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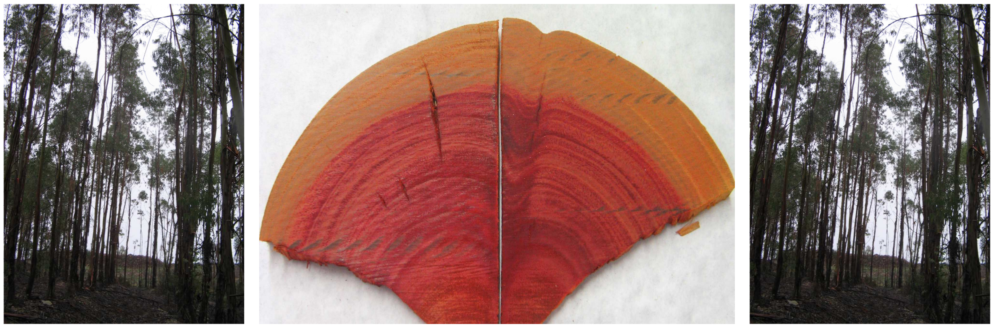

The influence of *Eucalyptus globulus* heartwood in pulp production

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Aos meus pais, Ana e Ângelo e ao meu irmão, Miguel.

RESUMO

Madeira de *Eucalyptus globulus* com 18 anos foi usada para estudar a influência do cerne e do borne na deslenhificação kraft (170ºC) com vários tempos de reacção (1 a 95 min). O cerne possuía maior conteúdo em extractivos (9,8 % *vs*. 3,9 %) e mais xilose (17,5 % *vs*. 13,7 %) mas idêntico teor em lenhina total (23,5 % *vs*. 24,3 %) comparativamente ao borne. Após 95 min de deslenhificação, o cerne apresentou menores rendimentos em pasta (52,4 % *vs*. 56,7 %) e com maior teor em lenhina residual (3,0 % *vs*. 1,2 %), enquanto que o conteúdo em xilose e glucose foi semelhante respectivamente, 12,6 % e 84,5 %. As pastas de borne apresentaram-se mais luminosas (L*, 67 a 80) do que as de cerne, mas não se verificaram diferenças em relação aos parâmetros de cor a* e b*. Dois modelos de cinética de deslenhificação foram aplicados: o consecutivo e o simultâneo. Ambos os modelos explicaram bem a cinética de deslenhificação do borne mas o modelo simultâneo explicou melhor a deslenhificação do cerne.

PALAVRAS CHAVE

Eucalyptus globulus, cerne, rendimento, propriedades das pastas, deslenhificação, cinética.

ABSTRACT

A 18-year-old *Eucalyptus globulus* tree was used to study the influence of heartwood and sapwood in kraft pulping along different reaction times (1 to 95 min). Heartwood had more extractives (9.8 % vs. 3.9 %) and more xylose content (17.5 % and 13.7 %) compared to sapwood, but no differences were found in total lignin content (23.5 % vs. 24.3 %). After 95 min, heartwood pulps had lower yields (52.4 % *vs*. 56.7 %) and higher residual lignin content (3.0 % *vs*. 1.2 %) but no differences were found in sugar content. Sapwood pulps presented higher luminosity (L*, 65 to 80), but no differences at a* and b* values. Two models of delignification kinetics were applied: consecutive and simultaneous. Both models explained well the delignification kinetics of sapwood but the simultaneous model explained better the heartwood delignification.

KEYWORDS

Eucalyptus globulus, heartwood, yield, pulp properties, delignification, kinetics.

RESUMO ALARGADO

Neste trabalho foi usada madeira de *Eucalyptus globulus* com 18 anos para estudar a influência do cerne e do borne na deslenhificação kraft (170ºC) ao longo de vários tempos de reacção (1 a 95 min). As fracções 20-40 mesh de borne e cerne foram caracterizadas por parâmetros químicos e ópticos. O cerne apresentou maior conteúdo em extractivos (9,8 % *vs*. 3,9 %), mas idêntico teor em lenhina total (23,5 % *vs*. 24,3 %) e apresentou uma percentagem mais elevada de xilose em relação ao borne (17,5 % *vs*. 13,7 %), enquanto o conteúdo em glucose foi superior neste último (81,1 % e 75,1 %). O cerne é mais amarelo que o borne respectivamente, 17 e 14, não apresentando diferenças nos parâmetros L* (83) e a* (3). A madeira de borne, por conter menor teor em extractivos comparativamente ao cerne, apresentou após 95 min de deslenhificação, rendimentos superiores (56,7 % *vs*. 52,4 %) e menor teor em lenhina residual respectivamente, 3,0 % e 1,2 %. O conteúdo em açucares totais foi semelhante em ambas as amostras: arabinose (0,5 %), manose (1,7 %) e galactose (0,8 %), glucose (84 %) e xilose (13 %). O borne apresentou valores de luminosidade (L*) mais elevados que o cerne, respectivamente, 66,5 e 74,5, não se verificando diferenças quanto aos parâmetros a* e b*. Foram aplicados dois modelos matemáticos baseados numa cinética de 1ª ordem, para explicar a remoção de lenhina. O modelo consecutivo descreveu a reacção de deslenhificação em duas fases: uma fase principal (que nas condições usadas inclui a fase inicial) mais rápida e onde é removida a maior parte da lenhina e uma fase residual, mais lenta. Quando aplicado ao borne, este modelo explicou na fase principal maior extracção de lenhina comparativamente ao cerne (86,0 % *vs*. 80,0 %), com uma constante de velocidade superior no borne ($k = 0{,}061\ min^{-1}$ *vs*. $k = 0{,}048\ min^{-1}$); na fase residual a extracção foi de respectivamente, 9,0 % e 7,0 % do total de lenhina, com constantes de velocidades correspondentes a 0,017 e 0,007 min^{-1}, permanecendo no cerne cerca de 13,0 % de lenhina na matriz lenhocelulósica e no borne apenas 5,0 %. O modelo simultâneo mostrou a existência de duas fracções da lenhina com diferente reactividade, uma mais reactiva e outra menos reactiva. O borne mostrou 76,0 % da lenhina mais reactiva (L_1) que foi removida a uma constante de velocidade k_1 de 0,077 min^{-1}, sendo a remoção de 24,0 % da lenhina menos reactiva (L_2) feita a um k de 0.018 min^{-1}. No cerne estas fracções representaram respectivamente, 71,0 % e 29,0 %, que apresentaram respectivamente constantes de velocidade: $k_1 = 0{,}080\ min^{-1}$ e $k_2 = 0{,}010\ min^{-1}$. Ambos os modelos explicaram bem a deslenhificação do borne (SQR = 0,041 *vs*. 0,033), enquanto que o modelo simultâneo explicou melhor a deslenhificação do cerne (SQR = 0,0030). Em conclusão, o cerne foi mais difícil de deslenhificar supondo-se que devido a diferenças anatómicas e químicas.

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1. Introduction

1.1. *Eucalyptus globulus* as a raw material for pulping

The species *Eucalyptus globulus* Labill. belongs to the *Mirtaceae* family, and is one of the nearly 500 species of the *Eucalyptus* genus (Cremer *et al*., 1984). The Latin *globulus* (a little button) refers to the shape of the operculum and the species has the common name Tasmanian Blue Gum. *E. globulus* was classified by the botanist Jacques-Julien de Labillardière when he arrived in Tasmanian in the XVIII century (Figure 1) and was proclaimed the floral emblem of Tasmania on 1962.

Figure 1. The illustration of *Eucalyptus globulus* published in 1800 and the botanist Labillardière (http://git-forestry-blog.blogspot.com/search/label/Blue%20Gum).

There are several species of *Eucalyptus* in Australia that are important for wood production (Turnbull and Pryor, 1984). In Portugal, the most important one is *E. globulus*, which was planted in the XIX century for timber production used for railway sleepers (Alves *et al.*, 2007). It was first used for pulping in 1925, in the Caima pulp mill and subsequently in 1957 in the Cacia pulp mill (Goes, 1978), and then expanded to other mills in Portugal.

E. globulus occupied a total area of 22 941 ha in 1965 (Goes, 1978), increased to 672 149 ha in 2005 and to 748 100 ha in 2006 (Celpa, 2005, 2006). In 2006, it represented 22% of the forest area of Portugal, distributed especially in the north and central coastal regions. A total of 152 537 ha are managed by the pulp industry. In 2006, from the overall wood consumed for pulping the majority belonged to eucalypt (5240 000 m^3 eq. without bark), and compared to 2005 represented an increase of 2 % in the pulp production using this species (Celpa, 2006).

The importance of eucalypt pulps in the world is also evident, as it has been increasingly dominating the world hardwood pulp markets. The total pulp production equals 10 million t/year and the annual increment of production amounts to 6%, twice as much as the general pulp production increment (Patt *et al.*, 2006).

Eucalyptus globulus combines fast growth under appropriate conditions with good tree form and excellent wood quality for pulp production, and high pulp yield, which result in pulps with excellent technical properties (Patt *et al.*, 2006), while offering a favourably low wood consumption in terms of volume due to its basic density (Pereira and Sardinha, 1984; Cotterill and Macrae, 1997). The growth rates may reach an average of 20 $m^3ha^{-1}year^{-1}$ in good site conditions, but are strongly influenced by soil water and mineral nutrient availability (Cromer and Williams, 1982; Pereira *et al.*, 1989; Miranda *et al.* 2006).

The characteristics that are most appreciated by the pulp industries are a high content in cellulose, and low contents in lignin and extractives (Trugilho *et al*., 2005). *Eucalyptus globulus* is well suited to kraft pulping because of its chemical characteristics. Low values of extractives content were referred by Kojima *et al.* (2008), ranging between 1.9 % to 6.8 %; Santos *et al*. (2006) reported 4.7 %, while Miranda *et al*. (2002c) obtained 3.7 % in 9-year-old trees, increasing to 5.0 %-8.7 % in 18-year-old trees (Miranda *et al*., 2003). Lignin content is low, ranging from 18.8 to 21.5 % (Pereira and Sardinha, 1984; Santos *et al*., 2004; Neto *et al*., 2004) with total lignin varying between 21.9 % and 27.0 % (Patt *et al*., 2006; Cotterill and Macrae, 1997; Gilarranz *et al.,* 1999; Miranda and Pereira, 2002c), and cellulose content is high (40.1-53.6 %, Pereira and Sardinha, 1984; Kojima *et al.*, 2008) as well as pentosan content (12.0-17.8 %) compared to other hardwoods (Pereira and Sardinha, 1984).

Other important factors are the fibre characteristics, such as fibre length, diameter and collapsibility. *E. globulus* is characterized by short fibres varying from 0.87 mm to 1.04 mm in length (Jorge *et al.*, 2000) and with a fibre width and wall thickness of respectively, 21.3 µm and 5.7 µm (Miranda *et al*., 2003). Miranda *et al*. (2003) reported for 18-year-old trees that fibres are shorter near the pith, increasing to the outside and are influenced by spacing. The wall thickness is higher than reported for 7-year-old trees (Miranda *et al*., 2001) indicating that wall thickness increases with age.

1.2. Heartwood and sapwood

Wood can be divided in two different physiological regions: sapwood and heartwood. Sapwood is the outer part of the trunk and contains almost 80 % of living cells; it is responsible for fluid conduction between roots and leaves, and participates in the respiration among other physiological processes (Bierman, 1996). Compared to heartwood, sapwood is less dark, has higher water content in green wood and has less extractives, but more starch that is accumulated in the ray cells and axial parenchyma cells (Hills, 1962; 1987).

Heartwood is found in the centre of the tree stems, after a certain age. It contains only dead cells, from where the accumulated substances were removed (e.g. starch) or transformed to protective substances, which give a darker coloration. These substances are extractives that can be removed from wood by extraction with solvents with different polarities (Fengel and Wegener, 1989). Heartwood is characterized by higher density, lower pH and less permeability compared to sapwood (Hills, 1987). During the formation of heartwood, the moisture content decreases with air replacing some of the water (Bierman, 1996).

The visual distinction between sapwood and heartwood can be defined or undefined. In the first case, heartwood delimitation in the transversal section is a curved line which may correspond to the growth rings or not. Heartwood can also be classified as regular or irregular, depending on its shape in the radial section being similar to the profile stalk or not (Hills, 1962; 1987).

1.2.1. Heartwood formation

The sapwood transformation in heartwood is complex, and still not totally explained (Buchanan *et al.*, 2000). Several theories have been presented. One is based on the natural aging and consequent death of parenchyma cells, starting with a gradual degeneration at the internal sapwood and ending at the transition area (Kramer and Kozlowski, 1960; Hillis, 1962; Desh and Dinwoodie, 1996). In sapwood, the ray parenchyma cells accumulate several organic compounds in the neighbour cell wall (such as tannins, gums, resins, and other coloured materials) which will originate heartwood cells (Kramer and Kozlowski, 1960; Hills, 1962; Desh and Dinwoodie, 1996; Buchanan *et al.*, 2000).

Several authors support the theory called “pipe-model”, proposed by Shinozaki *et al.* (1964), which explains heartwood formation by saying that the area of the tissues responsible for nutrient transportation (sapwood) in roots, stalks and branches is proportional to the leaf area (Grier and Waring, 1974; Albrektson, 1984). However some studies found that when a tree is pruned, the sapwood decrease does not match the leaf area removed (Margolis *et al.*, 1988; Lǻngström and Heliqvist, 1991). This is considered a static model due to several reasons, namely the assumption that sapwood area by leaf area is constant and that all sapwood cells have the same permeability rate and that every leaf has the same transpiration rate. Nikinmaa (1992) introduced a dynamic aspect to the relation between the leaf mass and the sapwood area, by admitting that sapwood could remain active after the decrease of leaf area and assumed that sapwood would only be inactive after the branch death. This will explain the difference between the increase of sapwood and the increase of aerial biomass.

Bamber (1976) proposed another theory based on the idea that heartwood formation is controlled by hormones produced by parenchyma cells at the cortex area. The hormones are transported through the ray cells to the pith, where they accumulate. When a certain hormone level is reached, the tree is induced to transform sapwood into heartwood.

Hillis (1980) considered that heartwood formation is due to the combination of two factors: the gradual decline of parenchyma cells in sapwood as a result of aging, and the distance between these cells and the active part of the stem.

Heartwood formation is also explained by other factors, such as enzymatic processes (Shah *et al.*, 1981; Datta and Kumar, 1987; Taylor *et al.*, 2002), air accumulation with consequent vascular cavitation (Harris, 1954), fungal attacks or accumulation of toxic substances (Hillis, 1962; Bamber, 1976, Hillis, 1987).

1.2.2. Factors affecting heartwood formation

Heartwood in a tree is determined by several factors (Bamber and Fukazawa, 1985; Hills, 1987; Taylor *et al.*, 2002). The genus and the species are two of them, but the age, the position in the tree, the growth rate, the silvicultural treatments are also considered important factors.

In some species, heartwood can be distinguished by colour differences, as in *Betula alleghaniensis*, *Betula lenta*, *Acer tartaricum*, but not in others, like in *Betula verucosa*, *Acer pseudoplatanu*s and *Acer platanoides* (Hillis, 1987). In *Eucalyptus*, heartwood proportion can be quite different, for example *E. urophyla* presents more heartwood than *E. pellita*, respectively, 52.8 % and 36.0 % (Semple *et al.*, 1999).

The age of heartwood formation is very important, and varies with genus and species. For example, in *Eucalyptus* it starts at 5 years of age (Hillis, 1972; Gominho *et al*., 2001), namely in *E. globulus* (Gominho and Pereira, 2000; 2005). In *Pinus ponderosa*, Hillis (1962) found that heartwood starts after 36 years, while in *Pinus pinaster* it starts after 18 years (Esteves *et al.*, 2005), and in *Pinus sylvestris* after 15 years (Björklund, 1999). Heartwood volume increases with age, as observed by Walker (1993) in *E. grandis*, with respectively 5 and 50 years, where it increased from 25% to 80%.

The growth rate is also one of the factors affecting heartwood development. In fact, the heartwood quantity is directly related to diameter growth as found by Wilkes (1991) in *Pinus radiata* and by Purkayastha *et al.* (1980) in *E. tereticornis*. In *E. globulus* the heartwood area was also positively correlated with stem radial growth (Gominho and Pereira, 2000; Miranda *et al*., 2006).

Silvicultural treatments can also influence heartwood development, such as pruning, as found by Margolis *et al.* (1988) with *Abies balsamea* or *Pinus sylvestries* (Lắngström and Heliqvist, 1991). The stand density is another factor, and for instance in a trial with *Pinus glauca* and *P. mariana*, reducing stand density increased heartwood (Yang and Hazenberg, 1992). Miranda *et al.* (on line) reported for 18-year-old *E. globulus* trees an increase of heartwood area with the increase of spacing, where in wide spacing (4x5) the heartwood area reached 206 cm^2, while in closer spacing (3x2), just 99 cm^2. The conclusion that eucalypt trees growing at higher plant densities present less heartwood was also examined by Gominho and Pereira (2005) in trees with 8.8 years of age, where heartwood reached 62 % of total tree height in wide spacing (3x3) and by Gominho and Pereira (2000) in 9 year-old trees where heartwood attained 60-75 % of total tree height varying with sites and within the tree decrease from the base to top. Miranda *et al.* (2006) found that irrigation and fertilization increased the proportion of heartwood in the stem.

1.2.3. Properties of heartwood and sapwood

Heartwood formation induces changes at anatomical and chemical levels which are responsible for different behaviour of sapwood and heartwood. The chemical modification is the most important one, and involves the production of extractives in parenchyma cells, followed by accumulation and transport through the bordered pit, to the neighbouring lignified cells. Heartwood presents more extractives of phenolic type (*e.g.* flavonoids) while sapwood is composed by starch, soluble sugars and triglycerides (Hillis, 1962).

As tree ages, an anatomical modification occurs and the pores in the wood become blocked with deposits and the sapwood turns into heartwood (Clark, 1978). In many hardwood species, tyloses are produced within the vessels. Tyloses (Figure 2) are defined as parenchyma cell outgrowths through a pit into the cavity of a vessel (Esau, 1960; Fahn, 1990). In softwoods, it involves the obstruction of bordered pits in tracheid cells (Hillis, 1962; Hillis, 1980). These anatomical changes decrease heartwood permeability to fluids (McIntosh, 1970; Bierman, 1996).

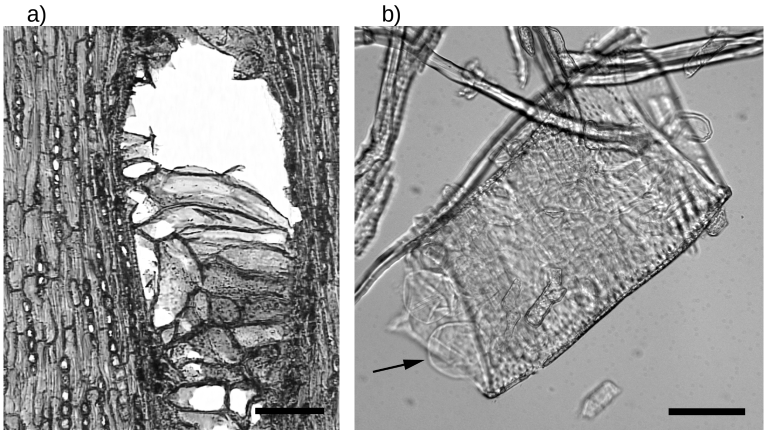

Figure 2. Tyloses present at *Q. suber* L, images obtained in optical microscope: a) tyloses in tangential section; – Scale bar = 100 µm; b) dissociate vessel with tyloses (→); Scale bar = 100 µm (Sousa, *et al.*, in press).

The extractives present in heartwood are acid, as for example, in *Eucalyptus* and *Quercus* pH is inferior to 3 (Hillis, 1987). Because of this, heartwood can be visually distinguished by application of indicator solutions, *e.g.* methyl orange. Due to the extractives, heartwood presents in general higher density compared to sapwood, although heartwood formation has no influence in wood mechanical resistance, because no modification at cell wall occurs (Kai, 1991).

In many species, the heartwood presence is an advantage for the tree. Some researchers suggest that the compounds accumulated in heartwood add durability, proposing the physiological importance of heartwood in the tree (Taylor *et al.*, 2002; Hills, 1987). The majority of the extractives accumulated in heartwood are toxic to microorganisms, while in sapwood the extractives (e.g. starch) are more susceptible of attack. Another important fact to heartwood natural durability is the obstruction of the cells, which difficult the biotic attacks.

As already pointed out, sapwood and heartwood present no differences related to physical and mechanical properties, but a higher amount of sapwood decreases the efficiency of tree growth, due to the dependence of higher levels of respiration (Chapman and Gower, 1991). In fact heartwood, as being constituted by dead cells, does not need maintenance although contributing to diameter growth (Ryan *et al.*, 1995).

Heartwood can be distinguished from sapwood by colour differences, but this is not always possible. To overcome this fact, several methods can be applied. A chemical method involves the pH differences between sapwood and heartwood (Campbell *et al.*, 1990; Winandy and Morrell, 1993; Clarke *et al.*, 1997). In this work the heartwood was detected by application of methyl orange as can be seen at Figure 3. There are also methods based in permeability differences, where the wood is immersed in water. More recently, some detection methods allow heartwood quantification in logs, such as X-rays (Grundberg, 1999) or infrared (Gjerdrum, 2002).

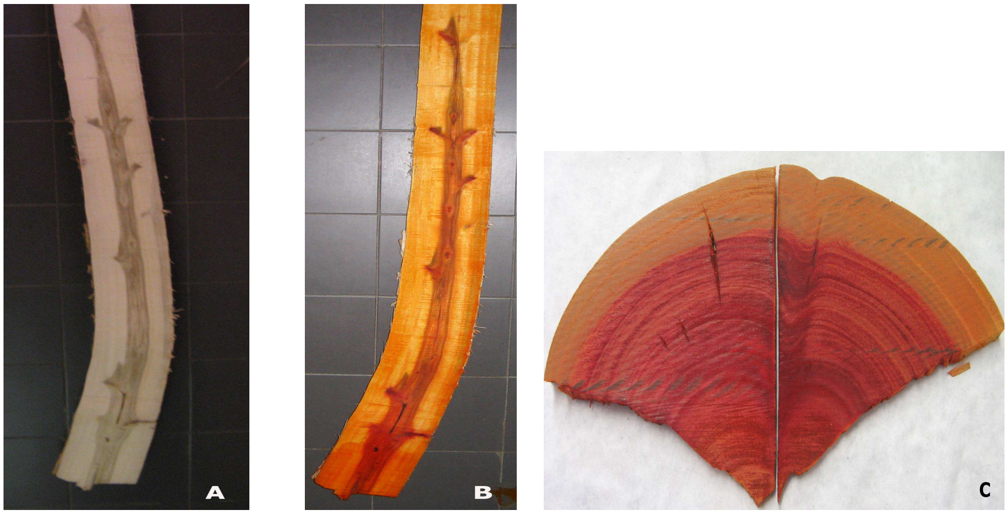

Figure 3. *E. globulus* wood: A – log showing sapwood and heartwood areas; B – the same log after application of methyl orange (used to increase distinction between both areas); C – transversal section of one wood disc after methyl orange application.

1.2.4. The influence of heartwood in pulping

Heartwood presence is negative in several aspects concerning pulp production and paper formation. The extractives in heartwood promote higher chemical consumption, reducing pulp yield and brightness (Higgins, 1984). The low permeability of heartwood makes more difficult the liquor circulation into the chips, reducing the lignin removal, while the accumulation of some extractives in the equipment as well as depositions on cellulosic fibres causes sticky and pitch problems (Kai, 1991; Campbell *et al.*, 1990; Higgins, 1984; del Rio *et al*., 1998).

On the contrary, sapwood is easier to pulp than heartwood (Nolan, 1970; Clark, 1978; Bierman, 1996) because it usually has less extractive matter and generally yields a lighter-coloured pulp (Clark, 1978).

Several authors used *Eucalyptus* to study heartwood influence in pulp production specially relating extractives content and pulp production (Miranda *et al.*, 2006; Miranda *et al*., 2007; Gominho, 2003; Mariani *et al.*, 2005). Miranda *et al*. (2007) obtained in 8-year-old *E. globulus* trees a negative correlation between extractives and pulp yield. Heartwood pulps presented lower yields compared to sapwood (mean values of 47.9 % *vs*. 52.1 %) due to higher extractives content, corresponding to a ratio of heartwood to sapwood extractives on average 1.8. In trees with 18 years of age, heartwood presented 1.6 % more extractives than sapwood, and pulp yield values were respectively, 52.1 % and 55.8 % (Miranda *et al*., 2006). The same behavior was observed by Gominho (2003) who compared pulp yield from extractive-free wood and wood with extractives, and found a tendency to decrease pulp yield with the presence of extractives.

Heartwood also influences pulp brightness due to the presence of extractives and lignin which will difficult the bleaching. Although no relation was obtained between extractives and brightness, samples with lower extractives content produced brighter pulps (Gominho, 2003).

Esteves *et al*. (2005) reported for *Pinus pinaster* chemical differences between heartwood and sapwood, in particular extractives content, respectively, of 19.7 % and 5.8 %, and their influence on pulping was negative, with lower yield values in heartwood (40.0 % *vs.* 49.7 %).

Although *Eucalyptus globulus* is the raw material commonly used for pulping in Portugal, little information is available about the effect of heartwood on kraft delignification.

1.3. Modeling of delignification kinetics

Lignin removal is the principal objective of chemical pulping and therefore optimized delignification kinetics is an important issue for pulping improvement. Lignin is a heterogeneous non-linear plant cell wall polymer, constituted by different structural elements and linkages that originate fractions, or moieties, with different stability, causing heterogeneity during the chemical process (Bierman, 1996). The kraft process is complex and involves many chemical reactions between the pulping chemicals (sodium hydroxide and sodium sulphide) and the components of wood (Dang and Nguyen, 2007). These chemical reactions degrade lignin, extractives and carbohydrates. The behavior of lignin is explained as a competition between degradation reactions, mainly those involving aryl ether cleavage, and condensation reactions, comprising addition of carbanions to quinone methide intermediates (Gierer, 1980). The degradation of lignin is accomplished by the liberation of α- and β-aryl ether structures (Clayton *et al.*, 1983).

Although those reactions are not fully understood, many models have been established to describe delignification kinetics (Gilarranz *et al*., 2002; Miranda and Pereira, 2002b; Santos *et al*., 1997, Pérez *et al.*, 2000). The expressions used were developed considering the lignin reaction as first-order (Kleppe, 1970; Gierer, 1980; Oliet *et al*., 2000) where the reaction velocity (or rate constant) is proportional to the concentration of lignin removed. The equation of lignin degradation in function of time is

$$-\frac{dL}{dt} = k_L * L$$

being L, the residual lignin in pulp; k_L, the rate constant and t, the reaction time (min). This equation can be integrated obtaining

$$\ln \frac{L}{L_0} = -k_L * t$$

where L_0 is the lignin present in the wood. The graphic representation of ln (L/L_0) *vs*. time is a straight line which the slope is ($-k_L$).

The dissolution of lignin can be described in three phases with different reaction rates: initial, bulk and residual.

The initial phase is characterized by the quick removal of lignin as a result of the cleavage of α and β–aryl ether bonds in the phenolic units, inducing a loss of 20-25 % of total lignin (Gellersted *et al.*, 1992; Miranda and Pereira, 2002b). The alkali consumption is high, with almost 50 % consumed in the hydrolysis of acetyl side groups associated to hemicelluloses, and in the removal of the carbohydrates by peeling reactions (Santos *et al.*, 1997; Clayton *et al.*, 1983; Labili and Pla, 1992). This phase is also characterized by the diffusion and extraction of low weight polymers. The delignification velocity depends on temperature but is independent of the reagents concentration (Vanchinathan and Krishnagopalan, 1995; Labidi and Pla, 1992; Gustafson, 1988; Nguyen and Dang, 2006).

The bulk phase is the period during which most of the lignin is removed, 70% (Gellersted *et al.*, 1992). In this phase, the reaction velocity is of 1st order relatively to the NaOH concentration (De Groot *et al.*, 1995; Labili and Pla, 1992; Pérez *et al.*, 2000). The lignin polymer is degraded by: cleavage of β–aryl ether bonds in the nonphenolic units, and of α and β–aryl ether bonds in the phenolic units, by condensation reactions and cleavage of carbon-carbon bonds. Although all these reactions occur, most of the lignin is removed due to the cleavage of β–aryl ether bonds in the phenolic units and then dissolved in the liquor (De Groot *et al.*, 1994; De Groot *et al.*, 1995; Labili and Pla, 1992; Hubbard *et al.*, 1992). The carbohydrates are removed by hydrolysis of glycosidic bonds (which reduces the degree of polymerization of cellulose), followed by peeling (which reduces yield), stopping reactions and cleavage of carbon-carbon bonds (Clayton *et al.*, 1983).

In the residual phase, the removal of lignin is slow, due to the cleavage of carbon-carbon bonds and condensation reactions; carbohydrates are also removed by cleavage of carbon-carbon bonds, and as in the bulk phase, cellulose polymerization decreases. The alkaline consumption is mainly due to the neutralization of the peeling reaction products (Santos *et al.*, 1997). The delignification velocity is also of 1st order relatively to the NaOH concentration.

The delignification can be interpreted as the dissolution of a single lignin species whose reaction mechanism changes as delignification proceeds, or as the dissolution of different lignin species with different reaction rates, which is the most common used (Oliet *et al.*, 2000). This hypothesis can also be divided in two interpretations: the most usual approach assumes that the different lignin species react consecutively and are removed in three phases: initial, bulk and residual (consecutive model); the other assumes that the lignin fractions react simultaneously with specific reaction velocities (simultaneous model).

1.3.1. Consecutive model

Several studies demonstrate that the rate of degradation and extraction of lignin, as well as the removal of carbohydrates, during alkaline pulping, is not uniform. The consecutive model is the most frequently applied to delignification, assuming that lignin is dissolved in three phases (initial, bulk and residual) with different reaction rates in each phase (Labidi and Pla, 1992; Oliet *et al.*, 2000). It is also assumed that lignin reacts consecutively during the delignification process according to a first-order kinetic model (Gillarranz *et al.*, 1999; Dolk *et al.*, 1989). The lignin that remains in the lignocellulosic matrix can be calculated using the initial material (L_0) and described as

$$\frac{L}{L_0} = a_{iL} \exp\left(-k_{iL} t\right) + a_{bL} \exp\left(-k_{bL} t\right) + a_{rL} \exp\left(-k_{rL} t\right)$$

L - the lignin present in the pulp; L_0 - lignin in wood at time zero; t - time (min); k_i - rate constant (min^{-1}) with i, b and r, corresponding to initial, bulk and residual phases; a_{iL} - mass fragments of the lignin removed in the initial phase; a_{bL} - mass fraction of the lignin removed in bulk phase; a_{rL} - mass fragments of the lignin removed in the residual phase.

The lignin removed in the three phases is assumed to be the result of the predominant cleavage of α-O-4 phenolic bonds, β-O-4 phenolic bonds and C-C bonds, respectively in the initial, bulk and residual phases.

Several authors applied the consecutive model reactions for the study of *Eucalyptus globulus* delignification, under kraft conditions (De Groot *et al.*, 1995; Santos *et al.*, 1997; Pérez *et al.*, 2000; Gilarranz *et al.*, 2002; Miranda and Pereira, 2002b) and organosolv (Gilarranz *et al.*, 1999; Miranda and Pereira, 2002b; Pereira *et al.*, 1986; Oliet *et al.*, 2000). In general, in kraft pulping the transition between initial to bulk phase can be distinguished at lower temperatures (100-120ºC), with lignin removal of 20-25 % (Santos *et al.*, 1997), while the transition from bulk to residual is recognized at higher temperatures (140-180ºC), with 97 % lignin conversion (Santos *et al.*, 1997) or 95 % (Pérez *et al.*, 2000).

1.3.2. Simultaneous model

The simultaneous model assumes that the different lignin fractions start to react at the same time at the beginning of pulping and continue to dissolve concurrently along the pulping progress (Dolk *et al.*, 1989; Labidi and Pla, 1992). Considering three different fractions of lignin with different reactivity, the total amount of lignin removed from the wood material (L) at an instant of cooking time (t) can be calculated from the equation:

$$L = L_{1,0} * \left(1 - \exp\left(-k_1 t\right)\right) + L_{2,0} * \left(1 - \exp\left(-k_2 t\right)\right) + L_{3,0} * \left(1 - \exp\left(-k_3 t\right)\right)$$

where $L_{1,0}$; $L_{2,0}$; $L_{3,0}$ are different lignin fractions with different reactivity, from the most reactive (1) to the less reactive (3), and k_n the reaction rate constants correspondent to each lignin fraction removed and can be calculated by the following equation

$$k_n = \ln\left(L_{n,0}/L_t\right)/\left(t_t - t_{n,0}\right)$$

where n = 1, 2 or 3; $L_{n,0}$ is the lignin (%) at time 0, L_t the lignin (%) at time t.

Several authors mentioned this model, but few applied it to *Eucalyptus* delignification. Gilarranz *et al.* (1999) proposed several equations, two referring to a simultaneous model approach and other two referring to a consecutive model approach, for *Eucalyptus globulus* organosolv delignification, but selected the consecutive model to explain the influence of temperature on the delignification rate.

A recent approach applying the simultaneous model was followed for the delignification of *Arundo donax* (Shatalov and Pereira, 2005) which could identify three lignin fractions (1, 2 and 3), which represented, respectively, 62 %, 22 % and 16 % of the total lignin. It also compared the simultaneous model with the consecutive model, and for *Arundo* the simultaneous model explained better the delignification.

2. Material and methods

2.1. Experimental site

The raw material used was obtained from one first-rotation *Eucalyptus globulus* tree, with 18 years of age. The plantation was established in 1986 with 3-month-old *E. globulus* seedlings, planted at 3mX3m spacing in Quinta do Furadouro, Óbidos, Portugal (Miranda *et al.*, 2006; Madeira *et al.*, 2002). The site is located in the central coastal region, approximately 10 km from the Atlantic Ocean (39º20'N, 9º15'W, 30 m of altitude). The climate is of the Mediterranean type, characterized by 607 mm annual rainfall, with mean maximum and minimum temperature, respectively 19.5 and 11.1ºC. The relative humidity during summer may be as high as 80 % at 9 a.m., and fogs are frequent (Madeira *et al.*, 2002). The soils are of low fertility and low organic carbon content (0.23 % to 0.28 %), mostly sandy and classified as Arenosols (Fontes *et al.*, 2006). A detailed description of the site and experimental design was presented elsewhere (Pereira *et al*., 1989).

2.2. Sampling

The tree chosen for this work belonged to an irrigation and fertilization trial, established by CELBI (at present, CAIMA), where several studies were performed (Pereira *et al*., 1989; Madeira *et al.*, 2002; Miranda *et al.*, 2006; Fontes *et al.*, 2006). One of them involved a total of 20 trees that were harvested and sampled by cutting discs at different heights (Miranda *et al.*, 2006). One of these 20 trees was selected for this study due to its high total extractive content (sapwood 3.9 % and heartwood 9.8 %).

This tree had 27.7 cm at DBH and a height of 36.1 m. A 10 cm thick disc was taken at 1.3 m, characterized by a total cross-sectional area of 423.6 cm^2 and a heartwood area of 293.5 cm^2. This disc was divided into two thinner discs with a saw. One was used to identify heartwood and sapwood areas with methyl orange (Gominho, 2003): heartwood area turned red (due to pH<4), as can be seen in Figure 4.a, and was used as reference for separation of heartwood and sapwood in the other disc. Analyses were performed on the individual heartwood and sapwood fractions.

2.3. Wood characterization

2.3.1. Basic density and bulk density

Basic density of heartwood and sapwood was determined using Tappi standards (Tappi 258 os-76) and calculated by dividing the oven-dry mass by the green (maximum swollen) volume. The green volume was determined by weighing in immersion in water, which is equal to the mass of the displaced water. The following formula was applied

$$\text{Basic density}\ \left(g.cm^{-3}\right) = \frac{\text{dry wood mass}\ (g)}{\text{green volume}\ \left(cm^{3}\right)}$$

For bulk density determination, wood was reduced to 20-40 mesh granulometric fraction (850 µm-425 µm, Figure 4.b), with a knife mill (Retsch SM 2000) and sieved (Retsch AS 200). The material was oven dried, weighted in a box of known volume, and the formula applied as

$$\text{Bulk density}\ \left(g.cm^{-3}\right) = \frac{\text{wood mass}\ (g)}{\text{volume}\ \left(cm^{3}\right)}$$

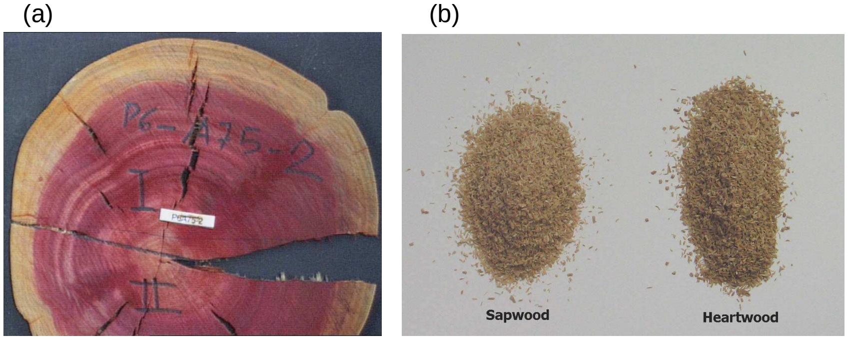

Figure 4. (a) Disc used for heartwood identification; (b) 20-40 mesh wood fraction used for pulping.

2.3.2. Chemical characterization

Sapwood and heartwood (20-40 mesh) material were chemically characterized in relation to total extractives, total lignin and sugar composition.

The extractives were determined with procedures adapted from Tappi 204 cm-97, in a soxhlet system with dichloromethane, ethanol and water in successive extractions. Total lignin was calculated by the sum of Klason lignin and soluble lignin, which were determined respectively, as adapted from Tappi 222 om-02 and Tappi UM 250 standards. The neutral sugars were determined after total hydrolysis as alditol acetates, by gas-liquid chromatography with a method adapted from Tappi 249 cm-00. The procedures was conducted in a GC (HP 5890A gas chromatograph) equipped with a FID detector, using helium as carrier gas (1 ml/min) and a fused silica capillary column S2330 (30 m x 0.32 mm i.d. x 0.20 µm film thickness). The column program temperature was 225-250ºC, with 5ºC/min heating gradient, the injector and detector temperature was 250 ºC, while split and septum purge were defined as 17.5ml/min and 2.5 ml/min, respectively. The volume inject was 0.3 µl and the run total time, 9 min. These conditions were established by several experiments, where the GC was calibrated with pure references compounds and inositol was used as internal standard in each run. Figure 5 presents a chromatogram of standard sugars and inositol that was used as reference for determination of retention time, sugar identification and quantification of the injected samples. A calibration factor was determined in a previous work for each sugar using the formula

$$\text{Calibration factor } (f) = \frac{Ai}{As} \times \frac{Ms}{Mi}$$

where Ai = chromatographic area of inositol peak, As = chromatographic area of the sugar peak; Ms = sugar mass (mg); Mi = inositol mass (mg).

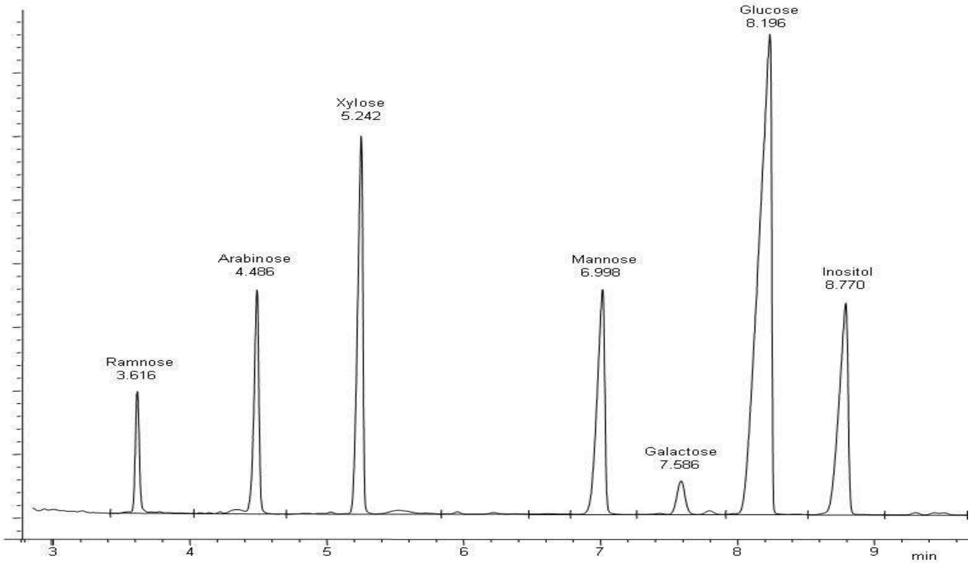

Figure 5. Standard sugars and inositol chromatogram (GC-FID) showing the retention times of each compound for the conditions used in this study.

2.3.3. Optical properties

Optical measurements were performed with a spectrophotometer (Minolta CM-3630) with d/0º geometry, which means that the illumination is diffuse and the measurement is made perpendicularly to the sample. The milled wood material was characterized by colour parameters of the L*a*b* CIE scale (Figure 6), using the software PaperControl ver.2 (2000). In CIE Lab colour scale, the L* axis represents nonchromatic changes in lightness from an L* value of 0 (black) to an L* value of 100 (white). The a* and b* parameters range in absolute value from 0 to 100, a* varying from red (positive values) and green (negative values); and b from yellow (positive values) to blue (negative values).

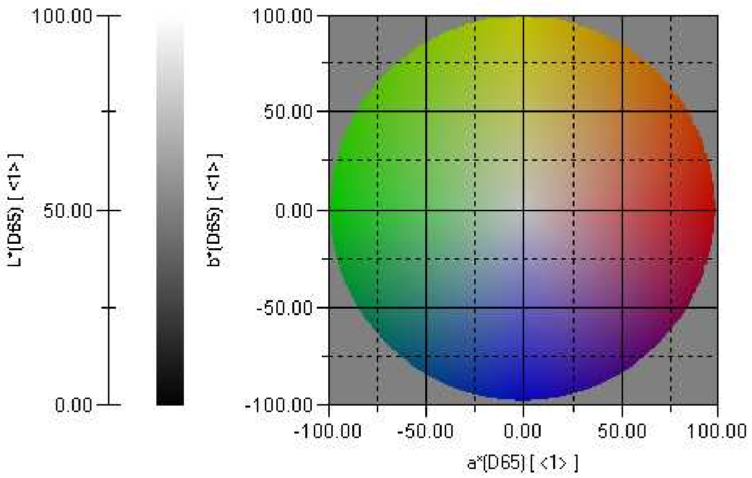

Figure 6. CIE L*a*b* colour scale.

2.4. Pulping

Sapwood and heartwood (20-40 mesh fraction) were dried and 5 g weighted for each batch of kraft pulping. The samples were placed in 100 ml stainless steel autoclaves (microdigesters) with kraft liquor and introduced in an oil bath with temperature control.

The pulping conditions were: liquor-to-wood ratio (mL/g) 4:1; sulfidity 30% (% as Na_2O); active alkali 20% (% as Na_2O); cooking at constant temperature of 170ºC. Heating time to temperature was 5 min. Pulping time at temperature was: 1, 3, 5, 10, 15, 20, 35, 35, 50, 65, 80 and 95 min.

After each pulping time, the autoclaves were removed from the oil bath and cooled in ice to stop the reaction. The sample was defibrated in a standard pulp ultrasound disintegrator (Dr Hielscher UP200H), thoroughly washed with de-ionised hot water, air-dried in an acclimatized room overnight (55 % relative humidity and 25ºC, as described in Tappi 402 os-70), dried and weighted for yield determination. All pulping experiments were replicated.

The material obtained from the delignification process was characterized by yield, lignin content and polysaccharides composition, and by colour parameters.

2.4.1. Yield

The delignified material yield (o.d.) was determined at each pulping time using the following formula

$$\text{Yield}\ (\%) = \frac{\text{mass of pulp}\ (\text{g})}{\text{mass of wood}\ (\text{g})}$$

The difference between the replicates was calculated and accepted for mean calculation when it was lower or equal to 0.5 %. Otherwise, pulping was repeated.

2.4.2. Chemical characterization

The samples were washed by extraction in a Soxhlet system with dichloromethane and water, with procedures adapted from Tappi 204 cm-97, to remove residual extractable material. The samples were dried and 1 g weighted and milled using a 0.05 sieve in a Retsch ZM 100 apparatus. Milling was necessary to homogenize the material, because at the early pulping stages the wood structure was still maintained.

The chemical determinations were performed as described for wood characterization.

2.4.3. Optical properties

The delignified material was characterized by the same colour parameters as in wood. Additionally delta values (Δ) of L*, a* and b* were calculated, as

$$\Delta L^* = L^*_{\text{sample}} - L^*_{\text{wood}}$$

$$\Delta a^* = a^*_{\text{sample}} - a^*_{\text{wood}}$$

$$\Delta b^* = b^*_{\text{sample}} - b^*_{\text{wood}}$$

Positive values of ΔL*, Δa* and Δb* mean that the samples are lighter, redder and yellower than the wood sample, while negative values represent darker, greener and bluer samples.

2.5. Modeling of delignification kinetics

2.5.1. Consecutive model

The delignification can be described by three consecutive phases (initial, bulk and residual) with different reaction velocities. The reaction rate of delignification at each pulping phase was mathematically described as a first order reaction with respect to lignin remaining in the pulps, and calculated as

$$\frac{L}{L_0} = \sum_{i=1}^{i=3} a_i \exp\left(-k_i\ t\right)$$

being a_i (experimental value) the lignin fraction susceptible to solubilization by the process in phase i, and k_i the corresponding rate constant; while i represents the reaction phase (i = 1, 2, 3).

First, the curve ln (L/L_0) was graphically represented and the phases defined. The a_i fractions were calculated by the difference of L/L_0 values at the beginning and the end of the corresponding i phase. The determination of k_i was made from a plot of the logarithm (L/L_0) versus time, which gives a straight line with slope representing k_i values.

2.5.2. Simultaneous model

The simultaneous model assumes that the different fractions (moieties) of lignin start to react at the same time since the beginning of pulping, and continue to dissolve simultaneously during pulping, although at different reaction rates, until at the end only the less reactive lignin species remains.

The logarithm of total lignin values (reported to wood material) was graphically represented during pulping. From this representation, the extraction of the less reactive lignin fraction (L_2) was visualized by drawing a straight line passing through the last value and the aligned previous values until obtaining the intercept parameter. The exponential of this intercept value is the percentage of the less reactive lignin present in the initial wood lignin. The corresponding velocity rate constant (k_2) was calculated by the following equation

$$k_2 = \ln\left(L_{2,0}/L_t\right)/\left(t_t - t_2\right)$$

where $L_{2,0}$ is the lignin at time 0 and L_t the lignin at time t.

Having determined the proportion of the less reactive lignin fraction (L_2) in the initial total lignin and its reaction rate, it was possible to calculate the amount of this fraction in the earlier pulping times, by applying the following equation

$$L_{n,t} = L_{2,0} * \left(\exp\left(-k_2 t\right)\right)$$

The subtraction of these values from the lignin at each point of time gives the points (L-L_2), which represents the next more reactive lignin fraction (L_1). The logarithm of these values is graphically represented describing the delignification without the less reactive lignin fraction. A straight line is drawn passing through these values, the intercept parameter is determined and the exponential of it gives the amount of the type of lignin fraction. The velocity rate constant of this stage is calculated as before. The analysis ends when the values obtained by subtraction represent a line and not a curve.

The total amount of lignin dissolved from the wood material (L) at an instant of cooking time (t) can be calculated from the equation:

$$L \;=\; L_{n\text{-}1,0} * \left(1 - \exp\left(-k_{n\text{-}1}t\right)\right) \;+\; L_{n,0} * \left(1 - \exp\left(-k_{n}t\right)\right)$$

where $L_{n-1,0}$ and $L_{n,0}$ are respectively the lignin fractions, from the more reactive (L_{n-1}) to the less reactive (L_n) and k the respective reaction rate constants.

The most suitable model was chosen after calculation of the sum of square residuals (SQR) which was obtained by the equation, $SQR \;=\; \sum_{n} E_n^{\,2}$ which was for this study

$$SQR \;=\; \sum_{t=0}^{95} \left[\; \left(L_t/L_0\right)_{\text{experimental}} \;-\; \left(L_t/L_0\right)_{\text{model}} \right]^2$$

3. Results

3.1. Heartwood and sapwood characterization

The physical, chemical and optical characterization of the 20-40 mesh wood fraction used for the delignification studies is presented in Table 1.

Heartwood and sapwood had the same value of basic density (0.74 g.cm^{-3}). The bulk density of chips was higher for heartwood them for sapwood (0.52 g.cm^{-3} *vs*. 0.44 g.cm^{-3}).

Table 1. Characterization of the *E. globulus* sapwood and heartwood material used for pulping.

	Sapwood	Heartwood
Basic density (g.cm^{-3})	0.74	0.74
Bulk density (g.cm^{-3})	0.44	0.52
Extractives (% o.d. wood)		
Dichloromethane	0.1	0.3
Ethanol	2.0	6.8
Water	1.8	2.7
Total	3.9	9.8
Lignin (% o.d. wood)		
Soluble	3.7	3.6
Klason	20.6	19.9
Total	24.3	23.5
Monosaccharides (% of total)		
Arabinose	1.2	1.3
Xylose	13.7	17.5
Mannose	1.7	2.7
Galactose	2.3	3.3
Glucose	81.1	75.1
Colour		
L*	82.9	82.9
a*	2.9	3.0
b*	13.9	16.6

Heartwood had more extractives (9.8 %) than sapwood (3.9 %). The difference was due to ethanol soluble material (6.8 % *vs*. 2.0 %) and also, but to a much smaller extent, to water soluble extractives (2.7 % *vs*. 1.8 %). Lignin content in sapwood and heartwood presented similar values, at respectively, 24.3 % and 23.5 %. The monossacharides composition of heartwood and sapwood was also similar, although heartwood showed slightly higher xylose and lower glucose content (17.5 % and 75.1 %) than sapwood (13.7 % and 81.1 %).

As regards colour, heartwood was more yellowish than sapwood, as confirmed by higher b* value (16.6 *vs*. 13.9).

3.2. Pulping

3.2.1. Yield

The 20-40 mesh fractions of sapwood and heartwood were submitted to kraft pulping during different cooking times. The obtained yields are presented in Table 2 and Figure 7. The solubilization of the wood material by pulping was very rapid in the initial reaction phase and somewhat higher in heartwood than in sapwood. After 1 min, the yield was 85.9 % and 92.6 %, for heartwood and sapwood, respectively, and after 5 min it was 74.9 % and 82.6 %. Similar yield values were obtained for heartwood and sapwood after 10 min (69.1 % and 68.7 %) and 20 min (60.9 % and 61.8 %). For longer reaction times, the yield obtained with sapwood was always higher than with heartwood: with 95 min pulp yield was 56.7 % and 52.4 % for sapwood and heartwood respectively.

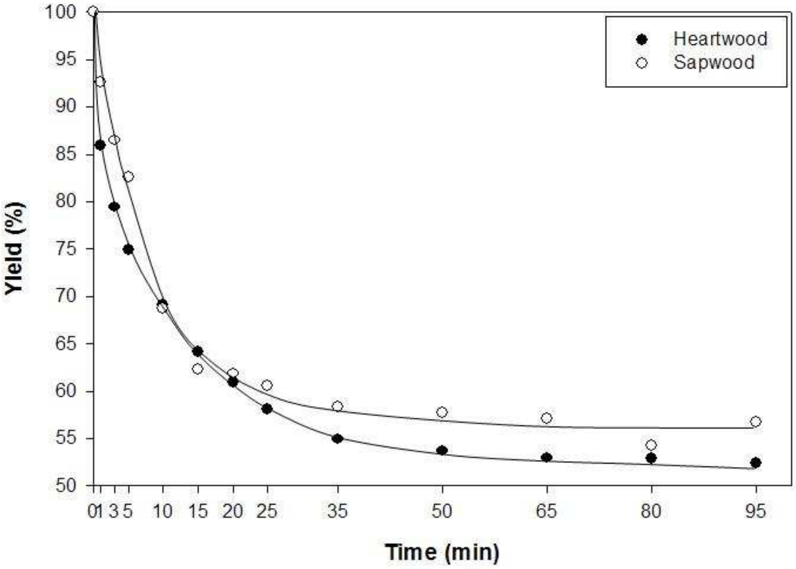

Figure 7. Effect of pulping time on total yield from sapwood and heartwood of *E. globulus*.

Figure 8 shows the macroscopical aspect of the wood samples after reaction with different pulping times. It can be seen that only after 35 min of delignification the fibres were separated and enough individualized to be networked in what can be considered as pulp. Before that time, the material was less delignified and the wood structure was maintained.

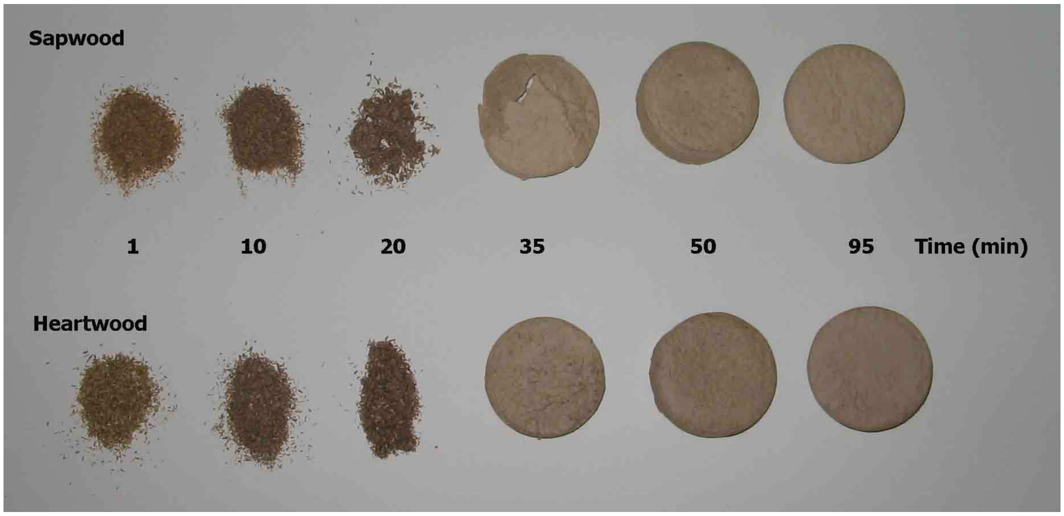

Figure 8. Samples of 20-40 mesh fractions of sapwood and heartwood of *E. globulus* after delignification with different times (1 to 95 min).

3.2.2. Chemical characterization

The delignified samples were chemically analysed and the results are shown in Table 2 and Table 3.

During pulping, lignin was progressively removed from the wood structure and the content in lignin of the pulped material decreased steadily, especially in the first stages of reaction. The behaviour of heartwood and sapwood in delignification, as regards content of residual lignin in the samples, was similar in the first part of pulping up to approximately 20 min reaction time, and subsequently sapwood showed lower residual lignin content. For example, after 15 min of pulping, the residual total lignin contained in the material was 11.0 % and 10.8 % in heartwood and sapwood respectively; after 20 min of pulping, it was 8.1 % and 8.9 % in sapwood and heartwood, and after 95 min, the total residual lignin was 3.0 % in heartwood and 1.2 % in sapwood. The differences between heartwood and sapwood in relation to residual lignin in the delignified samples were due to Klason lignin, since the acid soluble lignin showed similar values.

Table 2. Yield (% of o.d. wood) and lignin content (% o.d sample) of sapwood and heartwood, after delignification with different pulping times (mean of two samples).

	Sapwood				Heartwood			
	Yield	Lignin (% of sample)			Yield	Lignin (% of sample)		
Time (min)	(% of wood)	Soluble	Klason	Total	(% of wood)	Soluble	Klason	Total
Wood	100.0	3.7	20.6	24.3	100.0	3.6	19.9	23.5
1	92.6	3.7	19.3	23.0	85.9	3.8	18.8	22.6
3	86.5	3.3	18.1	21.4	79.4	3.2	17.3	20.5
5	82.6	3.3	16.2	19.5	74.9	3.2	15.0	18.2
10	68.7	2.3	9.2	11.6	69.1	2.4	11.9	14.3
15	62.3	1.8	9.2	11.0	64.1	2.0	8.8	10.8
20	61.8	1.5	6.6	8.1	60.9	1.4	7.5	8.9
25	60.5	1.1	2.8	3.9	58.1	1.4	4.8	6.2
35	58.3	0.7	2.7	3.4	54.9	0.9	3.8	4.7
50	57.7	0.7	1.4	2.1	53.7	0.8	3.2	4.0
65	57.1	0.7	1.0	1.6	52.9	0.6	3.1	3.7
80	54.3	0.7	0.6	1.3	52.9	0.6	2.9	3.5
95	56.7	0.8	0.3	1.2	52.4	0.7	2.3	3.0

The monossacharides composition is presented in Table 3. There were no significant differences between the samples after the various delignification times, although arabinose and galactose proportion decreased and glucose content increased with time. No differences were found between heartwood and sapwood.

Table 3. Monosaccharide composition (% of total neutral sugars) of sapwood and heartwood after delignification with different pulping times.

	Sapwood						**Heartwood**					
	Monosaccharide (%)						Monosaccharide (%)					
Time (min)	Arabinose	Xylose	Mannose	Galactose	Glucose	**Total**	Arabinose	Xylose	Mannose	Galactose	Glucose	**Total**
Wood	1.2	13.7	1.7	2.3	81.1	**100.0**	1.3	17.5	2.7	3.3	75.1	**100.0**
1	0.9	11.8	1.7	2.0	83.0	**100.0**	1.2	12.9	2.7	2.5	72.2	**100.0**
3	0.8	13.1	1.5	2.3	82.4	**100.0**	0.8	13.7	1.9	2.9	80.7	**100.0**
5	0.9	12.3	1.8	2.2	82.9	**100.0**	0.8	12.9	2.0	2.2	82.2	**100.0**
10	0.7	10.0	1.8	1.6	85.9	**100.0**	0.7	12.2	1.9	1.9	83.3	**100.0**
15	0.3	9.5	1.7	1.4	87.1	**100.0**	0.7	11.8	1.7	1.4	84.4	**100.0**
20	0.5	11.1	1.7	1.3	85.4	**100.0**	0.7	11.6	1.9	1.4	84.4	**100.0**
25	0.6	10.7	1.8	1.2	85.7	**100.0**	0.6	12.2	1.7	1.2	84.3	**100.0**
35	0.9	9.2	2.0	0.9	85.8	**100.0**	0.6	11.6	1.6	1.2	85.0	**100.0**
50	0.6	11.4	2.2	0.5	85.4	**100.0**	0.5	11.8	1.7	0.9	85.1	**100.0**
65	0.4	10.4	1.6	0.8	86.8	**100.0**	0.4	11.4	1.7	0.9	85.6	**100.0**
80	0.4	11.4	1.7	0.8	85.7	**100.0**	0.2	12.4	1.8	0.4	85.2	**100.0**
95	0.5	12.7	1.7	0.8	84.4	**100.0**	0.5	12.5	1.7	0.8	84.6	**100.0**

3.2.3. Optical properties

The colour characterization and the CIE L*a*b* parameters measured for each sample are presented in Table 4 and Figures 9 to 11.

Delignification reduced the L* value for both sapwood and heartwood samples. The values of delta lightness ($\Delta L^* = L^*_{wood} - L^*_{sample}$) show that all delignified samples were darker than the wood, with the less darker between 3 to 5 min with values of -5.9 (Figure 9). The delignified samples of sapwood were lighter (L*) than those of heartwood, as well as more reddish (values of a*) and less yellowish (values of b*).

Positive Δa* values, corresponding to reddish samples, were found in both sapwood and heartwood samples (Figure 10), although sapwood showed higher values, varying from 0 to 3 (close to red area), whereas heartwood varied from -2 (greener region) to 2 (reddish region). The delta b* values (Figure 11) show an increase in the initial pulping stages and a gradual reduction as pulping time increased. After 15 min, the heartwood material became bluer varying from -0.4 to -2.4, while sapwood maintained values near 0.

Table 4. Results from colour measurements of sapwood and heartwood samples after delignification with different pulping times. Values of L* a* b* parameters.

	Sapwood			Heartwood		
Time (min)	L*	a*	b*	L*	a*	b*
Wood	82.9	2.9	13.9	82.9	3.0	16.6
1	76.3	4.1	19.3	75.2	3.1	22.0
3	77.0	3.1	20.0	75.8	1.7	23.0
5	77.0	3.6	19.2	74.5	2.6	19.9
10	73.3	4.6	16.2	69.7	4.0	17.2
15	73.2	4.6	14.9	67.9	4.8	16.1
20	74.0	5.4	15.1	67.2	5.0	15.5
25	74.1	5.9	15.1	65.8	5.0	15.1
35	74.0	5.3	14.0	65.3	4.8	14.2
50	73.0	5.8	14.2	63.6	4.8	13.8
65	73.4	4.9	13.4	61.9	4.9	14.4
80	73.6	4.1	13.0	63.4	4.7	14.1
95	74.5	5.0	13.9	66.5	4.8	14.1

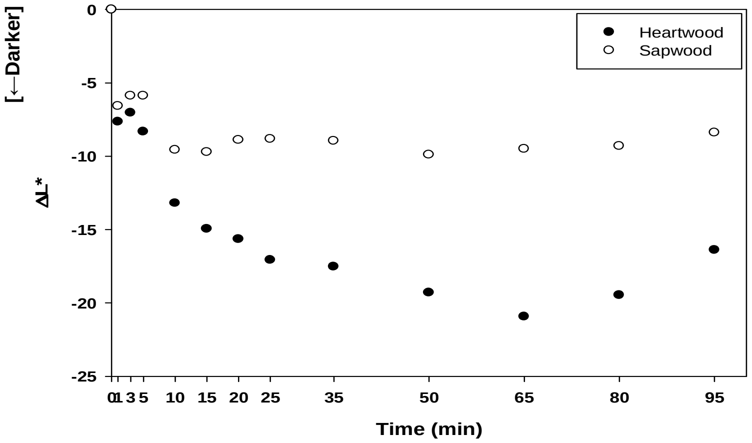

Figure 9. Values of ΔL* from sapwood and heartwood along the delignification period. Wood as reference.

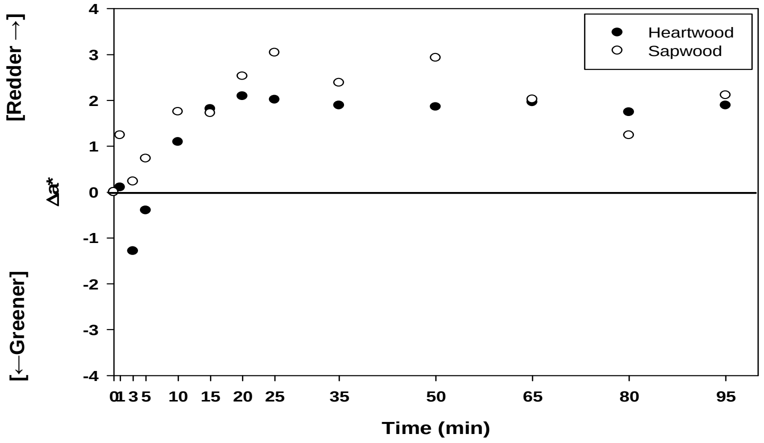

Figure 10. Delta a* values (CIE lab colour scale) of sapwood and heartwood during delignification.

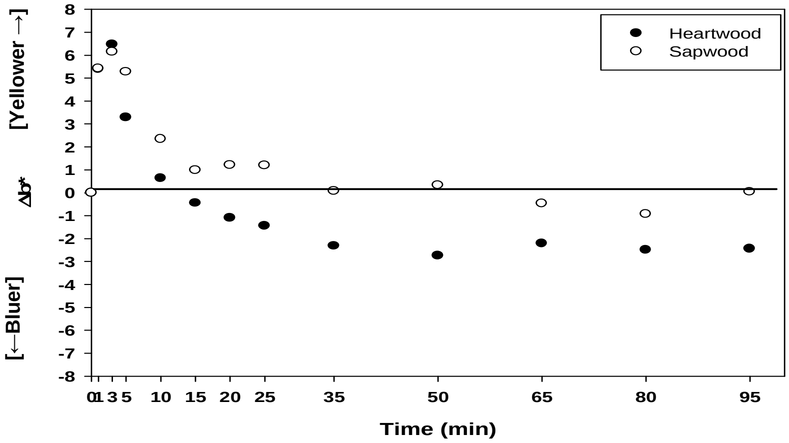

Figure 11. Delta b* values (CIE lab colour scale) of sapwood and heartwood samples during delignification.

3.2.4. Modelling of delignification kinetics

The content of lignin in the heartwood and sapwood samples decreased with reaction time (Table 2) and is shown graphically in Figure 12. The mathematical description of the kraft pulping process was made in relation to the delignification by analysing the results of lignin removal. Two modelling approaches were applied: the consecutive model and the simultaneous model.

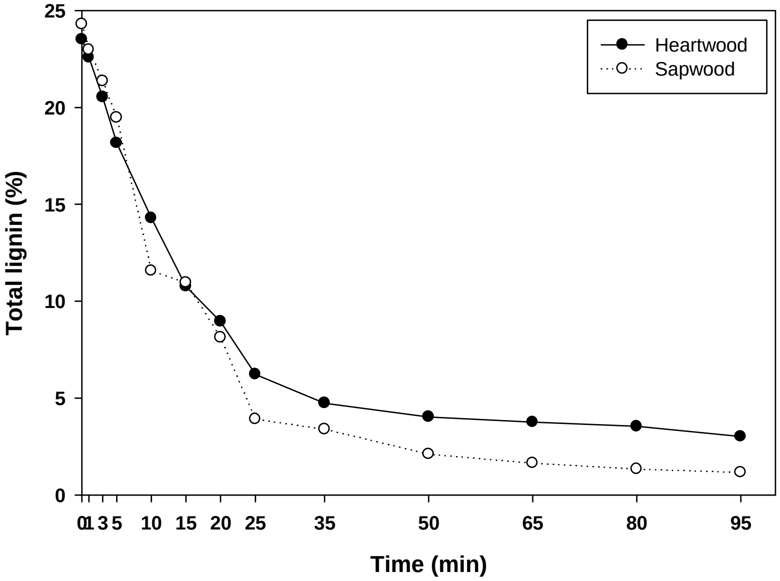

Figure 12. Lignin content of sapwood and heartwood samples with different reaction times.

3.2.4.1. Consecutive model

The consecutive approach assumes that the dissolution and removal of lignin proceeds in three phases, which occur consecutively, each of them characterized by a removal of lignin with different reaction rates.

A graphic representation of ln L/L_0 (where L = residual lignin; L_0 = initial lignin) *vs*. time is represented in Figure 13 and Figure 14, respectively for sapwood and heartwood. For both cases the initial phase of delignification could not be visualized and only two phases with different kinetics could be observed: the first included therefore the initial and bulk phases, and the second the residual phase.

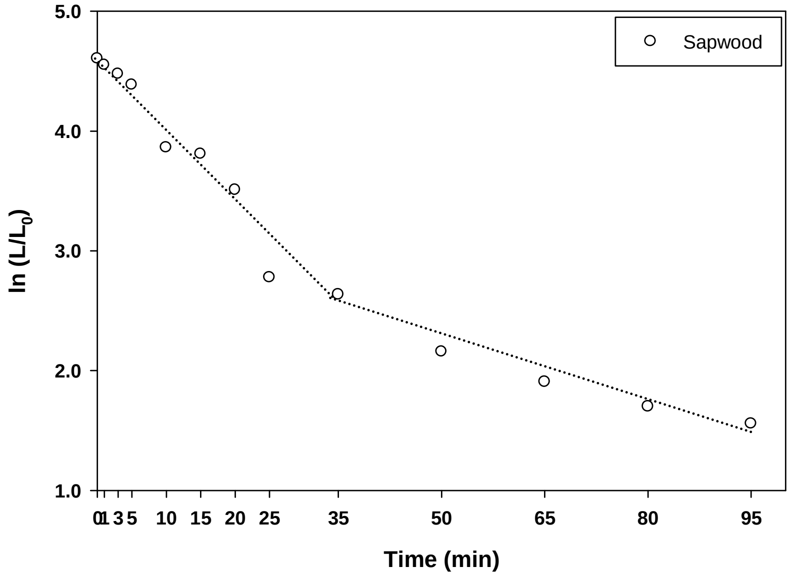

Figure 13. Logarithm variation of total lignin (L/L$_0$) for sapwood samples during delignification.

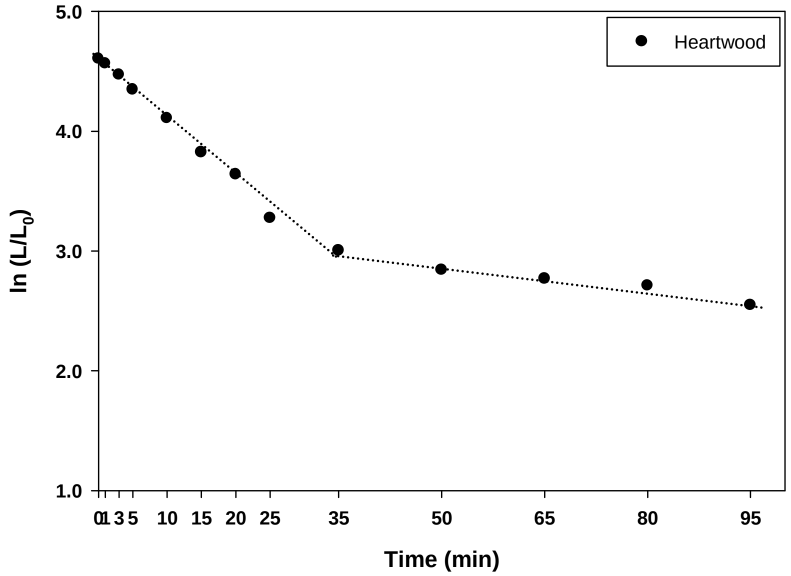

Figure 14. Logarithm variation of total lignin (L/L$_0$) for heartwood samples during delignification.

Table 5 presents the delignification rates (k) and the lignin fractions susceptible to solubilization (a_i) by the kraft process under the studied conditions. For sapwood (Figure 13) the first phase (initial and bulk) had a duration of 35 min, extracting 86% of the initial total lignin present in the wood, at a reaction rate characterized by a constant, k_{i+b}. of 0.061 min^{-1} ($R^2 = 0.961$). The residual phase removed 9 % of the initial lignin, at a lower reaction constant ($k = 0.017$ min^{-1}, $R^2 = 0.945$), while 5 % of the lignin remained in the lignocellulosic matrix after 95 min of pulping. For heartwood (Figure 14) less lignin was removed, the first phase (initial and bulk phases) lasted 35 min, extracting 80 % of the initial lignin, while the residual phase extracted 7 % and the residual lignin present in the pulp material after 95 min was 13 %. The reaction rate constants were, respectively, $k_{i+b} = 0.048$ min^{-1} ($R^2 = 0.991$) and $k_r = 0.007$ min^{-1} ($R^2 = 0.966$). The reaction rates and the fraction of lignin removed in both reaction phases were lower for heartwood than for sapwood. The mathematical expression for the total reaction can be described as:

$$L/L_0 = 0.86 \exp(-0.061t) + 0.09 \exp(-0.017t) + 0.05 \text{ for sapwood}$$

and

$$L/L_0 = 0.80 \exp(-0.048t) + 0.07 \exp(-0.007t) + 0.13 \text{ for heartwood}$$

Table 5. Reaction rate constants (k_i) and mass fractions (a_i) of sapwood and heartwood delignification. Delignification phases: i+b=initial and bulk; r=residual.

	Sapwood	Heartwood
a_{i+b}	0.86	0.80
k_{i+b} (min^{-1})	0.061 ($R^2 = 0.961$)	0.048 ($R^2 = 0.991$)
a_r	0.09	0.07
k_r (min^{-1})	0.017 ($R^2 = 0.945$)	0.007 ($R^2 = 0.966$)

The lignin values obtained by simulation using the obtained model equations were plotted versus the respective experimental values (Figure 15). There is an overall good correlation of experimental and modeled values, although slightly less in the late stages of pulping. For model validation the sum of square residuals (SQR) were determined (statistical criteria for data reproducibility) and the values obtained for sapwood and heartwood samples were respectively, 0.041 and 0.101. Sapwood delignification was better explained by this model, while heartwood was overestimated.

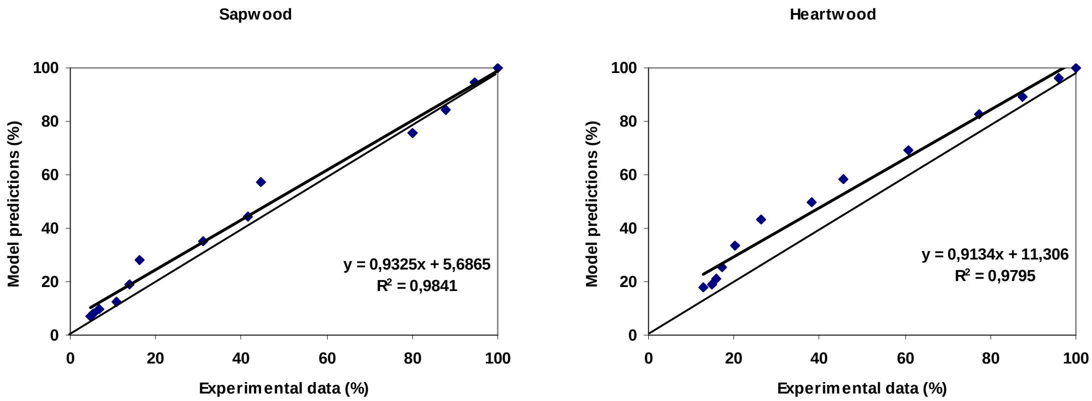

Figure 15. Reproduction of experimental data on lignin conversion by the consecutive model.

3.2.4.2. Simultaneous model

The simultaneous model assumes that the dissolution and removal of the different lignin fractions occur at the same time, although at different rate constants.

Figure 16 and Figure 17 present the logarithm of lignin content, respectively for sapwood and heartwood. A two-step analysis was enough to complete the kinetic description, corresponding to the presence of only two lignin fractions that behaved differently under these pulping conditions, L_1 and L_2. Their kinetics are represented by the two straight lines in the figures. In sapwood the less reactive lignin fraction L_2 corresponded to 24.2 % of the total lignin and was removed at a rate constant k_2 of 0.018 min^{-1}, while the more reactive lignin fraction L_1 was extracted with a higher rate ($k_1 = 0.077\ \text{min}^{-1}$) and represented 75.8 % of total lignin. The application of this model to the values obtained for sapwood gives the following equation

$$L = 75.8 * \left(1 - \exp\left(-0.077t\right)\right) + 24.2 * \left(1 - \exp\left(-0.018t\right)\right)$$

Heartwood presented the same behavior and also two types of lignin fractions. The less reactive lignin L_2 was approximately 29.4 % of the total lignin and was removed at a rate k_2 of 0.010 min^{-1}, while the more reactive lignin fraction L_1 represented 70.6 % and had a k_1 of 0.080 min^{-}1. The model equation for heartwood can be written as

$$L = 70.6 * \left(1 - \exp\left(-0.080t\right)\right) + 29.4 * \left(1 - \exp\left(-0.010t\right)\right)$$

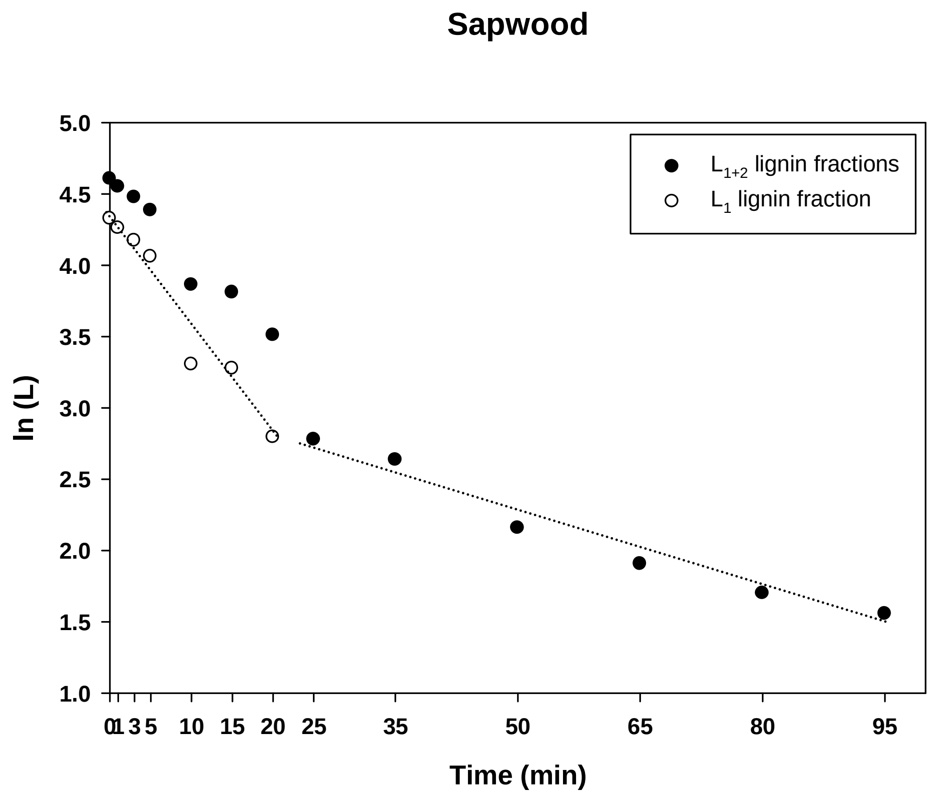

Figure 16. Delignification curves from sapwood samples. Straight lines represent lignin fractions.

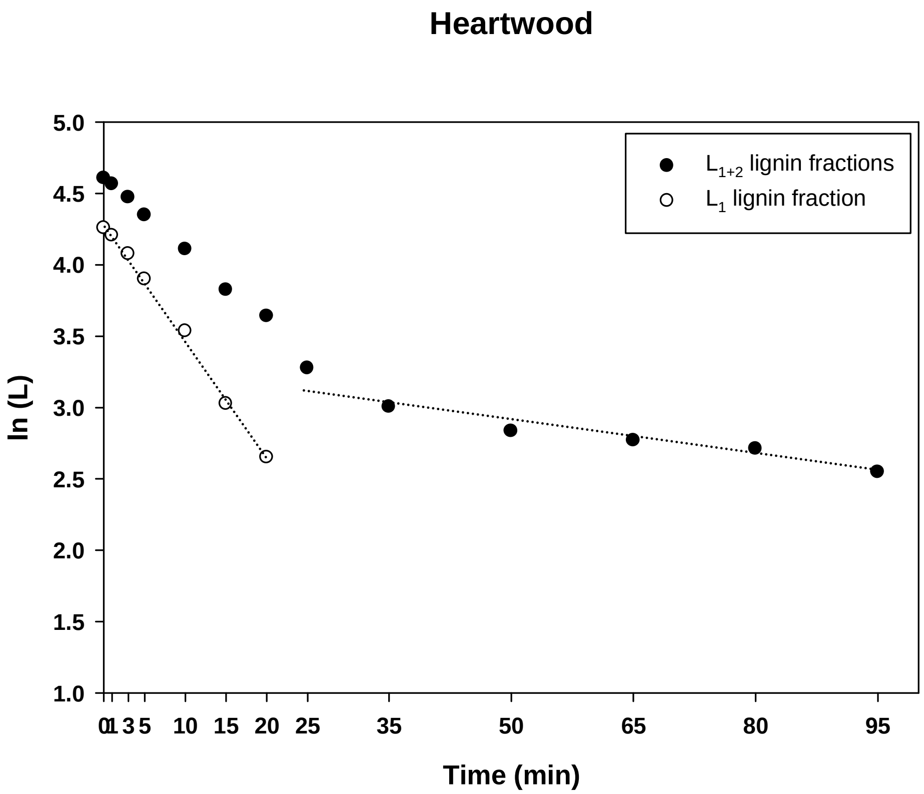

Figure 17. Delignification curves from heartwood samples. Straight lines represent lignin fractions.

The data obtained by the model and the experimental data were plotted (Figure 18). The correlation between them was high for heartwood and sapwood as shown by R^2 values of respectively, 0.994 and 0.984.The sum of square residuals (SQR) was also calculated and the values obtained were 0.033 and 0.009 for sapwood and heartwood, respectively.

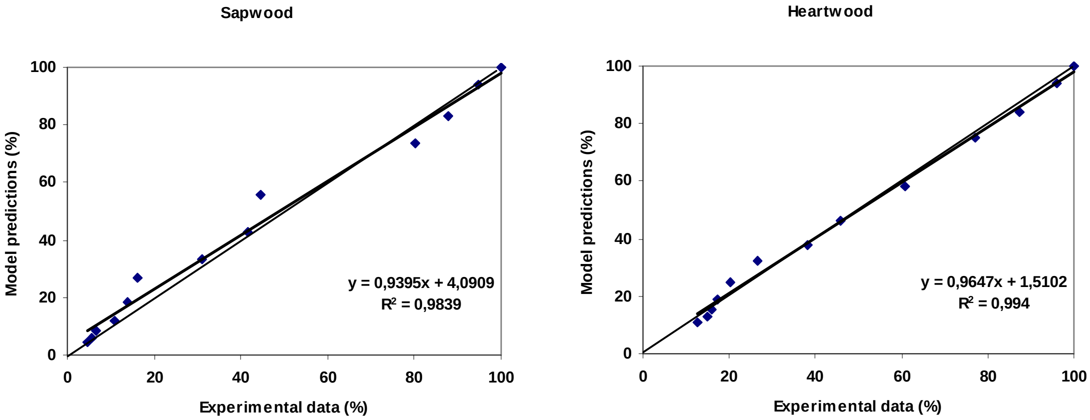

Figure 18. Reproduction of experimental data on lignin conversion by the simultaneous model.

4. Discussion

4.1. Heartwood and sapwood characterization

The basic density of sapwood and heartwood from *E. globulus* used in this study was 0.74 g.cm^{-3}. This value is higher than reported by other authors for *E. globulus* although it is in the broad range of values found for the *Eucalyptus* species growing in Australia forests (0.30-1.00 g.cm^{-3}, Higgins, 1984). For *E. globulus* trees with the same age of 18 years, Miranda *et al.* (2003) obtained lower wood basic density values, ranging from 0.57 to 0.59 g.cm^{-3}, while Valente *et al.* (1993) reported 0.45-0.62 g.cm^{-3} for trees with eight and twelve years, Cotterill and Macrae (1997) 0.53 g.cm^{-3} for ten-year-old trees, Miranda and Pereira (2002c) 0.53-0.55 for nine-year-old trees, and Gil *et al*. (1999) and Wimmer *et al.* (2002) 0.46 and 0.59 g.cm^{-3} for eight-year-old trees.

A wood basic density between 0.65 and 0.70 g.cm^{-3} was considered by Bootle (1983) as an economic advantage for pulping, because this wood occupies less volume per unit of papermaking material during transportation and more material can be treated per digester charge. Although wood density is one of the most studied wood variables, its influence on pulp properties is not significant in eucalypts (Trugilho *et al.*, 2005, Collins *et al.*, 1990).

It would be expected that because sapwood has thicker cell wall fibers it would have higher basic density compared to heartwood, as reported by Monteiro (2003) for *E. globulus* trees with 14 years of age (0.60 *vs*. 0.57 g.cm^{-3}). The similar value of 0.74 g.cm^{-3} obtained for both heartwood and sapwood, might be due to higher extractives deposition on heartwood fiber walls, that compensate the thicker sapwood cells.

One important chemical characteristic of wood is its content in extractives, whose presence is undesirable for pulping and papermaking. In general *E. globulus* has a moderate extractive content, *e.g*. 3.7 % total extractives in 9-year-old trees (Miranda *et al*., 2002c) although increasing with age to 5.0-8.7 % for 18-year-old trees (Miranda *et al*., 2003).

In this work the wood material was selected from a tree with a high extractive content in heartwood compared to sapwood (9.8 % vs. 3.9 %), essentially due to the contribution of ethanol extractives (6.8 % and 2.0 % respectively). Heartwood has more extractives than sapwood and some data are available for *E. globulus*: Gominho (2003) obtained in 9-year-old *E. globulus* trees, values of ethanol-extractives ranging from 1.8 % to 5.4 % in heartwood and 1.0 % to 1.5 % in sapwood. In 8-year-old trees values for ethanol extractives ranged from 1.9 % to 4.3 % in heartwood and 1.3 % to 2.2 % in sapwood (Miranda *et al*., 2007). Similar differences between heartwood and sapwood are found in other species in respect to total extractives, and Gominho *et al*. (2001) with urograndis eucalypt hybrid trees obtained 3.7 % and 7.6 % respectively, in sapwood and heartwood, where the main extractives were removed by ethanol respectively, 1.8 % and 3.9 %. In *E. grandis,* 5.1 % of extractives were found in sapwood and 5.6 % in heartwood (Mariani *et al*., 2005), and in *E. pilularis* 2.9 % and 8.4 % (Higgins, 1984). For total wood, Silva *et al.* (2005) attained with *E. grandis* respectively in 10 and 20-year-old trees 4.0 % and 6.3 %, showing the influence of a higher proportion of heartwood in the older trees.

Lignin content was similar in sapwood and heartwood respectively, 24.3 % and 23.5 %. These values are in the range of those reported for *E. globulus*, *e.g*. 21.9 % (Patt *et al.*, 2006, Gilarranz *et al.*, 1999), 25.5 % (Miranda and Pereira, 2002c) or 27.0 % (Cotterill and Macrae, 1997). *E. globulus* has lower lignin than other eucalypt species, a favourable characteristic for pulping, for example, 32.9 % in *E. degluta* and 33.7 % in *E. tereticornis* (Collins *et al.*, 1990), 29.0 % in *E. vitaminis* and 30.0 % in *E. grandis* (Cotterill and Macrae, 1997). Ona *et al*. (1997) studied the radial and axial variation in respect to lignin S/G ration in *E. globulus,* presenting higher ratio at pith area, decreasing with height. In *E. nitens*, Mariani *et al.* (2005) reported a lignin content of 21.8 % and 25.1 %, respectively in sapwood and heartwood. The content in extractives may obscure the composition of cell wall structural components; in our material, lignin in sapwood and heartwood represented respectively, 25.3 % and 25.8 % of extractive-free wood, in agreement with the general trend of higher lignin content in the inner part of the stem. This was also observed in maritime pine by Esteves *et al*. (2005) where heartwood-extractive free wood presented higher value than sapwood (28.7 % *vs.* 26.7 %).

The major monosaccharides were glucose and xylose that attained in sapwood respectively, 81.1 % and 13.7 %, and in heartwood, 75.1 % and 17.5 %. For *E. globulus* wood, mean values reported for glucose were 71.9 % (Miranda *et al*., 2003) and 75.3 % (Pinto *et al*., 2005a); and for xylose 28.4 % (Miranda *et al*., 2003) and 20.0 % (Pinto *et al*., 2005a).

Distinction of heartwood and sapwood by colour is one very common feature in most species and used as heartwood identification method. In *E. globulus*, heartwood is usually distinct from sapwood although often the difference is not very large and other methods are used for delimitation of heartwood (Gominho *et al*., 2004), as it was the case in the present study. In accordance, the CIELab colour measurements in sapwood and heartwood presented no difference in lightness (L*), and a* parameter (3.0), and the distinction occurred only at b* values, with heartwood more yellowish (positive b*) than sapwood (16.6 *vs*. 13.9). Mori *et al.* (2005) with *Eucalyptus* spp found differences between sapwood and heartwood in b* (18 *vs*. 22), a* (4-7 *vs.* 9-13) and L* (70 *vs*. 81) parameters.

4.2. Pulping

The primary objective of pulping is to remove lignin from wood, without depolymerization in great extent of polysaccharides (Clayton *et al.*, 1983) and therefore pulp yield is directly influenced by the lignin and cellulose contents (Patt *et al.*, 2006). The pulp yields obtained after 95 min pulping time (Table 2) are high at a mean value of 55 %, as it is usual for *E. globulus* wood. For example, Simão *et al*. (2005) reported 55.0 %, Miranda and Pereira (2002a) 56.2 %; Miranda and Pereira (2002c) 57.6 % to 58.5 %; Miranda and Pereira (2002b) 52.2 %; Wallis *et al.* (1996) 54.4 %; Patt *et al.* (2006) 54.6 %.

Pulp yield from heartwood was lower than from sapwood, respectively 52.4 % and 56.4 %. This difference was expected due to the higher content of extractives of heartwood and similar results have been reported already, *e.g*. Miranda *et al.* (2007) obtained 48.3 % for heartwood and 54.1% for sapwood, and Miranda *et al.* (2006) obtained 56.2 % and 57.4 %, respectively. The lower yield obtained from heartwood in relation to sapwood was also reported in other species: in *Acacia melanoxylon* 52.9 % and 56.2 % respectively (Lourenço *et al.*, 2008), in *E. grandis* composite samples where samples with more heartwood yielded less pulp (Mariani *et al.*, 2005). The same was observed with *P. pinaster* kraft pulps, 40.0 % and 49.7 %, respectively, for heartwood and sapwood (Esteves *et al*., 2005).

The fiber dissociation from the wood structure was only obtained for yield values less than 59 % for sapwood and 55 % for heartwood, representing a lignin removal of respectively, 86 % and 80 %, comparable to the yield results obtained by Miranda and Pereira (2002b) for *E. globulus* wood (60 %) although less lignin was removed (63 % during 35 min). Esteves *et al*. (2005) reported for pine heartwood a total yield of 40 % and 86 % lignin solubilization, while for sapwood respectively, 50 % and 84 % after 60 min.

Heartwood presents differences at chemical levels (extractives content) compared to sapwood, which are responsible for higher chemical consumption during pulping and higher residual lignin (3.0 % *vs*. 1.2 %, Table 2). Other authors studied the sapwood and heartwood behavior during delignification and obtained lower differences in respect to residual lignin content: *E. grandis* heartwood presented 2.6 % and sapwood 2.4 % (Mariani *et al.*, 2005) and *P. pinaster* the klason lignin represented respectively 4.2 % and 4.4 % (Esteves *et al.*, 2005).

In respect to sugar composition, sapwood and heartwood showed similar results, for example at 95 min, xylose and glucose content in both were respectively, 12.6 % and 84.5 %. These results can be compared with those reported by Pinto *et al*. (2005b) for *E. globulus* total wood where the percentage of glucose is similar to the obtained, 79.9 %, but xylose is higher, 18.8 %.

Compared to wood, all pulp samples were darker (Figure 19) due to the formation of lignin chromophores during pulping (Bierman, 1996). Other authors obtained for softwood kraft pulps L* varying from 68 to 71; a* from 5 to 7 and b*, 17 to 20 (Lachenal *et al.*, 2005). Birch kraft pulps were lighter, but less yellowish, compared to softwood kraft pulps (Lachenal *et al.*, 2005); for *E. globulus* commercial unbleached pulps, Lourenço (2003) reported respectively, 78, 4 and 16. In this study, heartwood pulps presented lower luminosity values (L*), ranging from 65 to 75, while sapwood values were around 75. Lourenco *et al.* (2008) with *Acacia melanoxylon* pulps obtained differences between heartwood and sapwood referring to lightness values respectively of 45-60 and 60-75.

Sapwood and heartwood delignified samples presented similar a* values, between 4 and 5, but presented differences at b* values, where sapwood became bluer (19.3-13.9) compared to heartwood (22.0-14.1). Lourenco *et al.* (2008) with *Acacia melanoxylon* pulps found smaller differences between sapwood and heartwood pulps: b* values were lower, 10 to 15, but similar a* values were attained (around 5).

Figure 19. Correlation between lightness (L*) in sapwood and heartwood delignified fractions and initial wood.

4.2.4. Modeling of delignification kinetics

4.2.4.1. Consecutive model

The application of a consecutive model to *Eucalyptus globulus* kraft pulping at 170ºC explained delignification in two phases, as shown by Labidi and Pla (1992), Gilarranz *et al.* (2002), as well as for organosolv delignification under the same temperature (Gilarranz *et al.*, 1999; Oliet *et al.*, 2000; Miranda and Pereira, 2002b). The initial phase was not identified at the high temperature of 170ºC that was used in this study, because it might be coincident with the heating period. An initial phase was observed by Chiang *et al.* (1988) with temperatures varying from 90 to 140ºC, who found that in this phase, 25 % of lignin was extracted in red oak and red alder, 20 % in aspen and sweetgum.

For *E. globulus* kraft delignification, the transition from bulk to residual delignification was observed at a lignin removal ranging from 94 % to 98 % (Gilarranz *et al.*, 2002) or 97 % (Santos *et al.*, 1997) at temperatures of 150 to 180ºC with several alkali concentrations. Miranda and Pereira (2002b) reported for delignification at 170ºC a lignin removal in the bulk phase of 66 % and 10 % in the residual phase, with rate constants of respectively, -0.035 and -0.0034 min^{-1}. In organosolv pulping, initial, bulk and residual phases represented a lignin extraction of respectively: 10, 69 and 21 % (Gilarranz *et al.*, 1999) or 9, 75 and 16 % (Oliet *et al.*, 2000); in the bulk and residual phases, respectively, 55 and 12 % of lignin were removed (Miranda and Pereira, 2002b).

In this study, delignification of sapwood and heartwood was explained by two phases, and in both, heartwood was more difficult to delignify. The bulk phase corresponded to a lignin removal of 86 % and 80 %, respectively for sapwood and heartwood and the residual phase to 9 % and 7 %. Heartwood samples retained more lignin in the solid matrix, 13 % *vs*. 5 %.

Several authors have studied the kraft pulping of *Eucalyptus globulus*, but no literature was found comparing sapwood and heartwood kinetics relatively to a consecutive model approach. For pine sapwood and heartwood delignification at 170ºC, Esteves *et al.* (2005) reported lower lignin removal in the bulk phase, respectively 59 % and 47 % for sapwood and heartwood, with more residual lignin present in the pulps, respectively, 11 % and 13 %. Pine heartwood was more difficult to delignify compared to eucalypt due to their differences at phenolic units. Pine is mostly constituted by guaiacyl (G) and p-hydroxyphenyl (H) (Saito *et al.*, 2005) and only in a minor degree (if at all) by syringyl (S) phenolpropanoid units (Obst and Landucci, 1986; Plomion *et al*., 2001), with a relation G:S:H of 95:0:5 (Alves, 2004). In *Eucalyptus globulus* the S:G ratio is high, ranging from 2.0 to 2.8 (Rodrigues *et al*., 2001). Because the S-type lignin is less condensed than G-lignin, eucalypt lignin is more easily solubilized during pulping (Ibarra *et al*., 2005) compared to pine.

4.2.4.2. Simultaneous model

Same authors refer a model where lignin fractions are removed at the same time, the simultaneous model (Dolk *et al.*, 1989; Labidi and Pla, 1992; Oliet *et al.*, 2000). Even though several references exist mentioning this approach, none was found applying it to *Eucalyptus globulus*. Two types of lignin were found regarding delignification kinetics: one more reactive lignin (L_1) that represented 71-76% of the lignin and a less reactive lignin (L_2) that represented 24-29% of the lignin. It may be possible that during the heating period a more reactive lignin was removed, but with this pulping temperature it could not be identified. The more reactive lignin (L_1) was easier to extract in sapwood compared to heartwood (75.8 % *vs*. 70.6 %), the inverse occurred for the less reactive lignin (L_2, 24.2 % *vs*. 29.4 %). The SQR analysis demonstrated that sapwood and heartwood delignification was well explained by this model with lower differences between the experimental data and the model predictions (0.033 *vs*. 0.030).

The only reference found applying a simultaneous model was for *Arundo donax* delignification at temperatures from 130 to 150ºC (Shatalov and Pereira, 2005). They could identify three different lignin fractions, the more reactive represented about 62 % of total lignin, the medium reactive lignin 22 % and the less reactive, 16 %. The simultaneous model explained better the delignification in *Arundo* compared to consecutive model, as tested by SQR (0.0036 *vs*. 0.0856).

The experimental values and those obtained by the two models are presented in Figure 20. It can be seen that sapwood delignification can be explained by both models, while heartwood delignification is better explained by the simultaneous model.

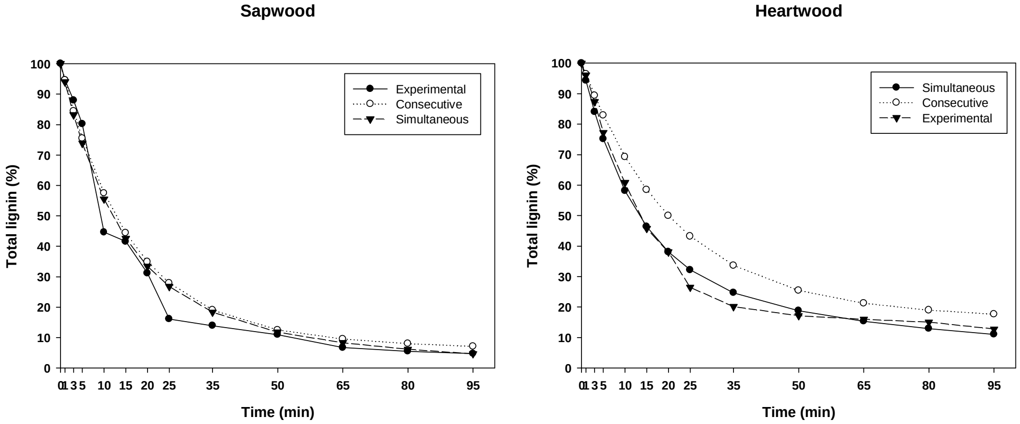

Figure 20. Comparison of total lignin remaining during pulping obtained by experimental data and by model simulations.

5. Conclusion

Eucalyptus globulus wood was used in this work to study the influence of heartwood and sapwood in delignication by kraft pulping. Heartwood had more extractives but similar lignin contents compared to sapwood and was more yellowish.

The major conclusions are:

- there were differences in pulping and in delignification between heartwood and sapwood;
- pulp yields were lower in heartwood in comparison to sapwood;
- heartwood was more difficult to delignify with more residual lignin in pulp;
- sapwood pulps were lighter than heartwood pulps, but in relation to a* and b* parameters no differences were found;
- heartwood delignification was better explained by a simultaneous kinetic model, while for sapwood both models could be applied;
- apparently sapwood delignification presented higher velocity reaction rates compared to heartwood when a consecutive model was applied but this difference was lower when the simultaneous model was used.

Further studies should be performed to better understand the differences of sapwood and heartwood in pulping. In relation to the delignification kinetics, lower temperatures should be tested to better explain the lignin removal, namely in the initial stages, with the calculation of other kinetics parameters, *e.g*. activation energy. The influence of liquor impregnation should also be tested using different chip sizes.

Another important issue is the influence of extractives, and their solubilisation during kraft pulping, namely in the initial phase, should be studied, also including discrimination by chemical composition. As regards the wood raw material there is a lack of information about the seasonality of extractives in commercial stands of *Eucalyptus globulus* and on their compositional variability.

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