Effect of Modified Cooking on Bleachability of *Eucalyptus globulus* and *Eucalyptus nitens*

Rudine Antes* and Olli P. Joutsimo

This work evaluates the effect of SuperBatch™ (SB), CompactCooking™ (CC), and Lo-Solids™ (LS) modified cooking concepts on pulp bleachability of *Eucalyptus globulus* and *Eucalyptus nitens*. *E. globulus* wood samples presented higher amounts of cellulose and *E. nitens* higher amounts of hemicellulose and acetone extractives. The same trend was observed in brownstock and in fully-bleached pulps. *E. globulus* wood sample presented lower amounts of lignin and higher S/G ratio than *E. nitens.* In the brownstock pulps, the amount of Hexenuronic Acids (HexA) and total lignin for *E. globulus* and *E. nitens* did not present significant difference variation in the contribution to kappa number 17±0.5. No significant differences were found in intrinsic viscosity among modified cooking methods in unbleached and in fully-bleached pulps. For both species, the CC produced pulps with the highest hemicelluloses content after cooking to the fully-bleached pulp. In this work, one cannot observe differences in bleachability of *E. globulus* and *E. nitens* caused by different modified cooking concepts.

Keywords: Pulping; Bleaching; Bleachability; Modified cooking; Hardwood; Eucalyptus globulus; Eucalyptus nitens; Kraft cooking; SuperBatch; CompactCooking; Lo-Solids

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INTRODUCTION

Printing, writing, and tissue paper grade pulps are made from fully-bleached fibers. Bleaching represents an important fraction of the manufacturing cost of these pulps (Martino *et al.* 2013). Several studies on bleachability of *Eucalyptus* pulps aimed to these grades have been published (Gustavsson *et al*. 1999; Pascoal Neto *et al*. 2000; 2002; Jiang *et al*. 2003; Colodette *et al*. 2007; Costa and Colodette 2007; Pedrazzi *et al*. 2010). The term 'bleachability' is defined in terms of the ease of bleaching pulp containing a given amount of residual lignin to a given target brightness. According to this definition, bleachability is the combined result of the ease with which the bulk of the residual lignin can be removed in the early stages of the sequence and the susceptibility of the last traces to removal or decolorization in the last stages (McDonough *et al.* 1997). It is useful to elaborate on this definition by subdividing the bleachability into at least two components. According to McDonough (1996), this is because chemical pulp bleaching sequences can be regarded as combinations of a delignifying partial sequence [the D_0 and (E_1) stage] and a brightening partial sequence [the D_1, E_2, and D_2 stages]. The industrial process to convert wood into bleached cellulosic fibers often involves two parts: first, the removal of 92 to 95% of lignin from wood with pulping liquor composed essentially of sodium hydroxide and sodium sulfide (Sjostrom 1993). The second part may use a variety of chemical compounds such as chlorine dioxide, ozone, and hydrogen peroxide. Alternatively, the bleaching can be carried out without chlorine-based chemicals using a totally chlorine free (TCF) bleaching sequence (Dence and Reeve 1996).

Duarte and Baptista (2003), Björklund *et al*. (2005), and Martino *et al*. (2013) referred in their work to the importance of chemical composition, cooking process parameters, and the utilization or not of extended oxygen delignification on bleachability of *Eucalyptus* pulps. Different pulping conditions can cause changes in chemical composition of the pulp, such as the nature of the residual lignin, carbohydrate composition, the soluble lignin content, the amount of lignin-carbohydrate complexes, and hexenuronic acids (HexA) present in kraft pulps of *Eucalyptus* sp. (Cardoso *et al*. 2002; Colodette *et al*. 2002; Duarte and Baptista, 2003; Colodette *et al*. 2007).

Pascoal Neto *et al*. (2002) reported in their work that pulping parameters, namely: active alkali, sulfidity, temperature, and liquor-to-wood ratio, significantly affect the bleachability of *Eucalyptus globulus* kraft pulps when they are bleached by a conventional ECF ($D_0E_1D_1E_2D_2$) bleaching sequence. The same authors concluded that bleachability can be related to the H-factor used in pulping. Low H-factors, obtained by variations in other parameters apart from temperature, afford pulps that are easier to bleach.

Even though there has been extensive research done on evaluation of how different wood composition and kraft pulping conditions can affect bleachability, there is a lack of evaluation how different modified cooking commercial technologies such as SB, CC, and LS affect the bleachability of *Eucalyptus globulus* and *E. nitens*. This is the objective of the present work.

EXPERIMENTAL

Materials

The unbleached pulp used in this work was produced from fresh chips of *E. globulus* and *E. nitens* from central Chile (Region VIII). The wood raw material age was chosen so that the wood basic density would be similar. The wood age with similar density was 12 years old for *E. globulus* (523 Kg/m^3) and 15 years old for *E. nitens* (507 Kg/m^3). The standard used to measure the basic density was TAPPI T 258 om 11 (2011b). The chip classification prior cooking followed the standard SCAN CM 40 (2001).

Methods

Cooking experiments

All the cooking experiments were performed at VTT Technical Research Centre of Finland. The laboratory-scale cooks were performed in a 30 liter water-jacketed circulation digester (Verdi) simulating three modifying cooking methods; SB, CC, and LS Cooking. The black liquors needed in the simulations were produced using 15 L digester electronically heated rotating autoclaves with the corresponding *Eucalyptus* species. The cooks for black liquor generation (only) were carried out at 160 ^{o}C with constant alkali charge of 17% EA as NaOH. The sulfidity of white liquor used in all cooks was 35%. For all the modified cooks, the kappa number target was 17±0.5. The cooking procedures for all modified cooks are described in Table 1.

The generalized cooking features of every modified cooking method can be summarized as:

SB: Reuse heat of cooking in the subsequent batches. Modified cooking chemistry (*i.e*., alkali profiling and low concentration of dissolved solids). Efficient use of residual and fresh cooking liquors.

CC: Maintain a low temperature during the impregnation stage. Maintain a high liquor to wood ratio and high sulfidity in the impregnation zone of the cook.

LS: Minimize the quantity and concentration of dissolved solids in the bulk and residual delignification phases.

How these modified pulping processes compare with one another with regards to the four rules of modified cooking (Hartler 1978) are presented in Table 2.

Table 1. Main Features Used in SB, CC, and LS Cooking Methods

Phase/Modified Cooking Type	SB	CC	LS
Impregnation Zone			
Temperature (°C)	90	115	105
Liquor to wood ratio	5:1	6:1	4:1
Alkali charge WL + BL as EA (%)	5	6.3	10.5
Time *E. globulus*/*E. nitens* (min)	40/40	60/60	45/45
Cooking Zone I			
Temperature (°C)	148 (HBL fill)	141	135
Liquor to wood ratio	4.25:1 (HBL fill)	6:1	4:1
Alkali charge as EA (%)	5 (HBL fill)	7	7.2
Time *E. globulus*/*E. nitens* (min)	60/60	90/100	20/20
Cooking Zone II			
Temperature (°C)	152 (Cooking circulation)	141	148
Liquor to wood ratio	5:1 (Cooking circulation)	3.8:1	4:1
Alkali charge as EA (%)	10.6 (Cooking circulation)	0.0	0.0
Time *E. globulus*/*E. nitens* (min)	34/40	90/100	100/100
Washing Zone			
Temperature (ºC)	80	NA	90
Washing Liquor to wood ratio	5:1	NA	4:1
Alkali charge as EA (%) or g/L (NaOH)	2.2%	NA	5.0 g/L
Time *E. globulus*/*E. nitens* (min)	90/90	60/60	40/40
Total Alkali charge in the cook as EA (NaOH) (%)	22.8	21.0	21.9

*NA = Not applicable

Table 2. The Four Rules of Modified Cooking Related to Cooking Methods

Rules of Modified Cooking	SB	CC	LS
(1) Leveled out OH^-	✓		
(2) High concentration of SH^-, especially at the beginning of the bulk phase	✓	✓	
(3) Low concentrations of dissolved lignin and sodium at the end of the cooking stage			✓
(4) Low cooking temperature		✓	

Bleaching conditions

The unbleached pulps were bleached at VTT in Finland using the bleaching sequence $D_0E_1D_1E_2D_2$. For each type of pulp, the sequence was applied to unbleached pulps having kappa Factor 0.20 before application of the D_0 stage. The following paragraphs present the bleaching conditions:

D-stages were performed in 18 L air bath reactors. Preheated pulp was initially added to the reactor, then water, and afterwards, acid or alkali for pH adjustment. After mixing, the pH was measured, chlorine dioxide was charged into the reactor, and the reactor immediately sealed. Pulp was first mixed for 4.5 min by a mixer in the reactor rotating at a speed of 30 rpm. During the reaction time, the reactor was periodically stirred (*i.e.*, stopped for 70 s, reversed rotation direction, and rotated for 30 s). After the reaction time, the final pH was measured of the pulp at the reaction temperature. The residual chlorine dioxide content of the bleaching filtrate was determined. The pulp was diluted and washed as described in the next section. The bleaching conditions of the various D stages are presented in Table 3.

Alkaline extraction stage (E) was performed in a Teflon coated 40 L reactor as follows. The pulp and most of the water were heated to the reaction temperature in a microwave oven and placed into the reactor. Alkali with additional water was charged, the pulp slurry was mixed one minute at 300 rpm, and the pH was measured. During the reaction time the pulp slurry was mixed every 20 min for 12 s at 300 rpm. After the reaction time, the final pH was measured of the pulp at the reaction temperature. The pulp was diluted and washed as described in the next section. The bleaching conditions of the E stages are presented in Table 3.

Pulp washing: Washing between the bleaching stages was performed using a standard laboratory procedure. Pulp was diluted to 5% consistency with deionized water, which was the same temperature as that of the preceding bleaching stage. After dewatering, the pulp was washed two times with cold deionized water with an amount equivalent to ten times the mass of the oven-dried pulp. Homogenization of pulp was done by hand.

Table 3. Main Bleaching Conditions

Parameters/Bleaching conditions of different cooking methods		*E. globulus*			*E. nitens*		
		SB	CC	LS	SB	CC	LS
D_0 Consistency 10%	ClO_2 Charge % act Cl	3.30	3.40	3.40	3.40	3.30	3.33
60°C, 60 min	H_2SO_4 charge, %	0.50	0.54	0.54	0.56	0.54	0.54
E_1 Consistency 10% 70°C, 60 min	NaOH charge %	1.36	1.35	1.38	1.36	1.32	1.33
D_1 Consistency 10%	ClO_2 Charge % act Cl	1.15	1.20	1.12	1.06	1.12	1.19
70°C, 120 min	NaOH charge, %	0.10	0.10	0.10	0.10	0.10	0.10
E_2 Consistency 10% 70°C, 60 min	NaOH charge %	0.80	0.80	0.80	0.80	0.80	0.80
D_2 Consistency 10%	ClO_2 Charge % act Cl	0.21	0.20	0.21	0.30	0.23	0.21
70°C, 180 min	H_2SO_4 charge, %	0.09	0.10	0.11	0.09	0.10	0.11

Handsheets (10 g bone-dried) for brightness and kappa number measurements were formed after bleaching stages by stabilizing the pH of the pulp slurries with SO_2 to 4.5 before forming the hand sheets. Testing methods were performed according to the follow standards: kappa number ISO 302 (2004):04, dry content of pulp ISO 638 (2008), Intrinsic viscosity ISO 5351 (2010) and brightness from split sheet surface ISO 2470-1 (2009). The detailed bleaching conditions are presented in Table 3.

Carbohydrates, Extractives, and Lignin Analysis

The carbohydrate analyses were performed using SCAN SCAN-CM 71:09 (2009). Acetone extracts were measured according to standard SCAN SCAN-CM 49:03 (2003). The two measurements were applied to unbleached and bleached pulps. The acid-insoluble lignin was measured using standard TAPPI T 222 om 11 (2011a). The acid-soluble lignin (ASL) was determined according to the standard TAPPI UM 250 um-83 (1999). In this method a solution, after filtering off the insoluble lignin was measured by a spectrophotometric method based on absorption of ultraviolet (UV) radiation at wavelength 205 nm. The total lignin was calculated as sum of both fractions. Statistical analysis was carried out using a confidence interval of 95% of the mean measurements or standard deviation (SD) when applicable. The software used in the calculation was Microsoft® Excel (2010 version).

RESULTS AND DISCUSSION

Wood Raw Material

The compositions of the two wood raw materials used in the experiment are presented in Table 4.

Table 4. Wood Raw Material Composition of *E. globulus* and *E. nitens*

Raw material composition (%)	*E. globulus*	*E. nitens*
Total lignin	24.9	26.4
Cellulose	50.6	48.3
Xylan	18.6	19.4
Glucomannan	2.6	2.4
Other carbohydrates	2.5	2.5
Acetone extractives	0.87	1.15
Syringyl and Guaiacyl (S/G) ratio	4.7	3.5

From Table 4 it can be observed that the *E. nitens* had a slightly higher lignin content, *i.e.*, 1.5% higher than *E. globulus*. The xylan content was also higher for *E. nitens* by 0.8%. Also, slightly higher amounts of extractives, *i.e.* 0.28%, were found in *E. nitens*. The composition of the lignin in the wood as the S/G group ratio was (4.7) for *E. globulus* and (3.5) *E. nitens*. Different hardwood species have been found to have different S/G ratios, which allows for the opportunity to improve process conditions (Santos *et al.* 2013).

Cooking Results

The ideal kappa number to terminate pulping and start bleaching has been a matter of debate. The controversy is only natural, since it depends on a large number of factors that include not only type of the wood but also pulping processes, the type and number of bleaching stages, the presence of oxygen delignification, and foremost on the price of wood

and bleaching chemicals. Kappa ranges from 17 to 20 have been considered ideal for hardwoods (Colodette *et al*. 2007). Table 5 presents a summary of the cooking results of *E. globulus* and *E. nitens* by the three modified pulping processes: H-Factor, kappa number, total yield, rejects, screen yield, intrinsic viscosity, and brightness.

Table 5. Summary Results of Different Cooking Methods

Cooking Technologies/Wood Species	*H factor/SD*	*Kappa number/SD*	*Total yield (%)/SD*	*Rejects (%)/SD*	*Screened yield (%)/SD*	*Brightness (%)/SD*	*Intrinsic Viscosity (mL/g)*
SB							
E. globulus	300/5.12	16.50/0.46	58.76/0.44	1.62/0.80	57.14/0.70	41.50/0.14	1590
E. nitens	315/3.98	17/0.32	57.89/0.40	1.33/0.40	56.56/0.45	39.36/0.06	1620
CC							
E. globulus	239/4.47	17/0.12	58.59/0.51	1.88/0.33	56.71/0.34	41.57/0.26	1660
E. nitens	262/5.20	16.5/0.10	57.22/0.23	1.13/0.13	56.09/0.22	40.33/0.10	1650
LS							
E. globulus	244/5.23	17/0.51	58.66/0.46	1.71/0.56	56.95/0.40	41.51/0.33	1600
E. nitens	273/4.78	16.5/0.14	56.84/0.37	1.19/0.21	55.65/0.38	39.84/0.17	1625

Results are average values ± standard deviation of two repetitions.

From the data in Table 5, it can be seen that the SB pulping required a slightly higher H-factor compared to CC and LS pulping. Also, *E. nitens* required a higher H-factor in order to reach the same targeted kappa number, and this was independent of the cooking methods employed. There were practically no differences among the total yields and rejects for *E. globulus* for the different modified cooking methods. The *E. globulus* wood afforded the highest screen yield, which was independent of cooking method.

Intrinsic pulp viscosities were measured from the brownstock in order to evaluate if there were any differences at kappa number 17±0.5 for both *Eucalyptus* species and for the three different cooking methods. The results are presented in Fig. 1.

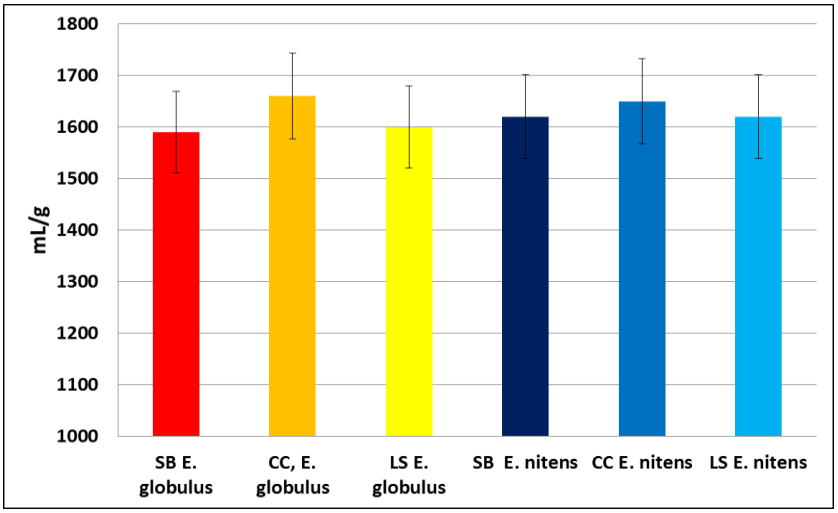

Fig. 1. Intrinsic viscosity of brownstocks at kappa 17±0.5. The error bars present 95% confidence interval of the mean value.

From the data given in Fig. 1, it can be observed that the intrinsic viscosities for the unbleached pulps were at the same level for all the modified cooking methods. There was only a small tendency regarding intrinsic viscosity that one can observe in CC-cooked

pulps. According to Hart *et al*. (2011), the slightly higher viscosity values of the CC are related to lower cooking temperature in comparison to other modified cooking methods. However considering the error bars presenting 95% confidence interval, one cannot conclude that there were differences in viscosities related to *Eucalyptus* species used in this experiment. Neither could it be concluded that there were differences related to the choice of modified cooking methods.

In terms of acetone extractives, *E. nitens* presented higher amounts than *E. globulus*, which was independent of modified cooking method employed (Fig. 2).

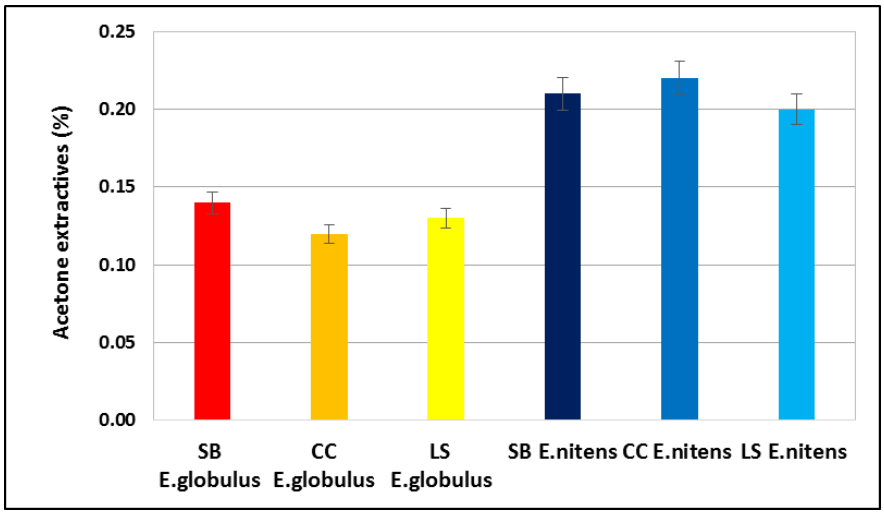

Fig. 2. Acetone extractives in brownstock at kappa 17±0.5. The error bars present 95% confidence interval of the mean value.

The difference presented in Fig. 1 may be related to wood species. Rencoret *et al*. (2007) showed that different lipophilic fractions in the wood composition may explain the differences of acetone soluble extractives in wood and in the pulp.

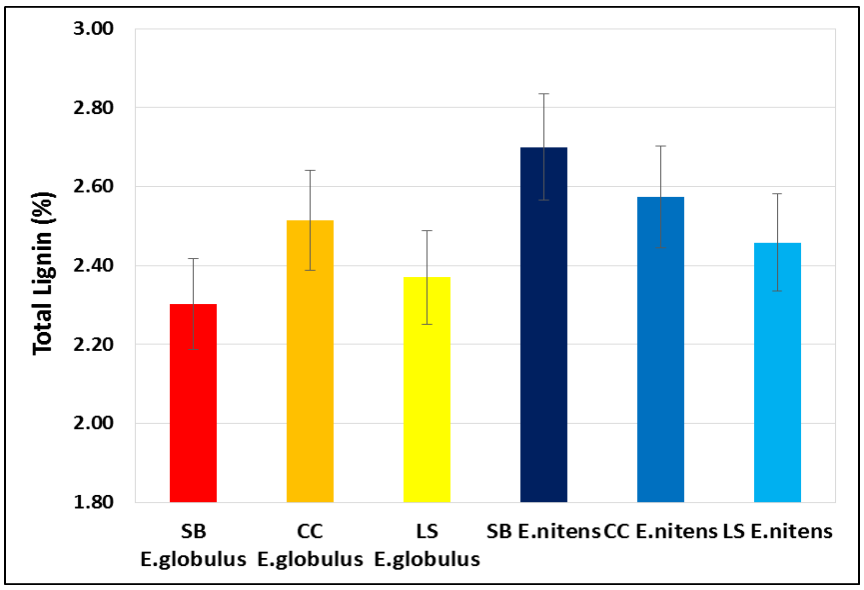

Fig. 3. Total lignin in % of brownstocks at kappa 17±0.5. The error bars present 95% confidence interval of the mean value.

Lignin Degradation

E. nitens pulps were also observed to have a higher amount of total lignin than *E. globulus* pulps (Fig. 3). This follows the same tendency coming from the wood chips. (Table 4).

In general, *E. nitens* pulps presented a tendency of a higher content of total lignin than *E. globulus* pulps. One reason for this could be that *E. globulus* has a higher syringyl/guaiacyl ratio than *E. nitens*, which is a possible reason why it is easier to delignify *E. globulus* that *E. nitens*. However considering the error bars, the only significant difference is related to the SB for *E. nitens*. Similar results were presented by Rencoret *et al*. (2007).

Hexenuronic Acid Formation

Hexenuronic acid (HexA) contents were measured for all unbleached pulps at kappa number 17±0.5. It was found that HexA groups contribute to the kappa number (Gellerstedt and Li 1996; Vuorinen *et al*. 1999) because they consume part of the potassium permanganate, as lignin does. Since pulp HexA content is largely affected by its xylan content, the removal of the latter may have significant impact on bleachability (Gomes *et al*. 2014). The HexA values found in this work are presented in (Fig. 4).

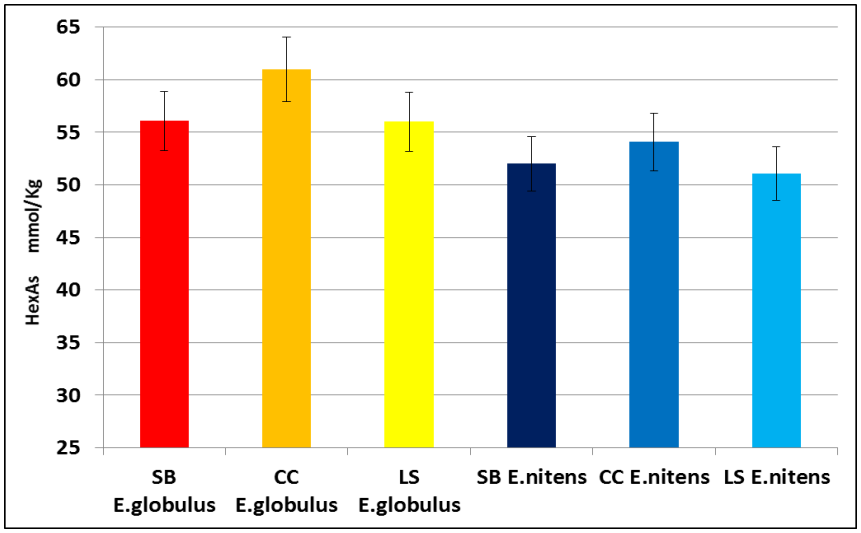

Fig. 4. HexA of brownstocks at kappa 17±0.5 for *E. globulus* and *E. nitens* for the three different cooking methods. The error bars present 95% confidence interval of the value.

E. globulus tended to be higher in HexA content than *E. nitens* brownstock; however, the differences were not statistically significant. According to Li and Gellerstedt (1997), every 10 mmol of HexA corresponds to 0.84 to 0.86 units of kappa number. As it is a linear relationship, both the HexA content and the kappa number follow the same trend. Under the conditions used in kraft pulping, 4-*O*-methylglucuronic acid in glucuronoxylans is partially converted into hexenuronic acid moieties by the β-elimination of methanol (Clayton 1963). The amount of HexA in the brownstocks is the result of two competitive processes: their formation and their degradation (Daniel *et al*. 2003). These unsaturated structures increase the consumption of bleaching chemicals (ozone, chlorine dioxide, and peracids), and decrease the brightness stability of pulps (Gustavsson and Al-Dajani 2000). Daniel *et al*. (2003), Colodette *et al* (2002), and Fatehi *et al* (2009), reported that the content of HexA in pulp increases with pulping time until delignification reaches 95%. It has been reported by Chai *et al*. (2001) that the degradation/dissolution of HexA dominates

over its formation only in the last part of the hardwood cooking process. The amount of this acid has shown a close dependency on the extension of the delignification process and, unlike softwood pulping, only decreased at kappa number below 12, which is not usually achieved in industrial practice (Pedroso and Carvalho 2003).

The significance of HexA in the overall kappa number may vary sharply, depending upon the pulp's initial kappa number. For example, kappa 14 and 18 brownstock samples containing equal amounts of HexA (*e.g.* 7.5 units kappa) will have 53.4% and 41.2% of their kappa represented by these acids, respectively. Thus, the impact of HexA on the overall kappa number is more significant for pulp at kappa 14 (Colodette *et al*. 2007). In this aspect the experiment evaluated the contribution of lignin and HexA for kappa number in Fig. 5.

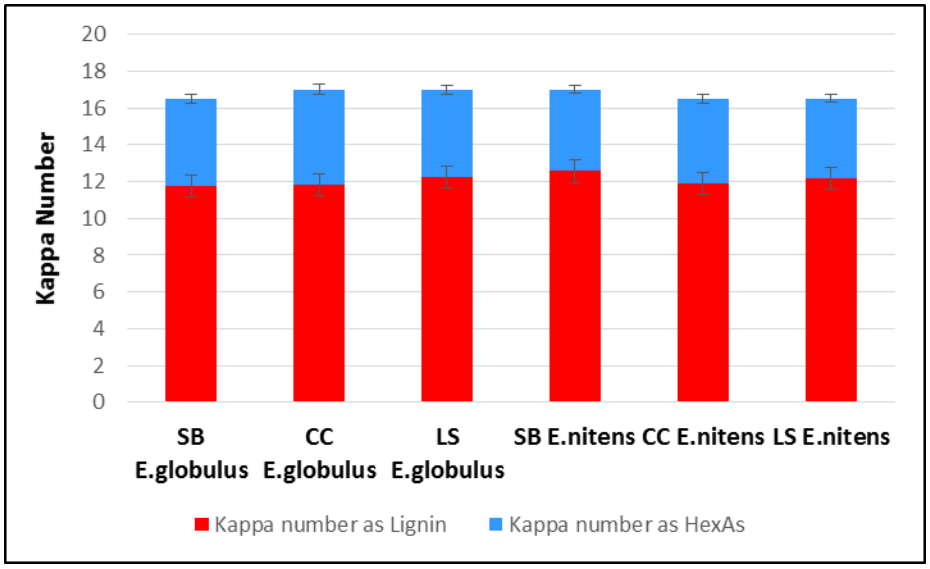

Fig. 5. HexA and total lignin of brownstocks representing kappa number 17±0.5 for *E. globulus* and *E. nitens* for the three different cooking methods. The error bars present 95% confidence interval of the value.

The HexA contribution to kappa number was found to be similar for all pulps and did not present a statistically significant difference. The same trend can be observed in total lignin of brownstock pulps presented in the same figure.

Carbohydrate Degradation

Figure 6 shows the carbohydrate composition of the brownstock pulps of *E. globulus* and *E. nitens* after SB, CC, and LS modified cooking methods at kappa number target 17±0.5.

Independent of the modified pulping process employed, *E. nitens* exhibited higher amounts of hemicelluloses (xylan, glucomannan, and other carbohydrates) than *E. globulus*. This higher proportion was also seen in the wood samples. The *O*-acetyl-4-*O*-methylglucuronic-xylans are the most important *Eucalyptus* hemicelluloses. Acetyl groups and 4-methylglucuronic acids are responsible for increasing the alkali consumption during pulp production (Magaton *et al*. 2011). The reason for increased pulp yield is based on Table 4, and the chemical composition of the unbleached pulps shown Fig. 6, which can be related to higher initial cellulose content of the *E. globulus* wood and lower guaiacyl lignin amount (Collins *et al*. 1990; Wallis *et al*. 1996; González-Vila *et al*. 1999; Del Río *et al*. 2005). Guaiacyl lignin requires higher H-factor in cooking when compared to

syringyl lignin. Therefore a lower cooking time of *E. globulus* produces lower cellulose degradation increasing the cooking yield. This is because a lower amount of cellulose is transformed into monosaccharides during the alkaline peeling reactions of kraft pulping.

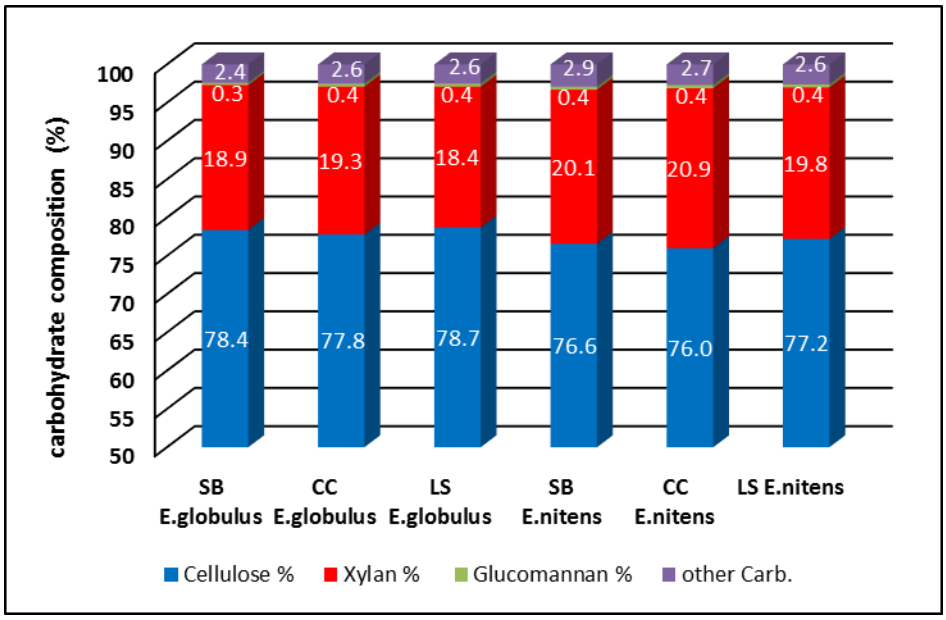

Fig. 6. Carbohydrate composition of brownstocks at kappa 17±0.5 for *E. globulus* and *E. nitens* for the three different cooking methods.

Bleaching Results

In this part of the study, the kappa number reduction and the brightness gain as a function of bleaching stage was determined for each wood species and modified pulping process. The kappa number after various bleaching stages of the $D_0E_1D_1E_2D_2$ did not show any clear tendencies related to the modified cooking method used to produce the resulting brownstock or to the wood species used Fig. 7.

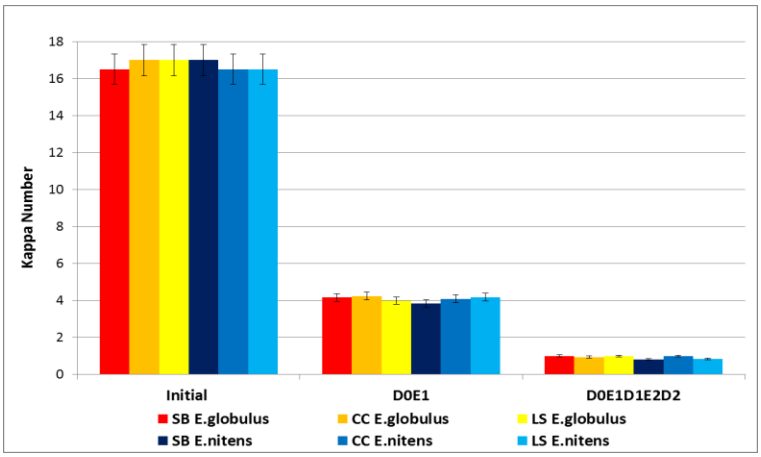

Fig. 7. Kappa numbers of *E. globulus* and *E. nitens* pulps during the $D_0E_1D_1E_2D_2$ bleaching. The error bars present 95% confidence interval of the value.

Similar observations to the kappa numbers were made regarding the brightness development after various bleaching stages of the $D_0E_1D_1E_2D_2$ sequence of *E. globulus* and *E. nitens* (Fig. 8). Independent of the cooking method employed, *E. globulus* exhibited

a slight tendency of higher brownstock brightness at a kappa number 17±0.5, though it was not statistically significant. After the D_0 stage and extraction (E_1), this trend was not observed in the other brightening stages. A similar observation with *E. globulus* pulps was reported by Pascoal Neto *et al*. (2002).

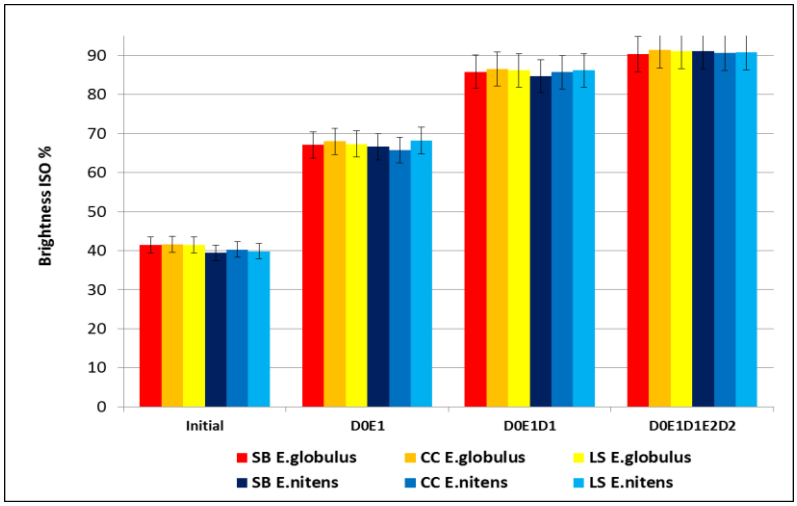

Fig. 8. ISO Brightness (%) development for *E. globulus* and *E. nitens* pulps during the $D_0E_1D_1E_2D_2$ The error bars present 95% confidence interval of the value.

One can obtain from Fig. 8 that when considering the two bleaching components (McDonough 1996), the delignifying partial (D_0E_1) and the brightening partial ($D_1E_2D_2$) both consumed the same amount of ClO_2 to reach a fully-bleached brightness of 90% ISO. One cannot conclude that there were statistically significant differences in the total ClO_2 consumption between the bleaching components among the three modified cooking methods employed or among the *Eucalyptus* species used in this work. The total ClO_2 consumption to reach a fully-bleached brightness of 90% ISO is present in the Fig. 9.

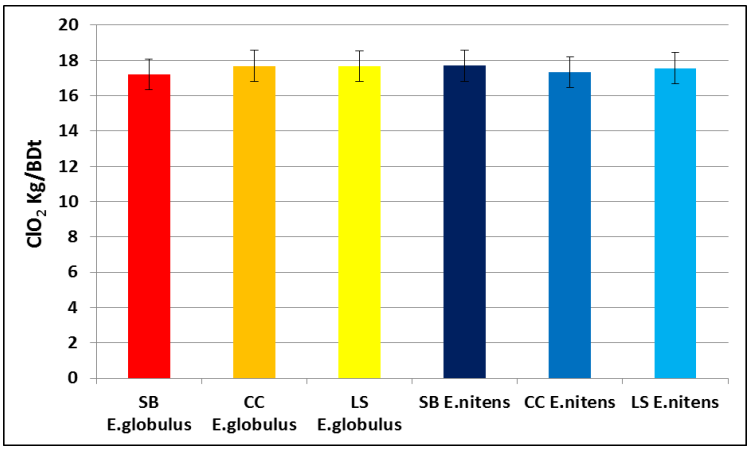

Fig. 9. Total ClO_2 consumption to bleach *E. globulus* and *E. nitens* pulps with 95% confidence intervals. The error bars present 95% confidence interval of the mean value.

The total consumption of chlorine dioxide for different pulps was 17.7±0.3. This indicated that the different cooking method had no effects on bleachability. The intrinsic viscosity after bleaching pulps to ISO 90% brightness was also measured, and the results are presented in the Fig. 10.

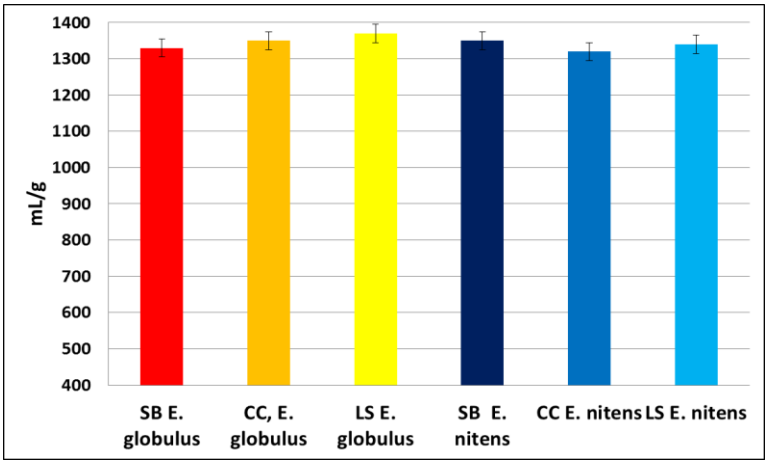

Fig. 10. Intrinsic viscosities of bleached pulps of *E. globulus* and *E. nitens*. The error bars present 95% confidence interval of the mean value.

When comparing these results to the intrinsic viscosity of unbleached pulps, bleached pulps present more even results among different *Eucalyptus species* and different cooking method. No statistically significant differences were observed. However, one can notice that the decrease in intrinsic viscosity of the CC modified method from brownstock to fully-bleach pulps was higher than for other modified cooking methods such as SB and LS. This should be to topic of future studies. The carbohydrate composition of bleached pulps are presented in Fig. 11 of the fully-bleached pulp.

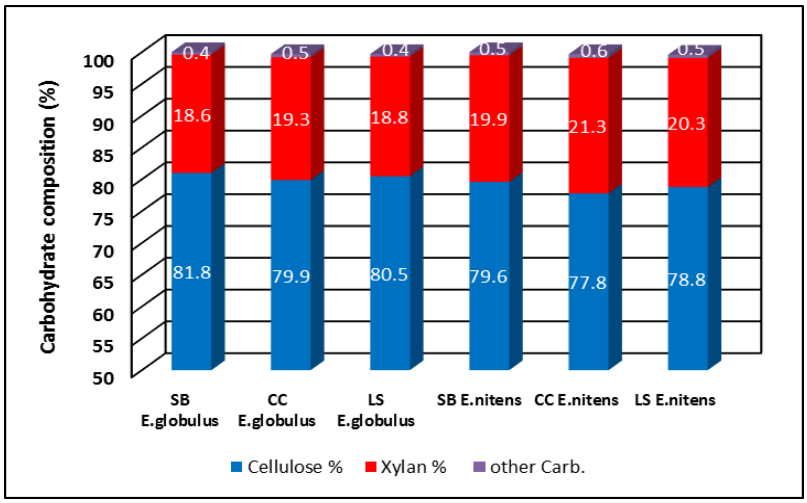

Fig. 11. Carbohydrate composition of fully-bleached pulps of *E. globulus* and *E. nitens*

These results follow the trend of wood raw material and brownstock. Independent of the cooking method employed, *E. nitens* exhibited higher amounts of hemicelluloses (xylan + glucomannan + other carbohydrates) compared to *E. globulus*. According to Gomes *et al*. (2014) it was found that pulp xylan content had no significant effect on bleachability. Fig. 12 shows the acetone extractives after the pulps are fully-bleached.

In terms of acetone extractives, *E. nitens* presented higher amounts than *E. globulus*, independently of the modified cooking method employed. This trend was maintained from the brownstock.

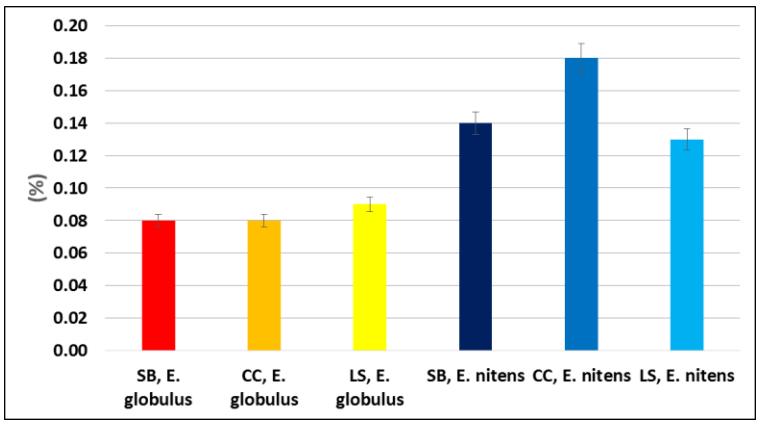

Fig. 12. Acetone extractives of fully-bleached pulps of *E. globulus* and *E. nitens* for the three different cooking methods. The error bars present 95% confidence interval of the mean value.

CONCLUSIONS

1. *E. globulus* wood presented a higher amount of cellulose, and *E. nitens* higher amounts of hemicellulose and acetone extractives. The same trend was found in brownstock and in fully-bleached pulps.
2. *E. globulus* presented a lower amount of lignin and a higher S/G ratio, which might be the reason why *E. globulus* needed lower H-Factor to reach the same kappa number level than *E. nitens* (17±0.5).
3. In the brownstock pulps the amount of (HexA) and total lignin for *E. globulus* and *E. nitens* did not present significant differences in the contribution to kappa number 17±0.5 for all modified cooking methods.
4. No significant differences were found in intrinsic viscosity among modified cooking methods in unbleached and in fully-bleached pulps.
5. For both *Eucalyptus* species, the CC modified cooking method produced pulps with the highest hemicelluloses content after cooking and fully-bleached pulp.
6. In this work it was not possible to observe differences in bleachability of *E. globulus* and *E. nitens* caused by different cooking methods.

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