6:

$$m_{Na_2S\cdot 9H_2O} = N_a \times m_{liq,d} \times \left[OH^-\right]_{liq,d} \times M_{Na_2S\cdot 9H_2O} \tag{3.6}$$

However, since the desired hydrosulphide ions concentration was, in this case, higher than the desired hydroxide ions concentration, NaHS (68%) was added according to equation 3.7:

$$m_{NaHS} = N_a \times m_{liq,d} \times \left(\left[HS^-\right]_{liq,d} - \left[OH^-\right]_{liq,d} \right) \times \frac{M_{NaHS}}{0.68} \tag{3.7}$$

The following steps were performed in the same way as in the "$[OH^-] > [HS^-]$" case. Nevertheless, when analysing equation 3.5, one can conclude that the hydrosulphide ions concentration in the primary liquor has to be sufficiently high so that the calculated NaOH quantity can be a positive value. Therefore, in order to obtain the desired white liquor, the excess addition of both $Na_2S{\cdot}9H_2O$ and NaHS for the preparation of the primary liquor had to be carefully executed.

3.1.1.2. Black liquor analysis

As previously mentioned, after filtration of the content of each autoclave, samples of each black liquor were collected as it is shown in the following figure.

Figure 3.4 – Black liquor samples collected after a series of cooking experiments.

Since all cooking experiments occurred under a high liquor-to-wood ratio, the active chemicals concentrations during digestion were maintained roughly constant, which means that the concentration of both hydroxide and hydrosulphide ions in the black liquor should be approximately the same as in its originating white liquor. Thus, after each cooking experiments series, one of the collected samples was selected and titrated according to the same procedure mentioned in section 3.1.1.1, in order to confirm the appropriate preparation of the white liquors used in the experiments.

3.1.1.3. Autoclave temperature rise rate

In order to obtain the temperature rise rate inside the autoclaves when these were rotating in the PEG bath, a temperature probe was placed inside an autoclave. The following figure presents the temperature variations over time obtained with 1.1 kg of white liquor in 2002 and the same amount of both water and white liquor[3] in 2008. Even though no wood was used in these measurements, the high liquor-to-wood ratio (200:1) used in the cooking experiments minimized the effect of the exothermic pulping reactions on temperature. Thus, the following measurements are still reliable.

[3] The white liquor used was prepared with NaOH and had a sodium concentration equal to the average of the ones in the liquors of the cooking experiments.

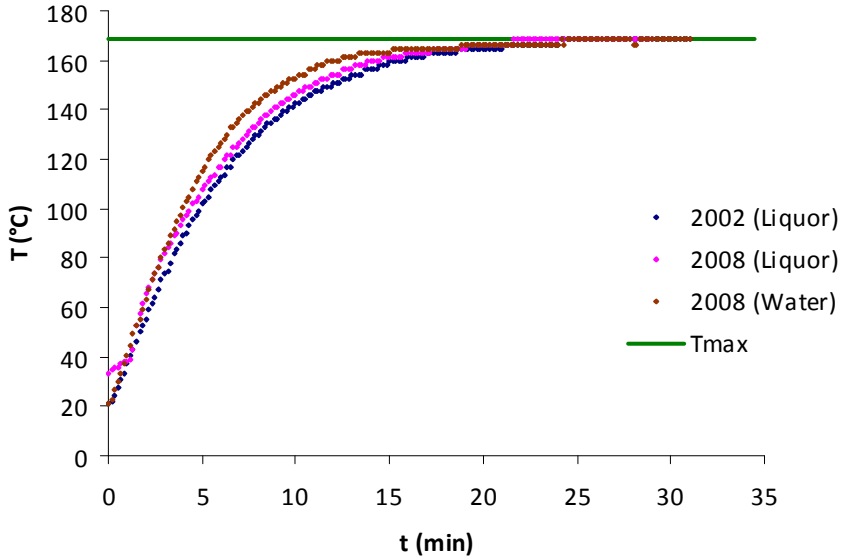


Figure 3.5 – Autoclave temperature rise rates obtained using both water and a white liquor.

Figure 3.5 shows that, in all experiments, it took approximately 25 minutes for the maximum temperature (168 °C) to be reached. Furthermore, during the first 17 minutes (roughly) the temperature rise obtained with white liquor in 2008 had a small delay in comparison to the one obtained in 2002. However, this delay should not significantly compromise the comparison between the results obtained for Scots pine sapwood and heartwood. In addition, by analysing the temperature rise with water and white liquor (2008), one can also conclude that the presence of ions slows the increase in temperature during approximately 17 minutes. The most likely reason for this is the fact that the presence of ions is responsible for an increase in viscosity, which decreases the heat transfer rate.

3.1.2. Lignin and carbohydrate analysis

Before analysing the wood residue samples using acid hydrolysis, approximately 250 mg of each sample were ground (Figure 3.6) and put in the oven, overnight, under a 105 °C temperature.

Figure 3.6 – a) wood residue samples; b) grinder used to grind the wood residue samples.

Afterwards, 200 mg of the dry material were transferred to 150 ml beakers and 3 ml of a 72% concentration sulphuric acid (H_2SO_4) were added in order to degrade cellulose and hemicelluloses into random oligomers. The content of the beakers was carefully stirred with glass rods and further evacuated for 15 minutes, so that a good impregnation of the acid into the solid residue was achieved. After placing the beakers in a 30 °C water bath for 60 minutes, 84 g of deionised water were added to each beaker. Thereafter, all the beakers were covered with aluminium lids and autoclaved at 125 °C for 60 minutes, with the purpose of dividing the previously mentioned oligomers into monomer units (i.e., arabinose, galactose, glucose, xylose and mannose).

After acid hydrolysis the content inside the beakers consisted of a heterogeneous solution of a solid residue (i. e., Klason lignin – KL) and dissolved carbohydrates and acid soluble lignin[4]. The content of each beaker was further filtrated and Klason lignin was analysed gravimetrically (see section 3.1.2.2), whereas acid soluble lignin content was determined by UV spectroscopy at 205 nm, assuming a value of 110 $dm^3 \cdot g^{-1} \cdot cm^{-1}$ for the absorptivity coefficient. The filtrate was diluted to two different concentrations. The more concentrated solutions were prepared adding the filtrate, 2 ml of 2000 mg/L fucose (internal standard) and water to 100 ml flasks. On the other hand, the less concentrated solutions were prepared adding 5 ml of the concentrated solutions, 9 ml of 200 mg/L fucose and water to 50 ml flasks[5]. Both concentrated and diluted solutions were transferred to vials, which were stored in a freezer for further analysis of the monomer content (i.e., fucose, arabinose, galactose, glucose[6], xylose and mannose). This was accomplished by using ion chromatography with a CarboPac™ PA1 column and a pulsed amperiometric detector (PAD) for both separation and detection of the previously mentioned monomers, in order to determine the content of the different polysaccharides in the solid residue (i.e., cellulose and hemicelluloses – xylan and glucomannan).

The following figure shows the general steps that constituted the lignin and carbohydrate analysis.

[4] Unlike Klason lignin, acid soluble lignin is the small amount of lignin that is soluble in acid.
[5] These were the solutions used to determine the acid soluble lignin content by UV spectroscopy.
[6] Since the amplitude of the detector was not sufficiently large to obtain the entire glucose peak for the analysis of the concentrated samples, the glucose content was determined using the diluted samples.

Figure 3.7 – Lignin and carbohydrate analysis steps: a) evacuation of the beakers; b) beakers placed in a 30°C water bath; c) autoclave; d) filtration of the content of a beaker; e) Klason lignin after filtration; f) concentrated and diluted solutions after filtration; g) HPLC; h) spectrophotometer used to measure the absorbance of the diluted solutions in order to calculate the acid soluble lignin content.

3.1.2.1. HPLC calibration

The calibration of the HPLC was performed using three concentrated standard samples and three diluted standard samples. The concentrated samples were used to obtain the calibration curves for arabinose, galactose, xylose and mannose, whereas the diluted samples were used to obtain the glucose calibration curve. The following table presents the concentrations of the solutions.

Table 3.2 – Concentrations of the different standard samples used for the calibration of the HPLC.

	Concentration (mg/L)					
Sample	**Fucose**	**Arabinose**	**Galactose**	**Glucose**	**Xylose**	**Mannose**
1c	40	10.5	8	550	60	80
2c	40	21	16	1100	120	160
3c	40	31.5	24	1650	180	240
1d	40	1.05	0.8	55	6	8
2d	40	2.1	1.6	110	12	16
3d	40	3.15	2.4	165	18	24

Since fucose was used as an internal standard, its concentration was fixed. Thus, for each chromatogram resulting from each analysed sample, the areas of the peaks of the other monomers were divided by the area of the fucose peak. These values and their corresponding concentrations (Table 3.2) were plotted and linearly adjusted in order to obtain the calibration curves for each monomer. This procedure was repeated for each series of measurements. The following figures show the calibration curves obtained for one of those series.

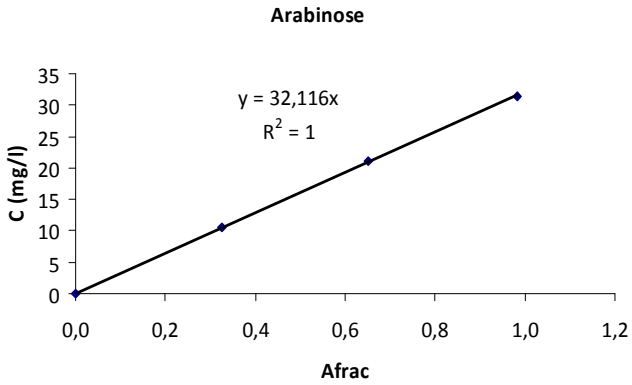


Figure 3.8 – Arabinose calibration curve.

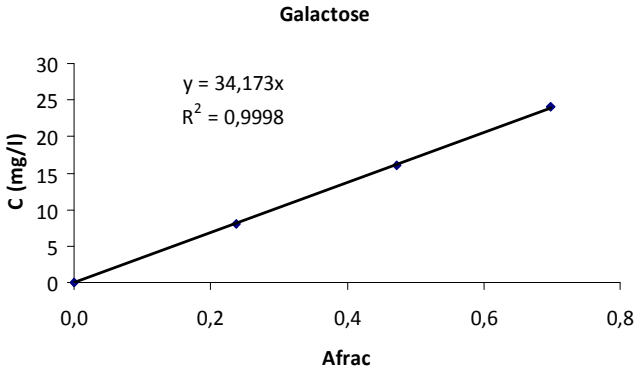


Figure 3.9 – Galactose calibration curve.

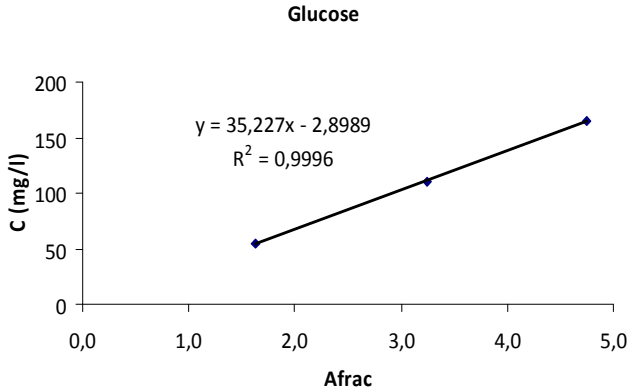


Figure 3.10 – Glucose calibration curve.

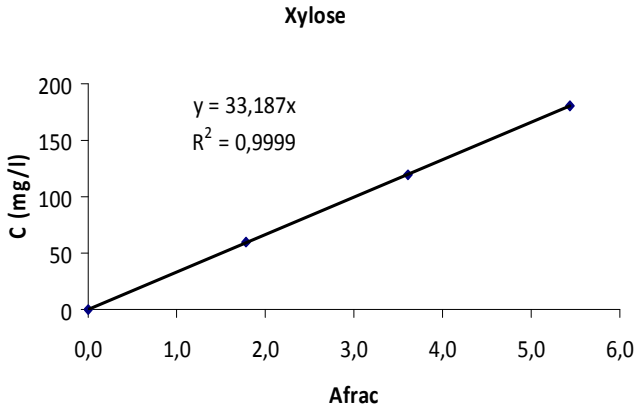


Figure 3.11 – Xylose calibration curve.

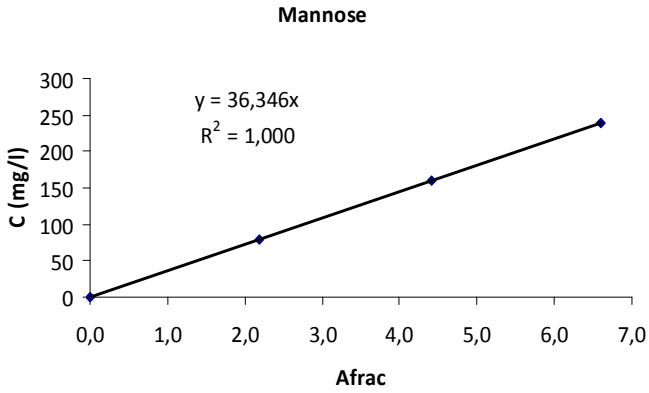


Figure 3.12 – Mannose calibration curve.

The calibration curves were used to determine the concentrations of the different monomers in the solutions prepared after separation of Klason lignin from the carbohydrate content.

3.1.2.2. Determination of Klason lignin and carbohydrate percentages on wood

As previously mentioned, after hydrolysis of the samples of wood residue obtained from the cooking experiments, the separation of Klason lignin from the carbohydrate containing liquid was achieved by filtration. Thus, in order to characterize the degree of delignification during Kraft cooking, the percentage of Klason lignin in relation to the initial quantity of wood used in the cooking experiments was calculated according to the following equation.

$$KL\ (\%\ on\ wood) = \frac{m_{lignin,wrh}}{m_{wrh}} \times Yield \qquad (3.8)$$

In order to determine the yield, the following equation can be used.

$$Yield\ (\%) = \frac{m_{wr}}{m_{wood\ meal}} \times 100 \qquad (3.9)$$

Equation 3.9 shows that the yield is defined as the ratio between the quantity of wood residue (dry weight) obtained after the cook and the quantity of its originating wood (dry weight).
On the other hand, the calculation of the carbohydrate percentages on wood (i.e., cellulose, glucomannan and xylan) was performed according to the following steps:

- The concentrations of the monomers in the solutions prepared after hydrolysis were determined using the areas of the peaks that resulted from the analysis of the vials on the HPLC and the calibration curves of each monomer.
- Since carbohydrates derive from anhydro sugars (i.e., arabinan, galactan, glucan, xylan and mannan), the amount of these compounds in the wood residue used for hydrolysis was determined as follows [Wigell *et al.* 2007]:

$$Arabinan\ (mg) = \frac{[Arabinose] \times V_{sol} \times a}{y} \qquad (3.10)$$

$$Galactan\ (mg) = \frac{[Galactose] \times V_{sol} \times a}{y} \qquad (3.11)$$

$$Glucan\ (mg) = \frac{[Glucose] \times V_{sol} \times a}{y} \qquad (3.12)$$

$$Xylan\ (mg) = \frac{[Xylose] \times V_{sol} \times a}{y} + \frac{M_{xylose}}{M_{MeGlA}} \times 0.001 \times$$
$$\times \frac{2}{3} \times m_{wrh} \times \left(0.0027 \times Yield^2 - 0.224 \times Yield + 5.5722\right) \qquad (3.13a)$$

$$Xylan\ (mg) = \frac{[Xylose] \times V_{sol} \times a}{y} \qquad (3.13b)$$

$$Mannan\ (mg) = \frac{[Mannose] \times V_{sol} \times a}{y} \qquad (3.14)$$

In equations 3.10 to 3.14, "a" is a parameter that results from the fact that when two monomer units are linked to each other a molecule of water is lost. Therefore, "a" is obtained by subtracting the molecular weight of water (approximately 18 g/mol) to the molecular weight of the monomer and dividing this by the molecular weight of the monomer. Furthermore, "y" is a correction factor for the fact that some monomers are further degraded during the acid hydrolysis procedure. The following table shows the values of the parameters "a" and "y".

Table 3.3 – Values of the parameters a and y.

	Monomer	$M_{monomer}$ (g/mol)	a	y
Pentosanes	Arabinose	≈ 150	0.88	0.944
	Xylose			0.899
Hexosanes	Galactose	≈ 180	0.90	0.952
	Glucose			0.974
	Mannose			0.926

In addition, equation 3.13a encloses a term that compensates the fact that two thirds of the bonding between xylose units and 4-O-methylglucuronic acid (MeGlcA) are not broken during acid hydrolysis, this meaning that part of the xylose is not detected on the HPLC. This part of equation 3.13a was obtained from Wigell *et al.* (2007) and it considers the variation of the content of 4-O-methylglucoronic acid with the total yield, during alkaline cooking of Scots pine, as it is shown in the following figure:

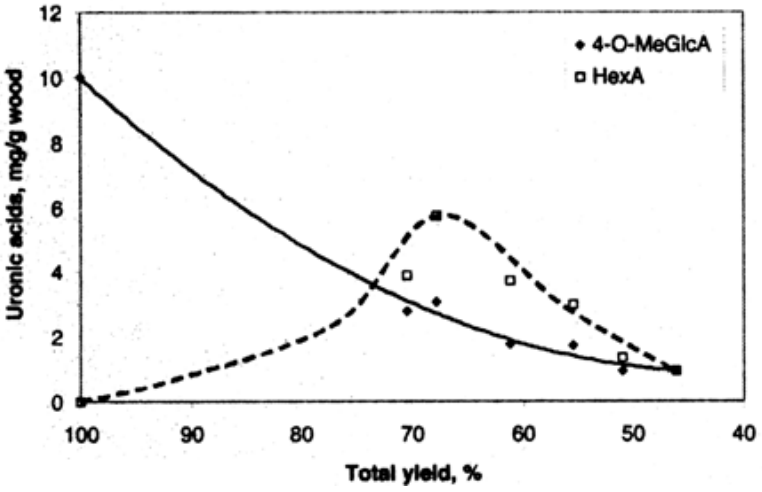


Figure 3.13 – Degradation and formation of uronic acids during alkaline cooking [Wigell *et al.* 2007].

However, since this kind of information was not available for Blue gum, equation 3.13b was used in this case.

- The following table shows the equations used for determining the amount of carbohydrates in the wood residue used for hydrolysis:

Table 3.4 – Calculation formulas for determination of cellulose, glucomannan and xylan contents in wood residues of Scots pine and Blue gum.

	Scots pine	Eq.	Blue gum	Eq.
Cellulose (mg)	$Glucan - \frac{1}{3.5} Mannan$	3.15a	$Glucan - \frac{1}{1} Mannan$	3.15b
Glucomannan (mg)	$Galactan + Mannan\left(1 + \frac{1}{3.5}\right)$	3.16a	$Mannan\left(1 + \frac{1}{1}\right)$	3.16b
Xylan (mg)	$Xylan + Arabinan + (MeGlcA + HexA)$	3.17a	$Xylan$	3.17b
Other carbohydrates (mg)	---		$Arabinan + Galactan$	3.18

Equations 3.15a to 3.17a were obtained from Wigell *et al.* (2007). Thus, for Scots pine, the glucomannan content was calculated as the sum of galactan, mannan and part of the glucan, assuming a molar ratio between mannose and glucose of 3.5:1 (see section 2.2.3.3). Moreover, the xylan content was determined as the sum of xylan, arabinan and uronic acids (i.e., 4-O-methylglucoronic acid and hexenuronic acid, which is formed during alkaline cooking from the first one). Furthermore, the cellulose content was calculated as the content of glucan, apart from its contribution to glucomannan.

On the other hand, equations 3.15b to 3.17b were adapted from equations 3.15a to 3.17a, considering the existing differences between hardwood and softwood components (see section 2.2.3) and a molar ratio between mannose and glucose in glucomannan of 1:1 [Rydholm 1966]. In order to complete the mass balance for Blue gum, arabinan and galactan were classified as “other carbohydrates”, as shown in Table 3.4 (equation 3.18). In addition, the content of uronic acids was also not counted in the determination of the amount of xylan.

- Finally, the carbohydrate percentages on wood were calculated according to the following equations:

$$Cellulose\,(\%\ on\ wood) = \frac{m_{cellulose,wrh}}{m_{wrh}} \times Yield \qquad (3.19)$$

$$Glucomannan\,(\%\ on\ wood) = \frac{m_{glucomannan,wrh}}{m_{wrh}} \times Yield \qquad (3.20)$$

$$Xylan\left(\%\ on\ wood\right)=\frac{m_{xylan,wrh}}{m_{wrh}}\times Yield \tag{3.21}$$

$$O.C.\left(\%\ on\ wood\right)=\frac{m_{o.c.,wrh}}{m_{wrh}}\times Yield \tag{3.22}$$

An example of calculation of Klason lignin and carbohydrate percentages on wood can be found in Appendix B.

4. Results and Discussion

This chapter presents the experimental results of this thesis, along with a discussion of those results. A comparison in terms of degree of delignification and degradation of hemicelluloses during Kraft cooking is established between Scots pine sapwood and heartwood, as well as between Scots pine and Blue gum.

4.1. Scots pine sapwood and heartwood

During Kraft cooking, the main goal is to degrade and solubilise lignin, regardless of the wood specie used for the production of pulp. Therefore, when comparing the digestion of different wood species or different wood parts (as sapwood and heartwood), the analysis of the variation of the degree of delignification over time is crucial.

Moreover, since the hemicellulose content is strongly affected during Kraft pulping, due to the fact that hemicelluloses are attacked by the active chemicals in the white liquor, it is also extremely important to observe the evolution of their degree of dissolution/degradation over time.

Thus, the figures presented in this section (Figures 4.1, 4.2 and 4.3) show the tendency of Klason lignin, glucomannan and xylan percentages on wood, during different Kraft cooking experiments.

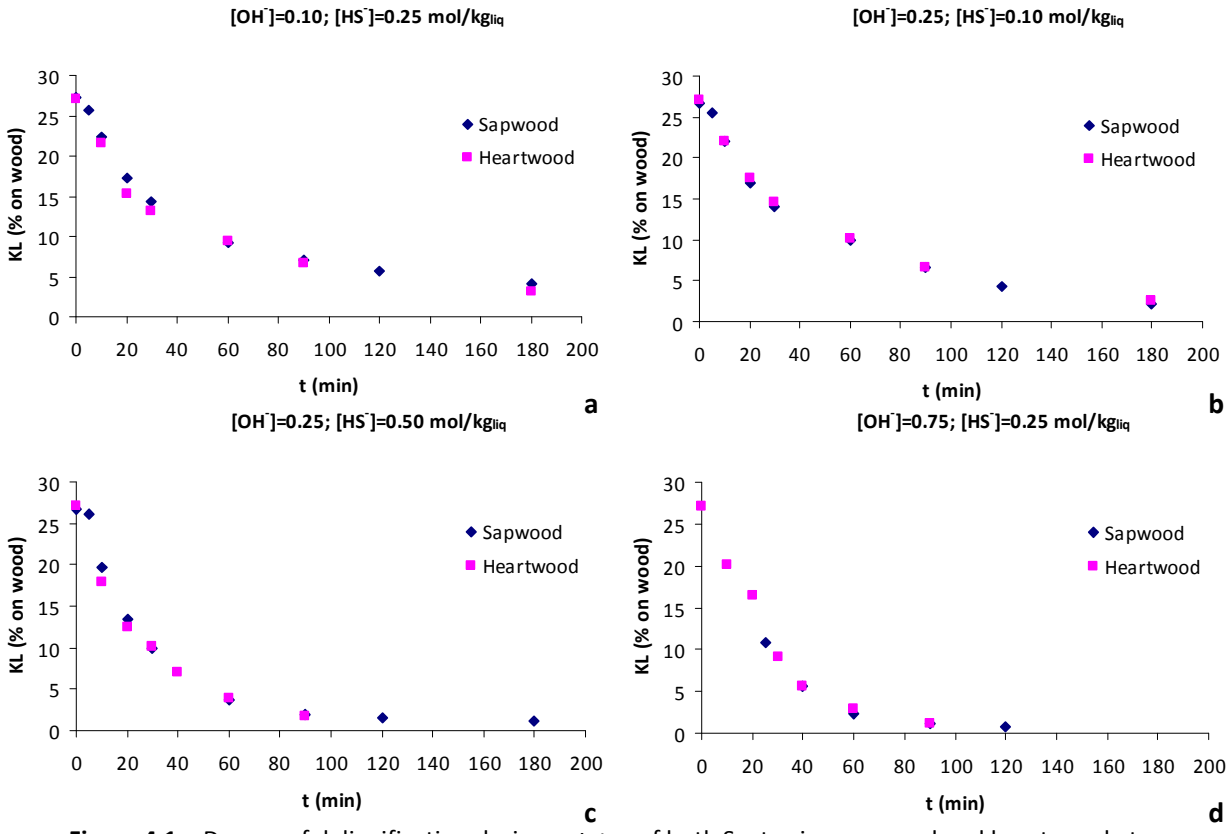


Figure 4.1 – Degree of delignification during pulping of both Scots pine sapwood and heartwood at a temperature of 168 °C and different hydroxide and hydrosulphide ion concentrations.

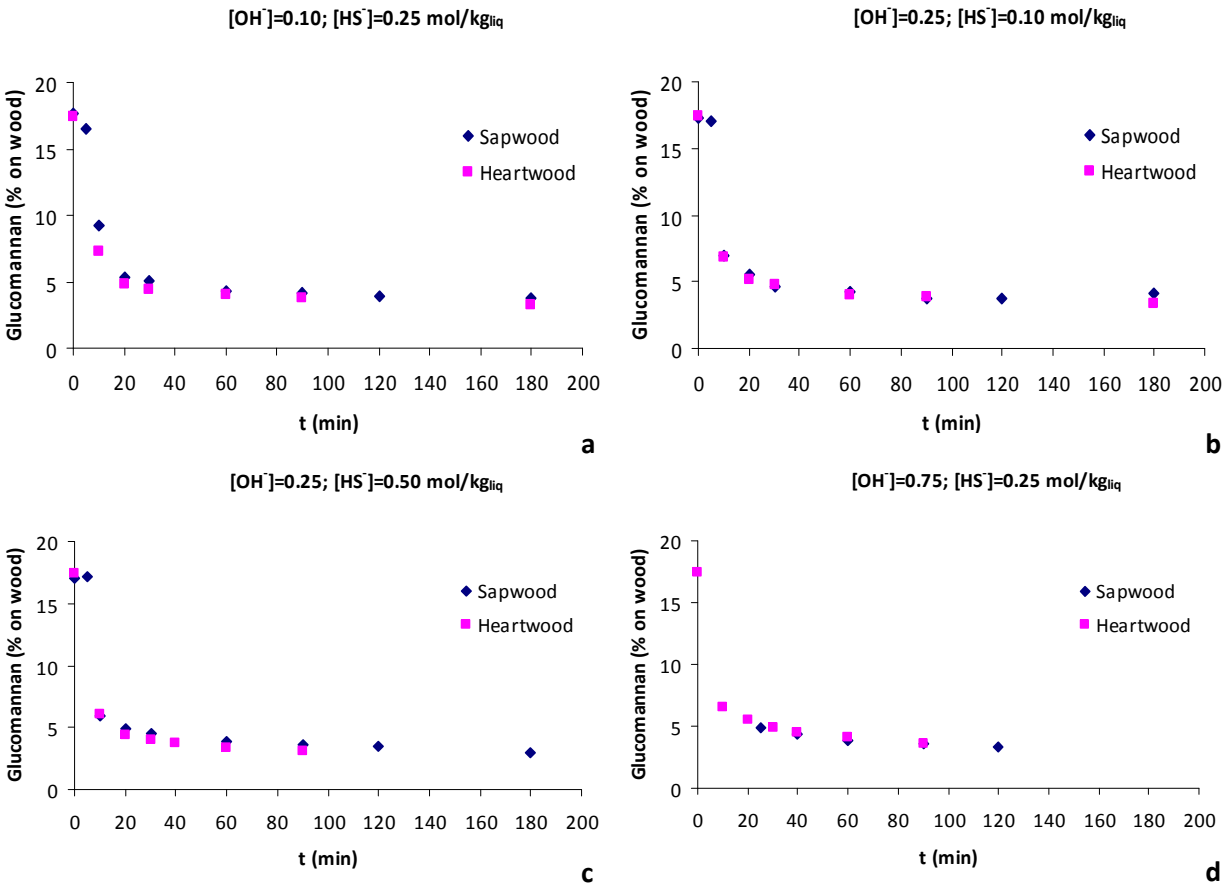


Figure 4.2 – Degree of dissolution/degradation of glucomannan during pulping of both Scots pine sapwood and heartwood at a temperature of 168 °C and different hydroxide and hydrosulphide ion concentrations.

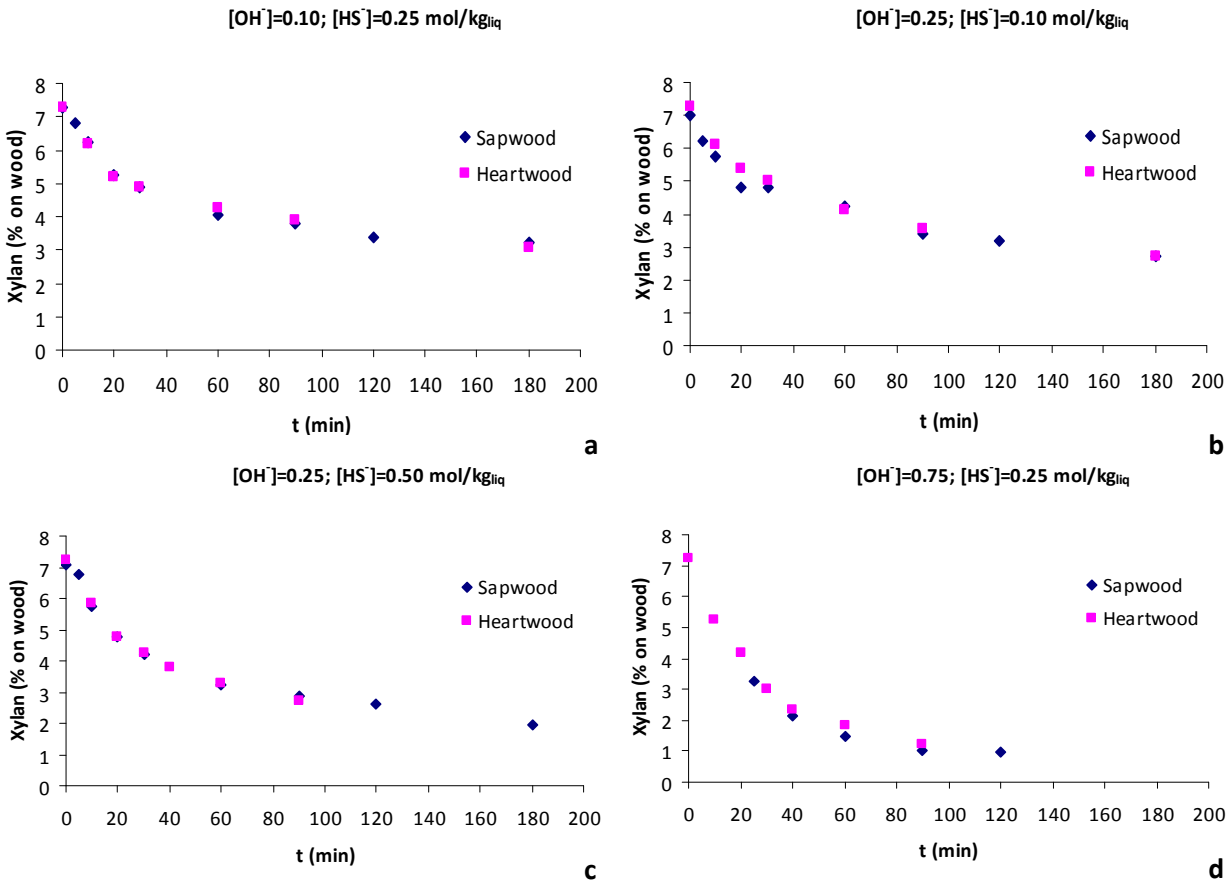


Figure 4.3 – Degree of dissolution/degradation of xylan during pulping of both Scots pine sapwood and heartwood at a temperature of 168 °C and different hydroxide and hydrosulphide ion concentrations.

When analysing Figures 4.1, 4.2 and 4.3, one verifies that Klason lignin, glucomannan and xylan percentages on wood have an almost coincident behaviour for both heartwood and sapwood during Kraft cooking. Thus, the deviations observed are essentially connected to experimental errors (e.g., lack of accuracy in the time of removing the autoclaves from the PEG bath, weight measuring mistakes and lignin and carbohydrate losses during the experimental work) and probably to the fact that sapwood and heartwood results were obtained by different operators.

Furthermore, by analysing the behaviour of the main wood components (apart from cellulose, which is less degraded during Kraft cooking), one can assume a similar behaviour for the overall yield. The conclusion in a study of pulping yield and delignification kinetics of heartwood and sapwood of Maritime pine [Esteves *et al.* 2005] states that lower yields are obtained for heartwood. Nevertheless, according to that study, this fact is related to the different content of wood extractives in sapwood and heartwood of the Maritime pine used (1.6 and 4.1 % on wood, respectively). However, the content of extractives in the Scots pine used in this thesis was approximately the same for both wood parts (≈ 1.4 % on wood), which can explain the result of practically equal yields during Kraft cooking. Thus, the result in the present study is in agreement with earlier results.

4.2. Scots pine and Blue gum

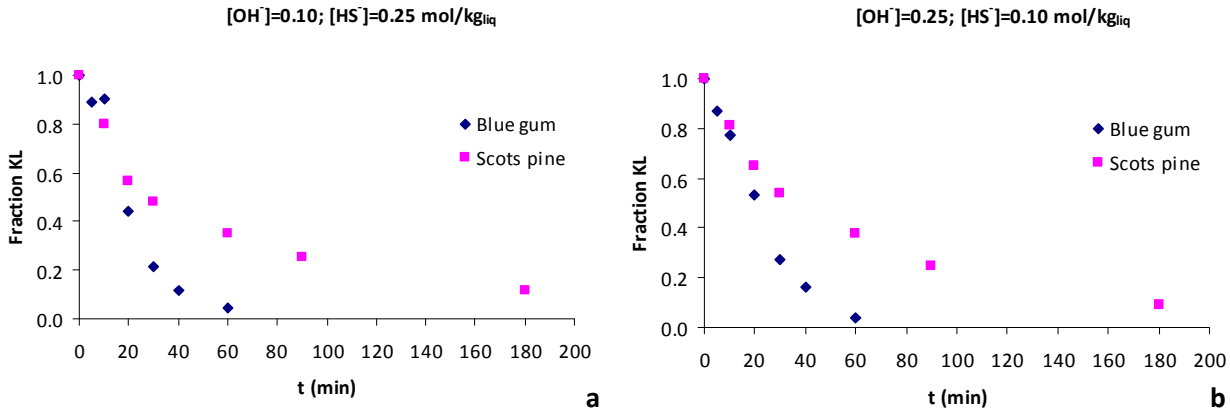
The existing differences in composition and structure of wood components between softwood and hardwood species imply a significant difference concerning their behaviour during Kraft cooking. The following table stresses the chemical composition differences for the particular case of Scots pine and Blue gum, presenting the initial compositions of their main components (excluding cellulose).

Table 4.1 – Percentage of the main wood components on both Scots pine and Blue gum (MV – measured value; LV – literature value [Sjöström 1993]).

Wood species	% Lignin		% Glucomannan		% Xylan	
	MV	LV	MV	LV	MV	LV
Scots pine	27.0	27.7	17.4	16.0	7.3	8.9
Blue gum	22.3	21.9	2.6	1.4	14.2	19.9

When observing Table 4.1, one can notice that there is a deviation between the values measured in this work (see calculation method in section 3.1.2.2) and the ones found in literature. However, since these values vary from tree to tree, depending on factors such as the place where each tree grows, the deviations observed are acceptable. Furthermore, one can also see that there is a higher content of lignin and glucomannan is present in Scots pine, whereas Blue gum has a higher content of xylan.

The following figures show a comparison of the results obtained for Blue gum and Scots pine heartwood regarding delignification and hemicellulose degradation over time. In order to simplify the analysis of the different behaviours observed for Scots pine and Blue gum, all results were normalized, because of the different initial values.



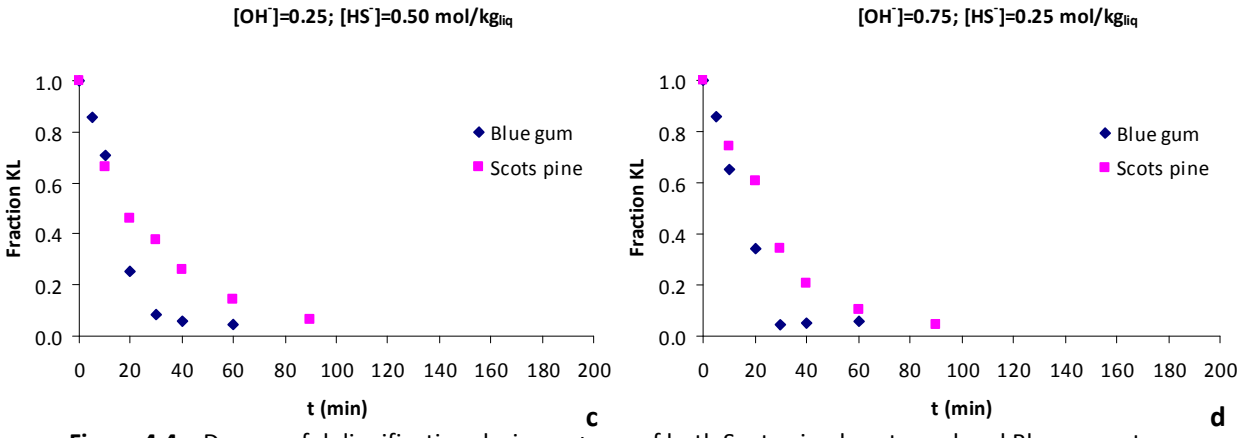


Figure 4.4 – Degree of delignification during pulping of both Scots pine heartwood and Blue gum at a temperature of 168 °C and different hydroxide and hydrosulphide ion concentrations.

As it is shown in Figure 4.4, delignification is much faster for Blue gum than for Scots pine. If both temperature and liquor composition are kept constant, it has been shown that a first order reaction behaviour can be applied in Kraft cooking [Teder 2004]. In table 4.2, the result of estimating the rate constants assuming a first order reaction behaviour is shown (see Appendix A).

Table 4.2 – Estimates of delignification rate constants and correspondent correlation coefficients for Scots pine and Blue gum.

Wood species	$[OH^-]$ (mol/kg_{liquor})	$[HS^-]$ (mol/kg_{liquor})	Corresponding Figure	k (min^{-1})	R^2
Scots pine	0.10	0.25	4.4a	$9.22x10^{-3}$	0.994
	0.25	0.10	4.4b	$1.19x10^{-2}$	0.998
	0.25	0.50	4.4c	$2.81x10^{-2}$	0.995
	0.75	0.25	4.4d	$3.38x10^{-2}$	0.991
Blue gum (168 °C)	0.10	0.25	4.4a	$5.24x10^{-2}$	0.995
	0.25	0.10	4.4b	$6.69x10^{-2}$	0.994
	0.25	0.50	4.4c	n.d.	n.d.
	0.75	0.25	4.4d	n.d.	n.d.
Blue gum (154 °C)	0.10	0.25	---	$1.72x10^{-2}$	0.975
	0.25	0.10	---	$2.10x10^{-2}$	0.998
	0.25	0.50	---	$3.98x10^{-2}$	1.000
	0.75	0.25	---	$4.24x10^{-2}$	0.994

Using the values shown in Table 4.2, the ratio between the delignification rate constants of Blue gum and Scots pine that correspond to the first two liquors (i.e., the ones corresponding to Figures 4.4a and 4.4b) show that, in these two cases, the delignification rate in Blue gum is approximately 5.6 times higher than the one in Scots pine. Due to the poor correlation coefficient obtained for the trend line associated to the liquors that correspond to Figures 4.4c and 4.4d, it was not possible to determine the rate constants for those two cooking experiments. However, when observing Figures 4.4.c and 4.4d, even though the deviations in delignification rate between Scots pine and Blue gum seem to be lower, hardwood lignin still degrades faster than the one in softwood. Thus, according to Chang & Sarkanen (1973), in their study regarding the effect of species on the rate of Kraft delignification, the fact that hardwood delignification rates are higher than the ones in softwood is explained by the higher content of syringylpropane units in hardwood lignin. This was also indicated by Chiang *et al.* (1988), in a study that compared softwood and hardwood Kraft pulping, who also stated that the structure of lignin, rather than its amount in wood, contributes to the faster delignification rate in hardwood.

Moreover, by comparing Figure 4.4a with 4.4d and 4.4b with 4.4c, one can also notice that the delignification rate of both wood species increases with an increase in the concentrations of hydroxide and hydrosulphide ions. This was expected since it is known that hydroxide ions are involved in the fragmentation reactions of lignin, whereas hydrosulphide ions promote the cleavage of the phenolic β-O-4 structures in lignin [Gellerstedt 2004].

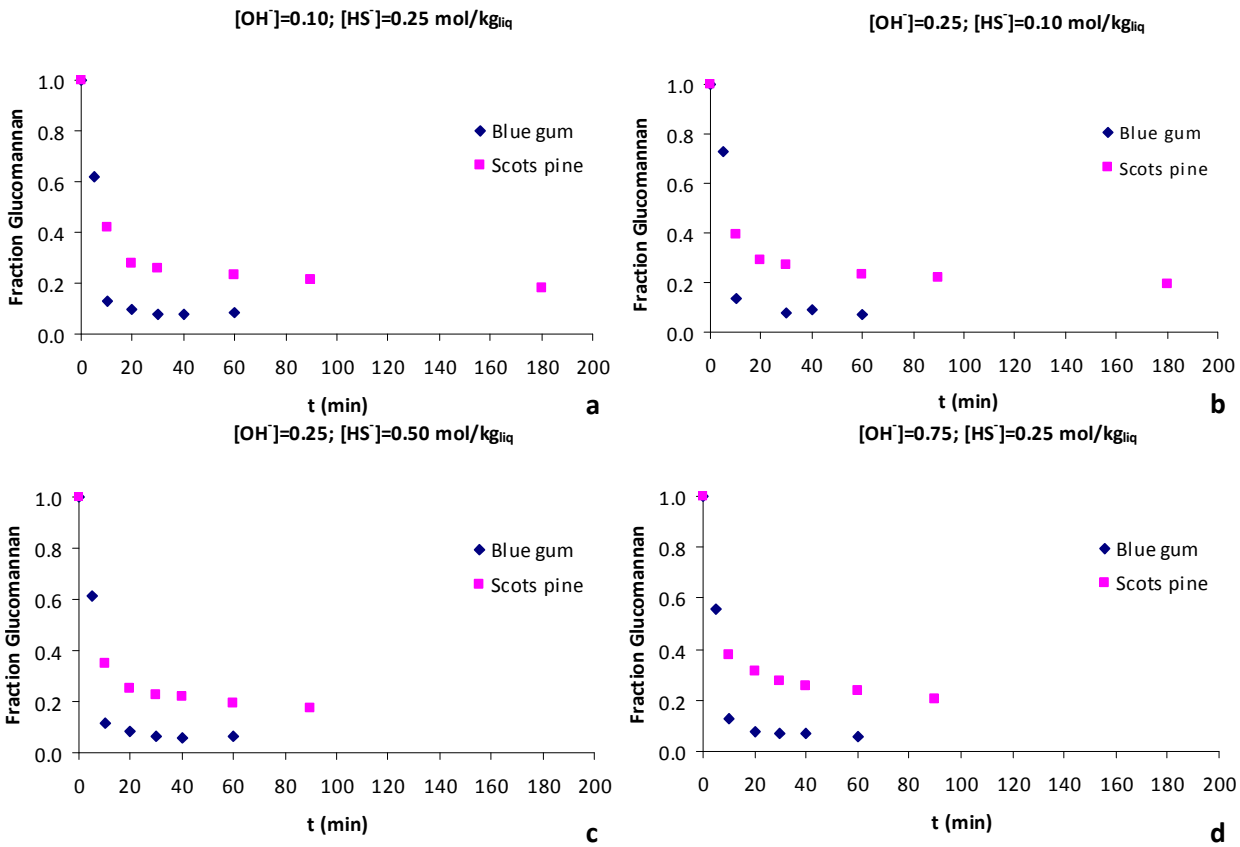
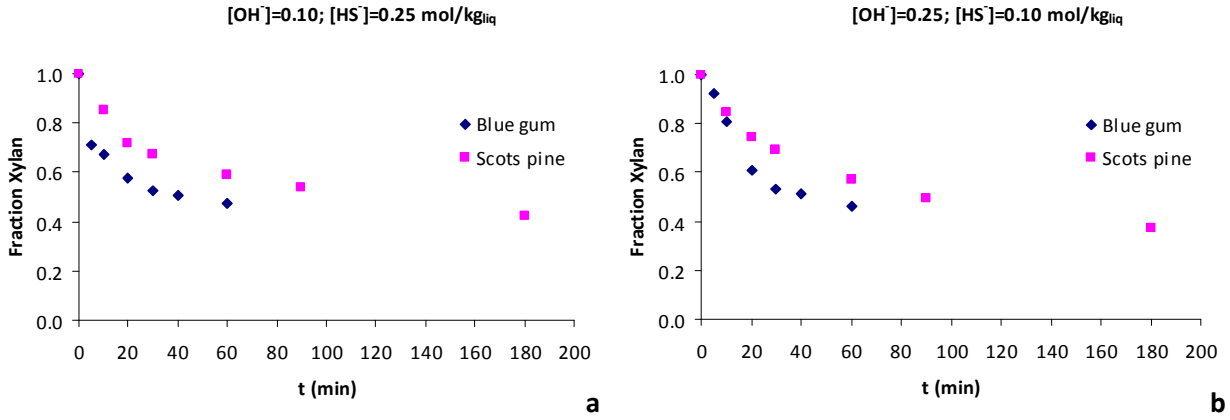


Figure 4.5 – Degree of dissolution/degradation of glucomannan during pulping of both Scots pine heartwood and Blue gum at a temperature of 168 °C and different hydroxide and hydrosulphide ion concentrations.

Figure 4.5 presents the variation of the degree of degradation of glucomannan over time. The analysis of the results shows that, for both wood species, a large amount of glucomannan is degraded during the initial part of the cook, but then a plateau is reached and the content of glucomannan stays approximately constant. Nevertheless, in the final part of the cook, the content of glucomannan in Scots pine is still approximately 20 % of its initial amount, whereas, in Blue gum, almost all glucomannan is degraded. According to information in literature, the rapid decrease in glucomannan content obtained during the initial part of the cook is mainly due to the peeling reactions (rather than dissolution), that have a noticeable reaction rate already at temperatures around 100°C (i.e., approximately 3 minutes reaction time – see section 3.1.1.3). These reactions keep chewing off sugar units of the glucomannan chain until a stopping reaction occurs [Brännvall 2004, Wigell *et al.* 2007]. Thus, the lower plateau observed for Blue gum may be due to the lower molecular weight of hardwood glucomannan, which might increase the efficiency of the peeling reactions, leaving almost no time for a stopping reaction to occur. On the other hand, in softwood glucomannan, with a higher molecular weight, a stopping reaction may happen before the glucomannan chain has been entirely degraded. In addition, possible interactions (either chemical or physical) between parts of glucomannan and the more resistant cellulose [Wigell *et al.* 2007] may also keep glucomannan protected from the alkali attack.

Moreover, when comparing Figures 4.5b with 4.5c, it seems that, for both wood species, variations in concentration of hydrosulphide ions do not cause any significant effect on the degradation rate of glucomannan. This is in accordance with the literature, since the effect of hydrosulphide ions on carbohydrate degradation is known to be very small [Gellerstedt 2004]. Furthermore, a comparison between Figures 4.5a and 4.5d shows that the concentration of hydroxide ions does not have any obvious influence on glucomannan degradation. This was also verified in a study of softwood hemicellulose degradation by Wigell *et al.* (2007) and may be due to the fact that peeling reactions occur in the presence of alkali, but their rate does not depend on the alkali concentration.



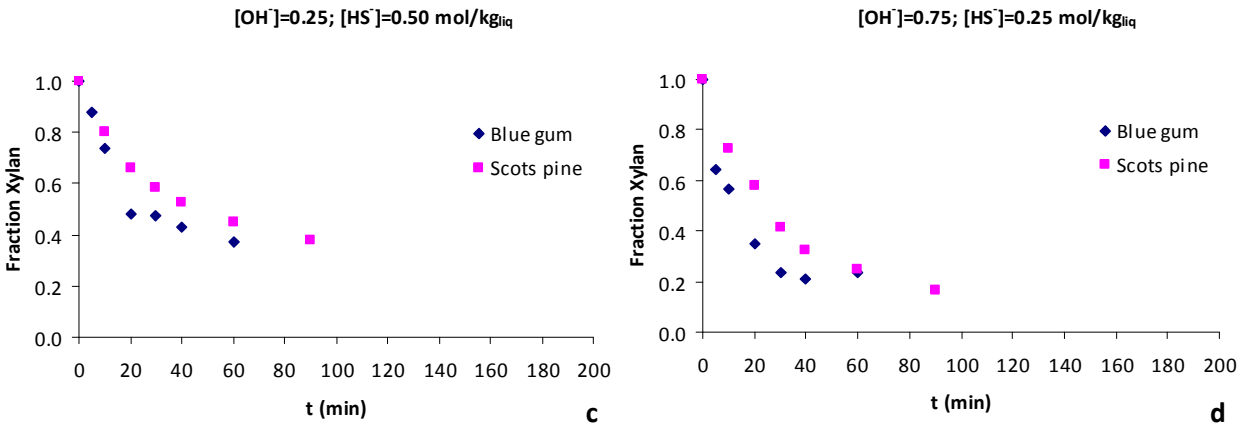
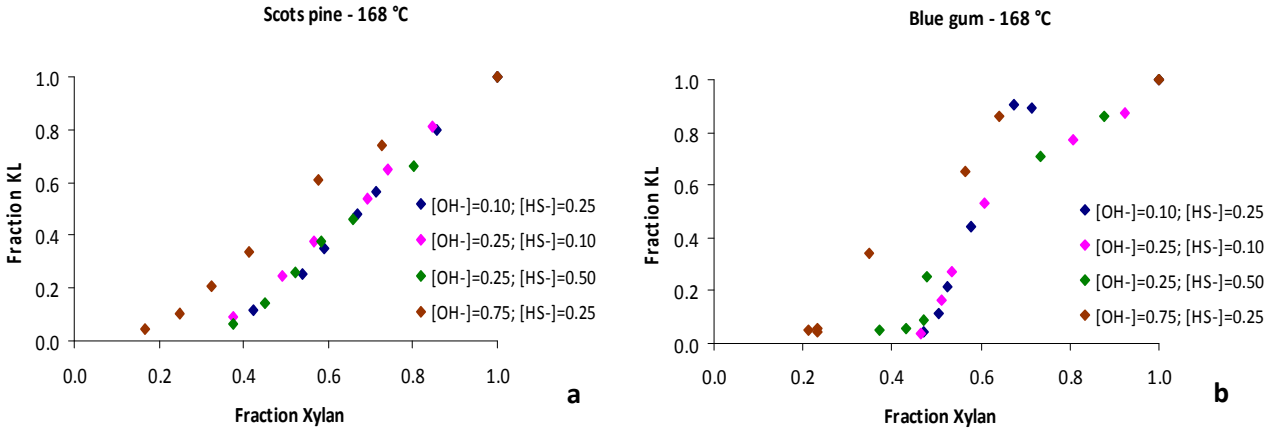


Figure 4.6 – Degree of dissolution/degradation of xylan during pulping of both Scots pine heartwood and Blue gum at a temperature of 168 °C and different hydroxide and hydrosulphide ion concentrations.

By analysing Figure 4.6, one can verify that, as occurred for lignin and glucomannan, a decrease in xylan content over time occurs for both Blue gum and Scots pine. Since it is known that peeling reactions are much less efficient in xylan than in glucomannan [Gellerstedt 2004], its decrease in content over time is mainly due to dissolution in alkaline environment. Therefore, when comparing Figure 4.6a with 4.6d, it is not surprising to see that an increase in hydroxide ions concentration is responsible for a higher loss in xylan content for both wood species. However, a comparison between Figures 4.6b and 4.6c shows that an increase in hydrosulphide ions concentration (which is known not to have any influence in carbohydrate degradation/dissolution) leads to a slight decrease in xylan content. Thus, the possible existence of LCCs (i.e., Lignin Carbohydrate Complexes), which has been suggested by several researchers, especially between xylan and lignin, may be a reason for the verified influence of hydrosulphide ions in xylan dissolution. The following figure presents the relation between lignin and xylan contents during Kraft cooking of both wood species.



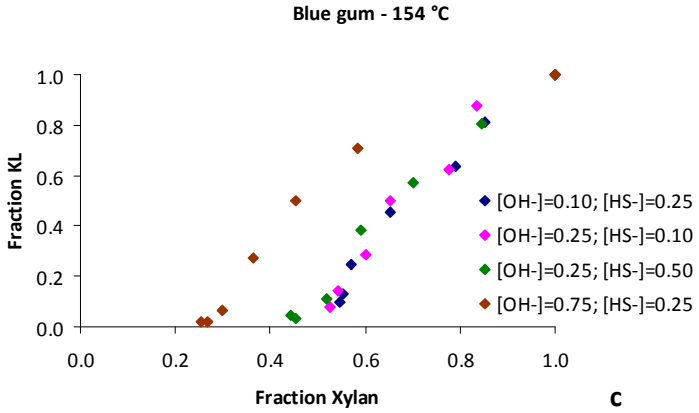


Figure 4.7 – Relation between lignin and xylan contents during Kraft cooking.

As was shown in a study by Wigell *et al.* (2007), Figure 4.7a shows a practically linear relation between the variation of xylan and lignin contents during Kraft cooking of Scots pine. On the other hand, this linear relation does not seem to occur in the same way for Blue gum (Figure 4.7b). In fact, for the two liquors with a hydrosulphide ions concentration of 0.25 mol/kg_{liquor}, xylan seems to be more affected during the first minutes of the cook, until an approximately linear relation between xylan and lignin contents starts. However, since it is difficult to make a clear analysis of the behaviour observed for the liquors with a hydroxide ions concentration of 0.25 mol/kg_{liquor}, the relation between lignin and xylan contents during Kraft cooking of Blue gum at 154 °C was also plotted (Figure 4.7c). Thus, when analysing Figure 4.7c, one can notice the existence of a relation closer to linearity, which does not make it unreasonable to assume the occurrence of both chemical and physical interactions between lignin and xylan, in both wood species. Consequently, the parts of xylan that are linked to lignin can also be affected by the presence of hydrosulphide ions, whereas the parts that are covered by lignin in the cell wall can remain there until that lignin is dissolved/degraded. Furthermore, the suggestion of strong interactions between xylan and cellulose might explain the reason why there is still xylan in the final part of the cook (Figures 4.6 and 4.7).

Moreover, Figures 4.6 and 4.7 also show that a way of keeping the xylan content high, in order to increase the overall yield, is to decrease the alkali concentration during Kraft cooking.

4.3. Effect of temperature on cooking of Blue gum

In order to analyse the effect of temperature on delignification and dissolution/degradation of both glucomannan and xylan during Kraft cooking of Blue gum, this wood species was cooked at two different temperatures (154 and 168 °C). The following figure presents the results obtained with a hydroxide ions concentration of 0.25 mol/kg_{liq} and a hydrosulphide ions concentration of 0.50 mol/kg_{liq}.

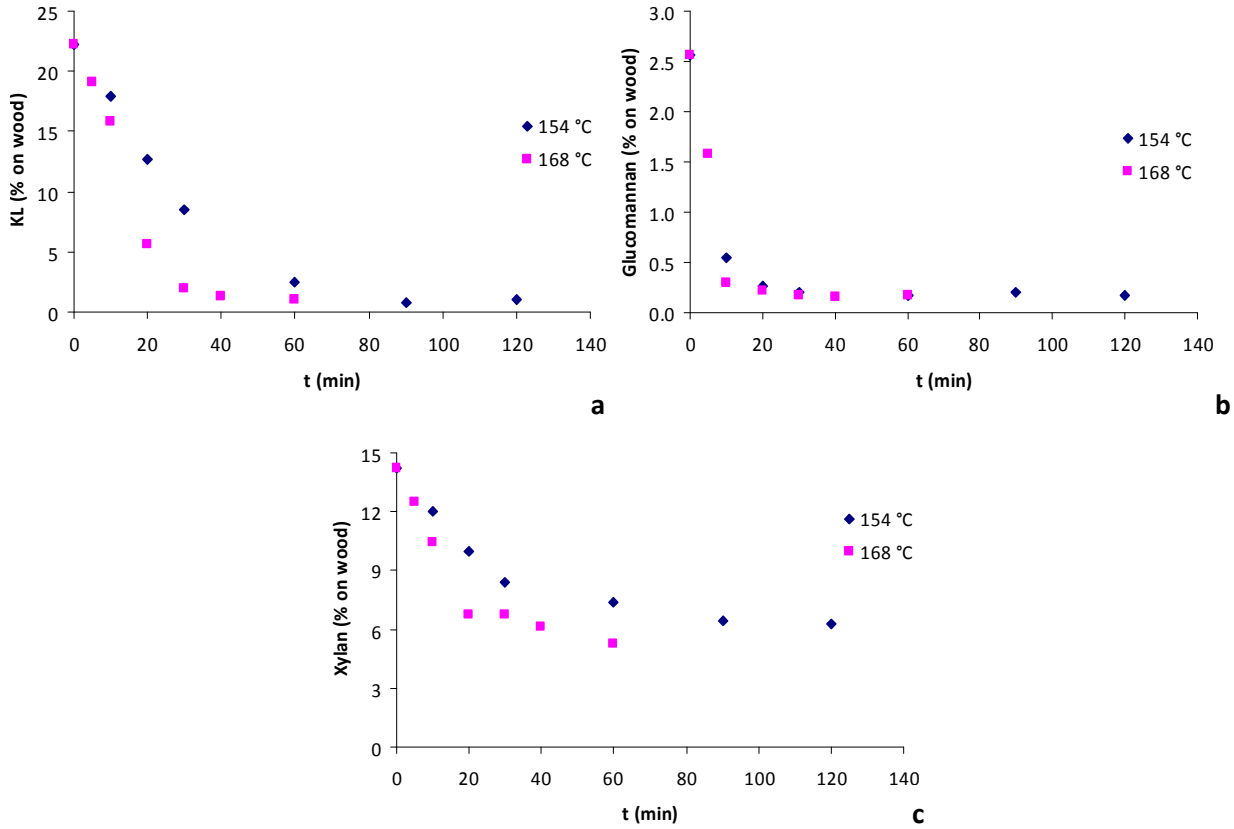


Figure 4.8 – Degree of dissolution/degradation of lignin (a), glucomannan (b) and xylan (c), during Kraft cooking, at 154 and 168 °C, $[OH^-]$=0.25 mol/kg_{liq}, $[HS^-]$=0.50 mol/kg_{liq}.

Figures 4.8a and 4.8c show that an increase in temperature from 154 to 168 °C is responsible for an increase in dissolution/degradation rate of lignin and xylan. Furthermore, the contents of lignin and xylan at the end of the cook also seem to be almost independent of the cooking temperature.

In addition, Figure 4.8b shows that the degradation rate of glucomannan only seems to increase with temperature during the initial phase of the cook. After that, the glucomannan content stays roughly constant and independent of temperature.

5. Conclusions

The main purpose of this thesis was to perform a comparison between Scots pine sapwood and heartwood, as well as between Scots pine and Blue gum, in terms of delignification and dissolution/degradation of glucomannan and xylan during Kraft cooking.

Regarding the first aim, it was verified that lignin, glucomannan and xylan showed an almost coincident behaviour during Kraft cooking of both Scots pine sapwood and heartwood. Nevertheless, since, in this thesis, the resistance to mass transfer phenomena was minimized, further works, which intend to study both kinetics and mass transfer phenomena, should still regard these two wood parts.

Moreover, concerning the comparison between Scots pine and Blue gum, even though an increase in the concentrations of the active chemicals was responsible for an increase in delignification rate for both wood species, determination of delignification rate constants showed that the rate of delignification of the hardwood species was approximately 5.6 times higher than the rate of the softwood species. This might be related to the existence of structural differences between hardwood lignin and softwood lignin, rather than to the lower amount of lignin in hardwood. Furthermore, in both wood species, a rapid decrease in glucomannan content, which was not affected by variations in the concentrations of hydroxide and hydrosulphide ions, was verified at the beginning of the cook, until a plateau was reached. However, the higher plateau observed in the case of Scots pine glucomannan might be due to its higher molecular weight, which means that a stopping reaction may occur. The suggestion of the existence of closer interactions between glucomannan and cellulose, in Scots pine, might also explain this fact. Concerning xylan, it was verified that its content in pulp decreased over time, which was mainly due to dissolution in alkaline environment. Thus, when higher alkali concentrations were used, the dissolution rate was also higher. In addition, the approximately linear relation between xylan and lignin contents, verified during Kraft cooking of Scots pine and Blue gum (at 168 °C and 154 °C, respectively), suggests the existence of interactions between these two components in both wood species. Thus, these interactions might be an explanation for the slightly negative effect on xylan content of an increase in the concentration of hydrosulphide ions. On the other hand, the existence of strong interactions between xylan and cellulose might explain the fact that a part of xylan still remains on the wood residue at the end of the cook.

Furthermore, the analysis of the effect of temperature on cooking of Blue gum showed that dissolution/degradation rates of lignin and xylan increased with an increase in temperature from 154 to 168 °C, but their contents at the end of the cook did not seem to depend on temperature variations. On the other hand, apart from a slight increase in the degradation rate of glucomannan at the beginning of the cook, caused by the same increase in temperature, glucomannan content did not seem to be affected by that temperature variation.

6. Final Assessment and Future Work

The lack of comparative studies between Kraft cooking of different wood parts and different wood species emphasizes the importance of the comparisons established in this work. Thus, the main aim of this thesis was achieved and one more step was taken in the attempt of increasing the knowledge of the physical and chemical mechanisms that are responsible for delignification and hemicellulose dissolution/degradation during the Kraft cooking stage. Nevertheless, much work remains until those underlying mechanisms are completely understood.

In order to increase the usefulness of this work, a comparison between Kraft cooking of Scots pine and Blue gum should be extended to a wider range of temperatures. Moreover, further research should also focus on the interactions between lignin and carbohydrates (e.g., LCCs), as well as on the interactions between cellulose and the hemicelluloses. The comprehension of these interactions might be a crucial factor for the production of paper pulps with higher quality.

Nomenclature

[Arabinose] – arabinose concentration obtained from the calibration curve of arabinose (mg/L).

[Galactose] – galactose concentration from the calibration curve of galactose (mg/L).

[Glucose] – glucose concentration from the calibration curve of glucose (mg/L).

[HCl] – concentration of hydrochloric acid solution used as a titrant (mol/dm^3).

$[HS^-]_{liq}$ – concentration of hydrosulphide ions in primary liquor (mol/kg_{liq}).

$[OH^-]_{liq}$ – concentration of hydroxide ions in primary liquor (mol/kg_{liq}).

$[HS^-]_{liq,\,d}$ – desired hydrosulphide ions concentration in white liquor (mol/kg_{liq}).

[Mannose] – mannose concentration from the calibration curve of mannose (mg/L).

$[OH^-]_{liq,\,d}$ – desired hydroxide ions concentration in white liquor (mol/kg_{liq}).

[Xylose] – xylose concentration from the calibration curve of xylose (mg/L).

a – parameter of the equations for determination of the amount of anhydro sugars.

HexA – hexenuronic acid.

k – delignification rate constant (min^{-1}).

KL – Klason lignin.

L – remaining lignin content.

L_0 – initial lignin content.

LCCs – lignin-carbohydrate complexes.

$m_{cellulose,wrh}$ – mass of cellulose in the wood residue used for hydrolysis (mg).

$m_{glucomannan,wrh}$ – mass of cellulose in the wood residue used for hydrolysis (mg).

$m_{lignin,wrh}$ – mass of lignin in the wood residue used for hydrolysis (mg).

m_{liq} – necessary mass of primary liquor in order to prepare the desired white liquor (kg).

$m_{liq,\,d}$ – desired mass of white liquor for each autoclave (kg).

$m_{liq,\,t}$ – mass of both primary and black liquor used for titration (g).

MeGlcA – 4-O-methylglucuronic acid.

M_{MeGlcA} – molecular weight of 4-O-methylglucuronic acid (g/mol).

$M_{monomer}$ – molecular weight of the monomer (g/mol).

m_{NaHS} – estimate of the necessary mass of sodium hydrosulphide for the preparation of the primary liquor (g).

M_{NaHS} – molecular weight of sodium hydrosulphide (g/mol).

m_{NaOH} – estimate of the necessary mass of sodium hydroxide for the preparation of the primary liquor (g).

M_{NaOH} – molecular weight of sodium hydroxide (g/mol).

$m_{Na2S\cdot9H2O}$ – estimate of the necessary mass of sodium sulphide for the preparation of the primary liquor (g).

$M_{Na2S\cdot9H2O}$ – molecular weight of sodium sulphide (g/mol).

$m_{o.c.,\ wrh}$ – mass of other carbohydrates in the wood residue used for hydrolysis (mg).

$m_{wood\ meal}$ – dry weight of wood meal used for each cooking experiment (g).

m_{wr} – mass of wood residue obtained after cooking (g).

m_{wrh} – mass of wood residue used for hydrolysis (mg).

$m_{xylan,wrh}$ – mass of xylan in the wood residue used for hydrolysis (mg).

M_{xylose} – molecular weight of xylose (g/mol).

N_a – number of autoclaves used in each cooking experiments series.

O.C. – other carbohydrates.

t – time (min).

$V_{HCl,\ HS^-}$ – volume of hydrochloric acid used for the titration of hydrosulphide ions in both primary and black liquors (ml).

$V_{HCl,\ OH^-}$ – volume of hydrochloric acid used for the titration of hydroxide ions in both primary and black liquors (ml).

V_{sol} – volume of the solutions prepared after separation of Klason lignin from the carbohydrate content (L).

y – correction factor for the acid hydrolysis yield.

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Tack så mycket!

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Appendix A – Delignification rate constants determination

The assumption of a first order delignification in remaining lignin can be made as long as the concentrations of hydroxide and hydrosulphide ions and temperature are constant during the cook. In this case, the first condition was practically true, due to the high liquor-to-wood-ratio used, and so was the second condition after 25 minutes (necessary time to reach the maximum temperature – 168 °C). Thus, the delignification rate constants were calculated according to the following method:

$$\frac{dL}{dt} = -kL \Leftrightarrow \int_{L_0}^{L} \frac{dL}{L} = -k \int_{0}^{t} dt \Leftrightarrow \ln(L) = -kt + \ln(L_0) \qquad (A.1)$$

Thus, according to equation A.1, for each series of cooking experiments, the data obtained after 25 minutes of cooking was selected and a linear adjust was made to the representation of the logarithm of the lignin content versus time. The slope obtained was the delignification rate constant.

Appendix B – Calculation examples

1. White liquor preparation

This section contains an example of the calculations associated to the preparation of a white liquor with a hydroxide and hydrosulphide ions concentrations of 0.25 and 0.50 mol/kg_{liq}, respectively, according to the equations shown in section 3.1.1.1.

Thus, using equations 3.6 and 3.7, the initial estimates of both $Na_2S{\cdot}9H_2O$ and NaHS quantities for the preparation of the primary liquor were:

$$m_{Na_2S\cdot 9H_2O} = N_a \times m_{liq,d} \times \left[OH^-\right]_{liq,d} \times M_{Na_2S\cdot 9H_2O}$$

$$m_{Na_2S\cdot 9H_2O} = 6 \times 1.1 \times 0.25 \times 240 = 396\ g$$

$$m_{Na_2S\cdot 9H_2O} = 420\ g \quad (excess)$$

$$m_{NaHS} = N_a \times m_{liq,d} \times \left(\left[HS^-\right]_{liq,d} - \left[OH^-\right]_{liq,d}\right) \times \frac{M_{NaHS}}{0.68}$$

$$m_{NaHS} = 6 \times 1.1 \times \left(0.50 - 0.25\right) \times \frac{56}{0.68} \approx 136\ g$$

$$m_{NaHS} = 200\ g \quad (excess)$$

After titration of 8.621 g of the primary liquor with the hydrochloric acid 1M solution, equations 3.2 and 3.3 were used to calculate the concentrations of the active chemicals in the primary liquor:

$$\left[OH^-\right]_{liq} = \frac{\left[HCl\right] \times V_{HCl,OH^-}}{m_{liq,t}}$$

$$\left[OH^-\right]_{liq} = \frac{1 \times 6.584}{8.621} = 0.764\ mol / kg_{liq}$$

$$\left[HS^{-}\right]_{liq} = \frac{\left[HCl\right] \times V_{HCl,HS^{-}}}{m_{liq,t}}$$

$$\left[HS^{-}\right]_{liq} = \frac{1 \times 16.762}{8.621} = 1.944\ mol/kg_{liq}$$

Finally, in order to obtain the necessary quantities of both primary liquor and NaOH for the preparation of the desired white liquor, equations 3.4 and 3.5 were used:

$$m_{liq} = \frac{\left[HS^{-}\right]_{liq,d} \times m_{liq,d}}{\left[HS^{-}\right]_{liq}}$$

$$m_{liq} = \frac{0.50 \times 1.1}{1.944} = 0.283\ kg$$

$$m_{NaOH} = M_{NaOH} \times m_{liq,d} \times \left(\left[OH^{-}\right]_{liq,d} - \frac{\left[OH^{-}\right]_{liq} \times \left[HS^{-}\right]_{liq,d}}{\left[HS^{-}\right]_{liq}} \right)$$

$$m_{NaOH} = 40.0 \times 1.1 \times \left(0.25 - \frac{0.764 \times 0.50}{1.944} \right) = 2.359\ g$$

The previously calculated quantities were mixed and water was added until a 1.1 kg weight was reached.

2. Klason lignin and carbohydrate % on wood

This section contains an example of the calculation of Klason lignin and carbohydrate percentages on wood for the 60 minutes cooking experiment of Blue gum, at 168 °C, using a hydroxide and hydrosulphide ions concentrations of 0.10 and 0.25 mol/kg_{liquor}, respectively.

Thus, using equations 3.8 and 3.9 from section 3.1.2.2, the KL % on wood was:

$$Yield\ (\%) = \frac{m_{wr}}{m_{wood\ meal}} \times 100$$

$$Yield\ (\%) = \frac{2.85}{5.50} \times 100 = 51.8$$

$$KL\,(\%\ on\ wood) = \frac{m_{lignin,wrh}}{m_{wrh}} \times Yield$$

$$KL\,(\%\ on\ wood) = \frac{3.8}{200.2} \times 51.8 = 0.98$$

Furthermore, the calculation of the carbohydrate percentages was performed according to the procedure shown in section 3.1.2.2. Thus:

- Amount of anhydro sugards (equations 3.10 to 3.14):

$$Arabinan\,(mg) = \frac{[Arabinose] \times V_{sol} \times a}{y}$$

$$Arabinan\,(mg) = \frac{1.89 \times 0.10 \times 0.88}{0.944} = 0.18$$

$$Galactan\,(mg) = \frac{[Galactose] \times V_{sol} \times a}{y}$$

$$Galactan\,(mg) = \frac{6.42 \times 0.10 \times 0.90}{0.952} = 0.61$$

$$Glucan\,(mg) = \frac{[Glucose] \times V_{sol} \times a}{y}$$

$$Glucan\,(mg) = \frac{161.04 \times 1.00 \times 0.90}{0.974} = 148.80$$

$$Xylan\,(mg) = \frac{[Xylose] \times V_{sol} \times a}{y}$$

$$Xylan\,(mg) = \frac{264.68 \times 0.10 \times 0.88}{0.899} = 25.91$$

$$Mannan\,(mg) = \frac{[Mannose] \times V_{sol} \times a}{y}$$

$$Mannan\,(mg) = \frac{4.16 \times 0.10 \times 0.90}{0.926} = 0.40$$

- Amount of carbohydrates (equations 3.15b to 3.18):

$$Cellulose\,(mg) = Glucan - \frac{1}{1} Mannan$$

$$Cellulose\,(mg) = 148.80 - 0.40 = 148.40$$

$$Glucomannan\,(mg) = Mannan\left(1 + \frac{1}{1}\right)$$

$$Glucomannan\,(mg) = 2 \times 0.40 = 0.80$$

$$Xylan\,(mg) = Xylan$$

$$Xylan\,(mg) = 25.91$$

$$O.C.\,(mg) = Arabinan + Galactan$$

$$O.C.\,(mg) = 0.18 + 0.61 = 0.79$$

- Carbohydrate % on wood (equations 3.19 to 3.22):

$$Cellulose\,(\%\ on\ wood) = \frac{m_{cellulose,wrh}}{m_{wrh}} \times Yield$$

$$Cellulose\,(\%\ on\ wood) = \frac{148.40}{200.2} \times 51.8 = 38.4$$

$$Glucomannan\left(\%\ on\ wood\right)=\frac{m_{glucomannan,wrh}}{m_{wrh}}\times Yield$$

$$Glucomannan\left(\%\ on\ wood\right)=\frac{0.80}{200.2}\times 51.8=0.2$$

$$Xylan\left(\%\ on\ wood\right)=\frac{m_{xylan,wrh}}{m_{wrh}}\times Yield$$

$$Xylan\left(\%\ on\ wood\right)=\frac{25.91}{200.2}\times 51.8=6.7$$

$$O.C.\left(\%\ on\ wood\right)=\frac{m_{o.c.,wrh}}{m_{wrh}}\times Yield$$

$$O.C.\left(\%\ on\ wood\right)=\frac{0.79}{200.2}\times 51.8=0.2$$