Effect of Modified Cooking on Chemical Composition of Pulps from *Eucalyptus globulus* and *Eucalyptus nitens*

Rudine Antes* and Olli P. Joutsimo

The effects of SuperBatch™ (SB), CompactCooking™ (CC), and Lo-Solids™ (LS) modified cooking processes on pulp properties of *Eucalyptus globulus* and *Eucalyptus nitens* were investigated. The syringyl/guayacil (S/G) lignin ratio in the wood of *E. globulus* was significantly higher (4.7) than that of *E. nitens* (3.5). From the brown stock pulps, the viscosity, total lignin, carbohydrate composition, acetone extractives, and hexenuronic acids were measured. For the same Kappa number level (17 ± 0.5), pulps from *E. globulus* needed lower H-factor. They also presented a higher brightness and more cooking rejects, independent of the cooking method. CC presented a slightly higher cooking yield and pulp viscosity compared to the other modified cooking methods. At the same Kappa number level, the pulps of *E. nitens* presented a greater amount of total lignin, whereas *E. globulus* presented a higher amount of hexenuronic acid content, independent of the cooking method.

Keywords: Pulping; Modified cooking; Hardwood; Eucalyptus; Chemical composition; Hemicelluloses; Kraft cooking; Syringyl/guayacil (S/G) lignin ratio

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INTRODUCTION

The kraft cooking process was developed in 1879 by Carl F. Dahl in Danzig, Prussia, Germany. Since then, many improvements were made in order to increase yield, reduce the chemical consumption, and improve strength. Over the last few decades, the focus has been to increase the yield and intensity of delignification in order to implement elemental chlorine free (ECF) and total chlorine free (TCF) bleaching sequences (Courchene 1998).

During conventional kraft cooking, white liquor ($NaOH + Na_2S$) and the wood chips are charged simultaneously into the digester. The mixture is heated under pressure for a specific period of time with the goal of reaching a desired degree of delignification. If the alkali concentration is very high in the beginning of the cooking process, high degradation of the carbohydrates may take place during the process. Investigators from the Royal Institute of Technology, and the Swedish Pulp and Paper Research Institute (Carnö and Hartler 1976; Hartler 1978; Nordén and Teder 1979; Teder and Olm 1981; Johansson *et al.* 1984) developed a more selective kraft process by introducing several modifications that are summarized as follows: (1) a "leveled-out" alkali concentration; (2) a high concentration of hydrogen sulfide ions, especially early in the bulk phase, (3) low concentrations of dissolved lignin and sodium ions, especially at the end of the cook; and (4) a low cooking temperature. These modifications allowed pulp producers to extend the cooking to lower kappa levels without significant loss of the pulp strength or yield. Several new pulping technologies for continuous and batch systems have been developed since the implementation of this modified kraft process, to include rapid displacement heating (RDH), black liquor impregnation (BLI), modified continuous cooking (MCC), extended modified continuous cooking (EMCC), and isothermal cooking (ITC). The most recent developments have resulted in Lo-Solids^{TM} (LS) and CompactCooking^{TM} (CC) modified continuous cooking technologies, which are currently the two primary continuous kraft cooking systems. SuperBatch^{TM}, (SB) has been used as a modified batch digester system. Based on cooking technology used in Chile, three digester types were selected to evaluate their performance on chemical composition of pulps from *E. globulus* and *E. nitens*: SuperBatch^{TM}, CompactCooking^{TM}, and Lo-Solids^{TM}.

SuperBatch^{TM} modified displacement cooking was introduced as a batch pulping process in which the objective was to reuse the heat from cooking in subsequent batches. In addition, SB combines the modified cooking chemistry alkali profiling, low content of dissolved matters, and efficient use of residual and fresh cooking chemicals (Uusitalo and Svedman 1999). Energy is saved by displacing hot liquors to tank farms, which are then reused in a subsequent cook. The process starts with filling the digester with chips and packing the digester as evenly as possible (Joutsimo 1997).

After chip filling, the digester is filled from bottom to top with a flow of black liquor having a low alkali concentration. To secure proper impregnation, the liquor is circulated with pumps through the screens and the digester is pressurized. In the next step, the temperature of the digester is increased by displacing the impregnation liquor with hot and high alkali-containing black liquor. The impregnation liquor is displaced to an impregnation liquor tank. The temperature of the digester is then raised to the cooking temperature using direct medium pressure steam.

During this phase, the cooking liquor is circulated from the digester middle screen to the top of the digester. The cook is finished by cold displacement from bottom to top when the H-Factor target is reached. The digester is discharged when the temperature reaches below 100 °C by cold displacement liquor. The discharge is done by using a discharge pump (Weckroth and Hiljanen 1997). In SB cooking, a well-performed hot black liquor and hot white liquor displacement gives the starting point for cooking with an even temperature and chemical profile inside the digester. The most important feature of SB cooking is the impregnation phase, in which the hydroxyl ion content is low and the hydrosulfite ion concentration is high. After the initial phase, the alkali profile is uniform. According to Uusitalo and Svedman (1999), these hydroxyl ion and sulfide ion profiles ensure low Kappa variation and excellent pulp properties.

CompactCooking^{TM} - In the continuous modified cooking process, impregnation of the wood chips is crucial to produce high quality pulp with a lower reject content than standard pulp (Hart *et al.* 2011). In modified cooking, CC of second generation (G2), the impregnation stage has been further improved by prolonging the treatment with low temperature in order to promote diffusion over consumption of cooking chemicals during the impregnation of the chips (Tran 2002). A significant part of the CC philosophy is to maintain a high liquor-to-wood ratio (L:W) and high sulfidity in the impregnation portion of cooking. To obtain these conditions, black liquor is taken from the upper side (extraction zone) of the digester and circulated back into the impregnation vessel, from which black liquor is extracted and sent to the evaporation area. An important feature in the cooking zone I (upper zone of digester) is that it has a high liquor-to-wood ratio, approximately 5:1 to 6:1. In cooking zone II (between wash extraction and main extraction), the liquor-to-wood ratio is decreased to 2:1.

Lo-Solids^{TM}: According to Marcoccia (1996), pulp quality can be improved by decreasing the dissolved solids, retention time in the digester, and cooking liquor concentration. This is the basis for LS cooking. The main objective of this modified cooking process is to minimize the quantity and concentration of dissolved solids in the bulk and residual delignification phases; therefore, LS cooking is based on multiple extractions, reposition, and dilution with preheated white liquor and washing liquor followed by each extraction. The reintroduction of the liquors (white and washing liquor) decreases the dissolved solids concentrations. The aim of reposition of liquor flows is to dilute the reaction products during cooking. This decreases the concentrations of residual products in the cooking bulk and residual delignification phases (Marcoccia *et al.* 1996). It has also been reported that LS improves selectivity (*i.e.*, higher viscosity-to-Kappa ratios at all Kappa numbers within the 10 to 18 range) and bleachability in mill operations compared to EMCC and conventional batch operations (Stanley and Marcoccia 2001).

Also compared to other cooking processes, LS cooking technology results in improved pulp strength and viscosity, increased digester extraction capacity, and enhanced digester washing performance. Decreases in cooking temperature, cooking chemical application, and bleaching chemical consumption have also been cited (Marcoccia *et al.* 1997). Other advantages include improved heat distribution, and thus greater uniformity of cooking, decreased scaling rates, and enhanced control and stability of the chip column movement within the digester (Marcoccia *et al.* 1997).

The objective of this work was to evaluate in the laboratory scale the effect of three modified cooking methods (SB, CC, and LS) on chemical composition of the Eucalyptus species planted and used to produce pulp in Chile, *E. globulus* and *E. nitens*. Their effects on cooking yield, chemical composition, lignin, hemicelluloses, and cellulose degradation were also considered.

EXPERIMENTAL

Materials

The wood used in this work was fresh chips of *E. globulus* and *E. nitens* from central Chile (VIII Region). The age of the wood was chosen so that the wood basic density would be at a similar level: 500 ± 20 kg/m^3. The ages were, for *E. globulus* 12 years old and for *E. nitens* 15 years old. To measure the basic density, the TAPPI T 258 om 11 (2011b) standard method was used. 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 procedures for modified cooking were performed in a forced circulation digester with a volume of 30 L. Heating of the digester was carried out with water jacket heating. The digester was used to generate black liquor, which was then used as the displacement liquor and wash liquor in LS modified cooking. This was done with the corresponding *Eucalyptus* species, and the cooking equipment used consisted of 15 L rotating batch digesters. The results presented in this work related with the cooks are average values of two repetitions of pulps with kappa number of 17±0.5. The heating of the batch cooking system was carried out with electronic control and electric heating of the digester jacket. The cooks for liquor generation were carried out at 160 °C and with a constant alkali charge of 17% EA (effective alkali) as NaOH. The sulfidity of the white liquors used in all cooks was 35%. For all the modified cooks, the target Kappa number was 17 ± 0.5. The cooking procedure for SB and the conditions are presented below in Fig. 1.

In the SB displacement cooking, 5 kg of wood chips was used. First, wood chips were impregnated with black liquor at a liquor-to-wood (L/W) ratio of 5:1 and with an alkali concentration of 18 g/L as EA. The impregnation time was 40 min, and the temperature was 85 °C. Total alkali was 23% as EA (NaOH). From the total, 5.3% (23% of total) was charged to the impregnation. The temperature of the hot black liquor (HBL) displacement was 148 °C and the alkali charge to HBL displacement was 5% (21.7% of total). The cooking temperature was 152 °C, and the alkali charge was 10.6%. The temperature in the final displacement was 40 °C, and the alkali charge was 2.1% of the total charge. The displacements were carried out in the following manner: (1) Impregnation liquor was added to the digester and then circulated; (2) The impregnation liquor was displaced with 18 L of HBL and then circulated; the L/W ratio decreased to 4.25; (3) Four liters of white liquor was added before cooking circulation, which increased the L/W ratio to 5.05; and (4) The HBL after cooking was displaced with 30 L of weak black liquor, and the cook was ended with a final L/W ratio of 5.

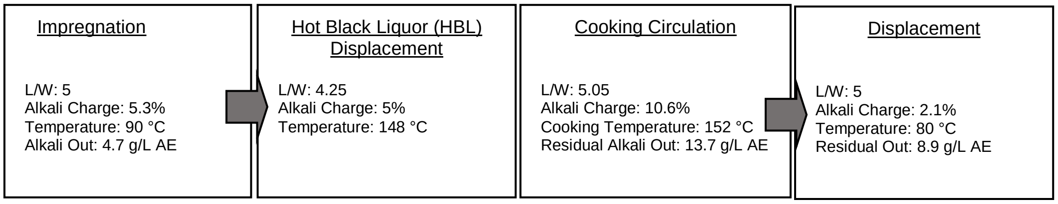

Fig. 1. Laboratory SuperBatch^{TM} cooking procedure. Arrows indicate displacement. L/W: liquor-to-wood; EA: effective alkali

The Compact Cooking simulation started with chip steaming at low steam pressure (3.5 bars) for 5 min. The chip surface temperature was increased to 105 °C. Impregnation time was 60 min at 105 °C, and from the total WL charge (13.3%), 47.3% was charged to impregnation together with black liquor, so that impregnation liquor concentration was 23.8 g/L as EA (NaOH) and L/W was 6:1. At the end of impregnation, the rest of the WL charge (7%) was used to displace 9 L of BL from the impregnation. The temperature was increased to 141 °C and maintained in this cooking zone I (CZ1) for 110 min.

The L/W ratio was decreased from 6:1 to 3.8:1 in the beginning of cooking zone II (CZ2). The temperature was maintained at 141 °C in CZ2 for 90 to 110 min. The cooking was finished by washing with water for 60 min when the temperature decreased to 40 °C. The compact cooking procedure is presented in Fig. 2.

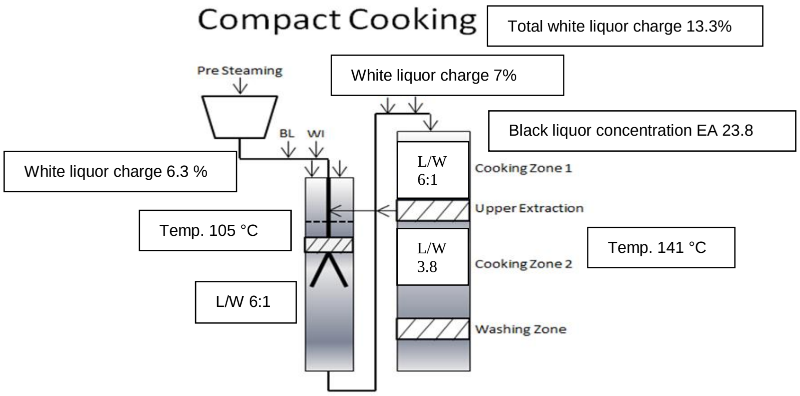

Fig. 2. Laboratory CC procedure. L/W: liquor-to-wood; EA: effective alkali

The delignification degree of the species *E. globulus* and *E. nitens* was adjusted by cooking time in cooking zones I and II. The LS cooking was initiated with chip steaming with low pressure steam (3.5 bars) for 15 min. The chip surface temperature was increased to 105 °C. The impregnation time was 45 min at 135 °C, and from the total WL charges (17.7%), 59.3% was charged to impregnation and the L/W was adjusted to 4:1 with BL with alkali concentration of 2.5 g/L EA. In the first cooking zone, the temperature was increased from 135 °C to 148 °C in 20 min. Black liquor from impregnation was displaced with washing liquor (washing liquor had an alkali concentration of 5 g/L EA) and WL charge of 7.2%, so that the final L/W ratio was 4:1. In cooking zone II, the temperature was kept at 148 °C for 100 min. Washing was then carried out with wash liquor, and the temperature was decreased with the L/W of 4:1 to 130 °C and then in 20 min to 90 °C, maintaining the L/W at 4. Finally, the cook was terminated by washing with water for 60 min when the temperature decreased to 40 °C. The LS cooking procedure is presented in Fig. 3.

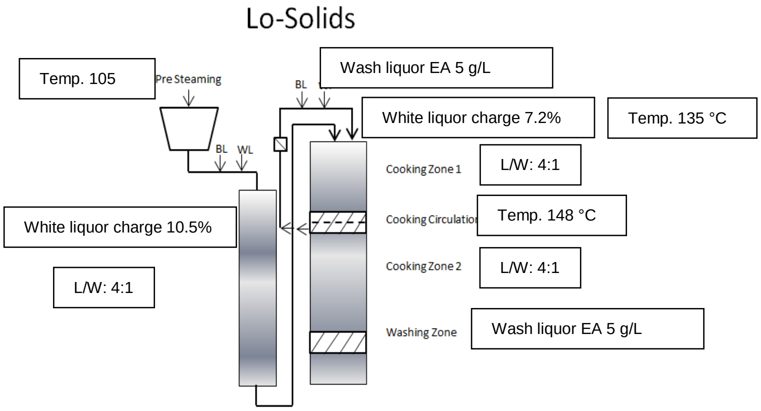

Fig. 3. Laboratory LS procedure. L/W: liquor-to-wood; EA: effective alkali

In the washing and screening of the pulps, special care was taken to avoid the loss of fines, *e.g.*, in washing, where fabrics were used to retain fines with the pulp. After cooking, the chips were disintegrated in a Wenberg type disintegrator. Pulp was washed in a screen basket, and outgoing washing filtrate was directed through a wire fabric with a mesh size of 70. The retained fines in the fabric were returned to the pulp. Cooking trials were carried out at VTT. The pulps were screened using the TAPPI T 275 sp 07 (2007) standard, and the dry matter content was measured using standard ISO 638 (2008). Standard ISO 302 (2004) was used for the Kappa number measurement, standard ISO 5351 (2010) was used for viscosity, and standard ISO 2470-1 (2009) was used for brightness. The primary features utilized in these modified lab cooking methods are presented in Table 1.

Table 1. 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

The general cooking features of each of the modified cooking methods can be summarized as follows:

SB: Reuse of heat of cooking in the subsequent batches.
Modified cooking chemistry (alkali profiling and low content of dissolved matters). Efficient use of residual and fresh cooking chemicals.

CC: Low temperature during the impregnation stage.
Maintaining a high liquor-to-wood ratio and high sulfidity in the impregnation portion of the cook.

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

The evaluation of how the four rules of modified cooking (Hartler 1978) comply with the three cooking methods can be seen in Table 2:

Table 2. 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		✓	

Hemicelluloses, lignin, and extractives analysis

The hemicelluloses, lignin, and extractives were analyzed from all of the brown stock pulps after cooking. Extractives were measured according to the SCAN standard CM 49 (2003). This standard method is utilized for the determination of non-volatile lipophilic matter in wood chips and pulp samples through gravimetric analysis. The method entails solid-liquid extractions with acetone in a Soxhlet extractor equipment for at least 16 or 24 cycles for pulp and wood respectively. For lignin analysis, total lignin were measured using a modified version of standard TAPPI T 222 om-11 (2011a). In this method, the total lignin is calculated by adding the amount of gravimetric lignin plus the acid soluble lignin.

The carbohydrates were measured according to SCAN CM 71 (2009). The method is used for quantification of the monosaccharides arabinose, glucose, galactose, xylose, and mannose in pulp by using acid hydrolysis as saccharification pretreatment and chromatography for further analysis. The S/G ratio was measured using the pyrolysis-gas-chromatography-mass spectrometry (Py-GC/MS) method described in detail by Ohra-aho *et al.* (2013). In this method, Py-GC/MS measurements were performed with a filament pulse pyrolyzer (Pyrola 2000, Pyrol AB, Sweden) connected to a GC/MS instrument (Varian 3800 GC/2000 MS, Agilent Technology, USA). About 100 µg of the sample was weighed accurately on an automatic ultramicrobalance (CHAN 29 Instruments Inc., Cerritos; USA) and placed directly on the filament, which contained a small cavity. The pyrolysis chamber maintained at 175 °C was purged with helium 18 mg/min to lead the pyrolysis products into the gas chromatography injector, which contained a split liner (Restek, 3.4 mm × 5.0 mm × 54 mm). A split injector maintained at 280 °C with a split ratio of 1:18 was used. The time to increase the temperature to 580 °C was set to 8 min, and total pyrolysis time was 2 s. The pyrolysis products were separated using a capillary column (J&W DB-1701, Agilent Technology, USA), using the following temperature program: initial temperature of 100 °C, incremental rate of 4 °C/min to 265 °C, and temperature held for 10 min. Helium was used as a carrier gas with a constant flow rate of 0.9 mL/liter. An ion trap mass spectrometer was used for the compound detection with a mass scan range of m/z 46 to 399 (EI 70 eV). The ion trap and transfer line temperature were set to 180 °C and 250 °C, respectively. The peak areas of lignin pyrolysis products were integrated and normalized to the weight of the sample. Co-eluted compounds numbered as 14/15, 23/24, and 25/26 were integrated using selected main ions (122 + 137 + 166 + /167 + 182, 123 + 151 + 178/124 + 137 + 180, 181 + 208/167 + 210), and the peak areas were corrected back to the total peak area using factors, which were calculated for the pure mass spectra of the compound (2/2.5, 2.7/3.1, 4.5/5.3). An average of at least two parallel measurements was calculated, and the peak areas of guaiacyl and syringyl lignin pyrolysis products were normalized to 100%. Confidence intervals of 95% of the mean of measurements were applied when applicable. The software used in the calculation was Microsoft Excel version 2010.

RESULTS AND DISCUSSION

Raw Material

Wood basic densities of *E. globulus* and *E. nitens* were found to be 523 kg/m^3 and 507 kg/m^3, respectively. The target of the experiment was 520±20 kg/m^3 for both species. The results that are presented are an average of 7 experiment results from a mix of 12 trees of each species. The results of measurements and the standard deviation are presented in Table 3.

Table 3. Average and Standard Deviation of Basic Density Measurement for Wood Samples of *E. nitens* and *E. globulus*

Measurement/Species	*E. globulus*	*E. nitens*
1	531	497
2	503	523
3	535	515
4	530	497
5	508	516
6	521	501
7	531	501
Average	**523**	**507**
Standard deviation	11.65	9.80

The results show the basic densities for both samples *E. globulus* and *E. nitens*. Based on the overlapping of some results, one can conclude that there was no significant difference in basic density between the two samples used in the cooking experiment. The standard deviation values of the basic density measurement were also in a very similar level. Table 4 presents the chemical composition of the raw material and relationship of the lignin structures syringyl (S) /guaiacyl (G) ratio.

Table 4. Chemical 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 3 it can be observed that *E. nitens* had a slightly higher lignin content, *i.e.*, 1.5% higher than *E. globulus*. The xylan content was also higher 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*. This topic has been intensively investigated and characterized (Rencoret *et al.* 2007, 2008) also using Py-GC/MS, with reported S/G ratios for *E. nitens* (3.9) and for *E. globulus* (4.1). Different hardwood species have been found to have different S/G ratios, which allows for the opportunity to improve process conditions (Santos *et al.* 2013a). It has been claimed that a higher S/G ratio impacts pulping and bleaching performance (Resquin *et al.* 2006; Oudia *et al.* 2007). According to Santos *et al.* (2013b), recent studies demonstrated that the S/G ratio varies not only among different species but even among clones of the same species, which can explain the different S/G ratios found in the literature. Another possibility for the variation in the S/G ratio results was proposed by Genuit *et al.* (1987); even though S/G ratios are widely used for the characterization of lignin, a study with model compounds showed indications that the β-aryl ether linkage of syringyl lignin is cleaved much more easily than guaiacyl lignin (Tsutsumi *et al.* 1995). It should be noted that pyrolysis, as with all degradation methods, overestimates the amount of (S) units (Sarkanen and Hergert 1971).

Cooking Results

Table 5 presents a summary of the cooking results with SB, CC, and LS.

Table 5. Modified Cooking Results of *E. nitens* and *E. globulus*

Cooking Technologies	*H factor/SD*	*Kappa number/SD*	*Total yield (%)/SD*	*Rejects (%)/SD*	*Screened yield (%)/SD*	*Brightness (%)/SD*	*Intrinsic Viscosity (mL/g)/SD*
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

Note: The table presents the results and the Standard Deviation (SD)

As shown in Table 4, the SB cooking method required a slightly higher H-Factor compared to the CC and LS cooking methods. Also, *E. nitens* required a higher H-Factor in order to reach the same Kappa number, independent of the cooking method. This is likely due to the higher S/G ratio for *E. globulus* than for *E. nitens*. There were also practically no differences between the measurements of total yield and reject amount for *E. globulus* within the different modified cooking methods. *E. globulus* presented the highest yield independently of the cooking method. This is explained by the higher S/G ratio of *E. globulus* and is supported by several authors (Collins *et al.* 1990; Wallis *et al.* 1996; González-Vila *et al.* 1999; Del Río *et al.* 2005). The reject levels of *E. nitens* were lower than those of *E. globulus*, independent of the cooking method applied.

Figure 5 presents the intrinsic viscosities of the unbleached pulps for SB, CC, and LS, considering a single experiment per sample.

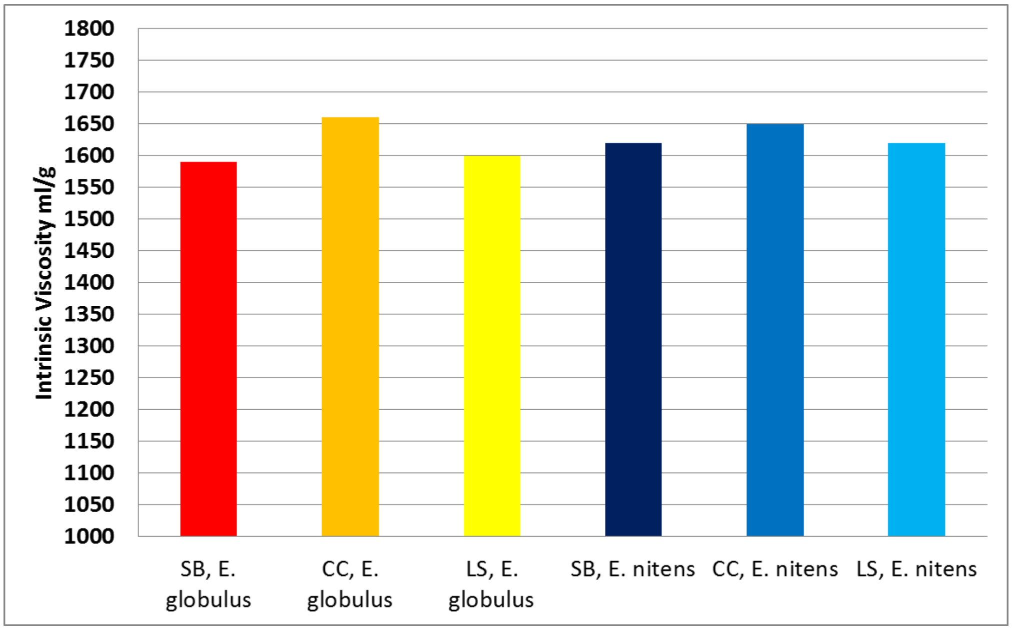

Fig. 5. Unbleached pulp intrinsic viscosity of *E. globulus* and *E. nitens* with 3 different cooking strategies

From Fig. 5, it can be deduced that the intrinsic viscosity for unbleached pulp is about the same for all the modified cooking methods. Only a small tendency in CC could be noted. This tendency of higher viscosity values of CC may be related to the lower cooking temperature and consequently the lower H-Factor in comparison with the other modified cooking methods (Hart *et al*. 2011).

Lignin Degradation

The objective of chemical pulping is to release the fibers by dissolving the lignin. This is achieved when the lignin is fragmented from the middle lamellae between the fibers and in the fiber cell wall, leading to the liberation of phenolic groups, and thus the hydrophobicity of the lignin is increased. Lignin is a heterogeneous polymer built by three types of monomeric phenolic structures: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) propane units (Lourenço *et al*. 2012).

Cleavage of β-O-4 linkages in phenolic structures is an important reaction during lignin degradation, and the extent of this cleavage is determined by the composition of the cooking liquor. A high content of hydrosulfide ions could promote this reaction during the bulk delignification phase, whereas a lower content benefits the competing formation of alkali-stable ethanol ether.

The cleavage of β-O-4 linkages without free phenols also contributes to the lignin fragmentation, although it is a slower reaction that only depends on the hydroxide ion concentration (Sjöström 1993). The results for total lignin of this study are presented in Figs. 6.

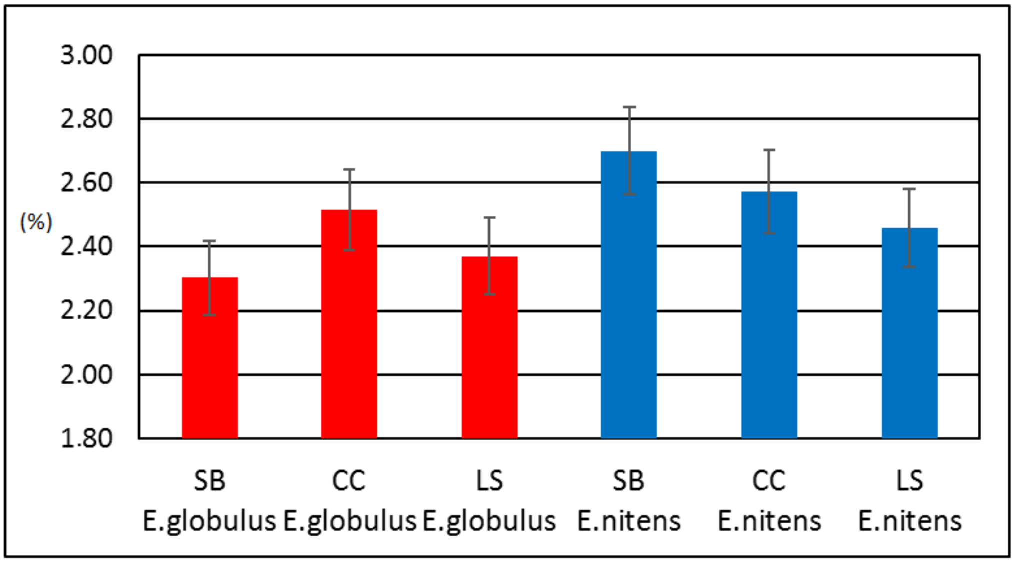

Fig. 6. Total lignin composition at a Kappa number of 17 ± 0.5. The error bars present the 95% confidence interval of the mean of the measurement.

Figure 6 shows that lignin content of the CC and LS cooked pulps at the kappa level (17 ± 0.5) were very similar. There was only a statistical difference (95% confidence interval) between *E. globulus* and *E. nitens* cooked with SB technology. According to Bierman (1996), different bonds and chemical moieties within the G-lignin and S-lignin macromolecules have different reactive stabilities, causing heterogeneity during the chemical pulping. The difference in the lignin content may derive from the difference in the S/G ratio, which is higher for *E. globulus* and for SB cooking. Hydroxyl ion concentration is relatively even throughout the whole cooking compared to CC and LS modified cooking. The high S-lignin is more reactive in the same hydroxyl concentration compared to G-lignin. For instance, the G-lignin is more resistant to cleavage, since it is characterized by the absence of a methoxyl group at C5 in the aromatic ring, and thus contributes to a lower depolymerization during pulping (Gutiérrez *et al*. 2006). A G-lignin rich will be more difficult to remove, while an S-lignin will be more easily cleaved and solubilized (González-Vila *et al*. 1999). The difference in the lignin content is probably a combination of the mentioned factors in case of the SB cooking.

Carbohydrate Degradation

The degradation of hemicelluloses is strongly temperature dependent, as both reaction rate and final yield are affected by the cooking temperature (Sjöström 1977). The yield difference arises from the decreased alkaline hydrolysis (less cellulose degradation) at lower cooking temperatures (around 140 °C), whereas the extent of the primary peeling is largely unaffected at this temperature. The yield differences at varying cooking temperatures are thus larger for xylan than glucomannan due to the stabilizing effect of arabinose side-groups toward endwise degradation (Whistler and BeMiller 1958; Sjöström 1977). This stabilizing effect decreases at higher temperatures (around 155 °C) as a result of substituent removal through alkaline hydrolysis, yielding additional secondary peeling (Simonson 1963; 1965; Hansson and Hartler 1968).

Aurell, Hansson, and Hartler (1965 and 1968) have shown that xylan degradation increases as a function of hydroxide ion concentration. The xylan degradation is caused by alkaline hydrolysis, which results into chain cleavage and removal of arabinose side groups. Also secondary peeling increases because of formed reduced end-groups. Similar phenomena has been reported by Ribe *et al*. (2010), *i.e.* the increased solubility of polysaccharide fragments at increased hydroxide ion concentrations. The carbohydrate composition after cooking in the brown stock pulp samples are presented in Fig. 7.

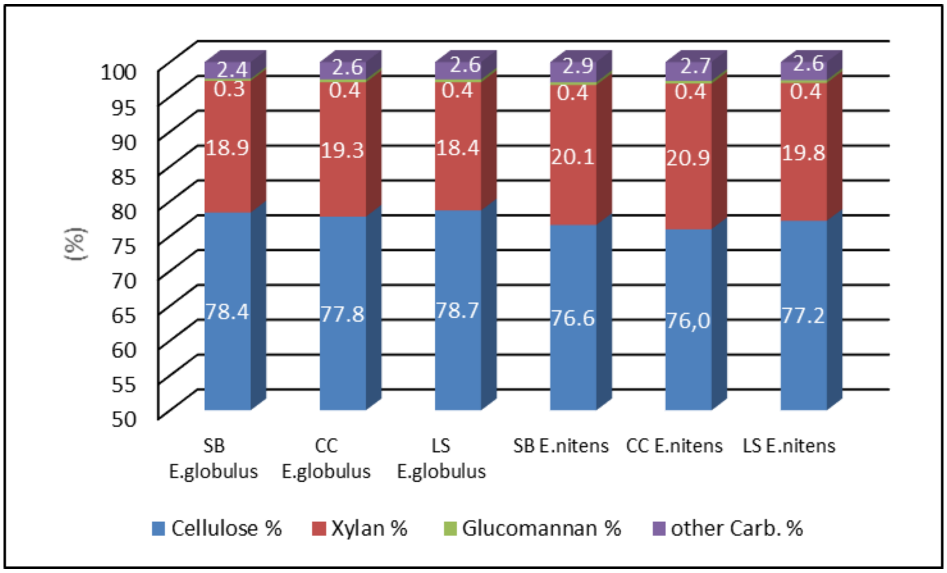

Fig. 7. Total carbohydrate composition at the same Kappa number of 17 ± 0.5

It can be concluded from Fig. 8 that *E. globulus* has higher amounts of cellulose compared to *E. nitens* in the brown pulps. It can also be concluded that *E. nitens* has a higher hemicellulose content in the brown pulps than does *E. globulus*. Studies have shown that the hydroxide ion concentration increases the removal of xylan during all the cooking stages (Aurell and Hartler 1965; Hansson and Hartler 1968). Figure 7 shows that LS cooking, which has highest hydroxide ion concentration, results in the lowest amount of xylan among all the modified pulping methods.

Hexenuronic Acid Formation

Eucalyptus kraft pulps produced by kinetically modified pulping processes contain very high amounts of hexenuronic acids (HexAs). The significance of HexAs in the overall kappa number may vary sharply, depending upon the pulp's initial kappa number. (Colodette *et al.* 2007). The hexenuronic acid measurement in brown pulps with a 95% confidence interval is presented in Fig. 8. HexAs are formed because of two main reasons: raw material and process parameters. According to Gomes *et al*. (2014), the HexAs content in pulps is largely affected by the xylan content. In the kraft pulping process, hexenuronic acid is formed by the elimination of methanol from 4-O-methylglucuronic acid groups (Gellerstedt and Li 1996). The formation rate of hexenuronic acid also depends on some operational variables of the process, including cooking time, temperature, and effective alkali concentration (Cadena *et al.* 2010); this explanation is supported by various authors (Buchert *et al.* 1995; Chai *et al.* 2001; Daniel *et al.* 2003; Simao *et al.* 2005).

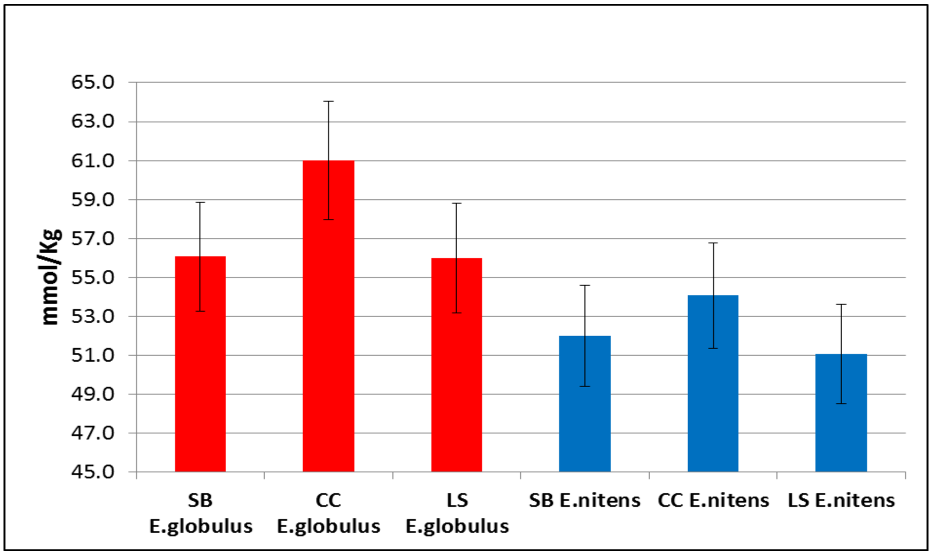

Fig. 8. The hexenuronic acid content in the pulp at the same Kappa number level of 17 ± 0.5. The error bars present a 95% confidence interval of the mean of the measurement.

As HexAs are formed during pulping, they may be simultaneously degraded in the alkaline medium or partially eliminated as a result of xylan dissolution; hence, the content of HexAs in unbleached alkaline pulps is the result of two competitive processes, *i.e.*, formation and degradation. At the final cooking temperature, the hexenuronic acid content in the pulp decreases continuously with time due to alkaline degradation and xylan dissolution (Gustavsson and Al-Dajani 2000). Even though the raw material *E. globulus* has a smaller amount of xylan (18.6%) compared to *E. nitens* (19.4%), independent of cooking method, *E. globulus* needed a smaller H-Factor than *E. nitens* in order to achieve the same kappa number. In this case, the smaller degradation of HexAs in the pulp of *E. globulus* may explain why its content of HexA was higher than *E. nitens*.

CONCLUSIONS

1. Based on a higher value of H-factor, SB technology consumes more energy to delignify at the same Kappa number level, independent of the raw material used in the experiment *E. globulus* and *E. nitens*.
2. At the same Kappa number (17 ± 0.5), the pulps of *E. nitens* presented a higher lignin content and lower brightness for all the cooking methods employed. By contrast, *E. globulus* presented a higher amount of rejects.
3. The amount of HexAs was higher for *E. globulus* than for *E. nitens* after applying the different cooking methods. The authors suggest that the smaller degradation of HexAs in the pulp of *E. globulus* due lower H-Factor may explain why its content of HexA was higher than for *E. nitens*.
4. An evening out of the hydroxyl ion concentration during kraft cooking will decrease G-lignin removal during cooking; this is especially the case in SB cooking.

5. Higher hydroxyl ion concentration from the initial phase of the cooking increases xylan degradation; this is observed in LS cooking.

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