VALÉRIA JUSTE GOMES

EFEITO DA NATUREZA QUÍMICA DE POLPAS KRAFT DE MADEIRAS DE FIBRAS CURTAS NO DESEMPENHO DOS ESTÁGIOS DE BRANQUEAMENTO COM OXIGÊNIO, HIDRÓLISE ÁCIDA A QUENTE E OZÔNIO

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

LISTA DE SIGLAS E ABREVIATURAS

A – estágio de hidrólise ácida à quente (hot acid hydrolysis)
adt – air dry tonnes
a-step – etapa de acidificação
ASL – acid soluble lignin
CEL – cellulolytic enzyme lignin
COD – chemical oxygen demand
cP – centipoise
D – estágio de branqueamento com dióxido de cloro (chlorine dioxide stage)
E. – Eucalyptus
e-step – etapa de extração
ECF – Elemental Chlorine Free
EP – estágio de extração alcalina com peróxido de hidrogênio
FPU – Filter paper unit
GC – gas chromatography
Glu – glucose
HC – high consistency (alta consistência)
HexA – hexenuronic acid (ácido hexenurônico)
ISO – International Standard Organization
MC – medium consistency (média consistência)
Mn – number average molecular weight
Mw – weight average molecular weight
MWL – milled wood lignin
NMR – nuclear magnetic resonance
OD – oven dry
odt – oven dry tonnes
P – estágio de branqueamento com peróxido de hidrogênio
PD – polydispersity
PhOH – free phenolic hydroxyl groups
P&W – print and write
Py-GC-MS – Pyrolysis - Gas Chromatography/Mass Spectrometry
S/V – syringaldehyde/vanillin ratio
TAPPI – Technical Association of the Pulp and Paper Industry
tas – tonelada absolutamente seca
TAT – time at temperature
TCF – Total Chlorine Free
tsa – tonelada seca ao ar
TTT – time to temperature
Xyl – xylose
Z – estágio de branqueamento com ozônio (ozone bleaching stage)
Z/E – estágio de branqueamento com ozônio seguido de extração alcalina sem lavagem

RESUMO

GOMES, Valéria Juste, D.Sc., Universidade Federal de Viçosa, maio de 2017. **Efeito da natureza química de polpas kraft de madeiras de fibras curtas no desempenho dos estágios de branqueamento com oxigênio, hidrólise ácida a quente e ozônio**. Orientador: Jorge Luiz Colodette.

A origem da madeira bem como o processo de polpação kraft tem efeito significativo na composição química da polpa, sendo verificada variações substanciais da relação lignina/HexA, do teor de ligninas contendo fenóis livres, da presença de complexos ligninas carboidratos etc. Essa composição química variada da polpa kraft afeta a sua alvura e como consequência a sua branqueabilidade frente aos processos químicos de branqueamento tradicionais. Por isso, é muito frequente se encontrar plantas de branqueamento inteiramente similares, consumindo o dobro dos reagentes de branqueamento em relação a outras, sendo essas diferenças explicadas pela composição química das polpas marrons. Porém, as variações de composição química da polpa bem como as suas consequências na operação de branqueamento são de difícil determinação. Correntemente, não existe um conhecimento claro de como resolver esse problema. Portanto, o objetivo deste trabalho foi investigar o impacto da composição química da polpa kraft derivada de madeiras de fibra curta, especialmente nas etapas de branqueamento tradicionais, tais como deslignificação com oxigênio, hidrólise ácida à quente e ozonólise.

Este trabalho se divide em três capítulos na forma de artigos, cobrindo os seguintes temas: (1) Importância da natureza química da lignina *versus* eficiência da deslignificação com oxigênio para polpas de fibras curtas; (2) efeito da química da polpa e das condições operacionais do estágios de hidrólise ácida e de ozonólise em média consistência na branqueabilidade de polpa kraft de eucalipto; (3) influência do pré-tratamento ácido da polpa kraft de eucalipto no desempenho do seu branqueamento ECF e TCF pelas sequências (aZe)DP e (aZe)(EP)P. No capítulo 1 foi realizada a caracterização química e estrutural da lignina isolada de polpas marrons provenientes de madeiras de várias espécies de fibras curtas e associá-las com o desempenho da deslignificação com oxigênio. Para isso, seis madeiras de fibras curtas foram submetidas ao cozimento kraft para se obter polpas marrons com número kappa em torno de 20. A lignina foi isolada a partir da madeira e da polpa marrom através de um coquetel enzimático para futura determinação de grupos fenólicos livres por RMN de fósforo. Após o cozimento, o conteúdo total de grupos fenólicos livres aumentou devido à quebra das ligações β-O-4. O estágio de deslignificação com oxigênio foi realizado em todas as polpas sob as mesmas condições e mostrou-se eficiente e seletivo. A eficiência foi calculada com base no número kappa, excluindo o conteúdo de HexA. Foi encontrada uma alta correlação entre a eficiência deste estágio e o conteúdo de estruturas fenólicas do tipo 5-substituídas (R^2 = 0,84), 5-livres (R^2 = 0,90) e totais (R^2 = 0,87), comprovando que os grupos fenólicos livres da lignina são os sítios reativos para a deslignificação com oxigênio. No capítulo 2 foram determinadas as condições ótimas para operação dos estágios A e Z/E, em média consistência, e avaliado o efeito da inserção deste estágio A à frente do estágio Z/E, sobre a remoção de HexA e lignina, usando como referência uma polpa não tratada com o estágio A. Para isso, os estágios A e Z/E foram otimizados. O estágio A causou significante remoção de kappa e HexA, sendo que a condição ótima para este estágio foi pH 3,0 e 90 °C. Após a polpa ser tratada pelo estágio ácido, as condições onde o estágio Z/E apresentou maior eficiência e seletividade foram pH 2,5 e 40 °C e pH 10,5 para a etapa de extração (etapa E). Os valores de remoção de kappa por quilograma de ozônio aplicados foram 1,04 e 1,18 para a polpa tratada pelo estágio A e polpa referência, respectivamente. Uma vez que o estágio A não decresceu a eficiência do estágio Z/E, tais estágios mostraram-se complementares ao invés de competitivos. O potencial do estágio A na economia de reagentes químicos de branqueamento é bastante significativo, dado que o número kappa das polpas após os estágios Z/E e AZ/E foram 5,5 e 1,1, respectivamente. Por fim, no capítulo 3 foi investigado o branqueamento ECF e TCF de polpas referência e pré-tratada com o estágio A, com as sequências (aZe)DP e (aZe)(EP)P, sendo o estágio Z em alta consistência, abordando o consumo de reagentes químicos e a qualidade da polpa branqueada. Foi realizado um estágio A à frente das sequencias ECF [A/(aZe)DP e A(aZe)DP] e TCF [A/(aZe)(EP)P e A(aZe) (EP)P] em uma polpa kraft de eucalipto. A quantidade de reagentes químicos poupados graças à adição o estágio A, sob condições otimizadas foram significantes (aproximadamente 7 kg de ClO_2/tsa). As propriedades de resistência das polpas branqueadas pelas sequências ECF (aZe)DP (referência) e A/(aZe)DP foram similares, enquanto que aquela branqueada pela sequência TCF A/(aZe)(EP)P apresentou propriedades inferiores à das polpas ECF.

ABSTRACT

GOMES, Valéria Juste, D.Sc., Universidade Federal de Viçosa, May, 2017. **Effect of pulp chemistry on oxygen, hot acid hydrolysis and ozone bleaching stages for hardwood kraft pulps**. Adviser: Jorge Luiz Colodette.

The wood origin as well as the kraft pulping process have a significant effect on the chemical composition of the pulp, with substantial variations in the lignin/HexA ratio, the content of free phenolic groups, the presence of lignin-carbohydrate complexes and so on. This varied chemical composition of kraft pulp affects its brightness and consequently its bleachability against the traditional bleaching chemical processes. Therefore, it is very common to find similar bleaching plant mills consuming double the bleaching reagents in relation to others, and these differences are explained by the chemical composition of the unbleached pulps. However, variations in the chemical composition of the pulp as well as their consequences in the bleaching operation are difficult to determine. Currently, there is no clear understanding of how to solve this problem. Therefore, the aim of this thesis was to investigate the impact of the chemical composition of kraft pulp derived from hardwoods, especially in the traditional bleaching stages, such as oxygen delignification, hot acid hydrolysis and ozone. This thesis is divided into three chapters, addressing the following topics: (1) Relevance of lignin chemistry on the oxygen bleaching stage efficiency of several hardwood samples, (2) Effect of pulp chemistry and the bleaching conditions of the hot acid hydrolysis and ozone stages at medium consistency on the bleachability of the eucalypt kraft pulp, and (3) Influence of eucalypt pulp pretreatment with hot acid hydrolysis on its ECF [(aZe)DP] and TCF [(aZe)(EP)P] bleaching performance. In the chapter 1 the isolated lignin from wood and kraft pulp from several hardwoods species was chemical and structural characterized and its features were associated with oxygen delignification performance. Following that, several hardwood samples were pulped under the same conditions, resulting in unbleached pulps with kappa number around 20. Isolated lignin was obtained from wood and unbleached pulp by a cellulolytic enzyme cocktail for free phenolic hydroxyl groups determination using ^{31}P NMR technic. After pulping, the content of total phenolic units increase because of breaking β-O-4 linkages. O-stage was carried out under the same conditions and showed a good efficiency and selectivity. The efficiency was calculated based on kappa number, subtracting HexA. A high correlation was found between O-stage efficiency and the content of 5-substituted (R^2 = 0.84), 5-free (R^2 = 0.90), and total PhOH (R^2 = 0.87), proving that free phenolic hydroxyl groups are the reactive site for oxygen delignification reactions. In the chapter 2 the optimum conditions of the A and Z/E were determined. The effect of A-stage before Z/E on the lignin and HexA removal was also investigated. A and Z/E stages were fully optimized using an oxygen delignified eucalypt kraft pulp. A-stage caused significant kappa and HexA drop, and the optimum condition for this stage being pH 3.0 and 90 °C. For A-stage pretreated pulp, the conditions for maximum Z/E-stage efficiency and selectivity were pH 2.5, 40 °C, and pH 10.5 for the alkaline extraction step (E). The values of kappa drop per kilogram of ozone applied were 1.04 and 1.18 for A-stage pretreated and reference pulps, respectively. Since the A-stage pretreatment did not decrease the (Z/E)-stage efficiency to a large extent, such stages are complementary rather than competitive. The potential of the A-stage pretreatment to save bleaching chemicals is quite large given that pulp kappa number after Z/E and AZ/E treatments were 5.5 and 1.1, respectively. In the chapter 3 the effect of hot acid hydrolysis on high consistency ozone bleaching and its application in a ECF [A/(aZe)DP and A(aZe)DP] and TCF [A/(aZe)(EP)P and A(aZe)(EP)P] sequences for eucalypt kraft pulp was evaluated, specially regarding reagents consumption and pulp quality. The A-stage removed a significant amount of HexA from the pulp, and the subsequent Z-stage remained efficient after completion of the A-stage. The chemical savings caused by the A-stage were significant (~7 kg ClO_2/adt). The strength properties of pulps bleached with the (aZe)DP (reference) and A/(aZe)DP ECF sequences were similar, but the TCF sequence A/(aZe)(EP)P delivered slightly lower strength properties than the ECF sequences.

INTRODUÇÃO GERAL

Atualmente, a principal fonte de matéria prima para produção de polpa celulósica é a madeira. Nas Américas do Norte e do Sul, as madeiras de fibras curtas, também chamadas de madeiras de *hardwoods*, são amplamente utilizadas para este fim. Mais de 100 milhões de toneladas de polpa celulósica são branqueadas anualmente, representando mais de 50% de toda a polpa produzida no mundo (Colodette e Gomes, 2015).

O processo predominante de conversão da madeira em polpa celulósica é o *kraft* (Gomide e Gomes, 2015), que consiste no tratamento dos cavacos com uma forte solução alcalina, composta de hidróxido de sódio e sulfeto de sódio, para individualização das fibras. A polpa celulósica oriunda deste cozimento possui uma cor característica marrom, devido à presença da lignina residual, sendo necessário que a mesma seja submetida a um processo denominado de branqueamento, a fim de se atingir valor de alvura compatíveis com as necessidades de mercado.

O branqueamento é um processo químico que se dá por vários estágios a fim de aumentar a alvura e promover a limpeza da polpa, através da remoção e/ou modificação dos grupos cromóforos e leucocromóforos residuais presentes na polpa (Colodette e Santos, 2015), sendo estes, em sua grande maioria, constituídos por lignina e ácidos hexenurônicos (HexA). A lignina residual se encontra bastante modificada e apresenta composição química e estrutural variada, possuindo diferentes relações S/V, teores de grupos hidroxílicos fenólicos livres e ligações β-aril-éter (Jiang et al., 1987; Prinsen et al., 2013). Além disso a lignina residual pode estar fortemente ligada aos carboidratos e possuir ligações condensadas do tipo carbono-carbono (Chang, 1992). Tudo isso afeta grandemente a reatividade da lignina.

Por outro lado, os ácidos hexenurônicos são formados durante o cozimento kraft pela conversão parcial dos grupos de ácidos 4-O-metil-α-D-glucourônicos, ligados covalentemente às xilanas da madeira, em grupos de ácido 4-deoxihex-4-enurônicos (HexA) via β-eliminação de uma molécula de metanol (Buchert et al., 1995; Li and Gellerstedt, 1996). Portanto, a remoção destes ácidos da polpa resulta em uma redução do consumo de reagentes eletrofílicos durante o branqueamento (Vuorinen et al., 1996).

No processo de branqueamento, são usados reagentes químicos que reduzem o número kappa da polpa e, ao mesmo tempo, elevam sua alvura. As polpas *kraft* de fibras curtas cozidas até números kappa entre 15-20 possuem teores de lignina na faixa de 1 a 3% (Andrade et al., 2013). O número kappa quantifica, além da lignina, os HexA e outras estruturas oxidáveis da polpa em menores quantidades. Em polpas previamente deslignificada com oxigênio de madeiras de folhosas, mais da metade do número kappa da polpa pode ser devido aos HexA (Colodette e Santos, 2015). Sendo assim, durante o branqueamento, são usados reagentes específicos para a remoção da lignina e dos HexA da polpa.

Além da lignina, os HexA também são responsáveis pelo consumo de reagentes químicos durante o branqueamento de polpa *kraft* (Vuorinen et al., 1996; Li and Gellerstedt, 1996; Jiang et al., 2000). O grande problema causado pela presença dos HexA é que eles reagem com compostos eletrofílicos, como o ozônio (O_3) e o dióxido de cloro (ClO_2) (Buchert et al., 1995; Suess, 2010), sendo que estes reagentes poderiam ser facilmente poupados com a adição de um pré-tratamento de hidrólise ácida a quente (estágio A).

Normalmente, a deslignificação com oxigênio (estágio O), também conhecida como branqueamento com oxigênio, é a primeira etapa de uma sequência de branqueamento, onde se utiliza oxigênio em meio fortemente alcalino e pressurizado, para remoção da lignina residual. A fração de lignina removida corresponde a 25-65% do número kappa da polpa não branqueada (Sixta et al., 2006). Nesta etapa, a remoção da lignina se dá principalmente pela oxidação dos grupos hidroxílicos fenólicos livres presentes na lignina (Gierer, 1986). No caso de polpas com alto teor de HexA, a eficiência deste estágio é bastante limitada, uma vez que o oxigênio não reage com estes ácidos (Colodette et al., 2007).

A remoção dos HexA através de um estágio A resulta numa significante economia de dióxido de cloro e de ozônio durante o branqueamento ECF, uma vez que estes ácidos reagem prontamente com compostos eletrofílicos. Devido à presença de um grupo carboxílico insaturado e um enol-éter em sua estrutura, os HexA reagem prontamente com eletrófilos, como o ozônio no caso deste estudo, sendo que esta reação é cerca de 2,4 vezes mais rápida do que com a lignina (Ventorim et al., 2008). Estes reagentes consumidos pelos HexA, que são de alto custo para as indústrias, poderiam ser poupados para oxidar de fato a lignina.

Sendo assim, a composição química das polpas, especialmente os conteúdos de lignina e HexA e o teor de ligninas contendo fenóis livres afeta a sua alvura e como consequência a sua branqueabilidade frente aos processos químicos de branqueamento tradicionais. Porém, as variações de composição química da polpa bem como as suas consequências na operação de branqueamento são de difícil determinação. Correntemente, não existe um conhecimento claro de como resolver esse problema. Portanto, o objetivo desta tese foi investigar o impacto da composição química da polpa kraft derivada de madeiras de fibra curta, especialmente nas etapas de branqueamento tradicionais, tais como deslignificação com oxigênio, hidrólise ácida à quente e ozonólise.

Diante disso, este trabalho se divide em três capítulos na forma de artigos, cobrindo os seguintes temas: (1) Importância da natureza química da lignina *versus* eficiência da deslignificação com oxigênio para polpas de fibras curtas; (2) efeito da química da polpa e das condições operacionais do estágios de hidrólise ácida e de ozonólise em média consistência na branqueabilidade de polpa kraft de eucalipto; (3) influência do pré-tratamento ácido da polpa kraft de eucalipto no desempenho do seu branqueamento ECF e TCF pelas sequências (aZe)DP e (aZe)(EP)P. No capítulo 1 foi realizada a caracterização química e estrutural da lignina isolada da polpa marrom proveniente da madeira de várias espécies de fibras curtas e associadas com o desempenho da deslignificação com oxigênio. No capítulo 2, foram determinadas as condições ótimas para operação dos estágios A e Z/E, em média consistência, e avaliado o efeito da inserção deste estágio A à frente do estágio Z/E, sobre a remoção de HexA e lignina, usando como referência uma polpa não tratada com o estágio A. Por fim, no capítulo 3 foi investigado o branqueamento ECF e TCF de polpas referência e pré-tratada com o estágio A, com as sequências (aZe)DP e (aZe)(EP)P, sendo o estágio Z em alta consistência, abordando o consumo de reagentes químicos e a qualidade da polpa branqueada. Foi realizado um estágio A à frente das sequencias ECF [A/(aZe)DP e A(aZe)DP] e TCF [A/(aZe)(EP)P e A(aZe) (EP)P] em uma polpa kraft de eucalipto.

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PAPER 1: EFFECTS OF LIGNIN CHEMISTRY ON THE PERFORMANCE OF THE OXYGEN BLEACHING STAGE

Abstract

The present work was focused on the chemical and structural characterization of the isolated lignin from wood and kraft pulp from six hardwoods species with the aim to determine associated features with oxygen delignification performance. Several hardwood samples were pulped under the same conditions, resulting in unbleached pulps with kappa number between 19.4-23.5 and viscosity between 1280-1485 dm^3/kg*. Isolated lignin was obtained from wood and unbleached pulp by a cellulolytic enzyme cocktail for free phenolic hydroxyl groups (PhOH) determination using* ^{31}P *NMR technic. The yield of CEL preparations from unbleached pulps were quietly low, but an investigation on its impact in the quantification of phenolic hydroxyl groups showed that yield was not a relevant factor. After pulping, the content of 5-substituted PhOH units increase while 5-free PhOH decrease, but the total PhOH units increase because of breaking ß-O-4 linkages during the delignification process. O-stage was carried out under the same conditions and showed a good efficiency and selectivity. The efficiency was calculated based on kappa number, subtracting HexA. A high correlation was found between O-stage efficiency and the content of 5-substituted* ($R^2 = 0.84$)*, 5-free* ($R^2 = 0.90$)*, and total PhOH* ($R^2 = 0.87$)*, proving that free phenolic hydroxyl groups are the reactive site for oxygen delignification reactions. When different hardwood species are compared, the HexA content did not influence the total oxygen bleaching efficiency* ($R^2 = 0.16$)*.*

1. INTRODUCTION

Oxygen bleaching stage (O-stage) is a well-established technology with environmental, technical and economic benefits. This stage allows the cooking to end at a higher kappa number, thus minimizing pulp yield losses as the reactions during the oxygen delignification are more selective than kraft cooking for pulps with low lignin contents. Furthermore, the oxygen delignification helps decreasing chemical consumption in subsequent bleaching stages (McDonough, 1986). With the aim to preserve the selectivity (lignin removal *versus* cellulose degradation), oxygen stage has limited the kappa number reduction to approximately 40 and 50% for hardwood and softwood pulps, respectively (Ji et al., 2009). For hardwood pulps, kappa number removal is typically limited to 40% only. Beyond this level, there is an increase on cellulose degradation (Argyropoulos, 2003). A reason for this limited kappa number reduction is the presence of hexenuronic acid (HexA), since HexA is countered in kappa number results and does not react with oxygen (Suess, 2010).

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).

The characteristics of lignin are among the most important features for understanding the mechanism of its removal from cell wall during chemical pulping and O-stage bleaching processes (Aguayo et al., 2015). To understand and improve the O-stage process, the chemistry involved in the delignification must be studied carefully (Yang et al., 2003). Some studies (Gellerstedt et al., 1999; Moe and Ragauskas, 1999; Asgari and Argyropoulos, 1998) have indicated that the structure of the residual lignin is not significant affected by the O-stage, since the significant changes in structure of the residual lignin was due to a loss of non-condensed phenolic units, occurring in a range of 50-60%, whereas C-5 condensed units were found to be around 50% less reactive to oxygen delignification than non-condensed phenolic units.

According to Gierer (1986), extensive studies using lignin model compounds have shown that phenolic hydroxyl groups play an important role in bleaching reactions with oxygen. Lignin removal by the oxygen delignification mainly occurs on the free phenolic structures, formed after *ß-O*-4 cleavage during the kraft pulping. Under the strong alkaline conditions, a proton is abstracted and these groups are converted into phenoxyl radicals by the oxygen attack. The radicals react with molecular oxygen, superoxide or hydroperoxide anions resulting in lignin fragmentation through the side chain elimination, ring-opening and demethoxylation reaction, which are dissolved in the liquor and converted into COD (Agarwal et al., 1999). A kinetic study of the oxygen delignification proposed that the reaction between the radical anion superoxide and phenoxyl radical preferably occurs at aromatic C3 position (Ji et al., 2009). Figure 1 shows the ring-opening reaction at C3 position, forming the *ortho* quinone and muconic acid structures (Asgari and Argyropoulos, 1998). During the oxygen delignification, the residual lignin solubilization is directly influenced by the hydrophilic groups content, since without then lignin would become practically insoluble in aqueous solutions (Gellerstedt et al., 1999).

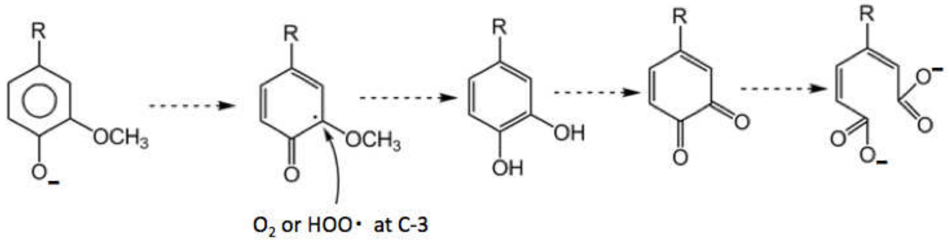

Figure 1. Scheme of the possible reaction of the free phenolic groups at C3 position during the oxygen bleaching at high temperature and alkaline conditions.

Although hardwood is the most important raw material for pulp and paper production, our knowledge of its lignin structure is not enough. Variations in the structure of lignin isolated from different hardwood species are much higher than that in softwoods, since the last contains predominately guaiacyl units, while hardwood lignin consists of various proportions of guaiacyl and syringyl units (Capanema et al., 2015). The oxygen delignification behavior of several hardwood samples can be better understood if an investigation of the residual lignin was done.

The present work is focused on the chemical and structural characterization of the isolated lignin from wood and kraft pulp from several hardwoods species with the aim to determine associated features with oxygen delignification performance. Following that, several hardwood samples were cooked under the same conditions and the resulting unbleached pulps with kappa number around 20 were submitted to the oxygen stage. Isolated lignin from wood and residual lignin from pulp were characterized by ^{31}P NMR. The unbleached and post oxygen bleached pulps were evaluated regarding quality and O-stage efficiency.

2. EXPERIMENTAL

2.1 Working plan

The flowchart presented in Figure 2 depicts the working plan. Six hardwood samples were submitted to kraft cooking with the aim to produce unbleached pulps for oxygen bleaching stage performance. Wood, unbleached, and oxygen bleached pulps were characterized. Isolated lignin from wood and unbleached pulp were also chemically characterized and its structural characterization was accomplished by ^{31}P NMR.

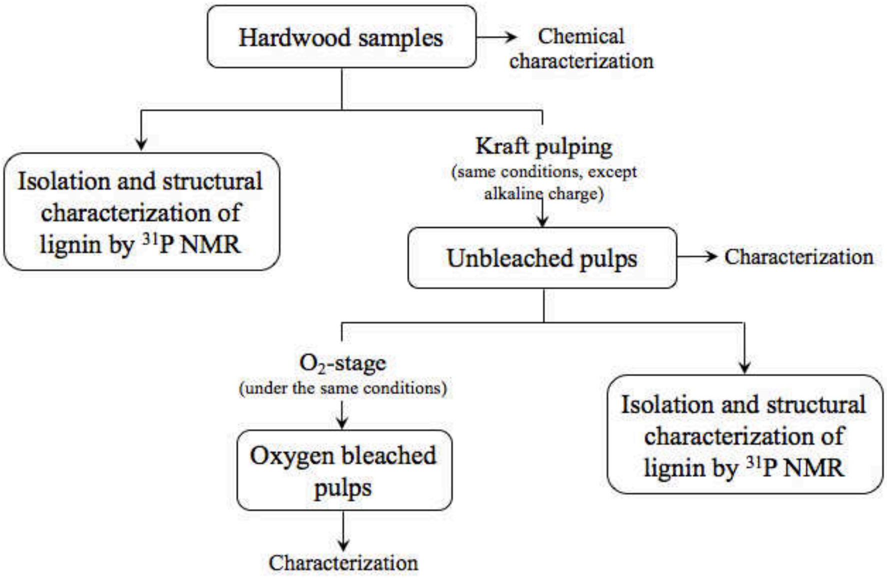

Figure 2. Flowchart for pulp production and oxygen bleaching stage.

2.2 Material

Wood samples of sweet gum (*Liquidambar styraciflua*), red oak (*Quercus rubra*), white oak (*Quercus alba*), *Eucalyptus benthamii*, yellow birch (*Betula alleghaniensis*), and white birch (*Betula papyrifera*) were received as chips from different pulp and paper mills around the world and ground in a Wiley mill, sieved, and the fraction which passed between 40 and 60 mesh screen was collected (knots and barks were removed) and used for the pulping process. For wood characterization and lignin isolation, the wood meals were extracted in a soxhlet for 24 h with benzene-ethanol 2:1 (v/v) (TAPPI T264 om-88).

2.3 Methods

2.3.1 Kraft pulping

The kraft pulping process of the woods was carried out in a M/K digester (Systems Inc., Massachusetts/USA) with capacity of 7.0 liters equipped with temperature controller and recirculation heater system, under the following conditions: ratio of liquid/wood 4:1, temperature 160 °C, H factor 800, sulfidity 25% and active alkaline charge adjusted to reach kappa number around 20. After pulping, the chips were placed in a stainless steel box of 150 mesh, thoroughly washed with water, and disintegrated in a laboratorial hydrapulper. The pulp was centrifuged to a consistency about 30% and stored in polyethylene bags. Pulping yield, kappa number (TAPPI T236 om-06), viscosity (TAPPI T230 om-08), HexA content (Tenkanen et al., 1999), and total lignin (Lin and Dance, 1992) was determined.

2.3.2 Oxygen delignification stage

The unbleached kraft pulps resulting from pulping process were submitted to oxygen delignification stage (O-stage). The O-stage was carried out in a pressurized cylindrical vessel. The vessel was preheated to 70-80 °C and charged with 200 grams (OD) of unbleached pulp, and the consistency was adjusted to 10% with distilled water and sodium hydroxide amount to desired charge (2.0%). A top with a collar was screwed onto the vessel. 100 psi of O_2 was added through a valve into the vessel and checked for leaks. The vessel was then placed in a preheated hot air oven. The vessel was on a rotating rack inside the oven. A temperature probe was placed on the top of the vessel to check temperature of the pulp inside the vessel. The vessel was heated to the desired temperature (100 °C) for 45 min (TTT) and kept at 100 °C for 30 min (TAT). After total time reaction (75 min), the vessel was placed in a cold-water vat and the pressure was released. Then, the pulp was washed, centrifuged to approximately 30% of consistency, and stored in polyethylene bags. O-stage efficiency, selectivity, kappa number (TAPPI T236 om-06), viscosity (TAPPI T230 om-08), and HexA content (Tenkanen et al., 1999).

2.3.3 Isolation of Cellulolytic Enzyme Lignin (CEL 96%) from wood

A planetary ball mill (Pulverisette, Fritsch, Germany) was used in this experiment instead of a vibratory ball mill used in Bjorkman's protocol. Two grams of extracted sawdust was milled for 6 h at 600 rpm using 17 ZiO_2 balls. The ball milled meal was then treated with cellulase and hemicellulase (purchased from Sigma) in a sodium acetate buffer solution at pH 4.5 for 72 h at 50 °C to a consistency of 5%. The enzyme charge was 20 FPU/g. After 72 h, the hydrolyzed material was centrifuged and the solid phase was collected, washed with buffer once and with water twice, and then freeze dried. The dried material was extracted with dioxane/water 96:4 (v/v) and the solvent was evaporated under vacuum at 35 °C. Then, the solid material was dried in a vacuum oven at 35 °C to obtain the CEL preparation.

2.3.4 Isolation of Cellulolytic Enzyme Lignin (CEL 96%) from unbleached pulps

The pulps were beaten in a PFI mill (TAPPI T248 cm-85) using 6,000 revolutions to improve the accessibility of the pulps toward cellulolytic enzymes. The pulps were dewatered to a consistency of about 30% and fluffed. For each sample, 200 grams (OD) of the fluffed pulp was divided in several Erlenmeyer flasks and the sodium acetate buffer at pH 4.5 was added. After mixing, the suspension was treated with cellulase and hemicellulase (purchased from Sigma) for 72 h at 50 °C. The enzyme charge was 20 FPU/g. After 72 h, the hydrolyzed material was acidified with hydrochloric acid solution to pH 3.0. The hydrolyzed material was centrifuged and the solid phase was washed with buffer once and twice with water, and then freeze dried. The dried material was extracted with dioxane/water 96:4 (v/v) and the solvent was evaporated under vacuum at 35 °C. Then, the solid material was dried in a vacuum oven at 35 °C to obtain the CEL preparation.

2.3.5 Nitrobenzene oxidation for S/V ratio determination

The S/V ratio determination was performed according to Chen (1992) with a slight modification. The extracted biomass samples (200 mg OD) were reacted with 7 mL of 2 mol/L NaOH and 0.4 mL of nitrobenzene. The reaction was carried out in a stainless-steel bomb heated in an aluminum block for 2.5 h at 170 °C. During the reaction, the stainless-steel bomb was removed every 30 min and shaken vigorously. Once the reaction was completed, the hot stainless-steel bomb was cooled down in cold water and 1 mL of internal standard was added (16 mg/mL of 5-iodovanillin in dioxane). The mixture was extracted with CH_2Cl_2 three times (30 mL each time), and the organic phase was discarded. The aqueous phase (alkali solution) was acidified with 2 mol/L HCl to pH around 2.5. Then, the acidified solution was further extracted with CH_2Cl_2 (30 mL each time) three times, and the organic phase was collected, dried with anhydrous Na_2SO_4 overnight, and then adjusted to 100 mL. After remove any trace of water, 1 mL of this solution was dried under rotary evaporator at 30 °C. The resulting solid sample was dissolved by adding 50 μL of pyridine and derivatized by adding 50 μL of N,O-bis(trimethylsilyl)trifluoroacetamide. The solution was heated for 15 min at 50 °C and the derivatized solution was directly analyzed by gas chromatography. Quantitative GC analysis was carried out on a HP 6890 GC equipped with flame ionization detector and HP-1 column (30 m x 0.32 mm x 0.25 μm). The components were analyzed under the following condition: injector temperature 200 °C, detector temperature 270 °C, carrier gas flow rate 2 mL helium/min, column held for 3 min at 120 °C, raised at 5 °C/min to 200 °C, followed by 10 °C/min to 260 °C and kept isothermal for 5 min. The S/V ratio was calculated by the molar ratio of syringaldehyde and syringic acid divided by the sum of vanillin and vanillic acid. The concentrations were found by a calibration curve.

2.3.6 ^{31}P NMR analysis

^{31}P NMR analysis was carried out for all species, using the CEL preparations, from wood and pulp. The analysis was performed using a Bruker Avance 300 MHz spectrometer according the procedure described by Granata and Argyropoulos, 1995. 40 mg of lignin sample was introduced into an appropriated vial and 500 μL of anhydrous pyridine/$CDCl_3$

mixture (1.6:1 v/v) was added to dissolve the lignin. Then, 200 μL of endo-N-hydroxy-5-norbornene-2,3-dicarboximide (e-NHI) solution (as internal standard) and 50 μL of chromium(III) acetylacetonate solution (serving as relaxation reagent) were added. Finally, 100 μL of the phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added, and the mixture was vigorously shaken, transferred into a NMR tube, and subjected to immediate ^{31}P NMR analysis.

2.3.7 Molecular weight distribution

The average molecular weight and distribution of the isolated lignin was determined by using gel permeation chromatography (GPC). The GPC system (Shimadzu, Kyoto, Japan) consisted of a LC-20AD pump, a CTO-20A oven equipped with a HR1 and a HR 5E Styragel columns (Waters, Milford, MA), a SPD-20A UV/Vis detector and a RID-10A reflective index detector. The oven was set to 35 °C and dual wavelength of 235 and 280 nm were used in all the experiments. The lignin samples were modified by acetylation before testing in order to ensure total solubility in THF solution (of 5 mg/L concentration). This mobile phase was set with a flow rate of 0.7 ml/min. A calibration curve was also created based on twelve polystyrene dispersions (PSS ReadyCal-Kit, Amherst, MA) with Mw in the range 266 to 252 kDa. A Shimadzu LC solution software was used for data processing.

2.3.8 Total lignin and sugar content

Approximately 100 mg of sample was hydrolyzed with 1.5 mL of 72% H_2SO_4 at room temperature for 120 min. The mixture was then diluted to 3% H_2SO_4 using deionized water, transferred to a vial, sealed, and autoclaved at 121 °C for 90 min. Klason lignin and acid-soluble lignin were determined for each specie by gravimetric determination. The sum of Klason lignin and acid-soluble lignin is reported as the total lignin content. The resulting suspension was filtered and analyzed for monomeric sugar content. The monomeric sugars were analyzed by a HPLC system (Agilent 1200), including a Shodex SP0810 column (8 x 300 mm, Showa Denko, Tokyo, Japan). The samples were eluted at 80 °C with Mili-Q water at a flow rate of 0.5 mL/min with peak detection using a refractive index detector, set at 35 °C. Before analysis, all samples were filtered through a 0.20 μm nylon syringe filter (Millipore, Billerica, MA). Sugar content was quantitatively determined by comparison with standards sugars.

3. RESULTS AND DISCUSSION

3.1 Wood chemical composition

Several hardwood species were received as chips from different pulp and paper mills around the world for this study. Firstly, chemical characterization of all wood samples was done and the results are given in Table 1. The six hardwoods investigated showed significantly different chemical compositions. Among the six hardwood samples, total carbohydrates content ranges from 54.7 to 74.3% with glucans and xylan as the major component. Glucans composed 38.1% (for white oak) to 46.0% (for white birch) of the total wood composition, while xylan varied from 11.3 (for *E. benthamii*) to 24.2% (for white birch). The values are according to Santos et al., 2011, who characterized several hardwood samples, including sweet gum and red oak, both presented in this study. *Betula* specie's (as white and yellow birch) are known to contain high amounts of xylans, as found in this study (Pinto et al., 2005). Total lignin content varied from 20.1 (for yellow birch) to 28.9% (for *E. benthamii*). S/V ratio, measured after nitrobenzene oxidation, was found to differ a little among the species, from 2.39 (for yellow birch) to 3.00 (for white birch).

Table 1. Wood chemical characterization

Samples	Sugars, %			Lignin, %			Uronic acid, %	S/V
	Glc	Xyl	Others	ASL	Klason	Total		
Sweet gum	42.1	14.8	4.6	2.2	20.6	22.8	5.5	2.70
Red oak	42.7	15.8	4.6	2.3	20.5	22.8	4.4	2.50
White oak	38.1	15.1	5.1	2.2	20.9	23.1	5.3	2.42
E. benthamii	40.0	11.3	3.7	1.6	27.3	28.9	5.8	2.63
Yellow birch	43.3	21.9	3.9	1.8	18.2	20.1	4.5	2.39
White birch	46.0	24.2	4.1	2.1	19.4	21.5	4.4	3.00

3.2 Isolated CEL from wood

Lignin from wood meals were then isolated after enzymatic treatment, as described previously, to obtain the CEL preparation. The method is based on carbohydrates removal by a cellulolytic enzyme cocktail (cellulase and hemicellulase) and the resulting solid material was extracted with dioxane/water 96%. In theory, lignin is the residue after carbohydrates dissolution. However, protein and carbohydrates can remain in the isolated material. The main advantage of this method is that there is minimal modification in lignin structure during its recovery and isolation (Argyropoulos et al., 2002; Maia and

Colodette, 2003; Chang 1992). Yield was calculated based on the total lignin content in wood and total lignin content after isolation and purification.

Table 2 shows yield and purity of CEL preparations from hardwood samples. Yield of CEL from wood meals varied from 20.1 (for white birch) to 33.3% (for red oak), and was independent of the lignin content in the wood ($R^2 = 0.0628$). There is no data in the literature about the effect of the CEL yield on the lignin structure for *hardwood* CEL preparations. However, wet chemistry, NMR, and FTIR spectroscopy studies demonstrated that the chemical structure of CEL and MWL (milled wood lignin) isolated from *softwood* in high yields (up to 65%) were very similar to those isolated in the usual yield (20-30%) (Capanema et al., 2015; Balakshin et al., 2008; Hu et al., 2006).

Table 2. Yield and purity of the isolated lignin (CEL preparation) from wood meal samples

	Sweet gum	Red oak	White oak	*E. benthamii*	Yellow birch	White birch
Yield*, %	22.8	33.3	22.8	29.4	28.9	20.1
CEL purity, %	81.6	79.2	77.6	82.2	81.0	79.4

*Based on total lignin in the wood and after isolation.

The main chemical functional groups in lignin are the hydroxyl, methoxyl, carbonyl and carboxylic groups. The proportion of these groups depends on the genetic origin and isolation processes applied. Functional group analysis can be used to determine the lignin structure (Mansouri and Salvadó, 2007) and ^{31}P NMR is often used for the quantitation of specific functionalities in lignin, such as hydroxyl groups (Lupoi et al., 2015). ^{31}P NMR spectra was carried out on the CEL material for characterization regarding free phenolic groups (PhOH) content. 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 are attributed to 5-substituted units (which include 5-5' condensed units), and those in the range of 140.3 to 137.2 ppm are assigned to non-condensed units (free C_5 position). The signals in the range of 135.6 to 134.0 are associated to carboxylic acid hydroxyl groups. Figure 3 and 4 shows, respectively, a typical ^{31}P NMR spectra from hardwood pulp and the reactions of hydroxyls groups present in lignin with phosphitylating reagent.

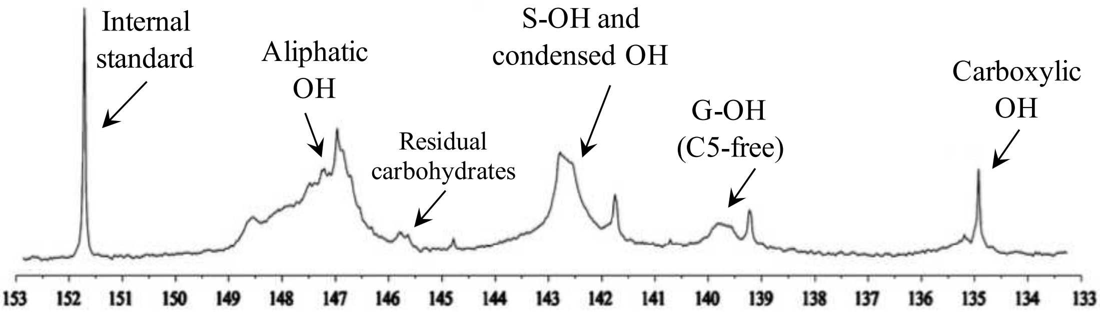

Figure 3. Typical ^{31}P NMR spectra from hardwood pulp (adapted from Prinsen et al., 2013).

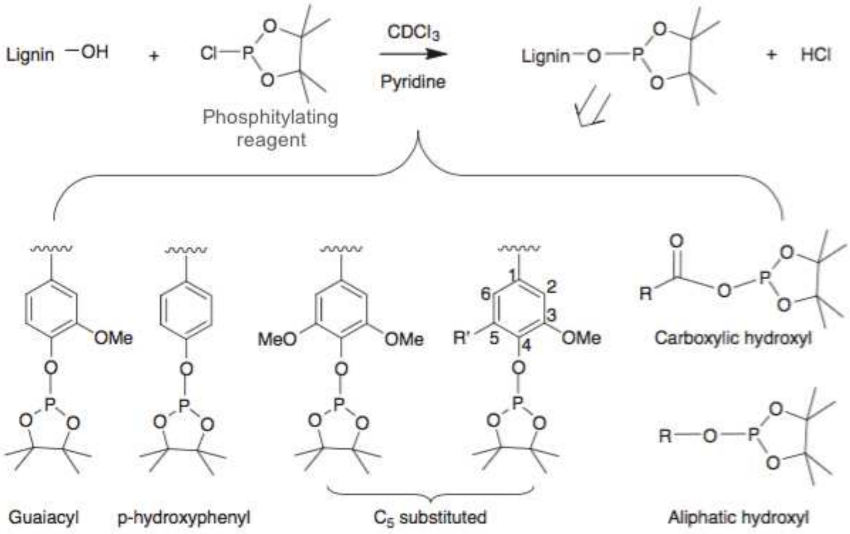

Figure 4. Scheme of the reactions of hydroxyls groups present in lignin with phosphitylating reagent.

The content of aliphatic, phenolic, and carboxylic hydroxyl moieties in CEL preparations obtained from wood samples are listed in Table 3. Among the various hydroxyl groups, the aliphatic hydroxyl signal is typically the dominant in lignin. A minor amount of carboxylic OH groups was observed. The relative proportions of such groups are usually dependent on the biomass species as well as the processing methods employed and it varied from 7.02 to 8.22 and 0.01 to 0.18 mmol/g of lignin, respectively. The total of 5-substituted and 5-free phenolic OH units varied widely from 0.97 to 2.33 mmol/g of lignin, for white birch and *Eucalyptus benthamii*, respectively. The importance of hydroxyl groups is associated to increase the solubility of lignin in aqueous solution since they turn lignin macromolecule more hydrophilic (Zhang, 2006).

Table 3. Aliphatic, phenolic and carboxylic hydroxyl groups content (mmol/g of lignin) determined by quantitative ^{31}P NMR in CEL isolated from wood samples

Samples	mmol/g lignin				
	Aliphatic OH	Phenolic OH groups			Carboxylic OH
		5-substituted	5-free	Total	
Sweet gum	7.41	0.61	0.74	1.35	0.13
Red oak	7.02	0.53	0.70	1.23	0.03
White oak	7.24	0.89	0.85	1.74	0.18
E. benthamii	7.65	0.88	1.14	2.02	0.08
Yellow birch	7.70	0.51	0.64	1.15	0.01
White birch	8.22	0.51	0.46	0.97	0.03

3.3 Kraft cooking of hardwood samples

Kraft cooking of the wood samples were performed under fixed conditions, except for the alkali charge, with the aim to produce brown pulps with similar degree of delignification (kappa number around 20) for the oxygen delignification study. Table 4 shows the results for kraft pulping, including the active alkaline charge needed to reach the desired kappa number. To cook all six wood samples, active alkaline charge varied from 13.5 to 16.0% and kappa number ranged from 19.4 to 20.0, except for white oak sample, which kappa number was found 23.5. Even using different values of alkaline charge for white oak sample, it was not possible decrease the kappa number, which lead us to believe that this sample has some property that was not investigated here. Red oak was the easiest to delignify whereas white birch and white oak woods required the highest amounts of pulping chemicals. The pulping yields (weight of unbleached pulp/weight of inicial wood) were significantly different among the wood species, ranging from 42.6 (for sweet gum) to 48.7% (for white birch), suggesting different patterns of wood polysaccharide degradation/retention. Although the S/V ratio and relative content of lignin in wood might contribute to the different pulping performances, the differences observed among the samples are clearly related to other factors, since these woods contained similar lignin content, except for *Eucalyptus benthamii* which contains the highest lignin amount. Furthermore, no correlation could be established between S/V ratio and the ease of pulping. However, the positive influence of S/V ratio on pulp yield and ease of pulping has been reported by other authors (Gomide et al., 2005; Gomes et al., 2008; Guerra et al., 2009; Santos et al., 2011). The hexenuronic acids content, measured according the method described by Tenkanen et al., 1999, varied from 36.7 to 52.3 mmol/kg of pulp. HexA formation might be influenced by pulping conditions and wood chemical characteristics, as uronic acids content (Morais, 2008; Zanão, 2016).

Table 4. Kraft pulping conditions* and results

Samples	A.A., %	Screened yield, %	Rejects, %	Kappa	HexA, mmol/kg	Viscosity, dm^3/kg
Sweet gum	15.0	42.6	5.54	20.0	47.5	1314
Red oak	13.5	42.9	7.28	20.0	36.7	1485
White oak	16.0	47.9	2.88	23.5	47.4	1386
E. benthamii	15.0	46.6	1.77	19.4	46.2	1304
Yellow birch	15.4	46.7	6.21	20.0	52.3	1400
White birch	16.0	48.7	1.52	19.8	49.2	1280

*H factor, sulfidity, and temperature were 800, 25%, and 160 °C, respectively.

3.4 Isolation of residual kraft lignin

Isolation of residual lignin from a chemical pulp has been a difficult task since the residual lignin content in pulp is relatively low and is probably linked chemically to the carbohydrates (Chang, 1992). The CEL samples used in this study was obtained from each unbleached kraft pulps, similar to wood CEL preparation method. The first difference was the step before enzymatic hydrolysis, where unbleached pulps were beaten in a PFI mill (instead of ball-milling) with the aim to convert shives into fibers and to improve the digestibility of the pulp towards cellulolytic enzymes, while avoid structural modifications (Chang, 1992). The second difference was the pH after enzymatic digestibility, which deserves a special attention. It was observed a very low yield of digested solid material for all six pulp samples, but after decrease the pH of the digested solution from 4.5 to 3.0, an increase of about 65% of yield was found in a study using red oak pulp sample. Thereafter, an investigation was done using only red oak sample to verify how CEL yield increase as the pH of digested solution decreases. Then, four different pH values were tested: 4.5 (regular pH, as reference), 4.0, 3.0, and 2.0. It was observed an increase of about 70% of yield when the pH reached 2.0 (data not presented). The reason is because a portion of the residual lignin becomes solubilized during the enzymatic treatment and must be precipitated from the filtrate by acidification (Chang, 1992).

The question now is: would the pH change the lignin characterization, specially regarding free phenolic groups content? After a ^{31}P NMR analysis, it was not found a considerable difference in free phenolic groups content (1.61-1.78 mmol/g of lignin), proving that yield is not a determinant factor to quantify PhOH groups. GPC analysis was also carried out on these samples to confirm the behavior of the macromolecule size precipitated under the different pH values. The results are presented in Table 5. It was observed a decrease in the molecular weight of the lignin when decrease the pH, confirming that a small size portions of residual lignin has been solubilized during the enzymatic treatment. However, as mentioned above, the different macromolecule size does not interpose on the PhOH groups content. Then, in this case, the main advantage of obtain a yield as higher as possible is turn the material handle.

Table 5. Molecular mass of CEL* from red oak pulp samples obtained at different pH values

Samples	Mn	Mw	PD
pH 4.0	2,510	12,440	5.0
pH 3.0	2,160	10,310	4.8
pH 2.0	1,240	5,150	4.2

*Acetylated lignin.

Yield and purity of CEL preparations obtained from all six unbleached pulp samples are presented in Table 6. Yield varied from 5.5 (for white oak) to 25.4% (for white birch), when the pH of the hydrolyzed solution was adjusted to 3.0. 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 probably cannot fully diffuse into dioxane/water solution (Jääskeläinen et al., 2003). ^{31}P NMR spectra was then carried out on these samples for characterization regarding free phenolic groups content.

Table 6. Yield and purity of the isolated lignin (CEL preparation) from unbleached pulp samples

	Sweet gum	Red oak	White oak	*E. benthamii*	Yellow birch	White birch
Yield*, %	13.9	24.1	5.50	16.7	16.2	25.4
CEL purity, %	65.9	62.9	57.3	67.3	61.3	79.4

*Based on total lignin content in the pulp and after isolation.

A special attention has been paid for free phenolic hydroxyl groups since it has demonstrated that they are one of the most significant reaction sites for oxygen delignification (Asgari and Argyropoulos, 1998). The contents of aliphatic, phenolic, and carboxylic hydroxyl moieties in CEL preparations obtained from the unbleached pulp samples are listed in Table 7.

Carboxylic hydroxyl groups varied from 0.17 (for red oak) to 0.68 mmol/g of lignin (for white oak). The values are much higher than woods (0.01-0.18 mmol/g, Table 3) since they are formed when lactones and esters present in wood are hydrolyzed, forming acid groups (Sjöström, 1993; Zhang, 2006). Same tendency was found by Prinsen et al., 2013, who investigated hydroxyl groups in MWL of a eucalypt hybrid before and after kraft cooking.

Aliphatic hydroxyl groups ranged from 8.72 (for white birch) to 15.5 mmol/g of lignin (for yellow birch), and are much higher for pulps than woods (Table 3). Once those groups are involved on the pulping delignification reactions, it was expected a significant decrease, as obtained by Prinsen et al., 2013 and Aguayo et al., 2015. However, the nature of aliphatic hydroxyl groups on the pulp is probably due to carbohydrates. Jääskeläinen et al., 2003 has shown that aliphatic hydroxyl can be originated from carbohydrates. They also showed that as more impurity and more carbohydrates content, more aliphatic hydroxyl groups were detected.

The total of 5-substituted units varied from 0.85 (for white birch) to 1.84 mmol/g of lignin (for sweet gum), while 5-free units varied from 0.24 (for white birch) to 0.57 mmol/g of lignin (for sweet gum). The resulting of total hydroxyl phenolic units was the sum of 5-subtituted and 5-free units and the total amount ranged from 1.09 (for white birch) to 2.41 mmol/g of lignin (for sweet gum). As expected, the 5-subtituted units, which include 5-5' condensed units, increased compared to the wood, while 5-free units decreased. The process of wood delignification involves the fragmentation of lignin macromolecules, which, almost invariably, is accompanied by competing condensation reactions (Liu et al., 2000). In summary, the total phenolic units increased after kraft cooking, once this process is well known to generate new phenolic groups because of breaking *ß*-*O*-4 linkages during the delignification process (Maia and Colodette, 2003).

The alteration in the content of phenolic moieties before and after the kraft cooking as cited above can be better explained by analyzing the Figure 5A-C.

Table 7. Aliphatic, phenolic and carboxylic hydroxyl groups content (mmol/g of lignin) determined by quantitative ^{31}P NMR in CEL isolated from unbleached pulp samples

Samples	mmol/g lignin				
	Aliphatic OH	Phenolic OH groups			Carboxylic OH
		5-substituted	5-free	Total	
Sweet gum	12.8	1.84	0.57	2.41	0.43
Red oak	15.1	1.21	0.40	1.61	0.17
White oak	14.2	1.56	0.51	2.07	0.68
E. benthamii	12.7	1.57	0.56	2.13	0.34
Yellow birch	15.5	1.30	0.45	1.74	0.29
White birch	8.72	0.85	0.24	1.09	0.30

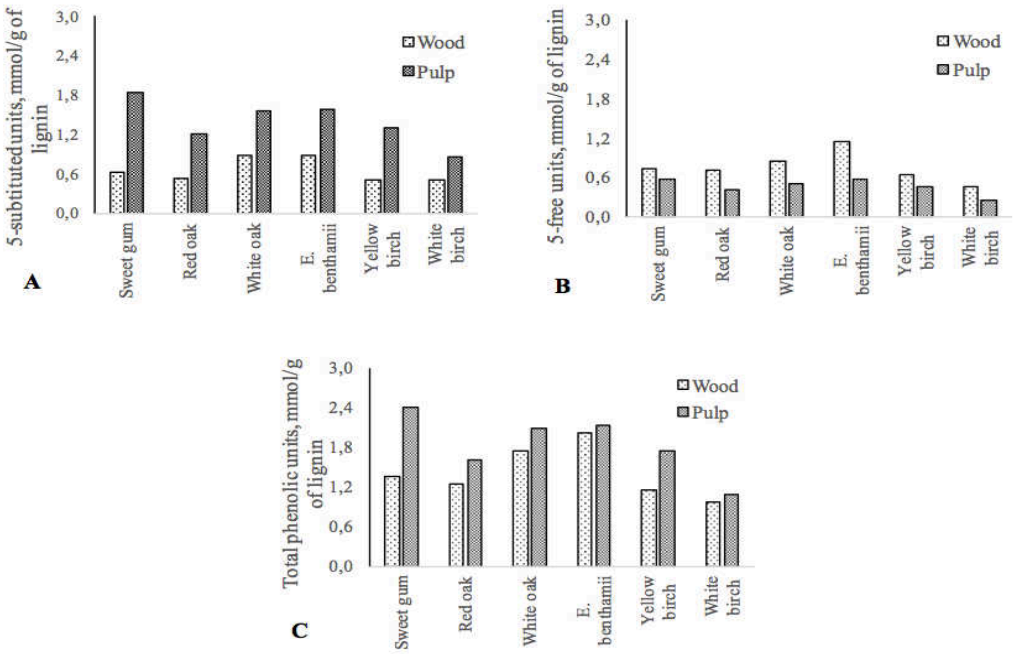

Figure 5. 5-substituted (A), 5-free (B) and total phenolic units (C) of isolated lignin in the wood and unbleached pulps samples.

3.5 Oxygen delignification stage

All unbleached pulp samples were submitted to an oxygen bleaching stage under fixed conditions and the results are presented in the Table 8. Less than 50% of the total kappa number was removed, since kappa number after O-stage varied from 10.3 to 12.2. At this level, acceptable losses in viscosity were found and the selectivity of the process, measured as kappa removed by 1 cP unit of viscosity drop, were preserved. Despite of the O-stage does not remove HexA, a decrease on this acid was observed, which can be explained by carbohydrate degradation, especially xylan, during the O-stage. It is well known that delignification rate for hardwood samples are limited to around 40%, and beyond this level, a significant cellulose degradation occurs (Argyropoulos, 2003). Since

HexA are not removed by the oxygen stage bleaching, the oxygen delignification efficiency was measured by the “true lignin kappa number”, which means that the equivalent HexA amount on kappa, considering the ratio of 10 mmol/kg HexA equals to 1 kappa number unit (Costa and Colodette, 2007), was subtracted of the kappa number and not included in the calculation. A high efficiency was observed, ranging from 48.3 to 59.7%, for white birch and white oak, respectively, indicating a good rate of lignin removal.

Table 8. Oxygen bleaching results and performance

	Sweet gum	Red oak	White oak	*E. benthamii*	Yellow birch	White birch
Kappa number	10.5	10.3	12.2	10.7	11.2	12.2
HexA, mmol/kg	43.1	31.0	39.2	43.2	44.7	45.0
Viscosity, dm^3/kg	1105	1300	1200	950	1178	1108
Kappa drop, %	47.5	48.5	48.1	44.8	44.0	38.4
Viscosity drop, dm^3/kg	209	185	186	354	222	172
Selectivity*	0.44	0.31	0.69	0.29	0.31	0.45
O-stage efficiency**, %	59.4	55.9	59.7	56.8	54.4	48.3

O-stage conditions: 2.0% of NaOH, temperature of 100 °C, TTT of 45 min, TAT of 30 min, pressure 100 psi, consistency 10%;

*Δ Kappa/ Δ viscosity (cP);

**Based on true lignin kappa number removal (excluding HexA), assuming that 10 mmol HexA/kg of pulp are equivalent to 1 kappa number.

According to Gellerstedt and Lindsfors, 1987 and Gellerstedt et al., 1999, two factors influence the lignin solubilization during the oxygen bleaching. The first one is the quantity of hydrophilic groups, since the lignin is practically insoluble in aqueous solution without these groups, and the second one is the reduction of the macromolecules size of the degraded lignin, which facilitates the transport of lignin out of the cell wall. From a reactivity point of view, free phenolic hydroxyl groups are the most important functionality in lignin and the phenolic phenylpropane units are preferably attacked (Toven and Gellerstedt, 1999). The O-stage efficiency, based on true lignin kappa number, *versus* 5-substituted, 5-free and total phenolic hydroxyl groups and its resulting correlation are presented in Figure 6A-C. As expected, the unbleached pulp samples with higher content of phenolic OH groups showed the higher O-stage efficiency, and a high and positive correlation was found, especially when only 5-free moieties are considered (Figure 6B). Even when only 5-substituted moieties are considered, a good correlation was found (Figure 6A), but some studies have indicated that condensed structures trends to inactivate the lignin toward oxygen delignification (Lucia et al., 2002). It is important to emphasize that 5-substituted moieties, for *hardwood* samples, include S-type lignin and 5-5’condensed lignin. The results obtained reinforces that free phenolic hydroxyl groups are the reactive site for oxygen delignification reactions, governing its efficiency. The O-stage efficiency based on total kappa number (which include HexA content) *versus* HexA content in unbleached pulps is presented in Figure 6D. A poor correlation was found ($R^2 = 0.1677$), meaning that HexA content is not a significant factor governing the oxygen bleaching efficiency when a wide range of hardwood species are under investigation.

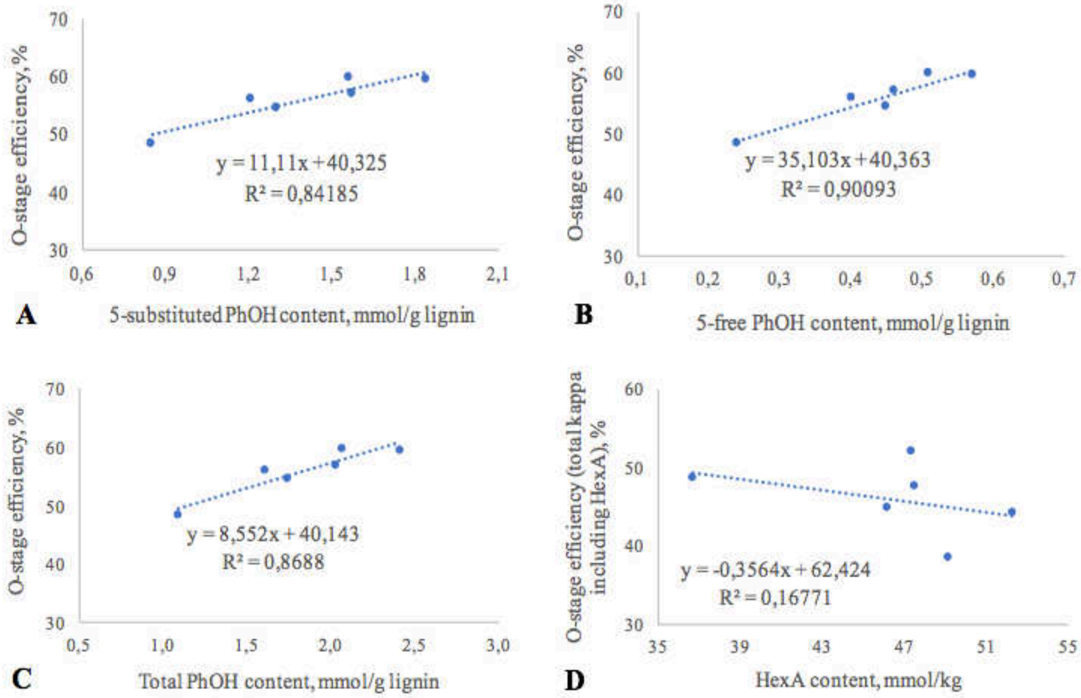

Figure 6. O-stage efficiency *versus* 5-substituted (A), 5-free (B) and total phenolic hydroxyl groups (C) and O-stage efficiency (based on total kappa number, including HexA) *versus* HexA content in unbleached pulps (D).

4. CONCLUSION

The six hardwood samples used in this study showed to differ widely regarding their chemical composition. ^{31}P analysis of CEL preparations from wood and pulp samples showed an increase in aliphatic, 5-substituted and carboxylic hydroxyl groups after pulping, and a decrease in 5-free phenolic hydroxyl groups. The yield of CEL preparations from unbleached pulps were quietly low, but an investigation on its impact in the quantification of phenolic hydroxyl groups showed that yield was not a relevant factor. The kraft pulping showed different yields for the same kappa number range, because of the wood chemical composition variation, keeping fixed conditions, except alkaline charge. The main objective of the kraft pulp was to produce unbleached pulps for oxygen bleaching investigation. The oxygen bleaching stage, carried out under fixed conditions, showed a good efficiency, and it was calculated based on true lignin kappa number. A high correlation was found between O-stage efficiency and the content of 5-substituted ($R^2 = 0.84$), 5-free ($R^2 = 0.90$), and total PhOH ($R^2 = 0.87$), proving that free phenolic hydroxyl groups are the reactive site for oxygen delignification reactions. When different hardwood species are compared, the HexA content did not influence on the total efficiency ($R^2 = 0.16$).

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PAPER 2: UM NOVO CONCEITO DE BRANQUEAMENTO DE POLPA KRAFT DE EUCALIPTO COM OZÔNIO EM MÉDIA CONSISTÊNCIA

Publicado em *Química Nova*, 40(1):54-59, 2017

Resumo

O efeito do pré-tratamento de hidrólise ácida a quente (estágio A) sob a performance do branqueamento com ozônio (estágio Z/E) em média consistência foi avaliado. Um plano experimental foi desenvolvido para otimização dos estágios A e Z/E em uma polpa kraft de eucalipto pré-deslignificada. O estágio A causou significante remoção de kappa e HexA, sendo que a condição ótima para estágio foi pH 3,0, 90 °C e 120 minutos de reação à consistência 10%. Para a polpa pré-tratada pelo estágio A, as condições onde o estágio Z/E apresentou maior eficiência e seletividade foram pH 2,5, 40 °C, 5,0 kg de O_3/tas para a etapa de ozonização (Z/) e pH 10,5 para a etapa de extração (etapa E). Os valores de remoção de kappa por quilograma de ozônio aplicados foram 1,04 e 1,18 para a polpa pré-tratada pelo estágio A e polpa referência, respectivamente. Uma vez que o estágio A não decresceu fortemente a eficiência do estágio Z/E, tais estágios mostram-se complementares ao invés de competitivos. O potencial do estágio A na economia de reagentes químicos de branqueamento é bastante significativo, dado que o número kappa das polpas após os estágios Z/E e AZ/E foram 5,5 (alvura 67,3 %ISO) e 1,1 (alvura 72,6 %ISO), respectivamente. O impacto do estágio A na performance de uma sequência de branqueamento, comparando as sequências Z/EDP e AZ/EDP será discutido em outra publicação.

1. INTRODUÇÃO

Por muitos anos, a lignina foi considerada o único componente da madeira responsável pelo consumo de reagentes químicos durante o branqueamento de polpa celulósica. No início dos anos noventa, a presença dos ácidos 4-desoxihex-4-enurônicos na polpa, chamados de hexenurônicos (HexA), foi confirmada pela técnica de Ressonância Magnética Nuclear e o seu efeito sobre o número *kappa* e consumo de reagentes químicos no branqueamento puderam ser estudados.[1,2] O grande problema causado pela presença dos HexA na polpa é que eles reagem com compostos eletrofílicos, como o ozônio e dióxido de cloro, usados durante o branqueamento.[3,4]

Os HexA são formados durante o cozimento alcalino devido à β-eliminação de metanol da estrutura dos ácidos 4-*O*-metil-α-D-glucourônicos, os quais estão ligados covalentemente às xilanas presentes na madeira (Figura 1).[2,5]

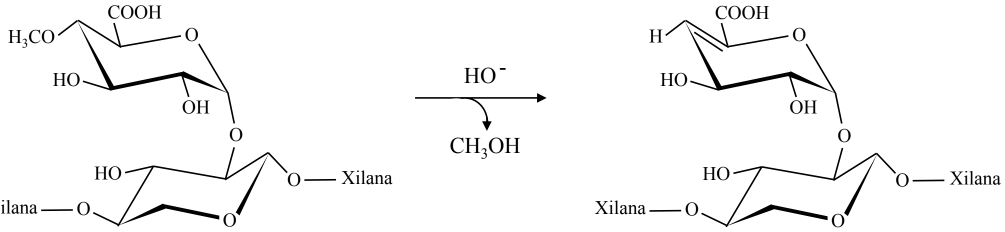

Figura 1. *Esquema da reação de formação dos HexA durante a polpação alcalina (adaptado de Li e Gellerstedt[2])*

Com o intuito de remover os HexA antes de se iniciar uma sequência de branqueamento, o estágio de hidrólise ácida a quente (estágio A) foi desenvolvido, resultando em significativa economia de reagentes químicos,[1,6,7] além de se tratar de uma técnica de baixo custo. O estágio A se baseia no tratamento da polpa com solução de ácido mineral (ácido sulfúrico, clorídrico ou nítrico) em pH 2,5-4 e temperaturas em torno de 85-105 °C.[8] Nestas condições, a estrutura do HexA se degrada, dando origem a estruturas derivadas do furano (Figura 2), que são então, solúveis em água.[1,2] Porém, mesmo nas mais severas condições, não é possível removê-los completamente. Uma parcela de aproximadamente 20% ainda permanece na polpa.[9] Condições extremas causariam perda de viscosidade, o que é indesejado no caso de uma polpa destinada a produção de papel de impressão e escrita. Suess[4] afirma que apenas metade dos HexA presentes na polpa podem ser removidos em um estágio ácido sem grave perda de viscosidade.

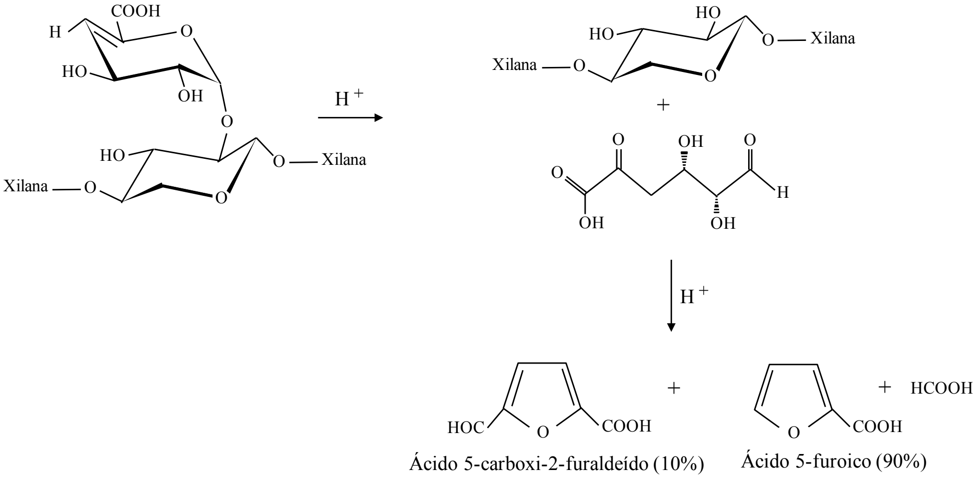

Figura 2. *Esquema reacional da hidrólise ácida dos HexA e seus derivados (adaptado de Li e Gellersdedt[2])*

Devido à presença de um grupo carboxílico insaturado e um enol-éter em sua estrutura, os HexA reagem prontamente com eletrófilos, como o ozônio, sendo que esta reação é cerca de 2,4 vezes mais rápida do que com a lignina.[10] Além de consumir ozônio, o qual poderia ser poupado para oxidar a lignina, a reação com os HexA gera quantidades significativas de ácido oxálico, como mostrado na Figura 3, que na presença de cálcio dá origem ao oxalato de cálcio, responsável por incrustações nos equipamentos.[11]

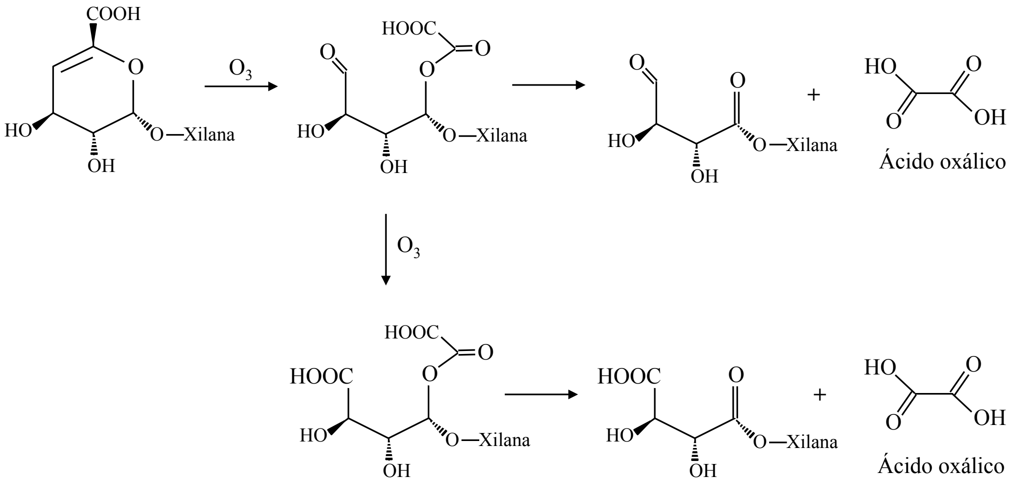

Figura 3. *Esquema reacional da formação do ácido oxálico através da reação entre os HexA e o ozônio (adaptado de Lino et al.[11])*

Pelo seu caráter eletrofílico, o ozônio reage rapidamente com a lignina residual, a qual é rica em estruturas insaturadas e aromáticas, levando à formação de grupos cetônicos e aldeídicos e também à clivagem do anel aromático, resultando num polímero hidrofílico que se solubiliza em água nas condições neutras ou alcalinas.[11-13] A Figura 4 exemplifica essas reações.

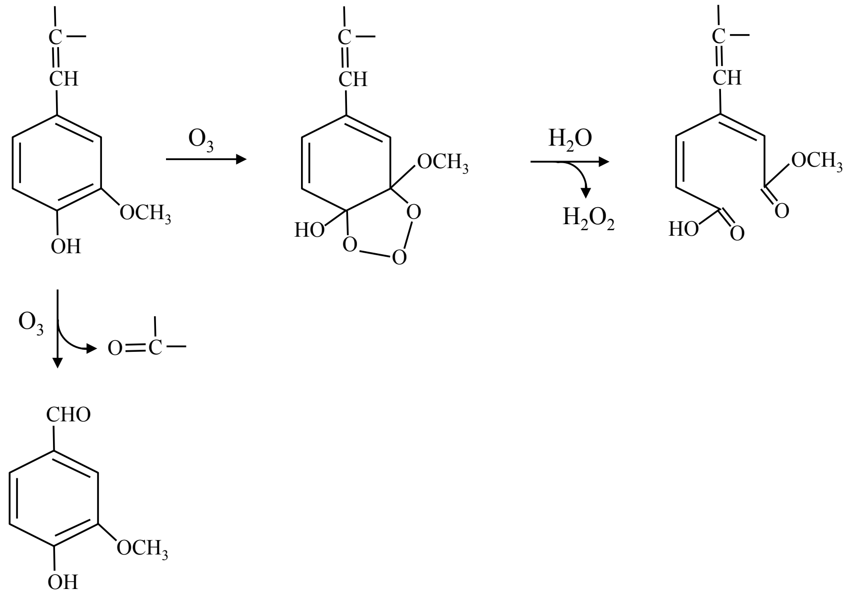

Figura 4. *Esquema reacional entre uma estrutura típica da lignina com o ozônio (adaptado de Lino et al.[11]).*

A reação do ozônio com as estruturas fenólicas de lignina também leva à formação de radicais livres, os quais são responsáveis pela degradação dos carboidratos da polpa, resultando em queda de viscosidade e consequentemente, perda de resistência das fibras.[14] Apesar do ozônio ser usado há anos nas indústrias como agente de branqueamento, ainda é necessário uma melhor compreensão das reações químicas e um ajuste refinado das condições utilizadas no processo.[15,16]

A prática industrial vem mostrando significativa economia de reagentes químicos no branqueamento com a adição de um estágio A antes do estágio Z/E.[17,18] Sendo assim, uma investigação mais profunda sobre a utilização deste estágio e sua influência na performance do subsequente estágio Z/E se torna necessária. O objetivo desse estudo foi determinar as condições ótimas do estágio A e Z/E e avaliar o efeito da inserção deste estágio A à frente do Z/E sobre a remoção de HexA e lignina, bem como seu impacto na viscosidade e alvura da polpa, usando para comparação, uma polpa de referência, onde não houve aplicação de estágio A.

2. EXPERIMENTAL

2.1 Material

Foi utilizada uma amostra de polpa *kraft* industrial de eucalipto, pré deslignificada com oxigênio. A polpa pré deslignificada apresentou as seguintes características iniciais: número *kappa* 11,4; viscosidade 1059 $dm^3\ kg^{-1}$; alvura 49,5 % ISO e HexA 56,3 mmol kg^{-1}.

2.2 Métodos

2.2.1 Aperfeiçoamento do estágio A

O aperfeiçoamento do estágio A foi realizado utilizando as seguintes condições: pH 2,5; 3,0; 3,5 e 4,0; temperatura 85, 90 e 95 °C; o tempo de reação e a consistência do estágio foram fixados em 120 minutos e 10%, respectivamente. A polpa foi acidificada com ácido sulfúrico para atingir o pH desejado, e então colocada em um reator/misturador Mark V (Quantum Technologies, EUA) com capacidade para 3,6 L. A polpa foi então aquecida até a temperatura desejada e mantida no reator sob agitação pelo tempo desejado. Em seguida, as polpas foram lavadas com 9 m^3 de $H_2O\ t^{-1}$ de polpa. A melhor condição foi determinada com base na remoção do HexA e na queda de viscosidade.

2.2.2 Aperfeiçoamento do estágio Z/E em média consistência (MC)

O aperfeiçoamento do estágio Z/ foi realizado utilizando as condições: pH de reação 2,5; 3,5 e 5,5; temperatura 40, 55 e 70 °C; o tempo de reação para a dosagem de ozônio desejada (5 kg de O_3 t^{-1} de polpa) foi fixado em 2 min. A polpa foi acidificada com ácido sulfúrico e então colocada em um reator/misturador Mark V (Quantum Technologies, EUA) com capacidade de 3,6 L e aquecida até a temperatura desejada, mantida sob agitação, sendo que o ozônio foi injetado durante o período de 2 minutos. Após a conclusão do estágio Z/, as amostras de polpa foram removidas do reator e o ozônio residual foi determinado. Em seguida, foi realizada uma extração (E), utilizando dois valores de pH diferentes (3,5 e 10,5) por 10 min a 65 °C e 10% de consistência. As polpas foram então lavadas com o equivalente a 9 m^3 de H_2O t^{-1} de polpa, e a escolha da melhor condição do estágio Z/E foi baseada na redução do número *kappa*, na remoção do HexA e na queda de viscosidade.

2.2.3 Estágio Z/E da polpa referência

A polpa *kraft* industrial pré deslignificada foi submetida ao estágio Z/E sem prévia aplicação do estágio A, seguindo as condições: carga de ozônio de 5 kg t^{-1}, tempo de reação 2 min, pH 3,5, temperatura 70 °C e consistência 10%. A extração foi realizada em pH 3,5 por 10 minutos a 65 °C e 10% de consistência. Por último, a polpa foi lavada com o equivalente a 9 m^3 de H_2O t^{-1} de polpa.

2.2.4. Procedimentos analíticos

As amostras de polpa foram analisadas de acordo com os seguintes procedimentos analíticos: número *kappa*: TAPPI T236 om-85, que se baseia na medição indireta de compostos oxidáveis da polpa por reação com permanganato de potássio (neste caso, lignina e HexA); viscosidade: TAPPI T230 om-94, baseada na medição da viscosidade da celulose, usando viscosímetro capilar, após sua dissolução em etilenodiamina cúprica; alvura ISO: TAPPI T525 om-86, valor numérico para o fator de reflectância da amostra de polpa à 457 nm; e teor de HexA: Tenkanen *et al.,* 1999,[19] método baseado na medição do ácido 2-furanocarboxílico à 245 nm, que é originado após hidrólise dos HexA em condições ácidas.

3. RESULTADOS E DISCUSSÃO

3.1 Aperfeiçoamento do estágio A

Embora as condições gerais para execução do estágio A já tenham sido estudadas por Vuorinen *et al.*,[1] é sempre interessante otimizar tais condições para uma nova amostra de polpa afim se obter o máximo proveito desse estágio.

A Tabela 1 mostra a redução do *kappa*, remoção de HexA, queda de viscosidade e ganho de alvura após o estágio A, para cada condição investigada. A remoção de HexA aumentou com a elevação da temperatura e diminuição do pH, como já citado em estudos anteriores[1,20], uma vez que eles são suscetíveis a hidrólise ácida gerando produtos solúveis em água. A redução do número *kappa* também aumentou nessas condições. Como o estágio A não remove grandes quantidades de lignina,[1] a diminuição do *kappa* pode ser explicada pela metodologia usada na sua determinação, que se baseia na quantificação, por titulação, de compostos oxidáveis na polpa usando permanganato de potássio em meio ácido, o qual oxida não só lignina, mas também os HexA.[21] Sendo assim, uma diminuição do número *kappa* pode não significar remoção de lignina, mas sim de HexA, como neste estudo. A queda de viscosidade e o ganho de alvura também aumentaram nessas condições (aumento da temperatura e diminuição do pH), as quais favorecem a degradação dos carboidratos pela hidrólise ácida e a remoção de pequenas frações de grupos cromóforos (lignina e HexA) neste estágio. A máxima redução do *kappa* (53,5%) e de HexA (74,6%) foi obtida a 95 °C e pH inicial 2,5. Contudo, essa condição resultou em significativa perda de viscosidade (253 dm^3 kg^{-1}). Condições severas como essas (baixo pH e alta temperatura) resultam em grave queda de viscosidade, uma vez que a celulose é sensível à hidrólise ácida devido às ligações glicosídicas entre os monômeros de glucose. A perda de viscosidade é uma das principais desvantagens do estágio A, devido à potencial perda nas propriedades de resistência se as condições empregadas não forem devidamente controladas.[6] Sendo assim, considerando que a condição de 90 °C e pH inicial 3,0 resultou em menor perda de viscosidade (141 dm^3 kg^{-1}) e ainda assim alta eficiência na redução de *kappa* (44,7%) e HexA (65,9%), esta condição foi escolhida para dar sequência a este estudo.

Tabela 1. Efeito da temperatura e pH inicial sobre a redução do *kappa*, remoção de HexA, queda de viscosidade e ganho e alvura após o estágio A

Temperatura de reação, °C	pH de reação	Redução de *kappa*, %	Remoção de HexA, %	Queda de viscosidade, $dm^3\ kg^{-1}$	Ganho de alvura, % ISO
85	2,5	35,4	44,1	182	5,0
	3,0	35,1	40,2	135	5,1
	3,5	33,0	41,6	136	4,9
	4,0	28,4	31,9	121	5,1
90	2,5	47,4	69,0	231	5,3
	3,0	44,7	65,9	141	5,0
	3,5	41,9	56,4	137	5,1
	4,0	38,4	52,0	101	4,8
95	2,5	53,5	74,6	253	5,4
	3,0	51,2	71,7	161	5,2
	3,5	48,3	67,4	131	5,2
	4,0	39,8	54,4	107	5,3

3.2 Aperfeiçoamento do estágio Z/E em média consistência (MC)

Após selecionado o ponto ótimo do estágio A, a polpa foi então submetida ao estágio Z/E em diferentes condições de pH e temperatura. A Figura 5 mostra os efeitos do pH e da temperatura do estágio Z/E sobre a redução do *kappa*, remoção de HexA, ganho de alvura e queda de viscosidade para as polpas extraídas em pH 3,5. Os valores máximos para redução de *kappa* e HexA com mínima perda de viscosidade foram encontrados em pH 2,5 e temperatura 40 °C, indicando que a máxima eficiência e seletividade do ozônio acontecem nessas condições. O ganho de alvura após o estágio Z/E também foi maximizado nestas condições (pH 2,5 e temperatura de 40 °C), o que está de acordo com o decréscimo do *kappa*. Resultados similares foram reportados anteriormente por outros pesquisadores.[22,23] A alta eficiência e seletividade em baixos valores de pH e temperaturas é explicado pela baixa decomposição do ozônio sob essas condições.[11] A seletividade do estágio de branqueamento com ozônio é muito dependente da formação de radicais livres, que por sua vez, é influenciada pelas condições operacionais do estágio, especialmente temperatura e pH.[24-26]

A mesma tendência foi observada para o estágio Z/E com extração em pH 10,5, como mostrado na Figura 6. Em geral, melhores resultados de redução de *kappa* e HexA foram obtidos quando a polpa foi extraída em pH 10,5 ao invés de pH 3,5 após a ozonização. As condições alcalinas favorecem a remoção de materiais oxidados, impactando positivamente na redução do *kappa* e HexA da polpa. O ganho de alvura diminuiu levemente para as polpas extraídas em pH 10,5, o que pode ser explicado pela conversão de frações fenólicas em quinonas devido às condições alcalinas da extração. Assim, as condições ótimas do estágio Z/E foram pH 2,5, temperatura de 40 °C e extração em pH 10,5.

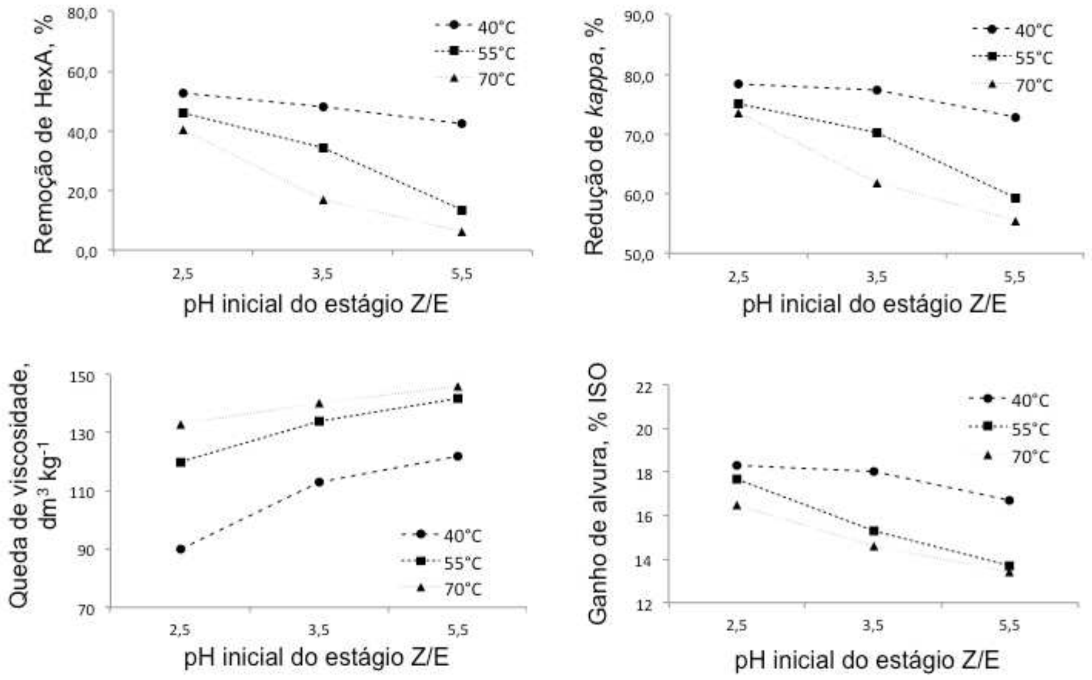

Figura 5. *Efeito do pH e temperatura sob a redução do kappa, remoção dos HexA, queda de viscosidade e ganho de alvura, após o estágio Z/E (extração em pH 3,5).*

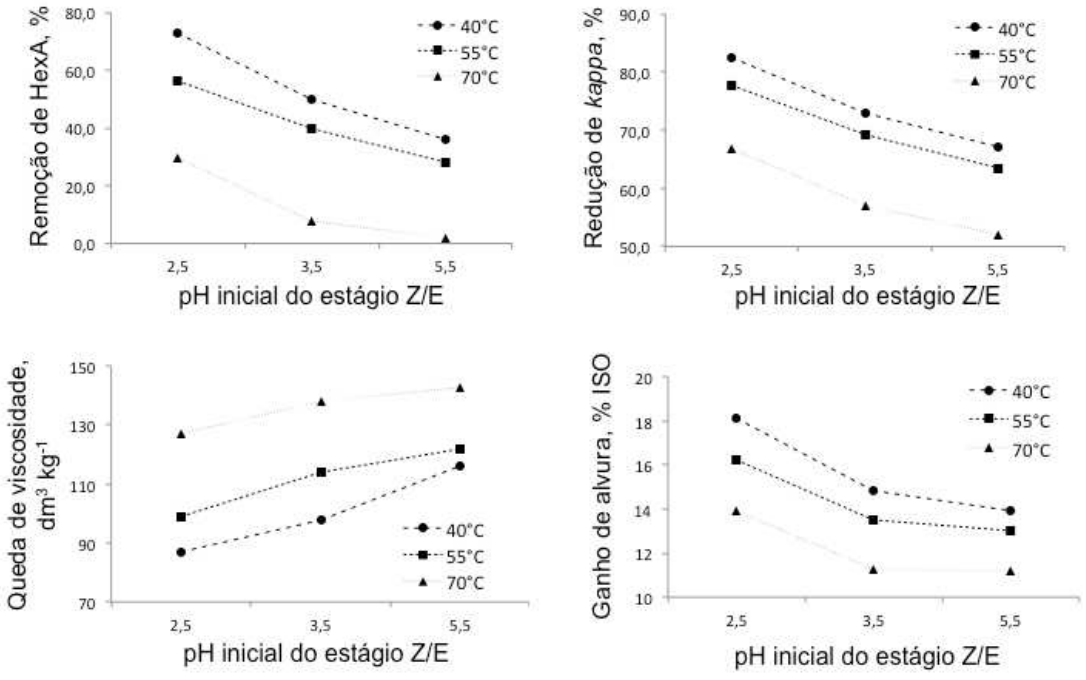

Figura 6. *Efeito do pH e temperatura sob a redução do kappa, remoção dos HexA, queda de viscosidade e ganho de alvura, após o estágio Z/E (extração em pH 10,5).*

Os resultados mostrados na Tabela 2 comparam a performance do estágio Z/E em polpas tratadas e não tratadas pelo estágio A. É importante notar que, no caso da polpa referência, o estágio Z/E foi realizado em condições operacionalmente favoráveis, como altas temperaturas. Assim, foi feita uma comparação entre as polpas tratadas e não tratadas pelo estágio A, sendo que o estágio Z/E da polpa referência foi realizado a 70 °C e o da polpa tratada pelo estágio A foi realizado a 40 °C (condição otimizada). Essa comparação é válida uma vez que alguns estudos mostraram que não há diferença significativa na performance do estágio Z em temperaturas na faixa de 40-60 °C.[15,16] Normalmente, as fábricas operam sua extração em pH 3,5, pois no caso de um subsequente estágio de branqueamento utilizando dióxido de cloro, já se tem a vantagem do baixo pH; este então foi o valor empregado no experimento de referência. Mas, para a polpa tratada pelo estágio A, o estágio Z/E foi realizado no pH ótimo, pH 2,5, e assim tem-se a vantagem da acidificação vinda do estágio ácido e também da melhor reação do ozônio com a lignina, que é mais eficiente e seletiva neste valor de pH.[23]

Tabela 2. Resultados do estágio Z/E para polpas tratadas e não tratadas pelo estágio A

Parâmetro	Estágio Z/E sob as condições ótimas*	Estágio Z/E sob a condição referência**
	Após estágio A	Sem prévio estágio A
Número kappa	1,1 ± 0,1	5,5 ± 0,1
HexA, mmols kg^{-1}	5,2 ± 0,1	23,4 ± 0,2
Viscosidade, dm^3 kg^{-1}	831 ± 2	840 ± 5
Alvura, % ISO	72,6 ± 0,1	67,3 ± 0,1
Redução do kappa, unidades kappa	5,2	5,9
Remoção de HexA, mmols kg^{-1}	14,0	32,9
Remoção de HexA, unidades kappa***	1,4	3,3
Remoção de lignina, unidades kappa	3,8	1,9
Queda de viscosidade, dm^3 kg^{-1}	87	219
Ganho de alvura, % ISO	18,1	17,8

* Etapa Z/ em pH 2,5, 40 °C, 10% de consistência e extração em pH 10,5

** Etapa Z/ em pH 3,5, 70 °C, 10% de consistência e extração em pH 3,5

*** Assumindo que uma unidade *kappa* equivale a 10 mmols de HexA kg^{-1} de polpa.[21]

Como no caso da referência, onde o estágio Z/E foi realizado em uma polpa sem prévio estágio A, o número *kappa* e o teor de HexA dessa polpa após o estágio Z/E foi bem maior do que aquela previamente tratada pelo estágio A. Em termos de redução do número *kappa*, os valores foram similares. Porém, a polpa referência tinha um alto teor de HexA em relação à polpa previamente tratada pelo estágio A (56,3 e 19,2 mmols kg^{-1}, respectivamente), fazendo com que 55,9% da carga de ozônio aplicada fosse gasta para remover HexA, enquanto que na polpa tratada pelo estágio A, o ozônio agiu direto na remoção de lignina (apenas 26,9% da carga de ozônio foi gasta para remover HexA), fazendo com que o estágio Z/E removesse o dobro de lignina quando a polpa foi tratada pelo estágio A (remoção de 1,9 e 3,8 unidades *kappa* como lignina, respectivamente). Assim, após o estágio Z/E, a alvura ISO da polpa referência foi 5,3% ISO mais baixa que a polpa tratada pelo estágio A. A queda de viscosidade para a polpa referência foi bem mais alta do que para a polpa tratada pelo estágio A. No entanto, o valor final de ambas foi próximo. O ganho de alvura através do estágio Z/E foi maior para as polpas tratadas pelo estágio A. Estes resultados indicam que polpas tratadas pelo estágio A fizeram com que o subsequente estágio Z/E fosse mais seletivo para remover lignina, com consequente aumento da alvura.

O número *kappa* reduzido por cada quilograma de ozônio aplicado foi de 1,04 (variação de 5,2 no número *kappa* antes e depois do estágio Z/E, sendo a carga de ozônio aplicada de 5,0 kg t^{-1}) a partir de um número *kappa* de entrada de 6,3 após o estágio A, e 1,18 (variação de 5,9 no número *kappa* antes e depois do estágio Z/E, sendo a carga de ozônio aplicada de 5,0 kg t^{-1}) a partir de um *kappa* de entrada de 11,4, sem o prévio estágio A. Era esperado que o estágio Z/E fosse pouco eficiente após o estágio A, mas considerando-se o significativo menor *kappa* de entrada, pode-se perceber que sua redução de 1,04 e 1,18 unidades *kappa* por quilograma de ozônio aplicado estão na mesma faixa. Em outras palavras, a implementação do estágio A não decresceu a eficiência do estágio Z/E. Assim, a hidrólise ácida à quente e o branqueamento com ozônio, neste estudo, não são técnicas competitivas, e sim complementares.

4. CONCLUSÃO

A condição ótima de reação para o estágio A foi 90 °C, pH 3,0 por 120 minutos a 10% de consistência, reduzindo o *kappa* de 11,4 para 6,3 e o teor de HexA de 56,3 para 19,2 mmols kg^{-1}, sendo a perda de viscosidade de 141 $dm^3\ kg^{-1}$.

A condição ótima do estágio Z/E foi 40 °C em pH 2,5 a 10% de consistência, usando 5 kg de O_3 t^{-1}, sendo o pH de extração 10,5, reduzindo o *kappa* de 6,3 para 1,1 e o teor de HexA de 19,2 para 5,2 mmols kg^{-1}, com perda de viscosidade de 87 $dm^3\ kg^{-1}$.

O estágio Z/E na polpa referência reduziu o número *kappa* de 11,4 para 5,2 e o teor de HexA de 56,3 para 23,4 mmols kg^{-1}, sendo a perda de viscosidade de 219 $dm^3\ kg^{-1}$.

Os estágios AZ/E e Z/E mostraram similar eficiência, sendo o número *kappa* reduzido por quilograma de ozônio 1,04 e 1,18 para as polpas pré-tratada e referência, respectivamente, tornando tais estágios complementares ao invés de competitivos.

A inserção de um estágio A aumenta significativamente a economia de reagentes químicos de branqueamento, dado que o número *kappa* após os estágios AZ/E e Z/E foram 1,1 (alvura 72,6% ISO) e 5,5 (alvura 67,3% ISO), respectivamente. O impacto do estágio A no branqueamento completo das polpas pelas sequências AZ/EDP e Z/EDP será discutida em uma futura publicação.

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PAPER 3: EFFECT OF EUCALYPT PULP PRETREATMENT WITH HOT ACID HYDROLYSIS ON (aZe)DP AND (aZe)(EP)P BLEACHING PERFORMANCE

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Abstract

The effect of pulp pretreatment with hot acid hydrolysis on high consistency ozone bleaching was evaluated. An experimental plan was set up involving the full optimization of the A-stage and its application in Elemental Chlorine Free – ECF – [A/(aZe)DP and A(aZe)DP] and Total Chlorine Free – TCF – [A/(aZe)(EP)P and A(aZe)(EP)P] sequences for eucalypt kraft pulp bleaching. The A-stage removed a significant amount of lignin and HexA from the pulp, and the subsequent Z-stage remained efficient after completion of the A-stage. The chemical savings caused by the A-stage were significant (~7 kg ClO_2/adt). The optimum conditions for the A-stage were pH 3.0, 90 °C for 120 min and 10% consistency. The strength properties of pulps bleached with the (aZe)DP (reference) and A/(aZe)DP ECF sequences were similar, but the TCF sequence A/(aZe)(EP)P delivered slightly lower strength properties than the ECF sequences. Fiber peeling studies indicated that the HexA present in the kraft pulp is not concentrated on the fiber surface as previously thought.

1. INTRODUCTION

Until the early 1990s, lignin was considered the only pulp component responsible for chemical consumption during bleaching. In 1994, the presence of hexenuronic acids (HexA) in pulp was confirmed by the NMR technique, and their effect on the pulp kappa number and bleaching chemical demand was determined.(1, 2) At the same time, the so-called hot acid hydrolysis process (A-stage) was developed, which is a commercial and inexpensive technique to remove HexA from pulp prior to bleaching, resulting in significant chemical savings.(1,3,4)

The use of ozone as a bleaching agent for fibrous materials, including those used for papermaking, was first described in 1889, when fibers were subjected to a gas mixture of chlorine and ozone.(5) However, the industrial production of ozone bleached pulp started in connection with increasing environmental pressure and the Total Chlorine Free (TCF) wave. Similar to many other new technologies, ozone bleaching did not immediately reach its optimal technical efficiency but faced several issues during its early years. With an improved mixing technology, a better understanding of ozone bleaching chemistry and the fine tuning of the whole process,(6, 7) the so-called ECF-Light bleaching sequences - including an ozone stage - made it possible to deliver a pulp quality similar to those produced by conventional ECF bleaching.(8)

Ozone bleached pulp capacity is currently over 8 million tonnes/year, accounting for 8% of the worldwide chemical bleached pulp capacity. Ozone bleaching has taken just 10 years to develop as a reliable and economically viable technology and can now be considered a mature bleaching process. Most mills using ozone today are operating Z-ECF bleaching as a result of the ease of installation and the economic benefits. More than 60% of the 26 mills made the choice of ozone bleaching after the year 2000. Three mills have already started new ozone bleaching stages in 2013. In Brazil, there are four fiber lines using ozone in sequences, such as O/OAZP, O/OZ/D(EPO)D, OAZDP and O(aZe)DP.

The implementation of so-called hot acid hydrolysis (A-stage) prior to ozone treatment (Z-stage) has been a matter of debate, particularly in eucalyptus kraft pulp bleaching. Some studies contend that the A-stage before the Z-stage decreases the efficiency of the latter.(9) Other studies indicate that the A-stage before the Z-stage is highly capital intensive because a washer would be required after the A-stage.(1) The fact of the matter is that ozone reacts fast with HexA and the ozone consumed by HexA could, in principle, be removed less costly by an A-stage.(10)

Because industrial practice has shown prodigious chemical savings after the addition of an A-stage ahead of the ZDP bleach plant,(9, 11) it is worth looking into this matter more deeply.

The objective of this study was to evaluate the effect of placing an A-stage, with and without washing, ahead of the (aZe)DP and (aZe)(EP)P sequences on the consumption of bleaching chemicals and pulp quality. The optimum conditions to run the A-stage prior to ozone bleaching were also determined. An experimental plan was set up involving full optimization of the A-stage and its application in the A/(aZe)DP, A(aZe)DP, A/(aZe)(EP)P and A(aZe)(EP)P sequences for the bleaching of an oxygen delignified eucalypt kraft pulp. As a reference, the (aZe)DP sequence without the A-stage was also performed. The effect of the (aZe)-stage e-step pH was also investigated. The impact of the A-stage was assessed on the basis of bleaching chemical demand to full brightness (90% ISO) and pulp quality.

2. EXPERIMENTAL

2.1 Material

An oxygen delignified eucalypt kraft pulp collected at the Jacarei fiberline C (FLC) last post-O_2 washer was used throughout the study. The main characteristics of the pulp are shown in Table 1.

Table 1. Pulp sample characterization

Analysis	Oxygen delignified eucalypt kraft pulp (FLC sample)
Kappa number	11.4
Viscosity, dm^3/kg	1059
ISO Brightness, %	49.5
HexA HUT, mmols/kg*	56.3
COD, kg/adt	14.1
Extractives in acetone, %	1.01

* According to Tenkanen(12) methodology

2.2 Methods

2.2.1 A-stage optimization

The A-stage optimization was carried out using the FLC pulp sample (Table 1). Four initial pH values (2.5, 3.0, 3.5 and 4.0) and three temperatures (85, 90 and 95 °C) were investigated at a fixed 120 min time interval at 10% consistency. The pulps were either dewatered to 35% consistency (unwashed) or washed with 9 m^3 H_2O/adt pulp and then dewatered to 35% consistency, depending on the subsequent bleaching. The optimum A-stage condition was determined on the basis of the drop in kappa number, the drop in total HexA, and the drop in viscosity across the stage. The pulp was acidified to the proper pH with sulfuric acid and placed in a Mark V mixer/reactor (Quantum Technologies, USA) 3.6 L Hastelloy bowl. The pulp was heated to the desired temperature under mixing and kept in the reactor for the desired reaction time, after which it was washed or dewatered.

2.2.2 (aZe)-stage procedure

The incoming pulp from the A-stage was acidified with H_2SO_4 to pH 2.5 at 10% consistency, let stand for 10 min at room temperature and dewatered to 35% consistency in a centrifuge (a-step). The pulp mat was then fluffed in a laboratory fluffer to increase fiber surface and reduce pulp flocks to a minimum. The fluffed pulp was placed into a 4 L glass flask attached to a rotating reactor assembled on a heating bath and treated with ozone for approximately 3 minutes at 40 °C until a charge of 5 kg O_3/adt pulp was added to the system (Z-stage). Residual ozone was collected in KI solution to calculate the actual ozone consumption in the reaction. After completion of the Z-stage, the pulp samples were removed from the glass flask and extracted at pH values of 3.5 and 10.5 for 10 min at 65 °C and 10% consistency (e-stage). The pulp samples were then washed with the equivalent of 9 m^3 H_2O/adt pulp. The performance of the (aZe)-stage was determined on the basis of the drop in kappa, HexA, and viscosity.

For the reference pulp, the (aZe)-stage followed the aforementioned procedure, but the reaction with ozone was carried out at 55 °C and pH 3.5 following the reference mill's operating conditions.

2.2.3 ECF bleaching with DP stages and TCF bleaching with (EP)P stages

The high consistency (aZe) treated pulps were further bleached with a sequence of a D followed by a P-stage (ECF technology) or with an (EP)- followed by a P-stage (TCF technology) targeting 90% ISO brightness. These stages were run under the following conditions: D-stage: ClO_2 charges of 6, 12 and 18 kg/adt (as Cl_2), 70 °C, 60 min, initial pH 3.5 and 10% consistency; P-stage (ECF): H_2O_2 charge of 10 kg/adt, 90 °C, (30+135) min, initial pH 10.5 and 10% consistency; (EP)-stage: H_2O_2 charge of 5 kg/adt, 90 °C, 80 min, initial pH 10.8 and 10% consistency; P-stage (TCF): H_2O_2 charges of 10, 15 and 20 kg/adt, 90 °C, (30+135) min, initial pH 10.8 and 10% consistency. For the reference pulp, the same aforementioned ECF bleaching conditions were used, except that the ClO_2 charge was 24 kg/adt (as Cl_2).

After bleaching with D- or P-stages, the pulps were washed with the equivalent of 9 m^3 H_2O/adt pulp. The bleaching performance and pulp quality were determined on the basis of total chemical consumption necessary to reach 90% ISO brightness, in addition to pulp HexA content, kappa number, viscosity, brightness, brightness reversion, and strength properties.

2.2.4 Pulp quality assessment

Pulp refining was carried out in a PFI mill on never-dried pulp samples at 1000, 1500 and 2000 revolutions. Hand sheets from the refined samples from the PFI mill and from the original unbeaten sample were prepared and tested for physical properties according to Tappi Standard Methods.

2.2.5 Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC-MS)

An aliquot of 100 mL of the A-stage filtrates (unwashed and super washed pulps A-stage filtrate) were lyophilized, resulting in approximately 100 µg of each sample. The pyrolysis of the lyophilized samples was performed in duplicate with a Pyr A-4 model (Shimadzu) microfurnace pyrolyzer coupled to a GC-MS apparatus (Shimadzu, model PQ5050A) using a fused silica capillary column (DB-5, 30 m x 0.25 mm ID, 0.25 µm film thickness). A finely divided sample (100 µg) was deposited in a small platinum cup that was then inserted into a quartz tube (2 mm x 40 mm) placed in the pyrolysis chamber. The pyrolysis was carried out at 550 °C for 10 s, as previously described.(13, 14, 15) The pyrolysis chamber was kept at 250 °C and purged with helium to transfer the pyrolysis products as quickly as possible to the GC column. The chromatograph oven was programmed to increase the temperature from 45 °C (4 min) to 240 °C at a rate of 4 °C min^{-1}. The final temperature was held for 20 min. The injector and GC-MS interface were kept at 200 °C. The mass spectrometer was operated in the electron impact ionization mode at 70 eV, and the mass scan range was 40 to 600 Da. The temperatures of the detector and the GC-MS interface were 250 and 290 °C, respectively. Compounds were identified by comparing their mass spectra with the GC-MS spectral library (Willey 333,000) and with data from the literature.(13, 16, 17)

2.2.6 Surface HexA determination

Surface HexA was determined by two different tests: (1) refining followed by fiber classification and (2) grinding in a high intensity shear blade mill followed by fiber classification. For the first test, pulp samples were passed through a Bauer MacNett Classifier to remove the original fines and then refined in a PFI mill at various intensities (0, 500, 1000, 1500, 2000, and 5000 revolutions). Next, the material was passed again through a Bauer MacNett Classifier and separated into fractions according to screen mesh of 20, 48, 100 and 200. For the second test, pulps were passed through a Bauer MacNett Classifier to remove the original fines. The dried pulps were then ground in a high shear blade mill (Ika A11 basic) for 30 seconds, and the material was passed through a Bauer

MacNett Classifier again, as in the first test. The HexA content was measured in all the fractions retained in the screens, including the fraction collected after 200 mesh sieve (fines). The sample utilized was the oxygen delignified eucalypt kraft pulp of the fiberline C containing 56.3 mmols HexA/kg.

2.2.7 Relative chemical costs calculation

The cost of the bleach chemicals of each sequence was calculated using the following reagent prices in US$/kg of reagent: O_3 = 2.00, ClO_2 = 1.50, H_2O_2 = 0.85, NaOH = 0.50, and H_2SO_4 = 0.10. The chemical charges of each reagent, in kg/adt pulp, were multiplied by their respective prices, and the total chemical cost of each sequence was derived. The value of 100 was attributed to the total chemical cost of the reference sequence, and the relative chemical costs of the other sequences were calculated relative to the value attributed to the reference.

2.2.8 Analytical procedures

Pulp and filtrate samples were analyzed according to Tappi, SCAN and other standard methods, as described in Table 2.

Table 2. Analytical procedures and respective standards

Analysis	Standards
Kappa number	TAPPI T236 om-85
Viscosity	TAPPI T230 om 94
Brightness	TAPPI T525 om 86
Total HexA (HUT)	According to Tenkanen(12) methodology
Total HexA (TAPPI)	TAPPI T 282 pm-07
Pulp COD	SCAN
Pulp metals content	SCAN-CM 38:96
Pulp extractives in acetone	ISO 14453
Pulp ash	Tappi T211
Pulp silica	Tappi T 244
Brightness Reversion	TAPPI UM-200
Laboratory beating of pulp	T 248 wd-97
Forming Hand sheets for Physical Tests of Pulp	T205 sp-95
Physical Testing of Pulp Hand sheets	T220 sp-96
Grammage of paper	T410 om-98
Thickness (caliper) of paper and paperboard	T411 om-97
Internal Tearing Resistance of Paper (Elmendorf)	T414 om-98
Tensile Breaking Properties of Paper	T494 om-96
Bursting Strength of Paper	T 403 om-97
Air Resistance	T 460 om-96
Opacity	T 519 om-96

3. RESULTS AND DISCUSSION

3.1 A-stage optimization

The main focus of this study was determining the impact of pulp pretreatment with an A-stage on the performance of the subsequent (aZe)DP and (aZe)(EP)P bleaching sequences. To be successful, proper A-stage optimization was required. Although the general conditions to run an A-stage are generally established,(1) it is always necessary to optimize such conditions for a given pulp to take the greatest advantage of such a stage. The A-stage optimization was conducted by varying the initial pH (2.5, 3.0, 3.5 and 4.0) and temperature (85, 90 and 95 °C) using constant reaction time (120 min) and consistency (10%).

Figure 1 shows the kappa removal, HexA removal, viscosity drop, and brightness gain across the A-stage for each set of conditions. The kappa and HexA removal increased with increasing temperature and decreasing pH, as has been shown in previous studies.(1, 18) As expected, the viscosity drop also increased with decreasing pH and increasing temperature, conditions that favor cellulose degradation by acid hydrolysis. The brightness gain across the A-stage was generally very small but tended to increase with increasing temperature and decreasing pH. Because small fractions of lignin are removed in the A-stage, an increase in pulp brightness is anticipated. The maximum kappa (53.5%) and HexA removal (74.6%) were achieved at 95 °C and initial pH 2.5, but this condition resulted in a significant viscosity drop (253 dm^3/kg). Because the condition that used a temperature of 90 °C and initial pH 3.0 resulted in a much lower viscosity loss (141 dm^3/kg) and still presented a high efficiency of kappa (44.7%) and HexA (65.9%) removal, it was chosen for the subsequent bleaching.

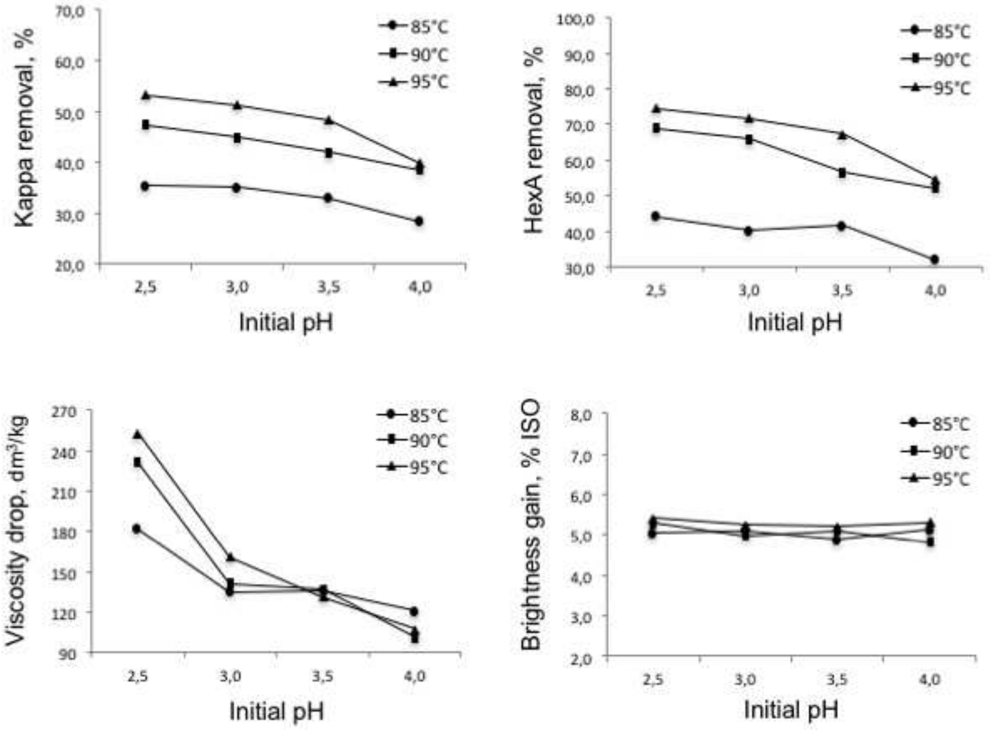

Figure 1. Effect of temperature and initial pH on kappa removal, HexA removal, viscosity drop and brightness gain across the A-stage (10% consistency, 120 min, acidification with H_2SO_4).

The A-stage is largely used for HexA removal at the start of bleaching after the oxygen delignification stage, especially for eucalypt pulps. The acid conditions of the A-stage (pH 2.5-3.5) also removes inorganic contaminants present in the pulp.(19) Table 3 shows the pulp mineral composition before and after the A-stage carried out under optimized conditions (90 °C and pH 3.0). The pulp ash and silica content decreased by 60.6% and 79.5%, respectively, across the A-stage. In addition, the content of magnesium and calcium were reduced by 93.4% and 89.3%, respectively. Furthermore, the removal of transition metals (Fe, Mn and Cu) was in the range of 29.5-48.8%. The efficient silica and calcium removal is desirable for minimizing scaling in the bleach plant, whereas the magnesium removal is undesirable given its positive effect on subsequent hydrogen peroxide bleaching stages.(20) The partial removal of transition metals is favorable because it decreases the formation of hydroxyl radicals in subsequent peroxide and ozone bleaching stages, thus preserving pulp viscosity.(21) The low manganese removal, in relation to Fe, a metal notoriously difficult to remove from pulp, may be explained by its very low concentration in the original pulp (4.4 mg/kg).(22)

Table 3. Pulp mineral removal across the A-stage*

	Metals, mg/kg					SiO_2, mg/kg	Ash, %
	Ca	Fe	Mn	Mg	Cu		
Oxygen delignified eucalypt kraft pulp	654	9.4	4.4	241	4.1	953	1.42
Pulp after A-stage	70.0	5.6	3.1	15.9	2.1	195	0.56
Reduction, %	89.3	40.4	29.5	93.4	48.8	79.5	60.6

* A-stage conditions: acidification with H_2SO_4, 90 °C, initial pH 3.0, 120 min, 10% consistency.

3.2 Effect of A-stage on lignin removal

The first studies of the A-stage technology indicated its large selectivity toward HexA, with only very small amounts of lignin being removed.(1) Later studies with beech kraft pulp,(23) in contrast, have shown significant removal of lignin across the A-stage in addition to HexA. The results of Table 4 show that a significant fraction of the kappa drop across the A-stage is not due to HexA but rather to lignin removal. The overall numbers in Table 4 show that 0.9-1.4 kappa units (18-32% of the kappa removed) were due to lignin. To verify if the A-stage actually removes lignin, the oxygen delignified eucalypt kraft pulp sample (kappa number 11.4, where 49.4% are due to HexA) was super washed with excess water until its carryover COD decreased from the original 14.1 kg/adt to approximately zero. The kappa number after super washing was 10.9, indicating that the kappa number due to the carryover was 0.5. After correcting for carryover and recalculating, it was determined that the A-stage kappa drop due to lignin decreased to 0.9-1.4 units (18-32% of the kappa removed). These numbers are still quite significant.

Table 4. Effect of temperature and initial pH on the removal of kappa, HexA and lignin across the A-stage (10% consistency, 120 min, acidification with H_2SO_4)

Temp. (°C)	Initial pH	Kappa number	Kappa removed, K units*	HexA removed, K units	Lignin removed, K units	Lignin removed, K units corrected for carryover**	Lignin Removed, K units %
85	2.5	7.4	4.0	2.45	1.55	1.05	26
85	3.0	7.4	4.0	2.24	1.76	1.26	32
85	3.5	7.6	3.8	2.31	1.49	0.99	26
85	4.0	8.2	3.2	1.77	1.43	0.93	29
90	2.5	6.0	5.4	3.86	1.54	1.04	19
90	3.0	6.3	5.1	3.68	1.42	0.92	18
90	3.5	6.6	4.8	3.15	1.65	1.15	24
90	4.0	7.0	4.4	2.90	1.50	1.00	23
95	2.5	5.3	6.1	4.17	1.93	1.43	23
95	3.0	5.6	5.8	4.01	1.79	1.29	22
95	3.5	5.9	5.5	3.76	1.74	1.24	23
95	4.0	6.9	4.5	3.03	1.47	0.97	22

*10 mmols/kg pulp HexA = 1 kappa unit
**pulp carryover (14.1 kg/adt) = 0.50 kappa units.

To confirm that this kappa fraction was indeed lignin, a new A-stage was carried out under the optimum condition (90 °C and pH 3.0) with the original unwashed (14 kg/adt COD) and super washed pulps. The filtrate of these two A-stages was collected and analyzed by Py-GC-MS to determine whether there were lignin traces in the filtrates. Table 5 shows the lignin-like compounds found in the A-stage filtrate of the original unwashed and super washed pulps by Py-GC-MS.

Table 5. Lignin-like compounds found in the A-stage filtrate of the original unwashed (14.1 kg/adt COD) and super washed pulps (~0 kg/adt COD) by Py-GC-MS

Unwashed pulp		Super washed pulp	
Lignin-like Compounds	Peak Area	Lignin-like Compounds	Peak Area
Guaiacol	0.19	Guaiacol	0.22
Syringol	0.74	Syringol	0.50
4-methylsyringol	0.14	4-methylsyringol	0.25
Acetoguaiacone	0.22	-	-
4-propenylsyringol	0.06	-	-
Acetosyringona	0.40	Acetosyringona	0.10
-	-	3-methoxy-cathecol	0.08
-	-	4-vinylsyringol	0.04
-	-	4-methylguaiacol	0.07
Total, %	**1.75**	**Total, %**	**1.26**

The Py-GC-MS analysis of the A-stage filtrates (washed and super washed pulp) revealed the presence of various lignin-like compounds, including guaiacol, syringol, 4-methylsyringol, acetoguaiacone, 4-propenylsyringol, acetosyringone, and 4-methylguaiacol. Although it was not possible to precisely measure the quantities of these compounds in the filtrates, the Py-GC-MS results gave clear evidence of the existence of lignin byproducts in the A-stage filtrate of the super washed pulp (no lignin carryover), indicating that the A-stage indeed removes lignin. The Py-GC-MS data did not allow for a quantitative determination of lignin removal across the A-stage, and other techniques based on the kappa number and HexA measurements are also imprecise. For example, Vuorinen(1) reports a ratio of 9.6 mmols/kg HexA per kappa unit, whereas Li and Gellerestedt(2) report a ratio of 11.6 mmols/kg HexA per kappa unit. The measurement of the kappa number itself accepts an error of 0.5 units. The fact of the matter is that lignin-like structures were found in the A-stage filtrate of super washed pulp by Py-GC-MS, which is proof that some lignin is removed in the A-stage, though the exact quantity remains to be determined.

3.3 (aZe)-stage results

The results presented in Table 6 compare the performance of the (aZe)-stages carried out on pulps treated and not treated with an A-stage. Two different scenarios were considered for the pulp treated with an A-stage: one in which the incoming pulp from the A-stage was only dewatered (unwashed) and another where the pulp was washed with the equivalent of 9 m^3 H_2O/adt pulp.

When the (aZe)-stage is applied to a pulp that was washed rather than unwashed after the A-stage, the performance of the (aZe)-stage is better, indicating that the remaining organic material from the A-stage affects the ozone bleaching performance. The amount of such material in a pulp at 35% consistency is not very small. Considering that the A-stage was carried out at 10% consistency and the pulp was dewatered to 35% consistency, approximately 80% of the liquid phase was removed during dewatering. Assuming that the organic matter is well distributed in the liquid phase that remained in the fiber, it is inferred that approximately 20% of the material hydrolyzed in the A-stage entered the (aZe)-stage. For the reference pulp, the (aZe)-stage was carried out on a pulp not treated with the A-stage. As a consequence, the (aZe) pulp kappa number and HexA were much higher than those of the pulps previously treated with the A-stage. The (aZe)-stage removed more lignin and less HexA in the pulp previously treated with the A-stage; the opposite was verified for the pulp not treated with the A-stage. The brightness gain across the (aZe)-stage was substantially higher for pulps previously treated with the A-stage. In summary, these results indicate that pulp pretreatment with the A-stage makes the subsequent (aZe)-stage more selective at removing lignin with consequent improved pulp brightness.

Table 6. Results of the (aZe)-stage for the A-stage unwashed pulp, the (aZe)-stage for the A-stage washed pulp, and the (aZe)-stage for the reference pulp (no A-stage)

Parameter	aZe-stage (Z-step at pH 2.5, 40^{o}C, 5 kg O_3/adt, 35% cst. e-step at pH 10.5)		aZe-stage (Z-step at pH 3.5, 55^{o}C, 5 kg O_3/adt, 35% cst. e-step at pH 3.5)
A-stage post-treatment	Dewatering	Washing	Reference - No A-stage
Kappa number	1.0	0.8	5.2
HexA, mmols/kg	5.0	4.8	22.8
Viscosity, dm^3/kg	823	817	830
Brightness, % ISO	73.6	76.3	67.7
Kappa drop, K units	5.3	5.5	6.2
HexA drop, K units*	1.4	1.4	3.4
Viscosity drop, dm^3/kg	95	101	229
Brightness gain, % ISO	19.1	21.8	13.8

*Assuming that one kappa unit is equivalent to 10 mmols HexA/kg pulp.(24)

The kappa drop per kg ozone varies between 1.06 and 1.1 from an inlet kappa of 6.3 after the A-stage and is 1.24 from an inlet kappa of 11.4 without the A-stage. Ozone was expected to be less efficient after the A-stage, but considering the significant lower kappa inlet, we can note that kappa drops of 1.04-1.1 and 1.24 are in the same range. In other words, implementation of an A-stage does not decrease the Z-stage efficiency. Thus, hot acid hydrolysis and ozone bleaching are not competing techniques but rather complementary ones.

3.4 Where are the HexA located in the fiber wall?

There is no clear evidence for the location of the HexA in the fiber wall. There have been claims that it may be more concentrated on the fiber surface as a result of xylan precipitation during cooking.(9) Because the mass transfer of ozone to the fiber during ozone bleaching is not very high, it is anticipated that ozone will react more readily on the fiber surface and therefore be consumed largely by the pulp HexA, which are purportedly more concentrated on the surface of the fiber. The experiments intended to prove that HexA are concentrated on the fiber surface showed no such evidence (Figure 2), and HexA are likely well distributed in the cell wall and not concentrated on the fiber surface. The sample utilized was the oxygen delignified eucalypt kraft pulp of the fiberline C containing 56.3 mmols HexA/kg (Table 1). Assuming that pulp refining causes peeling of the fiber surface, a significant decrease in pulp HexA content would be expected if they were highly concentrated on the fiber surface. However, the maximum HexA decrease achieved using the two fiber wall mechanical peeling techniques, PFI and high shear blade mill, were 0.5% (from 56.3 to 56.6 mmols HexA/kg) and 0.7% (from 56.3 to 56.7 mmols HexA/kg), respectively. These drops are much too low to make a case for large HexA concentrations on the fiber wall surface, especially considering that the HexA measurement technique used in this work(12) accepts errors of 5% on the readings.

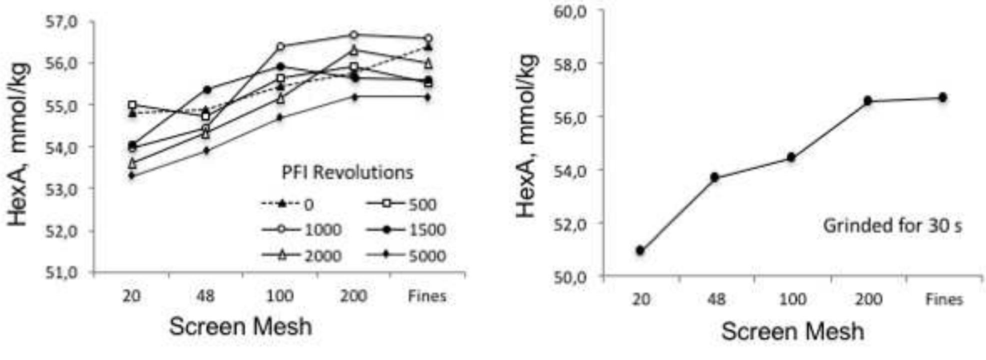

Figure 2. Effect of pulp refining intensity in a PFI mill and a high shear blade mill on the content of hexenuronic acids.

3.5 ECF bleaching with (aZe)DP, A/(aZe)DP and A(aZe)DP sequences

The reference pulp was bleached using the (aZe)DP sequence under typical conditions used commercially. Pulps produced under optimal A-stage and (aZe)-stage conditions were further bleached with a D- and a P-stage in sequence. The effect of the presence of a washing step between the A-stage and (aZe)-stage was investigated. Hence, the sequences A/(aZe)DP (no washing is represented by "/") and A(aZe)DP were compared**.** The effect of the extraction pH (e-step) after ozone bleaching was also considered. The average bleaching data are presented in Table 7.

In the bleaching sequences containing the A-stage, different performances were observed for the processes with and without washing (dewatering). The absence of a washing stage after the A-stage had a significant impact on pulp brightness, which was reduced from 91.4% ISO in the system with washing to 90.3% ISO in the system without washing, maintaining constant all the chemical charges (Tests #2 *vs* #3 in Table 7).

Table 7. ECF bleaching results

Sequence	(aZe)DP with 9.1 kg ClO_2/adt	A/(aZe)DP with 2.3 kg ClO_2/adt	A(aZe)DP with 2.3 kg ClO_2/adt	A/(aZe)DP with 3.8 kg ClO_2/adt	A(aZe)DP with 3.8 kg ClO_2/adt	A(aZe)DP with 2.3 kg ClO_2/adt
e-step pH	3.5	10.5	10.5	10.5	10.5	3.5
Test #	1	2	3	4	5	6
Z-stage cst.	35%	35%	35%	35%	35%	35%
ClO_2 (as ClO_2), kg/adt	9.1	2.3	2.3	3.8	3.8	2.3
O_3, kg/adt	5	5	5	5	5	5
H_2O_2, kg/adt	10	10	10	5	5	10
NaOH, kg/adt	12.3	21.5	21.5	20.0	20.0	13.8
H_2SO_4, kg/adt	9.8	19.1	19.1	19.1	19.1	18.4
ClO_2 consumption, %	100	100	99.5	99.5	99.2	99.5
H_2O_2 consumption, %	98.2	98.2	98.2	98.2	97.4	95.5
Brightness, % ISO	90.6	90.3	91.4	90.6	91.5	89.7
Reversion, % ISO	1.5	1.8	1.8	1.4	1.5	1.9
Viscosity, dm^3/kg	677	653	630	693	685	649
HexA, mmols/kg	2.8	3.6	3.7	2.5	2.6	3.6
Relative chemical cost*, %	100	88	87	80	80	78

* Corrected to 90.0% ISO brightness and assuming the following reagent prices in US$/kg: H_2SO_4 = 0.15; NaOH = 0.55; ClO_2 = 1.64; H_2O_2 = 0.55; O_3 = 2.37.

This result is explained by the negative effect of the A-stage carryover material on the performance of ozone bleaching. The pulp incoming from the A-stage at 10% consistency had its pH adjusted to the proper value with a small acid addition (a-step), was dewatered to 35% consistency, treated with ozone (Z-step), and extracted at either pH 3.5 or 10.5 (e-step). Therefore, approximately 20% (dewatering from 10 to 35% consistency) of the products from the HexA hydrolysis (ex: 2-furancarboxylic acid and 5-carboxy-2-furaldehyde) were present during the ozone reaction. These substances are known to consume ozone(1) and explain the poorer performance of the system without washing.

The pH of the extraction (e-step) following the ozone treatment also affected the (aZe)-stage performance. For the sequence A(aZe)DP, the final brightness values for the extractions at pH 3.5 and 10.5 were 89.7% and 91.4% ISO, respectively, for similar overall chemical charges in the bleaching (Tests #6 *vs* #3, Table 7). The significant benefit of the extraction at a higher pH is explained by a more thorough removal of materials (lignin, HexA) by alkali in the e-step. In addition to its potential oxidant savings (ClO_2 and/or H_2O_2) the extraction at the higher pH is advantageous for environmental reasons because the alkaline filtrate can be recirculated back to the post-oxygen washer.

The chemical savings due to the introduction of an A-stage followed by washing ahead of the (aZe)DP sequence can be realized by comparing the results of Test #1 with Test #6 in Table 6. The pulp bleached with the sequence (aZe)DP (Test #1) produced a brightness of 90.6% ISO with a ClO_2 charge of 9.1 kg/adt, whereas the pulp bleached with the A(aZe)DP sequence (Test #6) produced a brightness of 89.7% ISO with a ClO_2 charge of only 2.3 kg/adt pulp, maintaining constant all other chemical charges, except for acid and base. Although the brightness values are slightly different in the two scenarios, full brightness was achieved in both cases without an additional oxidant charge. In general, the bleached pulp viscosity was not largely affected by the insertion of an A-stage in the sequence, but the residual HexA concentration was slightly higher and caused an increase in pulp brightness reversion (Test #1 *vs* Tests #2, #3 and #6); the higher final HexA content in Tests #2, #3 and #6 is explained by the very low ClO_2 usage (2.3 kg/adt). To curb the reversion problem, the charge of ClO_2 was increased from 2.3 kg/adt (Tests #2, #3 and #6, Table 7) to 3.8 kg/adt with a consequent decrease in the H_2O_2 charge from 10 to 5 kg/adt (Tests #4 and #5, Table 7). By performing this change, the HexA concentration decreased to acceptable values and the reversion problem was resolved.

Overall, the implementation of the A-stage without subsequent washing allowed for a decrease in the ClO_2 demand from 9.1 kg/adt to 3.8 kg/adt and in H_2O_2 from 10 kg/adt to 5 kg/adt while maintaining pulp viscosity and brightness stability. However, there was an increase in the demand of NaOH and H_2SO_4 of approximately 8 and 10 kg/adt, respectively. The increase in acid demand is explained by the presence of an A-stage, while the increase in NaOH demand is explained by the e-step of the (aZe)-stage, which, in the (aZe)DP sequence, was done at pH 3.5 (current mill practice), whereas in the A/(aZe)DP sequence, it was done at pH 10.5.

The relative chemical costs for the sequences without and with the A-stage were determined to be 100 and 80 for Tests #1 and #4, respectively (Table 7). Therefore, the addition of an A-stage followed by proper optimization of the reference sequence, without inter-stage washing, decreased the overall cost of bleaching chemicals by 20%.

3.6 TCF bleaching with A/(aZe)(EP)P and A(aZe)(EP)P sequences

Pulps produced under the optimal A-stage and (aZe)-stage conditions were further bleached with (EP)- and P-stages in sequence. The effect of the presence of a washing step between the A-stage and (aZe)-stage was considered by comparing the sequences A/(aZe)(EP)P and A(aZe)(EP)P. The effect of the extraction pH (e-step) after ozone bleaching was also considered. The average bleaching data are presented in Table 8.

Different performances were observed for the processes with and without washing (dewatering). The absence of washing after the A-stage had a significant impact on pulp brightness, which was reduced from 90.6% ISO in the system with washing to 89.9% ISO in the system without washing, in spite of using an additional 5 kg H_2O_2/adt in the bleaching of the unwashed pulp (Tests #1 *vs* #2 in Table 8). This result is explained by the negative effect of carryover material from the A-stage on the ozone bleaching performance. The pH of the extraction following the ozone treatment had no effect on the overall bleaching performance. For the sequence A(aZe)(EP)P, the final brightness values for the extractions at pH 3.5 and 10.5 were 90.7% and 90.6% ISO, respectively, for similar overall chemical charges in the bleaching (Tests #2 *vs* #3, Table 8). The lack of an effect from the extraction pH is likely because an (EP)-stage was used subsequent to the (aZe)-stage, and this treatment performed the role of the extraction (e-step at pH 10.5).

Table 8. TCF bleaching results

Sequence	A/(aZe)(EP)P	A(aZe)(EP)P	A(aZe)(EP)P
e-step pH	10.5	10.5	3.5
Test #	1	2	3
Z-stage consistency, %	35	35	35
ClO_2 (as ClO_2), kg/adt	0	0	0
O_3, kg/adt	5	5	5
H_2O_2, kg/adt	25	20	20
NaOH, kg/adt	25.6	24.1	16.0
H_2SO_4, kg/adt	18.3	18.3	18.4
Brightness, % ISO	89.9	90.6	90.7
Reversion, % ISO	2.1	1.9	2.1
Viscosity, dm^3/kg	728	704	709
HexA, mmols/kg	5.5	5.7	6.5
Relative chemical cost*, %	117	103	93

* Corrected to 90.0% ISO brightness and assuming the following reagent prices in US$/kg: $H_2SO_4 = 0.15$; NaOH = 0.55; $ClO_2 = 1.64$; $H_2O_2 = 0.55$; $O_3 = 2.37$.

When comparing the reference sequence, (aZe)DP (Test #1, Table 7), with the A(aZe)(EP)P TCF sequence (Test #2, Table 8), significant oxidant savings were observed by operating with the latter. While in the former sequence, the 90.6% ISO brightness was achieved with 9.1 kg ClO_2/adt, 10 kg H_2O_2/adt, 9.8 kg H_2SO_4/adt and 12.3 kg NaOH/adt, the latter sequence achieved the same brightness with 20 kg H_2O_2/adt, 18.3 kg H_2SO_4/adt and 24.1 kg NaOH/adt.

The relative chemical costs for the reference sequence (Test #1 Table 7) and the optimized TCF sequences without (Test #2, Table 8) and with (Test #3, Table 8) inter-stage washing between the A- and (aZe)-stages were 100, 103 and 93.

In summary, the TCF sequences with and without intermediate washing between the A- and Z-stages were very competitive with the existing bleaching sequence, suggesting that with some additional research and optimization, the P&W industry will soon be able to implement a very competitive ozone-based TCF bleaching process.

The viscosity of the A(aZe)(EP)P bleached pulp was actually slightly higher than that of the (aZe)DP reference pulp, but the residual content of HexA and the brightness reversion were significantly higher. To decrease the content of HexA in the TCF pulp, stronger conditions would be required in the A-stage and/or larger dosages of ozone must be used in the (aZe)-stage.

3.7 Pulp refinability and strength properties

Reference (Test #1, Table 7), ECF (Test #2, Table 7), and TCF (Test #1, Table 8) bleached pulps with brightness values of approximately 90% ISO were tested for their refinability and strength properties. The refinability (Figure 3A) of the three pulps, measured as the relationship between energy consumption (Wh) and pulp drainage resistance (°SR), showed only slight differences among the three pulps. Up to approximately 30 °SR, the pulps behaved somewhat similarly. Over this value, there was a trend for less energy consumption for the TCF pulp, followed by the ECF and the reference. Normally, eucalypt pulps are not refined above 30 °SR, and therefore, the small differences observed in refinability are not very important. However, the properties of tear, burst, tensile and modulus of elasticity (Figures 3B-3E) were somewhat impaired by the A-stage, and this was particularly visible for the TCF bleached pulp; in the case of the ECF pulp, the strength losses in relation to the reference were almost insignificant. In addition, Figure 3F indicates higher air resistance values (less porosity) for the TCF pulp, followed by the ECF and reference pulps. The A-stage has been reported to cause slight strength impairment when operated at severe conditions.(3) In addition, in the case of the TCF pulp, the lower strength may have been caused by the harsh conditions used in the hydrogen peroxide stages. The TCF bleached pulp (Test #1, Table 8) was the one for which there was no washing after the A-stage. The lack of washing resulted in a pulp that was difficult to bleach and required the use of higher than usual peroxide doses in the P-stage; this may also have contributed to the strength impairment.

It is worth noting that the viscosities of the TCF pulps (Tests #1-3, Table 8) were actually higher than those of the reference (Test #1, Table 7) and ECF bleached (Tests #2-6, Table 7) pulps. However, the selected TCF sample (Test #1, Table 8) showed lower strength properties than those of the reference and ECF (Tests #1 and #2, Table 7) pulps. Thus, there may be other factors affecting the strength of the TCF bleached pulps that are beyond our comprehension at this stage.

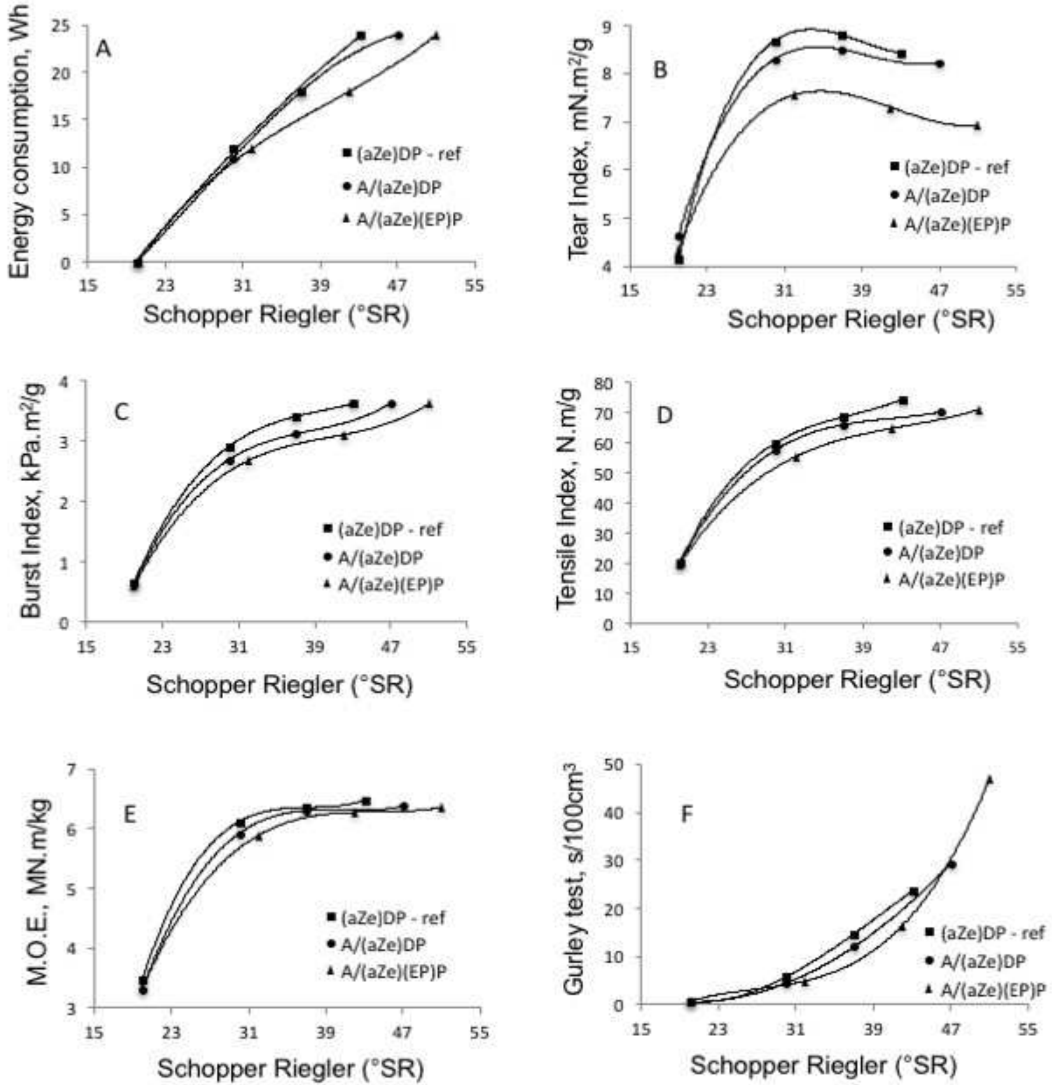

Figure 3. Refinability and strength property results for reference, ECF, and TCF bleached pulps as a function of drainage resistance (°SR). A: energy consumption, B: tear index, C: burst index, D: tensile index, E: modulus of elasticity, F: resistance to air passage.

4. CONCLUSIONS

The optimum A-stage conditions were 90 °C and pH 3.0 for a 120 min reaction at 10% consistency, reducing the kappa number from 11.4 to 6.3. Of the total kappa removed across the A-stage, approximately 70-80% is HexA and 20-30% is lignin. The presence of lignin-like structures was identified in the A-stage filtrate of a super washed pulp by Py-GC-MS. The HexA present in eucalypt pulps are likely well distributed in the cell wall and not concentrated on the fiber surface. The ozone stage showed similar efficiencies on pulps treated with the A-stage or not, with A- and Z-stages complementing each other in the removal of HexA and residual lignin as opposed to competing with each other. For the ECF bleaching, the insertion of an A-stage prior to the (aZe)DP sequence with inter-stage washing allows for savings for the 90% ISO brightness target. The approximately 90% ISO brightness target was achievable with the A/(aZe)(EP)P (25 kg H_2O_2/adt) and A(aZe)(EP)P (20 kg H_2O_2/adt) sequences, with some brightness stability penalty. The A-stage for ECF pulps caused only a slight decrease in refining energy demand, pulp porosity, and pulp strength properties (tensile, MOE, burst and tear). For TCF pulps, these effects were more significant.

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CONCLUSÕES GERAIS

Concluiu-se que a composição do número kappa, especialmente a sua relação ácidos hexenurônicos (HexA)/lignina residual, e o teor de grupos fenólicos livres da lignina têm influência significativa nos estágios de branqueamento com oxigênio, hidrólise ácida e ozonólise, aplicados à polpa kraft de fibras curtas. Apesar de os grupos fenólicos livres serem reconhecidos como centros de alta reatividade na lignina residual, este foi o primeiro estudo sistemático, envolvendo várias matérias-primas, que demonstrou o impacto positivo deles na eficiência da deslignificação com oxigênio. Fração significativa (~50%) do número kappa da polpa kraft de fibras curtas é composto de HexA, sendo o restante de lignina residual e outros materiais oxidáveis. Os HexA estão uniformemente distribuídos na parede celular, não sendo possível removê-los por simples tratamento mecânico das fibras. O tratamento de hidrólise ácida da polpa em pH 3,0 a 90 °C por 120 min é uma forma adequada para remoção parcial dos HexA da polpa. Enquanto removendo HexA da polpa por hidrólise ácida, remove-se também quantidade significativa (~18% do número kappa) de lignina solúvel em ácido. A remoção prévia dos ácidos hexenurônicos (HexA) da polpa kraft é uma etapa fundamental aos processos ECF-*light* e TCF com ozônio focalizados na produção de polpa branqueada de eucalipto de baixo custo e alta qualidade. Embora a remoção dos HexA pelo ozônio seja possível, ela é de custo proibitivo. A forma mais racional de remover HexA é previamente ao estágio de ozonólise, na etapa de hidrólise ácida. A eficiência da etapa de ozonólise não foi prejudicada pelo estágio A, e esta deve ser efetuada, preferencialmente, em tempo curto 1-2 min, pH 2,5 de temperatura de 40 °C, seguida de extração alcalina da polpa (pH 10,5, 65 °C, 10 min), não havendo a necessidade de lavagem da polpa entre a ozonólise e a extração alcalina.

ANEXOS DO CAPÍTULO 1

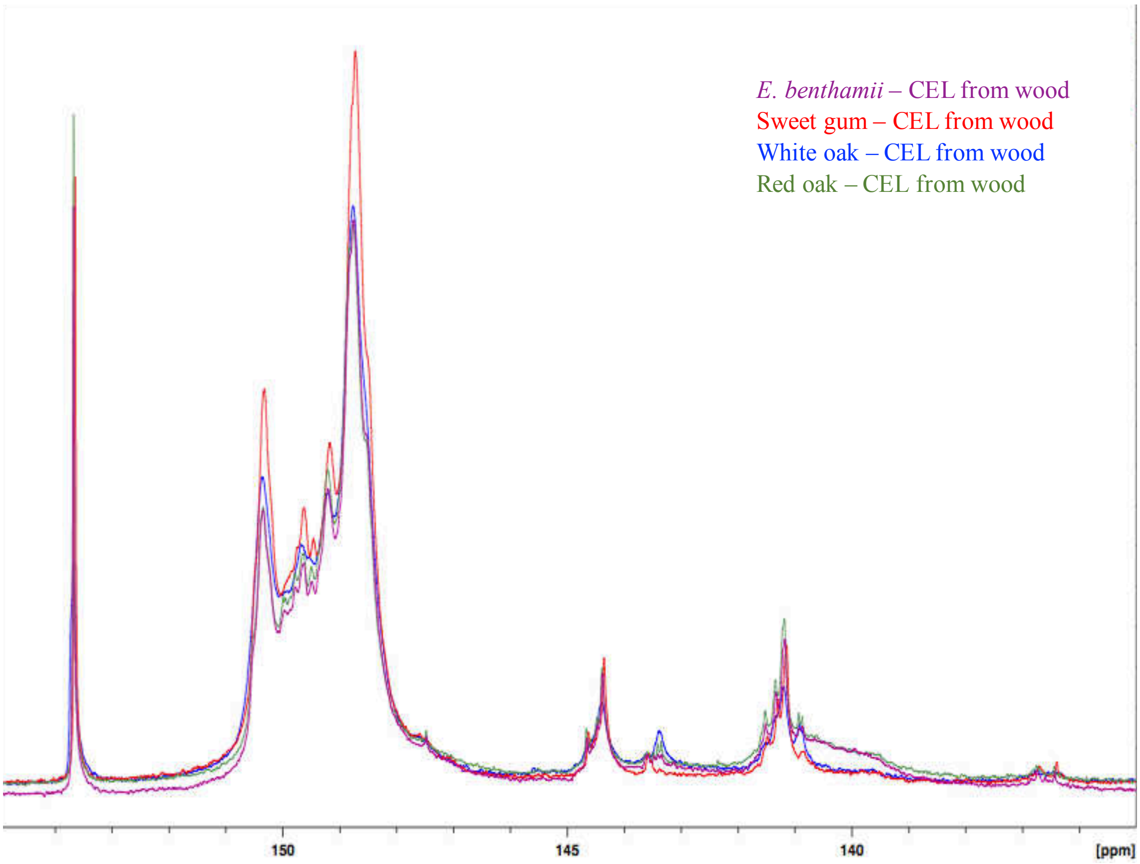

Figura 1A. Espectros de RMN de fósforo das amostras de lignina isolada (CEL) das madeiras de *E. benthamii*, sweet gum, white oak e red oak.

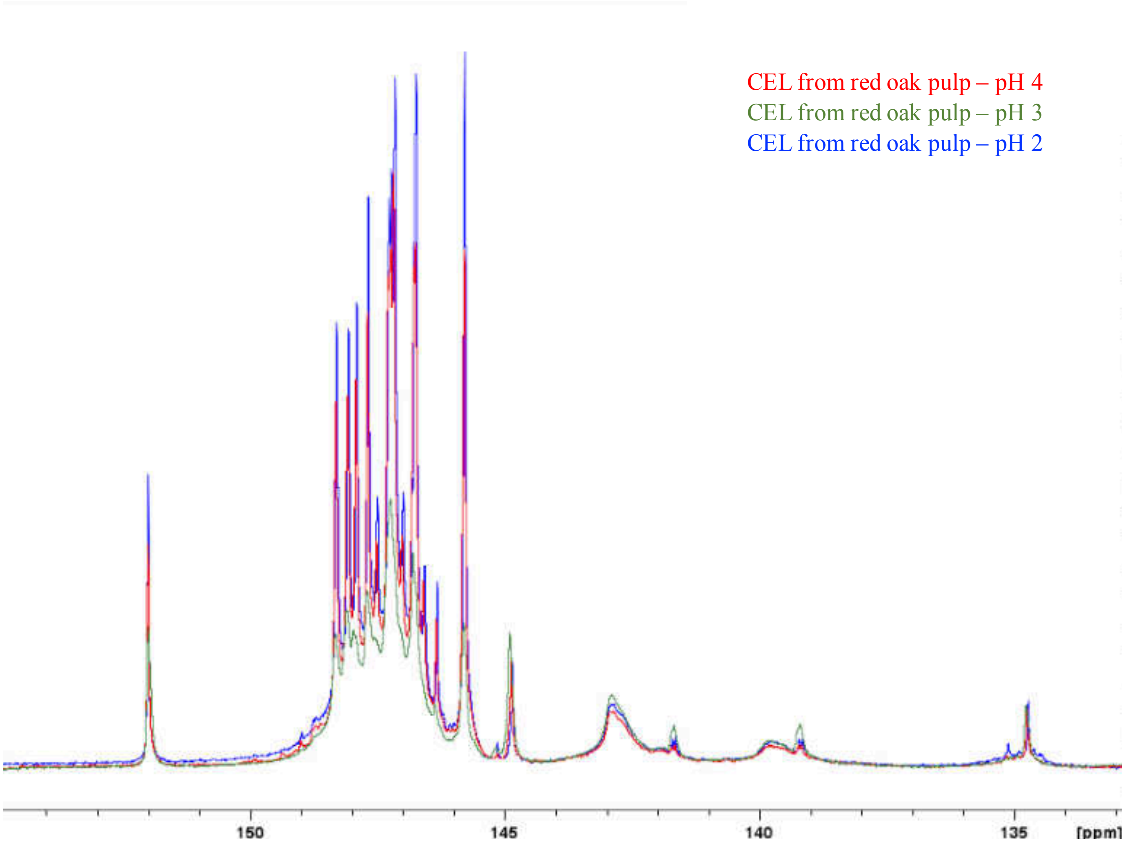

Figura 1B. Espectros de RMN de fósforo das amostras de lignina isolada (CEL) da polpa de red oak em diferentes valores de pH após a hidrólise enzimática.

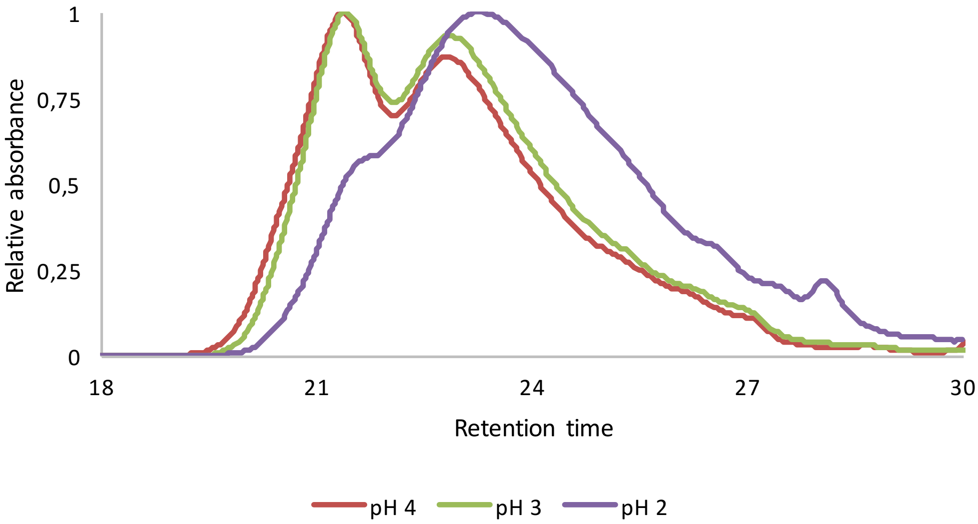

Figura 1C. Cromatograma das amostras de lignina isoladas da polpa de red oak em diferentes valores de pH após a hidrólise enzimática.

ANEXOS DO CAPÍTULO 3

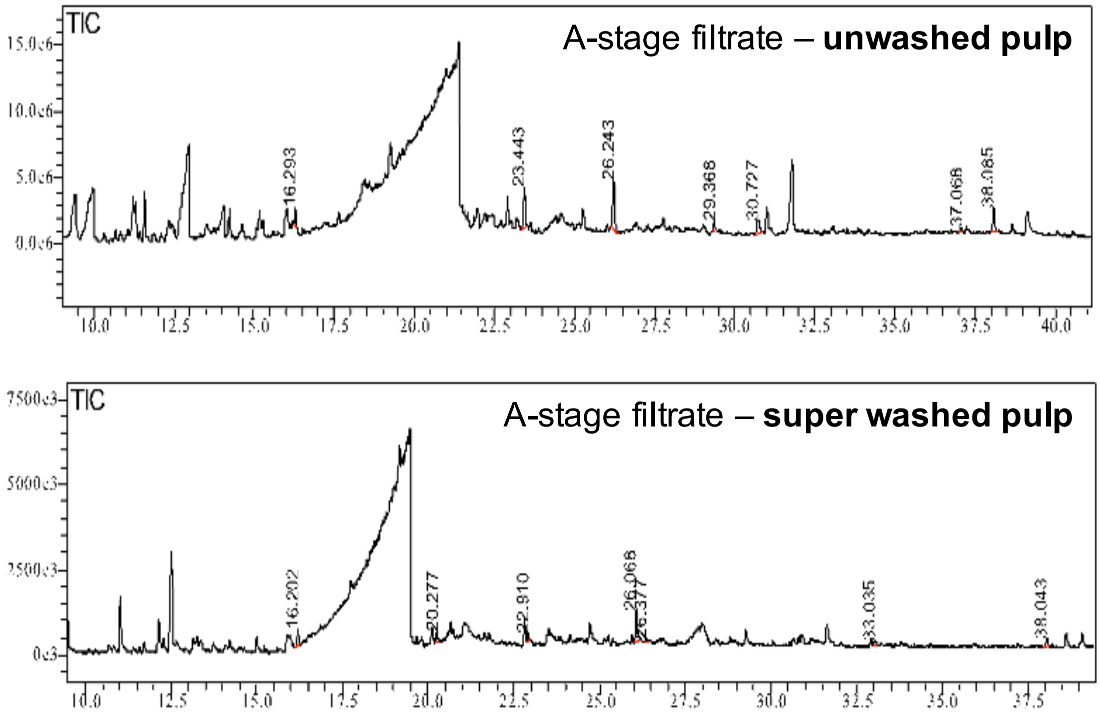

Figura 3A. Cromatograma Py-GC-MS dos filtrados ácidos do estágio A das amostras de polpas não lavadas e super lavadas.

Tabela 3A. Condições e resultados do branqueamento de referência – (aZe)DP

Conditions and Results	**Rep.**	**Bleaching stages**				
		a	**Z***	**e**	**D**	**P**
Consistency (%)	-	10	35	10	10	10
Time (min.)	-	10	2.5	10	60	165
Temperature (^{0}C)	-	25	55	65	70	90
O_3 (kg/adt)	-	-	5	-	-	-
ClO_2 such as Cl_2 (kg/adt)	-	-	-	-	24	-
H_2O_2 (kg/adt)	-	-	-	-	-	10
NaOH (kg/adt)	-	-	0	0	1.3	11.0
H_2SO_4 (kg/adt)	-	9.8	-	-	-	-
Final pH	A	3.5	3.5	3.5	2.5	10.3
	B	3.5	3.5	3.5	2.4	10.4
Reagent consumption (%)	A	-	96.8	-	100	97.9
	B	-	96.3	-	100	98.5
Kappa number	A	-	-	5.2	-	0.36
	B	-	-	5.2	-	0.30
Brightness ISO (%)	A	-	-	67.7	83.9	90.6
	B	-	-	67.7	84.0	90.6
Reversion brightness ISO (%)	A	-	-	-	-	1.5
	B	-	-	-	-	1.5
Viscosity (dm^3/kg)	A	-	-	830	-	676
	B	-	-	830	-	678
HexA (mmoles/kg)	A	-	-	22.5	-	2.9
	B	-	-	23.1	-	2.7

Tabela 3B. Condições e resultados do branqueamento ECF – A/(aZe)DP

Conditions and Results	Rep.	Bleaching stages									
		A/	**a**	**Z***	**e**	**D**	**D**	**D**	**P**	**P**	**P**
Consistency (%)	-	10	10	35	10	10	10	10	10	10	10
Time (min.)	-	120	10	2.7	10	60	60	60	165	165	165
Temperature (^{0}C)	-	90	25	40	65	70	70	70	90	90	90
O_3 (kg/adt)	-	-	-	5	-	-	-	-	-	-	-
ClO_2 such as Cl_2 (kg/adt)	-	-	-	-	-	6	12	18	-	-	-
H_2O_2 (kg/adt)	-	-	-	-	-	-	-	-	10	12	15
NaOH (kg/adt)	-	-	-	-	11.0	-	-	-	10.5	12	16
H_2SO_4 (kg/adt)	-	12.1	6.3	-	-	0.70	0.53	0.44	-	-	-
Final pH	A	3.0	-	2.5	10.4	3.9	4.0	4.0	10.5	10.4	10.4
	B	3.1	-	2.6	10.4	3.9	4.1	4.0	10.4	10.4	10.5
Reagent consumption (%)	A	-	-	-	94.0	100	-	-	98.0	97.0	95.0
	B	-	-	-	95.8	100	-	-	98.3	95.0	92.0
Kappa number	A	6.3	-	-	1.0	-	-	-	0.33	0.32	0.27
	B	6.3	-	-	0.9	-	-	-	0.34	0.33	0.29
Brightness ISO (%)	A	54.4	-	-	73.6	85.7	89.2	89.4	90.3	90.0	90.6
	B	54.4	-	-	73.5	85.5	89.4	89.5	90.3	90.4	90.2
Reversion brightness ISO (%)	A	-	-	-	-	-	-	-	1.8	1.9	1.9
	B	-	-	-	-	-	-	-	1.7	1.8	1.8
Viscosity (dm^3/kg)	A	917	-	-	820	-	-	-	650	653	630
	B	919	-	-	826	-	-	-	656	656	641
HexA (mmol/kg)	A	19.2	-	-	4.9	-	-	-	3.6	-	-
	B	19.1	-	-	5.0	-	-	-	3.5	-	-

Tabela 3C. Condições e resultados do branqueamento TCF – A/(aZe)(EP)P

Conditions and Results	**Rep.**	**Bleaching stages**							
		A	**a**	**Z***	**e**	**EP**	**P**	**P**	**P**
Consistency (%)	-	10	7.9	35	10	10	10	10	10
Time (min.)	-	120	10	1	10	90	165	165	165
Temperature (^{0}C)	-	90	25	40	65	80	90	90	90
O_3 (kg/adt)	-	-	-	5	-	-	-	-	-
ClO_2 such as Cl_2 (kg/adt)	-	-	-	-	-	-	-	-	-
H_2O_2 (kg/adt)	-	-	-	-	-	5	10	15	20
NaOH (kg/adt)	-	-	-	-	11.0	4.1	6.8	9.0	10.5
H_2SO_4 (kg/adt)	-	12.1	6.3	-	-	-	-	-	-
Final pH	A	3.0	-	2.5	10.3	10.6	10.6	10.5	10.3
	B	3.1	-	2.6	10.4	10.5	10.6	10.4	10.3
Reagent consumption (%)	A	-	-	-	96.0	92.6	89.0	88.9	88.6
	B	-	-	-	96.6	93.2	90.3	90.1	89.0
Kappa number	A	6.3	-	-	1.1	0.81	0.49	0.44	0.44
	B	6.3	-	-	1.1	0.85	0.50	0.44	0.42
Brightness ISO (%)	A	54.4	-	-	72.6	83.0	85.1	89.0	89.9
	B	54.4	-	-	72.6	82.9	85.3	89.2	89.9
Reversion brightness ISO (%)	A	-	-	-	-	-	-	-	2.1
	B	-	-	-	-	-	-	-	2.1
Viscosity (dm^3/kg)	A	917	-	-	831	740	735	730	728
	B	919	-	-	831	746	738	733	729
HexA (mmoles/kg)	A	19.2	-	-	5.2	-	-	-	5.6
	B	19.1	-	-	5.2	-	-	-	5.4