Modeling and Optimization of *Eucalyptus globulus* Bark and Wood Delignification using Response Surface Methodology

Duarte M. Neiva,* Jorge Gominho, and Helena Pereira

Statistical models and optimization of *Eucalyptus globulus* Labill. wood and bark delignification were achieved using response surface methodology (RSM). A central composite design was outlined to model the simultaneous influence of active alkali (*AA*), reaction temperature (*T*), and reaction time (*t*) on pulp yield (η) and kappa number (*k*) during the kraft pulping of wood and bark. Experimental results were fitted to a second-order polynomial with linear interaction of factors. The statistical models showed high coefficients of determination for both wood (R^2_η = 0.991, R^2_k = 0.975) and bark (R^2_η = 0.993, R^2_k = 0.984). Using these models, the optimum conditions to attain a pulp with the highest yield at an acceptable kappa number (below 17) were determined. For wood, the pulp yield was 51.6% (51.5% predicted) and the kappa number was 16.1 (16.9 predicted) under optimized conditions (*AA* = 21%, *T* = 151 ºC, and *t* = 118 min). For bark, the pulp yield was 51.3% (51.0% predicted) and the kappa number was 19.4 (16.9 predicted) under optimized conditions (*AA* = 15%, *T* = 166 ºC, and *t* = 114 min). The degree of polymerization (DP) of the carbohydrates for the optimized pulps, 1430 and 1151 for wood and bark, respectively, suggests low levels of polysaccharide degradation. The bark delignification showed similar behavior to wood.

Keywords: Response surface methodology (RSM); Eucalyptus globulus; Bark; Wood; Delignification; Kraft pulping

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INTRODUCTION

Shortage of raw material is an important issue for the pulping industries in some regions due to the worldwide increasing demand for and price of wood. In Europe, for example, the industry continues to rely on 20% imported pulpwood (UNECE/FAO, 2011/12). Wood cost is the largest contributor to total pulp production cost, ranging between 55 and 70% (ForestIndustry.com). Studies have examined alternative or complementary raw material sources, either by focusing on new lignocellulosic species or by using residual materials, which are rich in fibers that have similar characteristics to wood (Gominho *et al*. 2001; Jiménez *et al*. 2005; Khiari *et al*. 2010; Miranda *et al*. 2012).

Eucalyptus globulus bark appears to be a good candidate due to its chemical similarity to wood (Pereira 1988) and high average fiber proportion, as well as availability, as it accounts for 7 to 20% of the stem's dry weight (Pereira *et al*. 2010). Regarding the main cell types, *E. globulus* bark has 22 to 39% fiber cells as opposed to an average of 61% for the stem wood (Pereira *et al*. 2010). An advantage of utilizing bark is the fact that this material is already at the industrial site where log debarking takes place. Currently, bark is mostly burned as fuel in steam boilers to generate electricity and energy, but this biomass residue has been the focus of recent studies within the biorefinery concept. For instance, in the EU research project that supports this manuscript (AFORE), bark was studied as a source of high-value compounds previous to pulping or burning (Domingues *et al.* 2011; Santos *et al.* 2012).

In the 1960s and 1970s, a whole-tree utilization concept led to an increase in research on the use of bark in pulp and paper production (Foelkel *et al*. 1977; Brito *et al*. 1978). These studies suggested that bark increased the demand for chemicals in the delignification and bleaching steps and produced a pulp with low quality. However, even with those detrimental effects, the addition of low amounts of bark (normally below 10%) would have economic benefits to the industries in periods of short pulpwood supply.

Presently, less attention has been given to the potential of bark for pulp production. Miranda *et al*. (2012) studied the incorporation of bark and tops into the wood pulping of *E. globulus*. The authors pulped different percentages of bark (5 to 15%) with the wood and achieved yields of 52 to 56.8% with kappa numbers of 18 to 20.

Despite the abundant literature regarding the kraft pulping of *E. globulus* wood and bark, there have been few mathematical modeling or optimization investigations to relate the principal process variables with the quality of the resulting pulp. Nevertheless, optimization studies have been done for other species and other delignification processes (Gominho *et al*. 2001; Vanderghem *et al*. 2012; Dong and Fricke 1996; Gilarranz *et al*. 1998; Ligero *et al*. 2008).

In this work, we used response surface methodology (RSM) to model the delignification process variables for both wood and industrial bark. Response surface methodology is one of the most common optimization methods employed in chemical and biochemical processes (Bas and Boyaci 2007), mostly because it enables the analysis of the effects of multiple independent variables simultaneously while requiring a small number of experiments. Specifically, the delignification process variables of active alkali concentration (*AA*), reaction temperature (*T*), and time (*t*) were analyzed for their effects on pulp yield and kappa number.

EXPERIMENTAL

Sampling

Wood chips and industrial bark of *Eucalyptus globulus* were obtained from the Portucel Soporcel Group pulp mill (Setúbal, Portugal). The bark was previously sifted with a 6-mm sieve to remove undesired material (soil and dirt), and both materials were fractionated using a knife mill, screened to a size ranging between 2 and 10 mm, and homogenized into single lots to avoid substantial differences in composition. The wood chips had an average dimension of 8 mm x 3 mm x 2 mm. The industrial bark, which comprised bark and trace amounts of wood from the debarking process, had a smaller average dimension.

Chemical Analysis

Wood and bark samples from the homogenized lots were milled and screened to a 40- to 60-mesh particle size range.

The ash content of the samples was determined by TAPPI standard method T15 os-58. The extractives in the samples were obtained by utilizing a Soxhlet apparatus that used dichloromethane, ethanol, and water solvent extractions in succession; each extraction lasted 16 h. The extraction thimbles containing the samples were oven dried and weighed between each extraction to gravimetrically obtain the corresponding extractive content.

The holocellulose content of the extractive-free samples was determined using the modified chlorite method (Rowell 2005).

Prior to measuring the lignin content, the extractive-free material was treated with 1% NaOH for 1 h followed by hot water washing until reaching neutral pH, as described elsewhere (Mendes *et al*. 2013), to remove tannins and other polyphenols. The insoluble (Klason) and soluble lignin content of the extractive-free and tannin-free samples were determined according to TAPPI standard methods T222 om-88 and UM 250 om-83, respectively.

The monosaccharide composition was determined based on the neutral sugars monomers present in the hydrolysate from the insoluble lignin analysis, after their derivatization to alditol acetates and separation by gas chromatography, according to a method adapted from TAPPI standard 249 cm-00.

All analyses were performed in duplicate and reported as the average percentage of the original oven-dried samples, except for the monosaccharides composition results, which were reported as percentage of total sugars.

Pre-treatment

Pre-treatment of the wood and bark was conducted with water in a stainless steel batch reactor with fluid recirculation (*ca.* 4 L) and a liquid to oven-dry solid ratio of 20/1. The heating time to temperature (140 °C) was set to 45 min, and the isothermal period was set to 45 min. At the end of the pre-treatment, the liquid was discarded and the solid was thoroughly washed, oven dried, weighed, and properly stored.

The hydrolysate was analyzed in an Aminex HPX-87H HPLC column to determine the carbohydrates composition.

Pulping

Kraft pulping was conducted under isothermal conditions in small (*ca.* 100 mL) stainless steel digesters, rotated in a mineral oil bath with temperature control. The white liquors were prepared with reagent grade NaOH (98%) and Na_2S (>90%). The cooking conditions were: 5 g of oven dry material load; liquor-to-solid ratio of 10:1; 25% sulfidity (as Na_2O); and 5 min heating time to temperature. The high liquor-to-solid ratio used when compared to industrial standards (*i.e.*, 4:1) was due to the high hydration capacity of the bark, which would prevent the total impregnation of the solid sample (Foelkel *et al*. 1977).

The process variables were active alkali (*AA*) as Na_2O (12 to 28%), reaction temperature (143 to 177 ºC), and reaction time (40 to 140 min). At the end of the cooking, the digesters were removed from the oil bath and cooled in ice. The solid residue was washed with 200 mL of hot water and defibrated in a laboratory blender. The resulting pulp was separated from the solution by vacuum filtration and further washed until neutral pH was obtained.

Pulp Characterization

Delignification yield was calculated after weighing the oven-dry pulp and reported as a percentage of the original oven-dry samples prior to the pre-treatment.

The kappa number of the pulp was determined according to TAPPI Useful Test Method UM 246 with one additional step in the procedure. The pulps were milled in a centrifugal mill to dimensions below 0.15 mm to ensure the complete oxidation reaction of lignin during the kappa number test.

The degree of polymerization of the pulps was determined using cupriethylenediamine (CED), as described in SCAN-CM 15:88 test method.

Statistical Experimental Design and Model Development

Response surface methodology (RSM) was used to define and determine the relationships between process (*i.e.*, independent) variables of active alkali ($15\% < AA < 25\%$), reaction temperature ($150\ °C < T < 170\ °C$), and reaction time ($60\ \text{min} < t < 120\ \text{min}$) to the response (*i.e.*, dependent) variables of pulp yield (yield) and kappa number (kappa).

A central composite circumscribed design was chosen since it provides high quality predictions over the entire design space, while requiring few experimental points. This design uses $2n$ factorial points that estimates the linear and interaction terms, $2n$ axial (or star) points that estimates the quadratic terms and four center points that, besides providing an internal estimate of error, also estimate the quadratic terms. The n term represents the number of independent variables.

Because the process variables have different range intervals and units, normalization is required prior to implementing the statistical design. Equation (1) was used to normalize the parameters:

$$X = \frac{x_i - \bar{x}}{(x_{max} - x_{min})/2} \tag{1}$$

where X is the normalized parameter, x_i is the natural value, $\overline{x}$ is the average value in the considered interval, and $x_{\max}$ and $x_{\min}$ are its limits. For the axial points, the distance to the center of the design was $\alpha = 1.682$ due to the rotatability property conferred by it, meaning that the precision of the predicted response at any given point is equal to all points equidistant from the coded origin of the design.

Experimental results were fitted to a second order polynomial equation using multiple regression analysis through the least square method. The result was a model that can be written as follows:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j \tag{2}$$

where Y is the predicted response, X_i and X_j the coded independent variables, and β_0, β_i, β_{ii}, and β_{ij} are the regression coefficients for intercept, linear, quadratic, and interaction terms, respectively. The statistical significance of the overall model and coefficients was determined by analysis of variance. Experimental design and statistical analysis were performed with Statistica® 6.0 (StatSoft, USA) and all figures were done with Matlab® R2011a (MathWorks, USA).

RESULTS AND DISCUSSION

Chemical Composition

The chemical compositions of the wood and bark samples are shown in Table 1. The ash content of bark was 1.96%, which is lower than some previously reported values for *Eucalyptus globulus*, *e.g.*, 4.7% (Vázquez *et al*. 2008) and 4.9% (Yadav *et al*. 2002), but similar to other reported values, *e.g.*, 2.9% (Miranda *et al*. 2012) and 2.3% (Mota *et al*. 2012, Pereira 1988). The wood had nearly five times less ash (0.42%) than bark, which is in agreement with published results (Queiroz 1973; Pereira and Sardinha 1984). Bark contains more total extractives than wood (6.02% *vs*. 4.36%), mainly water-soluble compounds (3.02% *vs*. 1.65%). Wood had a higher content of Klason and soluble lignin than bark, which is corroborated by previous research reports (Miranda *et al*. 2012; Pereira 1988). The 1% NaOH treatment used to remove the tannins prior to the lignin measurement allows a more accurate determination of the lignin content, as explained by Mendes *et al.* (2013). In fact, tannins tend to precipitate during the acidic treatment and be accounted for as Klason lignin.

The total amount of polysaccharides (determined as holocellulose) for both materials were almost identical (around 74%). Similar values of cellulose plus pentosans for *E. globulus* wood and bark were reported in the literature: respectively 78.6% and 79.7% (Miranda *et al.* 2012) and 72.9% and 67.1% (Pereira 1988). Table 2 shows the carbohydrate composition for the wood and bark; although very similar, the bark has a lower content of xylose, a main constituent of the hemicelluloses, and a slightly higher content of glucose.

Table 1. Chemical Composition of *Eucalyptus globulus* Wood and Bark Industrial Chips as Percentage of Oven-Dried Material

	Wood	**Bark**
Ash	**0.42**	**1.96**
Total Extractives	**4.36**	**6.02**
Dichloromethane	0.78	1.20
Ethanol	1.93	1.80
Water	1.65	3.02
Total lignin	**21.36**	**18.53**
Klason lignin	17.04	14.97
Soluble lignin	4.32	3.56
Holocellulose	**74.52**	**74.21**

Table 2. Carbohydrate Composition of *Eucalyptus globulus* Wood and Bark Industrial Chips as Percentage of Total Sugars

	Wood (%)	**Bark (%)**
Arabinose	0.9	1.2
Xylose	20.0	17.4
Mannose	1.8	1.6
Galactose	2.1	2.3
Glucose	75.2	77.5

Pre-treatment

The hydrothermal pre-treatment removed 4.09% and 7.23% from wood and from bark, respectively, on an oven-dry mass basis. This procedure was performed to wash away the debris and contaminants, mostly from the industrial bark, and also to reduce part of the extractives in the samples because they have a detrimental effect on both response variables (pulp yield and kappa number) (Lourenço *et al.* 2010; Higgins 1984). The low temperature and reaction time were chosen to prevent the degradation and removal of hemicelluloses and cellulose from the fibers (Duarte *et al.* 2012; Garrote *et al.* 2003). The removal of hemicelluloses (determined as solubilized xylose, arabinose and acetic acid) was 4.5% and 6.0% of the total hemicelluloses in the wood and bark, respectively, while the glucose in the hydrolysate was 0.4% and 0.5% of the total amount of glucose determined for wood and bark, respectively.

Experimental Design Analysis and Model Fitting

The effect of active alkali (*AA*, 15 to 25%), reaction temperature (*T*, 150 to 170 °C), and reaction time (*t*, 60 to 120 min) on pulp yield and kappa number for wood and bark of *E. globulus* were investigated using a central composite design. The conditions used and the factors range intervals were chosen in order to contain the average industrial conditions for *E. globulus* wood pulping. All pulp yield results were reported as percentage of the initial oven dry material prior to the pre-treatment.

The experimental design, factors, and obtained responses are shown in Table 3. It is worthwhile to mention that the values used for the variables selected for the models correspond to points located in the second and third phases of the kraft pulping, *i.e.* the bulk and residual periods of pulping.

Table 3. Experimental Design with Natural and Coded Factor Variables, and Dependent Variables Response for Wood and Bark Delignification

	Run	Natural Variables			Coded Variables			Wood		Bark	
		AA (%)	*T* (°C)	*t* (min.)	*AA* (%)	*T* (°C)	*t* (min.)	Yield (%)	kappa	Yield (%)	kappa
Factorial runs 2^3	1	15	150	60	-1	-1	-1	58.2	51.1	59.3	63.4
	2	15	150	120	-1	-1	+1	54.3	31.2	56.5	44.7
	3	15	170	60	-1	+1	-1	51.9	16.7	51.3	18.5
	4	15	170	120	-1	+1	+1	49.7	12.7	50.2	11.0
	5	25	150	60	+1	-1	-1	52.0	25.8	54.8	52.0
	6	25	150	120	+1	-1	+1	51.1	14.2	52.1	37.4
	7	25	170	60	+1	+1	-1	47.8	10.6	47.8	20.0
	8	25	170	120	+1	+1	+1	46.6	8.8	45.0	11.0
Axial runs	9	12	160	90	$-\alpha$	0	0	55.8	43.4	55.3	42.0
	10	28	160	90	$+\alpha$	0	0	48.0	10.7	47.9	22.9
	11	20	143	90	0	$-\alpha$	0	55.6	41.5	57.5	67.1
	12	20	177	90	0	$+\alpha$	0	46.8	10.4	47.5	10.9
	13	20	160	40	0	0	$-\alpha$	52.4	24.7	53.7	45.2
	14	20	160	140	0	0	$+\alpha$	49.5	12.0	49.5	15.7
Center runs	15(C)	20	160	90	0	0	0	50.3	12.5	50.4	26.1
	16(C)	20	160	90	0	0	0	50.8	12.1	50.6	23.8
	17(C)	20	160	90	0	0	0	50.6	12.9	50.7	25.1
	18(C)	20	160	90	0	0	0	49.6	12.9	50.5	25.3

The minimum and maximum yields for wood and bark were, respectively, 47 to 58% and 45 to 59%, with kappa numbers ranging 9 to 51 and 11 to 63, respectively. These values suggest a larger variance in both parameters for the bark. The values for wood are in agreement with Carvalho *et al.* (2000), who reported ranges of 48.0 to 64.4% for yield and 7 to 70 for kappa number, under similar cooking conditions. In a study of bark suitability for kraft pulping, Miranda *et al.* (2012) reported a pulp yield of 47.2% with kappa number of 36.1.

The experimental data were used to estimate the coefficients of the second order polynomial equations (Eqs. 3 to 6), the corresponding coefficients of determination (R^2), and adjusted coefficients of determination (Adj R^2), where X_1 is the active alkali, X_2 is the reaction temperature, and X_3 is the reaction time:

$$\begin{aligned} Yield_{Wood} &= 226.78 - 2.53X_1 + 0.023X_1^2 - 1.42X_2 + 0.0031X_2^2 - 0.249X_3 + 0.0003X_3^2 - 0.0056X_1X_2 \\ &+ 0.0033X_1X_3 + 0.0007X_2X_3 \end{aligned} \tag{3}$$

R^2=0.991 ; Adj R^2=0.980

$$\begin{aligned} Yield_{Bark} &= 314.95 - 0.971X_1 + 0.0163X_1^2 - 2.66X_2 + 0.0071X_2^2 - 0.2004X_3 + 0.0004X_3^2 \\ &- 0.0013X_1X_3 + 0.0007X_2X_3 \end{aligned} \tag{4}$$

R^2=0.993 ; Adj R^2=0.986

$$\begin{aligned} Kappa_{Wood} &= 1752.59 - 22.41X_1 + 0.178X_1^2 - 16.447X_2 + 0.04X_2^2 - 2.31X_3 + 0.002X_3^2 + 0.081X_1X_2 \\ &+ 0.009X_1X_3 + 0.011X_2X_3 \end{aligned} \tag{5}$$

R^2=0.975 ; Adj R^2=0.948

$$\begin{aligned} Kappa_{Bark} &= 1778.525 - 12.266X_1 + 0.085X_1^2 - 17.532X_2 + 0.044X_2^2 - 1.651X_3 + 0.002X_3^2 \\ &+ 0.051X_1X_2 + 0.007X_2X_3 \end{aligned} \tag{6}$$

R^2=0.984 ; Adj R^2=0.969

The coefficient and adjusted coefficient of determination were above 0.94 for all models, indicating a strong correlation between the predictors and the response variables. Interpretation of R^2 should, however, be done with caution since a large value does not necessarily imply that the regression model accurately describes the relationship between the predictors and the responses. Figure 1 shows the experimental results plotted against the model results, with the points aligned around the 45° line, thus suggesting that the model defines the true behavior of the system and that the model can be used for interpolation (Myers and Montgomery 1995).

These plots showed that most of the wood pulps obtained had kappa numbers below 17, while there were only four bark pulps that fell below 17 kappa, which suggested that bark needs more intense pulping conditions than wood to reach the same delignification level.

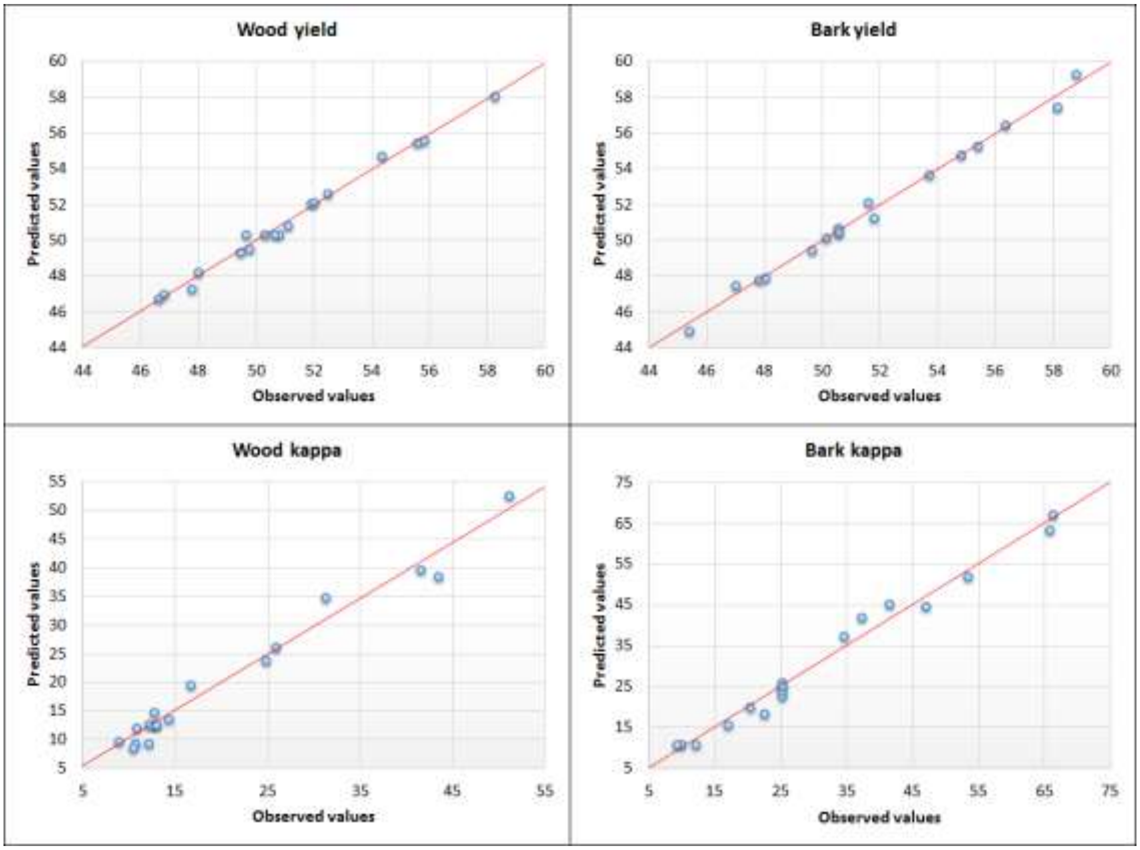

Fig. 1. Observed *vs.* predicted values of pulp yield and kappa number for wood and bark

Figure 2 shows the Pareto charts of standardized effects. In all the models, temperature was the most relevant factor. This implies that temperature was the key parameter in the pulping process, at least within the interval in which this experiment took place. This finding is not surprising, given that during the bulk phase the rate of delignification is chemically controlled, as opposed to the initial phase, which is mostly diffusion-controlled (Gierer 1980). The effects of temperature in batch kraft cooking were studied by Jain and Mortha (2008), who reported increases in the delignification rate by two to three-fold per 10 ºC increase in reaction temperature. Isabel and Pereira (2002) reported, for *E. globulus* wood kraft pulping, that the proportion of lignin removed in the bulk phase ranged from 66% to 74%, with an increase of temperature from 170 ºC to 180 ºC, respectively.

Coefficients for the interaction terms *AA*/*T* and *AA*/*t* were non-significant at the 95% confidence level for bark yield (Eq. 4) and bark kappa number (Eq. 6), respectively, and therefore were discarded. For most coefficients, the respective *p*-value statistic was below 0.05 (right side of the vertical line), although a few have higher *p*-values, such as the quadratic time term and *AA*/*t* interaction term. Normally, these exceptions would be discarded from the equations but they were kept since their inclusion increased the value of the Adj R^2.

The pulp yield and kappa number were inversely affected by all the process variables – active alkalinity, reaction time and temperature - indicating that increasing any of these independent variables would result in a decrease in yield or kappa number.

The quadratic terms of the variables were all positive, indicating that the predictor variables interact with themselves following a U-shaped function. On the other hand, the paired-variables interaction terms ranged between positive and negative values, *e.g.* the temperature-time interaction was positive, but the sign of the interactions involving alkalinity varied. Although their underlying chemical justification was not found in the literature, these interaction terms were statistically significant and were maintained in the models.

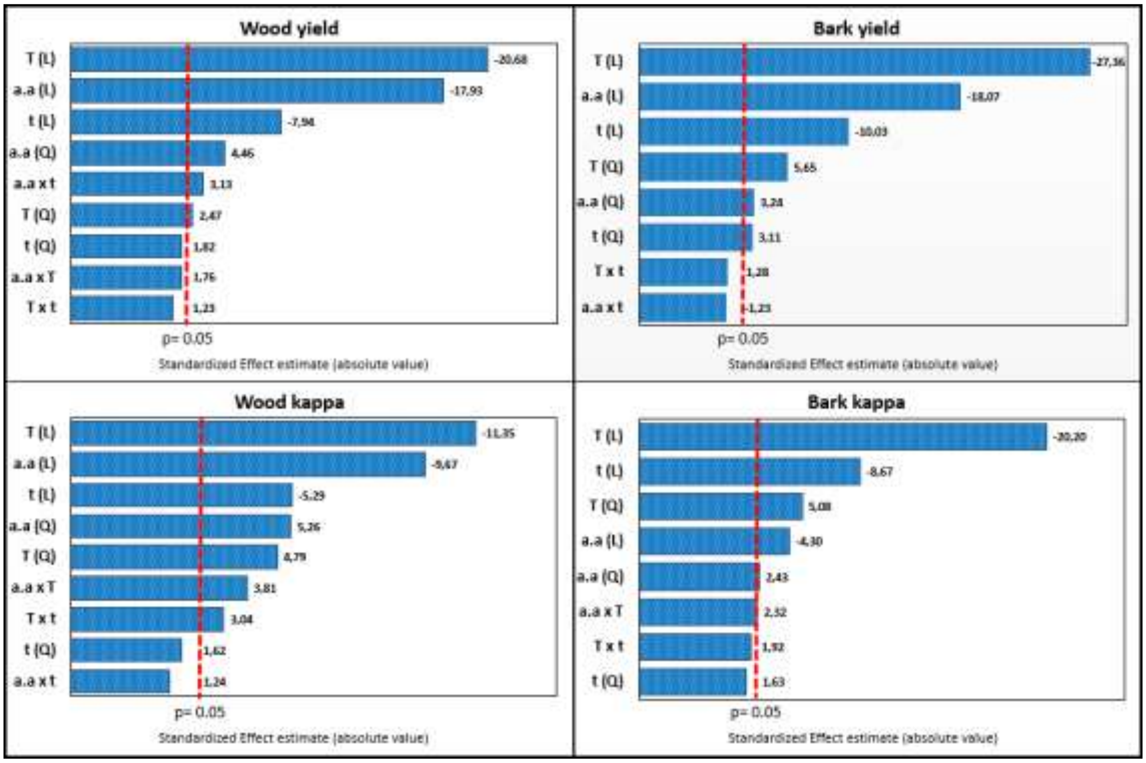

Fig. 2. Pareto charts of standardized effects of pulp yield and kappa number for wood and bark

Response Surface

Figures 3 and 4 show the response surfaces obtained from Eqs. 3 to 6, while fixing active alkali at three distinct points (*AA* = 15%, 20%, and 25%). The response surfaces correspond mainly to the bulk phase of the pulping and to the beginning of the residual phase for the more intense reaction conditions. At the harsher cooking conditions the kappa number decrease started to slow down, while the yield continued to decrease at a considerable rate. Under such conditions, the selectivity of lignin reaction decreased, while the attack on the carbohydrates continued.

The bulk phase of pulping is where most of the lignin is removed, while carbohydrate degradation continues but at a lower rate than during the initial phase. The residual phase is characterized by slow delignification, increased carbohydrate degradation, and increased consumption of alkali (Gustafson *et al.* 1983). In a study of *E. globulus* wood, Miranda and Pereira (2002) found that the rate of delignification is approximately 10 times slower in the residual phase than in the bulk phase.

Pulp yield response surfaces (Fig. 3) showed similarities for both wood and bark, varying between 58.1 to 46.7% and 58.8 to 45.4%, respectively. Because the quadratic terms were all positive (Eqs. 3 and 4), the concavity of the surfaces is turned up, meaning that the variation of the yield will decrease when increasing the factors. For example, the variation in yield for wood was -3.3% between *T* = 150 ºC and *T* = 160 ºC (*AA* = 15%, *t* =

60 min) and -2.7% between T = 160 ºC and T = 170 ºC (AA = 15%, t = 60 min). For bark, these values corresponded to -4.8 and -2.8%, respectively. Changes in yield were more pronounced for lower values of all factors. Considering the same intervals of temperature, but at higher active alkali and time (AA = 25%, t = 120 min), the same applied and the variation was -2.4% and -1.7%, and -3.8% and -2.4% for wood and bark, respectively. For the remaining factors, the same behavior was observed.

A comparison of wood and bark plots suggested that for wood, AA has a higher impact at lower temperature and shorter time, contrary to bark, where the higher impact occurred at higher temperature and longer time.

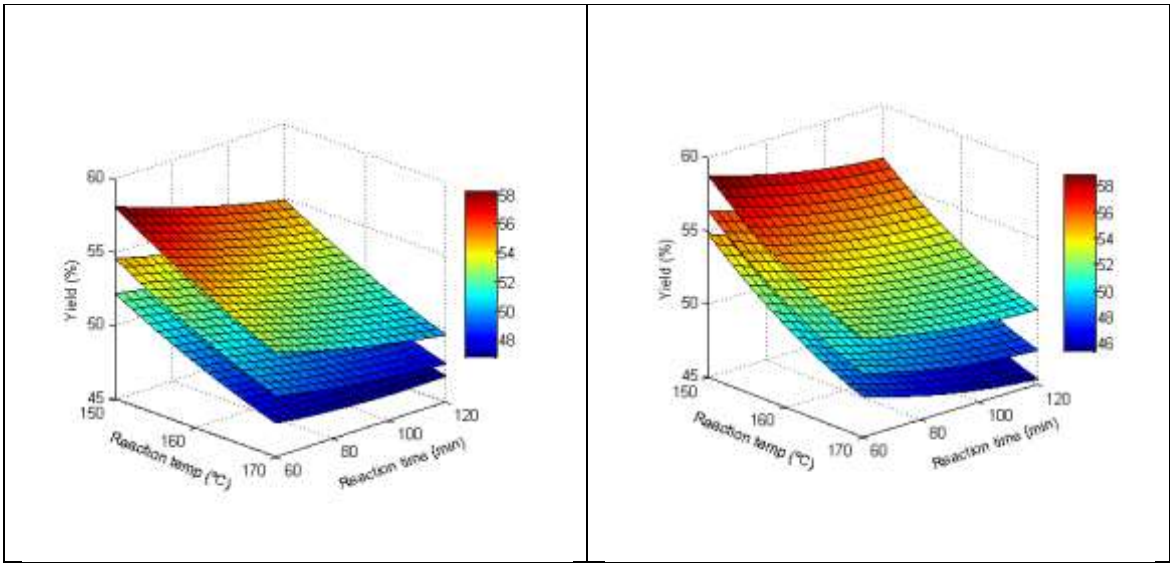

Fig. 3. Response surfaces for wood (left) and bark (right) yield, as a function of reaction temperature, reaction time and active alkali. Surfaces from top to bottom correspond to AA = 15%, 20%, and 25%, respectively.

Pulp kappa number response surfaces (Fig. 4) showed that the behavior of wood and bark is somewhat different, varying between 52.6 to 7.9 and 65.6 to 8.9, respectively. The kappa number for the bark pulps was highly dependent on the variation of temperature, leading to a response surface with a sharp slope, and showing a much lower amount of pulp delignification at lower temperatures and shorter time than wood. One possible explanation is that the activation energy for the delignification of bark is higher than that for wood, although there are no studies in bark kinetics to support this. On the other hand, the influence of active alkali on kappa number appeared to be much lower for bark, showing its highest variation (-12) at the milder temperatures and shorter times. The corresponding variation of active alkali for wood at the same conditions produces a variation of -26.

For wood, active alkali plays an important role in the variation of kappa at shorter times and lower temperature conditions; as these factors increase, the variation becomes smaller, especially above 20% active alkali. According to Júnior and Almeida (2004), active alkali higher than 20% had little influence on the decreasing of kappa number of the ensuing pulp.

Regarding reaction time, the results show that its influence on kappa number for both wood and bark was almost the same at the lowest temperature and active alkali, which was approximately -18 kappa units (Δt = 60 min). This value remained constant when increasing the active alkali for bark (since the interaction term *AA*/*t* was discarded from Eq. 6) and diminished slightly for wood (-12 at *AA* = 25%). When the reaction temperature was higher, the influence of increasing time decreased, having no apparent influence for wood at the maximum temperature. Dong and Fricke (1996) showed for slash pine that cooking times above 70 min between 160 and 180 ºC had little impact on the pulp's kappa number. These results show that at higher temperature and alkalinity the delignification of wood already reached the residual phase with the shortest reaction time tested.

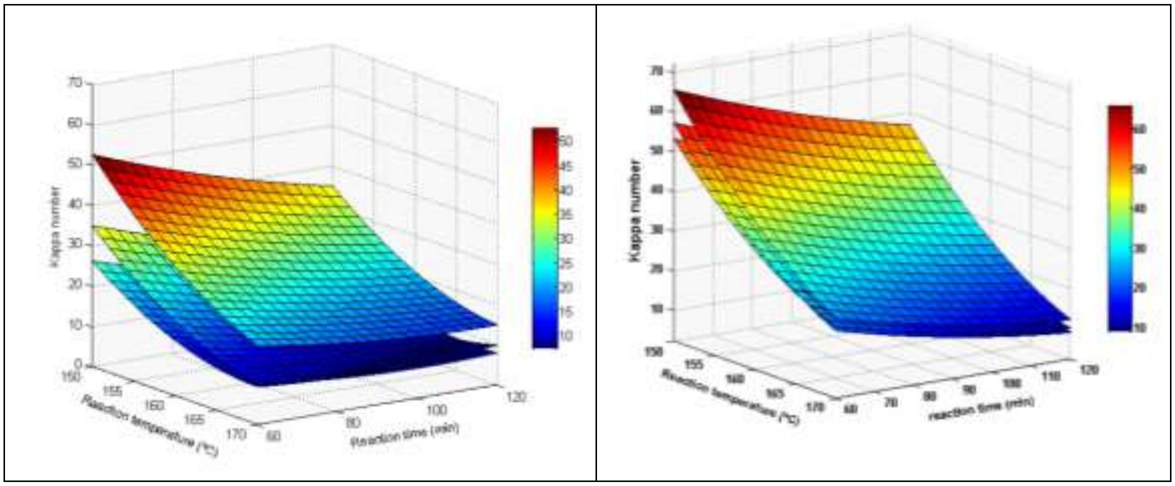

Fig. 4. Response surfaces for wood (left) and bark (right) kappa number, as a function of reaction temperature, reaction time and active alkali. Surfaces from top to bottom correspond to *AA* = 15%, 20%, and 25%, respectively.

Optimization of the Parameters

The optimization of the pulping parameters to achieve the maximum yield with the minimum kappa proved to be unfeasible because both response variables monotonically decreased for the chosen factors intervals. This suggested that for a maximum yield, the respective kappa was also at a maximum, resulting in partially cooked pulp, whereas the minimum pulp yield was obtained at the lowest kappa number.

A decision was made to impose a constraint with the kappa number (*i.e.*, 16 to 17) to obtain a pulp similar to those industrially produced. Results from the optimization within these boundaries are presented in Table 4. After the determination of the optimized factors, wood and bark were pulped in triplicate experiments to determine the real predictability of the model.

Table 4. Optimized Parameters and Experimental Results at Parameter Values

	Factor values			**Experimental**			**With Model**	
	AA (%)	T (°C)	t (min)	Yield (%)	kappa	DP	Yield (%)	kappa
Wood	21	151	118	51.5±0.3	16.1±0.2	5155±254	51.6	16.9
Bark	15	166	114	51.3±0.4	19.4±0.1	3995±188	51.0	16.9

The models showed that for the same kappa number, the best yield was similar for wood and bark, although the yield was slightly lower for bark (51.0 *vs*. 51.6%). The conditions at which wood and bark achieved their maximum pulp yield were, however, different, regarding active alkali and temperature, but the reaction times were similar.

The experimental results for wood bark pulp yield appeared to be consistent with the model, while the bark experimental kappa number was higher than that determined with the model. The present results suggested that *E. globulus* bark is suitable for pulp production, though additional analyses are required to determine its characteristics for paper production. Extrapolations should also be carried with caution since the models are only valid within the specific kraft laboratory conditions used to construct them.

The selectivity of kraft pulping is determined by the amount of polysaccharide degradation versus delignification (Sixta 2006). The amount of polysaccharide degradation was assessed for both wood and bark optimized pulps through the degree of polymerization (DP), which was calculated from the pulps intrinsic viscosity. The wood and bark pulps had DP values of 5155 and 3995, respectively. The higher DP values of the wood pulp suggested less cellulose degradation, which can possibly be explained by the lower pulping temperature in comparison with the bark.

CONCLUSIONS

1. *Eucalyptus globulus* Labill. wood and bark are similar in their structural chemical components; however, bark contains higher levels of ash and extractives, which are detrimental for pulping.
2. Statistical modeling, which employed response surface methodology (RSM), identified that pulping temperature was the most relevant factor for the delignification of wood and bark; the active alkali level had a lower influence on bark delignification than that observed for wood.
3. RSM was used to define the optimum set of reaction conditions for maximum yield at a given kappa number. Experimental results corroborated the predictions derived from the mathematical models.
4. Overall, the results from this study suggested that *E. globulus* bark can be delignified to produce pulps similar to wood chips with respect to pulp yield and kappa number. The pulping conditions for bark should be specifically adjusted and are not the same as those for wood.

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