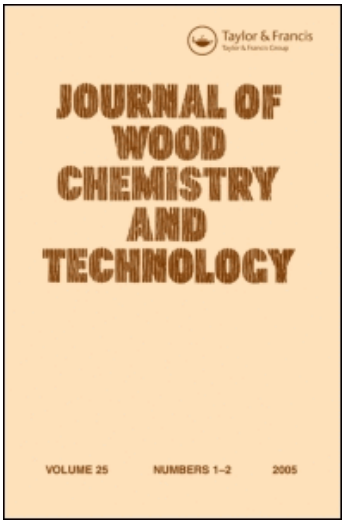

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Pulping Yield and Delignification Kinetics of Heartwood and Sapwood of Maritime Pine

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Abstract: In maritime pine (*Pinus pinaster* Ait.), heartwood represents a substantial part of the tree stem at final harvest age (80 years) corresponding to 42% at the base of the stem wood diameter and decreasing upward. The rate of heartwood formation was estimated at 0.35 rings/year, beginning at 18 years of age. Differences in the chemical composition between heartwood and sapwood were mainly in the extractives, 19.7% and 5.8%, respectively. The lignin content was 23.1% and 24.5% in the heartwood and sapwood, respectively. Pulping yield of the heartwood was lower

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than that of the sapwood (40.0% vs. 49.7%) and was negatively correlated with the extractives content. Extraction of heartwood prior to pulping increased the pulp yield and the delignification (lower residual lignin in pulps). Pulping kinetics showed lower yields for heartwood at all pulping stages, the difference occurring especially in the initial reaction phase. However, delignification rate constants were similar for heartwood and sapwood ($3.1 \times 10^{-2}\,\mathrm{min}^{-1}$ and $2.7 \times 10^{-2}\,\mathrm{min}^{-1}$ for the main delignification phase for sapwood and heartwood, respectively), with a lower activation energy for sapwood (68.3 vs. $90.0\,\mathrm{kJ \cdot mol}^{-1}$). The presence of heartwood decreases the raw-material quality for pulping and this should be taken into account when harvesting trees for pulping processes.

Keywords: *Pinus pinaster* Ait., maritime pine, heartwood, sapwood, extractives, kraft pulp yield, delignification kinetics, activation energy

INTRODUCTION

The formation of heartwood in the inner part of the stem of most tree species is accompanied by the accumulation of extractives and loss of conducting properties. Heartwood is usually characterized by a darker color, and shows the presence of tyloses and the absence of starch and of living cells.[1]

In spite of its importance in wood processing, heartwood is usually not taken into account as a quality parameter in forest management and tree breeding. For many important species little is known about heartwood development and accumulation of extractives, as well as its impact on utilization, for example, pulping. This is the case for maritime pine (*Pinus pinaster* Ait.), an important softwood species in southern Europe, covering approximately 3.4 millions ha in Portugal, Spain, and France. Maritime pine is used for timber and for kraft pulp production, but little is known about the heartwood content of the stems.[2–4]

The effects of heartwood are in direct relation with the accumulation of extractives and their composition.[5] A higher content of extractives increases the consumption of pulping chemicals and reduces the pulp yield. The darker color usually associated with heartwood also decreases pulp brightness and thus, negatively impacts bleaching. The relationship between extractives and heartwood has been examined for *Pinus contorta*[6,7] and *P. echinata.*[8] For *P. banksiana*, Wong et al.[9] investigated the pulping kinetics of extractive-free wood, including determining the average activation energy, and did not find significant differences between the heartwood and sapwood.

The objective of this study was to evaluate the heartwood development and extractive accumulation in maritime pine (*Pinus pinaster* Ait.) and to examine the influence of heartwood and sapwood on kraft pulping yields and on the delignification kinetics.

MATERIAL AND METHODS

Wood Material

Three trees of maritime pine (*Pinus pinaster* Ait.) were harvested at the age of approximately 80 years in the Leiria pine forest, located in the central coastal area of Portugal. Wood discs were taken at different stem heights: at the base, breast height (1.30 m above ground) and at 5%, 15%, 35%, and 65% of total tree height. The trees' heights were 22.9, 22.0, and 21.9 m, and breast heights (b.h.) corresponded to *ca.* 6% of tree height.

The heartwood was clearly visible on the cross section of all wood discs by its darker brown color. The measurements on the wood discs, made on the north and south radial directions, included the determination of the width of heartwood and sapwood and of the corresponding number of annual rings. The heartwood and sapwood fractions were separated on each wood disc with a chisel. The wood samples were milled in a knife mill, sieved, and the 40–60 mesh fractions were kept for chemical analysis and micropulping.

To study the pulping kinetics of heartwood and sapwood, small wood chips (approximately $2 \times 2 \times 5$ mm) were prepared manually with a chisel from each fraction of the breast height disc of the three trees and thoroughly homogenized.

Chemical Composition

The total extractives content was determined by successive Soxhlet extraction using dichloromethane (6 h), ethanol (16 h), and water (16 h). The extractives content was determined gravimetrically after each solvent extraction.

The lignin content was determined on the extractive free samples by FTIR spectroscopy following the methodology developed by Rodrigues et al.[10] for *Eucalyptus globulus.* The samples were dried and milled in a vibratory ball mill (Mixer Mill MNMz, Retsch) for 30 min and dried over P_2O_5. Approximately 1.8 mg of wood meal were mixed with 350 mg KBr, ball milled during 20 s, and used to prepare 13 mm diameter pellets in a standard pellet device. Spectra were recorded using a BIORAD FTS 165 infrared spectrometer with 64 scans per sample and reference pellets of pure KBr prepared for each set of 6–8 wood samples in order to guarantee similarity of recording conditions. The peaks at wave numbers of $1510\,cm^{-1}$ and $1375\,cm^{-1}$ were used for measurement and reference, respectively. The calibration and validation of FTIR data were performed using Klason lignin determination as the reference method ($r^2 = 0.95$).

Micropulping

The heartwood and sapwood samples were separated into two aliquots, one to be pulped directly, and the other to be pulped after extraction (successively with dichloromethane, ethanol and water, as described earlier). Pulping was carried out in 10-mL rotating stainless reactors that were immersed in an oil bath at 170°C, using 1 g of wood previously equilibrated at 23°C and 50% relative humidity for one week. The pulping conditions were as follows: active alkali, 22% (as Na_2O); sulfidity, 10%; liquor-to-wood ratio, 6 : 1; and pulping time, 2 h. After reaction the reactors were cooled in an ice bath. The solids were manually beaten with a glass bar for 30 s, filtered, and thoroughly washed with 500 mL of distilled water. The solids were air-dried overnight at room temperature and further at 103 $\pm$ 3°C. Yields were determined on the basis of the oven-dry mass of wood meal charged to the reactor. The solids were analyzed for kappa number using the microkappa method (TAPPI UM 246) on a 100 mg aliquot, and for Klason lignin content (TAPPI 13 os-54) on a 50 mg aliquot.

Pulping Kinetics

The heartwood and sapwood small wood chips were pulped in 100-mL rotating stainless reactors immersed in a thermostatted oil bath using 10 g samples. The pulping conditions were as follows: active alkali, 19% (as Na_2O); sulfidity, 19%; and liquor-to-wood ratio, 6 : 1. Three pulping temperatures (160, 170, and 180°C) were used and the reaction time at pulping temperature varied from 5 to 150 min. The heating time of the reaction mixture to the pulping temperature was 5 min.

After reaction, the reactors were cooled in an ice bath. The resulting solids were washed with water, disintegrated in a mixer at 7500 rpm, kept in water suspension over night, washed, and filtered on a Buchner funnel. The solids were air dried overnight, and further oven dried at 103 $\pm$ 3°C. Yields were determined on the basis of the oven dry mass of wood chips charged to the reactor. The solids were milled (Retsch SMI) and 300 mg aliquots of the 40–60 mesh fractions were used for Klason lignin determinations (TAPPI 13 os-54). The rate of delignification was described mathematically in each pulping phase by a first order reaction with respect to the lignin remaining in the lignocellulose matrix as follows:

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

where L/L_0 is the fraction of lignin remaining in the solid residue, L_0 the lignin in the initial wood, a_i is the fraction of lignin susceptible to solubilization by the process, and k_i is the corresponding rate constant, with i

representing the reaction phase (i = 1,2,3). The values of a_i were calculated from the L/L_0 values for the beginning and the end of the corresponding i phase. In each reaction phase, a plot of residual lignin as ln L/L_0 versus time gave a straight line with the slope representing the value of k_i (min^{-1}).

The activation energy of the delignification was determined using the Arrhenius equation. With k_i as the rate constant for phase i, E_{ai} the activation energy ($kJ \cdot mol^{-1}$), R the gas constant ($8.314\,kJ \cdot K^{-1} \cdot mol^{-1}$) and T the absolute temperature (K), a plot of $\ln(k_i)$ versus $1/T$ was a straight line with the slope equal to E_{ai}/R.

RESULTS AND DISCUSSION

Heartwood Content

Heartwood was present in all the samples taken at all stem height levels. It showed a rich brown color, clearly distinguishable from the light and yellowish brown sapwood. The heartwood diameter decreased regularly along the stem from base upward (Figure 1), whereas the width of sapwood remained constant within the tree at approximately 10 cm. In proportion of total diameter, heartwood represented 42% at the base and 22% at the 65% height level.

The development of heartwood in the maritime pine trees followed the decreasing pattern from base upward previously found for this species[2–4,11] as well as for other pine species, for example, *P. contorta*,[12] *P. banksiana*,[13] *P. radiata*,[14] *P. sylvestris*,[15] and *P. canariensis.*[16]

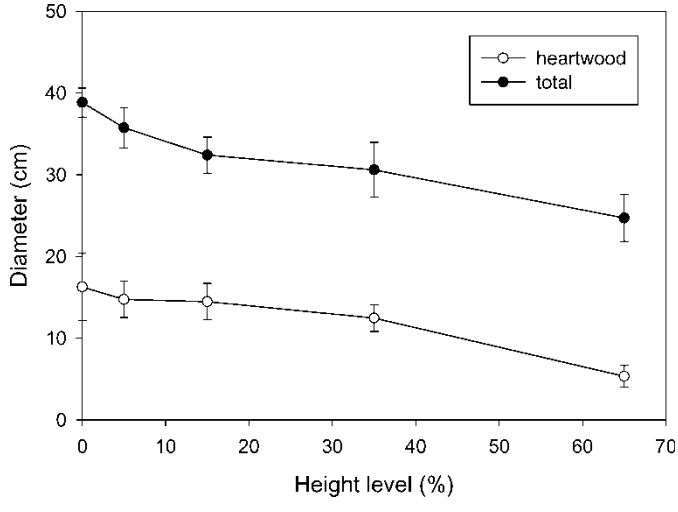

Figure 1. Variation of the total diameter and the heartwood diameter along the stem of the maritime pine trees. The points are the mean values with the standard deviation indicated.

The maximum number of annual rings in the heartwood was found at the stem base, between 16 and 25, and decreased along the stem to 4 to 7 rings at the uppermost level that was studied (Figure 2) where the total number of rings was 32 to 36. The average rate of heartwood formation was calculated as 0.35 ring/year. Plotting the number of heartwood rings as a function of cambial age, as given by the total number of rings at each height level, and fitting the data to a linear model ($y = -5.60 + 0.32x$; $r^2 = 0.75$) allowed us to estimate the age of heartwood initiation at 18 years. Heartwood is reported to be formed at a nearly constant annual ring rate after a certain initial age, which in pines has been estimated between 15 and 25 years for *P. sylvestris*[15,17] and 30 years for *P. canariensis.*[16]The results obtained in the present study are in agreement with the values estimated for the heartwood initiation age of maritime pine of 13 and 21 years.[2,11]

Maritime pine trees with ages below 30 years will contain only a limited amount of heartwood, therefore not having a significant effect on the pulping quality. This is usually the case when thinning and cutting pine trees for pulpwood. However, trees will develop substantial amounts of heartwood content with age and the evaluation of older trees as pulping material should take this fact into account.

Chemical Composition

The extractives and lignin content of the heartwood and sapwood of the maritime pine are given in Table 1. Heartwood contained more extractives than sapwood:

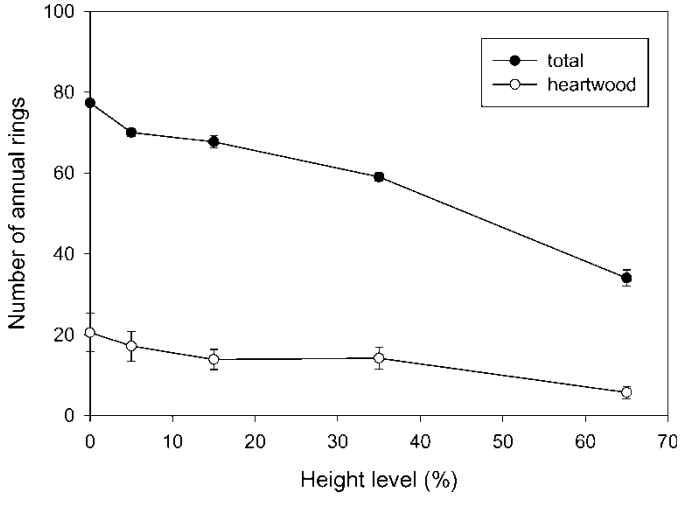

Figure 2. Variation of the number of annual rings in the cross section and in the heartwood along the stem of the maritime pine trees. The points are the mean values with the standard deviation indicated.

Table 1. Extractives and lignin in heartwood and sapwood of maritime pine. Mean of 18 samples with the standard deviations in parentheses

	Heartwood	Sapwood
Extractives, % wood		
Total	19.7 (7.9)	5.8 (2.4)
Dichloromethane	4.1 (5.3)	1.6 (1.2)
Ethanol	2.6 (2.7)	1.1 (0.4)
Water	13.0 (2.5)	3.0 (1.2)
Lignin, % wood	23.1 (1.4)	24.5 (0.4)
Lignin, % extractive-free wood	28.7 (1.2)	26.7 (0.9)

on average total extractives corresponded to 5.8% of sapwood and 19.7% of heartwood. Water soluble extractives were a relatively higher proportion in heartwood, for example, 66% and 52% of the total extractives, respectively, in heartwood and sapwood. Similar differences between sapwood and heartwood have been found in other pine species, that is, *P. echinata*[8]and *P. contorta.*[6] Values for total extractives ranged from 1.9 to 2.2% and from 10 to 12% in sapwood and heartwood, respectively, of *Pinus contorta.*[7]

The heartwood contained less lignin than the sapwood (23.1% and 24.5% in relation to wood) but the differences between the two fractions were not statistically significant. Some contradictory results are found in the literature regarding the lignin content in heartwood and sapwood. For *P. contorta*, Campbell et al.[6] also reported no differences between sapwood and heartwood, whereas for *P. taeda* higher lignin contentwas found in heartwood by Ritteer and Fleack.[18]

It is noteworthy that lignin content calculated relative to extractive-free wood is higher in heartwood than in sapwood (28.7% vs. 26.7%, Table 1). It is known that in general lignin content varies radially in the tree with higher values in the juvenile innermost region.[19] This agrees with the values found here of higher lignin content in heartwood, because heartwood corresponds to the inner part of the wood cross section. Therefore the fact that the lignin content of heartwood was slightly lower than that of sapwood when expressed in percent of total wood mass (Table 1) is the result of a higher amount of extractives in heartwood in relation to sapwood (nearly 4 times more extractives). This could explain the sometimes contradictory results for lignin content in heartwood and sapwood referred to in the literature.

Pulp Yield and Residual Lignin

Table 2 shows the average kraft pulp yield, residual lignin, and kappa number of pulps obtained from extracted and unextracted samples of maritime pine heartwood and sapwood. The pulp yield obtained with sapwood was higher than with heartwood both for extracted and unextracted samples. The difference between heartwood and sapwood pulp yields was larger for the

Table 2. Pulp yield, residual lignin, and kappa number for kraft pulping of heartwood and sapwood of maritime pine. Mean of 18 samples with the standard deviations in parentheses

	Pulp yield % of wood	Residual klason lignin, % pulp	Kappa number
Heartwood	40.0 (2.4)	4.2 (1.5)	37.2 (4.5)
Sapwood	49.7 (3.0)	4.4 (1.5)	38.0 (3.8)
Extracted heartwood	44.8 (1.9)	2.5 (0.5)	19.4 (1.7)
Extracted sapwood	48.5 (2.1)	2.6 (0.5)	21.1 (1.6)

unextracted samples: 40.0% vs. 49.7% for the unextracted samples and 44.8% vs. 48.5% for the extracted samples, respectively.

Removal of the extractives had opposite effects on the mean pulp yield for heartwood and sapwood. For heartwood the yield obtained with extracted material averaged 4.8% more than with unextracted material, the difference being statistically very significant ($p < 0.001$). For sapwood the pulp yield obtained with the unextracted material was higher by 1.2% in relation to the extracted material, the difference being statistically significant ($p = 0.023$). When comparing the ratios of pulp yields obtained from extracted and unextracted wood, mean values of 1.12 (± 0.01) and 0.98 (± 0.08) were obtained for heartwood and sapwood, respectively.

Pulp yield correlated negatively with the extractives content ($y = 53.12 - 0.67x$; $r^2 = 0.796$; $P < 0.001$) (Figure 3). These results are in

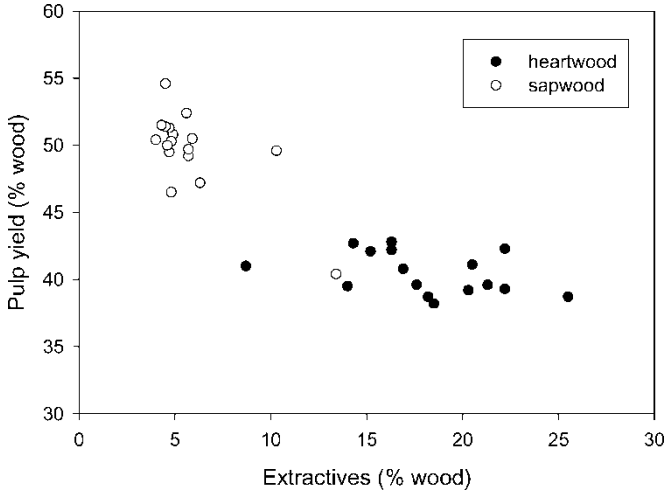

Figure 3. Variation of pulp yield with the extractives content in sapwood and heartwood of maritime pine.

agreement with the negative influence of heartwood extractives on pulp yields. For eucalypts extractives have been considered as the main parameter to define pulp yield[20] and good correlations between water extractives and pulp yield were obtained for *E. globulus*,[21] *E. camaldulensis*,[22] and *E. grandis*. [23]

The presence of extractives also lowered the extent of delignification and less residual lignin was found in the pulps obtained with extracted material (e.g., 2.5% and 4.4% residual lignin in extracted and unextracted sapwood, respectively). However, this influence was not directly related to the absolute extractive content because differences could not be found between the delignification degree of unextracted heartwood and sapwood pulps (residual lignin of 4.2% and 4.4%, respectively). The increased removal of lignin should be the result of the solvent extraction and the treatment temperature (i.e., 100°C for water extraction) that act as a pre-treatment for lignin removal in the subsequent pulping.

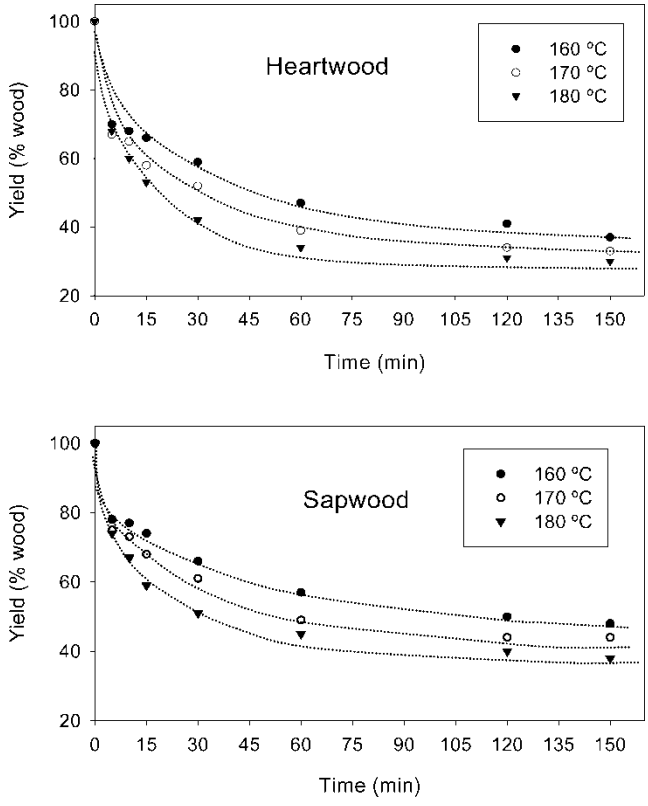

Figure 4. Pulp yield versus time for kraft pulping of maritime pine heartwood and sapwood at 160, 170, and 180°C.

Pulping and Delignification Kinetics

The variation in yield with pulping time at the three temperatures is given in Figure 4 for the sapwood and heartwood of maritime pine. The kinetic curves of heartwood and sapwood displayed similar patterns with a three-stage process: a rapid initial phase, corresponding to approximately 5 min pulping time, with a high mass loss (yields of 67% and 75%, respectively, for sapwood and heartwood were obtained at 170°C after 5 min); a second phase when most of the mass losses occurred corresponding to approximately 60 min pulping time (39% for heartwood and 49% for sapwood at 170°C); and a final stage where the mass loss proceeded at a slower rate.

In comparison to sapwood, pulping yields of heartwood were lower for the same reaction time and temperature, for example, 33% yield was obtained after 150 min at 170°C from heartwood, as compared to 44% from the sapwood fraction. The yield difference was mainly the consequence of the relatively higher mass loss of heartwood in the initial pulping phase.

The kinetics of delignification were studied by following the amounts of lignin removed from the wood during pulping and were analyzed on the basis of the proportion of the total lignin removed with time (Table 3). Lignin solubilization occurred at a faster rate for the higher temperatures almost to complete removal, that is, 98% with 160 min pulping at 170°C and 180°C. Roughly one third of the lignin was removed in the initial phase of pulping. Final delignification values at each temperature were the same for heartwood and sapwood. Wong et al.[9] also found a negligible difference in lignin solubilization between sapwood and heartwood in *Pinus banksiana*. However, differences between heartwood and sapwood occurred in the initial phase for 160°C and 170°C with a lower lignin solubilization in heartwood, for example, after 5 min at 170°C, 27% lignin was removed from heartwood and 37% from sapwood.

Table 3. Lignin solubilization (% of initial lignin) during kraft pulping of heartwood and sapwood of maritime pine at 160, 170, and 180°C

	Heartwood			Sapwood		
Time (min)	160°C	170°C	180°C	160°C	170°C	180°C
5	23.7	26.9	33.9	30.1	36.6	33.2
10	27.4	35.0	42.5	33.8	38.1	44.8
15	31.8	43.5	53.5	37.4	48.5	66.1
30	47.2	52.7	76.6	48.7	56.4	89.3
60	71.8	86.3	93.7	68.9	83.9	95.1
120	86.7	96.6	98.0	87.0	95.2	97.0
160	91.4	97.9	98.4	91.1	97.1	98.7

Previous studies on delignification kinetics have considered two (or three) simultaneous first order processes with different reaction rates corresponding to different fractions of lignin that are solubilized at different rates: one easily soluble and the other with more difficulty.[24–27] A similar pattern was found in this study for heartwood and sapwood kraft pulping, with two successive delignification phases after an initial stage corresponding to a main delignification stage and a final delignification stage. The plots of the adjusted logarithmic residual lignin content against time indicated first-order processes and the parameters k_i (estimated value for the rate constant) were calculated by linear regression (Table 4).

The increase in the delignification rate constant with temperature was moderate for the main delignification phase (by a factor of 2.3 and 3.2 between 160 and 180°C for sapwood and heartwood, respectively) and smaller for the final delignification, especially for sapwood where no consistent effect of temperature on the k_2 rate constant was found. The delignification rate in the main phase was higher than in the final phase but only by a factor of 1.3 to 2.0, except for sapwood at 180°C where the difference was much larger. This is not what typically happens with other wood species that may show large differences between the rate constants of the main and final delignification phases, for instance, for *Eucalyptus globulus* the delignification in the final stage proceeds at a rate approximately one-tenth of the main phase.[28] This may be explained by a more homogeneous chemical composition of maritime pine lignin, partly derived from its predominantly guaiacylic monomeric composition (90 to 96% G units).

There were no large differences in the delignification rate constants obtained for heartwood and sapwood (Table 4). The fact that the kinetics of lignin solubilization in heartwood and sapwood of maritime pine were similar suggests that the differences in pulp yields obtained from heartwood

Table 4. Reaction rate constants for the main (k_1) and final (k_2) delignification phases and the respective fractions of solubilized lignin for kraft pulping of heartwood and sapwood of maritime pine

		Sapwood		Heartwood	
		a_1	k_1	a_1	k_1
Main phase	160°C	0.48	0.0195	0.39	0.0160
	170°C	0.59	0.0306	0.47	0.0271
	180°C	0.60	0.0446	0.62	0.0514
		a_2	k_2	a_2	k_2
Final phase	160°C	0.20	0.0148	0.22	0.0127
	170°C	0.11	0.0157	0.13	0.0164
	180°C	0.05	0.0085	0.04	0.0274

and sapwood are explained by solubilization of other components, that is, the extractives.

The activation energy for the main delignification phase was $90.0\,kJ \cdot mol^{-1}$ ($r^2 = 0.988$) and $68.3\,kJ \cdot mol^{-1}$ ($r^2 = 0.997$) for heartwood and sapwood, respectively. The activation energies found in this study are in the range of reported values for other species, but only one reference could be found in the literature comparing heartwood and sapwood. Wong et al.[9] reported values between 85.2 and $92.0\,kJ \cdot mol^{-1}$ for sapwood and between 89.6 and $90.6\,kJ \cdot mol^{-1}$ for heartwood of *Pinus banksiana*. Most of the values published refer to mixed wood chips: $80\,kJ \cdot mol^{-1}$and $101\,kJ \cdot mol^{-1}$ for spruce wood,[29,30] $125.0\,kJ \cdot mol^{-1}$ for southern pine,[31] $143.6\,kJ \cdot mol^{-1}$ for the hemp woody core,[32] $129\,kJ \cdot mol^{-1}$ for western hemlock,[25] 143.1 $kJ \cdot mol^{-1}$ for *Populus trichocarpa*,[27]and $83.5\,kJ \cdot mol^{-1}$ for *Eucalyptus globulus*.[28]

Overall, heartwood in maritime pine showed poorer chemical and pulping properties than sapwood (i.e., higher content of extractives, lower pulp yield) and the extent of its presence should be carefully monitored in pulpwood raw-material procurement.

CONCLUSIONS

In maritime pine, heartwood represented a substantial part of the tree stem at the final harvest age and showed an extensive accumulation of extractives. In pulping, heartwood had lower yields in comparison to sapwood during all the pulping stages and especially in the initial phase, but the final delignification of heartwood and sapwood was similar. The pulping differences of heartwood and sapwood were related to the presence of extractives. The presence of heartwood decreases the raw-material quality for pulping and this should be taken into account when harvesting trees for pulpwood.

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