ROBISNÉA ADRIANA RIBEIRO

INFLUÊNCIA DO ÁLCALI EFETIVO RESIDUAL DO COZIMENTO KRAFT DE EUCALIPTO NO RENDIMENTO, NA BRANQUEABILIDADE E NA COMPOSIÇÃO QUÍMICA DA POLPA E DA LIGNINA RESIDUAL

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Agroquímica para obtenção do título de *Doctor Scientiae*.

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SUMÁRIO

RESUMO

RIBEIRO, Robisnéa Adriana, D.Sc., Universidade Federal de Viçosa, março de 2019. **Influência do álcali efetivo residual do cozimento kraft de eucalipto no rendimento, na branqueabilidade e na composição química da polpa e da lignina residual.** Orientador: Jorge Luiz Colodette. Coorientador: Silvio Vaz Júnior.

O impacto do álcali efetivo residual (AER) e do grau de deslignificação da polpa no rendimento da polpa kraft de eucalipto, branqueabilidade, e na sua composição química, particularmente para os grupos hidroxílicos e carboxílicos da lignina, analisados por espectroscopia de RMN de ^{31}P, foi investigado neste estudo. Foram avaliados neste estudo as madeiras de *Eucalyptus globulus* x *Eucalyptus nitens* hybrid, *Eucalyptus nitens*, *Eucalyptus globulus* e *Eucalyptus urophylla x Eucalyptus grandis* hybrid. As madeiras de eucalipto foram cozidas com números kappa de 14 ± 1, 18 ± 1, 22 ± 1 e 26 ± 1, utilizando duas faixas diferentes de álcali efetivo residual(AER): baixo-AER (1-2 g L^{-1}) e alto-AER (8-9 g L^{-1}). Em geral, os cozimentos com baixo teor de AER levam a polpas com maior rendimento, maior viscosidade, maior teor de xilanas, e menor teor de ácido hexenurônico (HexA) e menor alvura, em relação as polpas cozidas emalto-AER. Além disso, os cozimentos com baixo teor de AER requereram cerca de 20% menos de álcali efetivo para atingir o número kappa alvo, apesar de demandarem cerca de 50% mais fator-H. Tendências semelhantes foram observadas para todas as madeiras e os números kappa avaliados, mas o grau de deslignificação variou substancialmente entre as madeiras;*E. globulus* foi a madeira mais fácil de deslignificar. Houve uma tendência de maior rendimento de polpa marrom para os cozimentos terminados em um elevado número kappa, na faixa de 14-26, mas o rendimentodepurado livre de lignina e HexA foram aproximadamente semelhantes na faixa de kappa de 18-26 para um dado tipo de madeira. A lignina remanescente nas polpas a partir do cozimento do híbrido de *E. urophylla* x *E. grandis* em baixo-AER (1-2 g L^{-1}) e alto-AER (8-9 g L^{-1}) foi analisada para os grupos hidroxílicos e carboxílicos. Em ambos os cenários, as comparações foram feitas com polpas de número kappa variando na faixa de 14-26. As ligninas residuais da polpa foram isoladas por lignina enzimática celulolítica (CEL) e suas distribuições de grupos funcionais foram examinadas usando a espectroscopia de RMN de ^{31}P. Análises de ligninas residuais indicaram que as polpas a partir dos cozimento combaixo-AER possui altos teores de grupos hidroxílicos alifáticos, exceto para as polpas de númerokappa 14, maiores teores de grupos hidroxílicos fenólicos e grupos carboxílicos em relação as polpas derivadas de cozimentos com alto-AER.As polpas de cozimento com baixo teor de AERem relação às de alto-AER apresentarameficiência do estágio-O ligeiramente maior (2% a 4%), apesar de exigirem 5% a 10% mais cloro ativo total (CAT) para alcançar a alvura desejada de 90% ISO quando branqueada pela sequência D(EP)D. No entanto, a estabilidade de alvura da polpa foi pouco afetada. A branqueabilidadedas polpas produzidas a partir de cozimentos em baixo-AERforam menores do que para as polpas produzidas a partir de cozimentos em alto-AER, principalmente quando considerado o intervalo de número kappa de 22 a 26, para um determinado tipo de madeira.

ABSTRACT

RIBEIRO, Robisnéa Adriana, D.Sc., Universidade Federal de Viçosa, March, 2019. **Influence of residual effective alkali from eucalypt kraft cooking on yield pulping, bleachability and chemical composition of pulp and residual lignin.**Advisor: Jorge Luiz Colodette. Co-advisor: Silvio Vaz Júnior.

The impact of residual effective alkali (REA) and pulp delignification degree on *Eucalyptus* kraft pulp yield, bleachability, and in the chemical composition, particularly for lignin hydroxyl and carboxyl groups analyzed by quantitative ^{31}P-NMR spectroscopy was investigated in this study. Itwas evaluated in this study the woods of *Eucalyptus globulus* x *Eucalyptus nitens* hybrid, *Eucalyptus nitens*, *Eucalyptus globulus* and *Eucalyptus urophylla x Eucalyptus grandis* hybrid. The eucalypt woods were cooked to kappa numbers of 14±1, 18±1, 22±1 and 26±1 using two different ranges of REA, namely: Low-REA (1-2 g L^{-1}) and High-REA (8-9 g L^{-1}). In general, the low-REA cooks lead to pulps of higher yield, viscosity and xylans content and lower brightness and hexenuronic acid (HexA) content, in relation to the high-REA cooks. In addition, the low-REA cooks required about 20% less effective alkali to achieve the target kappa, in spite of demanding about 50% more H-factor. Similar trends were observed for the other woods and kappa values evaluated, but the level of gains varied substantially among woods and delignification degrees. Among the various woods, *E. globulus* was the easiest to delignify. There was a trend of higher brown pulp yield for the cooks terminated at higher kappa in the range of 14-26, but the lignin-HexA free screen yields were about similar in the kappa range of 18-26 for a given wood type. The lignin remaining in the pulps from*E. urophylla* x *E. grandis* hybrid cooked in Low-REA (1-2 g L^{-1}) and High-REA (8-9 g L^{-1}) were analyzed for hydroxyl and carboxyl groups. In both case scenarios, the comparisons were done with pulps of kappa number varying in the range of 14-26. The pulp residual lignins were isolated by cellulolytic enzyme lignin (CEL) and their functional group distributions examined using quantitative 31P-NMR. Analysis of residual lignins isolated from Low-REA and High-REA cooking of kappa number 14, higher contents of phenolic hydroxyl groups, carboxylic acid groups in relation to the high-REA pulps.The pulps from low-REA cooks showed slightly higher O-stage efficiency (2%-4%), in spite of demanding

about 5% to 10% more total active chlorine (TAC) for attaining the target brightness of 90% ISO when bleached by D(EP)D sequence.Howeveer,pulp brightness stability was somewhat affected. Bleachability for the pulps produced from low-REA were smaller than those from high-REA cooks,mainly in the kappa number range of 22 to 26, for a given wood type.

APRESENTAÇÃO

Esta tese está apresentada na forma de três artigos, sendo que o primeiro deles teve como objetivoavaliar o impacto do álcali efetivo residual baixo e alto (1-2 e 8-9 g L^{-1}NaOH) e o grau de deslignificação da polpa (número kappa 14-26) sobre o desempenho do cozimento kraft de quatro madeiras de eucalipto normalmente usadas na fabricação de celulose.

O segundo teve como objetivoinvestigar as mudanças nos grupos funcionais da lignina residual (hidroxílicos e carboxílicos) da polpa kraft quando o cozimento kraft foi terminado em álcali efetivo residual baixo e alto (1-2 e 8-9 g L^{-1}NaOH), aplicado a um híbrido de *Eucalyptus urophylla* x *Eucalyptusgrandis.*

O terceiro artigo teve como objetivo avaliar o impacto do álcali efetivo residual baixo e alto (1-2 e 8-9 g L^{-1}NaOH) na branqueabilidade de polpasproduzidas a partir de quatro madeiras.

Paper 1: Effect of residual effective alkali on *Eucalyptus* kraft pulp yield and chemistry

Paper 2: Chemical study of kraft lignin during alkaline delignification of *E. urophylla* x *E. grandis* hybrid in low and high residual effective alkali

Paper 3: Effect of residual effective alkali on the *Eucalyptus* kraft pulp bleachability

INTRODUÇÃO GERAL

A polpação Kraft é o processo mais amplamente utilizado para a produção de polpas químicas (Gullichsen & Fogelholm, 2000). Os cavacod de madeira são tratados com uma forte solução alcalina composta principalmente de íons HO^- e HS^-, em temperaturas na faixa de 150 - 170 °C. Neste processo, a lignina é efetivamente degradada (aproximadamente 90-95% da lignina é removida) em fragmentos solúveis em álcali (Pinto et al., 2005). Vários parâmetros do processo influenciam a química e a eficiência da deslignificação alcalina, incluindo tempo/temperatura (fator H), carga alcalina efetiva (AE), sulfidez, etc. Esses parâmetros afetam as características da polpa resultante quanto à natureza e conteúdo de seus principais componentes, nomeadamente: celulose, hemiceluloses e lignina (Colodette et al., 2002).

O processo kraft apresenta uma série de vantagens quando comparado a outros processos, especialmente em termos de resistência da fibra. As desvantagens também estão presentes, sendo a principal delas uma perda no rendimento da polpa causada pela instabilidade e degradação dos carboidratos durante a reação alcalina,que ocorrem, principalmente por hidrólise e eliminação sequencial dos grupos terminais redutores (Nieminen et al., 2014).

As hemiceluloses são mais suscetíveis à hidrólise alcalina que a celulose, devido ao seu baixo grau de polimerização, estado amorfo e acessibilidade ao licor de polpa. Portanto, a degradação da hemicelulose é responsável por uma parte significativa da perda de rendimento total observada durante a produção de celulose Kraft (Clark, 1985; Sjöström, 1993). A principal hemicelulose da madeira de folhosas é o O-acetil-4-O-metilglucuronoxilana (Hutterer et al., 2016). Para minimizar essas perdas, é importante ter uma boa e confiável compreensão do processo (Froass et al., 1998).

As principais abordagens para evitar a perda de rendimento são: retardar ou evitar as reações de degradação de carboidratos, aumentar a taxa de deslignificação e melhorar o fenômeno de transferência de massa durante o cozimento (Colodette e Gomes, 2014).

Reduzir o álcali efetivo residual (AER) no final do cozimento aparece como uma alternativa interessante para melhorar o desempenho do cozimento kraft, uma vez que permite um maior rendimento de polpa pela precipitação de xilanas sobre as fibras, além de diminuir a carga de álcali efetivo(AE) utilizada no processo (Colodette eGomes, 2014; Goyal, 2017). Em aplicações industriais, oAER pode variar entre 4-18 g/L. No entanto, o intervalo de 7-9 g/L éo mais comum. Para algumas indústrias, o AER pode ser diminuído sem impactos negativos na operação do ciclo de recuperação kraft (Colodette e Gomes, 2014). O cozimento Kraft em baixo AER pode realmente apresentar certas vantagens econômicas, pois a baixa demanda de AE implica uma menor carga de caustificação diminuindo,dessa forma, os custos no ciclo de recuperação (Goyal, 2017; Hanson e Hartler, 1969; Hanna, 1998)

O cozimento Kraft em baixoAER pode ter algum impacto na química e na estrutura da lignina residual que permanece na polpa, com consequências nas operações subsequentes de deslignificação com oxigênio e branqueamento (Matsushita, 2015).

Portanto, para desenvolver processos seletivos de deslignificação/ branqueamento, que atende aos altos requisitos de uma polpa química branqueada no que diz respeito à adaptação ambiental, economia de energia e estabilidade do processo, é essencial entender como a lignina residual pode ser afetada pelo cozimento com baixo e altoAER e qual o impacto disso na operação de branqueamento.

A lignina pode ser vagamente definida como um polímero tridimensional contendo vários grupos funcionais que afetam sua reatividade. Estes incluem grupos metoxílicos, carbonílicos, carboxílicos e hidroxílicos que se ligam a porções aromáticas ou alifáticas, em várias quantidades e proporções, conduzindo a diferentes composições e estruturas de lignina(Mancera et al., 2011). Apenas uma pequena proporção dos grupos hidroxílicos fenólicos está livre, já que a maioria está ocupada em ligações, com ligações vizinhas de fenilpropano.

O principal objetivo do branqueamento é remover as estruturas residuais de lignina e cromóforo da polpa. O aumento da alvura da polpa durante o processo de fabricação resulta em menores custos com produtos químicos de branqueamento e reduz o impacto ambiental dos processos de branqueamento à base de dióxido de cloro. Tais razões explicam a ampla aceitação das tecnologias de processos kraft modificados na indústria de celulose e papel nos últimos anos.

A composição de carboidratos da polpa, o conteúdo de lignina álcali-lixiviável e grupos fenólicos, complexos de lignina-carboidrato e HexA presentes em polpas kraft de madeira de *Eucalyptus* são provavelmente os fatores subjacentes que afetam a branquabilidade e a estabilidade de alvura de polpas branqueadas, mas sua importância relativa não é claramente entendida para a polpa kraft deeucalipto. Uma melhor compreensão do efeito das condições de polpação na química da polpa pode levar a melhores formas de produzir polpa kraft branqueada de eucalipto.

A fragmentação da macromolécula de lignina, durante o processo de cozimento, prossegue através da clivagem das ligações que mantêm as unidades fenilpropano juntas. Como as ligações carbono - carbono (C - C) são estáveis em condições alcalinas, a clivagem das ligações oxigênio - carbono (C - O - C) é a reação mais significativa no processo de cozimento. Na lignina residual da polpa kraft, 25% a 40% das estruturas aromáticas têm sido relatadas como fenólicas (Gellerstedt e Lindfors, 1984). A presença desses grupos hidroxílicos aumenta a hidrofilicidade dos fragmentos de lignina na operação de deslignificação e branqueamento com oxigênio.

De acordo com Gellerstedt e Lindsfors(1987) e Gellerstedt et al., (1999), dois fatoresinfluenciam a solubilização da lignina durante o branqueamento com oxigênio. O primeiro é a quantidade de grupos hidroxílicos, uma vez que a lignina é praticamente insolúvel em solução aquosasem estes grupos, e o segundo é a redução do tamanho das macromoléculasde lignina degradada, o que facilita o transporte de lignina para fora da parede celular. Do ponto de vista de reatividade, os grupos hidroxílicos fenólicos livres são os grupos funcionais mais importantesna lignina (Toven e Gellerstedt, 1999).

Em comparação com a lignina de madeira nativa, as ligninas kraft residuais e dissolvidas têm um maior conteúdo de grupos fenólicos livres (com ligninas dissolvidas com uma quantidade significativamente maior de tais grupos), uma menor quantidade de ligações β-O-4 (em ligninas residuais são encontradas cerca de 15% da quantidade mensurada em uma amostra de lignina de madeira) e uma proporção razoavelmente grande de átomos de carbono saturados de cadeia lateral com ligações apenas com carbono e hidrogênio (Prinsen et al., 2013; Gellerstedt et al., 2004). Ligninas residuais extraídas a partir de polpas com baixo teor de lignina (número kappa baixo) tendem a conter menos grupos hidroxílicos alifáticos e estruturas β-O-4, e maiores teores de grupos hidroxílicos fenólicos, ácidos carboxílicos e estruturas condensadas em comparação com as ligninas a partir de polpas de elevado teor de lignina (número kappa maior) (Froass, 1996). Uma das principais alterações que ocorrem durante o cozimento kraft convencional é um enriquecimento progressivo de ácidos carboxílicos e grupos hidroxílicos fenólicos condensados (Gellerstedt e Lindfors, 1991). No final do cozimento kraft, a lignina residual contém três vezes mais grupos fenólicos C-5 condensados do que aqueles presentes na amostra de lignina de madeira inicial (Gellerstedt and Lindfors, 1991).

Tradicionalmente, a lignina a partir de polpa não branqueada pode ser isolada por meio de um coquetel de enzimas celulolíticas que removem celulose e hemicelulose da polpa, deixando a maior parte da lignina como resíduo sólido (Argyropoulos et al., 2002) A elucidação de detalhes estruturais de ligninas residuais constitui o desafio mais importante e pré-requisito para melhorias adicionais na tecnologia de cozimento kraft. As mudanças na estrutura da lignina residual refletem as reações que ocorrem durante as operações de cozimento. Com esse conhecimento, relações confiáveis de estrutura-propriedade podem ser estabelecidas, o que, por sua vez, cria a base para melhorar ainda mais a seletividade e a eficiência da tecnologia de cozimento kraft.

Neste contexto, o objetivo deste estudo foi avaliar o impacto do álcali efetivo residual baixo e alto (1-2 e 8-9 g L^{-1} NaOH), do cozimento kraft de eucalipto e grau de deslignificação da polpa (número kappa 14 à 26) no rendimento da polpa marrom e desempenho do processo de branqueamento livre de cloro (ECF), além de fornecer uma visão mais aprofundada sobre como o álcali efetivo residual variável pode afetar os grupos funcionais da lignina residual da polpa (grupos hidroxílico e carboxílico).

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PAPER 1:EFFECT OF RESIDUAL EFFECTIVE ALKALI ON *EUCALYPTUS* KRAFT PULP YIELD AND CHEMISTRY

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ABSTRACT

The impact of residual effective alkali (REA) and pulp delignification degree on Eucalyptus kraft pulp yield and chemistry was investigated. In this study four types of eucalypt clones were evaluated. The eucalypt woods were cooked to kappa numbers of 14±1, 18±1, 22±1 and 26±1 using two different ranges of REA, namely: low-REA (1-2 g L^{-1}) and high-REA (8-9 g L^{-1}). In general, the low-REA cooks lead to pulps of higher yield, viscosity and xylans content and lower brightness and hexenuronic acid (HexA) content, in relation to the high-REA cooks. In addition, the low-REA cooks required about 20% less effective alkali to achieve the target kappa, in spite of demanding about 50% more H-factor. Similar trends were observed for the other woods and kappa values evaluated, but the level of gains varied substantially among woods and delignification degrees. Among the various woods, *E. globulus* was the easiest to delignify. There was a trend of higher brown pulp yield for the cooks terminated at higher kappa in the range of 14-26, but the lignin-HexA free screen yields were about similar in the kappa range of 18-26 for a given wood type.

Keywords:Yield; kappa number; *Eucalyptus*.

1. INTRODUCTION

Kraft pulping is the most widely used process for production of chemical pulps (Gullichsen & Fogelholm, 2000). Wood chips are treated with a strong alkaline solution composed mainly of HO^- and HS^- ions, at temperatures about 150 – 170 °C (Pinto, et al., 2005). Several process parameters influence the chemistry and efficiency of alkaline delignification, including time/temperature (H-factor), effective alkali charge (EA), sulfidity, etc. These parameters affect the characteristics of the resulting pulp regarding the nature and content of its main components, namely: cellulose, hemicelluloses and lignin (Colodette et al., 2002).

During the kraft process, wood delignification is accompanied by simultaneous and undesirable dissolution of carbohydrates mainly by alkaline hydrolysis and sequential elimination of the terminal reducing end groups(Nieminen et al., 2014). Hemicelluloses are more susceptible to alkaline hydrolysis than cellulose due to their low degree of polymerization, amorphous state, and accessibility to the pulping liquor. Therefore, the loss of hemicelluloses is responsible for a significant part of the total yield loss observed during Kraft pulping (Clark, 1985; Sjöström, 1993). The main hardwoods hemicellulose is the O-acetyl-4-O-methylglucuronoxylan (Hutterer et al., 2016).

Increment in pulp yield is a major goal of a chemical process, since it allows increased mill throughput and reduced specific wood consumption. For this purpose, the main approaches to meet such goal are: retarding or avoiding the carbohydrate degradation reactions, increasing delignification rate, and enhancing the mass transfer phenomenon during cooking (Colodette and Gomes, 2014). In this context, lowering the residual effective alkali (REA) at end of cook appears as an interesting alternative to enhance kraft pulping performance, since allows a higher pulp yield by xylan precipitation onto the fibers (Goyal, 2017; Pinto et al., 2005). Currently the REA varies between 4 to 18 g/L for various mills. However, the range of 7-9 g/L is more common. For some mills the REA target can be lowered without affecting the operation of evaporator and the recovery boiler (Goyal, 2017).

Kraft cooking at low-REA presents certain economic advantages because the low EA demand implies less causticizing load, thus decreasing costs in the recovery cycle (Goyal, 2017; Hansson and Hartler 1969; Hanna et al.1998). On the other hand, there are some drawbacks. Cooking at low-REA demands higher H-factors, which can be provided by either increasing the cooking reaction time or the temperature. However, the increase in temperature results in larger steam consumption and therefore is economically disadvantageous (Nesselrodt, et. al., 2015).

Another issue related to low-REA cooking is the potential risk of lignin precipitation, which may have considerable consequences in the bleaching costs and in the pulps bleachability as well as in the black liquor management due its increased viscosity with consequent system (Goyal, 2017; Hansson and Hartler 1969; Hanna et al.1998). However, Goyal (2017) showed that the cooking with low-REA did not show any appreciable difference of bleachability of the pulps, between pulps cooked with low-REA compared to high-REA pulps, and always results in higher pulp yield at a given delignification degree. Based on these results, a range of REA is recommended no loss on bleaching and with satisfactory pulp yield. Therefore, when considering low-REA cook one must balance the benefits and drawbacks.

Another important aspect linked to the increment in pulp yield is the kappa number itself. A very old cooking rule states that terminating a cook at high kappa number results in high pulp yield (Segura et al., 2016; MacLeod, 2007). Although this rule is very true when comparing total pulping yields, it is not so reliable for comparing to screened yields. Yield comparisons at different kappa numbers are usually not fair unless the results are compared at fixed REA and only lignin and HexA-free screen yield (Lignin HexA- free screen yield) be considered. Fair cooking yield comparison shall be done with the screened yield and not total yield because rejects are not fibers and they are usually discarded or very poorly reused in subsequent pulping cycles. In addition, if bleached pulp grades are sought after, one must compare the screen yields discounting their contents of lignin and HexA, the so-called lignin and HexA-free screened yield. This is necessary because during bleaching both lignin and HexA are largely removed and their weight shall not be accounted for in the yield measurements.

Besides, it is of paramount importance that cooking results be compared at similar REA, otherwise the yield results are meaningless (Colodette and Gomes, 2014). The only way to meet these constraints is by playing with both effective alkali charge and cooking time-temperature (H-factor) so that at the end of the cook, different kappa numbers are achieved at similar REA. This is exactly what was done in this study and it is a novelty in relation to previous studies.

In addition, wood type can also substantially affect pulp yield, as well as quality of the brown pulp, because *Eucalyptus* wood-fiber characteristics may vary substantially among the various species and clones as well as with age (Magaton et al., 2009). Thus, the pulping can affect in different way its composition, like as residual lignin nature, pulp carbohydrate composition, and the contents of alkali-leachable lignin and HexA present in hardwood kraft pulps (Colodette, 2002). Therefore, in this study was used four different types of Eucalyptus wood, typically used in pulp manufacture, for the greater reliability of the results obtained.

In this context, the objective of this study was to evaluate the impact of low and high residual effective alkali (1-2 and 8-9 g L^{-1} NaOH), and pulp degree of delignification (kappa number 14-26) on the performance of kraft cooking *Eucalyptus* woods typically used in pulp manufacture.

2. MATERIALS AND METHODS

The feedstock consisted of wood chips from *E. urophylla* x *E. grandis* hybrid, seven year old, grown in Brazil, and wood chips from *E. nitens* and *E. globulus*, sixteen years old, *E nitens* x *E. globulus* hybrid, twelve years old, all grown in Chile. The chips were classified according and air-dried conditioned SCAN-CN 40:94 standard procedure, dried to about 15% moisture, and stored for further use. A fraction of the air-dried accepts were used to evaluate the wood chemical composition. The chips were converted into sawdust in a knife-mill (Willey Co, USA), classified according to TAPPI T257cm-85 standard and air-dried to ~10% moisture.

The chemical composition was carried out on extractive-free wood sawdust (T280 pm-99). The contents of acid-soluble lignin (Goldschmid, 1971), acid-insoluble lignin (T222 om-97), lignin syringyl/guaiacyl ratio (Lin and Dence, 1992), ash content (Tappi 211 om-93), sugars content (Wallis et al., 1996), total uronic acid (Scott 1979) and acetyl groups (Solár et al., 1987) were quantified. The wood basic density was measured according to SCAN-CM46:92 standard procedures.

The kraft cooking of the four eucalyptus woods was performed in duplicate in a 7-L MK digester with 500 g of chips, oven dry (od) equivalent. The cooks were carried out with a liquor/wood ratio of 4 L:1 kg, 30% sulfidity, maximum temperature of 165 °C, 70-min time-to-temperature and variable effective alkali charge and time-at-temperature to meet the kappa number targets of 14±1, 18±1, 22±1 and 26±1 and the low (1-2 g L^{-1} NaOH) and high (8-9 g L^{-1} NaOH) residual effective alkali (REA) for the various woods. By varying the time at the maximum temperature of 165 °C (H-factor) and the EA charge applied, using the trial-and-error technique, it was possible to meet the desired REA ranges at given kappa numbers. At the end of each cook, the chips were discharged and disintegrated in a 20-L hydrapulper at 2% consistency, washed and screened in an equipment (Voith Co., Germany) garnished with a flat screened of 0.2 mm slots, and at the end of this stage the rejects were collected. The screened pulps were analyzed for extractives content (TAPPI T280 pm-99), ash content (TAPPI T-211 om-93), total uronic acid (Scott 1979) kappa number (TAPPI T236 cm-85), HexA content (TAPPI T282 pm-07), viscosity (SCAN-CM 15:99), pentosans (TAPPI T280 om-99), sugar composition (SCAN- CM 71:09) and brightness (T525 om-92). From the values of kappa number and HexA, the corrected kappa number values (only lignin) were determined according to the procedure described by Li and Gellerstedst (1997). The black liquor was analyzed for residual effective alkali (SCAN-N 33:94).

3. RESULTS

3.1.Basic density and chemical composition of wood

Basic density and chemical composition of the various *Eucalyptus* woods investigated in this study are presented in Table 1.

Table 1. Basic density and chemical composition of *Eucalyptus* wood

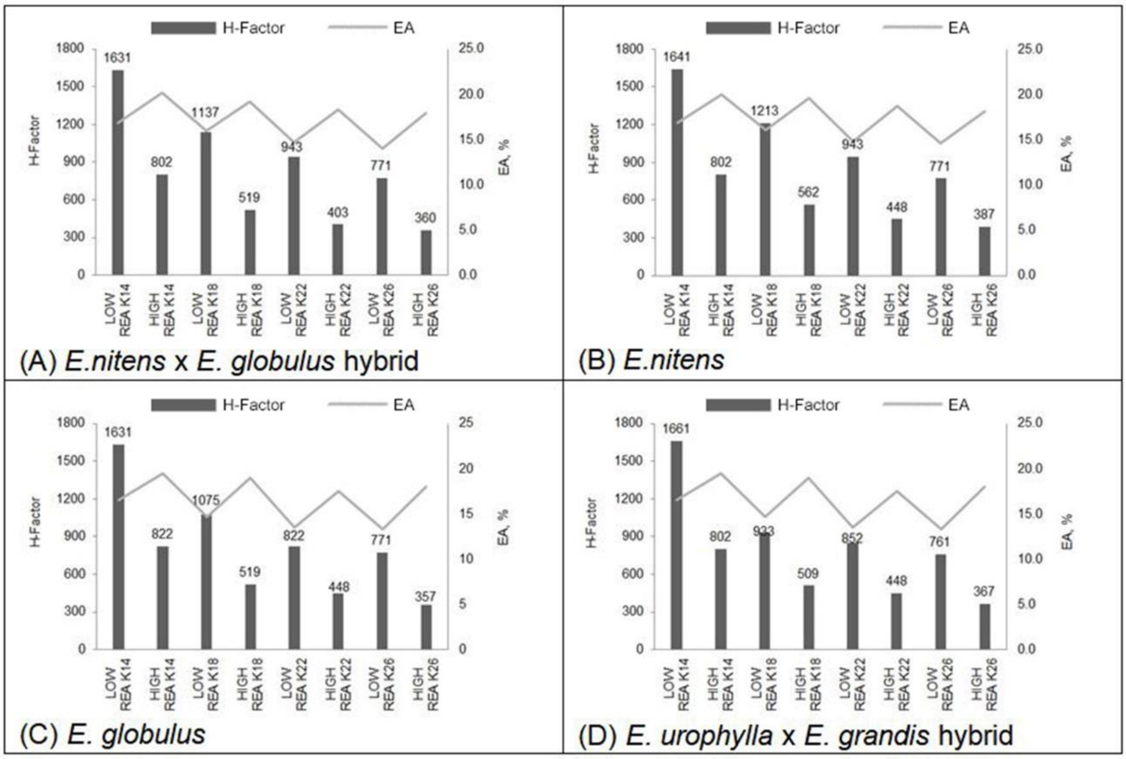
Wood trait	*E. nitens* x *E. globulus* hybrid	*E. nitens*	*E. globulus*	*E. urophylla* x *E. grandis* hybrid
Basic density, kg m^{-3}	493	521	562	452
Ash, %	0.31	0.21	0.31	0.26
Extractives in acetone, %	1.9	1.5	2.2	1.3
Acid-insoluble lignin, %	20.6	20.7	19.5	24.0
Acid-soluble lignin, %	5.6	5.0	5.2	4.1
Total lignin, %	26.2	25.7	24.7	28.1
Lignin S/G ratio	4.7	3.4	4.8	2.9
Acetyl Groups, %	2.5	2.3	2.3	2.1
Total uronic acids, %	2.7	3.1	2.5	2.8
Glucans, %	48	49	52.0	52.1
Xylans, %	16.2	16.7	14.2	11.6
Galactans, %	0.9	0.9	1.4	1.3
Mannans, %	1.2	1.4	1.0	0.8
Arabinans, %	0.3	0.2	0.3	0.2
Total Sugar, %	66.6	68.2	68.9	66
Cellulose[a], %	46.8	47.6	51.0	51.3
Hemicelluloses[b], %	25.0	26.0	22.7	19.6

Cellulose[a] = total glucans – glucans from glucomannans (1/1); hemicelluloses[b] = xylans + mannans + galactans + arabinans + (2 x glucans from glucomannans) + uronic acids + acetyl groups.

3.2. Kraft pulping

3.2.1. *Impact of REA, kappa number and wood type on EA charge and H-factor requirements*

The values of H-factor and EA charge required to achieve kappa numbers of 14-26, with low-REA and high-REA, for the four wood types are show in Figure 1.



(A) *E.nitens* x *E. globulus* hybrid

(B) *E.nitens*

(C) *E. globulus*

(D) *E. urophylla* x *E. grandis* hybrid

Figure 1. Effect of low and high residual effective alkali and kappa number variations on effective alkali charge and H factor requirements in kraft pulping of four Eucalyptus woods.

3.2.2. Impact of REA, kappa number and wood type on lignin-HexA free pulp screen yield

By considering pulps of different kappa numbers and similar REA, it was possible to investigate the impact of kappa number on lignin-HexA free screen yield and establish why different kappa numbers produce different yields (Table 2).

Table 2. Effect of kappa number on screened yield and lignin HexA-free yields in low-REA and high-REA kraft pulping of four eucalypt woods

Parameter and Results								
E. nitens x *E. globulus* hybrid								
Kappa Number	14		18		22		26	
REA, g/L	1.0	8.2	1.2	8.1	1.0	8.3	1.1	8.0
Black liquor pH	12.1	12.8	12.1	12.7	12.2	12.8	12.1	12.8
Screen yield, %	51.7	50.8	52.7	51.6	53.1	51.7	53.1	51.1
[a]L-HexA free Screen yield, %	50.3	49.4	50.9	49.9	51.0	49.7	50.6	48.8
Reject, %	0.0	0.2	1.3	1.2	2.6	3.0	4.0	4.5
[b]Δ due to decrease REA	0.9		1.0		1.3		1.8	
E. nitens								
Kappa Number	14		18		22		26	
REA, g/L	1.3	8.0	1.0	8.9	1.0	9.0	1.0	8.4
Black liquor pH	12.1	12.7	12.1	12.8	12.2	12.8	12.2	12.8
Screen yield, %	52.2	51.4	54.1	53.0	54.9	53.5	54.6	52.8
[a]L-HexA free Screen yield, %	50.9	50.0	52.4	51.3	52.8	51.4	52.1	50.4
Reject, %	0.1	0.3	0.3	0.4	1.1	1.1	2.8	3.0
[b]Δ due to decrease REA	0.9		1.1		1.4		1.7	
E. globulus								
Kappa Number	14		18		22		26	
REA, g/L	1.3	8.2	1.2	8.1	1.0	8.5	1.0	8.7
Black liquor pH	12.2	12.7	12.1	12.7	12.1	12.8	12.1	12.8
Screen yield, %	53.9	53.0	54.8	53.7	55.1	53.7	54.9	53.2
[a]L-HexA free Screen yield, %	52.4	51.6	52.9	51.9	52.9	51.6	52.3	50.7
Reject, %	0.1	0.3	1.5	1.2	3.0	3.2	3.8	4.4
[b]Δ due to decreased REA	0.9		1.0		1.3		1.6	
E. urophylla x *grandis* hybrid								
Kappa Number	14		18		22		26	
REA, g/L	2.0	9.0	1.8	9.0	1.0	8.3	1.1	9.0
Black liquor pH	12.1	12.8	12.1	12.7	12.1	12.7	12.1	12.8
Screen yield, %	52.5	52.0	53.7	52.7	54.3	52.9	54.3	52.4
[a]L-HexA free Screen yield, %	51.1	50.6	51.9	51.0	52.2	50.8	51.8	50.0
Reject, %	0.0	0.2	0.4	0.6	1.2	1.5	2.1	2.3
[b]Δ due to decreased REA	0.5		0.9		1.3		1.8	

[a]Lignin-HexA Free Screen Yield = Screen yield – (lignin yield + HexA yield). [b]ΔLignin-HexA Free Screen Yield due to decrease REA.

3.2.3. Impact of REA, kappa number and wood type on brown pulp chemical and physical compositions

The brown pulp chemical and physical characteristics are reported in Figure 2, Figure 3 and Table 3. The brown pulp xylan content refer to the xylan backbone only.

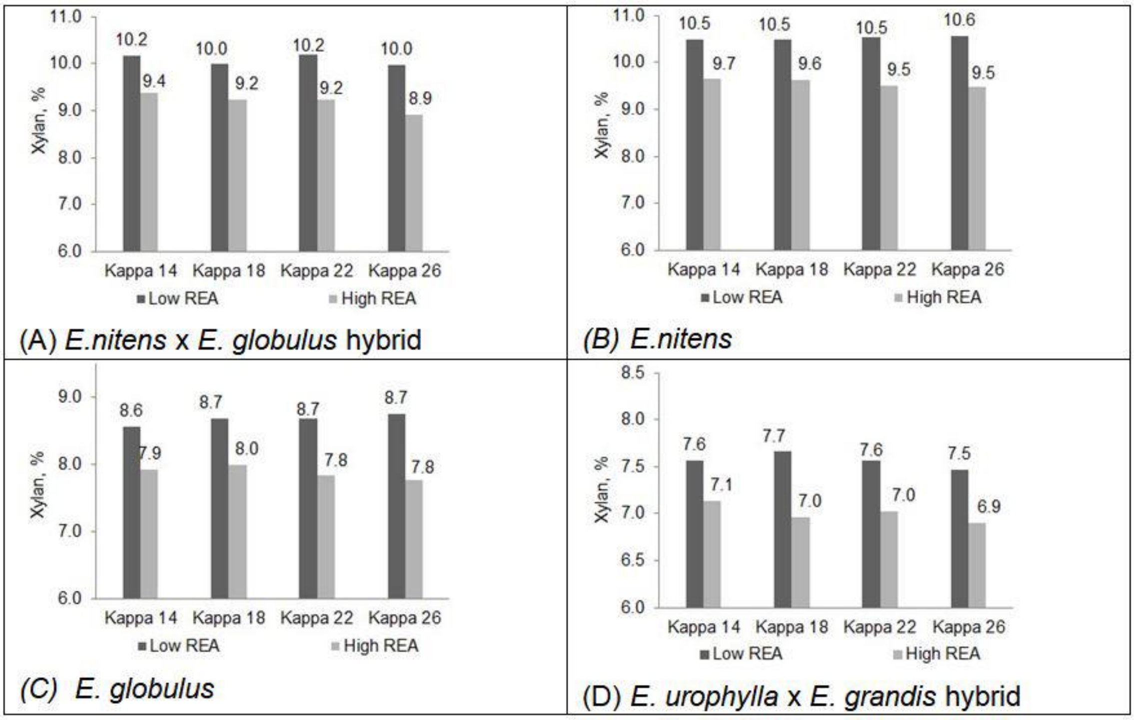


Figure 2. Effect of low and high REA and kappa number variations on pulp xylan backbone contents in kraft pulping of four eucalypt woods.

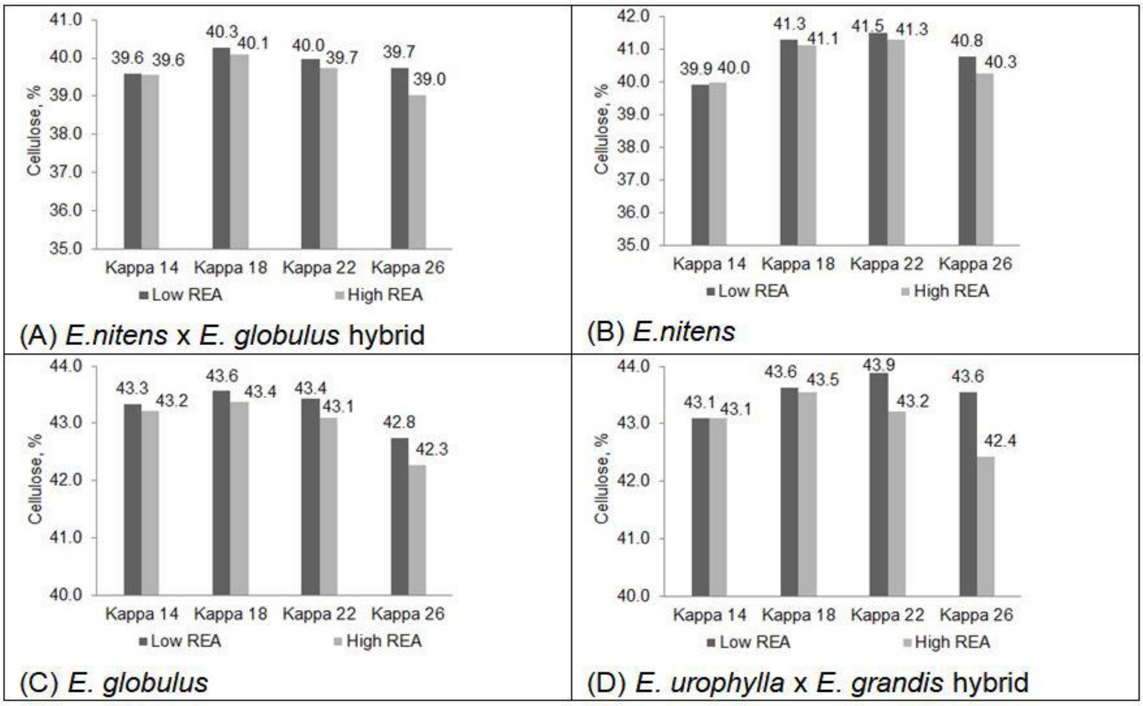


Figure 3. Effect of low and high REA and kappa number variations on pulp cellulose contents in kraft pulping of four eucalypt woods.

Table 3. Contents of lignin, HexA and MeGlcA and physical characteristic of unbleached pulps, viscosity and brightness, derived from cooks to kappa numbers of 14-26 at low-REA and high-REA of four *Eucalyptus* wood species

Parameter and Results								
E. nitens x E. globulus hybrid								
Kappa Number	14		18		22		26	
REA, g L^{-1}	1.0	8.2	1.2	8.1	1.0	8.3	1.1	8.0
[a]Lignin content, %	1.2	1.3	2.0	1.9	2.7	2.6	3.4	3.2
HexA content, %	1.0	1.10	0.92	0.99	0.78	0.91	0.65	0.86
MeGlcA, %	1.1	0.9	1.3	1.1	1.6	1.4	1.9	1.6
Viscosity, dm^3 kg^{-1}	1059	990	1189	1096	1280	1181	1389	1270
Brightness, %ISO	33.0	35.6	30.4	34.1	29.2	32.9	28.4	32
E. nitens								
Kappa Number	14		18		22		26	
REA, g L^{-1}	1.3	8.0	1.0	8.9	1.0	9.0	1.0	8.4
[a]Lignin content, %	1.3	1.2	2.0	1.9	2,7	2.6	3.3	3.2
HexA content, %	0.97	1.10	0.91	0.95	0.80	0.88	0.73	0.84
MeGlcA, %	1.0	0.8	1.2	1.0	1.4	1.2	1.6	1.3
Viscosity, dm^3 kg^{-1}	1035	967	1191	1100	1292	1176	1400	1280
Brightness, %ISO	33.4	37.8	31.3	36.2	30.4	34.8	29.9	34.3
E. globulus								
Kappa Number	14		18		22		26	
REA, g L^{-1}	1.3	8.2	1.2	8.1	1.0	8.5	1.0	8.7
[a]Lignin content, %	1.4	1.3	2.0	1.9	2.7	2.6	3.4	3.2
HexA content, %	0.86	0.92	0.81	0.86	0.72	0.84	0.64	0.81
MeGlcA, %	1.1	0.9	1.3	1.0	1.5	1.2	1.6	1.4
Viscosity, dm^3 kg^{-1}	1090	1034	1184	1110	1309	1190	1425	1277
Brightness, %ISO	29.3	31.9	28.0	31.4	26.7	28.5	24.8	27.7
E. urophylla x grandis hybrid								
Kappa Number	14		18		22		26	
REA, g L^{-1}	2.0	9.0	1.8	9.0	1.0	8.3	1.1	9.0
[a]Lignin content, %	1.3	1.1	1.9	1.8	2.6	2.5	3.4	3.1
HexA content, %	1.1	1.2	1.0	1.1	0.86	1.1	0.65	1.0
MeGlcA, %	0.9	0.8	1.2	1.0	1.4	1.2	1.6	1.4
Viscosity, dm^3 kg^{-1}	1009	963	1180	1130	1311	1240	1400	1330
Brightness, %ISO	34.8	37.4	32.9	36.8	31.2	35.7	29.9	34.2

[a]Lignin content = 0.15 x (k – 0.086 x C_{HexA}), where k is the kappa number, and C_{HexA} is HexA content in mmol/kg (Li & Gellerstedt,1997).

4. DISCUSSION

4.1. Wood density and chemical composition

Basic densities were very different among the samples. The highest and lowest measured densities were for *E. globulus* (562 kg m^{-3}) and *E. urophylla* x *E. grandis* hybrid (452 kg m^{-3}), respectively. These density values are typical of *Eucalyptus* woods used in pulp manufacture in South America (Gomide et al, 2005). The acetone extractivecontents varied in the range of 1.3-2.2%, with maximum and minimum values for *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively. In general, these levels of extractives may be considered low compared to other tropical hardwoods (Gomide et al, 2005).

The ash content, which corresponds to the wood inorganic materials, was similar for *E. nitens* x *E. globulus* hybrid, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, with value of 0.3%, while for *E. nitens*, the ash content was slightly smaller, with value of 0.2%. Total carbohydrate content ranged from 66% to 69%, with glucan and xylan as the major components. There were slight variations in the contents of arabinans, galactans and mannans among the various wood species but overall the contents of these sugars were irrelevant, which is positive given their low stability throughout kraft cooking. Glucans content varied in the range of 48-52% with the higher values for *E. globulus* and the hybrid of *E. grandis* x *E. urophylla*.

The xylan contents varied in the range of 11.6-16.7% with higher values for *E. nitens* and the hybrid of *E. globulus* x *E. nitens*. Similar trends have been reported elsewhere (Magaton et al., 2006; Pinto et al., 2005). Total wood lignin content varied from 24% to 28% with the lowest value for *E. globulus* and the highest for *E. urophylla* x *E. grandis* hybrid. The lower content of lignin in *E. globulus* compared to others wood has been reported elsewhere (Santos et al., 2012; Pinto et al., 2005; Rencoret et al., 2007; Magaton et al., 2006).

The low wood lignin content is quite favorable for bleached pulp production because it reduces wood and chemical demand, which are the most relevant production costs components (Gomide 2005; Pinto et al., 2005; Rencoret et al., 2007). The wood contents of acetyl (2.1-2.5%) and uronic acid (2.5-3.1%) groups were in the range of values reported elsewhere (Magaton et al., 2009). More acetyl groups were found in the woods containing more xylans as should have been expected.

However, this trend was not observed for the uronic acids. In fact, the *E. urophylla* x *E. grandis* hybrid wood, which contained only 11.6% xylans, presented 2.8% of uronic acid groups, while the *E. nitens* x *E. globulus* hybrid had 16.2% xylans and only 2.7% uronic acids. The cellulose (46.8-51.3%) and hemicelluloses (19.6-26%) contents were very different among the various wood samples. The highest and lowest cellulose contents were measured for *E. urophylla* x *E. grandis* hybrid (51.3%) and *E. nitens* x *E. globulus* hybrid (46.8%), respectively. For hemicelluloses content, the highest and lowest values were measured for *E. nitens* (26%) and *E. urophylla* x *E. grandis* hybrid (19.6%), respectively.

4.2.Kraft pulping

4.2.1. Impact of REA, kappa number and wood type on EA charge and H-factor requirements

It is observed that the EA charge and H-factor were largely influenced by the target REA, with higher H-factors and low EA charge requirements for the low-REA cooks and the opposite for the high-REA cooks. Kraft cooking at low-REA presents certain economic advantages because the low EA demand implies less causticizing load, thus decreasing costs in the recovery cycle. In addition, cooking with low EA tend to preserve carbohydrates during cooking with potential yield and pulp viscosity gains (Pinto et. al., 2005). On the other hand, cooking at low-REA demands higher H-factors, which can be provided by either increasing the cooking reaction time or the temperature. In a mill scale, the natural choice would be increasing the temperature because the increase in reaction time would decrease mill throughput.

Therefore, when considering low-REA cook one must balance the cost savings due to reduced causticizing load against the increase in steam consumption or the increase in reaction time (Nesselrodt et. al., 2015). This is a difficult calculation to be mendeadly when we consider the different needs of mills. For some mills the REA target can be lowered without affecting the cost the operation of evaporation, the recovery boiler and mill throughput. For example, for some mills, the lower white liquor requirement, hence, an energy savings in lime kiln, is a positive factor if recovery boiler limited. This can permit the increase in reaction time can be possible without change about costs.

In average, considering all four woods, the low-REA cooks required about 20% less effective alkali to achieve the target kappa in relation to the high-REA cooks. For example, for the *E. urophylla* x *E. grandis* hybrid wood, the low-REA cooks allowed for EA charge savings of 26 and 15% for kappa numbers 26 and 14, respectively, in relation to the high-REA cooks. However, low-REA cooks demanded, in average, about 50% more H-factor in relation to the high-REA cooks, considering all four *Eucalyptus* woods and kappa number values. The maximum and minimum H-factor increases due to low-REA cooks were 57% and 45% for *E. nitens* x *E. globulus* hybrid cooked at kappa 22 and 18, respectively. In addition, in the kappa number range investigated, 14-26, the EA charge and H-factor requirements tend to decrease as the reduction of delignification degree. No significant effect of wood type was observed on EA charge and H-factor requirements for a given REA and kappa number value.

4.2.2. Impact of REA, kappa number and wood type on lignin-HexA free pulp screen yield

In order to compare pulping screedned yield at different kappa numbers, the REA at the end of the cooks must be similar and only lignin and HexA-free screen yield must be considered. The only way to meet these constraints is by playing with both effective alkali charge and cooking time-temperature (H-factor) so that at the end of the cook, different kappa numbers are achieved at similar REA. This is exactly what was done in this study.

Various studies have indicated that higher brown pulp screen yields are obtained when cooking is terminated at higher kappa numbers (Segura et al., 2016; Colodette and Gomes, 2014; Colodette et al., 2007). This trend was also found in our study, except for kappa number 26, due to high reject content, as can be seen in Table 2. However, if one considers the lignin-and HexA-free screen yield (bleached yield), this trend is not so clear. The results presented in Table 2 show that the lignin-HexA free screen yield tend to remain similar with increasing kappa number, regardless of raw material and REA, except for the kappa number 14 pulp that showed lower yields in relation to those of kappa 18-26 pulps. For example, for *E. urophylla* x *E. grandis* hybrid cooked at low-REA, the lignin- and HexA-free yields were of 51.1, 51.9, 52.2 and 51.8% for kappa numbers of 14, 18, 22 and 26, respectively. Thus, the removal of lignin is the main cause of yield decrease in the kappa range of 18-26. For the kappa number 26, the reject content increased in relation to other kappa numbers, this is explaining the decreasing of the yield.

According to Santiago (2008), a decreasing in the effective alkali charge leads to increased pulping yield and selectivity thereof. This behavior was notable in this paper, since an increase maximum of 1.8% in the lignin- and HexA-free pulp screen yield was achieved at kappa number 26 for the low-REA cook, for both hybrids of *E. nitens* x *E. globulus* and *E. urophylla* x *E. grandis* woods. For kappa number 18, more commonly required by mill, a smaller yield gains were achieved in the order of 1.0% for *E. nitens* x *E. globulus* hybrid, 1.1% for *E. nitens*, 1.0% for *E. globulus* and 0.9% for *E. urophylla* x *E. grandis* hybrid (Table 2). The cooking with low residual effective alkali results higher yield, likely due to improved preservation of hemicelluloses and/or partial precipitation of dissolved xylans onto the fibers (Santiago and Neto, 2008; Colodette, et al., 2002).

As the pulping conditions, among woods, were very similar for a fixed kappa number, yield comparisons among the various woods is fair and possible. The maximum values of lignin-HexA free screen yields were 52.9, 52.8, 52.2 and 51.0% from *E. globulus* (kappa number 18)*, E. nitens*, *E.urophylla* x *grandis* hybrid, *E. nitens* x *E. globulus* hybrid (kappa number 22), respectively. It is worth noting that at the high-REA the same yield trends among the various woods was observed, except the absolute yield values were in general lower. *E. globulus* gave the highest yields and the *E. globulus* x *E. nitens* hybrid the lowest. The relative content of lignin in wood certainly contribute to different pulping performances of different *Eucalyptus* species, and, the differences observed between *E. globulus* and *E. nitens* x *E. globulus* hybrid are clearly related to this factor (Table 1). Also, it is worth noting that, despite there is the potential risk of lignin precipitation at low-REA cooking, that did not occur in this study, since the black liquor pH was about 12.2. According to Gomes (2001), at normal cooking conditions, the lignin precipitation occurs in pH lower that 12, being considerable in pH 9.5 In addition, the low-REA cooks can positively impact on other black liquor properties, with energy savings in black liquor evaporation due to high ratio organic to inorganic present in black liquor (Goyal, 2017; Hanna, 1998; Hanson and Hartler, 1969).

4.2.3. Impact of REA, kappa number and wood type on brown pulp chemical and physical compositions

The two main components of brown pulps are cellulose and hemicelluloses, with lignin and HexA representing a very small fraction of the pulp on a weight basis. The xylans are synonym of hemicelluloses in *Eucalyptus* kraft pulp. The contents of xylan backbone in the original woods were 16.2, 16.7, 14.2 and 11.6% for *E. nitens* x *E. globulus* hybrid, *E. nitens, E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively (Table 1).

The xylan backbone contents in the brown pulps produced in different kappa numbers at low-REA and high-REA, on wood weight, varied from 8.9-10.2, 9.5-10.6, 7.8-8.7, 6.9-7.7% for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively. Hence, it is clear that the xylans retained in the pulp correlates to the original xylan backbone content present in the wood. Significant amounts of the xylan backbone were lost across kraft cooking, with the effect being more significant for the high-REA cooks.

The xylan backbone loss across pulping, for the various kappa numbers and wood types, represented from 3.9% to 6.2% (wood basis) for low-REA cooks and from 4.5% to 7.3% (wood basis) for the high-REA cooks. In the low-REA cooks, considering all four kappa values, the relative xylan losses were 38, 37, 39 and 35%, respectively, for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid. In the high-REA cooks, the relative xylan losses were about 5% higher being 43, 43, 44 and 40%, respectively, for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid. No significant effect of kappa number value was observed on xylan retention for a given REA value, regardless of wood type. For example, for the *E. globulus* wood cooked at low-REA, the increase of kappa number from 14 to 26 resulted xylan losses of 39%, in both cases. Similar trends were observed for the other wood types.

No effect on xylan removal in different kappa numbers, for the various *Eucalyptus* woods are explained by the REA, which was carefully kept constant. On the other hand, when the focus is to analyze the effect of REA, the low-REA cooks led to smaller xylans losses, suggesting that effective alkali charge play a key role in the stability and retention of this polysaccharide during the pulping process. Previous works concerning the impact low-REA cooks on carbohydrate dissolution of unbleached pulp have demonstrated significantly increased both total yield and viscosity, for similar kappa number, which was mainly attributed to higher carbohydrates retention, especially xylan (Santiago, 2008; Achrén et al., 1998).

The contents of cellulose in the original woods were 46.8, 47.6, 51.0 and 51.3% for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively (Table 1). The cellulose contents in the brown pulps produced in different kappa numbers at low-REA and high-REA, on wood weight, varied from 39.0-40.3, 39.9-41.5, 42.3-43.6 and 42.4-43.9% for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively. Hence, it is clear that the cellulose retained in the pulp correlates to the original cellulose content present in the wood.

A smaller amount of the cellulose was lost across kraft cooking when compared to loss of xylan backbone, with the effect being more significant for the high-REA cooks. The cellulose loss across pulping, for the various kappa numbers and wood types, represented from 6.7% to 7.8% (wood basis) for low-REA cooks and from 7.0% to 8.3% (wood basis) for the high-REA cooks. In the low-REA cooks, considering all four kappa values, the relative cellulose losses were 15.0, 14.1, 15.3 and 15.1%, respectively, for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid. In the high-REA cooks, the relative cellulose losses were in average 0.6% higher being 15.4, 14.7, 15.7 and 16.2%, respectively, for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid.

No significant effect of kappa number value was observed on cellulose retention for a given REA value, regardless of wood type, except for kappa number 26. For example, for the *E. globulus* wood cooked at low-REA, the increase of kappa number from 14 to 26 resulted cellulose losses of 15.1 and 16.1%, respectively. Similar trends were observed for the other wood types.

The no effect on cellulose removal in different kappa numbers, for the various *Eucalyptus* woods are explained by the fixed REA, which was carefully kept constant. Already the difference found for kappa number 26 can be explained due to higher amount of reject obtained in the cooking. On the other hand, when the focus is to analyze the effect of REA, the low-REA cooks led to smaller celluloses losses, suggesting that effective alkali charge play a key role in the stability and retention of this polysaccharide during the pulping process. The higher cellulose loss in the high-REA cooks is explained by enhanced secondary peeling reactions in the presence of higher alkali concentration. In addition to xylans and cellulose, *Eucalyptus* brown pulp contains minor quantities of lignin, HexA and MeGlcA.

The lignin contents in the brown pulp produced in different kappa numbers and at low-REA and high-REA was calculated according to Li & Gellerstedt (1997). Higher amounts of the lignin were obtained for the low-REA cooks. The lignin content for the various kappa numbers and the four wood types, represented from 1.4% to 3.4% for low-REA cooks and from 1.1% to 3.1% for the high-REA cooks. As expected, the lignin content trends to increase as the kappa number increases in the range of 14-26. For example, for the *E. globulus* wood cooked at low-REA, the increase of kappa number from 14 to 26 resulted lignin content increase of 1.4 to 3.4%. Similar trends were observed for the other wood types. In general, no significant effect of wood type was observed on lignin content for a given REA and kappa number value, except to *E. globulus* that present the higher values of lignin, since HexA content was the smallest. The effect on lignin content at low and high cooks, for the various *Eucalyptus* woods and different kappa numbers are explained by lignin precipitation(Colodette, 2002). On the other hand, when the focus is to analyze the effect of kappa number and wood type on lignin content, there are clear trend that the increase of the kappa number lead to increases lignin content regardless of wood. However, the lignin content at kappa number fixed, to a given wood type, depends of HexA content formed during pulping (Magaton et al., 2008).

Higher amounts of the HexA were obtained for the high-REA cooks. The HexA content for the various kappa numbers and the four wood types, represented from 0.64 to 1.1% for low-REA cooks and from 0.81 to 1.2% for the high-REA cooks. In the kappa number range investigated, the HexA content increases as delignification proceeds. For example, for the *E. globulus* wood cooked at low-REA, the increase of kappa number from 14 to 26 resulted HexA decrease of 0.86 to 0.64%. Similar trends were observed for the other wood types. In general, no significant effect of wood type was observed on HexA content for a given REA and kappa number value, except to *E. globulus* that present the lower values of HexA.

The smaller HexA content found in low-REA cooks in relation to high-REA cooks can be associated to decrease of the reactions rate HexA formation, since the

EA charge is smaller to achieve target REA and the rate of formation/degradation of HexA was shown to depend essentially on HO^- (Gomide 2005; Hutterer et al., 2017). On the other hand, HexA content in pulps increased along the kraft pulping process due to adjusted the pulping time to obtain a target kappa number, while keeping the other pulping parameters at partially constant levels (Bergnor-Gidnert et al., 1998). The smaller amount of HexA in *E. globulus* in relation the others *Eucalyptus* species can be due to varying contents of 4-O-methyl-glucuronoxylans among species that influences the amount of HexA formed (Magaton et al., 2008).

The most of the uronic acids groups, present in hardwood, are 4-0-methylglycouronic acid group (MeGlcA). Therefore, it was assumed in this study, that the uronic acid quantified in the pulp are all 4-O-methylglycouronic acid group (MeGlcA). Higher amounts of the MeGlcA were obtained for the low-REA cooks. The MeGlcA content for the various kappa numbers and the four wood types, represented from 1.1 to 1.9% for low-REA cooks and from 0.8 to 1.3% for the high-REA cooks. In the kappa number range investigated, as kappa number decreases, the MeGlcA also decreases. For example, for the *E. globulus* wood cooked at low-REA, the increase of kappa number from 14 to 26 resulted MeGlcA increase of 1.1 to 1.6%. Similar trends were observed for the other wood types. In general, no significant effect of wood type was observed on MeGlcA content for a given REA and kappa number value, except to *E. nitens* x *E. globulus* hybrid that presented values slightly higher to kappa numbers 22 and 26.

The higher MeGlcA content found in low-REA cooks in relation to high-REA cooks can be associated to smaller xylans losses and decreased formation rate of HexA, since the MeGlcA are the precursors of HexA (Gomes et al., 2014; Magaton, 2008). On the other hand, MeGlcA content in pulps increased as the kappa number increases due to adjusted the pulping time (decreasing of H-factor) to obtain a target kappa number, while keeping the other pulping parameters at partially constant levels (Monrroy et al., 2008). The higher amount of MeGlcA in *E. nitens* x *E. globulus* hybrid in relation the others *Eucalyptus* species can be due to varying contents of 4-O-methyl-glucuronoxylans among species that influences the remaining amount of MeGlcA in pulp (Magaton et al., 2008).

A clear tendency of viscosity improvement in pulps from low-REA cooks was observed, representing relative estimated viscosity gains of 93 $dm^3\ kg^{-1}$ for *E. nitens* x *E. globulus* hybrid, 91 $dm^3\ kg^{-1}$ for *E. nitens*, 74 $dm^3\ kg^{-1}$ for *E. globulus* and

50 dm^3 kg^{-1} for *E. urophylla* x *E. grandis* hybrid in relation to pulps from high-REA cooks, when cooked to kappa number 18. The viscosity gains increase as the kappa number increases. For example, considering all four woods, the pulps cooked to kappa number 26 from low-REA cooks had the viscosity gains of about 120 dm^3 kg^{-1}. In the kappa number range investigated, 14-26, the viscosity loss increases as the kappa number decreases (delignification increases). For example, for the *E. globulus* wood cooked at low-REA, the decrease of kappa number from 26 to 14 resulted viscosity decrease of 1425 to 1090 dm^3 kg^{-1}. Similar trends were observed for the other wood types. In general, no significant effect of wood type was observed on viscosity for a given REA and kappa number value.

The higher viscosity values found in pulps from low-REA cooks in relation to high-REA cooks is associated to higher preservation of cellulose due to possible decrease of alkaline hydrolysis reactions and consequently the secondary peeling reactions in the cellulose chains(Santiago, 2008; Santiago and Neto, 2008). On the other hand, viscosity in pulps decreased along the kraft pulping process due to higher degradation of the carbohydrate chains (Gomide et al., 2011). Similar viscosity values found among the four wood types, for a given REA and kappa number value, can be due to keeping the pulping parameters at partially constant levels.

A negative impact on pulp brightness was caused by the decrease of REA concentration in the pulping process. For example, for the *E. globulus* wood cooked in kappa number 18, the cooks at low-REA in relation to high-REA resulted brightness decrease of 31.4 to 28%ISO. As expected, in the kappa number range investigated, 14-26, the brightness increases as delignification proceeds. For example, the decrease of kappa number from 26 to 14 for the *E. globulus* wood cooked at low-REA, resulted brightness increase of 24.8 to 29.3% ISO. Similar trends were observed for the other wood types. Significant effects of wood type were observed on brightness for a given REA and kappa number value, mainly for *E. urophylla* x *E. grandis* hybrid (32.9% ISO) and *E. globulus* (28% ISO) that present the higher and the smaller brightness, respectively, for brown pulps produced in kappa numbers 18 and at low-REA.

The smaller brightness obtained in pulps from low-REA cooks in relation to high-REA cooks can be explained by the decrease in the content of aliphatic hydroxyl groups and the carboxyl groups in the residual lignin(Colodette et al., 2002). It was reported by Aurell and Hartler (1965) as well, that a low residual alkali concentration in the cook gives rise to pulps with a low brightness due to a formation of chromophoric structures in the lignin. Also, Hartler and Norrström (1969) demonstrated that applying a high H-factor to reach a given kappa number is accompanied by a low residual amount of β-O-4 structures in the residual lignin. On the other hand, brightness in pulps decreased as the reduction of delignification degree due to higher amount of residual lignin in the pulp (Gustavsson, 2006). The different brightness values found among the wood types studied, to a given REA and kappa number value can be explained by HexA and lignin content that composing the kappa number (Costa and Colodette, 2007).

5. CONCLUSION

This study investigates the effect of residual effective alkali (low and high) and pulp degree of delignification (kappa 14-26) on the performance of kraft cooking of four Eucalyptus woods. Regardless of wood type, low-REA cooks required about 20% less effective alkali than high-REA ones to achieve the target kappa values. Among the various woods, *E. globulus* was the easiest to delignify. There was a trend to higher brown pulp screen yields for the cooks terminated at higher kappa number, in the range of 14-26, but the lignin-HexA free screen yields were about similar in the kappa range of 18-26. At 18±1 kappa, the low-REA cooks showed higher pulp yield (1.0%), xylan yield (0.8%), cellulose yield (0.2%) and viscosity (90 dm^3 kg^{-1}), in relation to the high-REA ones. There was a trend for higher preservation of pulp MeGlcA and lower formation of HexA in the low-REA cooks, with the opposite occurring for the high-REA ones. Low-REA cooks produced pulps of lower brightness.

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PAPER 2: CHEMICAL STUDY OF KRAFT LIGNIN DURING ALKALINE DELIGNIFICATION OF *E. urophylla X E. grandis* HYBRID IN LOW AND HIGH RESIDUAL EFFECTIVE ALKALI

Submetido em: **ACS Sustainable Chemistry & Engineering**

ABSTRACT

Chips from a *E. urophylla* x *E. grandis* hybrid were subjected to kraft cooking using two different approaches: low and high residual effective alkali. The lignin remaining in the pulps were analyzed for hydroxyl and carboxyl functional groups. For both pulping cases the kappa number varied between 14 and 26. Significant yield gains were observed when kraft cooking was terminated with low residual effective alkali (L-REA) in contrast to high residual effective alkali (H-REA) at a given kappa number. The L-REA pulps also tended to contain higher lignin and smaller HexA contents than the H-REA pulps at a given kappa number. Cellulolytic enzyme lignin (CEL) was isolated from the studied pulp's residual lignins and their hydroxyl functional group distributions were quantified using a method involving ^{31}P-NMR. Analysis of residual lignins isolated from L-REA and H-REA cooking indicated that L-REA had high contents of aliphatic hydroxyl groups up to kappa number 14. In addition, the L-REA lignin preparations also contained higher contents of phenolic hydroxyl groups and carboxylic acid groups in relation to the H-REA pulps. This work demonstrates the varied lignin chemistry one can expect when varying residual effective alkali levels during kraft pulping and how this parameter can influence downstream unit operations and overall process performance.

Keywords: Residual Lignin; Delignification Process; Unbleached Pulp; Chemical characterization; ^{31}P-NMR analysis.

1. INTRODUCTION

Lignin consists of three phenylpropanoid monomers, namely coniferyl, sinapyl, and *p*-coumaryl alcohols, which are linked via C-C or C-O-C bonds formed by radical coupling reactions during cell wall biosynthesis.[1] These structures are of note because they are more resistant to cleavage in most pulping and bleaching reaction media than, for example, β-O-4 moieties.[2-8] Lignin can be loosely defined as a three-dimensional polymer containing a wide variety of functional groups, all of which impacts its reactivity in towards various processing technologies. Examples of lignin functional groups include methoxyl, carbonyl, carboxyl, and hydroxyl groups linking to aromatic or aliphatic moieties, each with various amounts and proportions which lead to different compositions and structures of lignin across biomass or after being subjected to chemical processing. Importantly, only a small proportion of lignin's phenolic hydroxyl groups are free in its native state because most of these groups are involved in linkages with neighboring phenylpropane moieties[9] (Figure 1).[10]

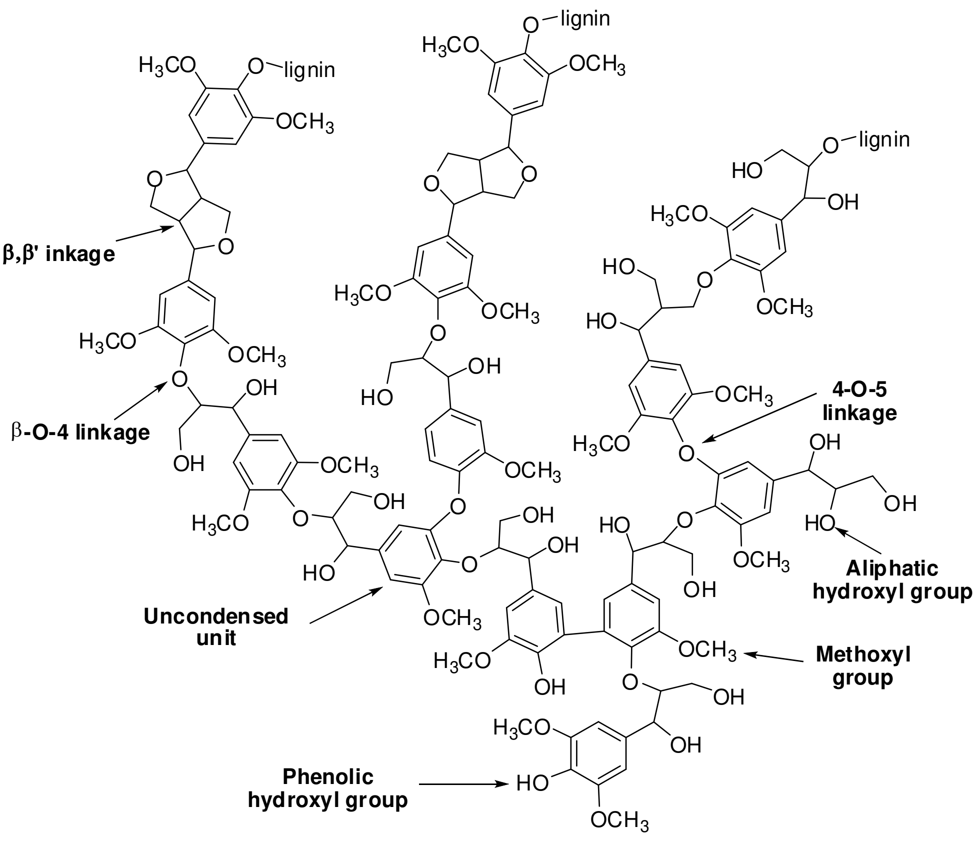


Figure 1. Some possible reactive sites of hardwood lignin (adapted from Ralph and Landucci, 2010).[10]

In terms of industrial chemical extraction modification of lignin, the alkaline kraft cooking process is the dominant global process. Employing a combination of sodium hydroxide and sodium sulfide at high temperatures (e.g., 150-170 °C), lignin is effectively degraded (approximately 90-95% of the lignin is removed) into alkali-soluble fragments affording pulp fibers that are predominantly composed of cellulose and hemicellulose. This material is suitable for the manufacture of paper and other related products. The kraft cooking brings a number of advantages when compared to other processes, especially in terms of fiber strength. Disadvantages are also present, the major one being a loss in pulp yield caused by carbohydrate instability and degradation during the alkaline reaction. In order to minimize those losses, it is important to have a good and reliable understanding of the process.[11]The process conditions, such as, cooking time, temperature and effective alkali charge, can be critical in this aspect and therefore, require special attention.[12]

Increases to pulp yield are a major goal of a cooking process, because improvements allow for increased mill throughput and reduced specific wood consumption. The main approaches to meet such goal are retarding or avoiding carbohydrate degradation reactions, increasing delignification levels, and improving mass transfer during cooking.[13] Lowering the residual effective alkali (REA) at end of cook is an interesting alternative to enhance kraft cooking performance, because doing so allows for a higher pulp yield by inducing xylan precipitation onto the fibers, in addition to decreasing the effective alkali (EA) charge to cook the wood.[13,14] In industrial applications, REA may vary between 4 to 18 g L^{-1}. However, the range of 7 to 9 g $L^{-1}$is more common. For some mills the REA target can be lowered without negative impacts upon operation of the black liquor recovery cycle.[14] Kraft cooking at L-REA can actually present certain economic advantages because the lowered EA demand implies less causticizing load, thus decreasing costs in the recovery cycle.[14-16]

Kraft cooking at L-REA likely also exerts some impact upon the chemical structure of the residual lignin remaining within the pulp, leading to consequences in subsequent operations such as oxygen delignification or other bleaching techniques.[17]Therefore, in order to develop a selective delignification/bleaching processes which meets the stringent requirements of a bleached chemical pulp with regard to environmental adaption, energy economy and process stability, it is essential to understand how the residual lignin can be affected by the cooking with low and high REA. The main goal of subsequent bleaching is to remove residual lignin and chromophore structures from pulp, therefore it is expected that differences in lignin structure will translate to effects on bleaching operations. The ease of bleaching operations is highly dependent on the relative abundance, structure, and reactivity of the lignin fragments present therein.

The fragmentation of the lignin macromolecule, during the process, proceeds through the cleavage of the linkages holding the phenylpropane units together. As the carbon to carbon bond (C – C) are stable in alkaline conditions, the cleavage of oxygen - carbon bonds (C – O – C) are the most significant reaction in the cooking process. Under alkaline conditions the phenolic group ionizes and increases the reactivity of the structure. On the other hand, etherified structure is much less reactive site in the alkaline pulping process.[18] The reactivity of β-O-4 depends on whether the structure is phenolic or etherified (i.e. nonphenolic) (Figure 2). The presence of these hydroxyl groups increases the hydrophilicity of the lignin fragments in the oxygen delignification and bleaching operation.

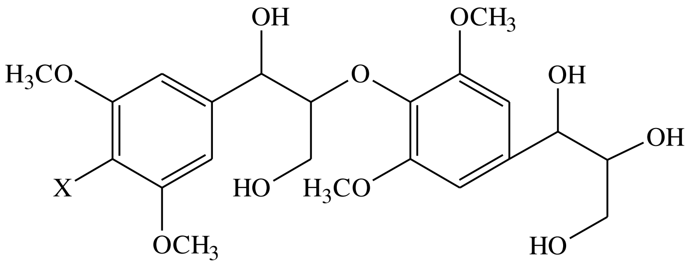


Figure 2. Lignin polymers can be terminated by a *p*-hydroxyl group or connected to additional lignin species, referred to as “phenolic” (X = OH) and “non-phenolic” (X = O-lignin) groups, respectively.[19]

Compared to native wood lignin, residual and dissolved kraft lignins have higher quantities of free phenolic groups (with dissolved lignins having a significantly greater amount), lower abundance of β-O-4 linkages (in residual lignins about 15% of the amount found in a wood lignin sample), and a fairly large proportion of saturated side-chain carbon atoms with bonds only to carbon and hydrogen.[20,21] Unavoidably, a certain portion of β-O-4 units is converted into alkali stable enol ether structures during the course of kraft cooking. Towards the end of a kraft cook the relative amounts of biphenyl (5-5) and biphenyl ether (4-O-5) structures in lignin increase whereas guaiacyl end-groups decrease. In addition, it is known that the residual lignin contains increasing amounts of carbohydrates as the cook proceeds. This indicates that delignification is becoming less lignin-selective and the lignin being solubilized at late stages of the cook has a more branched and/or cross-linked structure and fewer hydrolysable β-O-4 units. All these structural changes hinder further fragmentation, causing the residual lignin to be unreactive towards pulping chemicals. Residual lignin, compared to native lignin, is unreactive due to a low quantity of aryl ether linkages and the prevalence of condensed structures.[22] Residual lignins extracted from pulps having low lignin content (low kappa number) tend to contain fewer aliphatic hydroxyl groups and β-O-4 structures and higher contents of phenolic hydroxyl groups, carboxylic acid groups, and condensed structures compared to lignin from pulps with higher lignin content (higher kappa number).[22] One of the major changes occurring during the course of conventional kraft cooking is a progressive enrichment of carboxylic acids and condensed phenolic hydroxyl groups.[23] Toward the end of a kraft cook, the residual lignin contains three times more C-5 condensed phenolic groups than those present in the starting wood lignin sample.

Traditionally, lignin from unbleached pulp is isolated by a cellulolytic enzyme cocktail that removes cellulose and hemicellulose from the pulp, leaving the residual solid lignin as more extractable into lignin-favoring solvents (e.g. DMSO and aqueous 1,4-dioxane).[24] Elucidation of structural details from residual lignins constitutes the most important challenge and prerequisite for further improvements to kraft cooking technologies. The changes in the residual lignin structure reflect the reactions taking place during the selected cooking operations. With this knowledge, reliable structure-property relationships can be established, which in turn creates the basis for further improving the selectivity and efficiency of kraft cooking.

The goal of this study was to provide further insight into how varying residual effective alkali might affect pulp residual lignin functional groups (hydroxyl and carboxyl groups) and the performance of the kraft cooking from *Eucalyptus grandis* × *Eucalyptus urophylla* wood.

2. MATERIAL AND METHODS

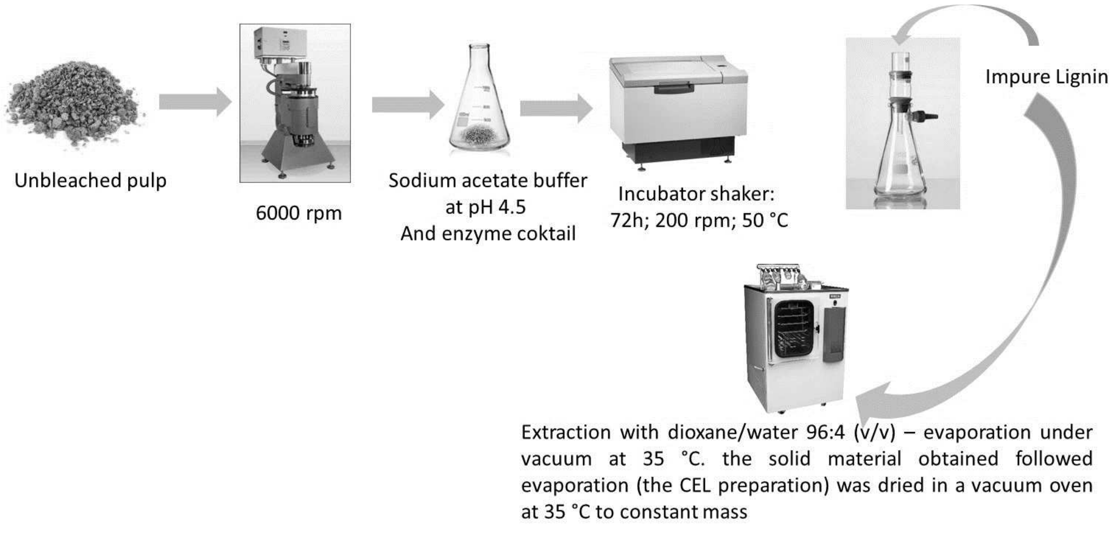
Eucalyptus urophylla x *Eucalyptus grandis* hybrid wood chips were cooked to kappa 14, 22 and 26. Cooking processes were terminated at low (1-2 g L^{-1}) and high (8-9 g L^{-1}) residual effective alkali. These two cooking approaches are henceforth designated as L-REA and H-REA, respectively. Both the wood and the unbleached pulps at kappa 14, 22 and 26 were characterized. Isolated lignin from unbleached pulps was also chemically characterized, with its functional characterization performed using quantitative ^{31}P-NMR. All experiments were run in duplicate.

The feedstock consisted of wood chips obtained from seven-year-old *E. urophylla* x *E. grandis* hybrid trees grown in Brazil. The chips were classified according to SCAN-CN 40:94[25] standard procedure and air-dried. In order to determine the wood's chemical composition, a fraction of the air-dried accepted chips were converted into sawdust using a knife-mill (Willey Co, USA), classified according to TAPPI T257cm-12[26] standard, and air-dried to ~10% moisture.

The chemical composition was carried out on extractive-free wood meal (TAPPI T280 pm-99)[27]. The contents of acid-insoluble lignin (TAPPI T222 om-97)[28], acid-soluble lignin (Goldschmid, 1971)[29], lignin syringyl/guaiacyl (Lin and Dence, 1992)[30], ash content (Tappi 211 om-93)[31], sugars composition (Wallis et al., 1996)[32], total uronic acid (Scott, 1979)[33] and acetyl groups (Solár et al., 1987)[34] were quantified. The wood basic density was measured according to the SCAN-CM46:92[35] standard procedure.

Kraft cooking was performed in duplicate in a 7-L MK digester with 500 g of chips, oven dry (od) equivalent. Cooking processes were carried out at a liquor/wood ratio of 4 L:1 kg, 30% sulfidity, maximum temperature of 165 °C, 70-min time-to-temperature and variable effective alkali charge and time-at-temperature to meet the kappa number targets of 14±1, 22±1 and 26±1 and L-REA (1-2 g L^{-1} NaOH) and H-REA (8-9 g L^{-1} NaOH). At the end of each cook, the chips were discharged and disaggregated in a 20-L hydrapulper at 2% consistency, then washed and screened using equipment (Voith Co., Germany) garnished with a flat screen of 0.2 mm slots. At the end of this stage the rejects were collected. Screened pulps were analyzed for extractives content (TAPPI T280 pm-99)[27], ash content (Tappi 211 om-93)[31], kappa number (TAPPI T236 cm-85)[36], HexA (TAPPI T282 pm-07)[37], viscosity (SCAN-CM 15:99)[38], total uronic acid (Scott, 1979)[33], sugar composition (Wallis et al., 1996)[31] and brightness (T525 om-92)[39]. From the values of kappa number and HexA, the corrected kappa number values (only lignin) were determined according to the procedure described by Li and Gellerstedst (1997).[40] The black liquor was analyzed for residual effective alkali (SCAN-N 33:94).[41]

Residual kraft lignin isolation is showed in Figure 3.The pulps were beaten in a PFI mill (TAPPI T248 cm-85)[42] using 6,000 revolutions to improve the digestibility of the pulps toward cellulolytic enzymes. For enzymatic hydrolysis of each sample, 50 grams (oven dry, od) of the pulp was divided across several Erlenmeyer flasks and a sodium acetate buffer (pH 4.5) was added. An enzyme cocktail of Cellic CTec 2 and Cellic HTec 2 (Novozymes, USA) with activity of 117 FPU mL^{-1} was used. Hydrolysis was performed in an environmental incubator shaker (New Brunswick Scientific, USA) operating at 50 °C and 200 rpm under the following conditions: 5% w/v consistency in a 50 mmol L-1 acetate buffer (pH 4.5) with an enzyme dosage of 20 FPU per dry g substrate. After 72 hours, hydrolysis was ceased and the hydrolyzed material was first washed extensively with acetate buffer and then water. The vessels used to wash the samples were vortexed between each wash and centrifuged at 20,000 rpm (Avanti J-E High-Speed Centrifuge, Beckman Coulter, USA) to ensure enzyme removal from the substrate. This was repeated 3 times for each wash. After washing, dried material was extracted with dioxane/water 96:4 (v/v) until resultant filtrate reached visual transparency. The entirety of the extraction solvent was next evaporated under vacuum at 35 °C. Finally, the solid material obtained followed evaporation (the CEL preparation) was dried in a vacuum oven at 35 °C to constant mass.



Extraction with dioxane/water 96:4 (v/v) – evaporation under vacuum at 35 °C. the solid material obtained followed evaporation (the CEL preparation) was dried in a vacuum oven at 35 °C to constant mass

Figure 3. Residual kraft lignin isolation

Quantitative ^{31}P-NMR spectra were obtained on a Brüker Avance 300 MHz spectrometer, following published procedures by Granata and Argyropoulos, 1995.[43]

Pyridine/$CDCl_3$ (1.6/1 v/v) was used as the solvent, endo-N-hydroxy-5-norbornene-2,3-dicarboximide (e-NHI) as the internal standard, chromium (III) acetylacetonate as the relaxation reagent, and as the phosphitylation reagent used the 2-chloro-4,4,5,5- tetramethyl1,2,3-dioxaphospholane.

3. RESULTS AND DISCUSSION

3.1.Wood Basic Density and Chemical Composition.

Basic density and chemical composition of the *E. urophylla* x *E. grandis* hybrid wood investigated are presented in Table 1.

Table 1. Wood basic density and chemical composition

Basic density, kg m^{-3}	**452 ±1.40**
Ash, %	0.26 ±0.02
Extractives in acetone, %	1.30 ±0.03
Acid-insoluble lignin, %	24.0 ±0.00
Acid-soluble lignin, %	4.10 ±0.01
Total lignin, %	28.1 ±0.01
Lignin S/G ratio	2.90 ±0.07
Acetyl groups, %	2.10 ±0.14
Total uronic acids, %	2.80 ±0.07
Glucans, %	52.1 ±0.13
Xylans, %	11.6 ±0.15
Galactans, %	1.30 ±0.06
Mannans, %	0.80 ±0.01
Arabinans, %	0.20 ±0.00
Total sugar, %	66.0 ±0.10
Cellulose[a], %	51.3 ±0.10
Hemicelluloses[b], %	19.6 ±0.10

[a]Cellulose = total glucans – glucans from glucomannans (1/1); [b]hemicelluloses = xylans + mannans + galactans + arabinans + (2 x glucans from glucomannans) + uronic acids + acetyl groups.

Basic density in this study (452 kg m^{-3}) was very similar to that reported by Souza et al. (2017)[44], who observed the same number, and Vivian et al. (2017)[45] that observed basic density value of 447 kg m^{-3}. These values are typical of *Eucalyptus* woods used in pulp manufacture in South America. The acetone extractives content was 1.3%. In general, these levels of extractives can be considered low compared to other hardwoods.[44] The ash content, which corresponds to the wood inorganic materials, was only 0.26%. Total carbohydrate content was 66% (w/w), with glucan and xylan serving as the major carbohydrate components. The contents of arabinans, galactans and mannans were irrelevant, which is positive given their instability throughout Kraft cooking. Glucans and xylan contents were of 52.1% and 11.6%, respectively. Similar numbers (52.1% glucans and 11.4% xylans) have been reported by Pinto et al. (2012)[12] in a study with *E. urophylla* × *E. grandis* wood. Evtuguin and Neto (2007)[46] working with the same hybrid wood found values of 48.6% glucans and 11.3% xylans. Beyond carbohydrates, the wood sample of this study contained 28.1% of total lignin, a value quite close to the value of 27.9% reported by Pinto et al. (2012)[12] who used the same eucalyptus hybrid wood. The wood's lignin content affects process yield and chemical demand, which are the most relevant production cost components.[12, 45, 47] Finally, the wood's contents of acetyl (2.1%) and uronic acid (2.8%) groups were in the range of values previously reported.[48]

3.2.Kraft Cooking

Kraft cooking of the *E. urophylla* x *E. grandis* hybrid wood was carried out in a way that kappa numbers of 14, 22 and 26 were achieved under two different approaches, namely: L-REA in the range of 1-2 g L^{-1} and H-REA in the range of 8-9 g L^{-1}. In order to achieve such goal, the EA charge and the time-at-temperature were varied, maintaining constant the liquor to wood ratio of 4L: $1kg^{-1}$, the sulfidity at 30% and the maximum temperature at 165 °C. By varying the time at the maximum temperature of 165 °C (H-factor) and the EA charge applied (using a trial-and-error technique), it was possible to meet the desired REA ranges at given kappa numbers. The metrics of cooking performance and unbleached pulp characterizations are presented in Table 2.

It was observed that the EA charge and H-factor were largely influenced by the target REA, with higher H-factors and low EA charge requirements for the L-REA cooks and the opposite for the H-REA cooks. On average, L-REA cooks required about 20% less EA to achieve the target kappa in comparison to the H-REA ones. For example, the L-REA cook allowed for EA charge savings of 26% and 15% for kappa numbers 26 and 14 (respectively) compared to the H-REA cooks. However, the L-REA cooks demanded, on average, about 50% higher H-factor than

H-REA when considering all kappa number values evaluated. It is worth noting that there exists a potential risk of lignin precipitation when cooking was terminated at L-REA conditions. However, this phenomenon did not occur in this study because the black liquor pH values were above 12 for all experiments. According to Gomes (2001),[49] at normal cooking conditions, there is no lignin precipitation at pH values of 12 or higher, but precipitation can be severe at pH approximately9.5.

In order to compare yields at different kappa numbers, the REA at the end of the cooks must be similar, regardless of the kappa number value, and the lignin and HexA-free screen yield must be considered. Fair cooking yield comparisons should be done with the screen yield and not total yield because rejects are not fibers and they are usually discarded or inefficiently reused in subsequent pulping cycles. In addition, if bleached pulp grades are sought after, one must compare the screen yields discounting their contents of lignin and HexA (a so-called “lignin-HexA free screened yield”). This is necessary because during bleaching both lignin and HexA are largely removed and their weight shall not be accounted for in the yield measurements. The only way to meet these constraints is by playing with both effective alkali charge and cooking time-temperature (H-factor) so that at the end of the cook different kappa numbers are achieved at similar REA. This is precisely what was done in this study. If one considers lignin-and HexA-free screen yield (bleached yield), the values tend to remain similar with increasing kappa number, except for the kappa number 14 pulp that showed lower yields than kappa 22-26 pulps (Table 2). Thus, the removal of lignin rather than carbohydrates, is the main cause of yield decrease when going from kappa 26 to 22. It was also observed that terminating the cook at low residual effective alkali leads to increased pulp yield.[50] At kappa number 26 the lignin- and HexA-free pulp screen yield was 1.8% higher for the L-REA cook than the H-REA one. The cook terminated at L-REA resulted in higher yield due to improved preservation of hemicelluloses and/or partial precipitation of dissolved xylans onto the fibers.[51,52]

There was a trend observed in which higher preservation of MeGlcA (4-O-methylglucuronic acid) and lower formation of HexA (hexenuronic acid) in the L-REA pulps could be found compared to H-REA pulps. Pulp HexA contents for the various kappa numbers were in the range of 0.65 to 1.1% for L-REA cooks and 1.0 to 1.2% for the H-REA cooks. On the other hand, pulp MeGlcA content varied in the range of 0.9 to 1.6% for L-REA and from 0.8 to 1.4% for H-REA. For the kappa number range investigated, was found that as kappa number decreased, the HexA content increased and the MeGlcA content decreased. The lower HexA quantities found in the L-REA pulps (versus H-REA pulps) can be explained by lower conversion of MeGlcA into HexA due to the lower EA charges applied. The rate of formation/degradation of HexA has been shown to depend essentially on [OH^-]. This also explains the higher MeGlcA content found in the L-REA pulps over the H-REA pulps.[45-55] HexA content in pulps increased with decreasing kappa number due to decreased cooking time while keeping the other cooking parameters at constant levels[56], with the opposite occurring for MeGlcA contents.[57]

Lignin contents in the brown pulps produced at different kappa numbers and at the L-REA and H-REA cooking conditions were calculated according to Li and Gellerstedt (1997).[40] Overall it was found that higher amounts of lignin were present in the L-REA pulps. The lignin content for L-REA pulps were between 1.3% and 3.4% (kappa number 14-26), and from 1.1% to 3.1% (kappa number 14-26) for the H-REA pulps. As expected, the lignin content increased with increasing kappa number (range of 14-26). Importantly, a given pulp's lignin content at a fixed kappa number depends on pulp HexA content [36]. In our work, L-REA pulps had lower HexA quantities than the H-REA pulps. As a consequence, L-REA pulps had more lignin. The higher lignin content of the L-REA pulps also caused a decrease in brightness. For example, for the cooking done to kappa number 22, L-REA pulp had a brightness decrease of 35.7 to 31.2 %ISO compared to H-REA pulp.As expected, the brightness increases as delignification proceeded. It was reported by Aurell and Hartler (1965),[58] that cooking at L-REA gives rise to pulps of low brightness due to formation of chromophoric structures in the lignin molecules. Also, Hartler and Norrström (1969)[59] demonstrated that applying a high H-factor to reach a given kappa number is accompanied by a low residual amount of β-O-4 structures in the residual lignin.[7]

Table 2. Cooking performance and unbleached pulp characterization.

Kappa number, units	**14**		**22**		**26**	
REA, g L^{-1}	**2.0**	**9.0**	**1.0**	**8.3**	**1.1**	**9.0**
Cooking performance						
Effective alkali, %	16.5	19.5	13.5	17.5	13.3	18.0
H-Factor	1661	802	852	448	761	367
[a]Lignin-HexA-free screen yield, %	51.1	50.6	52.2	50.8	51.8	50.0
Black liquor pH	12.1	12.8	12.1	12.7	12.1	12.8
Reject, %	0.0	0.2	1.2	1.5	2.1	2.3
Unbleached pulp characterization						
HexA content, mmol kg^{-1}	66	74	55	66	41	63
MeGlcA, %	0.9	0.8	1.4	1.2	1.6	1.4
[b]Lignin content, %	1.3	1.1	2.6	2.5	3.4	3.1
Brightness, %ISO	34.8	37.4	31.2	35.7	29.9	34.2

[a]Lignin-HexA Free Screen Yield = Screen yield – (lignin yield + HexA yield).
[b]calculated according to Li and Gellerstedt (1997).[39]

3.3.Isolation of Residual Kraft Lignin

Lignin isolation from chemical pulps has been a difficult task since the residual lignin content in pulp is relatively low and is probably linked chemically to the carbohydrates.[60] In this study, additional steps were taken for the purpose of improving isolated lignin yields. This included beating unbleached pulps in a PFI mill with the aim to convert shives into fibers and to fibrillate the fiber surfaces to improve enzymatic digestibility of the pulp while avoiding inducing chemical structural changes.[60] In addition, experiments were performed to understand how pH of the sodium acetate buffer varied over the time period of enzymatic digestion. Thus, the objective was test the relation between the concentrations of the buffer components and the yield of the enzymatically digested solid material (impure lignin). Importantly, it was reported by Chang (1992)[60] that the residual lignin becomes solubilized during the enzymatic treatment and must be precipitated from the filtrate by acidification. Based on this, it was employed an acidification step to the liquid phase after enzymatic digestion in hopes to precipitate any newly solubilized lignin. Table 3 shows the results of this analysis: the quantities of impure residual lignin (recovered as an insoluble residue) after enzymatic digestion under different scenarios: i) two differentpH of the sodium acetate buffer; ii) acidification of the filtrate after enzymatic digestion.

Enzymatic hydrolysis was carried out with sodium acetate buffer at pH 4.5 and 4.9, using pulp samples of kappa number 22 produced at L-REA and H-REA. It was observed that a slightly lower yield of digested solid material was procured at pH 4.9 in contrast to pH 4.5. Specifically, these values were 2.3% and 2.7% for L-REA pulp, and 2.5% and 2.9% for H-REA pulp. In addition, the lignin recovery was lowin the solid material digested at pH 4.9. The sugar and protein contents were very similar in both cases, representing from 13 to 17.2% and 18.4 to 21.7% for the H- and L-REA pulps, respectively. Thus, the optimal pH of the two levels investigated was pH 4.5.

Also was investigated the effect of acidifying the enzymatic hydrolyzate filtrate after the digestion time period. After enzymatic hydrolysis, the pH was lowered to pH 2 through addition of HCl. Despite this increasing the solid yield and successfully inducing lignin precipitation, a large amount of sugar and protein impurities were also newly quantifiable. According to some authors, residual lignin isolated by means of enzymatic hydrolysis has been found to contain a relatively high amount of carbohydrates and proteins.[61,62] It is believed the first (carbohydrates) originate from the limited ability of enzymes to hydrolyze lignin-carbohydrate linkages,[63] while the latter (enzymes) is assigned to the enzymes themselves which were used to hydrolyze the pulp. Based on these findings, was concluded that not performing acidification was most favorable for representative lignin isolation in the case of our highly specific study.

Table 3. Lignin, sugar and protein content after enzymatic hydrolysis in two different approachesusing pulp samples of kappa number 22, produced at L-REA and H-REA

REA, g L^{-1}	**pH (acetate) solution)**	**Solid remaining, %**	**lignin recovery*, %**	**Sugar, %**	**Protein, %**
	Enzymatic digestion in two different pH of the sodium acetate buffer				
1.0	4.5	2.7	64	14.9	18.4
8.3		2.9	58	17.2	20.7
1.0	4.9	2.3	56	13.0	21.7
8.3		2.5	51	14.7	21.3
	Enzymatic digestion followed by a*cidification* of the filtrate				
1.0	4.5	4.7	50	45.0	23.4
8.3		4.7	54	46.5	22.0

*Based on total lignin content in the pulp.

Table 4 presents the yield and purity of CEL preparations obtained from all six unbleached pulp samples. The purities of CEL were calculated by summing the acid-insoluble (Klason lignin)[28] and acid soluble lignin[29] contents of each pulp. Yield varied from 11.1 (kappa number 14 from H-REA cooking) to 34.2% (kappa number 26 from L-REA cooking). The yield of enzymatic residual lignin from eucalypt pulps was relatively low, attaining 34% in unbleached kraft pulp[64], but the lignins obtained exhibited high purity and likely maintained an unaltered chemical structure due to the pre-processing steps employed[52]. The fairly low yield can partly be explained by the mass transfer limitations. Despite enzymatic treatment, most of the lignin in kraft pulp is located inside the fiber wall, and this lignin is probably unable to fully diffuse into the dioxane/water solution from its fiber-embedded locations.[65]In spite of our struggling yields, still was chose to quantify the hydroxyl content of the CELs in effort to better understand how varying REA affects the functionality of residual lignin in kraft pulps.

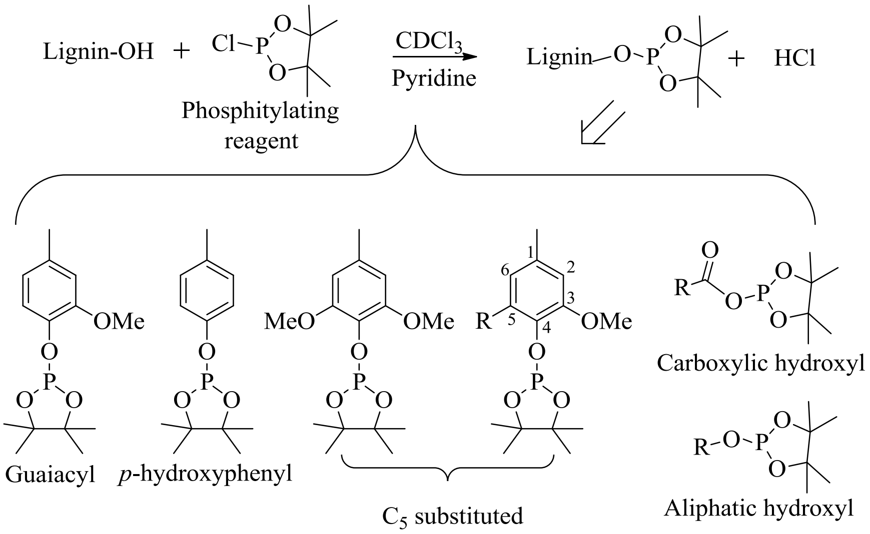
Table 4. Yield and purity of the isolated lignin (CEL preparation) from unbleached pulp samples.

Kappa number, units	**14**		**22**		**26**	
REA, g L^{-1}	2.0	9.0	1.0	8.3	1.1	9.0
Yield*, %	12.4	11.1	27.7	20.8	34.2	21.7
CEL purity, %	83.9	74.3	79.0	61.0	77.3	82.5

*Based on total lignin in the pulp after isolation.

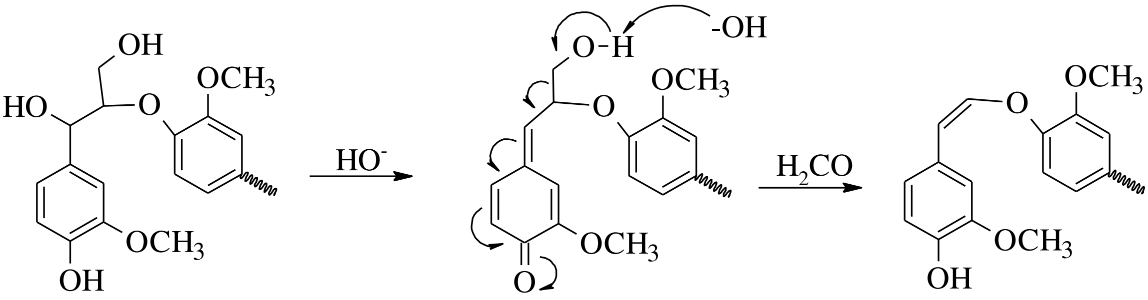
3.4.Characterization of Lignin by ^{31}P-NMR

Critical functional groups present in lignin, including, carboxylic acids, phenolic, and aliphatic hydroxyl groups, were precisely quantified using a ^{31}P-NMR technique. Changes in the relative proportions of these functional groups provide critical information on the nature of the reactions involved in the applied cooking operations.[66] The following discussion attempts to evaluate how these functional groups change in kraft pulps, depending upon the cooking conditions employed and the level of residual lignin remaining in the pulp. Table 5 show the contents of aliphatic, phenolic, and carboxylic hydroxyl of the residual lignins isolated in this study from the unbleached pulp samples. The values were corrected for lignin content in each isolate to provide more specific quantification. All signals in the range of 149.2 to 145.0 and 144.3 to 137.2 ppm are associated with aliphatic and phenolic hydroxyl groups, respectively. In the phenolic hydroxyl region, the signals in the range of 144.3 to 140.3 ppm can be attributed to 5-substituted units (which include 5-5' condensed units), and those in the range of 140.3 to 137.2 ppm were assigned to non-condensed units (free C5 position). The signals in the range of 135.6 to 134.0 are associated to carboxylic acid groups. Scheme 1 show the reactions of hydroxyls groups present in lignin with phosphitylating reagent.



Scheme 1. Scheme of the reactions of hydroxyls groups present in lignin with phosphitylating reagent.

The aliphatic hydroxyl content of lignin is mainly comprised of primary and secondary hydroxyl groups located on $C^{γ}$ and $C^{α}$ of the phenylpropane side chain of lignin (Figure 1). The loss in aliphatic hydroxyl groups can be attributed, in part, to the loss of the primary hydroxyl group of the phenyl propane chain as formaldehyde during the cooking process (Scheme 2).[67] Therefore the degree to which lignin is modified during kraft cooking is presumably related to the content of aliphatic hydroxyl groups. This is exactly what our results indicated. The residual lignin of both L- and H-REA pulps contained reduced aliphatic hydroxyl contents as delignification proceeded. Specifically, the values of 5.30 and 7.15 (mmol g^{-1} lignin) were found for the kappa numbers 14 and 26 pulps cooked at L-REA, respectively. In addition, the content of lignin aliphatic OH groups was higher in the pulps cooked at L-REA (except that which was cooked to kappa number 14), in contrast with the pulps cooked at H-REA conditions. This can be explained due to the fact that cooking at L-REA demands a lower effective alkali charge to achieve the target kappa. In the case of the kappa number 14, the lower content of lignin aliphatic OH groups can be associated to the longer cooking time employed. Consequently, there was lower HO^- availability in the reaction medium so the reaction rate for loss of γ-carbon was reduced. Decreasing residual alkali increased aliphatic OH content by about 7% for the kappa numbers 22 and 26. It is worth noting that aliphatic OH groups tend to increase lignin reactivity and thus improving the pulp bleachability.[66]



Scheme 2. Loss of γ-carbon during kraft pulping (adapted from Froass et al., 1998).

The most important lignin fragmentation reaction during alkaline cooking is the cleavage of the β-aryl ether linkage. This reaction fragments the lignin polymer and simultaneously liberates a new phenolic hydroxyl group.[68] As a result, residual lignins and solubilized lignins from kraft pulping have a greater quantity of phenolic groups than native wood lignin.[69] The ^{31}P-NMR method used in this work not only measures total phenolic content, but also distinguishes between these groups the structures of guaiacyl-non-condensed and C5-substituted (S-units and 5-condensed G units). Table 5 lists the contents of C5-substituted units, free C5 units and total phenolic content in each lignin isolate. In hardwoods, the phenolic groups in C5-substituted guaiacyl units have similar chemical environments as the phenolic groups in syringyl units, and their corresponding signals partially overlap. All previous works reporting the phenolic groups of hardwoods by ^{31}P-NMR expressed both types of phenol groups as their sum. As expected, a clear trend involving increasing phenolic contents as delignification proceeded was observed in our findings. This result is also reported in others studies.[22,51] For example, the total phenolic groups content of the residual lignins cooked in H-REA at kappa numbers 26 and 14, respectively, are of 1.66 and 2.30 (mmol g^{-1} lignin). At the same kappa number, the content of phenolic hydroxyl groups was higher for the pulps cooked at L-REA in contrast to pulps cooked at H-REA. Decreasing REA from 9 g L^{-1} to 1 g L^{-1} increased total phenolic group content by about 24% for the kappa number 26. However, at kappa number 14, phenolic contents appeared to level off with the decreasing residual alkali, with values of 2.34 and 2.30 (mmol g^{-1} lignin) for the L-REA and H-REA cooks, respectively. The observation that the content of phenolic hydroxyl groups is increasing as delignification proceeds implies that the residual lignin is still undergoing cleavage of the remaining aryl ether linkages. The levelingof the phenolic content in the residual lignins of the L-REA and H-REA cooks (kappa number 14), suggests that additional aryl ether cleavage is minimal, likely due to the very low kappa numbers.[22] Other changes that occurred during the course of conventional kraft cooking were progressive enrichment of C5-substituted groups (condensed phenolic hydroxyl) compared to the C5-free groups (guaiacyl phenolic content). The greater increase in condensed phenolic suggests that the majority of new phenolic groups created are of the C5 condensed type, and/or some of the phenolic structures have undergone condensation reactions. If the greater increase in the condensed phenolic content originated from the cleavage of condensed aryl ether linkages, then the results seem to suggest that a significant portion of the non-phenolic structures in residual lignin is of the condensed (C5 substituted) type.[11]

The residual lignin contains an increasing quantity of carboxylic acid groups as delignification proceeds, varying from 0.10 (for kappa number 26) to 0.41 mmol g^{-1} of lignin (for kappa number 14). The same trend was found by Prinsen et al., 2013,[20] who investigated hydroxyl groups in MWL (milled wood lignin) of a eucalypt hybrid before and after kraft cooking. At the same kappa number, the content of carboxylic acid groups was higher for the pulps cooked at L-REA conditions in contrast to pulps cooked at H-REA. Decreasing residual alkali from 9 g L^{-1} to 1 g L^{-1} increased carboxylic acid content by about 29% for the kappa number 14. However, at kappa number 26, the carboxylic acid groups content appeared to level off with the decreased residual alkali, with values of 0.14 and 0.10 (mmol g^{-1} lignin) for the L-REA and H-REA cooking, respectively. Finally, the content of *p*-hydroxyphenyl was considerably lower in all samples compared to contents of C5-substituted groups (condensed phenolic hydroxyl) and the C5-free groups (guaiacyl phenolic content). This observation is likely due to the lignin constituency of the hardwood hybrids used being overwhelmingly comprised of G and S units.

Table 5. Aliphatic, phenolic and carboxylic hydroxyl groups content (mmol g^{-1} of lignin) determined by quantitative ^{31}P-NMR in CEL isolated from unbleached pulp samples.

Kappa number, units	**14**		**22**		**26**	
REA, g L^{-1}	**2.0**	**9.0**	**1.0**	**8.3**	**1.1**	**9.0**
	mmol g^{-1} of lignin					
Aliphatic OH	5.30	6.26	6.99	6.56	7.15	6.67
C5-substituted units	1.79	1.85	1.64	1.53	1.69	1.22
free C5 units	0.48	0.45	0.46	0.43	0.45	0.40
Total phenolic OH	2.33	2.30	2.13	2.01	2.17	1.66
para Ph OH	0.06	0.00	0.03	0.05	0.03	0.04
Carboxylic OH	0.41	0.27	0.16	0.13	0.14	0.10

4. CONCLUSIONS

The L-REA leaded a high pulp yield, less alkali consumption, in addition to improve pulp quality in relation to the H-REA ones. A 1.8% maximum yield increase (kappa number 26±1) was observed for the L-REA pulps in relation to the H-REA ones. The effective alkali charge decreased about 20% when compared to the charge used to obtain H-REA. Besides, the L-REA resulted in a higher pulp viscosity, indicating a lower degradation of cellulose chains along the pulping. ^{31}P-NMR analysis of CEL preparations from each pulp sample showed that residual lignin structure differs depending upon the lignin content of the pulp and the cooking protocol employed. It was found that low kappa pulps contain less aliphatic hydroxyl groups and more phenolic hydroxyl groups and carboxylic acid groups compared to higher kappa pulps. L-REA pulps had high contents of aliphatic hydroxyl groups, except for pulps of kappa number 14, and higher contents of phenolic hydroxyl and carboxylic acid groups compared to the H-REA pulps. The loss in aliphatic hydroxyl groups was attributed, in part, to the loss of the primary hydroxyl group of the phenyl propane chain as formaldehyde during the cooking process. New phenolic hydroxyl group are formed by cleavage of the β-aryl ether linkage. Our findings demonstrate the expected changes to lignin that will affect downstream kraft pulping operations when varying REA during kraft cooking.

5. ACKNOWLEDMENTS

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PAPER 3:EFFECT OF RESIDUAL EFFECTIVE ALKALI ON THE EUCALYPTUS KRAFT PULP BLEACHABILITY

ABSTRACT

The impact of residual effective alkali (REA) and pulp delignification degree on bleaching process was investigated. In this study four types of eucalypt clones were evaluated. The eucalypt woods were cooked to kappa numbers of 14±1, 18±1, 22±1 and 26±1 using two different ranges of REA, namely: low-REA (1-2 g L^{-1}) and high-REA (8-9 g L^{-1}). In general, the low-REA cooks lead to pulps of higherviscosity and xylans content, lower brightness and hexenuronic acid (HexA) content and high contents of aliphatic hydroxyl groups up to kappa number 14, higher contents of phenolic hydroxyl groups and carboxylic acid groups, in relation to the high-REA cooks. In addition, the pulps from low-REA cooks showed slightly higher O-stage efficiency (2%-4%), in spite of demanding about 5% to 10% more total active chlorine (TAC)for attaining the target brightness of 90% when bleached by D(EP)D sequence, but pulp brightness stability was somewhat affected. The pulps from low-REA cooks showed higher brightness reversion than those from cooks at high-REA, but these values tended to be acceptable.Similar trends were observed for the all woods and kappa values evaluated.

Keywords: Delignification efficiency; Bleaching; Total active chlorine;

1. INTRODUCTION

Bleachability is defined as the chemical requirement to bleach the pulp to a given brightness degree. The higher the bleachability of a given pulp the lower the quantity of bleaching chemicals needed to reach a given brightness degree (for example 90% ISO brightness). There are many variables that affect the bleachability, but, surely the cooking process is between these variables (Colodette et al., 2002).

Kraft pulping is the most widely used process for production of chemical pulps (Gullichsen and Fogelholm, 2000). Employing a combination of sodium hydroxide and sodium sulfide at high temperatures (e.g., 150-170 °C), lignin is effectively degraded (approximately 90-95% of the lignin is removed) into alkali-soluble fragments affording pulp fibers that are predominantly composed of cellulose and hemicellulose. The kraft cooking brings a number of advantages when compared to other processes, especially in terms of fiber strength. Disadvantages are also present, the major one being a loss in pulp yield caused by carbohydrate instability and degradation during the alkaline reaction. In order to minimize those losses, it is important to have a good and reliable understanding of the process (Clark, 1985; Sjöström, 1993).

Those investigating in this field have made many attempts to increase pulp yield and bleachability. Most of the processes proposed are either effective to increase yield or to increase bleachability, but not both at the same time. As a matter of fact, many of the alternate methods proposed to increase pulp yield result in decreased pulp bleachability (Colodette et al., 2002).

The pulping and bleaching performance is highly dependent on the relative abundance, structure, and relative stability/reactivity of the wood biopolymers, i.e., lignin, cellulose, and hemicelluloses. In particular, different hardwoods can require significantly different pulping and bleaching conditions to achieve the same extent of delignification and degree of brightness, respectively. The reasons behind such different behaviors are not completely understood (Pinto et al, 2005).

Significant changes in kraft pulping technology in the last decade have been sparked by the need to increase pulp yield and reduce bleaching chemical consumption. The process conditions, such as, cooking time, temperature and effective alkali charge, can be critical in this aspect and therefore, require special attention, since cooking conditions can affect pulp residual lignin and pulp carbohydrate composition, including variations in hemicellulose and hexenuronic acid contents.

Lowering the residual effective alkali (REA) at end of cook is an interesting alternative to enhance kraft cooking performance, because doing so allows for a higher pulp yield by inducing xylan precipitation onto the fibers, in addition to decreasing the effective alkali (EA) charge to cook the wood (Goyal, 2017; Colodette and Gomes, 2014). Kraft cooking at Low-REA likely also exerts some impact upon the chemical structure of the residual lignin remaining within the pulp, leading to consequences in subsequent operations such as oxygen delignification or other bleaching techniques (Matsushita, 2015).

The main goal of subsequent bleaching is to remove residual lignin and chromophore structures from pulp. Increasing pulp bleachabillity during the manufacturing process results in decreased bleach chemical costs and reduces environmental impact of chlorine dioxide based bleaching processes. Such reasons explain the widespread acceptance of modified kraft process technologies in the pulp-and-paper industry in the last few years.

Studies have demonstrated that cooking at low-REA led to higher carbohydrates preservation, while high-REA cooks has been shown to cause extensive degradation and dissolution of xylan chains (Goyal, 2017; Pinto et al., 2005; Aurell, 1964). Pulp carbohydrate composition, and the contents of alkali-leachable lignin, lignin-carbohydrate complexes residual lignin, and HexA present in hardwood kraft pulps are likely the underlying factors affecting bleachability and brightness stability of bleached pulps, but their relative importance is not clearly understood for eucalyptus kraft pulp. A better understanding of the effect of pulping conditions on pulp chemistry may lead to better ways to produce bleached eucalyptus kraft pulp.

In this context, the objective of this study was to evaluate the impact of kraft cooking Eucalyptus woods at low and high residual effective alkali (1-2 and 8-9 g L^{-1} NaOH), and pulp degree of delignification (kappa number 14-26) on the performance of chlorine-free (ECF) bleaching process.

2. MATERIAL AND METHODS

Unbleached pulps at kappa 14, 18, 22 and 26 were produced from *E. urophylla* x *E. grandis* hybrid wood chip, seven year old, grown in Brazil, and wood chip of *E. nitens* and *E. globulus*, sixteen years old, *E nitens* x *E. globulus* hybrid, twelve years old, all grown in Chile. Cooking processes were terminated at low (1-2 g L^{-1}) and high (8-9 g L^{-1}) residual effective alkali. These two cooking approaches are henceforth designated as low-REA and high-REA, respectively. The cooking process were detailed in Ribeiro et al., 2019. The unbleached pulps were characterized and submitted to oxygen delignification stage (O-stage) and bleaching step by D-(EP)-D sequence. All experiments were run in duplicate

The unbleached pulps chemical composition was carried out on kappa number (TAPPI T236 cm-85), viscosity (T230 om-94), brightness (TAPPI 525 om-92), hexenuronic acid content (TAPPI T282 pm-07) and sugars content (Wallis et al., 1996). The hydroxyl and carboxyl groups content by ^{31}P-NMR (Granata and Argyropoulos, 1995) was carried out only to the pulps from *E. urophylla* x *E. grandis* hybrid wood.

The O-stage was performed with 65 g of pulp, oven dry (od) equivalent, in an electrically heated laboratory rotary reactor, equipped with 4 individual reactors with a capacity of 1.5 liters each. The oxygen delignification was carried out at a consistency of 11.5%, 100 °C, 60 min, using four different charges of oxygen and sodium hydroxide, according to the unbleached pulp kappa number. The oxygen and sodium hydroxide dosages were the same to 1.6, 1.8, 2.0, 2.2% for the pulps with kappa number of 14, 18, 22 and 26, respectively. The pulp was added to each of the reactor capsules along with the sodium hydroxide and water to complete of consistency. The oxygen was added when the temperature was reached. After the reaction time a sample of the residual filtrate was collected for pH analysis and the pulps were washed with distilled water equivalent to 9 m^3 t^{-1} of pulp. Across the O-stage pulps were analyzed for kappa number (TAPPI T236 cm-85), HexA (TAPPI T282 pm-07), viscosity (SCAN-CM 15:99) and brightness (T525 om-92).

The first chlorine dioxide stage (D) was carried out at a 11% consistency, 90 ºC, 120 minutes, and a kappa factor of 0.21. The EP stage was carried out at a t 11% consistency, 85 ºC, 75 minutes, and hydrogen peroxide charge of 0.44% by pulp weights. The final dioxide chlorine stage (D) was carried out at a 11% consistency, 80 ºC, and 90 minutes. Bleaching stages were carried out at a water bath with temperature control with 150 g oven-dry pulp, in polyethylene bags. The control of pH in bleaching stages was achieved through small additions of NaOH or H_2SO_4 to reach final pH of 3.0, 11 and 5.5 for D_0, EP and D_1 stages, respectively. Between each stage the pulps were washed with distilled water equivalent to 9 m^3 t^{-1} of pulp. After the reaction time a sample of the residual filtrate was collected for pH analysis and reagent consumption. Bleached pulps were analyzed for kappa number (TAPPI T236 cm-85), viscosity (SCAN-CM 15:99) and brightness (T525 om-92), reversion brightness (TAPPI UM200).

3. RESULTS AND DISCUSION

3.1. Unbleached pulp chemical and physical compositions

Unbleached pulp chemical and physical composition and residual lignin hydroxyl and carboxyl groups content are reported in Table 1 and 2. The results will be discussed as to, HexA content, viscosity, brightness, cellulose and xylan contents and hydroxyl and carboxyl groups content.

Higher amounts of the HexA were obtained for the high-REA cooks. The HexA content for the various kappa numbers and the four wood types, represented from 0.64 to 1.1% for low-REA cooks and from 0.81 to 1.2% for the high-REA cooks. In the kappa number range investigated, the HexA content increases as delignification proceeds, regardless of wood type. In general, no significant effect of wood type was observed on HexA content for a given REA and kappa number value, except to *E. globulus* that present the lower values of HexA. The smaller HexA content found in low-REA cooks in relation to high-REA cooks can be associated to decrease of the reactions rate HexA formation, since the EA charge is smaller to achieve target REA and the rate of formation/degradation of HexA was shown to depend essentially on HO^- ions (Gomide 2005; Hutterer et al., 2017). HexA content in pulps decreased with increasing kappa number due to decreased cook time, while keeping the other cooking parameters at constant levels (Bergnor-Gidnert, 1998). The smaller amount of HexA in *E. globulus* in relation the others *Eucalyptus* species can be due to varying contents of 4-O-methyl-glucuranoxylans among species that influences the amount of HexA formed (Magaton et al., 2008).

A clear tendency of viscosity improvement in pulps from low-REA cooks was observed, representing relative estimated viscosity gains of 93 $dm^3 kg^{-1}$ for *E. nitens* x *E. globulus* hybrid, 91 $dm^3 kg^{-1}$ for *E. nitens*, 74 $dm^3 kg^{-1}$ for *E. globulus* and 50 $dm^3 kg^{-1}$ for *E. urophylla* x *E. grandis* hybrid in relation to pulps from high-REA cooks, when cooked to kappa number 18. The viscosity gains increase as the kappa number increases. In the kappa number range investigated, 14-26, the viscosity loss increases as the kappa number decreases (delignification increases). In general, no significant effect of wood type was observed on viscosity for a given REA and kappa number value. The higher viscosity values found in pulps from low-REA cooks in relation to high-REA cooks is associated to higher preservation of carbohydrates due to possible decrease of alkaline hydrolysis reactions and consequently the secondary peeling reactions in the cellulose chains(Santiago, 2008; Santiago and Neto, 2008). On the other hand, viscosity in pulps decreased along the kraft pulping process due to higher degradation of the carbohydrate chains (Gomide et al., 2011). Similar viscosity values found among the four wood types, for a given REA and kappa number value, can be due to keeping the pulping parameters at partially constant levels.

A negative impact on pulp brightness was caused by the decrease of REA concentration in the pulping process. As expected, in the kappa number range investigated, 14-26, the brightness increases as delignification proceeds, regardless of wood type. Significant effects of wood type were observed on brightness for a given REA and kappa number value, mainly for *E. urophylla* x *E. grandis* hybrid (32.9% ISO) and *E. globulus* (28% ISO) that present the higher and the smaller brightness, respectively, for unbleached pulps produced in kappa numbers 18 and at low-REA. The smaller brightness obtained in pulps from low-REA cooks in relation to high-REA cooks can be due to the higher lignin content present in these pulps, since the low-REA pulps had less HexA than the high-REA ones. Another possible cause was reported by Aurell and Hartler (1965) as well, that a low residual alkali concentration in the cook gives rise to pulps with a low brightness due to a formation of chromophoric structures in the lignin. Also, Hartler and Norrström (1969) demonstrated that applying a high H-factor to reach a given kappa number is accompanied by a low residual amount of β-O-4 structures in the residual lignin. Brightness in pulps decreased as the reduction of delignification degree due to higher amount of residual lignin in the pulp (Gustavsson, 2006). The different brightness values found among the wood types, to a given REA and kappa number value can be explained by HexA and lignin content that composing the kappa number, since the pulp lignin content at a fixed kappa number depends on pulp HexA content (Costa and Colodette, 2007).

The cellulose contents in the brown pulps produced in different kappa numbers at low-REA and high-REA, on wood weight, varied from 39.0-40.3, 39.9-41.5, 42.3-43.6 and 42.4-43.9% for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively. It is known that a smaller amount of the cellulose is lost across kraft cooking when compared to loss of xylan backbone. But, it is still possible observed that this effect was slightly higher for the high-REA cooks. The cellulose content in the unbleached pulp, for the various kappa numbers and wood types, was, in average, about 0.3% higher for low-REA cooks in relation to the high-REA cooks. No significant effect of kappa number value, except to kappa number 26, was observed on cellulose retention for a given REA value, regardless of wood type. The no effect on cellulose retention in different kappa numbers, for the four woods type are explained by the fixed REA, which was carefully kept constant. Already the difference found for kappa number 26 can be explained due to higher amount of reject obtained in the cooking. On the other hand, when the focus is to analyze the effect of REA, the low-REA cooks led to higher celluloses preservation, suggesting that effective alkali charge play a key role in the stability and retention of this polysaccharide during the pulping process. The small cellulose preservation in the high-REA cooks is explained by enhanced secondary peeling reactions in the presence of higher alkali concentration.

The xylans are synonym of hemicelluloses in *Eucalyptus* kraft pulp. The xylan backbone contents in the brown pulps produced in different kappa numbers at low-REA and high-REA, on wood weight, varied from 8.9 to 10.2; 9.5 to 10.6; 7.8 to 8.7 and 6.9 to 7.7% for *E. nitens* x *E. globulus* hybrid, *E. nitens*, *E. globulus* and *E. urophylla* x *E. grandis* hybrid, respectively. It is known that significant amounts of the xylan backbone are lost across kraft cooking. But, this effect was more significant for the high-REA cooks. The xylan backbone content in the unbleached pulp, for the various kappa numbers and wood types, was, in average, about 0.8% higher for low-REA cooks in relation to the high-REA cooks. The maximum increase of xylan backbone content due to low-REA cooks was of 1.1% for *E. nitens* x *E. globulus* hybrid and the minimum increase was 0.4% for *E.urophylla* x *E.*

grandis hybrid, cooked at kappa 26 and 14, respectively. No significant effect of kappa number value was observed on xylan retention for a given REA value, regardless of wood type. No effect on xylan retention in different kappa numbers, for the four woods types are explained by the REA, which was carefully kept constant. On the other hand, when the focus is to analyze the effect of REA, the low-REA cooks led to higher xylans preservation, suggesting that effective alkali charge play a key role in the stability and retention of this polysaccharide during the pulping process. Previous works concerning the impact low-REA cooks on carbohydrate dissolution of unbleached pulp have demonstrated significantly increased both total yield and viscosity, for similar kappa number, which was mainly attributed to higher carbohydrates retention, especially xylan (Santiago, 2008; Achrén et al., 1998).

Table 1. Chemical and physical composition of unbleached pulp

Parameter and Results								
E. nitens x *E. globulus* hybrid								
Kappa Number	14		18		22		26	
REA, g L^{-1}	1.0	8.2	1.2	8.1	1.0	8.3	1.1	8.0
HexA content, mmol kg^{-1}	63	68	58	62	49	57	41	54
Viscosity, dm^3 kg^{-1}	1059	990	1189	1096	1280	1181	1389	1270
Brightness, %ISO	33.0	35.6	30.4	34.1	29.2	32.9	28.4	32
Cellulose, %	39.6	39.6	40.3	40.1	40.0	39.7	39.7	39.0
Xylans, %	10.2	9.4	10	9.2	10.2	9.2	10	8.9
E. nitens								
Kappa Number	14		18		22		26	
REA, g L^{-1}	1.3	8.0	1.0	8.9	1.0	9.0	1.0	8.4
HexA content, mmol kg^{-1}	61	67	57	60	50	55	46	53
Viscosity, dm^3 kg^{-1}	1035	967	1191	1100	1292	1176	1400	1280
Brightness, %ISO	33.4	37.8	31.3	36.2	30.4	34.8	29.9	34.3
Cellulose, %	39.9	40.0	41.3	41.1	41.5	41.3	40.8	40.3
Xylans, %	10.5	9.7	10.5	9.6	10.5	9.5	10.6	9.5
E. globulus								
Kappa Number	14		18		22		26	
REA, g L^{-1}	1.3	8.2	1.2	8.1	1.0	8.5	1.0	8.7
HexA content, mmol kg^{-1}	54	58	51	55	45	53	40	51
Viscosity, dm^3 kg^{-1}	1090	1034	1184	1110	1309	1190	1425	1277
Brightness, %ISO	29.3	31.9	28.0	31.4	26.7	28.5	24.8	27.7
Cellulose, %	43.3	43.2	43.6	43.4	43.4	43.1	42.8	42.3
Xylans, %	8.6	7.9	8.7	8.0	8.7	7.8	8.7	7.8
E. urophylla x *grandis* hybrid								
Kappa Number	14		18		22		26	
REA, g L^{-1}	2.0	9.0	1.8	9.0	1.0	8.3	1.1	9.0
HexA content, mmol kg^{-1}	66	74	63	66	55	66	41	63
Viscosity, dm^3 kg^{-1}	1009	963	1180	1130	1311	1240	1400	1330
Brightness, %ISO	34.8	37.4	32.9	36.8	31.2	35.7	29.9	34.2
Cellulose, %	43.1	43	43.6	43.5	44	43.2	43.7	42.4
Xylans, %	8.0	7.6	8.3	7.5	8.1	7.6	8.1	7.6

Critical functional groups present in lignin, including, carboxylic acids, phenolic, and aliphatic hydroxyl groups, were precisely quantified using a ^{31}P-NMR technique. Changes in the relative proportions of these functional groups provide information on the nature of the reactions involved cooking operations and how that can implicate in the oxygen delignification and bleaching operation (Gellerstedt et al., 1988). Table 2 show the contents of aliphatic, phenolic, and carboxylic hydroxyl of the residual lignins isolated in this study from the unbleached pulp obtained from *E. urophylla* x *E. grandis* hibryd cooked at low and high REA.

The residual lignin of both low-REA and high-REA pulps contained reduced aliphatic hydroxyl contents as delignification proceeded. Specifically, the values of 5.30 and 7.15 (mmol g^{-1} lignin) were found for the kappa numbers 14 and 26 pulps cooked at low-REA, respectively. In addition, the content of lignin aliphatic OH groups was higher in the pulps cooked at low-REA (except that which was cooked to kappa number 14), in contrast with the pulps cooked at high-REA conditions.

As expected, a clear trend involving increasing phenolic contents as delignification proceeded was observed in our findings. This result is also reported in others studies (Froass, 1996; Colodette, 2002). For example, the total phenolic groups content of the residual lignins cooked in high-REA at kappa numbers 26 and 14, respectively, are of 1.66 and 2.30 (mmol g^{-1} lignin). At the same kappa number, the content of phenolic hydroxyl groups was higher for the pulps cooked at low-REA in contrast to pulps cooked at high-REA. Decreasing REA from 9.0 g L^{-1} to 1.1 g L^{-1} increased total phenolic group content by about 24% for the kappa number 26. However, at kappa number 14, phenolic contents appeared to level off with the decreasing residual alkali, with values of 2.34 and 2.30 (mmol g^{-1} lignin) for the low-REA and high-REA cooks, respectively.

The residual lignin contains an increasing quantity of carboxylic acid groups as delignification proceeds, varying from 0.10 (for kappa number 26) to 0.41 mmol g^{-1} of lignin (for kappa number 14). The same trend was found by Prinsen et al., 2013, who investigated hydroxyl groups in MWL (milled wood lignin) of a eucalypt hybrid before and after kraft cooking. At the same kappa number, the content of carboxylic acid groups was higher for the pulps cooked at low-REA conditions in contrast to pulps cooked at high-REA. Decreasing residual alkali from 9 g L^{-1} to 1 g L^{-1} increased carboxylic acid content by about 29% for the kappa number 14. However, at kappa number 26, the carboxylic acid groups content appeared to level off with the decreased residual alkali, with values of 0.14 and 0.10 (mmol g^{-1} lignin) for the low-REA and high-REA cooking, respectively.

It is worth noting that aliphatic OH groups tend to increase lignin reactivity and thus improving the pulp bleachability (Gierer, 1970) Besides, several studies have demonstrated that the phenolic units of lignin are one of the most significant reaction sites for oxygen delignification. The primary interaction of alkali with these structures generates anions that are candidate structures for attack by oxygen and its coexisting species (Asgari and Argyropoulos, 1998).

Table 2. Aliphatic, phenolic and carboxylic hydroxyl groups content (mmol g^{-1} of lignin) determined by quantitative ^{31}P-NMR in CEL isolated from unbleached pulp samples.

Kappa number, units	**14**		**22**		**26**	
REA, g L^{-1}	**2.0**	**9.0**	**1.0**	**8.3**	**1.1**	**9.0**
	mmol g^{-1} of lignin					
Aliphatic OH	5.30	6.26	6.99	6.56	7.15	6.67
C5-substituted units	1.79	1.85	1.64	1.53	1.69	1.22
free C5 units	0.48	0.45	0.46	0.43	0.45	0.40
Total phenolic OH	2.33	2.30	2.13	2.01	2.17	1.66
para Ph OH	0.06	0.00	0.03	0.05	0.03	0.04
Carboxylic OH	0.41	0.27	0.16	0.13	0.14	0.10

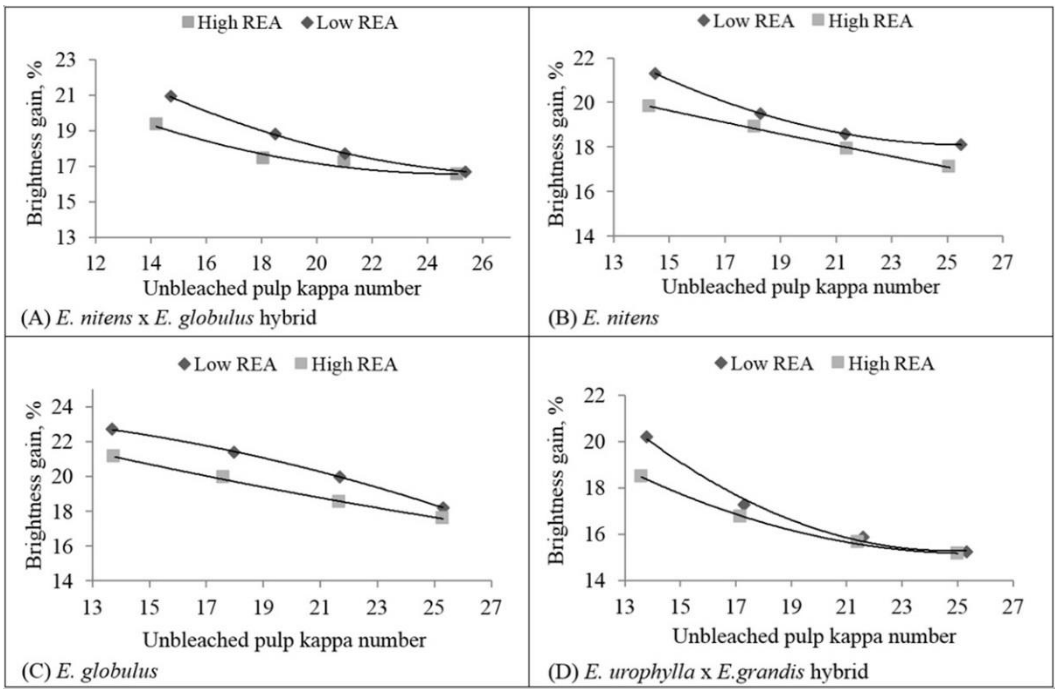
3.2. Oxygen delignification stage

The oxygen delignification step results are summarized in Table 3 and will be discussed as to, kappa drop, viscosity drop, brightness gain, overall efficiency and efficiency based only on the true lignin kappa number.

A similar tendency viscosity across the O-stage pulps in relation to unbleached pulps was observed, i.e., the across the O-stage pulps from low-REA cooks had higher viscosity values than found in relation to across the O-stage pulps from high-REA cooks. In the kappa number range investigated, 14-26, the viscosity values increase as the kappa number increases. In general, no significant effect of wood type was observed on viscosity for a given REA and kappa number value, except to the pulps from *E. globulus*, that have viscosity values superior to pulps from others woods. The viscosity drops across the O-stage varied in the range of 118 to 365 dm^3 kg^{-1} and 96 to 300 dm^3 kg^{-1} for pulps from low-REA and high-REA, respectively, when cooked to kappa number 14 to 26. The viscosity drop was lower for the pulps cooked at high-REA, which had lower viscosities to begin with. In general, no significant effect of wood type was observed on viscosity drop for a given REA and kappa number value. The higher viscosity values found across the O-stage pulps from low-REA cooks in relation to high-REA cooks, regardless of wood type or kappa number occurred because these pulps had higher initial viscosities due to higher preservation of carbohydrates during the cooking process. In the kappa number range investigated, 14-26, the pulps viscosity is higher for the kappa number high due to old and very well-known concept that higher kappa numbers pulps present higher viscosities (Colodette et al., 2007). Similar viscosity values found among the four wood types, except to the pulps from *E. globulus*, for a given kappa number value, are consequences its initial viscosities and for keeping the O-stage parameters at partially constant levels. Viscosity drop in pulps increased as kappa number increases due to a very old rule states that higher viscosities values to begin O-stage results in higher viscosity drop (Colodette et al., 2002).

As can be noted in Figure 1, a negative impact on pulp brightness was caused by the decrease of REA concentration in the cooking process and this effect has persisted for across the O-stage pulp. However, the pulps cooked at low-REA showed higher brightness gain in relation to those cooked to high-REA, with values varied in the range of 22.7 to 15.2% ISO and 18.5 to 15.1% ISO, considering all four kappa values and the four woods type, to low and high cooks, respectively. In the kappa number range investigated, 14-26, the brightness gain decreases as kappa number increases. Significant effects of wood type were observed on brightness gain for a given REA and kappa number value, mainly for *E. urophylla* x *E. grandis* hybrid, kappa number 26, (15.2% ISO) and *E. globulus*,kappa number 14, (22.7% ISO) that present the smaller and the higher brightness gain, respectively, for across the O-stage produced from low-REA cooks.

The higher brightness gain obtained in pulps from low-REA cooks in relation to high-REA cooks may be traced to the higher content of alkali-leachable lignin present in the pulps cooked at low residual alkali (Colodette et al., 2002). Brightness gain in pulps decreased as kappa number increases due to formation of certain oxygen-derived free radicals, which may give rise to cellulose oxidation and formation of carboxyl groups in the pulp (Oliveira et al., 2006). Hence, it was anticipated that very overall efficiency of the O-stage could decrease brightness gain. The different brightness values found among the wood types studied, to a given REA and kappa number value can be explained by HexA and lignin content that composing the kappa number (Costa and Colodette, 2007).


(A) *E. nitens* x *E. globulus* hybrid

(B) *E. nitens*

(C) *E. globulus*

(D) *E. urophylla* x *E.grandis* hybrid

Figure 1. Effect of low and high REA and kappa number variations on oxygen delignification brightness gain in unbleached pulps from four eucalypt woods.

Across the O-stage pulps from cooks at low-REA, regardless of wood type, showed higher kappa drop than those from cooks at high-REA, especially to high kappa numbers. For example, for the *E. nitens* wood cooked at kappa number 26, the decrease of REA from 1.0 to 8.4 resulted increase kappa drop of 1.0 units. Similar trends were observed for the other wood types. In the kappa number range investigated, 14-26, the kappa dropincreases as kappa number increases, regardless of REA. In relation to wood type, was observed a slight difference on kappa drop, for a given REA and kappa number value, mainly for the hybrids of *E.urophylla* x *E. grandis* and *E. globulus* and *E.nitens*, that present the smaller and the higher kappa drop, respectively.

The higher kappa drop obtained in pulps from low-REA cooks in relation to high-REA cooks may be traced to the higher content of alkali-leachable lignin present in the pulps cooked at low residual alkali (Colodette et al., 2002). The lower end pH of the cooks conducted to a low-REA may not have been sufficient to extract all the lignin fragments cleaved during the bulk delignification phase. These lignin fragments were removed in the subsequent O-stage, thus increasing the overall kappa drop. Conversely, when the cook ended at a high-REA, most of the lignin fragments were removed from the fibers during the pulping operation itself with only a small fraction remaining to be alkali-leached in the oxygen delignification stage.

As can be noted in Figure 2 and 3, pulps produced from cooks at low-REA showed slightly higher overall O-stage efficiency (2%-4%) than those from cooks at high-REA, regardless of wood type. The same trend was observed for efficiency based only on the true lignin kappa number (0.7%-3%). In the kappa number range investigated, 14-26, the overall O-stage efficiency increases as kappa number increases, regardless of wood type or REA, with the opposite occurring for the efficiency based only on the true lignin kappa number, i.e., the efficiency based only on the true lignin kappa number decreases as kappa number increases, regardless of wood type or REA. In relation to wood type, was observed a significant difference in theoverall O-stage efficiency, for a given REA and kappa number value, mainly for the of *E. globulus* (43.5%-56.1%), and *E. globulus* x *E. nitens* hybrid (40.8%-50.8%), that present the higher and the smaller overall O-stage efficiency, respectively. For the efficiency based only on the true lignin kappa number, for a given REA and kappa number value, the *E. urophylla* x *E. grandis* hybrid (57.8%-72.6%), and *E. globulus* x *E.nitens* hybrid (59.3%-66.8%), have presented the higher and the smaller efficiency, respectively.

It is known that the main factors affecting the oxygen delignification efficiency of *Eucalyptus* kraft pulp, as measured by the percentage kappa drop across the O-stage, are kappa number, HexA content and carryover to the bleaching plant and phenolic hydroxyl groups content. The higher O-stage efficiency or efficiency based only on the true lignin kappa number obtained in pulps from low-REA cooks in relation to high-REA cooks may be traced to the higher content of alkali-leachable lignin present in the pulps cooked at low residual alkali, since the lower end pH of the cooks conducted to a low-REA may not have been sufficient to extract all the lignin fragments cleaved during the bulk delignification phase (Colodette et al., 2002). These lignin fragments were removed in the subsequent O-stage, thus increasing the overall kappa drop. Conversely, when the cook ended at a high-REA, most of the lignin fragments were removed from the fibers during the pulping operation itself with only a small fraction remaining to be alkali-leached in the oxygen delignification stage.

Besides, this behavior also can be associated to phenolics groups amounts in the residual lignin from pulps by low-REA cooks and high-REA cooks. In order to find an explanation for this behavior, the cellulolytic enzyme lignin (CEL) was isolated from the pulp's cooked from *E. urophylla* x *E.grandis* hibryd at kappa number 22 and 26 and their hydroxyl functional group distributions were quantified using a method involving ^{31}P-NMR. It was found that the residual lignin isolated from pulp cooked at high-REA had a smaller content of C5-substituted units, free C5 units and, consequently,smaller total phenolic content(Table 2)than the corresponding lignin from pulp cooked at low-REA, regardless of kappa number. This is consistent with the fact that a much longer cooking time was required in the preparation of pulp from low-REA cooks resulting in a larger degree of degradation of the lignin, a larger amount of phenolic hydroxyl groups (Gellerstedt and Lindfors, 1987) and greater possibilities for the formation of structures with unsaturated carbons (Gierer et al. 1972). A high content of phenolic hydroxyl groups increases the degree of delignification in the oxygen stage, since are the main sites for oxygen reactions, and this explain the slightly higher efficiency based solely on lignin (Gellerstedt and Lindfors, 1987).

In the kappa number range investigated, the overall oxygen delignification efficiency increases with increasing kappa number, but the efficiency based only on the true lignin kappa number tend to decrease. The lignin from higher kappa pulps, regardless REA, showed contain less free phenolic hydroxyl groups than the lower kappa ones, which are the main sites for oxygen reactions, and this explain the slightly lower efficiency based solely on lignin (Gellerstedt, 1996). However, the higher kappa pulps contained more lignin available for reaction than the lower kappa ones because of their similar or lower HexA content. Therefore, the higher kappa pulps produced higher overall oxygen delignification efficiency than the lower kappa ones, given that HexA do not react with oxygen (Vuorinen et al., 1996).

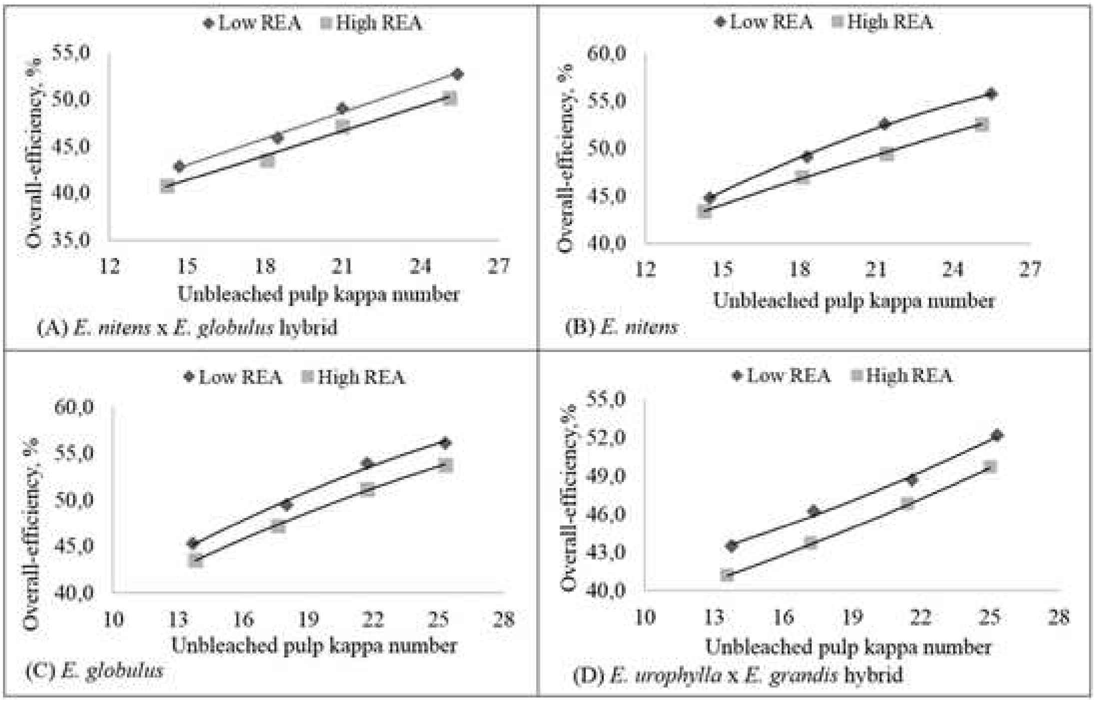


Figure 2. Effect of low and high REA and kappa number variations on overall oxygen delignification efficiency in unbleached pulps from four eucalypt woods.

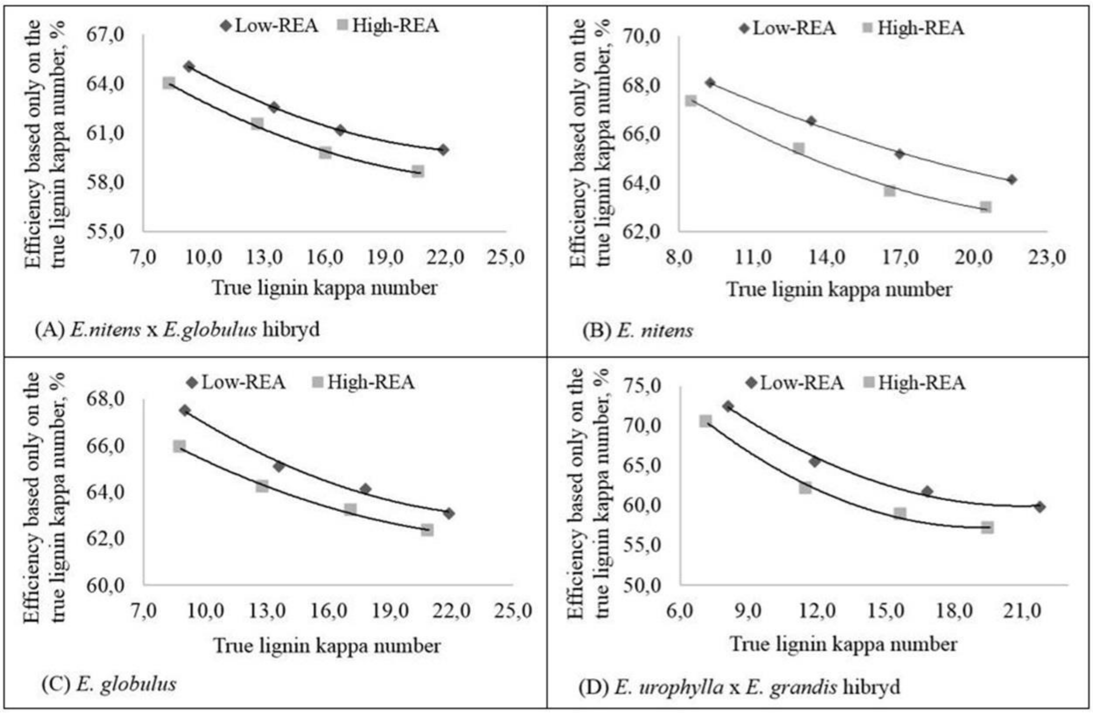


Figure 3. Effect of low and high REA and kappa number variations on oxygen delignification efficiency based only on the true lignin kappa number in unbleached pulps from four eucalypt woods.

Table 3. Oxygen bleaching results and performance

Parameter and Results								
E. nitens x E. globulus hybrid								
REA, g L^{-1}	1	8.2	1.2	8.1	1	8.3	1.1	8
Unbleached kappa number	14	14	18	18	22	22	26	26
Kappa number across O-stage	8.4	8.4	10	10.2	10.7	11.1	12	12.5
Viscosity, dm^{3} kg^{-1}	941	893	1010	956	1048	990	1073	1006
Brightness, %ISO	53.9	57.8	52.0	51.5	46.9	50.5	45.0	49.2
Kappa drop, unit	6.3	5.8	8.5	7.9	10.3	9.9	13.4	12.9
Viscosity drop, dm^{3} kg^{-1}	118	97	179	140	232	201	316	264
Efficiency, %	42.9	40.8	45.9	43.6	49.0	47.1	52.8	50.8
Gain of Brightness, %ISO	20.9	22.2	21.6	17.4	17.7	17.6	16.6	17.2
E. nitens								
REA, g L^{-1}	1.3	8	1	8.9	1	9	1	8.4
Unbleached kappa number	14	14	18	18	22	22	26	26
Kappa number across O-stage	8.0	8.1	9.3	9.6	10.1	10.8	11.3	11.9
Viscosity, dm^{3} kg^{-1}	914	860	994	933	1017	942	1035	980
Brightness, %ISO	54.7	57.6	50.8	55.1	49.0	52.7	48.0	51.4
Kappa drop, unit	6.5	6.2	9.0	8.5	11.1	10.7	14.2	13.2
Viscosity drop, dm^{3} kg^{-1}	121	107	197	167	275	234	365	300
Efficiency, %	44.8	43.4	49.2	47.0	52.4	49.8	55.7	52.6
Gain of Brightness, %ISO	21.3	19.8	19.5	18.9	18.6	17.9	18.1	17.1
E. globulus								
REA, g L^{-1}	1.3	8.2	1.2	8.1	1	8.5	1	8.7
Unbleached kappa number	14	14	18	18	22	22	26	26
Kappa number across O-stage	7.5	7.8	9.1	9.3	10.0	10.6	11.1	11.7
Viscosity, dm^{3} kg^{-1}	966	938	1018	980	1061	1018	1125	1063
Brightness, %ISO	52.0	53.0	49.4	50.3	46.7	47.0	43.0	45.5
Kappa drop	6.2	6.0	8.9	8.3	11.1	11.1	14.0	13.6
Viscosity drop, dm^{3} kg^{-1}	124	96	166	130	248	172	300	214
Efficiency, %	45.3	43.5	49.4	47.2	52.6	51.2	55.8	53.8
Gain of Brightness, %ISO	22.7	21.1	21.4	18.9	20	18.5	18.2	17.6
E. urophylla x grandis hybrid								
REA, g L^{-1}	2	9	1.8	9	1	8.3	1.1	9
Unbleached kappa number	14	14	18	18	22	22	26	26
Kappa number across O-stage	7.8	8.0	9.3	9.7	11.1	11.4	12.1	12.6
Viscosity, dm^{3} kg^{-1}	891	850	978	944	1079	1039	1119	1075
Brightness, %ISO	55.0	55.9	50.2	53.5	47.1	51.3	45.1	49.3
Kappa drop	6.0	5.6	8.0	7.5	10.5	10.0	13.2	12.4
Viscosity drop, dm^{3} kg^{-1}	118	113	202	186	232	201	281	255
Efficiency, %	43.5	41.2	46.2	43.6	48.6	46.7	52.2	49.6
Gain of Brightness, %ISO	20.2	18.5	17.3	16.7	15.9	15.6	15.2	15.1

3.3.Bleaching process

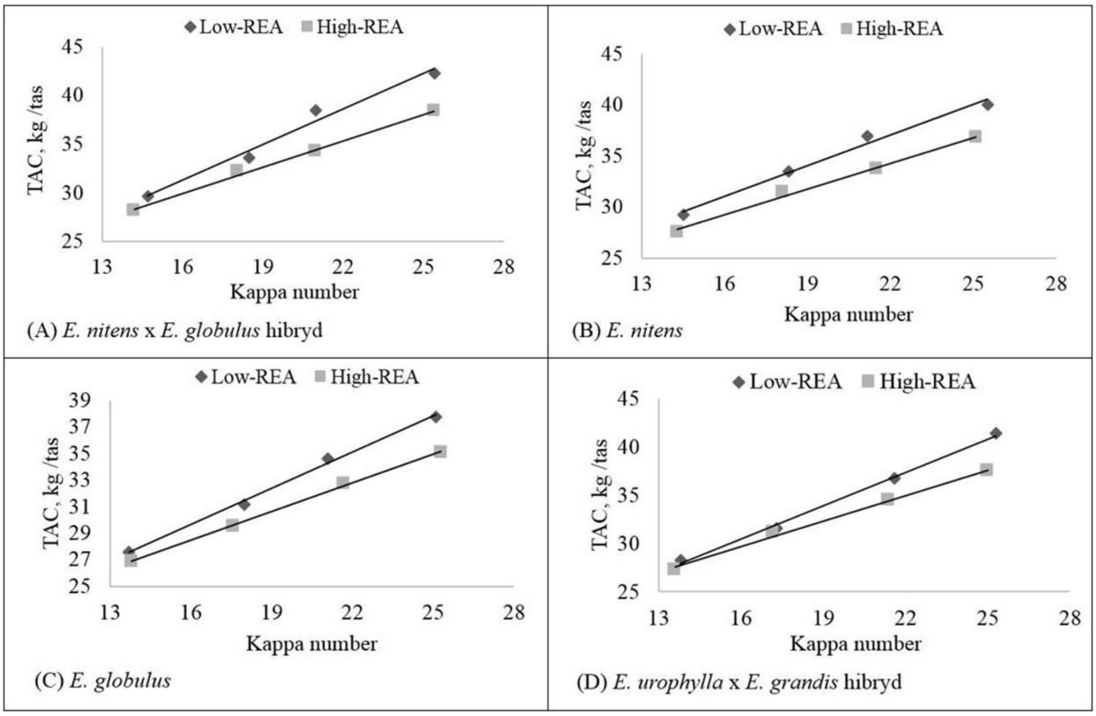
The bleaching results by sequence D(EP)Dfor the brightness of 90% ISO are summarized in Table 4, and will be discussed as to, final kappa number, viscosity, brightness reversion, total active chlorine and bleachability.

The bleached pulps produced from cooks at low-REA showed smaller final kappa number than those from cooks at high-REA, for a given unbleached pulp kappa number value and wood type. In the kappa number range investigated, 14-26, the bleached pulps final kappa numbertend to decreases as kappa number increases, regardless of wood type or REA. No significant effect of wood type was observed on final kappa number. The final kappa number obtained in bleached pulps is due to HexA content present in this pulp, since kappa number in this brightness degree is compound, especially, by HexA. This explain the high final kappa number in bleached pulps from high-REA cooks in relation to low-REA cooks, since to results previous showed original pulps from high-REA cooks contained high HexA content. In the relation to decreases pulps final kappa number as unbleached pulp kappa number increases, this explanation is also plausible.

The bleached pulps viscosities produced from cooks at low-REA showed slightly higher, (until 60 $dm^3 kg^{-1}$) than those from cooks at high-REA, for a given kappa number value and wood type. In the kappa number range investigated, 14-26, the viscosity increases as kappa number increases, regardless of wood type or REA. A slight difference in theviscosity was observed among the *Eucalyptus* wood, for a given REA and kappa number value, but, the*E. globulus* (814 $dm^3 kg^{-1}$ - 1032 $dm^3 kg^{-1}$) and *E. urophylla* x *E. grandis* hybrid (674 $dm^3 kg^{-1}$ - 931 $dm^3 kg^{-1}$) stand outfor present the higher and the smaller viscosity, respectively. It is interesting to note that pulps of high initial viscosities experienced greater losses across bleaching than low viscosity ones. The viscosity values of bleached pulps, regardless REA, wood type or kappa number final reflected the viscosities initial in unbleached pulps and tend to be acceptable.

The pulps produced from low-REA cooks showed slight increase on brightness reversion than those from cooks at high-REA, for a given kappa number value and wood type. In general, it was not observed a clear trend for brightness reversion in the kappa number range investigated, 14-26, regardless of wood type or REA. No significant effect of wood type was observed on brightness reversion for a given REA and kappa number value.Reversion values in the range of 1.7 to 2.9 were obtained in the whole spectrum of treatments and no clear trend was possible to derive. In any case, this reversion amplitude is rather low and all pulps can be considered of high brightness stability. The cooking conditions (low- and high-REA) hadsomewhat effect on brightness reversion for pulps from cooks at low-REA thatcan be due to smaller HexA content in these pulps.

As, can be noted in Figure 4, the bleached pulps from low-REA cooks consumed more total active chlorine (TAC) than those from high-REA cooks, mainlyin the range of 22 to 26, regardless of wood type. These pulps consumed about 10% more TAC required for attaining the target brightness of 90% ISO when bleached by D(EP)D sequence. In the kappa number range investigated, 14-26, the TAC increases as kappa number increases, regardless of wood type or REA. In relation to wood type, was observed a significant difference in TAC, for a given REA and kappa number value, mainly for the*E. globulus* (27.6%-37.8%), and *E. globulus* x *E. nitens* hybrid (29.7%-44.3%), that present the smaller and the higher TAC, respectively. Eucalyptus pulp chemical consumptions is affected by the kappa number composition. At a given kappa number, different chemical consumptions are observed for different pulps depending upon their contents of HexA, lignin and other oxidizable structures (Costa and Colodette 2002; Buchert et al., 1997; Jiang et al., 2000). The higher TAC obtained in pulps from low-REA cooks in relation to high-REA cooks can be explained on the basis of the residual lignin content in the pulp unbleached, since the pulps from low-REA cooks contains higher residual lignin content. The higher residual lignin content in high kappa numbers also explain the increase of TAC obtained for these pulps.



(A) *E. nitens* x *E. globulus* hibryd

(B) *E. nitens*

(C) *E. globulus*

(D) *E. urophylla* x *E. grandis* hibryd

Figure 4. Effect of low and high REA and kappa number variations on TAC across O-stage pulps from four eucalypt woods.

In this work bleachability has been defined as the kappa number entering the bleach plant subtracted for final kappa number across bleach plant divided by total active chlorine (TAC) required for attaining the target brightness of 90% ISO. Total active chlorine was defined by the following equation: TAC = (ClO_2*2.63 + H_2O_2*2.09). The factors 2.63 and 2.09 are simple conversions of ClO_2 and H_2O_2 into active Cl_2 based on their oxidation equivalents.

Bleachability for the pulps produced from low-REA were smaller than those from high-REA cooks, mainly in the kappa number range of 22 to 26, for a given wood type. It was observed a clear trend bleachability increases in the kappa number range investigated, 14-26, regardless of wood type or REA. In general, no significant effect of wood type was observed on bleachability for a given REA and kappa number value. The smaller bleachability found for pulps from low-REA cooks for the same kappa number, mainly for kappa number range of 22 to 26, can be due to higher TAC amount required for attaining the target brightness. In the kappa number range investigated, 14-26, the total amount of TAC required to fully Lbleach the pulp (90.0% brightness) decreased with kappa number decrease. However, the relative amount of oxidant required per kappa number unit reduction, increased (bleachability decreased), showing that ClO_2 oxidizable structures (contributing to kappa number in pulp) became less reactive as their contents in pulp decreased.

Table 4. Bleaching results and performance for D(EP)D sequence

Parameter and Results								
E. nitens x E. globulus hybrid								
REA, g L^{-1}	1	8.2	1.2	8.1	1	8.3	1.1	8
Unbleached kappa number	14	14	18	18	22	22	26	26
Kappa number across O-stage	8.4	8.4	10	10.2	10.7	11.1	12	12.5
Final kappa number	1.4	1.6	1.4	1.6	0.6	1.4	0.5	1.2
Viscosity, dm^3 kg^{-1}	769	738	898	858	952	897	990	930
Brightness reversion, %ISO	2.0	1.7	2.0	1.9	2.2	1.8	1.9	1.8
Total active chlorine, kg tas^{-1}	29.7	28.2	33.6	32.2	38.5	34.3	42.3	38.3
*Bleachability	0.24	0.24	0.26	0.27	0.26	0.28	0.27	0.29
E. nitens								
REA, g L^{-1}	1.3	8	1	8.9	1	9	1	8.4
Unbleached kappa number	14	14	18	18	22	22	26	26
Kappa number across O-stage	8.0	8.1	9.3	9.6	10.1	10.8	11.3	11.9
Final kappa number	1.5	2.1	1.2	1.6	0.9	1.5	0.6	0.9
Viscosity, dm^3 kg^{-1}	802	768	887	848	930	883	975	920
Brightness reversion, %ISO	2.5	2.2	2.9	2.5	2.8	2.7	2.6	2.1
Total active chlorine, kg tas^{-1}	29.2	27.5	33.5	31.5	37	33.7	40	36.8
*Bleachability	0.22	0.22	0.24	0.25	0.25	0.28	0.27	0.30
E. globulus								
REA, g L^{-1}	1.3	8.2	1.2	8.1	1	8.5	1	8.7
Unbleached kappa number	14	14	18	18	22	22	26	26
Kappa number across O-stage	7.5	7.8	9.1	9.3	10.0	10.6	11.1	11.7
Final kappa number	1.2	1.6	1.1	1.8	1.1	1.8	1.2	2
Viscosity, dm^3 kg^{-1}	822	814	910	882	980	931	1032	979
Brightness reversion, %ISO	2.7	2.4	2.6	2.3	2.5	2.1	2.6	2.1
Total active chlorine, kg tas^{-1}	27.6	26.9	31.2	29.5	34.7	32.8	37.8	35.1
*Bleachability	0.23	0.23	0.24	0.25	0.26	0.27	0.27	0.28
E. urophylla x grandis hybrid								
REA, g L^{-1}	2	9	1.8	9	1	8.3	1.1	9
Unbleached kappa number	14	14	18	18	22	22	26	26
Kappa number across O-stage	7.8	8.0	9.3	9.7	11.1	11.4	12.1	12.6
Final kappa number	1.6	2.1	1.6	1.9	1.3	1.6	0.8	1.3
Viscosity, dm^3 kg^{-1}	702	674	807	772	914	868	985	931
Brightness reversion, %ISO	2.4	2.3	2.8	2.4	1.9	1.8	2.4	2.0
Total active chlorine, kg tas^{-1}	29.7	27.8	34.5	31.9	39.1	35.5	43.3	39.1
*Bleachability	0.22	0.22	0.24	0.25	0.27	0.28	0.27	0.30

*Bleachability = (Δ kappa number (Kappa number across O-stage - Final kappa number)/Total active chlorine)

4. CONCLUSION

The low-REA leaded a higher pulp viscosity, xylan yield, cellulose yield and smaller brightness and HexA content, in relation to the high-REA ones. ^{31}P-NMR analysis of CEL preparations from *E. urophylla* x *E. grandis* hibryd pulp sample showed that low kappa pulps contain less aliphatic hydroxyl groups and more phenolic hydroxyl groups and carboxylic acid groups compared to higher kappa pulps. Low-REA pulps had high contents of aliphatic hydroxyl groups, except for pulps of kappa number 14, and higher contents of phenolic hydroxyl and carboxylic acid groups compared to the high-REA pulps.The pulps from low-REA cooks showed slightly higher O-stage efficiency (2%-4%), in spite of demanding about 5% to 10% more total active chlorine (TAC)for attaining the target brightness of 90% ISO, but pulp brightness stability was somewhat affected. Bleachability for the pulps produced from low-REA were smaller than those from high-REA cooks, mainly in the kappa number range of 22 to 26, for a given wood type.Our findings demonstrate that varying residual effective alkali in the cooking process might affect the performance of the bleaching for the eucalyptus wood.

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CONCLUSÃO GERAL

Este estudo investigou o efeito do álcali efetivo residual (baixo- e alto-AER) e do grau de deslignificação da polpa (kappa 14 a 26) no desempenho do cozimento kraft de quatro madeiras de eucalipto, na branqueabilidade e na composição química da polpa e da lignina residual. Independentemente do tipo de madeira, os cozimentos em baixo-AER exigiram,aproximadamente, 20% menos álcali efetivo e 50% mais fator-H do que os cozimentos em alto-AER para atingir os valores kappa desejado. Entre as várias madeiras estudadas, o *E. globulus* foi o mais fácil de deslignificar. Houve uma tendência para maiores rendimentos depuradopara os cozimentos terminados em maior número kappa, mas os rendimentosdepurado, livre de lignina-HexA, foram semelhantes para o intervalo denúmero kappa de 18 a 26. Nonúmero kappa 18 ± 1, os cozimentos em baixo-AER apresentaram maior rendimento de polpa (1,0%), rendimento de xilana (0,8%), rendimento de celulose (0,2%) e viscosidade (90 dm^3 kg^{-1}), em relação aos cozimentos em alto-AER. Houve uma tendência de maior preservação de MeGlcA e menor formação de HexA para as polpa obtidas dos cozimentos em baixo-AER, com o inverso ocorrendo para os de alta-AER. Os cozimentos em baixo-AER produziram polpas de menor alvura. A análise por RMN de ^{31}P a partir das preparações de CEL de cada amostra de polpa provenientes do cozimento do hibrído de *E. urophylla* x *E. grandis* mostrou que a estrutura da lignina residual difere dependendo do teor de ligninana polpa e do cozimento empregado. Verificou-se que as polpas de baixos números kappa contêm menos grupos hidroxilícos alifáticos e mais grupos hidroxilícos fenólicos e grupos ácido carboxílico em comparação com as polpas de altos números kappa. As polpas a partir dos cozimentos em baixo-AER apresentaram altos teores de grupos hidroxilícos alifáticos, com exceção das polpas de número kappa 14, e maiores teores de grupos hidroxilícosfenólicos e de ácidos carboxílicosem comparação com as polpas de alto-AER. A perda de grupos hidroxilas alifáticos foi atribuída, em parte, à perda do grupo hidroxilíco primário da cadeia de fenilpropano. Novos grupos hidroxílicos fenólicos são formados por clivagem da ligação éter-arila. As polpas de cozimento com baixo teor de AER em relação às de alto-AER apresentaram eficiência do estágio-O ligeiramente maior (2% a 4%), apesar de exigirem 5% a 10% mais cloro ativo total (CAT) para alcançar a alvura desejada de 90% ISO quando branqueada pela sequência D(EP)D. No entanto, a estabilidade de alvura da polpa foi pouco afetada. A branqueabilidade das polpas produzidas a partir de cozimentos em baixo-AER foram menores do que para as polpas produzidas a partir de cozimentos em alto-AER, principalmente quando considerado o intervalo de número kappa de 22 a 26, para um determinado tipo de madeira. Os resultados demonstram que o álcali efetivo residual variável no processo de cozimento, para madeiras de eucalipto, pode afetar, principalmente, o rendimento da polpa, os grupos funcionais da lignina residual (grupos hidroxila e carboxila) eo desempenho do processo de branqueamento.

ANEXOS DO PAPER 1

Quadro 1A. Resultados do processo de cozimento a partir do híbrido de *E. urophylla* x *E. grandis*

Amostra		Rep.	AE, %	FH	Temp., ºC	Nº Kappa	Rendimentos, %			Alvura, %ISO	Visc., dm³/Kg	Licor Negro	
							Depurado	Rejeito	Total			AER, g/L	pH
Híbrido de *E. urophylla* x *E. grandis*	Kappa 14 Baixo AER	A	16,5	1661	165	13,8	52,5	0,0	52,5	34,7	1009	2,1	12,3
		B	16,5	1661	165	13,9	52,5	0,0	52,5	34,9	1009	2,0	12,3
		Média	16,5	1661	165	13,8	52,5	0,0	52,5	34,8	1009	2,0	12,3
	Kappa 18 Baixo AER	A	14,7	933	165	17,2	53,6	0,4	54,0	32,9	1181	1,9	12,2
		B	14,7	933	165	17,4	53,8	0,4	54,2	32,9	1180	1,7	12,2
		Média	14,7	933	165	17,3	53,7	0,4	54,1	32,9	1180	1,8	12,2
	Kappa 22 Baixo AER	A	13,5	852	165	21,6	54,2	1,2	55,5	31,1	1312	1,0	11,8
		B	13,5	852	165	21,5	54,3	1,2	55,5	31,3	1310	1,1	12,0
		Média	13,5	852	165	21,6	54,3	1,2	55,5	31,2	1311	1,0	11,9
	Kappa 26 Baixo AER	A	13,3	761	165	25,3	54,1	2,5	56,6	29,9	1401	1,1	11,9
		B	13,3	761	165	25,3	54,5	2,3	56,8	29,9	1400	1,1	11,9
		Média	13,3	761	165	25,3	54,3	2,4	56,7	29,9	1400	1,1	11,9
	Kappa 14 Alto AER	A	19,5	802	165	13,6	52,0	0,2	52,2	37,2	965	9,0	12,6
		B	19,5	802	165	13,7	52,0	0,2	52,2	37,6	961	9,1	12,6
		Média	19,5	802	165	13,6	52,0	0,2	52,2	37,4	963	9,0	12,6
	Kappa 18 Alto AER	A	19,0	509	165	17,2	52,7	0,6	53,3	36,8	1135	9,0	12,6
		B	19,0	509	165	17,2	52,7	0,6	53,3	36,9	1125	9,1	12,6
		Média	19,0	509	165	17,2	52,7	0,6	53,3	36,8	1130	9,0	12,6
	Kappa 22 Alto AER	A	17,5	448	165	21,4	53,1	0,8	53,9	35,8	1240	8,2	12,5
		B	17,5	448	165	21,5	52,7	1,0	53,7	35,6	1240	8,4	12,6
		Média	17,5	448	165	21,4	52,9	0,9	53,8	35,7	1240	8,3	12,6
	Kappa 26 Alto AER	A	18,0	367	165	25,0	52,3	1,9	54,2	34,2	1331	9,0	12,5
		B	18,0	367	165	25,1	52,5	1,9	54,4	34,3	1330	9,0	12,6
		Média	18,0	367	165	25,0	52,4	1,9	54,3	34,2	1330	9,0	12,6

Quadro2A. Resultados do processo de cozimento a partir de *E. nitens*

Amostra		Rep.	AE, %	FH	Temp., ºC	Nº Kappa	Rendimentos, %			Alvura, %ISO	Visc., dm^3/Kg	Licor Negro	
							Depurado	Rejeito	Total			AER, g/L	pH
E. nitens	Kappa 14 Baixo AER	A	16,9	1641	165	14,5	52,2	0,1	52,3	33,4	1033	1,5	12,1
		B	16,9	1641	165	14,5	52,2	0,1	52,3	33,4	1037	1,1	12,3
		Média	16,9	1641	165	14,5	52,2	0,1	52,3	33,4	1035	1,3	12,2
	Kappa 18 Baixo AER	A	16,1	1213	165	18,2	54,0	0,3	54,3	31,4	1194	1,1	11,8
		B	16,1	1213	165	18,4	54,2	0,3	54,5	31,2	1188	1,0	11,9
		Média	16,1	1213	165	18,3	54,1	0,3	54,4	31,3	1191	1,0	11,8
	Kappa 22 Baixo AER	A	14,8	943	165	21,3	54,9	1,0	55,9	30,5	1290	1,0	11,9
		B	14,8	943	165	21,3	54,9	1,2	56,1	30,4	1294	1,0	11,9
		Média	14,8	943	165	21,3	54,9	1,1	56,0	30,4	1292	1,0	11,9
	Kappa 26 Baixo AER	A	14,6	771	165	25,4	54,7	2,8	57,5	30,0	1400	1,1	12,0
		B	14,6	771	165	25,6	54,6	2,8	57,4	29,8	1401	1,0	12,1
		Média	14,6	771	165	25,5	54,6	2,8	57,4	29,9	1400	1,0	12,0
	Kappa 14 Alto AER	A	20,0	802	165	14,2	51,5	0,3	51,8	37,9	968	8,1	12,7
		B	20,0	802	165	14,4	51,3	0,3	51,6	37,8	966	8,0	12,7
		Média	20,0	802	165	14,3	51,4	0,3	51,7	37,8	967	8,0	12,7
	Kappa 18 Alto AER	A	19,6	562	165	18,1	53,1	0,4	53,5	36,2	1100	8,9	12,7
		B	19,6	562	165	18,1	52,9	0,5	53,4	36,2	1101	8,9	12,7
		Média	19,6	562	165	18,1	53,0	0,4	53,4	36,2	1100	8,9	12,7
	Kappa 22 Alto AER	A	18,7	448	165	21,4	53,4	1,2	54,6	34,9	1178	9,0	12,7
		B	18,7	448	165	21,5	53,6	1,0	54,6	34,8	1174	9,1	12,7
		Média	18,7	448	165	21,4	53,5	1,1	54,6	34,8	1176	9,0	12,7
	Kappa 26 Alto AER	A	18,1	387	165	25,1	52,9	3,0	55,9	34,2	1280	8,3	12,7
		B	18,1	387	165	25,1	52,7	3,1	55,8	34,4	1280	8,5	12,7
		Média	18,1	387	165	25,1	52,8	3,0	55,8	34,3	1280	8,4	12,7

Quadro3A. Resultados do processo de cozimento a partir de *E.globulus*

Amostra		Rep.	AE, %	FH	Temp., ºC	Nº Kappa	Rendimentos, %			Alvura, %ISO	Visc., dm^3/Kg	Licor Negro	
							Depurado	Rejeito	Total			AER, g/L	pH
E.globulus	Kappa 14 Baixo AER	A	16,5	1631	165	13,6	53,8	0,1	53,9	29,4	1090	1,4	12,1
		B	16,5	1631	165	13,8	54,0	0,1	54,1	29,2	1091	1,2	12,3
		Média	16,5	1631	165	13,7	53,9	0,1	54,0	29,3	1090	1,3	12,2
	Kappa 18 Baixo AER	A	15,0	1075	165	18,1	54,7	1,6	56,3	28,0	1185	1,2	12,1
		B	15,0	1075	165	18,0	54,9	1,4	56,3	28,1	1183	1,3	12,2
		Média	15,0	1075	165	18,0	54,8	1,5	56,3	28,0	1184	1,2	12,2
	Kappa 22 Baixo AER	A	14,1	822	165	21,7	55,3	3,0	58,3	26,6	1309	1,0	11,8
		B	14,1	822	165	21,7	54,9	3,0	57,9	26,8	1309	1,0	12,0
		Média	14,1	822	165	21,7	55,1	3,0	58,1	26,7	1309	1,0	11,9
	Kappa 26 Baixo AER	A	13,8	771	165	25,4	54,9	3,8	58,7	24,8	1427	1,1	12,0
		B	13,8	771	165	25,2	54,9	3,8	58,7	24,9	1423	1,0	11,9
		Média	13,8	771	165	25,3	54,9	3,8	58,7	24,8	1425	1,0	12,0
	Kappa 14 Alto AER	A	19,7	822	165	13,8	53,1	0,3	53,4	31,8	1034	8,2	12,7
		B	19,7	822	165	13,9	52,9	0,3	53,2	32,0	1035	8,2	12,8
		Média	19,7	822	165	13,8	53,0	0,3	53,3	31,9	1034	8,2	12,7
	Kappa 18 Alto AER	A	19,6	519	165	17,6	53,6	1,3	54,9	30,4	1110	8,0	12,7
		B	19,6	519	165	17,6	53,8	1,1	54,9	30,4	1111	8,2	12,7
		Média	19,6	519	165	17,6	53,7	1,2	54,9	30,4	1110	8,1	12,7
	Kappa 22 Alto AER	A	18,3	448	165	21,6	53,7	2,4	56,1	28,6	1190	8,4	12,7
		B	18,3	448	165	21,8	53,7	2,2	55,9	28,4	1190	8,6	12,7
		Média	18,3	448	165	21,7	53,7	2,3	56,0	28,5	1190	8,5	12,7
	Kappa 26 Alto AER	A	18,0	357	165	25,3	53,3	4,5	57,8	27,7	1280	8,8	12,7
		B	18,0	357	165	25,3	53,2	4,3	57,5	27,7	1274	8,6	12,7
		Média	18,0	357	165	25,3	53,2	4,4	57,6	27,7	1277	8,7	12,7

Quadro 4A. Resultados do processo de cozimento a partir do híbrido de *E.nitens* x *E. globulus*

Amostra		Rep.	AE, %	FH	Temp., ºC	Nº Kappa	Rendimentos, %			Alvura, %ISO	Visc., dm^3/Kg	Licor Negro	
							Depurado	Rejeito	Total			AER, g/L	pH
Híbrido de *E. nitens* x *E. globulus*	Kappa 14 Baixo AER	A	16,8	1631	165	14,8	51,7	0,0	51,7	33,0	1060	1,1	11,8
		B	16,8	1631	165	14,6	51,7	0,0	51,7	33,1	1058	1,0	11,9
		Média	16,8	1631	165	14,7	51,7	0,0	51,7	33,0	1059	1,0	11,8
	Kappa 18 Baixo AER	A	16,0	1137	165	18,5	52,6	1,3	53,9	30,2	1189	1,1	11,9
		B	16,0	1137	165	18,5	52,8	1,3	54,1	30,6	1189	1,2	12,3
		Média	16,0	1137	165	18,5	52,7	1,3	54,0	30,4	1189	1,2	12,1
	Kappa 22 Baixo AER	A	14,7	943	165	21,0	53,3	2,6	55,9	29,2	1283	1,1	11,4
		B	14,7	943	165	21,1	52,9	2,5	55,4	29,2	1277	1,0	11,3
		Média	14,7	943	165	21,0	53,1	2,6	55,7	29,2	1280	1,0	11,4
	Kappa 26 Baixo AER	A	14,0	771	165	25,5	53,0	4,0	57,0	28,6	1390	1,0	11,3
		B	14,0	771	165	25,3	53,1	4,0	57,1	28,2	1388	1,2	11,3
		Média	14,0	771	165	25,4	53,1	4,0	57,1	28,4	1389	1,1	11,3
	Kappa 14 Alto AER	A	20,2	802	165	14,3	50,8	0,2	51,0	35,6	990	7,9	13,3
		B	20,2	802	165	14,1	50,8	0,2	51,0	35,7	991	8,4	12,9
		Média	20,2	802	165	14,2	50,8	0,2	51,0	35,6	990	8,2	13,1
	Kappa 18 Alto AER	A	19,2	519	165	18,2	51,5	1,2	52,7	34,1	1094	7,9	12,7
		B	19,2	519	165	18,0	51,7	1,1	52,8	34,1	1098	8,3	12,7
		Média	19,2	519	165	18,1	51,6	1,2	52,8	34,1	1096	8,1	12,7
	Kappa 22 Alto AER	A	18,3	403	165	21,0	51,8	3,0	54,8	32,8	1179	8,1	12,7
		B	18,3	403	165	21,1	51,6	3,0	54,6	33,0	1183	8,5	12,7
		Média	18,3	403	165	21,0	51,7	3,0	54,7	32,9	1181	8,3	12,7
	Kappa 26 Alto AER	A	17,9	360	165	25,1	51,1	4,6	55,7	32,0	1270	8,0	12,7
		B	17,9	360	165	25,1	51,1	4,4	55,5	32,1	1270	8,1	12,7
		Média	17,9	360	165	25,1	51,1	4,5	55,6	32,0	1270	8,0	12,7

ANEXOS DO PAPER 2

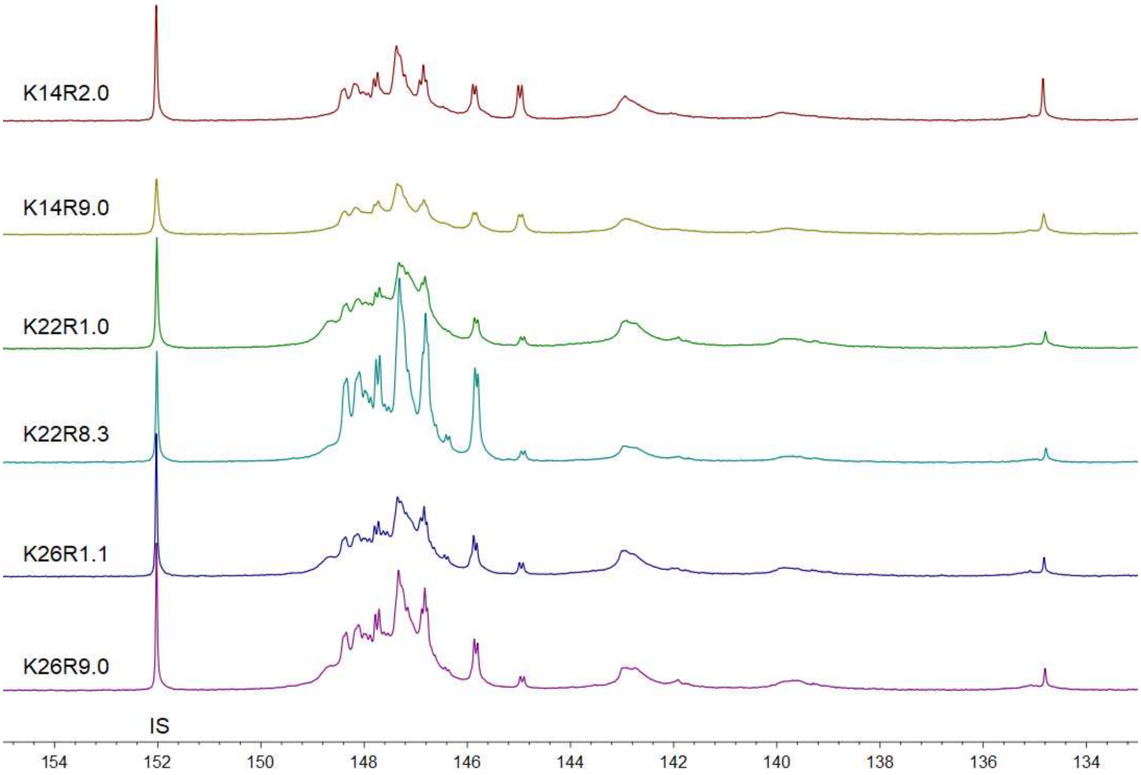

Figura 1B. Espectros de RMN de fósforo das amostras de lignina isolada (CEL) das polpas não branqueadas a partir do cozimento, em baixo e alto alcáli efetivo residual, dohibído de *E. urophylla* x *E. grandis*em números kappa de 14, 22 e 26.

ANEXOS DO PAPER 3

Quadro 1C. Resultados da deslignificação com oxigênio da polpa obtida pelo processo de cozimento a partir do híbrido de*E. urophylla* x *E. grandis* em baixo álcali efetivo residual para os kappa 14, 18, 22 e 26

Condições e Resultados	Pré O_2			
Kappa marrom	14	18	22	26
Consistência, %	11,5	11,5	11,5	11,5
Tempo, min	60	60	60	60
Temperatura, ºC	100	100	100	100
Pressão, Kpa	750	750	750	750
O_2, Kg/t	16	18	20	22
NaOH, Kg/t	16	18	20	22
pH	10,0	10,6	9,9	9,8
	10,2	10,6	10,0	9,6
Média	11,1	10,6	10,0	9,7
Alvura, %ISO	55,1	50,3	47,1	45,0
	55,0	50,1	47,1	45,2
Média	55,0	50,2	47,1	45,1
Número Kappa	7,7	9,3	11,0	12,0
	7,8	9,3	11,2	12,2
Média	7,8	9,3	11,1	12,1
Viscosidade, dm^3/Kg	893	978	1078	1117
	889	978	1081	1121
Média	891	978	1079	1119

Quadro 2C. Resultados da deslignificação com oxigênio da polpa obtida pelo processo de cozimento a partir do híbrido de*E. urophylla* x *E. grandis* em alto álcali efetivo residual para os kappa 14, 18, 22 e 26

Condições e Resultados	Pré O_2			
Kappa marrom	14	18	22	26
Consistência, %	11,5	11,5	11,5	11,5
Tempo, min	60	60	60	60
Temperatura, ºC	100	100	100	100
Pressão, Kpa	750	750	750	750
O_2, Kg/t	16	18	20	22
NaOH, Kg/t	16	18	20	22
pH	11,0	10,8	10,5	9,5
	11,2	10,7	10,5	9,3
Média	11,1	10,8	10,5	9,4
Alvura, %ISO	55,9	53,4	51,4	49,3
	55,9	53,6	51,2	49,3
Média	55,9	53,5	51,3	49,3
Número Kappa	8,0	9,6	11,5	12,6
	8,0	9,8	11,4	12,5
Média	8,0	9,7	11,4	12,6
Viscosidade, dm^3/Kg	853	943	1035	1081
	847	945	1043	1069
Média	850	944	1039	1075

Quadro 3C. Resultados da deslignificação com oxigênio da polpa obtida pelo processo de cozimento a partir de *E. nitens* em baixo álcali efetivo residual para os kappa 14, 18, 22 e 26

Condições e Resultados	Pré O_2			
Kappa marrom	14	18	22	26
Consistência, %	11,5	11,5	11,5	11,5
Tempo, min	60	60	60	60
Temperatura, ºC	100	100	100	100
Pressão, Kpa	750	750	750	750
O_2, Kg/t	16	18	20	22
NaOH, Kg/t	16	18	20	22
pH	10,8	10,8	10,2	10,0
	11,0	10,8	10,3	10,1
Média	10,9	10,8	10,2	10,0
Alvura, %ISO	54,7	50,9	49,0	48,1
	54,7	50,7	49,0	48,0
Média	54,7	50,8	49,0	48,0
Número Kappa	8,0	9,4	10,1	11,3
	8,1	9,2	10,1	11,3
Média	8,0	9,3	10,1	11,3
Viscosidade, dm^3/Kg	910	994	1019	1035
	918	993	1015	1035
Média	914	994	1017	1035

Quadro 4C. Resultados da deslignificação com oxigênio da polpa obtida pelo processo de cozimento a partir de *E. nitens* em alto álcali efetivo residual para os kappa 14, 18, 22 e 26

Condições e Resultados	Pré O_2			
Kappa marrom	14	18	22	26
Consistência, %	11,5	11,5	11,5	11,5
Tempo, min	60	60	60	60
Temperatura, ºC	100	100	100	100
Pressão, Kpa	750	750	750	750
O_2, Kg/t	16	18	20	22
NaOH, Kg/t	16	18	20	22
pH	11,0	10,9	10,3	10,0
	10,8	10,9	10,2	10,1
Média	10,9	10,9	10,2	10,0
Alvura, %ISO	57,6	55,1	52,6	51,5
	57,6	55,1	52,8	51,4
Média	57,6	55,1	52,7	51,4
Número Kappa	8,1	9,5	10,9	11,9
	8,1	9,6	10,7	11,9
Média	8,1	9,6	10,8	11,9
Viscosidade, dm^3/Kg	859	936	943	983
	861	930	942	978
Média	860	933	942	980

Quadro 5C.Resultados da deslignificação com oxigênio da polpa obtida pelo processo de cozimento a partir de *E.globulus* em baixo álcali efetivo residual para os kappa 14, 18, 22 e 26

Condições e Resultados	Pré O_2			
Kappa marrom	14	18	22	26
Consistência, %	11,5	11,5	11,5	11,5
Tempo, min	60	60	60	60
Temperatura, ºC	100	100	100	100
Pressão, Kpa	750	750	750	750
O_2, Kg/t	16	18	20	22
NaOH, Kg/t	16	18	20	22
pH	11,0	11,5	11,4	9,9
	11,1	11,5	11,6	9,8
Média	11,0	11,5	11,5	9,8
Alvura, %ISO	52,0	49,5	46,7	43,0
	52,1	49,4	46,7	43,1
Média	52,0	49,4	46,7	43,0
Número Kappa	7,6	9,1	10,1	11,0
	7,4	9,1	10,0	11,2
Média	7,5	9,1	10,0	11,1
Viscosidade, dm^3/Kg	963	1018	1063	1126
	969	1019	1059	1124
Média	966	1018	1061	1125

Quadro 6C. Resultados da deslignificação com oxigênio da polpa obtida pelo processo de cozimento a partir de *E.globulus* em alto álcali efetivo residual para os kappa 14, 18, 22 e 26

Condições e Resultados	Pré O_2			
Kappa marrom	14	18	22	26
Consistência, %	11,5	11,5	11,5	11,5
Tempo, min	60	60	60	60
Temperatura, ºC	100	100	100	100
Pressão, Kpa	750	750	750	750
O_2, Kg/t	16	18	20	22
NaOH, Kg/t	16	18	20	22
pH	11,0	11,7	10,1	10,2
	11,1	11,7	10,0	10,4
Média	11,0	11,7	10,0	10,3
Alvura, %ISO	53,0	50,2	47,0	45,5
	53,0	50,4	47,1	45,5
Média	53,0	50,3	47,0	45,5
Número Kappa	7,8	9,3	10,6	11,8
	7,7	9,3	10,5	11,6
Média	7,8	9,3	10,6	11,7
Viscosidade, dm^3/Kg	935	980	1020	1066
	941	981	1016	1060
Média	938	980	1018	1063

Quadro 7C. Resultados da deslignificação com oxigênio da polpa obtida pelo processo de cozimento a partir do híbrido de *E.nitens* x *E. globulus* em baixo álcali efetivo residual para os kappa 14, 18, 22 e 26

Condições e Resultados	Pré O_2			
Kappa marrom	14	18	22	26
Consistência, %	11,5	11,5	11,5	11,5
Tempo, min	60	60	60	60
Temperatura, ºC	100	100	100	100
Pressão, Kpa	750	750	750	750
O_2, Kg/t	16	18	20	22
NaOH, Kg/t	16	18	20	22
pH	10,8	10,7	9,8	10,3
	11,0	10,7	10,0	10,3
Média	10,9	10,7	9,9	10,3
Alvura, %ISO	53,8	52,0	47,0	45,1
	54,0	52,1	46,8	45,0
Média	53,9	52,0	46,9	45,0
Número Kappa	8,4	10,1	10,7	12,0
	8,5	10,0	10,7	12,1
Média	8,4	10,0	10,7	12,0
Viscosidade, dm^3/Kg	942	1008	1051	1073
	940	1012	1046	1073
Média	941	1010	1048	1073

Quadro 8C. Resultados da deslignificação com oxigênio da polpa obtida pelo processo de cozimento a partir do híbrido de *E.nitens* x *E. globulus* em alto álcali efetivo residual para os kappa 14, 18, 22 e 26

Condições e Resultados	Pré O_2			
Kappa marrom	14	18	22	26
Consistência, %	11,5	11,5	11,5	11,5
Tempo, min	60	60	60	60
Temperatura, ºC	100	100	100	100
Pressão, Kpa	750	750	750	750
O_2, Kg/t	16	18	20	22
NaOH, Kg/t	16	18	20	22
pH	11,5	10,0	10,5	10,1
	11,3	10,0	10,5	10,0
Média	11,4	10,0	10,5	10,0
Alvura, %ISO	57,8	51,6	50,6	49,3
	57,9	51,4	50,4	49,2
Média	57,8	51,5	50,5	49,2
Número Kappa	8,4	10,3	11,0	12,5
	8,5	10,2	11,2	12,5
Média	8,4	10,2	11,1	12,5
Viscosidade, dm^3/Kg	890	955	990	1006
	896	956	991	1006
Média	893	956	990	1006

Quadro 9C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. urophylla x E grandis hybrid* em baixo álcali efetivo residual e número kappa 14

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7	-	0,9	0,5	-	0,9
ClO_2 $_{\text{como } ClO2}$ kg/t	6,23	-	1	2	3	1,0
pH final	3,1	10,5	5,4	5,5	5,4	5,5
Consumo de Reagentes, %	100	85,9	-	-	-	85,3
	100	86,0	-	-	-	85,2
Média	100	85,9	-	-	-	85,3
Número Kappa	-	2,5	-	-	-	1,6
	-	2,4	-	-	-	1,6
Média	-	2,5	-	-	-	1,6
Alvura A.D., % ISO	73,6	86,5	90	90,6	91,3	90,0
	73,5	86,4	90	90,5	91,4	90,0
Média	73,6	86,5	90	90,6	91,4	90
Reversão de Alvura, % ISO	-	-	-	-	-	2,4
	-	-	-	-	-	2,4
Média	-	-	-	-	-	2,4
Viscosidade (dm^3/kg)	-	-	-	-	-	702
	-	-	-	-	-	702
Média	-	-	-	-	-	702

Quadro 10C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. urophylla x E grandis hybrid* em alto álcali efetivo residual e número kappa 14.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	6,5	-	1,1	0,9	0,7	0,8
ClO_2 $_{\text{como } ClO2}$ kg/t	6,39	-	0,5	1	1,5	0,5
pH final	4	10,5	5,4	5,5	5,5	5,5
Consumo de Reagentes, %	100	73,4	-	-	-	67,2
	100	73,4	-	-	-	67,2
Média	100	73,4	-	-	-	67,2
Número Kappa	-	2,8	-	-	-	2,1
	-	2,7	-	-	-	2,0
Média	-	2,8	-	-	-	2,1
Alvura A.D., % ISO	74,2	86,9	90,0	90,5	90,9	90,0
	74,2	86,8	90,0	90,6	91,0	90,0
Média	74,2	86,9	90,0	90,6	91,0	90
Reversão de Alvura, % ISO	-	-	-	-	-	2,3
	-	-	-	-	-	2,2
Média	-	-	-	-	-	2,3
Viscosidade (dm^3/kg)	-	-	-	-	-	672
	-	-	-	-	-	676
Média	-	-	-	-	-	674

Quadro 11C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. urophylla x E grandis hybrid* em baixo álcali efetivo residual e número kappa 18.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7	-	1,1	0,9	0,7	0,8
ClO_2 $_{\text{como ClO2}}$ kg/t	7,43	-	0,5	1	1,5	1,1
pH final	3,5	10,5	5,5	5,4	5,5	5,5
Consumo de Reagentes, %	100	69,6	-	-	-	80,5
	100	69,6	-	-	-	80,5
Média	100	69,6	-	-	-	80,5
Número Kappa	-	2,7	-	-	-	1,6
	-	2,6	-	-	-	1,6
Média	-	2,7	-	-	-	1,6
Alvura A.D., % ISO	70,3	86,3	89,4	89,8	90,4	90,0
	70,4	86,4	89,4	89,9	90,5	90,0
Média	70,4	86,4	89,4	89,9	90,5	90
Reversão de Alvura, % ISO	-	-	-	-	-	2,8
	-	-	-	-	-	2,7
Média	-	-	-	-	-	2,8
Viscosidade (dm^3/kg)	-	-	-	-	-	800
	-	-	-	-	-	814
Média	-	-	-	-	-	807

Quadro 12C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. urophylla x E grandis hybrid* em alto álcali efetivo residual e número kappa 18.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	6,5	-	1,1	0,9	0,7	1,1
$ClO_{2\ \text{como ClO2}}$ kg/t	7,75	-	0,5	1	1,5	0,6
pH final	3,1	10,5	5,4	5,5	5,5	5,5
Consumo de Reagentes, %	100	64,8	-	-	-	67,2
	100	64,7	-	-	-	67,2
Média	100	64,8	-	-	-	67,2
Número Kappa	-	3,0	-	-	-	1,9
	-	2,9	-	-	-	1,8
Média	-	3,0	-	-	-	1,9
Alvura A.D., % ISO	72,2	87,2	89,8	90,7	90,9	90,0
	72,1	87,3	89,7	90,7	90,8	90,0
Média	72,2	87,3	89,8	90,7	90,9	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,4
	-	-	-	-	-	2,4
Média	-	-	-	-	-	2,4
Viscosidade (dm^3/kg)	-	-	-	-	-	782
	-	-	-	-	-	782
Média	-	-	-	-	-	782

Quadro 13C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. urophylla x E grandis hybrid* em baixo álcali efetivo residual e número kappa 22.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7	-	0,9	0,5	-	0,6
ClO_2 $_{\text{como } ClO2}$ kg/t	8,863	-	1	2	3	1,6
pH final	3,3	10,5	5,5	5,6	5,5	5,5
Consumo de Reagentes, %	100	81,2	-	-	-	93,2
	100	81,2	-	-	-	93,2
Média	100	81,2	-	-	-	93,2
Número Kappa	-	2,5	-	-	-	1,3
	-	2,5	-	-	-	1,2
Média	-	2,5	-	-	-	1,3
Alvura A.D., % ISO	66,4	86,0	89,6	90,2	90,6	90
	66,3	85,9	89,5	90,3	90,5	90
Média	66,4	86	89,6	90,3	90,6	90
Reversão de Alvura, % ISO	-	-	-	-	-	1,9
	-	-	-	-	-	1,8
Média	-	-	-	-	-	1,9
Viscosidade (dm^3/kg)	-	-	-	-	-	914
	-	-	-	-	-	914
Média	-	-	-	-	-	914

Quadro 14C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. urophylla x E grandis hybrid* em alto álcali efetivo residual e número kappa 22.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	6,5	-	1,1	0,9	0,7	1,1
ClO_2 $_{\text{como } ClO2}$ kg/t	3,59	-	0,5	1	1,5	0,5
pH final	3,1	10,5	5,5	5,4	5,5	5,5
Consumo de Reagentes, %	100	85,2	-	-	-	67,3
	100	85,2	-	-	-	67,3
Média	100	85,2	-	-	-	67,3
Número Kappa	-	2,8	-	-	-	1,6
	-	2,7	-	-	-	1,5
Média	-	2,8	-	-	-	1,6
Alvura A.D., % ISO	69,9	87,3	90	90,4	90,7	90
	69,9	87,3	90	90,3	90,8	90
Média	69,9	87,3	90	90,4	90,8	90
Reversão de Alvura, % ISO	-	-	-	-	-	1,8
	-	-	-	-	-	1,8
Média	-	-	-	-	-	1,8
Viscosidade (dm^3/kg)	-	-	-	-	-	886
	-	-	-	-	-	900
Média	-	-	-	-	-	888

Quadro 15C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. urophylla x E grandis hybrid* em baixo álcali efetivo residual e número kappa 26.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7	-	1,1	0,9	0,7	0,2
$ClO_{2\ \text{como}\ ClO2}$ kg/t	9,66	-	1	2	3	2,6
pH final	3,4	10,5	5,5	5,5	5,6	5,5
Consumo de Reagentes, %	100	75,0	-	-	-	82,2
		75,0	-	-	-	82,2
Média	100	75,0	-	-	-	82,2
Número Kappa	-	2,6	-	-	-	0,8
	-	2,6	-	-	-	0,7
Média	-	2,6	-	-	-	0,8
Alvura A.D., % ISO	65,4	84,9	88,8	89,4	90,3	90
	65,3	84,9	88,7	89,5	90,3	90
Média	65,4	84,9	88,8	89,5	90,3	90
Reversão de Alvura, % ISO	-	-	-	-	-	2,4
	-	-	-	-	-	2,3
Média	-	-	-	-	-	2,4
Viscosidade (dm^3/kg)	-	-	-	-	-	980
	-	-	-	-	-	990
Média	-	-	-	-	-	985

Quadro 16C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. urophylla x E grandis hybrid* em alto álcali efetivo residual e número kappa 26.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	5,5	-	1,1	0,9	0,7	1,0
$ClO_{2\ \text{como ClO2}}$ kg/t	10,06	-	0,5	1	1,5	0,70
pH final	3,2	10,5	5,4	5,5	5,5	5,5
Consumo de Reagentes, %	100	77,3	-	-	-	65,8
	100	77,3	-	-	-	65,8
Média	100	77,3	-	-	-	65,8
Número Kappa	-	2,8	-	-	-	1,3
	-	2,8	-	-	-	1,2
Média	-	2,8	-	-	-	1,3
Alvura A.D., % ISO	68,0	86,9	89,8	90,2	90,7	90
	68,0	86,8	89,7	90,3	90,7	90
Média	68	86,9	89,8	90,3	90,7	90
Reversão de Alvura, % ISO	-	-	-	-	-	2,0
	-	-	-	-	-	2,0
Média	-	-	-	-	-	2,0
Viscosidade (dm^3/kg)	-	-	-	-	-	960
	-	-	-	-	-	950
Média	-	-	-	-	-	955

Quadro 17C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. globulus*em baixo álcali efetivo residual e número kappa 14.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	0,9	0,5	-	0,9
ClO_2 como ClO_2 kg/t	6,0	-	1	2	3	1,0
pH final	3,3	10,5	5,5	5,4	5,5	5,5
Consumo de Reagentes, %	100	78,9	-	-	-	97,7
	100	78,9	-	-	-	97,7
Média	100	78,9	-	-	-	97,7
Número Kappa	-	3	-	-	-	1,2
	-	2,9	-	-	-	1,1
Média	-	3	-	-	-	1,2
Alvura A.D., % ISO	75,1	85,2	90,0	90,3	90,7	90,0
	75,0	85,1	90,0	90,2	90,6	90,0
Média	75,1	85,2	90	90,3	90,7	90
Reversão de Alvura, % ISO	-	-	-	-	-	2,7
	-	-	-	-	-	2,7
Média	-	-	-	-	-	2,7
Viscosidade (dm^3/kg)	-	-	-	-	-	822
	-	-	-	-	-	822
Média	-	-	-	-	-	822

Quadro 18C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. globulus*em alto álcali efetivo residual e número kappa 14.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	1,1	0,9	0,7	1,1
ClO_2 $_{\text{como ClO2}}$ kg/t	6,2	-	0,5	1	1,5	0,5
pH final	2,9	10,5	5,4	5,5	5,6	5,5
Consumo de Reagentes, %	100	72,7	-	-	-	67,2
	100	72,7	-	-	-	
Média	100	72,7	-	-	-	
Número Kappa	-	2,5	-	-	-	1,6
	-	2,4	-	-	-	1,6
Média	-	2,5	-	-	-	1,6
Alvura A.D., % ISO	73,4	86,9	90,0	90,5	90,9	90,0
	73,4	86,8	90,0	90,4	90,9	90,0
Média	73,4	86,9	90,0	90,5	90,94	90
Reversão de Alvura, % ISO	-	-	-	-	-	2,4
	-	-	-	-	-	2,3
Média	-	-	-	-	-	2,4
Viscosidade (dm^3/kg)	-	-	-	-	-	810
	-	-	-	-	-	819
Média	-	-	-	-	-	814

Quadro 19C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. globulus* em baixo álcali efetivo residual e número kappa 18.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^0C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	9	-	0,9	0,5	-	0,9
$ClO_{2\ \text{como ClO2}}$ kg/t	7,3	-	1	2	3	1,1
pH final	3,5	10,5	5,5	5,4	5,4	5,5
Consumo de Reagentes, %	100	69,5	-	-	-	95,04
	100	69,5	-	-	-	
Média	100	69,5	-	-	-	
Número Kappa	-	2,6	-	-	-	1,1
	-	2,6	-	-	-	1,1
Média	-	2,6	-	-	-	1,1
Alvura A.D., % ISO	74,7	87,1	89,9	90,6	91,2	90,0
	74,6	87,1	89,8	90,5	91,2	90,0
Média	74,7	87,1	89,9	90,6	91,2	90
Reversão de Alvura, % ISO	-	-	-	-	-	2,6
	-	-	-	-	-	2,5
Média	-	-	-	-	-	2,6
Viscosidade (dm^3/kg)	-	-	-	-	-	910
	-	-	-	-	-	910
Média	-	-	-	-	-	910

Quadro 20C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. globulus*em alto álcali efetivo residual e número kappa 18.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	9	-	1,2	1,1	1	1,2
$ClO_{2\ \text{como ClO2}}$ kg/t	7,4	-	0,3	0,6	0,9	0,3
pH final	3	10,5	5,6	5,5	5,5	5,5
Consumo de Reagentes, %	100	75,0	-	-	-	80,1
	100	75,0	-	-	-	80,1
Média	100	75,0	-	-	-	80,1
Número Kappa	-	2,9	-	-	-	1,8
	-	2,8	-	-	-	1,7
Média	-	2,9	-	-	-	1,8
Alvura A.D., % ISO	74,9	86,6	90,0	90,6	91,2	90,0
	74,9	86,5	90,0	90,4	91,2	90,0
Média	74,9	86,6	90	90,6	91,2	90
Reversão de Alvura, % ISO	-	-	-	-	-	2,3
	-	-	-	-	-	2,3
Média	-	-	-	-	-	2,3
Viscosidade (dm^3/kg)	-	-	-	-	-	882
	-	-	-	-	-	882
Média	-	-	-	-	-	882

Quadro 21C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. globulus*em baixo álcali efetivo residual e número kappa 22.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^0C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	8,5	-	0,9	0,5	-	0,6
$ClO_{2\ \text{como ClO2}}$ kg/t	8,0	-	1	2	3	1,7
pH final	3,7	10,5	5,6	5,5	5,4	5,5
Consumo de Reagentes, %	100	78,1	-	-	-	90,4
	100	78,1	-	-	-	90,4
Média	100	78,1	-	-	-	90,4
Número Kappa	-	2,7	-	-	-	1,1
	-	2,6	-	-	-	1,0
Média	-	2,7	-	-	-	1,1
Alvura A.D., % ISO	73,1	84,8	89,8	90,1	91,1	90,0
	73,0	84,7	89,7	90,1	91,1	90,0
Média	73,1	84,8	89,8	90,1	91,1	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,4
	-	-	-	-	-	2,5
Média	-	-	-	-	-	2,5
Viscosidade (dm^3/kg)	-	-	-	-	-	970
	-	-	-	-	-	990
Média	-	-	-	-	-	980

Quadro 2C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. globulus*em alto álcali efetivo residual e número kappa 22.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	1,1	0,9	0,7	1,1
ClO_2 $_{\text{como ClO2}}$ kg/t	8,5	-	0,5	1	1,5	0,5
pH final	3,2	10,5	5,5	5,5	5,6	5,5
Consumo de Reagentes, %	100	75,0	-	-	-	89,8
	100	75,0	-	-	-	89,8
Média	100	75,0	-	-	-	89,8
Número Kappa	-	2,9	-	-	-	1,8
	-	2,8	-	-	-	1,7
Média	-	2,9	-	-	-	1,8
Alvura A.D., % ISO	74,1	87,1	90	90,3	90,6	90,0
	74,1	87,1	90	90,1	90,7	90,0
Média	74,1	87,1	90	90,3	90,7	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,1
	-	-	-	-	-	2,0
Média	-	-	-	-	-	2,1
Viscosidade (dm^3/kg)	-	-	-	-	-	931
	-	-	-	-	-	931
Média	-	-	-	-	-	931

Quadro 23C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. globulus*em baixo álcali efetivo residual e número kappa 26.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	8,5	-	0,9	0,5	-	0,5
ClO_2 $_{\text{como } ClO2}$ kg/t	8,86	-	1	2	3	2,0
pH final	3,4	10,5	5,5	5,4	5,5	5,4
Consumo de Reagentes, %	100	82,0	-	-	-	79,5
	100	82,0	-	-	-	79,5
Média	100	82,0	-	-	-	79,5
Número Kappa	-	2,7	-	-	-	1,2
	-	2,7	-	-	-	1,1
Média	-	2,7	-	-	-	1,2
Alvura A.D., % ISO	67,8	85,1	88,7	90,0	90,8	90,0
	67,8	85,0	88,8	90,0	90,7	90,0
Média	67,8	85,1	88,8	90	90,8	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,6
	-	-	-	-	-	2,5
Média	-	-	-	-	-	2,6
Viscosidade (dm^3/kg)	-	-	-	-	-	1010
	-	-	-	-	-	1014
Média	-	-	-	-	-	1012

Quadro 24C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. globulus*em alto álcali efetivo residual e número kappa 26.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	8,5	-	1,1	0,9	0,7	1,1
$ClO_{2\ \text{como ClO2}}$ kg/t	9,34	-	0,5	1	1,5	0,5
pH final	3,2	10,5	5,5	5,4	5,5	5,5
Consumo de Reagentes, %	100	71,1	-	-	-	83,6
	100	71,1	-	-	-	83,6
Média	100	71,1	-	-	-	83,6
Número Kappa	-	3,0	-	-	-	2,0
	-	2,9	-	-	-	2,0
Média	-	3,0	-	-	-	2,0
Alvura A.D., % ISO	70,7	87,1	90	90,3	90,7	90,0
	70,6	87,0	90	90,2	90,6	90,0
Média	70,7	87,1	90	90,3	90,7	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,1
	-	-	-	-	-	2,1
Média	-	-	-	-	-	2,1
Viscosidade (dm^3/kg)	-	-	-	-	-	979
	-	-	-	-	-	979
Média	-	-	-	-	-	979

Quadro 25C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. Nitens*em baixo álcali efetivo residual e número kappa 14.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	0,9	0,5	-	0,8
$ClO_{2\ \mathrm{como\ ClO2}}$ kg/t	6,4	-	1	2	3	1,2
pH final	3,2	10,5	5,6	5,5	5,5	5,5
Consumo de Reagentes, %	100	72,7	-	-	-	78,4
	100	72,7	-	-	-	78,4
Média	100	72,7	-	-	-	78,4
Número Kappa	-	3,0	-	-	-	1,5
	-	3,0	-	-	-	1,4
Média	-	3,0	-	-	-	1,5
Alvura A.D., % ISO	75,2	86,1	89,9	90,4	91,1	90,0
	75,2	86,1	89,9	90,4	91,1	90,0
Média	75,2	86,1	89,9	90,4	91,1	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,5
	-	-	-	-	-	2,4
Média	-	-	-	-	-	2,5
Viscosidade (dm^3/kg)	-	-	-	-	-	812
	-	-	-	-	-	804
Média	-	-	-	-	-	808

Quadro 26C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. Nitens*em alto álcali efetivo residual e número kappa 14.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	1,1	0,9	0,7	1,1
ClO_2 $_{\text{como ClO2}}$ kg/t	6,5	-	0,5	1	1,5	0,50
pH final	3,1	10,5	5,6	5,5	5,4	5,5
Consumo de Reagentes, %	100	75,0	-	-	-	67,2
	100	75,0	-	-	-	67,2
Média	100	75,0	-	-	-	67,2
Número Kappa	-	2,8	-	-	-	2,1
	-	2,8	-	-	-	2,0
Média	-	2,8	-	-	-	2,1
Alvura A.D., % ISO	76,7	87,2	90,0	90,4	90,7	90,0
						90,0
Média	76,7	87,2	90	90,4	90,7	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,2
	-	-	-	-	-	2,1
Média	-	-	-	-	-	2,2
Viscosidade (dm^3/kg)	-	-	-	-	-	770
	-	-	-	-	-	764
Média	-	-	-	-	-	768

Quadro 27C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. Nitens*em baixo álcali efetivo residual e número kappa 18.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	0,9	0,5	-	0,6
$ClO_{2\ \text{como ClO2}}$ kg/t	7,4	-	1	2	3	1,8
pH final	3,5	10,5	5,4	5,5	5,4	5,5
Consumo de Reagentes, %	100	49,2	-	-	-	86,4
	100	49,2	-	-	-	86,4
Média	100	49,2	-	-	-	86,4
Número Kappa	-	3,0	-	-	-	1,2
	-	3,0	-	-	-	1,2
Média	-	3,0	-	-	-	1,2
Alvura A.D., % ISO	74,2	84,8	89,1	90,2	91,1	90,0
	74,2	84,7	89,0	90,3	91,1	90,0
Média	74,2	84,8	89,1	90,3	91,1	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,9
	-	-	-	-	-	2,8
Média	-	-	-	-	-	2,9
Viscosidade (dm^3/kg)	-	-	-	-	-	878
	-	-	-	-	-	878
Média	-	-	-	-	-	878

Quadro 28C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. Nitens*em alto álcali efetivo residual e número kappa 18.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	1,1	0,9	0,7	1
ClO_2 $_{\text{como ClO2}}$ kg/t	7,7	-	0,5	1	1,5	0,8
pH final	3,1	10,5	5,5	5,4	5,5	5,5
Consumo de Reagentes, %	100	58,6	-	-	-	77,3
	100	58,6	-	-	-	77,3
Média	100	58,6	-	-	-	77,3
Número Kappa	-	3,0	-	-	-	1,6
	-	2,9	-	-	-	1,5
Média	-	3,0	-	-	-	1,6
Alvura A.D., % ISO	74,6	86,4	89,4	90,2	90,9	90,0
	74,5	86,3	89,5	90,3	90,9	90,0
Média	74,6	86,4	89,5	90,3	90,9	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,4
	-	-	-	-	-	2,5
Média	-	-	-	-	-	2,5
Viscosidade (dm^3/kg)	-	-	-	-	-	850
	-	-	-	-	-	846
Média	-	-	-	-	-	848

Quadro 29C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. Nitens*em baixo álcali efetivo residual e número kappa 22.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	0,9	0,5	-	0,3
ClO_2 $_{\text{como ClO2}}$ kg/t	8,1	-	1	2	3	2,5
pH final	3,6	10,5	5,5	5,5	5,4	5,5
Consumo de Reagentes, %	100	53,9	-	-	-	89,6
	100	53,9	-	-	-	89,6
Média	100	53,9	-	-	-	89,6
Número Kappa	-	2,8	-	-	-	0,9
	-	2,7	-	-	-	0,8
Média	-	2,8	-	-	-	0,9
Alvura A.D., % ISO	71,2	84,7	88,7	89,7	90,3	90,0
	71,2	84,6	88,8	89,7	90,2	90,0
Média	71,2	84,7	88,8	89,7	90,3	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,8
	-	-	-	-	-	2,8
Média	-	-	-	-	-	2,8
Viscosidade (dm^3/kg)	-	-	-	-	-	917
	-	-	-	-	-	917
Média	-	-	-	-	-	917

Quadro 30C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. Nitens*em alto álcali efetivo residual e número kappa 22.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	1,1	0,9	0,7	1
ClO_2 $_{\text{como ClO2}}$ kg/t	8,6	-	0,5	1	1,5	0,7
pH final	3,2	10,5	5,5	5,5	5,5	5,5
Consumo de Reagentes, %	100	70,3	-	-	-	77,7
	100	70,3	-	-	-	77,7
Média	100	70,3	-	-	-	77,7
Número Kappa	-	3,0	-	-	-	1,5
	-	2,9	-	-	-	1,4
Média	-	3,0	-	-	-	1,5
Alvura A.D., % ISO	70,9	86,8	89,8	90,4	91,2	90,0
	70,8	86,9	89,7	90,4	91,3	90,0
Média	70,9	86,9	89,8	90,4	91,3	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,7
	-	-	-	-	-	2,7
Média	-	-	-	-	-	2,7
Viscosidade (dm^3/kg)	-	-	-	-	-	883
	-	-	-	-	-	882
Média	-	-	-	-	-	883

Quadro 31C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. Nitens*em baixo álcali efetivo residual e número kappa 26.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	0,9	0,5	-	0,4
ClO_2 $_{\text{como ClO2}}$ kg/t	9,02	-	1	2	3	2,33
pH final	3,6	10,5	5,5	5,5	5,5	5,5
Consumo de Reagentes, %	100	68,0	-	-	-	83,3
	100	68,0	-	-	-	83,3
Média	100	68,0	-	-	-	83,3
Número Kappa	-	2,4	-	-	-	0,6
	-	2,4	-	-	-	0,5
Média	-	2,4	-	-	-	0,6
Alvura A.D., % ISO	70,8	85,7	89,2	89,7	90,4	90,0
	70,7	85,6	89,3	89,8	90,3	90,0
Média	70,77	85,7	89,3	89,8	90,4	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,5
	-	-	-	-	-	2,6
Média	-	-	-	-	-	2,6
Viscosidade (dm^3/kg)	-	-	-	-	-	965
	-	-	-	-	-	955
Média	-	-	-	-	-	960

Quadro 32C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *E. Nitens*em alto álcali efetivo residual e número kappa 26.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	0,9
H_2SO_4, kg/t	7,5	-	0,9	0,5	-	*
$ClO_{2\text{ como }ClO2}$ kg/t	9,50	-	1	2	3	1,0
pH final	3,4	10,5	5,5	5,5	5,5	5,5
Consumo de Reagentes, %	100	61,7	-	-	-	77,7
	100	61,7	-	-	-	77,8
Média	100	61,7	-	-	-	77,8
Número Kappa	-	2,8	-	-	-	0,9
	-	2,7	-	-	-	0,8
Média	-	2,8	-	-	-	0,9
Alvura A.D., % ISO	70,5	86,5	90	90,5	90,9	90,0
	70,4	86,5	90	90,4	90,9	90,0
Média	70,5	86,5	90	90,5	90,9	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,1
	-	-	-	-	-	2,0
Média	-	-	-	-	-	2,1
Viscosidade (dm^3/kg)	-	-	-	-	-	915
	-	-	-	-	-	925
Média	-	-	-	-	-	920

Quadro 33C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira do hibído de *E.nitens* x *E.globulus*em baixo álcali efetivo residual e número kappa 14.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	0,9	0,5	-	0,9
$ClO_{2\ \text{como ClO2}}$ kg/t	6,7	-	1	2	3	1,1
pH final	3,7	10,5	5,4	5,5	5,5	5,5
Consumo de Reagentes, %	100	65,6	-	-	-	72,7
	100	65,6	-	-	-	72,6
Média	100	65,6	-	-	-	72,7
Número Kappa	-	3,2	-	-	-	1,4
	-	3,1	-	-	-	1,3
Média	-	3,2	-	-	-	1,4
Alvura A.D., % ISO	74,8	86,3	89,9	90,6	91,1	90,0
	74,7	86,3	89,9	90,5	91	90,0
Média	74,8	86,3	89,9	90,6	91,1	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,0
	-	-	-	-	-	1,9
Média	-	-	-	-	-	2,0
Viscosidade (dm^3/kg)	-	-	-	-	-	763
	-	-	-	-	-	775
Média	-	-	-	-	-	769

Quadro 34C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira do hibído de *E.nitens* x *E.globulus* em alto álcali efetivo residual e número kappa 14.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	8	-	1,2	1,1	1	1,1
$ClO_{2\ \text{como}\ ClO2}$ kg/t	6,7	-	0,3	0,6	0,9	0,5
pH final	3,4	10,5	5,5	5,5	5,4	5,5
Consumo de Reagentes, %	73,4	57,0	-	-	-	67,2
	73,3	57,0	-	-	-	67,4
Média	73,4	57,0	-	-	-	67,3
Número Kappa	-	2,9	-	-	-	1,6
	-	2,8	-	-	-	1,5
Média	-	2,9	-	-	-	1,6
Alvura A.D., % ISO	75	86,5	89,5	90,1	90,8	90,0
	74,9	86,4	89,5	90,1	90,7	90,0
Média	75	86,5	89,5	90,1	90,8	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	1,7
	-	-	-	-	-	1,6
Média	-	-	-	-	-	1,7
Viscosidade (dm^3/kg)	-	-	-	-	-	731
	-	-	-	-	-	725
Média	-	-	-	-	-	728

Quadro 35C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira do hibído de *E.nitens* x *E.globulus* em baixo álcali efetivo residual e número kappa 18.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	8	-	0,9	0,5	-	0,8
ClO_2 $_{\text{como ClO2}}$ kg/t	8,0	-	1	2	3	1,3
pH final	3,7	10,5	5,5	5,5	5,3	5,5
Consumo de Reagentes, %	100	71,1	-	-	-	79
	100	71,1	-	-	-	79,1
Média	100	71,1	-	-	-	79,1
Número Kappa	-	2,7	-	-	-	1,4
	-	2,6	-	-	-	1,3
Média	-	2,7	-	-	-	1,4
Alvura A.D., % ISO	73,5	85,8	89,7	90,6	90,7	90,0
	73,5	85,7	89,7	90,5	90,7	90,0
Média	73,5	85,8	89,7	90,6	90,7	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	1,9
	-	-	-	-	-	2,0
Média	-	-	-	-	-	2,0
Viscosidade (dm^3/kg)	-	-	-	-	-	890
	-	-	-	-	-	894
Média	-	-	-	-	-	892

Quadro 36C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de do hibrído de *E. nitens x E. glubulos* em alto álcali efetivo residual e número kappa 18.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	1,2	1,1	1	1,1
$ClO_{2\ \text{como}\ ClO2}$ kg/t	8,1	-	0,3	0,6	0,9	0,6
pH final	3,7	10,5	5,3	5,5	5,5	5,5
Consumo de Reagentes, %	100	70,3	-	-	-	72,7
	100	70,3	-	-	-	72,5
Média	100	70,3	-	-	-	72,6
Número Kappa	1,6	3,1	-	-	-	1,6
	1,6	3,0	-	-	-	1,5
Média	1,6	3,1	-	-	-	1,6
Alvura A.D., % ISO	73	86,2	89,8	90,0	90,2	90,0
	72,9	86,1	89,7	90,0	90,2	90,0
Média	73	86,2	89,8	90	90,2	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	1,9
	-	-	-	-	-	1,9
Média	-	-	-	-	-	1,9
Viscosidade (dm^3/kg)	-	-	-	-	-	844
	-	-	-	-	-	852
Média	-	-	-	-	-	848

Quadro 37C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira de *Híbrido* em baixo álcali efetivo residual e número kappa 22.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	0,3	-
H_2SO_4, kg/t	7,5	-	0,5	-	-	0,2
ClO_2 $_{\text{como ClO2}}$ kg/t	8,5	-	2	3	4	2,6
pH final	4,1	10,5	5,6	5,5	5,5	5,5
Consumo de Reagentes, %	100	93,8	-	-	-	89,9
	100	93,8	-	-	-	89,6
Média	100	93,8	-	-	-	89,8
Número Kappa	-	3,2	-	-	-	0,6
	-	3,1	-	-	-	0,5
Média	-	3,2	-	-	-	0,6
Alvura A.D., % ISO	69,3	83,8	89,5	90,3	90,9	90,0
	69,2	83,8	89,4	90,3	90,8	90,0
Média	69,3	83,8	89,5	90,3	90,9	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,2
	-	-	-	-	-	2,1
Média	-	-	-	-	-	2,2
Viscosidade (dm^3/kg)	-	-	-	-	-	940
	-	-	-	-	-	944
Média	-	-	-	-	-	942

Quadro 38C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira do hibrído de *E. nitens x E. glubulos* em alto álcali efetivo residual e número kappa 22.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7,5	-	1,1	0,9	0,7	1
ClO_2 $_{\text{como } ClO_2}$ kg/t	8,9	-	0,5	1	1,5	0,7
pH final	4	10,5	5,4	5,5	5,5	5,5
Consumo de Reagentes, %	100	93,0	-	-	-	68,8
	99,9	93,0	-	-	-	68,9
Média	100	93,0	-	-	-	68,9
Número Kappa	-	3,1	-	-	-	1,4
	-	3,0	-	-	-	1,4
Média	-	3,1	-	-	-	1,4
Alvura A.D., % ISO	74,11	86,7	89,8	90,4	90,7	90,0
	74,10	86,6	89,8	90,3	90,6	90,0
Média	74,11	86,7	89,8	90,4	90,7	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	2,2
	-	-	-	-	-	2,1
Média	-	-	-	-	-	2,2
Viscosidade (dm^3/kg)	-	-	-	-	-	890
	-	-	-	-	-	904
Média	-	-	-	-	-	897

Quadro 39C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira do hibrído de *E. nitens x E. glubulos* em baixo álcali efetivo residual e número kappa 26.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	0,3	-
H_2SO_4, kg/t	8	-	0,5	-	-	-
ClO_2 $_{\text{como ClO2}}$ kg/t	9,58	-	2	3	4	3,0
pH final	3,5	10,5	5,5	5,5	5,5	5,5
Consumo de Reagentes, %	100	89,8	-	-	-	87,7
	100	89,8	-	-	-	87,9
Média	100	89,8	-	-	-	87,8
Número Kappa	-	2,5	-	-	-	0,5
	-	2,4	-	-	-	0,4
Média	-	2,5	-	-	-	0,5
Alvura A.D., % ISO	68,1	82,7	89,7	90	90,4	90,0
	68	82,6	89,7	90	90,3	90,0
Média	68,1	82,7	89,7	90	90,4	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	1,9
	-	-	-	-	-	1,8
Média	-	-	-	-	-	1,9
Viscosidade (dm^3/kg)	-	-	-	-	-	976
	-	-	-	-	-	984
Média	-	-	-	-	-	980

Quadro 40C. Resultados do branqueamento D-(EP)-D para a polpa derivada do cozimento da madeira do hibrído de *E. nitens x E. glubulos* em alto álcali efetivo residual e número kappa 26.

Condições e Resultados	**Do**	**EP**	**D1**	**D1**	**D1**	**D1- Inter.**
Consistência, %	11	11	11	11	11	11
Tempo, min	120	75	90	90	90	90
Temperatura, ^{0}C	90	85	80	80	80	80
Fator kappa	0,21	-	-	-	-	-
H_2O_2, kg/t	-	4,4	-	-	-	-
NaOH, kg/t	-	8,0	-	-	-	-
H_2SO_4, kg/t	7	-	1,1	0,9	0,7	0,8
$ClO_{2\ \text{como}\ ClO2}$ kg/t	9,98	-	0,5	1	1,5	1,1
pH final	3,6	10,5	5,5	5,5	5,5	5,5
Consumo de Reagentes, %	100	86,7	-	-	-	65,8
	99,9	86,7	-	-	-	65,6
Média	100	86,7	-	-	-	65,7
Número Kappa	-	3,0	-	-	-	1,2
	-	2,9	-	-	-	1,1
Média	-	3,0	-	-	-	1,2
Alvura A.D., % ISO	71,7	86,7	89,4	89,9	90,8	90,0
	71,7	86,6	89,3	89,9	90,7	90,0
Média	71,7	86,7	89,4	89,9	90,8	90,0
Reversão de Alvura, % ISO	-	-	-	-	-	1,9
	-	-	-	-	-	1,8
Média	-	-	-	-	-	1,9
Viscosidade (dm^3/kg)	-	-	-	-	-	933
	-	-	-	-	-	937
Média	-	-	-	-	-	935