Effect of pulping conditions in uronic and hexenuronic acids concentration in kraft pulps of *Eucalyptus globulus*

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Abstract

Hexenuronic acids (HexA) are formed during kraft pulping from the 4-O-methylglucuronic acid (GlcA) present in the xylans of the hemicellulose. The HexA affected the kappa number determination, reacted with some electrophilic bleaching chemicals, increasing their consumption and decreasing brightness stability of bleached pulps. In this work, different kraft pulping conditions: active alkali 15% and 20%, H-factor 200 - 2500 h and cooking temperature 155ºC and 165ºC, were evaluated to determine the effect in uronic and hexenuronic acids amount in kraft pulps from *E. globulus* planted in Chile. The amount of GlcA in *E. globulus* wood was 5.1% and its removal from wood chips varied between 30% and 60% during cooking. A signifficant influence of temperature and active alkali concentration on HexA formation in *E. globulus* kraft pulps was observed. For H-factor higher than 500, the HexA content is higher at 155ºC in pulps produced with 15% and 20 % AA than at 165ºC for the same alkali concentrations. For cookings with 15% of AA, the amount of HexA in pulps increases with the increase of the H-factor and for cookings with 20% AA, the amount of HexA decreases for an H-factor higher than 550. The maximal concentration of HexA observed was 73 mmol/kg pulp for cookings with 15% AA, 155ºC and H-factor 930. The minimal HexA value was 25 mmol/kg pulp for cookings with 20% AA, 165ºC and H-factor 2300. The results obtained in the present work showed that the contribution of the HexA to the kappa number varied from 5% to 60% and it is more signifficative in pulps with low residual lignin amount.

Keywords: *Eucalyptus globulus*, hexenuronic and uronic acids, kraft pulping.

Resumo

Os ácidos hexenurônicos (HexA) são formados durante a polpação kraft a partir do ácido 4-O-metil glucurônico (GlcA) presente nas xilanas da hemicelulose. Os HexA afetam a determinação do número kappa, reacionam com alguns reactivos eletrofílicos utilizados no branqueamento, aumentando seu consumo e diminuindo a estabilidade da alvura das polpas branqueadas. Neste trabalho, diferentes condições de polpação kraft: álcali ativo 15% e 20%, fator H 200 - 2500 h e temperatura de cozimento 155ºC e 165ºC, foram avaliadas para determinar o efeito no conteúdo de ácidos urônicos e hexenurônicos em polpas kraft de *E. globulus* plantado no Chile. A quantidade de GlcA na madeira de *E. globulus* foi de 5.1% e sua remoção dos cavacos de madeira variou entre 30% e 60% durante o cozimento. Uma influência significativa da temperatura e da concentração de álcali ativo foi observada na formação de HexA nas polpas kraft de *E. globulus*. Para fatores H maiores que 500, o teor de HexA é maior a 155ºC para polpas produzidas com 15% e 20% AA do que a 165ºC para as mesmas concentrações de álcali. Para cozimentos com 15% de AA a quantidade de HexA nas polpas aumenta com o aumento do fator H e para cozimentos com 20% de AA, a quantidade de HexA decresce para fatores H maiores a 550. A concentração máxima de HexA observada foi de 73 mmol/kg polpa para cozimentos com 15% AA, 155ºC e fator H de 930. O valor mínimo de HexA foi de 25 mmol/kg polpa para cozimentos com 20% AA, 165ºC e fator H de 2300. Os resultados obtidos no presente trabalho mostram que a contribuição dos HexA no número kappa varia entre 5% e 60% e é mais significativa em polpas com baixo conteúdo de lignina residual.

Keywords: *Eucalyptus globulus*, ácidos hexenurônicos e urônicos, polpação kraft.

Introduction

Eucalyptus spp. is an important raw material used for the production of writing and printing papers and, specifically *E. globulus*, represents the main source of short fibre for the pulp and paper industry of Chile. The kraft pulping process is the most widely used for the industrial production of chemical pulps (Gullichsen and Fogelholm, 1999) corresponding to approximately 80% of the worldwide production of cellulosic pulp (Ferris and Ragauskas, 2000). During kraft pulping, hexenuronic acids (HexA) are formed from the 4-O-methylglucuronic acid (GlcA) of the xylan chains of the hemicellulose (Chai et al., 2001a). The presence of these acids affects the kappa number determination causing an overestimation of the residual lignin in pulp, had negative effect in the bleaching and in the brightness stability (Chai et al., 2001a,b; Simão et al., 2005; Jiang et al., 2001). For this reason the study of formation and elimination HexA has been of fundamental importance in pulp production plants. HexA formation is more pronounced in hardwoods than in softwoods due to the high amount of glucuronoxylans in the hemicellulose composition of hardwoods (Biermann, 1993). The formation/degradation of HexA during pulping is affected by the several cooking conditions, as hydroxyl ion concentration, pulping time and temperature (Vourinen et al., 1999; Chai et al., 2001b,c). Pedroso and Carvalho (2003) and Simão et al. (2005) described that the temperature and alkali charge have strong influence in the evolution of HexA content in *Eucalyptus globulus* pulps than the sulfidity. In this work, different kraft pulping conditions were evaluated to determine the effect of these conditions in uronic acids degradation and hexenuronic acids formation during kraft pulping of *E. globulus* planted in Chile.

Experimental

Kraft pulping

E. globulus kraft pulps were produced by cooking industrial size wood chips in a 1000-mL Parr reactor. Each cooking was carried out with 50 g of wood chips (dry basis) and 250 mL of cooking liquor which composition was 15% or 20% of active alkali and 25% of sulfidity (expressed in NaOH equivalents). The reactor was heated at 1.6ºC/min until the pulping temperature of 155ºC or 165ºC. Cooking time was varied from 30 to 180 min with the objective to achieve different H-factors (200 - 2500 h) and pulps with different amounts of residual lignin and hexenuronic acids. After cooking, the pulp was disintegrated in a TAPPI laboratory blender, thoroughly washed with tap water and centrifuged. Total pulp yield was determined based on the weight of the pulp divided by the weight of the wood chips (both in dry basis) multiplied by 100%. Kappa number of pulps was determined following the standard procedure described in TAPPI test method T-236 om-99.

Chemical composition of wood

Approximately 1.5 g of milled wood samples (in triplicate) was extracted in a Soxhlet with ethanol/toluene 1:2 for 8 h, washed with ethanol and re-extracted with ethanol 95% for another 8 h in a Soxhlet apparatus. Extracted wood samples or kraft pulps were hydrolyzed with 72% (w/w) sulfuric acid at 30ºC for 1 h (300 mg of sample and 3 mL of acid). The acid was diluted to a final concentration of 3% (w/w) with the addition of 79 mL of water, and the mixture was autoclaved at 121ºC for 1 h. The residual material was cooled and filtered through porous glass filter n^{o} 3. Solids were dried at 105ºC until constant weight and determined as insoluble lignin. Soluble lignin concentration in the aqueous fraction was determined by measuring the absorbance at 205 nm and using the value of 105 L/g.cm as the absorptivity of soluble lignin. Total lignin was the sum of soluble and insoluble lignin. The concentrations of monomeric sugars in the soluble fraction were determined by HPLC using a BIORAD HPX-87H column at 45ºC, eluted at 0.6 mL/min with 5 mol/L sulfuric acid.

Glucuronic acids were quantified in the wood and pulps hydrolizates by using the colorimetric method proposed by Blumenkrantz and Asboe-Hansen (1973) and using galacturonic acid as standard. One mL of the acid hydrolyzate was added to a test tube immersed in ice with 6 mL of a solution containing 0.0125 mol/L sodium tetraborate in concentrated sulfuric acid. The tube was shaken in vortex and placed in a water bath at 100ºC for 15 min. The hydrolyzate was cooled in cold water with ice. After cooling, 200 μL of m-hydroxydiphenyl solution (0.15% in 0,5% NaOH) was added in the tube and after 5 min of reaction, the absorbance was read at 520 nm. For the blank solution, the m-hydroxydiphenyl was replaced by 200 μL of 0.5% NaOH.

Hexenuronic acid quantification

Hexenuronic acid content in pulps was quantified by the colorimetric method using dual-wave UV spectrophotometry analysis as proposed by Chai et al. (2001a). Approximately 0.05 g of air-dried pulp

with known moisture content was weighed and placed in a 20 mL vial containing 10 mL of the hydrolysis solution (0.6% of mercuric chloride and 0.7% of sodium acetate). The sealed vial was hand shaken for mixing and then heated at 65ºC in a water bath for 45 min. The solution was cooled to the room temperature, filtered by a nitrocellulose filter with 0.22 µm pore and the UV absorption of the solution was measured in a 10 mm path length silica cell at two wavelengths, 260 nm and 290 nm. The same fresh hydrolysis solution was used as the blank in UV absorption measurements. The HexA content in pulp was calculated using the dual-wavelength formula (Equation 1), where C_{HexA} is the content of hexeneuronic acid groups in pulp (mmol/kg); 0.287 is the calibration factor for the method; A_{260} and A_{290} are the measured absorption intensities at 260 nm and 290 nm, respectively; 1.2 is the relationship between the lignin absorption at the two wavelengths; V is the volume of the hydrolysis solution (mL) and w is the oven-dried weight of the pulp sample (g).

$$C_{HexA}(mmol/kgpulp) = 0.287\frac{(A_{260nm} - 1.2A_{290nm})V}{w} \quad (1)$$

Results and Discusion

Figure 1 and 2 shows the total pulping yield and kappa number, respectively, for *E. globulus* kraft pulps produced with two different active alkali concentrations (15% and 20%) and temperature (155ºC and 165ºC) in a wide range of H-factors (200 - 2500 h). For cookings with 15% AA the pulp yield varied from 58% to 51%, and kappa number from 32 to 12, while for cookings with 20% AA the pulp yield was from 64% to 46% and the kappa number from 62 to 9.

The amount of glucuronic acids (GlcA) in *E. globulus* wood was 5.1%, a similar value to that reported by Simão et al. (2005). During the kraft pulping process the amount of GlucA in pulps is influenced for both, alkali charge and temperature (Figure 3). The GlcA removal from wood chips varied between 30 and 60%, remaining in the pulps an amount of 3% to 3.6% (on wood basis) at 155ºC and 2% to 3.2% (on wood basis) at 165ºC. The dissolution of low molar mass xylan, the cleavage of glycosidic bonds between xylose and methyl glucuronic acid units and the formation of HexA are the reasons commonly pointed out to explain the GlcA decrease in pulps (Simão et al., 2005).

A signifficant influence of temperature and active alkali concentration on HexA formation in *E. globulus* kraft pulps was observed (Figure 4). For H-factor higher than 500, the HexA content is higher at 155ºC for 15% and 20 % of AA than at 165ºC. For cookings with 15% of AA the amount of HexA in pulps increases with the increase of the H-factor. For cookings with 20% AA the amount of HexA decreases for an H-factor higher than 550, indicating that the degradation of the HexA is higher than its formation. The maximal value of HexA concentration observed was 73 mmol/kg pulp for cookings carried out with 15% AA, 155ºC and H-factor 930. The minimal HexA value was 25 mmol/kg pulp for a cooking at 20% AA, 165ºC and H-factor 2300. These results were in agreement with the previously published by Daniel et al. (2003), that reported the influence of alkali charge on the HexA content in kraft pulps for *E. globulus* from Portugal. The authors showed that HexA amount increases for active alkali concentrations between 14% and 17% and decreases for concentrations from 17% to 24% AA (the maximal concentration evaluated). Simão et al. (2005) also described that the temperature and the alkali charge had strong influence on the HexA content in *E. globulus* kraft pulps and that sulfidity has none or little effect. Both authors reported that for AA concentrations higher than 20% the HexA concentration in pulps decreases with the increase of the cooking time and temperature.

Figure 5 shows that HexA increases with the decrease of the kappa number for pulpings with 15% and 20% of AA at 155ºC and 15% of AA at 165ºC. Nevertheless, for reactions with 20% of AA and carried out at 165ºC the HexA content decreases when the kappa number is lower than 10. However, in an industrial kraft cooking the kappa number of eucalyptus pulping is around 15 - 18, reaching low values only after a O_2 delignification or bleaching step. In this case, a pulp with kappa number of 15 presents between 50 to 65 mmol of HexA/kg of pulp, that can be considered a high concentration of HexA.

As mentioned before, the importance of the study of HexA formation and degradation during kraft pulping is based on the contribution of these acids in the determination of kappa number by the reaction with potassium permanganate, causing an overestimation of the real amount of the residual lignin on pulp. Buchert et al (1996), Li and Gellesterdt (1998) reported that HexA could contribute until 50% of the kappa number of kraft pulps from Northern Scandinavian woods. Chai et al (2001b) informed that the HexA contribution in kappa number for hardwood pulps is less than 10% for pulps with kappa number higher than 40, nevertheless this contribution can be until 70% in pulps with kappa number around 10. In order to verify how much of the HexA concentration represents the kappa

number in pulps obtained in this work, we applied a correction factor as proposed by Vourinen et al. (1999). According to the linear correlation found by these authors, the contribution of 10 meq HexA/kg of pulp correspond to 1.05 units of kappa. From the results obtained in the present work and based the estimation proposed, the contribution of the HexA varied from 5% to 60% to the kappa number of the kraft pulps. This contribution is more signifficant at low kappa numbers, wich are the normally necessary for the production of bleached pulps. For example, in the range of kappa number 15 - 20 the HexA represents 40% - 60% of the kappa number, while for a kappa 30, the HexA represents 20% of the kappa number.

According to the results obtained, low amount of HexA in *E. globulus* kraft pulps was obtained only in pulps produced at high severe conditions (high alkali charge, high temperature and high H-factor). Despite low kappa numbers were also obtained in these conditions, the pulp yield was also low, that is a drawback for a process carried out in these conditions. This study has contributed to provide more useful information about the effects of pulping conditions on the evolution of the GlucA and HexA during kraft pulping of *E. globulus*.

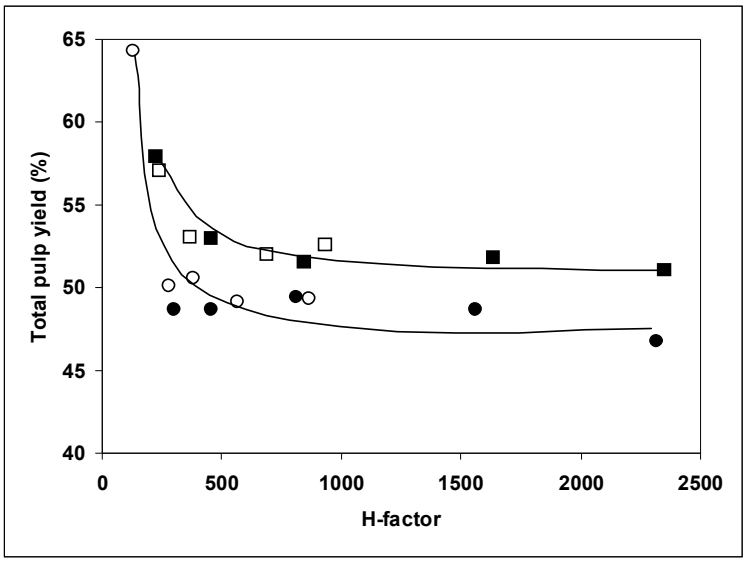

Figure 1. Total pulp yield of *E. globulus* kraft pulps obtained under different cooking conditions, 15% AA/155ºC (white squares), 15% AA/165ºC (black squares), 20% AA/155ºC (white circles) and 20% AA/165ºC (black circles).

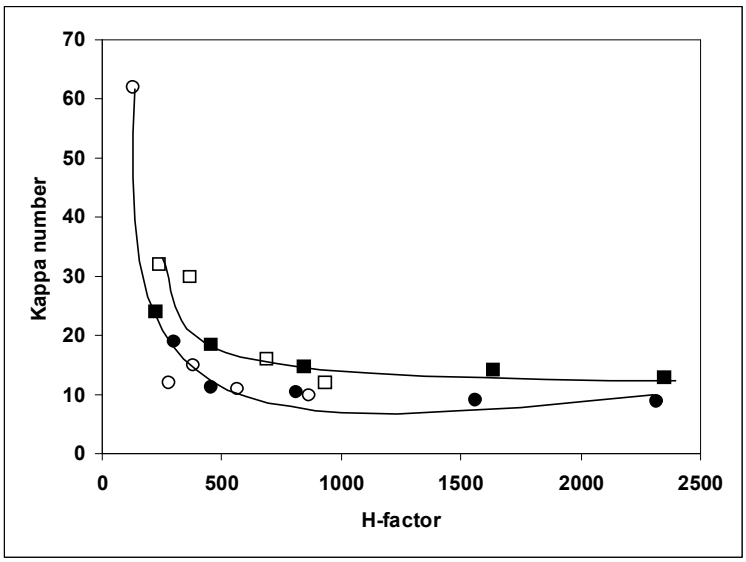

Figure 2. Kappa number of *E. globulus* kraft pulps obtained under different cooking conditions, 15% AA/155ºC (white squares), 15% AA/165ºC (black squares), 20% AA/155ºC (white circles) and 20% AA/165ºC (black circles).

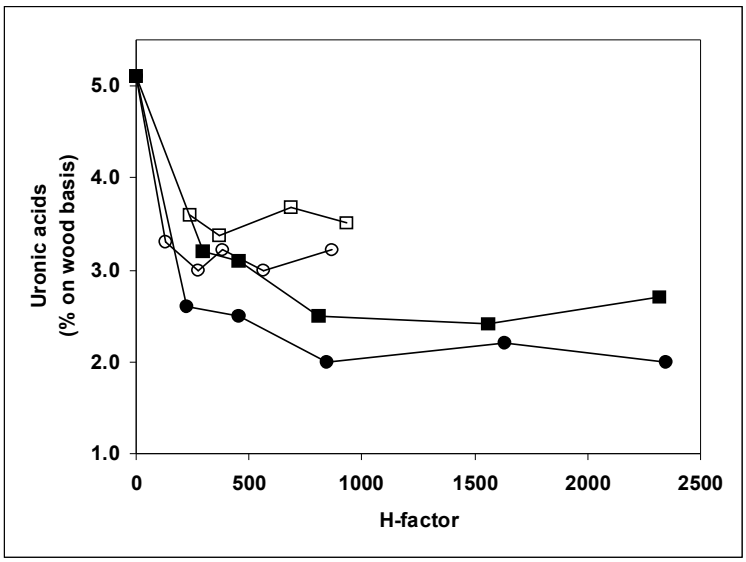

Figure 3. Uronic acids amount in *E. globulus* kraft pulps obtained under different cooking conditions, 15% AA/155ºC (white squares), 15% AA/165ºC (black squares), 20% AA/155ºC (white circles) and 20% AA/165ºC (black circles).

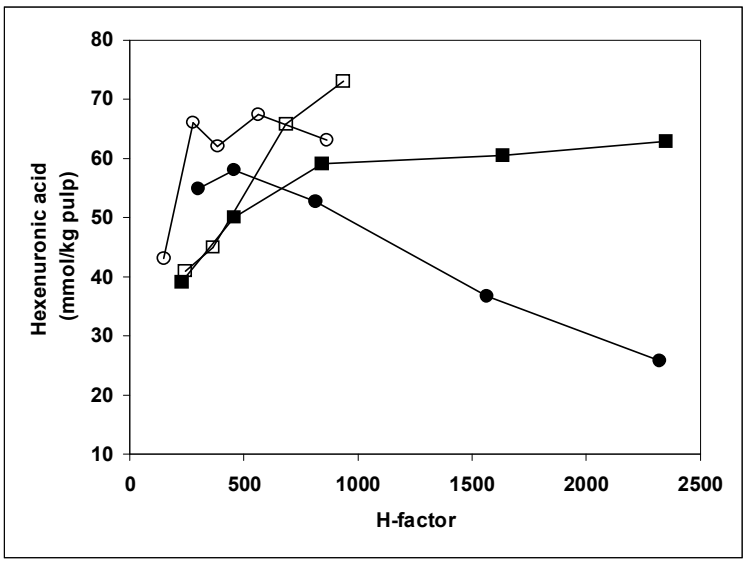

Figure 4. Hexenuronic acids amount in *E. globulus* kraft pulps obtained under different cooking conditions, 15% AA/155ºC (white squares), 15% AA/165ºC (black squares), 20% AA/155ºC (white circles) and 20% AA/165ºC (black circles).

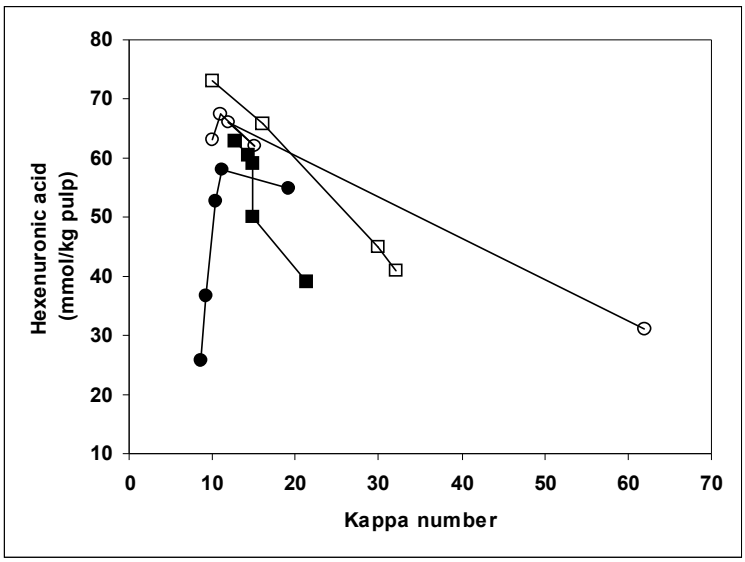

Figure 5. Hexenuronic acids amount in *E. globulus* kraft pulps with different kappa numbers and obtained under different cooking conditions, 15% AA/155ºC (white squares), 15% AA/165ºC (black squares), 20% AA/155ºC (white circles) and 20% AA/165ºC (black circles).

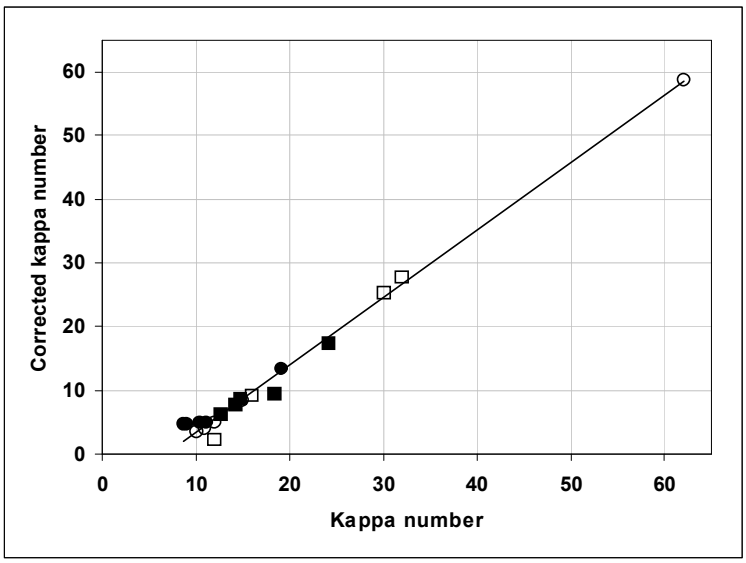

Figure 6. Kappa number of *E. globulus* kraft pulps vs corrected kappa number in *E. globulus* kraft pulps obtained under different cooking conditions, 15% AA/155ºC (white squares), 15% AA/165ºC (black squares), 20% AA/155ºC (white circles) and 20% AA/165ºC (black circles). Corrected kappa number calculated according to Vuorinen et al. (1999): 10 meq HexA/kg pulp = 1.05 units of kappa number.

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