MARCELA FREITAS ANDRADE

CARACTERIZAÇÃO E UTILIZAÇÃO DO BAGAÇO DE CANA-DE-AÇÚCAR E CAPIM-ELEFANTE PARA PRODUÇÃO DE POLPA SOLÚVEL E PAPEL DE IMPRESSÃO E ESCRITA

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

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BIOGRAFIA

Marcela Freitas Andrade, nasceu em 03 de junho de 1986, em Viçosa, Minas Gerais.

Em 2003, concluiu o 2^o grau no Colégio Equipe, em Viçosa, Minas Gerais.

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RESUMO

ANDRADE, Marcela Freitas, D.Sc., Universidade Federal de Viçosa, fevereiro de 2014. **Caracterização e utilização do bagaço de cana-de-açúcar e capim-elefante para produção de polpa solúvel e papel de impressão e escrita**. Orientador: Jorge Luiz Colodette. Coorientadores: José Lívio Gomide e Rubens Chaves de Oliveira.

Nos últimos anos, tem havido crescente tendência para se utilizar mais eficientemente os resíduos e culturas agroindustriais tais como o bagaço de cana-de-açúcar e o capim elefante. Alguns exemplos de aplicações desses materiais incluem produção de bioenergia, de bioetanol e de polpas celulósicas para papéis e para dissolução. Dada a grande variabilidade do bagaço de cana e do capim elefante, suas aplicações requerem estudo detalhado da composição química e morfológica de suas fibras; no caso particular do bagaço-de-cana, é também importante conhecer as diferenças entre as frações principais dessas fibras, o córtex e a medula. Um dos componentes menos conhecidos do bagaço (córtex e medula) é a lignina, sendo esse desconhecimento uma grande barreira ao sucesso dos processos de desconstrução dessa biomassa. O uso da técnica de Ressonância Magnética Nuclear Bidimensional (2D RMN) permite avaliação pormenorizada da lignina desses materiais e foi usada com sucesso nesse estudo. O objetivo principal dessa tese foi caracterizar, pormenorizadamente, a química e a morfologia das fibras do bagaço de cana (córtex e medula) e do capim elefante e avaliar os seus potenciais na produção de polpa celulósica para papel (bagaço e capim) e para dissolução (bagaço). A tese está dividida em 5 capítulos distintos, a saber: (1) caracterização química e morfológica do bagaço de cana (córtex e medula) e do capim elefante; (2) caracterização detalhada da estrutura da lignina do córtex do bagaço de cana pela técnica de 2D RMN; (3) avaliação do córtex do bagaço de cana para produção de polpa solúvel; (4) avaliação do córtex do bagaço de cana para produção de papéis de impressão e escrita; (5) avaliação do capim elefante para produção de papéis de impressão e escrita. O capítulo 1 teve como objetivo caracterizar, detalhadamente, a composição química das duas frações do bagaço (córtex e medula) e determinar a morfologia das fibras e a composição estrutural da lignina do córtex. O conteúdo de celulose, hemiceluloses e lignina das frações córtex e medula do bagaço variaram significativamente entre si, com o córtex apresentando mais celulose e hemiceluloses e menos lignina, minerais e extrativos. A lignina da fração córtex apresentou elevados teores de PCAs (ácidos cinâmicos). A análise morfológica da fração córtex do bagaço indicou ser um material composto por fibras curtas, semelhante às de madeiras de folhosas. O objetivo do capítulo 2 foi obter preparações de lignina do bagaço (córtex e medula) por técnica de alto rendimento e analisar suas estruturas detalhadas pela espectroscopia semi-quantitativa de RMN bidimensional. Duas frações de lignina foram isoladas, lignina de madeira moída (MWLc) e lignina de enzima celulolítica (CEL96), do material original (córtex e medula) como tal e após ele ter sido extraído com álcali para remover os ácidos *p*-cumárico e ferúlico. As quatro amostras de lignina e os dois extratos alcalinos foram analisadas por RMN 2D. O rendimento do isolamento da lignina da preparação CEL96 foi muito maior do que o da preparação MWLc. O conteúdo de ácido *p*-coumárico presente no extrato alcalino foi maior que o conteúdo de ácido ferúlico. O pico de correlação da ligação β-O-4' foi o sinal de ligação entre unidades mais importante encontrado em todas as frações da lignina isolada. Foi verificado que ambas as preparações, MWLc e CEL96, do córtex e da medula contêm elevadas quantidades de ácidos *p*-hidroxicinâmicos (*p*HCAs). O objetivo do capítulo 3 foi avaliar a o potencial do córtex do bagaço (fração fibras) para a produção de polpas para dissolução. A fração córtex foi quimicamente caracterizada e convertida em polpa marrom com dois diferentes graus de deslignificação (número kappa 16,9 e 9,2) pelo processo de pré-hidrólise seguido de polpação soda (PHS). As polpas resultantes foram completamente branqueadas pela sequência O-D-(EP)-D-P e avaliadas quanto as suas principais características para polpa solúvel. A produção de polpa solúvel foi possível pelo processo PHS independente do número kappa inicial, sendo o kappa 16,9 mais desejável, pelo maior rendimento de polpa solúvel. A polpa solúvel do córtex de bagaço, produzida pelo processo PHS em qualquer dos dois níveis de kappa, apresenta baixa viscosidade e teor relativamente alto de cinzas, o que limita seu uso para certas aplicações de polpa solúvel; algum sistema de desmineralização da polpa no final do branqueamento é requerido. O objetivo do capítulo 4 foi avaliar o potencial da fração córtex do bagaço de cana de açúcar para a produção de polpas para papéis de imprimir e escrever. A fração córtex do bagaço (fração fibras) foi convertida em polpas marrons com dois diferentes graus de deslignificação (número kappa 17,5 e 10,8) pelo processo soda e as polpas resultantes foram completamente branqueadas pela sequência O-D*-(EP)-D e caracterizadas quanto as suas refinabilidades, drenabilidades e propriedades físico-mecânicas. As polpas branqueadas e cozidas pelo processo soda com números kappas 17,5 e 10,8 apresentaram similares valores de refinabilidade, resistência à drenagem e propriedades de resistência (tração, arrebentamento e rasgo). Ambas as polpas marrons obtidas a partir do córtex do bagaço de cana-de-açúcar foram apropriadas para a produção de papéis de imprimir e escrever, no entanto, a polpa marrom de maior número kappa foi economicamente mais atraente dado o seu rendimento de polpação superior. O principal objetivo do capítulo 5 foi caracterizar química e morfologicamente o capim elefante e avaliar o potencial das suas fibras para a produção de polpa para papéis de impressão e escrita. O capim elefante foi convertido em polpas marrons com dois diferentes graus de deslignificação (número kappa 17,5 e 10,6) pelo processo soda e as polpas resultantes foram completamente branqueadas pela sequência O-D*-(EP)-D e caracterizadas quanto as suas refinabilidades, drenabilidades e propriedades físico-mecânicas. O capim elefante se caracterizou pelo baixo teor de lignina e relativamente alto teor de minerais e extrativos, em relação à madeira de eucalipto, por exemplo. A análise morfológica do capim elefante indicou ser um material de fibra curta, semelhante a madeiras de folhosas. As polpas cozidas pelo processo soda até números kappa 17,5 e 10,6 e branqueadas apresentaram valores similares de refinabilidade e resistência à drenagem, mas o índice de tração e arrebentamento foram maiores para a polpa com número kappa 17,5. Porém, ambas as polpas são apropriadas para a produção de papéis de imprimir e escrever, sendo a de maior número kappa economicamente mais atraente dado o seu rendimento de polpação superior, sem significativo aumento da demanda de reagentes químicos de branqueamento.

ABSTRACT

ANDRADE, Marcela Freitas, D.Sc., Universidade Federal de Viçosa, February, 2014. **Characterization and utilization of sugar cane bagasse and elephant grass to produce dissolving pulp and printing and writing paper.** Adviser: Jorge Luiz Colodette. Co-advisers: José Lívio Gomide e Rubens Chaves de Oliveira.

In recent years, there has been an increasing trend towards more efficient utilization of agro-industrial residues and crops, such has sugar cane bagasse and elephant grass. Some examples of applications of these materials include bioenergy, bioethanol and pulps for paper and dissolving. Given the great variability of sugarcane bagasse and elephant grass, its applications require a detailed study of the chemical and morphological composition of the fibers, in the particular case of sugar cane bagasse, is also important to know the differences between the main fractions of these fibers, the depithed and pith. One of the least known components of bagasse (depithed and pith) is the lignin, and this lack is the major barrier to the success of the biomass deconstruction processes. The use of the technique of Nuclear Magnetic Resonance dimensional (2D NMR) allows detailed assessment of the lignin these materials and was successfully used in this study. The main goal of this thesis was to characterize in detail the chemistry and morphology of the fibers of bagasse (pith and depithed) and elephant grass and evaluate their potential for production of paper pulp (bagasse and elephant grass) and dissolving pulp (bagasse). The thesis is divided into 5 distinct chapters, namely: (1) Chemical and morphological characterization of sugarcane bagasse (depithed and pith) and elephant grass, (2) detailed characterization of the lignin structure of the depithed bagasse by 2D NMR technical, (3) evaluation of the depithed bagasse for production of dissolving pulp, (4) evaluation of the depithed bagasse for production of printing and writing paper grade pulp, (5) evaluation of elephant grass for production of printing and writing paper grade pulp. On the first chapter the main goals were characterizing the chemical (depithed and pith), morphological (fibers fraction) and the structural composition of the depithed bagasse lignin by 2D NMR. The cellulose, hemicelluloses and lignin contents in the two materials varied significantly, with the depithed fraction presenting more cellulose and hemicellulose and less lignin, extractives and minerals. The lignin composition of the depithed bagasse showed very high contents in PCAs (cinnamic acids contents). The morphological analyses of the depithed bagasse indicated a short fiber material, similar to hardwoods. On the second chapter the main objective was to obtain a lignin preparation (depithed and pith) by technica high yield and analyze the detailed structural with a semi quantitative 2-dimensional spectroscopy. Two lignin fractions were isolated, from the two starting materials: milled wood lignin (MWLc) and cellulolytic enzyme lignin (CEL96) as such and after it has been extracted with alkali to remove the *p*-coumaric and ferulic acids. The four lignin samples and the two alkaline extracts were analyzed by 2D NMR. The isolation yield of CEL96 was far higher than of MWLc preparations. The *p*-coumaric acid content was higher than ferulic acid content in the alkali extraction liquor. The *β*-O-4´ linkage correlation peak was the most prominent inter-unit linkage signal found throughout all isolated lignin fractions. Both MWLc and CEL96 from both fractions DB and P contain high amounts of *p*HCAs. On the third chapter the goal was evaluating the potential of the depithed bagasse for production of dissolving grade pulps. The depithed bagasse was chemically characterized and converted into brown pulp of two different extents of delignification degrees (kappa 16.9 and 9.2) by the pre-hydrolysis soda process (PHS). The resulting pulps were fully bleached by the O-D-(EP)-D-P sequence and evaluated for their main dissolving pulp characteristics. The production of dissolving pulp was possible for PHS process independent of the initial kappa number, being the kappa 16.9 most, due the highest yield of soluble pulp. The depithed bagasse soluble pulp produced by the HSP process in either of two levels kappa has low viscosity and relatively high ash content, which limits their use for certain applications of dissolving pulp, some demineralization of the pulp at the end of the bleaching is required. On the fourth chapter the main goal was evaluating the potential of the depithed bagasse for the production of printing and writing paper. The depithed bagasse was cooked by the soda process to two different degrees of delignification (kappa 17.5 and 10.8). The resulting pulps were fully bleached by the O-D*-(EP)-D sequence and characterized for their beatability, drainability and physical-mechanical properties. The bleached soda pulps cooked to 17.5 and 10.8 kappa number showed similar refinability, resistance to drainage and strength properties (tensile, burst and tear). Both brownstock pulps obtained from depithed sugar cane bagasse were suitable for the production of printing and writing paper grades; however, the higher kappa brownstock was more economically attractive given its higher pulping yield. The main goal of the fifth chapter was characterizing chemically and morphologically the elephant grass, and evaluating the potential of the fibers for production of printing and writing paper grade pulp. The elephant grass was chemically and morphologically characterized and cooked by the soda process to two different degrees of delignification (kappa 17.5 and 10.6). The resulting pulps were fully bleached by the O-D*-(EP)-D sequence and characterized for their beatability, drainability and physical-mechanical properties. The elephant grass was characterized by the low lignin content and relatively high content of minerals and extractives in relation to eucalyptus wood, for example. The morphological analyses of the elephant grass indicated a short fibered material, similar to hardwoods. The bleached soda pulps cooked to 17.5 and 10.6 kappa number showed similar refinability and resistance to drainage, but the tensile and burst index were higher for the 17.5 kappa pulp. Both brownstock pulps obtained from elephant grass biomass were suitable for the production of printing and writing paper grades; however, the higher kappa brownstock was more economically attractive given its higher pulping yield, without significantly increased of chemical demand for bleaching.

Introdução Geral

Em sua rica biodiversidade vegetal, o Brasil conta com espécies não madeireiras de grande potencial para uso no contexto de produção de polpas celulósicas especiais, tais como polpas para dissolução e para papéis de imprimir e escrever. Nesse sentido, um estudo sobre o bagaço de cana-de-açúcar e o capim-elefante, que são fontes de biomassa lignocelulósica de grande produtividade no Brasil, é de grande relevância, visto que são matérias-primas renováveis, abundantes, e de fácil acesso. Por exemplo, as produtividades da cana-de-açúcar (60-80 t/ha/ano, base úmida) e do capim-elefante (40-60 t/ha/ano, base seca) estão entre as maiores do mundo, com boas perspectivas de crescer ainda mais.

A cana-de-açúcar (*Saccharum officinarum*) é uma gramínea perene, originária da Ásia e muito bem adaptada na maioria dos climas tropicais e subtropicais. O Brasil é o maior produtor de cana-de-açúcar no mundo, seguido pela China, Índia, Tailândia e Austrália. Em 2011/12, o Brasil produziu cerca de 571 milhões de toneladas de cana-de-açúcar em 8,4 milhões de hectares de terra, com uma produtividade média de aproximadamente 68 t/ha (Conab, 2012). Toda esta produção resulta em um resíduo de 80 milhões de toneladas de bagaço, anualmente. Uma grande fração deste bagaço é queimada dentro das usinas de açúcar e etanol para produzir vapor e energia. A outra fração restante pode ser utilizada para produção de polpas celulósicas especiais e para outras aplicações, por exemplo, em biorrefinaria. A indústria brasileira de cana-de-açúcar é altamente competitiva, uma vez que é baseada na agricultura de alto nível tecnológico, instalada em condições muito favoráveis de clima e solo, utiliza equipamentos fabricados no país e pode facilmente expandir devido às grandes áreas cultiváveis disponíveis. Por isso, antecipa-se um crescimento significativo da disponibilidade de bagaço para outras aplicações, além da queima direta para geração de vapor e energia.

O capim-elefante (*Pennisetum purpureum*) também é uma gramínea perene, natural da África, e adaptada a climas tropicais como o brasileiro. A cultura de capim-elefante é altamente eficiente na fixação de CO_2 (gás carbônico) atmosférico durante o processo de fotossíntese para a produção de biomassa vegetal. Esta característica é típica de gramíneas tropicais que crescem rapidamente e fazem ótimo uso da água do solo e da energia solar para a produção de biomassa vegetal. Além disso, deve-se destacar que o capim-elefante, por apresentar um sistema radicular bem desenvolvido, pode contribuir de forma eficiente para aumentar o conteúdo de matéria orgânica do solo ou o sequestro de carbono no solo. A produtividade aproximada do capim-elefante no Brasil é em torno de 40-50 ton/ha/ano, base seca (Mazzarella, 2007). Por ser uma espécie de rápido crescimento e de alta produção de biomassa vegetal, o capim-elefante apresenta um alto potencial para uso não apenas como fonte alternativa de energia, mas é também atrativo para produção de polpas celulósicas especiais.

A polpação soda é tradicionalmente o processo de cozimento químico mais utilizado para várias matérias-primas não madeireiras, incluindo o bagaço de cana-de-açúcar e capim-elefante (Khristova et al., 2006; Enayati et al., 2009). A introdução de uma pré-hidrólise antes de qualquer processo de polpação alcalina ajuda a produzir polpa com um teor elevado de alfa celulose e com baixo teor de hemiceluloses (Behin e Zeyghami, 2009). A fração córtex do bagaço é um material lignocelulósico fibroso com potencial para a produção de polpas de celulose para dissolução. Polpas para dissolução exigem um elevado grau de pureza e são usadas para a produção de derivados de celulose, tais como o nitrato de celulose, acetato de celulose, metil-celulose, rayon, carboximetilcelulose, entre outros. Em comparação com outros tipos de polpa de celulose, a celulose para dissolução contém muito pouco ou nenhuma lignina, contém baixo teor de hemiceluloses e níveis muito baixos de celulose degradada.

O Brasil é um importante produtor mundial de papel. Em 2011, o setor posicionou-se como 9º produtor mundial de papel e, em 2012, produziu 10,1 milhões de toneladas do produto (Bracelpa, 2013). O bagaço de cana-de-açúcar e capim-elefante tornam-se matérias-primas de grande interesse para a produção de papéis de imprimir e escrever, visto que são materiais fibrosos renováveis e possuem relativamente altos conteúdos de carboidratos em sua constituição. Em adição, suas fibras são geralmente comparadas a fibras de eucalipto, que é uma matéria prima já consolidada para essa finalidade (Casey, 1980). Segundo Foelkel (1998), as propriedades requeridas para a produção de papéis de impressão e escrita são: maciez, opacidade, formação, porosidade, capacidade de impressão, resistência e estabilidade dimensional. Estas propriedades podem ser obtidas com fibras curtas, tais como as fibras de eucalipto, bagaço e capim.

Os principais componentes da parede celular das madeiras e das plantas herbáceas são a celulose, hemicelulose e lignina. Sabe-se que o bagaço de cana-de-açúcar é constituído por cerca de 40-50% de celulose, 20-30% de hemicelulose, 18-25% de lignina, 3-7% de extrativos e 1-3% de minerais (Andrade and Colodette, 2014; Mosier et al., 2005; Aguilar et al., 2002). Já para o capim-elefante, o conteúdo de celulose, hemicelulose, lignina, extrativos e minerais são de aproximadamente 40%, 30%, e 18,0%, 15% e 7%, respectivamente (Madakadze, et al, 2010; Gomes, et al, 2013). Embora o conhecimento desta composição seja desejável para as aplicações destes materiais em processos que envolvem desconstrução química, ela não é suficiente. O conhecimento mais detalhado da composição orgânica e inorgânica desses materiais, especialmente no que tange à estrutura da lignina é de vital importância para uma utilização racional do bagaço e do capim-elefante.

A lignina é uma macromolécula aromática, constituída de unidades de hidroxifenil, guaiacil e siringil, é o terceiro polímero natural mais abundante presente na natureza. Informações disponíveis sobre ligninas de plantas herbáceas, tais como o bagaço da cana, ainda são muito escassas e os estudos se concentram geralmente ligados a madeiras. A maioria dos métodos de análise da lignina requer o isolamento de lignina a partir de materiais lignocelulósicos. Os principais problemas no isolamento da lignina estão associados com a estrutura complexa de parede celular e a interação dos seus componentes. Como a lignina está ligada a polissacarídeos, não é possível isolar a lignina pura sem qualquer clivagem química. Um procedimento de isolamento adequado deve produzir uma preparação de lignina representante e minimizar as alterações estruturais durante o isolamento. Assim pela técnica de espectroscopia de Ressonância Magnética Nuclear Bidimensional (2D RMN) torna-se possível a análise da estrutura da lignina na íntegra com menor perda da informação original causada pelos processos usuais de preparação da amostra.

Nos últimos anos, tem havido crescente tendência para se utilizar mais eficientemente os resíduos e culturas agroindustriais tais como o bagaço de cana-de-açúcar e o capim-elefante. Alguns exemplos de aplicações desses materiais incluem produção de bioenergia, de bioetanol e de polpas celulósicas para papéis e para dissolução. Dada a grande variabilidade do bagaço de cana e do capim-elefante, suas aplicações requerem estudo detalhado da composição química e morfológica de suas fibras; no caso particular do bagaço de cana, é também importante conhecer as diferenças entre as frações principais dessas fibras, o córtex e a medula. Um dos componentes menos conhecidos do bagaço (córtex e medula) é a lignina, sendo esse desconhecimento uma grande barreira ao sucesso dos processos de desconstrução dessa biomassa. O uso da técnica de Ressonância Magnética Nuclear Bidimensional (2D RMN) permite avaliação pormenorizada da lignina desses materiais e foi usada com sucesso nesse estudo.

O objetivo principal dessa tese foi caracterizar, pormenorizadamente, a química e a morfologia das fibras do bagaço de cana (córtex e medula) e do capim-elefante e avaliar os seus potenciais na produção de polpa celulósica para papel (bagaço e capim) e para dissolução (bagaço). A tese está dividida em 5 capítulos distintos, a saber: (1) caracterização química e morfológica do bagaço de cana (córtex e medula) e do capim elefante; (2) caracterização detalhada da estrutura da lignina do córtex do bagaço de cana pela técnica de 2D RMN; (3) avaliação do córtex do bagaço de cana para produção de polpa solúvel; (4) avaliação do córtex do bagaço de cana para produção de papéis de impressão e escrita; (5) avaliação do capim elefante para produção de papéis de impressão e escrita.

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CAPÍTULO 1

Chemical and Morphological Characterization of Sugar Cane Bagasse

Abstract

In view of the growing sugar cane industry in Brazil, there has been great interest in the utilization of the left over bagasse for other uses, in addition to burning it for its caloric value. A thorough physical and chemical characterization of the bagasse, particularly regarding its lignin structure is relevant for a more rational utilization of the bagasse in the production of printing and writing pulp grades, dissolving pulp, ethanol and power. The main goal of this study were characterizing the chemical (pith and fibers fractions), morphologic (fibers fraction) properties of the sugar cane bagasse and the structural of the depithed bagasse lignin by 2D NMR. Industrial whole bagasse was separated into two fractions: pith and depithed bagasse. The pith was only characterized chemically. The depithed bagasse was chemically and morphologically characterized. The cellulose, hemicelluloses and lignin contents in the two materials varied significantly. The lignin composition of the depithed bagasse showed very high contents in PCAs. The depithed bagasse lignin presented fractions with different structural monomer distributions. The morphological analyses of the depithed bagasse indicated a short fiber material, similar to hardwoods.

Keywords

Sugar cane bagasse, chemical characterization, morphological characterization.

1. Introduction

In view of the growing sugar cane industry in Brazil, there has been great interest in the utilization of the left over bagasse for other uses, in addition to burning it for its caloric value. A thorough physical and chemical characterization of the bagasse, particularly regarding its lignin structure is relevant for a more rational utilization of the bagasse in the production of printing and writing pulp grades, dissolving pulp, ethanol and power.

Among the many agricultural fibers used for pulp manufacture, sugar cane bagasse is the one with most promise. Bagasse is easily accessible and readily available in many countries. Brazil is the world-leading producer of sugar cane (*Saccharum officinarum*). In 2011/12, the average productivity of sugar cane in Brazil was 68 tons/ha [1]. About 80 million tons of bagasse is generated per year in 8.4 million hectares of land [1]. About 90% of the bagasse is burnt within the ethanol and sugar mills to produce energy for steam and electricity [2], with about 10% being wasted. This wasted material can potentially be used for producing high-added value pulp.

The sugar cane bagasse is a low cost raw material and has a high carbohydrate content (51%-78%) [3-7]. Because of its low ash content (2%-3%), bagasse offers numerous advantages in comparison to other crop residues such as rice straw and wheat straw, which contain ~17.0% and 11.0% of ash, respectively, [8]. In addition it provides longer fiber than straw, low refining energy consumption, and good sheet formation, as well as paper smoothness [9]. These are relevant raw material traits for pulp production and other industrial uses. The bagasse pulp is generally comparable to hardwood pulps [10].

The properties of felting index, flexibility coefficient, wall fraction, ratio between length and thickness, and the Runkel can facilitate the understanding the cellulose pulps characteristics, related with resistances properties [11]. The fiber variables responsible for determining the physical characteristics and quality of pulp and paper are classified under fiber morphological aspects. Sugar cane bagasse fibers has length and diameter similar to that hardwoods fibers [12, 13].

Since the sugar cane bagasse is a promising raw material, a comprehensive study of chemical composition was performed. The main goal of this study were characterizing the chemical (pith and fibers fractions), morphologic (fibers fraction) properties of the sugar cane bagasse and the structural of the depithed bagasse lignin by 2D NMR.

2. Experimental

2.1. Working plan

Figure 1 depicts the working plan. The two fractions of the sugar cane bagasse (pith and fibers) were separated in a hammer mill. The whole bagasse, pith and depithed bagasse were chemically characterized. The depithed bagasse fraction (fibers) was also morphologically characterized and the structural characterization of the isolated lignin from the depithed bagasse was accomplished by 2D NMR.

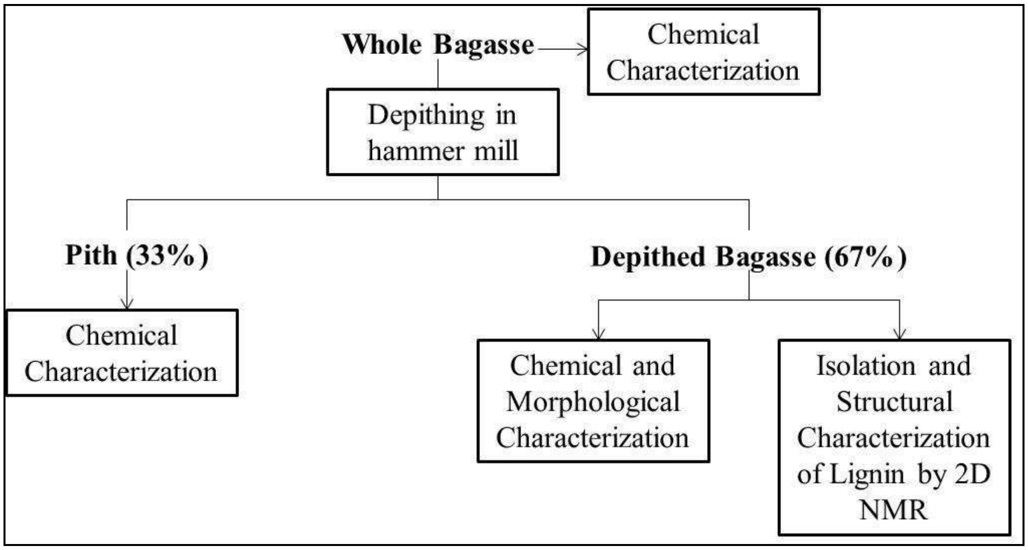

Figure 1. Working plan for bagasse fractionation.

2.2. Material

About 150 kg of industrial whole bagasse was provided by a Brazilian pulp mill. About 100 kg of the whole bagasse was separated into two fractions (pith and depithed bagasse) by a hammer mill. The pith fraction represented 33%, while the other 67% remained as the depithed bagasse. The pith, depithed bagasse and whole bagasse were dried to about 85% dryness in a conditioning room (23.0 ± 1.0°C and 50.0 ± 2.0% moisture) and stored in polyethylene bags for further use. The air-dried samples of pith, depithed bagasse and whole bagasse were ground in a Wiley mill and sieved, and the fraction that passed through a 40 mesh screen but was retained by a 60 mesh screen was collected.

2.3. Methods

2.3.1. Chemical characterization and isolation and structural characterization of lignin from sugar cane bagasse biomass

The following procedures were used for chemical analysis from pith and depithed bagasse fractions: moisture content (TAPPI T 264 om-88), total extractives content (TAPPI T 264 cm-97), acid soluble lignin [14], Klason lignin [15], lignin syringyl/guaiacyl ratio [16], preparation of biomass for sugar analysis (TAPPI T 249 cm-85), sugar analysis [17], acetyl groups [18], uronic acids [19], silica (TAPPI T245 cm-98) and ash (TAPPI 211 om 93).

From the depithed bagasse fraction, two different isolation methods were used to obtain lignin fractions: milled non-wood lignin (MWL) and cellulolytic enzyme lignin (CEL96). Crude milled non-wood lignin (MWLc) was isolated according to the classical method [20]. A planetary ball mill (Pulverisette 7, Fritsch, Germany) was used in the current experiment in contrast to a vibratory ball mill utilized in Björkman's protocol. The extracted sawdust (2g) was subjected to ball milling at 4 hours and at 600 rpm using ZrO_2 bowls and 17 ZrO_2 balls. The obtained non-wood meal was extracted with dioxane (96% v/v) and the solvent was then evaporated under vacuum at 35°C. Finally, the solid matter was dried in a vacuum oven at 35°C to obtain MWLc preparations.

The non-wood meal obtained after planetary ball milling (same Björkman's protocol as MWLc above) was treated with a cellulase (from *Trichoderma viride,* 9.1 U/mg solid) in an acetate buffer solution (pH 4.5) at 45°C for 48 h. The enzyme charge was 500 U/g non-wood substrate.

The 2D HSQC NMR spectra were carried out according to Balakshin *et al*., [21]. The spectra were acquired at sample concentration of *ca* 10% either on a Bruker AVANCE 500 MHz spectrometer equipped with a BBI probe with a cryoplatform and a Bruker 5 mm

ID CPTCI (^{1}H / ^{13}C / ^{15}N/D) cryo-probe with Z-Axis gradient. The acquisition parameters used on the 500 MHz spectrometer were: 160 transients (scans per block) were acquired using 1 K data points in F2 (^{1}H) dimension for an acquisition time of 151 ms and 256 data points in F1 (^{13}C) for an acquisition time of 7.68 ms for a total of 20 h. A coupling constant $^1J_{\mathrm{C-H}}$ of 147 Hz was used. The 2D data sets were processed with 1 K × 1 K data points using a Qsine window function in both dimensions.

2.3.2. Morphological characterization of depithed bagasse

The morphological analyses were performed from depithed bagasse fraction, after hydration and mild agitation for complete fiber individualization. Microscopic slides were prepared and images were captured with a video microscope equipped with image analysis software (model SZ - STS, Olympus, Japan). A small amount of colorant (Astra blue) was added for better visualization of the fibers. Approximately 100 whole fibers were measured. The following fiber biometric traits were measured: length, width, lumen diameter and cell wall thickness. Fiber length was measured using a 70X magnification, whereas the other traits were measured using 1000X magnification. The variation coefficient was taken at every 25 measurements. The data obtained from the various measurements were transferred to a computer spreadsheet program (Microsoft Excel 2007) to determine statistical parameters (*e.g.*, averages, standard deviations, and variation coefficients).

From the fiber biometry measurements, mathematical inferences were performed to determine other fiber properties, namely:

Felting Index (FI) = relation between fiber length (FL) and fiber width (FW),

$$(FI) = (FL/FW)*1000 \quad (1)$$

Where, 1000 is a conversion factor of μm to mm.

Flexibility Coefficient (FC) = relation between lumen diameter (LD) and fiber width (FW),

$$(FC) = (LD/FW)*100 \quad (2)$$

Where, 100 is a conversion factor for percentage.

Wall Fraction (WF), relation between wall thickness (WT) and fiber width (FW),

$$(WF) = (2*WT/FW)*100, \quad (3)$$

Where, 100 is a conversion factor for percentage.

Ratio length/thickness (L/T) = relation between fiber length (FL) and wall thickness (WT):

$$(L/T) = (FL/WT)*1000 \quad (4)$$

Where, 1000 is a conversion factor of μm to mm.

Runkel Index (RI) = relation between wall thickness (WT) and lumen diameter (LD),

$$(RI) = (2*WT/LD) \quad (5)$$

The analysis of coarseness, fiber number/gram and fines content were carried out in a particle size analyzer, which is Galai equipment, CIS-100 model.

3. Results and Discussion

3.1. Chemical characterization of sugar cane bagasse biomass

Three different fractions of the sugar cane bagasse biomass were characterized, namely: pith, depithed bagasse and whole bagasse. The proportions of pith and depithed bagasse after separation in the hammer mill were 33% and 67% on the basis of the whole bagasse dry weigh, respectively. The contents of cell wall structural constituents (cellulose, hemicelluloses and lignin) in the pith, depithed bagasse and whole bagasse varied significantly (Table 1), with the pith showing higher lignin and lower xylans and glucans contents than the depithed bagasse. Xylans are the main component of the hemicellulose of pith and depithed bagasses with trace amounts of galactans, mannans and arabinans.

The content of xylans in the pith (12.4%) is only about half of that present in the depithed bagasse (22.1%), while the glucan content were 37.8% and 43.4%, respectively, for the pith and the depithed bagasse. The acetyl group content in the pith, 0.5%, was much lower than that in the depithed bags, 2.6%; however, the contents of uronic acids of these materials were similar.

The pith presented much larger amounts of non-structural constituents (extractives and inorganics) versus the depithed bagasse. Most of the total inorganic material was composed of silica, particuarlly with the pith bagasse fraction. The whole bagasse presented structural and non-structural chemical composition in between the pith and depithed bagasse ones, reflecting their proportions in the whole bagasse.

Table 1. Chemical Composition of sugar cane bagasse in percentage of biomass dry weight

Analyses , %	Whole Bagasse	Pith	Depithed Bagasse
Klason lignin	21.3	23.2	20.2
Acid soluble lignin	1.2	1.0	1.4
Total lignin	22.5	24.2	21.6
Glucans	41.6	37.8	43.4
Xylans	18.9	12.4	22.1
Galactans	0.5	0.6	0.5
Mannans	0.0	0.0	0.0
Arabinans	1.2	0.9	1.4
Uronic acids	1.0	0.9	1.0
Acetyl	1.9	0.5	2.6
Total Sugars*	65.0	52.9	71.1
Ash	4.0	9.5	1.3
Silica	2.7	7.5	0.4
Extractives	8.5	13.4	6.1
Grand Total, %**	100	100	100

*include glucans, xylans, galactans, mannans, arabinans, uronic acids and acetyl groups.

**include total lignin, total sugars, ash and extractives.

Lignin content of this bagasse was similar to values reported in literature. Values in the range of 19%-24% were reported by Hurter [22]. Luz *et al.*, [23] have reported values of 43.8%, 28.6%, 23.5%, 1.3% and 2.8% for cellulose, hemicelluloses, lignin, ash and other components, respectively. High ash contents on bagasse have been reported by Wolf [5]. The very high content of extractives in the pith fraction has been reported elsewhere [4, 5 and 24].

Considering the pith has low fiber content and rather inadequate chemical composition to make pulp, this fraction was excluded for the next analyzes in this study. The remainder of this study focused on the depithed bagasse fiber fraction. The high extractive and inorganic contents are quite challengeable for pulp production.

From the depithed bagasse fraction, two different isolation methods were used to obtain lignin fractions: MWLc and CEL96. Both lignin fractions were analyzed by 2-dimensional NMR spectroscopy. Table 2 shows the isolation yield from MWLc and CEL96 preparations. The isolation yield of CEL96 was far higher than of MWLc. This means that the enzymatic digestion of the carbohydrates increases the accessibility for the dioxane 96% solvent.

Table 2. Yield from MWLc and CEL96 preparations

Preparation	Preparation yield, %
DB - MWLc	29.8
DB - CEL96	68.1

Wood lignins mainly contain guaiacyl (G) and syringyl (S) units, whereas the lignins of non-woody plants contain all three units: *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S). In non-wood materials, *p*-coumaric and ferulic acids are attached to lignin and hemicelluloses *via* ester and ether bonds forming lignin/phenolics–carbohydrate complexes.

The most abundant lignin linkages are *β*-O-4 ether bonds followed by *β*-5 and *β*-*β*' structures. In non-wood materials, where *p*-coumaric acid (*p*-CA) is ester-linked to the *γ*-carbon of the lignin side-chain we can find an acylated version of *β*-O-4' ethers.

The monomeric ratios, cinnamic acids contents (PCAs) and the ratios of the different inter-unit linkages are shown in Table 3. Regarding the S:G:H ratio, the differences in the S and G units were relevant. Regarding PCAs the estimated content was very high for both lignins (>50%) and the ferulic acid (FA) content is higher in MWLc than CEL96, while the *p*-CA content is higher in CEL96 than MWLc preparations. In MWLc and CEL preparations the ratio FA/*p*-CA was always in favor of *p*-CA (stronger for CEL than MWLc).

Table 3. S:G:H ratio, content of PCAs and relative abundances of inter-unit linkages

Lignin sample	Aromatic Rings					Interunit Linkages		
	Percentage					Percentage		
	S:G:H	PCAs	FA	*p*-CA	Ratio FA/*p*-CA	*β*-O-4'	*β*-5'	*β*-*β*'
DB-MWLc	54/42/4	60.3	19.2	41.0	0.468	83	10	2
DB-CEL96	49/47/4	52.8	7.0	45.8	0.154	82	9	1

Depithed bagasse lignins of herbaceous crops are known to be structurally different from those of softwood or hardwoods. The PCAs are also attached to lignin *via* acid-labile ester bonds and serve as bridges lignin and hemicelluloses [25]. The depithed bagasse lignin presented fractions with different structural monomer distributions. The lignin composition showed very high contents in PCAs.

3.2. Morphological characterization of depithed bagasse

Table 4 shows the average fiber dimensions for the depithed bagasse brownstock after soda pulping to 17.5 kappa.

Table 4. Depithed bagasse fiber dimensions in the soda brownstock with a 17.5 kappa number.

Dimension	Statistic	Depithed Bagasse Soda Pulp (17.5 Kappa)
Fiber length, mm	Average	1.44
	Standard Deviation	0.5
	C.V., %	34.9
Fiber width, µm	Average	21.3
	Standard Deviation	6.5
	C.V., %	30.5
Lumen diameter, µm	Average	15.5
	Standard Deviation	5.8
	C.V., %	37.8
Wall thickness, µm	Average	2.9
	Standard Deviation	1.3
	C.V., %	43.6

The average fiber length, fiber width, lumen diameter and wall thickness of the depithed bagasse were similar to results that have been reported by Carvalho [26] and Boechat [27]. In general, the fiber morphology of bagasse is somewhat similar to those of many hardwoods, thus being qualified as a short-fibered material [26, 27]. The values shown for the wall thickness were much lower in relation to lumen diameter. It is anticipated that pulp fibers produced from this raw material will have high collapsibility and low drainability, in addition to good bonding capacity. Other significant information can be obtained from the fiber morphology data through the correlations among the various fiber dimensions. Table 5 shows the relations calculated based on the average value of each morphological parameter measured in Table 4. These calculated relationships help with the understanding the influence of fiber morphology on paper formation and sheet physical properties [11]. Fibers with a high Runkel index and wall fraction, and a low flexibility coefficient are more rigid; these relationships correlate to tear resistance, which is a property dependent on the intrinsic strength of the fiber. However, tensile and burst indexes are properties that depend on fiber bonding [11].

The depithed bagasse soda pulp fibers exhibited a Runkel index of 0.37 % and wall fraction of 27.2%; these values are lower than those reported for eucalypt woods, which were 1.10-2.67 and 52-73%, respectively [11]. The pulp's fiber flexibility coefficient value was higher than that reported for eucalypt woods. Pulps of high flexibility coefficient produce more inter-fiber bonding during beating, which increase tensile and burst strengths. The felting index for depithed bagasse soda pulp was similar to that reported by Carvalho [26], but was higher than that of eucalypt wood fibers [11]. The length/thickness ratio of the depithed bagasse soda pulp was higher (496.6) than that of eucalyptus wood fibers (145-196) [11] and bagasse biomass fibers (329) [26].

Table 5. Relations of morphological properties.

Relationship	Depithed Bagasse Soda Pulp - Kappa 17.5	Bagasse Biomass [11]	Eucalyptus Hybrids [26]
Felting index	67.6	69.0	48.0 - 59.0
Flexibility coefficient, %	72.8	58.0	28.0 - 47.0
Wall fraction, %	27.2	42.0	52.0 - 73.0
Ratio length/thickness	496.6	329.0	145.0 - 196.0
Runkel index	0.37	0.73	1.10 - 2.67

Table 6 shows the results of fiber coarseness, fiber population per unit mass, and fiber fines content for depithed bagasse soda pulp and eucalyptus hybrids kraft pulps. The coarseness of the depithed bagasse fibers was lower than values reported in the literature for eucalypt kraft pulps. The coarseness is closely related to the fiber wall thickness and increases with increasing wall thickness (Ferreira et al., 2003). The fiber population (fibers/gram) of depithed bagasse pulp was somewhat similar to those observed for eucalypt pulps. The fines content of the depithed bagasse pulp (12.0%) was higher than the values commonly reported in the literature for eucalypt pulps. This is explained by the presence of significant parenchyma cells in the bagasse pulp, in spite of being depithed. Pulps containing higher fines content and high number of fibers per gram of pulp, coupled with low fiber coarseness and thin-walled fibers, will likely exhibit high resistance to drainage at the wet end of the papermachine.

Table 6. Analysis of depithed bagasse soda pulp fiber suspension carried out in Galai Cis-100 system.

Fiber Analysis	Depithed Bagasse Soda Pulp Kappa 17.5	Eucalyptus Hybrids Kraft Pulp [28]	Eucalyptus Hybrids Kraft Pulp [29]
Coarseness, mg/100m	4.3	6.4	7.6
Fibers number/gram, millions	25.8	23.7	22.0
Fines content, %	12.0	6.2	14.7

4. Conclusions

- The contents of cell wall structural constituents in the three bagasse materials varied significantly, with the pith showing significantly higher lignin, and lower xylans and glucans contents than the depithed bagasses.
- The pith presented much larger amounts of extractive and inorganic contents in relation to depithed bagasse.
- The depithed bagasse lignin composition by 2D NMR analysis showed very high contents of phenolic cinnamic acids (PCAs).
- The morphological analyses of the depithed bagasse (fiber fraction) indicated a short fiber material, similar to hardwoods.

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CAPÍTULO 2

Isolation and 2D NMR Characterization of Lignin from Sugar Cane Bagasse

Abstract

The aim of this study was a detailed evaluation of sugar cane bagasse (depithed and pith fractions) lignin structure. Lignin preparations of high yields with little changes in the lignin structure were obtained by two different techniques and analyzed by semi-quantitative 2-dimensional (2D) NMR spectroscopy for a detailed structural characterization. This work was divided in two parts: In the first part the study, 2D NMR spectroscopy analyses were carried out on lignin from depithed and a pith fraction of sugar cane bagasse fractions isolated from the original materials, namely: milled wood lignin (MWLc) and cellulolytic enzyme lignin (CEL96). In the second part an alkaline extraction of the original material was performed prior to lignin isolation and the contents of *p*-coumaric (*p*CA) and ferulic acid (FA) in the alkali extraction liquor were determined. The residue of the alkaline extraction was equally processed as the first part of the study. The isolation yield of CEL96 was far higher than of MWLc preparations. The enzymatic digestion of the carbohydrates increases the accessibility for the solvent. The *p*-coumaric acid content was higher than ferulic acid content in the alkali extraction liquor. The *β*-O-4´ linkage correlation peak was the most prominent inter-unit linkage signal found throughout all isolated lignin fractions. Both MWLc and CEL96 from both depithed and pith fractions contain high amounts of p-hydroxy-cinnamic acids (*p*HCAs). The ratio FA/*p*CA in all lignins isolated before alkali extraction is strongly in favor of *p*CA; after alkali extraction this ratio is shifted towards FA.

Key words

Sugar cane bagasse, 2D NMR, lignin.

1. Introduction

In recent years, there has been an increasing trend towards more efficient utilization of agro-industrial residues, including the residue from sugar cane (*Saccharum officinarum*) which is the bagasse. Several processes and products have been reported that utilize sugar cane bagasse as a raw material. Biomass from grasses, such as sugar cane bagasse, is the largest renewable source for the production of bio-products and biofuels, and it is available in high amounts at relatively low cost. The available information about lignins of herbaceous crops is scattered and the available reviews generally address wood lignins.

The main components of wood and herbaceous cell walls are cellulose, hemicelluloses and lignin. Lignin is the third most abundant natural polymer present in nature. There are 3 main groups of lignins: (1) the lignins of softwoods (gymnosperms), (2) the lignins of hardwoods (angiosperms) and (3) the lignins of grasses (non-woody). Lignin is an amorphous polymer consisting of phenylpropane units, and their precursors are three aromatic alcohols namely *p*-coumaryl (1), coniferyl (2) and sinapyl alcohol (3) (Figure 1). The respective aromatic constituents of these alcohols in the polymer are called *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) moieties. The lignin content, composition and structure vary widely among different plant species, among individuals, and even in different tissues of the same individual.

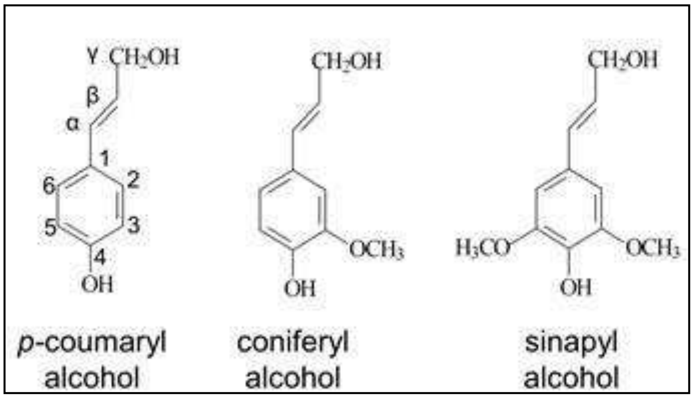

Figure 1: The lignin precursors that are the basic building blocks for all lignin-containing vascular plants.

Wood lignins mainly contain guaiacyl and syringyl units, whereas the lignins of non-woody plants contain all three units (H, G, S). Lignin is always associated with carbohydrates (in particular with hemicelluloses) via covalent bonds at two sites: α-carbon and C-4 in the benzene ring, and this association is called lignin–carbohydrate complexes (LCC). In herbaceous plants or non-wood biomass, *p*-hydroxycynnamic acids (*p*HCAs) like *p*-coumaric (*p*CA) and ferulic acids (FA) are attached to lignin and hemicelluloses via ester and ether bonds as bridges between them forming lignin/phenolics–carbohydrate complexes (Baucher et al., 1998; Sun et al., 2002, cited by Buranov and Mazza, 2008). Because of this chemical nature of lignin, it is practically impossible to extract lignins in pure form.

Most methods for lignin analysis require the isolation of lignin from lignocellulosic materials. The main problems in lignin isolation are associated with the complex structure of the cell wall and the interaction of its components. As almost all lignin is linked to polysaccharides, it is not possible to isolate pure lignin without any chemical cleavage. An appropriate isolation procedure should produce a representative lignin preparation and minimize structural changes during isolation. Generally, two approaches are used to isolate lignin from lignocellulosics: acidolysis methods and extraction of lignin after ball milling and/or enzymatic hydrolysis of carbohydrates. Although the acidolytic methods are quite fast and produce lignin preparations of high purity, the acidic conditions employed trigger some changes in lignin structures. Enzymatic hydrolysis cannot be directly applied to lignocellulosic materials, and a preceding efficient milling of the sample is required. During ball milling significant degradation of polysaccharides occurs along with a certain breakdown of the lignin macromolecule (Balakshin et al., 2011).

Extraction of the milled wood with 96% dioxane produces milled wood lignin (MWL). Enzymatic hydrolysis of carbohydrates in the milled wood followed by dioxane extraction produces cellulolytic enzyme lignin (CEL). Isolation of MWL and CEL from softwoods is a rather reliable and robust procedure (Capanema et al., 2004; Balakshin et al., 2011). However, the transfer of the already acquired knowledge to non-wood materials still has to be investigated. In the case of non-wood, such as sugar cane bagasse, comprehensive lignin studies are quite limited. A better understanding on the isolation of lignin and its structure and representativeness is required to better understand its behavior during chemical conversions that lead to products such as biofuels.

The proposal of this study was detail structural analysis of sugar cane bagasse (depithed and pith fractions):

1- Milling of the extractive free pith and depithed bagasse in a planetary ball mill for different periods of time (~4h – 15h).
2- Analysis of the milled material by nitrobenzene oxidation.
3- Isolation of lignin from the different milled materials by aqueous dioxane extraction after ball milling and after enzymatic hydrolysis.
4- Alkali extraction for determination of the amount of *p*-coumaric and ferulic acid.
5- Structural characterization of the lignin fractions by carbon 2D NMR.

The main objective was to obtain a lignin preparation with a yield as high as possible and changes in the lignin structure as low as possible and analyze the lignin preparations with a semi quantitative 2D NMR spectroscopy for a detailed structural characterization.

2. Experimental

2.1. Working plan

This work was divided in two parts: In the first part a detailed study of the structure of lignin from depithed and a pith fraction of sugar cane bagasse was done. Two lignin fractions were isolated, from the two starting materials: milled wood lignin (MWL) and cellulolytic enzyme lignin (CEL96) and then, both preparations were analyzed by 2-dimensional NMR spectroscopy (Figure 2). In the second part an alkaline extraction was performed prior to lignin isolation and the contents of *p*-coumaric and ferulic acid in bagasse were determined (Figure 3A). The residue of the alkaline extraction was equally processed as the plant material in the first part of the study (Figure 3B).

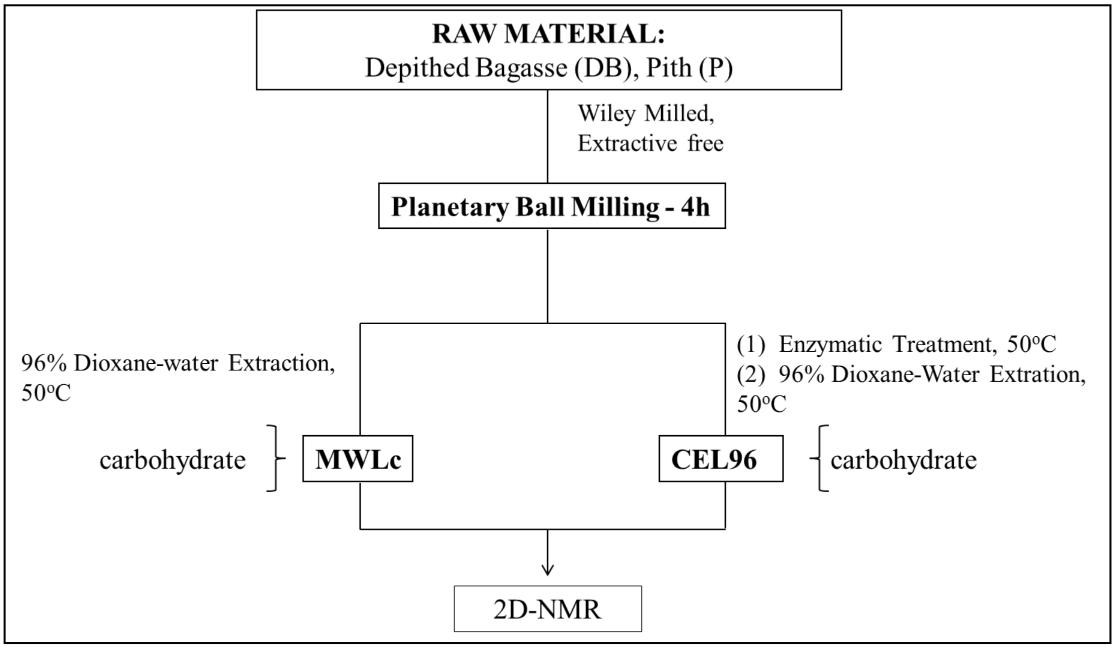

Figure 2: Isolation and structural characterization of the lignin from sugar cane bagasse (organization of tasks).

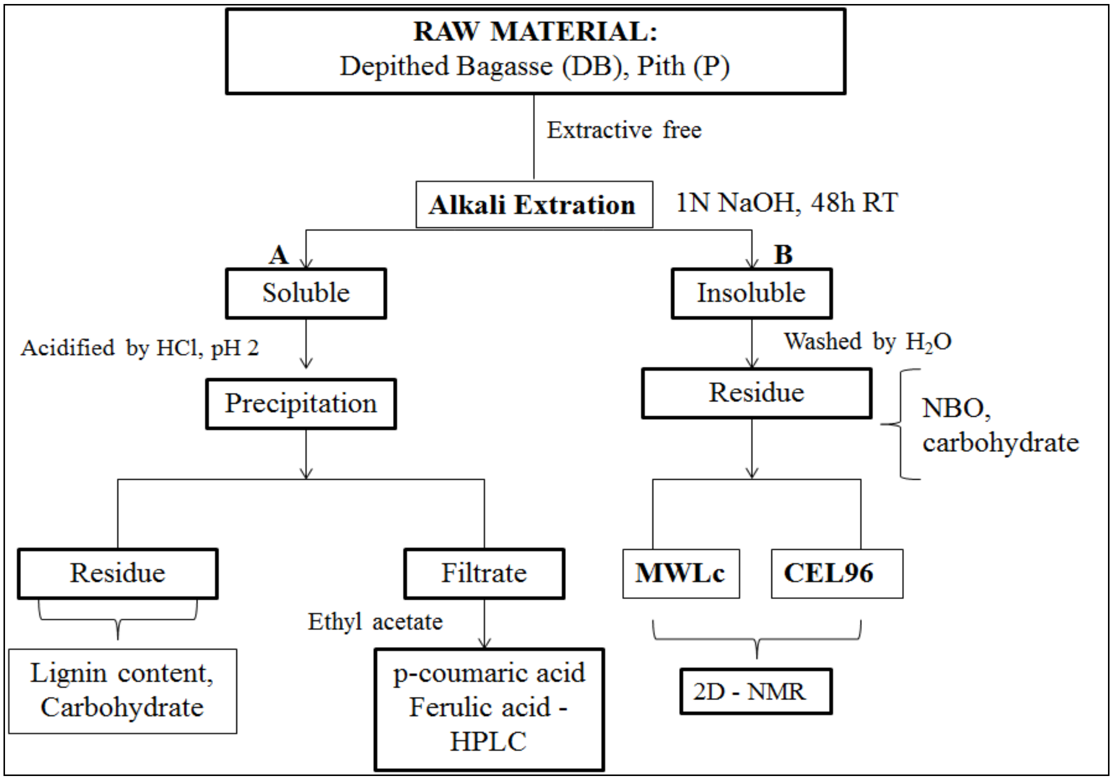

Figure 3: Alkaline extraction procedure for the determination of the amount of p-coumaric and ferulic acid (A) and subsequent isolation and structural characterization of the lignin (B) (organization of tasks).

2.2. Material

About 150 kg of industrial whole bagasse was provided by a Brazilian pulp mill. About 100 kg of the whole bagasse was separated into two fractions (pith and depithed bagasse) by a hammer mill. The pith fraction represented 33% while the other 67% remained as depithed bagasse. The pith, depithed bagasse and whole bagasse were dried to about 85% dryness in an acclimated room (23.0 ± 1.0^{o}C and 50.0 ± 2.0% moisture) and stored in polyethylene bags for further use. The air-dried samples of pith, depithed bagasse and whole bagasse were ground in a Wiley mill and sieved, and the fraction that passed through a 40 mesh screen but was retained by a 60 mesh screen was collected.

2.3. Methods

2.3.1. Isolation of milled non-wood lignin (MWL)

Crude milled non-wood lignin (MWLc) was isolated according to the classical method (Bjorkman, 1956). A planetary ball mill (Pulverisette 7, Fritsch, Germany) was used in the current experiment in contrast to a vibratory ball mill utilized in Bjorkman's protocol. The extracted sawdust (2g) was subjected to different ball milling times (~ 4h - 15h) at 600 rpm using ZrO_2 bowls and 17 ZrO_2 balls. The obtained non-wood meal was extracted with dioxane (96% v/v) and the solvent was then evaporated under vacuum at 35°C. Finally, the solid matter was dried in a vacuum oven at 35°C to obtain MWLc preparations.

2.3.2. Isolation of cellulolytic enzyme lignin (CEL 96)

The non-wood meal obtained after planetary ball milling (same conditions as MWLc) was treated with a cellulase (from Trichoderma viride, 9.1 U/mg solid, purchased from Sigma) in an acetate buffer solution (pH 4.5) at 50°C for 48 h. The enzyme charge was 500 U/g wood. After the enzymatic hydrolysis, the solid material was separated by centrifugation, washed with the buffer solution followed by deionized water and then freeze dried. The dried material was extracted with 96% dioxane and processed by the same procedure as used for MWLc.

2.3.3. Carbohydrate content and sugar composition of MWL and CEL 96.

Due to the limited amount of isolated MWL, a modified protocol for sugar analysis was developed and performed according to Balleirini et al., 2012. The lignin sample (10 mg) was swollen in 0.214 mL of 72% H_2SO_4 at room temperature for 2 h. The sample was then diluted with 8.0 mL of deionized water and placed in the 105°C oven for 3.5 h. After completion of the reaction, the sample was cooled down and the internal standard (fucose) was added. The acidic sample was neutralized by passing through an OnGuard IIA cartridge from Dionex. The neutralized sample was injected into a high-performance anion-exchange chromatograph with pulsed amperometric detection (HPAE-PAD) on a Dionex IC-3000 chromatography system, using a guard column (Carbo-Pac PA1, 2 mm × 50 mm i.d.) and an analytical column (Carbo-Pac PA1, 2 mm × 250 mm i.d.). Water was used as eluent at the flow rate of 1.0 mL/min and the column temperature was maintained at 18°C. The postcolumn used 40 mM NaOH at a flow rate of 1.0 mL/min to improve detection by pulsed amperometry.

2.3.4. Nitrobenzene Oxidation

Nitrobenzene oxidation for S/V ratio determination was performed according to Chen, 1992. Non-wood meals (200 mg, 40−60 mesh) were reacted with 7 mL of 2 N NaOH (aq) and 0.4 mL of nitrobenzene in a stainless steel bomb at 170°C for 2.5 h. After 2.5 h, the hot stainless steel bomb was cooled down immediately by ice water, and 1 mL of 5-iodovanillin (80 mg in 5 mL dioxane) was added as internal standard. The reaction mixture was extracted with CH_2Cl_2 four times and the organic phase (CH_2Cl_2 phase) was discarded. The remaining aqueous phase (alkali solution) was then acidified with 2 N HCl to pH 2−3. The acidified solution was further extracted again with CH_2Cl_2 three times, and this organic phase (CH_2Cl_2 phase) was collected for analysis. The CH_2Cl_2 phase was dried over Na_2SO_4(s) and the volume was adjusted to 100 mL. One milliliter of this solution was dried by rotatory evaporation at 30°C. The dried product was dissolved in 50 μL of pyridine, and

50 μL of N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) was added, and the solution was shaken for 15 min at 50 °C. The derivatized mixture was then directly injected (2 μL) into the GC. Quantitative GC analysis was carried out on a HP 6890 GC equipped with a flame ionization detector and HP-1 column (30 mm × 0.32 mm i.d., 0.25 μm). The injection temperature was 200°C, the detector temperature was 270°C, and the column flow rate was 2 mL of helium/min. The column was 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 at 260°C for 5 min. S/V was determined by the molar ratio of the amount of syringaldehyde divided by the sum of vanillin and vanillic acid. Syringic acid was not included, since the amount was negligible in all cases.

2.3.5. Alkaline extraction

Because sugar cane bagasse lignin is known to contain γ-esters of p-coumaric and ferulic acids (Ralph and Landucci, 2010), the amount of the two esters in the sample was determined according to published methods (Min, et al., 2014). The extracted sawdust (2g) was subjected to alkaline treatment with 1N NaOH for 48 hours at room temperature and the residue was washed by water until neutral. Isolation of the lignin fractions MWLc and CEL 96 was done both before and after removal of the hydroxycinnamic esters.

2.3.6. NMR Spectra

The 2D HSQC NMR spectra were carried out according to Balakshin et al., 2011. The spectra were acquired at sample concentration of *ca* 10% either on a Bruker AVANCE 500 MHz spectrometer equipped with a BBI probe with a cryoplatform and a Bruker 5 mm ID CPTCI (^{1}H / ^{13}C / ^{15}N/D) cryo-probe with Z-Axis gradient. The acquisition parameters used on the 500 MHz spectrometer were: 160 transients (scans per block) were acquired using 1 K data points in F2 (^{1}H) dimension for an acquisition time of 151 ms and 256 data points in F1 (^{13}C) for an acquisition time of 7.68 ms for a total of 20 h. A coupling constant $^1J_{C–H}$ of 147 Hz was used. The 2D data sets were processed with 1 K × 1 K data points using a Qsine window function in both dimensions.

3. Results and Discussion

3.1. Isolation of preparations

The isolation yields of MWLc and CEL 96 from the two sugar cane bagasse fractions, depithed (DB) and pith (P), at different ball milling times (~ 4h - 15h) are shown in Figure 4A and B, for depithed and pith, respectively, based on lignin content in the respective starting material.

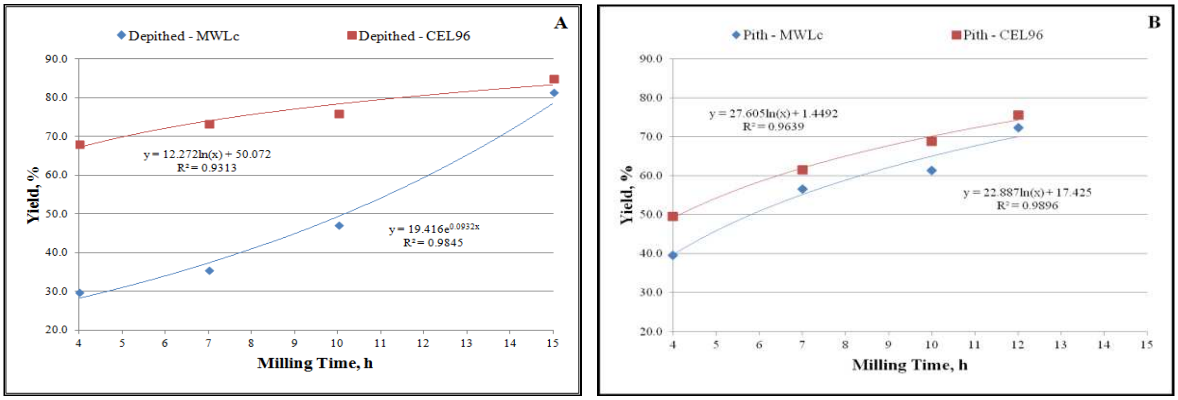

Figure 4: Isolation yield of MWLc and CEL 96 from the two sugar cane bagasse fractions depithed bagasse (A) and pith (B) at different milling times.

The yields of the preparations are proportional to the energy applied during ball milling (intensity and milling time). The milling intensity was fixed to 600 rpm and the milling time was adjusted to provide sugar cane bagasse fractions (depithed and pith) MWLc preparations with a yield around 30%. The milling time of 4 hours was chosen to continue the experiments. The yield of MWLc from the pith (P) at the same milling time (4h) was higher than for the depithed fraction (Table 1). Enzymatic hydrolysis before solvent extractions allowed isolating around 30% additional lignin as a CEL preparation for depithed bagasse and about 10% more for the pith fraction compared to the MWLc yield.

Table 1: The yields and sugar compositions.

Preparation	Preparation yield, %	Sugars, % sample	Sugar composition, %					
			Rha	Ara	Xyl	Man	Gal	Glc
DB - 4H - MWLc	29.8	12.2	0.0	1.0	9.9	0.0	0.1	1.2
P - 4H - MWLc	39.6	18.3	0.0	1.2	10.6	0.1	0.2	6.2
DB - 4H - CEL96	68.1	9.4	0.0	1.3	7.0	0.0	0.1	1.0
P - 4H - CEL96	49.6	7.3	0.0	1.0	5.0	0.0	0.1	1.3

It is notable that the carbohydrate content in CEL96 was smaller than in MWLc. This could be due to the celullase enzyme remove part of the carbohydrate. The depithed bagasse and pith contain xylan as main sugars constituents. Their amounts were about 81% and 58% of total sugars in the depithed and pith MWLc preparations. The amounts of the others sugars, especially arabinans and galactans, in the depithed and pith CEL96 were similar as compared to the depithed and pith MWLc preparations. Similar tendency about CEL96 preparation was related by Balakshin et al., 2011.

The results of nitrobenzene oxidation after ball milling of depithed bagasse and pith are given in Table 2.

Table 2: Total aldehyde yield and S/V and H/V ratios of depithed bagasse and pith after nitrobenzene oxidation.

Sample	Total Lignin Content (%)	Yield of H,V & S on % of lignin	S/V	H/V
DP - 4H	21.8	35.6	0.9	0.7
DP - 7H	21.8	35.5	0.9	0.7
DP - 10H	21.8	34.1	0.9	0.7
DP - 12H	21.8	34.1	0.9	0.7
P - 4H	24.1	28.3	1.2	1.0
P - 7H	24.1	28.4	1.1	1.1
P - 10H	24.1	26.3	1.1	1.0
P- 15H	24.1	27.7	1.1	1.0

The results of the nitrobenzene oxidation showed that the milling time does not interfere with the yields and with the S/V and H/V ratios, i.e., similar values were found for different milling times studied in the depithed and pith fractions of the bagasse. According to Fujimoto et al. 2005, little degradation of the lignin aromatic rings occurs during ball milling. The yields of H, V and S for depithed bagasse were higher than yields for pith, while the S/V and H/V ratios were lower.

3.2. Alkaline extraction

Because non woody lignin is known to contain γ-esters of *p*-coumaric and ferulic acids, the amount of the two esters in each sugar cane bagasse fractions were determined according to published methods (Min et al., 2014). An alkaline extraction (AE) protocol was used to determine the content of *p*-coumaric acid and ferulic acid present in the lignin of the sugar cane bagasse fractions (Table 3). The alkaline extraction (NaOH 1N) was performed for 48 hours under constant agitation at room temperature.

Table 3: Contents of *p*-coumaric and ferulic acid

Sample	CA (mg)	FA (mg)	Lignin (g)	% CA/lignin	% FA/lignin	% TA/lignin
DB	1.9	0.3	2.2	1.8	0.3	2.1
P	1.6	0.2	2.4	1.9	0.2	2.1

*Note: CA = *p*-coumaric acid; FA = ferulic acid; TA = total acid

The results show that the content of *p*-coumaric acid was higher than of ferulic acid. According to Scalbert et al., 1985, cited by Buranov and Mazza, 2008, ferulic acid is present in smaller amounts and can be linked either through ether or ester linkages. Studies of lignin structure after the removal of γ-esters are important since these esters play an important role in the lignin structure from sugar cane bagasse.

3.3. Chemical characterization

All chemical analyses of sugar cane bagasse components and lignin isolation were done both before and after removal of γ-esters. The yield obtained after alkaline extraction was 64% and 54% for depithed and pith, respectively. The determined yields were used to calculate the contents of the chemical constituents based on the extractive-free original sample.

Table 4 shows the chemical composition of the original samples and after alkaline extraction. The contents of cell wall components (cellulose, hemicelluloses and lignin) in the pith and depithed bagasse varied significantly, with the pith showing higher lignin and lower xylan and glucan contents than the depithed bagasse. Xylans are the main hemicelluloses of pith and depithed bagasses, while the contents of galactans, mannans and arabinans of these materials are rather low.

Table 4: Chemical composition of the extractive-free original samples and the samples extracted with alkali.

Sample	% Ara	% Gal	% Glu	% Xyl	% Total sugars	% Soluble Lignin	% Insoluble Lignin	% Total Lignin
DB	1.7	0.4	43.5	24.2	69.8	1.8	20.0	21.8
P	0.9	0.4	36.5	15.4	53.2	1.6	22.6	24.1
DB-AE*	0.7	0.0	35.1	7.0	42.8	0.7	6.8	7.4
P-AE*	0.0	0.0	24.6	2.7	27.3	0.5	10.9	11.4

*Note: Values based on the extractive-free original sample. The acetone was utilized for remove to extractive.

The lignin contents of the bagasse in original samples are similar to values reported in the literature. Values in the range of 19%-24% were reported by Hurter, 1998 and Luz et al., 2007. The alkaline extraction values were calculated based on the alkaline extraction yield. It can be observed that the lignin contents were lower after the alkaline extraction as well as the carbohydrate contents.

The delignification in depithed bagasse fraction after alkaline extraction was stronger than in pith fraction. The big part of the sugar was extractable in the alkali, 39% of

DB sugars and 49% of P sugars. The soda acts degrading carbohydrates and breaking the chains of cellulose and hemicelluloses. The xylans contents were more removed than the glucans contents, and the xylan removal in P was stronger than in DB fraction. The mannose and rhamnose contents were not detected in the samples.

Table 5 shows the results of the nitrobenzene oxidation analysis of the original sample and after alkali treatment. Nitrobenzene oxidation converts uncondensed units of lignin to vanillin (V), syringaldehyde (S), and *p*-hydroxybenzaldehde (H). While the total aldehydes yield (V + S + H) gives an indication of the relative degree of condensation in lignin, the ratios of the three aldehydes reveal the ratios of the three lignin precursors in the uncondensed units.

Table 5: Results from nitrobenzene oxidation of the original sample (DB and P) and after alkaline extraction (DB – AE and P – AE).

Sample	Total Lignin Content (%)	Yield of H,V & S on % of lignin	S/V	H/V
DB	21.8	36.2	1.0	0.6
P	24.1	26.5	1.2	1.0
DB - AE	10.6	38.7	0.9	0.1
P - AE	21.1	9.3	0.5	0.1

The yield of H, V and S for depithed bagasse after alkaline extraction was slightly higher than yield for depithed without alkaline extraction, while the S/V and H/V ratios were lower. Regarding the pith fraction, the yield of H, V and S after alkaline extraction was lower than yield without alkaline extraction, while the S/V and H/V ratios remained lower.

3.4. Isolation of preparations after AE

As for the starting material without alkali treatment, the material after alkali extraction (and milling for 4 hours in a planetary ball) was as well subjected to MWLc and CEL96 isolation and the respective yields are shown in Table 6.

Table 6: The yields and sugar contents of MWLc and CEL96 after alkaline extraction of the starting material

Preparation	Preparation yield, %	Sugars, % sample	Sugar contents %					
			Rha	**Ara**	**Xyl**	**Man**	**Gal**	**Glc**
DB - MWLc	14.1	7.6	0.0	0.8	1.7	0.0	0.2	4.9
P - MWLc	6.0	9.4	0.0	0.4	1.3	0.2	0.1	7.4
DB - CEL96	59.9	2.3	0.0	0.2	0.9	0.0	0.0	1.2
P - CEL96	11.3	2.8	0.0	0.1	0.8	0.0	0.0	1.9

The values in Table 6 show that the enzymatic hydrolysis for isolation of CEL96 was more effective to the alkali-extracted material than for isolation of MWLc after AE. It is also notable that the carbohydrate content of the lignin preparations decreased after alkali extraction which means that a part of the carbohydrates is extractable by alkali as well. It was observed that xylans were the main sugars removed by the effect of alkali. Their amounts were about 22% and 14% of total sugars in the depithed and pith MWLc preparations (after AE), respectively, while the glucans content were about 65% and 79% of total sugars in the same preparations. The amounts of the xylans after AE in the depithed and pith CEL96 were more significant (39% and 29%, respectively) as compared to the depithed and pith MWLc preparations. While the amounts of the others sugars, especially arabinans, mannans, galactans and glucans, in the depithed and pith CEL96 were more insignificant as compared to the depithed and pith MWLc preparations. Comparing to the isolation yields in Table 1, the yields of MWLc and CEL96 isolated from the alkali-extracted starting material were lower.

3.5. Structural characterization of lignin

The isolated preparation were analyzed on a 500 MHz NMR spectrometer and the table 7 shows the lignin structural characteristics as ratio of monomers, like S:G:H ratio, the contents of *p*-hydroxycinnamic acids (*p*HCAs), *p*-coumaric acid (pCA) and ferulic acid (FA), tricin contents and the relative abundances of inter-unit linkages from MWLc and

CEL96 preparations from depithed bagasse (DB) and the pith fraction (P) before and after alkaline extraction (AE):

Table 7: S:G:H ratio, contents of *p*HCAs, *p*CA and FA, tricin contents and the relative abundances of inter-unit linkages from MWLc and CEL96 preparations from DB and P before and after alkaline extraction (AE):

Lignin sample		**Aromatic rings (%)**						**Interunit linkages (%)**			
		S:G:H	***p*HCAs**	**FA**	***p*CA**	**ratio FA/*p*CA**	**Tricin**	***β-O-4'***	***β-5'***	***β-β'***	***β-β' THF***
DB	**MWLc**	54 / 42 / 4	60.3	19.2	41.0	0.468	3.6	83	10	2	6
	MWLc AE	53 / 40 / 7	28.9	15.5	13.3	1.166	1.7	83	10	4	3
P	**MWLc**	55 / 31 / 14	68.6	15.0	53.6	0.280	1.0	85	9	1	6
	MWLc AE	41 / 40 / 19	14.7	8.1	6.5	1.246	0.6	82	10	4	4
DB	**CEL96**	49 / 47 / 4	52.8	7.0	45.8	0.154	1.7	82	9	1	8
	CEL96 AE	49 / 45 / 6	9.1	6.8	2.3	3.010	0.8	87	9	2	2
P	**CEL96**	55 / 36/ 9	68.2	7.9	60.3	0.130	0.8	84	9	1	6
	CEL96 AE	49 / 29 / 22	12.9	4.3	8.6	0.503	0.8	90	6	2	2

For semi-quantitative analysis the 2D correlation peaks were integrated and compared using MestReNova v6.0.2 NMR processing software. Signal assignment was done according to the literature (Ralph et al. 2004; del Rio et al. 2008; Martínez et al. 2008; Kim and Ralph 2010; del Rio et al. 2012). In the aromatic region (δ_C/δ_H 90−150/6.0−8.0) of the HSQC spectra (Figure 5 and Table 9) the monomeric ratio of the lignin macromolecule was estimated from the C_2-H_2 correlations from S, G and H units as well as *p*CA and FA contents were estimated from their C_2-H_2 cross signal (del Rio et al. 2012). The Tricin content was estimated from the C_2-H_2 correlations of its syringyl moiety. The structures of the above mentioned lignin structures are depicted in Figure 6. Based on the volume integrals of the correlation peaks of the lignin monomers the relative monomeric ratio of the assumed lignin macromolecule was calculated. The *p*CA and FA content was calculated as a percentage of the sum of regular lignin monomers (S + G + H). In the same manner the tricin content was determined as a percentage of the sum of regular lignin units (Table 7).

Secondly, from the aliphatic-oxygenated region (δ_C/δ_H 50−90/2.5−5.8 ppm) important information about the different lignin inter-unit linkages can be found. The C_α-H_α correlations were used for estimation of the relative abundances of side-chains involved in the different forms of inter-unit linkages. The *β*-O-4´ linkage (A) correlation peak was the most prominent inter-unit linkage signal found throughout all isolated lignin fractions. Weaker signals from phenylcoumaran (*β*-5´) (B) and resinol (*β*-*β*´) (C) structures could be identified as well as from *γ*-acylated *β*-*β*´ tetrahydrofuran substructures (*β*-*β*´ *THF)* (C´). Xylan signals (i.e. X_5 at δ_C/δ_H 62.6/3.37 ppm and 3.82 ppm) and lignin side chain signals of acylated *γ*-carbons (δ_C/δ_H 62.5/3.70-4.30 ppm) were also found in this region, the latter confirming the presence of *γ*-acylated substructures. Further, signals of acetylated xylan structures (X'_2 and X'_3) were found in the MWLs fractions in contrast to the CEL96 fractions, indicating association with different xylans.

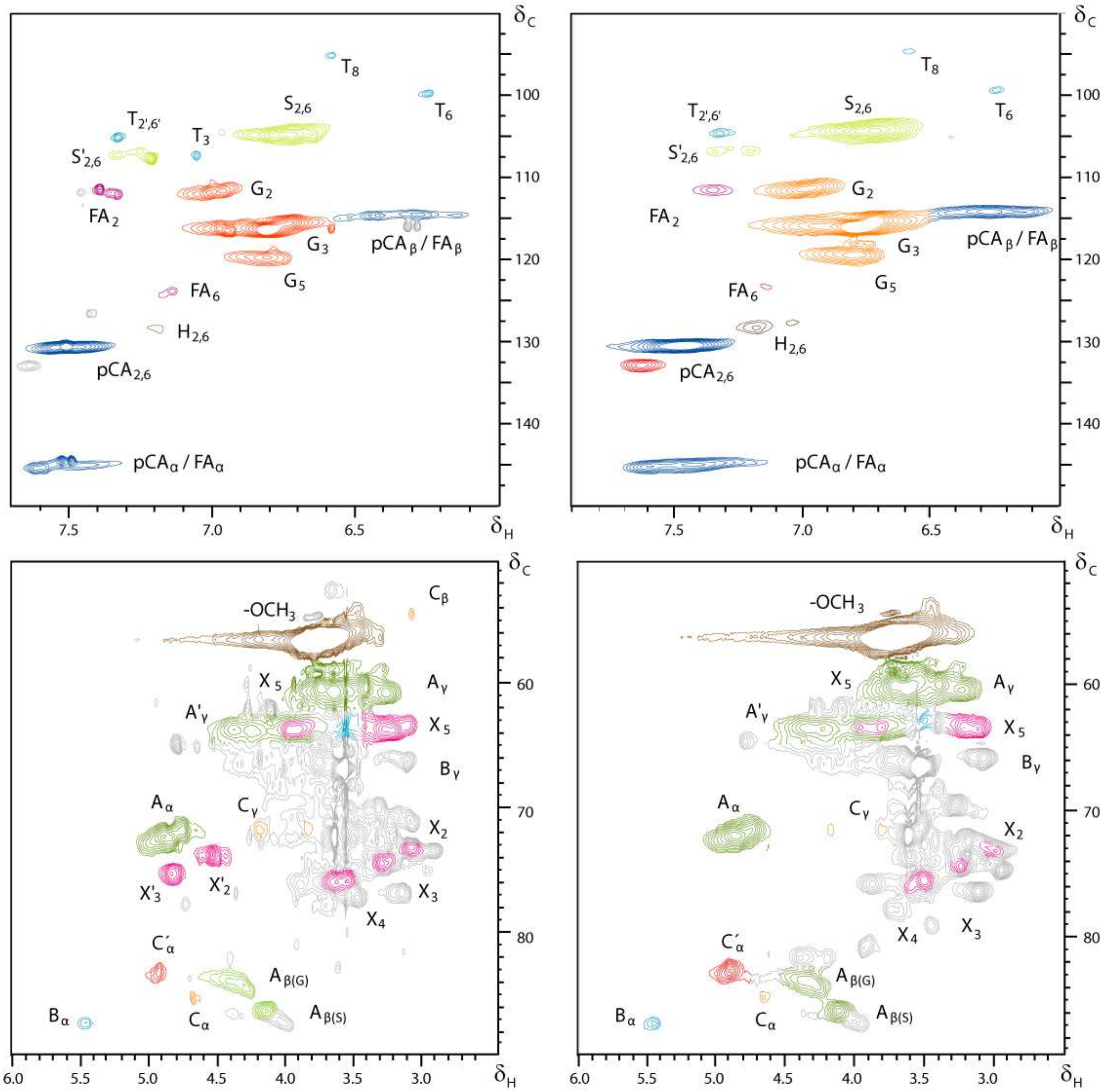

Figure 5: Expanded aromatic (δ_C/δ_H 90−150/5.0−7.7 ppm) and side chain (δ_C/δ_H 50−90/2.5−5.8 ppm) regions in the 2D HSQC NMR spectra of MWLc (left) and CEL (right), both isolated after 4 h ball milling. For signal assignments see Table 8. In Figure 6 the identified lignin substructures are depicted.

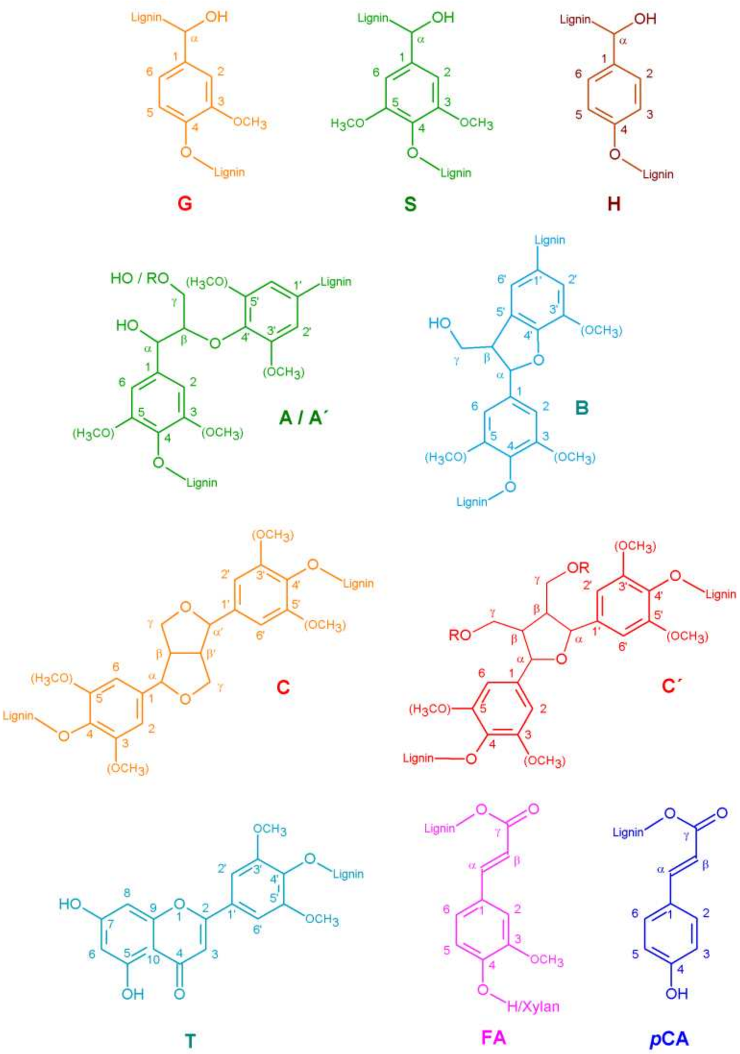

Figure 6: Lignin substructures considered for structural elucidation: (**S**) syringyl units, (**G**) guaiacyl units, (**H**) *p*-hydroxyphenyl units, (***p*CA**) *p*-coumaric acid (ester), (**FA**) ferulic acid (ester), (**A**) *β*-O-4´ substructures, (**B**) phenylcoumaran *β*-5´ substructures, (**C**) resinol *β*-*β*´ substructures, (**C´**) *γ*-acylated *β*-*β*´ tetrahydrofuran substructures, (**T**) tricin.

Comparing the monomeric ratios of the MWLc from depithd bagasse (DB) and the pith fraction (P) big differences in the G unit and H unit ratio can be found. The ratio of G units is much lower and the ratio of H units is much higher in the MWLc from P. For the CEL96 preparation the same trend can be observed, additionally higher ratio of S units in the CEL from P was observed (Table 7). Both MWLc and CEL96 from both fractions DB and P contain high amounts of *p*HCAs where *p*CA is strongly dominating over FA and the ratio FA/pCA is even more in favor of *p*CA in CEL96. Further, low tricin contents in the range of 0.8-3.6% could be determined. The relative abundances of the most important inter-unit linkages are in a very narrow range for MWLc and CEL96 from DB and P. Strikingly, an unusual high ratio of *γ*-acylated *β-β´* tetrahydrofuran structures (*β-β´ THF)* was found. The high amounts of *p*HCAs may strongly influence the *β-β´* coupling during lignin synthesis making a ring closure resulting in an usual resinol strucuture (C) impossible (del Río et al. 2008; Martínez et al. 2008).

Alkaline extraction before lignin isolation results in higher H unit ratios for all four lignin fractions. Observing the monomeric ratio the lignin fractions isolated from P seem much more affected by the alkaline extraction. MWLc from P after AE has a much lower S unit ratio and a much higher G unit ratio. For CEL from P there is also a strong decrease in S units after AE, but G units are decreasing here as well while the ratio of H units is much higher. As the ratio FA/*p*CA in all lignins isolated before AE, after AE this ratio is strongly shifted towards FA (Table 7). Comparing the contents of FA and *p*CA in CEL96 from DB isolated before and after AE, it can be seen that FA is almost untouched by the AE while *p*CA is almost completely removed, confirming that *p*CA is mainly ester-bound to the lignin macromolecule while FA is predominantly ether-bound (Ralph et al. 1994; Buranov and Mazza, 2008). Further, FA is removed to a higher extent by AE in the lignin preparations isolated from DB compared to the respective fractions from P, indicating that in the lignins from DB also contain ester-bound FA. Another effect of the AE and the resulting ester hydrolysis can be seen in the ratio of *β-β´ THF* substructures which are much less abundant in the lignin fractions isolated from the alkaline extracted bagasse fractions.

Table 8: Signal assignments of the $^{13}C-^{1}H$ correlation peaks in the 2D HSQC NMR spectra of the isolated sugar cane bagasse lignin fractions.

δ_C/δ_H (ppm)	assignment (label)
50.5 / 2.60	C_β-H_β in *γ*-acylated *β-β´* tetrahydrofuran substructures (**C´**$_\beta$)
53.2 / 3.44	C_β-H_β in phenylcoumaran *β*-5' substructures (**B**$_\beta$)
53.5 / 3.10	C_β-H_β in *β-β'* resinol substructures (**C**$_\beta$)
60.0 / 3.12-3.90	C_γ-H_γ in *γ*-hydroxylated *β*-O-4' substructures (**A**$_\gamma$)
62.5 / 3.70-4.30	C_γ-H_γ in *γ*-acylated *β*-O-4' substructures (**A'**$_\gamma$)
62.6 /3.37 and 3.82	C_5-H_5 in β-D-xylopyranoside (**X**$_5$)

63.8 / 3.61	C_{γ}-H_{γ} in phenylcoumaran β-5' substructures ($\mathbf{B_{\gamma}}$)
71.3 / 4.81	C_{α}-H_{α} in β-O-4' substructures ($\mathbf{A_{\alpha}}$) linked to a G unit
71.0 / 3.83 and 4.16	C_{γ}-H_{γ} in β-β' resinol substructures ($\mathbf{C_{\gamma}}$)
72.9 / 3.14	C_2-H_2 in β-D-xylopyranoside ($\mathbf{X_2}$)
73.5 / 4.61	C_2-H_2 in 2-O-acetyl-β-D-xylopyranoside ($\mathbf{X'_2}$)
74.1 / 3.32	C_3-H_3 in β-D-xylopyranoside ($\mathbf{X_3}$)
74.9 / 4.91	C_3-H_3 in 2-O-acetyl-β-D-xylopyranoside ($\mathbf{X'_3}$)
75.6 / 3.63	C_4-H_4 in β-D-xylopyranoside ($\mathbf{X_4}$)
83.4 / 4.93	C_{α}-H_{α} in γ-acylated β-β' tetrahydrofuran substructures ($\mathbf{C'_{\alpha}}$)
82.8 / 5.12	C_{β}-H_{β} in α-oxidized β-O-4' substructures ($\mathbf{A_{ox\ \beta}}$)
83.6 / 4.45	C_{β}-H_{β} in β-O-4' substructures ($\mathbf{A_{\beta(H)}}$) linked to a H unit
84.1 / 4.27	C_{β}-H_{β} in β-O-4' substructures ($\mathbf{A_{\beta(G)}}$) linked to a G unit
85.4 / 4.64	C_{α}-H_{α} in resinol β-β' substructures ($\mathbf{C_{\alpha}}$)
87.1 / 4.02	C_{β}-H_{β} in β-O-4' substructures ($\mathbf{A_{\beta(S)}}$) linked to a S unit
88.0 / 5.48	C_{α}-H_{α} in phenylcoumaran β-5' substructures ($\mathbf{B_{\alpha}}$)
94.8 / 6.58	C_8-H_8 in tricin ($\mathbf{T_8}$)
99.5 / 6.23	C_6-H_6 in tricin ($\mathbf{T_6}$)
103.8 / 6.70	$C_{2,6}$-$H_{2,6}$ in syringyl units ($\mathbf{S_{2,6}}$)
104.7 / 7.30	$C_{2,6}$-$H_{2,6}$ in tricin ($\mathbf{T_{2,6}}$)
105.3 / 7.03	C_3-H_3 in tricin ($\mathbf{T_3}$)
106.3 / 7.31	$C_{2,6}$-$H_{2,6}$ in oxidized (C_{α}=O) syringyl units ($\mathbf{S'_{2,6}}$)
110.8 / 6.95	C_2-H_2 in guaiacyl units ($\mathbf{G_2}$)
111.1 / 7.33	C_2-H_2 in ferulic acid (ester) ($\mathbf{FA_2}$)
115.4 / 6.78	C_5-H_5 in guaiacyl units ($\mathbf{G_5}$)
114.5 / 6.67	$C_{3,5}$-$H_{3,5}$ in p-coumaric acid (ester) ($\mathbf{pCA_{3,5}}$)
118.9 / 6.79	C_6-H_6 in guaiacyl units ($\mathbf{G_6}$)
122.2 / 7.15	C_6-H_6 in ferulic acid (ester) ($\mathbf{FA_6}$)
127.2 / 7.19	$C_{2,6}$-$H_{2,6}$ in p-hydroxyphenyl units ($\mathbf{H_{2,6}}$)
128.5 / 7.19	$C_{2,6}$-$H_{2,6}$ in p-coumaric acid (ester) ($\mathbf{pCA_{2,6}}$)
144.8 / 7.50	C_{α}-H_{α} in p-coumaric acid (ester) ($\mathbf{pCA_{\alpha}}$) and ferulic acid (ester) ($\mathbf{FA_{\alpha}}$)

4. Conclusions

- The isolation yield after 4 hours in planetary mill of CEL96 preparation was far higher than of MWLc preparations. The enzymatic digestion of the carbohydrates increases the accessibility for the solvent.
- The *p*-coumaric acid content was higher than ferulic acid content in the alkali extraction liquor.
- The lignin contents in the bagasse fractions were lower after the alkaline extraction as well as the carbohydrate contents. A big part of the sugars was extractable in alkali.
- The *β*-O-4´ linkage correlation peak was the most prominent inter-unit linkage signal found throughout all isolated lignin fractions.
- Both MWLc and CEL96 from both fractions DB and P contain high amounts of *p*HCAs.
- Alkaline extraction before lignin isolation results in higher H unit ratios for all four lignin fractions. The monomeric ratio of the lignin fractions isolated from P seems much more affected by the alkaline extraction.
- The ratio FA/*p*CA in all lignins isolated before AE is strongly in favor of *p*CA, after AE this ratio is strongly shifted towards FA.

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CAPÍTULO 3

Dissolving pulp production from Sugar Cane Bagasse

Abstract

The main goal of this study was characterizing the sugar cane bagasse two main fractions: pith and depithed bagasse, and evaluating the potential of the depithed for production of dissolving grade pulps. The depithed bagasse was chemically characterized and converted into brown pulp of two different extents of delignification' degrees (kappa 16.9 and 9.2) by the pre-hydrolysis soda process, which consists of bagasse treatment with hot water (15 min at 180^{o}C) followed by conventional soda pulping. The resulting pulps were fully bleached by the O-D-(EP)-D-P sequence and evaluated for their main dissolving pulp characteristics. The contents of cellulose, hemicelluloses and lignin in the pith and depithed bagasse varied significantly. For example, the lignin S:G:H of the pith and depithed bagasse were 1.0:1.6:1.8 and 1.0:2.1:2.0, respectively. The pre-hydrolysis pretreatment terminated at pH 3.4 and removed 29% of the depithed bagasse weight. The pre-hydrolysis soda process improves the xylan removal but decreases pulp yield. The bleached pulps showed similar glucans (~95%), xylans (~5.0%), ash (~0.4%), silica (~0.15%) and α-cellulose content (~92%) regardless of kappa number. The low viscosity values and the high ash and silica contents limit the uses of the bagasse pulps for certain dissolving grades applications, but it is useful for production of viscose rayon and CMC derivatives after some demineralization. The elucidation of the pith lignin S:G:H ratio and the production of high yield (35.1%) dissolving pulp from depithed bagasse fraction without bleaching cost penalties are the main novelties of this paper.

Keywords

Sugar cane bagasse, dissolving pulp, pre-hydrolysis, soda pulping.

1. Introduction

In recent years, there has been an increasing trend towards more efficient utilization of agro-industrial residues, including sugar cane bagasse. Several processes and products have been reported that utilize sugar cane bagasse as a raw material. These include production of dissolving pulp, paper pulp, ethanol and power (Pandey, et al., 2000).

The sugar cane (*Saccharum officinarum*) is a perennial grass, originating from Asia, but well adapted in most tropical and subtropical climates. Brazil is the largest producer of sugar cane in the world, followed by China, India, Thailand and Australia. In 2011/12, Brazil produced 571 million tons of sugar cane on 8.4 million ha of land, with an average productivity of 68 tons/ha (Conab, 2012). About 50.3% of this production was used to manufacture ethanol (22.9 billion liters), 47.3% to make sugar (36.9 million tons) and 2.4% was used to produce alcoholic beverages/candies (Conab, 2012). Wastes from sugar cane agro-industry are produced in large quantities. Hence about 140 kg of bagasse on a dry weight basis (CTC, 2012). This way, about 80 million tons of bagasse is generated per year in 8.4 million hectares of land (Conab, 2012).

Bagasse consists of approximately 40-50% cellulose and 20-30% of hemicelluloses and 18-25% lignin. Xylose is the main carbohydrate found in the hemicellulose fraction, representing about 80% of total sugars from hemicellulose (Aguilar et al., 2002; Mosier et al., 2005). Because of its low ash content (1-3%), bagasse offers numerous advantages in comparison to other crop residues such as rice straw and wheat straw, which contain ~17 and 11.0% of ash, respectively, (Pandey et al., 2000).

Sugar cane bagasse is a lignocellulosic material with potential for dissolving pulp production, especially when integrated into biorefinery processes (Wolf Ld., 2011). Dissolving pulps require a high degree of purity and are used for production of cellulose derivatives such as cellulose nitrate, cellulose acetate, methyl cellulose, rayon, carboxymethylcellulose among others. Compared to other types of paper pulp, dissolving pulp contains very little or no lignin, low hemicellulose content and very low levels of degraded cellulose.

There are different requirements of alpha cellulose content for different final uses of the dissolving pulp. According to Wizani et al. (1994), the desired alpha cellulose contents for rayon/cellophane, cellulose acetate and nitrocellulose are 90-92, 95-97 and 98%, respectively. All these derivatives require pulps containing very low or no lignin, low hemicelluloses and very low degraded cellulose.

According to Dhamodaran (2003), the chain-like high molecular weight cellulose polymer can be transformed into fibers or films of desired properties by spinning, casting, rolling, or extruding, from a melt or from solution. The natural and renewable cellulose polymer frequently occurs as fibers that are too short for textile uses. It cannot however be converted directly into longer fibers or into film because it can neither be melted nor simply dissolved in a solvent owing to strong hydrogen bonding in the material. A suitable cellulose derivative must first be prepared before it is possible to form a spinning solution from which cellulose can be regenerated. The commercially used systems for this purpose are the viscose process, to a lesser extent the cuprammonium and acetate process.

Soda pulping is traditionally the most used chemical pulping process for various non-wood raw materials including bagasse (Khristova et al. 2006; Enayati et al. 2009). The introduction of auto-hydrolysis (pre-hydrolysis) prior to any alkaline pulping process helps to produce pulp with a satisfactorily high content of alpha cellulose and with low hemicelluloses content (Behin and Zeyghami, 2009).

The novelty of this paper is the thorough chemical evaluation of the sugar cane bagasse pith fraction including lignin S:G:H ratio, which to the best of our knowledge has never being published. Also, the demonstration of the feasibility of producing high yield (35.1%) dissolving pulp from depithed bagasse fraction of sugar cane bagasse by terminating the cook at a kappa number higher than usual (kappa ~17) without significant penalty in bleaching cost.

The main goal of this study was characterizing the sugar cane bagasse two main fractions (pith and fibers), and evaluating the potential of the fibers for production of dissolving grade pulps.

2. Experimental

2.1. Working plan

Figure 1 depicts the working plan. The two fractions of the sugar cane bagasse (pith and fibers) were separated in a hammer mill and were characterized chemically. The whole bagasse was also characterized. The depithed bagasse fraction (fibers) was converted into brown pulp of two different delignification degrees (kappa 16.9 and 9.2) by the pre-hydrolysis soda process. The resulting pulps were fully bleached by the O-D-(EP)-D-P sequence and evaluated for their main dissolving pulp characteristics.

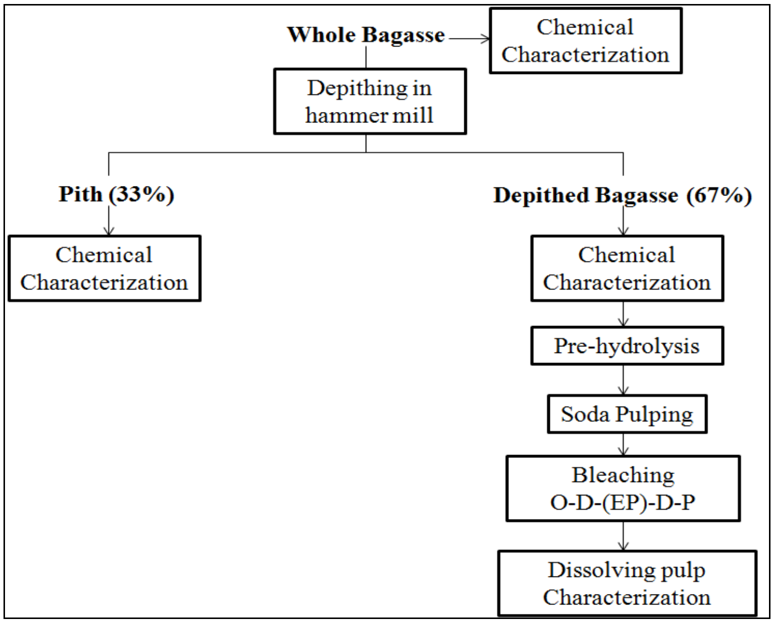

Figure 1. Working plan for bagasse fractionation, characterization and dissolving pulp production using the pre-hydrolysis soda process.

2.2. Material

About 150 kg of industrial whole bagasse was provided by a Brazilian pulp mill. About 100 kg of the whole bagasse was separated into two fractions (pith and depithed bagasse) by a hammer mill. The pith fraction represented 33% while the other 67% remained as depithed bagasse. The pith, depithed bagasse and whole bagasse were dried to about 85% dryness in an acclimated room ($23.0 \pm 1.0^{o}C$ and $50.0 \pm 2.0\%$ moisture) and stored in polyethylene bags for further use. The air-dried samples of pith, depithed bagasse and whole bagasse were ground in a Wiley mill, sieved, and the fraction that passed through a 40 mesh screen and was retained in the 60 mesh screen was collected, air dried and stored in wide mouth sealed flasks.

2.3. Methods

2.3.1. Chemical characterization of pith, depithed bagasse and whole bagasse

The following procedures were used for chemical analysis: moisture content (TAPPI T 264 om-88), total extractives content (TAPPI T 264 cm-97), acid soluble lignin (Goldschinid, 1971), Klason lignin (Gomide and Demuner, 1986), lignin syringyl/guaiacyl ratio (Lin and Dence, 1992), preparation of biomass for sugar analysis (TAPPI T 249 cm-85), sugar analysis (Wallis et al., 1996), acetyl groups (Solar et al., 1987), uronic acids (Scott, 1979), silica (TAPPI T 245 cm-98) and ash (TAPPI 211 om 93).

2.3.2. Pre-hydrolysis of the depithed bagasse

The pre-hydrolysis of the depithed bagasse was carried out in a M/K digester (Systems Inc., Massachusetts - USA) with a capacity of 7 liters, equipped with forced circulation and heat exchanger devices. It was conducted using the following parameters: ratio of water/biomass 8:1 l/kg, temperature 180°C, 60 min to temperature and reaction time of 15 min at temperature. The pre-hydrolysis experiments were carried out according to Colodette et al., 2011. Optimal conditions were identified for the various raw materials on the basis of yield, xylans removal and cellulose molecular weight. Note that the bagasse samples were not washed after the pre-hydrolysis treatment; they were immediately treated with the soda pulping process. The following procedures were used for analysis of the pre-hydrolyzed material: total extractives content (TAPPI T 264 cm-97), acid soluble lignin (Goldschinid, 1971), Klason lignin (Gomide and Demuner, 1986), lignin syringyl/guaiacyl ratio (Lin and Dence, 1992), preparation of biomass for sugar analysis (TAPPI T 249 cm-85), sugar analysis (Wallis et al., 1996), acetyl groups (Solar et al., 1987), uronic acids (Scott, 1979), silica (TAPPI T 245 cm-98) and ash (TAPPI 211 om-93).

2.3.3. Soda pulping

The soda pulping of the depithed bagasse was carried out in the same equipment used for the pre-hydrolysis treatment, aimed at producing pulps with two different delignification degrees (16.9 and 9.2), using the following parameters: ratio of liquor/biomass 8:1 l/kg, maximum temperature 180°C, time to maximum temperature of 60 min, time at maximum temperature of 20 min, and 12.5 and 15.0% alkali charges, to reach kappa number 16.9 and 9.2, respectively.

After cooking, the chips were placed in stainless steel screen box of 150 mesh and were washed thoroughly with running water. The disintegration of the fibers was performed in a laboratorial "hydrapulper" of 25 liters capacity. The pulp was classified in a "Voith" laboratorial screener equipped with 0.20 mm slotted plate, centrifuged to a consistency of about 30% and then stored in polythene bags. The following procedures were used for soda pulp analysis: Brightness (TAPPI T452 om-08), kappa number (TAPPI T236 om-06), viscosity (TAPPI T230 om-08), sugar analysis (Wallis et al., 1996), silica (TAPPI T245 cm-98) and ash (TAPPI 211 om-93).

2.3.4. ECF Bleaching

The two pulps resulting from the pre-hydrolysis soda process at kappa 16.9 and 9.2 were fully bleached by the O-D_0-(EP)-D_1-P sequence, where: O = simple stage oxygen delignification; D_0 = chlorine dioxide delignification stage; (EP) = alkaline extraction with hydrogen peroxide; D_1 = chlorine dioxide bleaching stage; P = hydrogen peroxide bleaching stage. Table 1 describes the conditions used in each bleaching stage. The O stage was carried out in a Teflon-lined Mark V (Quantum Technologies Inc.) mixer/reactor, with samples of 300g absolutely dry pulp. The desired charges of $MgSO_4$, NaOH and O_2 were added to the reactor, in this order, after the desired temperature was reached. After the total reaction time elapsed, the system was depressurized and the pulp discharged. The D_0 and D_1 stages were carried out in polyethylene bags. The bleaching liquor containing ClO_2, H_2O, NaOH or H_2SO_4 was added to the pulp at room temperature. The application of sulfuric acid or sodium hydroxide to control the pH was determined in previous experiments with mini-samples of pulp. After hand mixing in polyethylene bags, the material was heated in a microwave oven to the desired temperature and transferred to a steam bath with temperature control and was maintained for the time predetermined. The same procedure aforementioned was used in the (EP) and P stages, except for the bleaching liquor that in this case was comprised of H_2O, NaOH, H_2O_2 added to the pulp in this order.

After each bleaching stage, the residual liquor was extracted for pertinent analysis and the pulp samples were washed with an equivalent of 9m^3 of distilled warm water per ton of dry pulp. All experiments were run in duplicate.

Table 1. General conditions used for bleaching of the kappa 16.9 and 9.2 pre-hydrolysis soda pulps

Parameters	**Kappa Number 16.9**					**Kappa Number 9.2**				
	O	**D**	**(EP)**	**D**	**P**	**O**	**D**	**(EP)**	**D**	**P**
Consistency, %	10	12	12	12	10	10	12	12	12	10
Temperature, °C	105	60	80	80	80	105	60	80	80	80
Time, min	60	40	90	120	120	60	40	90	120	120
Pressure, kPa	600	-	-	-	-	600	-	-	-	-
O_2, kg/odt	20.0	-	-	-	-	20.0	-	-	-	-
ClO_2, as Cl_2, kg/odt	-	28.0	-	10.0	-	-	26.0	-	10.0	-
H_2O_2, kg/odt	-	-	3.0	-	5	-	-	3.0	-	5.0
NaOH, kg/odt	20.0	-	8.0	0.8	7	15.0	-	8.0	0.8	7.0
H_2SO_4, kg/odt	-	1.0	-	-	-	-	2.0	-	-	-
$MgSO_4$, kg/odt	1.5	-	1.5	-	-	1.5	-	1.5	-	-

Brightness (TAPPI T452 om-08), brightness reversion (TAPPI UM200), kappa number (TAPPI T236 om-06) and viscosity (TAPPI T230 om-08) were measured for characterization of the depithed bagasse pulps after each stage of bleaching.

2.3.5. Dissolving pulp characterization.

The bleached dissolving pulps were characterized for their contents of alpha cellulose (TAPPI T203 om-93), sugars (Wallis et al., 1996), silica (TAPPI T245 cm-98) and ash (TAPPI 211 om-93).

2.3.6. Statistical analysis

The statistical analysis was performed using the Statistic 7.0 software. A variance analysis was carried out using a significance level of 5%. The tested hypotheses were the following:

H_0: all averages are equal, there is no significant difference between samples, and
Ha: At least one of the averages is statistically different from the others.

When the ANOVA showed significant differences among the samples, the Tukey test was applied.

3. Results and Discussion

3.1. Chemical characterization of sugar cane bagasse biomass

The contents of cell wall structural constituents (cellulose, hemicelluloses and lignin) in the pith, depithed bagasse and whole bagasse varied significantly (Table 2), with the pith showing higher lignin and lower xylans and glucans contents than the depithed bagasses. Xylans are the main hemicelluloses of pith and depithed bagasses, with the contents of galactans, mannans and arabinans of these materials being rather low. The whole bagasse presented structural chemical composition intermediate between the pith and depithed bagasse pulp, reflecting their proportions in the whole bagasse.

The content of xylans in the pith (12.4%) is only about half of that present in the depithed bagasse (22.1%) while the glucans contents were 37.8% and 43.4%, respectively, for pith and depithed bagasse. The lignin S/G ratio for pith and depithed bagasse were similar in the range of 50/50%. The acetyl group content in the pith (0.5%) was much lower than that in the depithed bagasse (2.6%), but the contents of uronic acids of these materials were similar.

The pith presented much larger amounts of non-structural constituents (extractives and minerals) in relation to depithed bagasse. The amount of ethanol/toluene extractives and minerals in the pith were 13.4 and 9.5%, respectively, against 6.1 and 1.3% in the depithed bagasse, respectively. The silica was responsible for 78.9% and 30.8% of the pith and depithed bagasse mineral contents, respectively. The whole bagasse presented non-structural chemical composition in between the pith and depithed bagasse ones, reflecting their proportions in the whole bagasse.

Table 2. Chemical Composition of sugar cane bagasse in percentage of biomass dry weight

Analyses , %	Whole Bagasse	Pith	Depithed Bagasse
Klason lignin	21.3	23.2	20.2
Acid soluble lignin	1.2	1.0	1.4
Total lignin	22.5	24.2	21.6
Lignin H:G:S	1.0 : 1.9 : 1.9	1.0 : 1.6 : 1.8	1.0 : 2.1 : 2.0
Glucans	41.6	37.8	43.4
Xylans	18.9	12.4	22.1
Galactans	0.5	0.6	0.5
Mannans	0.0	0.0	0.0
Arabinans	1.2	0.9	1.4
Uronic acids	1.0	0.9	1.0
Acetyl	1.9	0.5	2.6
Total Sugars**	65.0	52.9	71.1
Ash	4.0	9.5	1.3
Silica	2.7	7.5	0.4
Extractives	8.5	13.4	6.1
Grand Total, %**	100	100	100

*include glucans, xylans, galactans, mannans, arabinans, uronic acids and acetyl groups.

**include total lignin, total sugars, ash and extractives.

Lignin content of this bagasse was similar to values reported in literature. Values in the range of 22%-23% were reported by Rainey, (2009). Luz et al. (2007) have reported values of 43.8%, 28.6%, 23.5%, 1.3% and 2.8% for cellulose, hemicelluloses, lignin, ash and other components, respectively. High ash contents on bagasse have been reported by Wolf, 2011. The very high content of extractives in the pith fraction has been reported elsewhere (Wolf, 2011; Pitarelo, 2007).

Considering the low content of fibers in the pith and rather inadequate chemical composition for making dissolving pulp, this fraction was not considered for this application. The high extractive and mineral contents are quite challenging for dissolving pulp production. Besides causing a variety of operational problems (scaling, corrosion, pitch deposition, chemical degradation during bleaching, recovery boiler plugging, etc), minerals and extractives may cause severe difficulties during utilization of the dissolving pulp for production of cellulose derivatives, if not properly removed during the process.

3.2. Pre-hydrolysis Treatment

In this study, the pre-hydrolysis pretreatment with hot water showed 71.0% yield and a final pH of 3.4. During the pre-hydrolysis, acetic acid is released from O-acetyl groups in the xylans, which lowers the pH of the extract to value in the range of 3-4 (Chen et al., 2010). Table 3 shows the characteristics of the pulps before and after the pre-hydrolysis treatment as well as the values of mass loss for each biomass component across the treatment.

Table 3. Chemical Composition of depithed bagasse, in percentage of biomass dry weight, before and after the pre-hydrolysis treatment and material loss across the pre-hydrolysis treatment*

Analyses , %	Depithed Bagasse	Pre-hydrolyzed* Depithed Bagasse	Material Loss Across Pre-hydrolysis
Klason lignin	20.2	18.0	36.7
Acid soluble lignin	1.4	0.7	64.5
Total lignin	21.6	18.7	38.5
Lignin H:G:S	1.0 : 2.1 : 2.0	1.0 : 1.9 : 1.7	-
Glucans	43.4	61.0	0.2
Xylans	22.1	10.5	66.3
Galactans	0.5	0.0	100.0
Mannans	0.0	0.0	-
Arabinans	1.4	0.2	89.9
Uronic acids	1.0	0.2	85.8
Acetyl	2.6	1.1	69.9
Total Sugars**	71.1	72.9	27.2
Ash	1.3	0.8	53.3
Silica	0.4	0.5	11.3
Extractives	6.1	7.6	11.5
Grand Total, %***	100	100	-
Yield, %	-	71	-

*pre-hydrolysis pretreatment: water/biomass: 8:1 l/kg, temperature: 180°C, time to temperature: 60 min, time at temperature: 15 min.

**includes glucans, xylans, galactans, mannans, arabinans, uronic acids and acetyl groups.

***include total lignin, total sugars, ash and extractives.

The pre-hydrolysis pretreatment terminated at pH 3.4 and removed 29% of the depithed bagasse weight. The remaining 71% material was comprised of lignin, xylans, glucans, arabinans, acetyl groups, uronic acids, inorganics, silica, and extractives. The losses of the components across the pre-hydrolysis were significant; only the loss of glucans was insignificant (Table 3).

The pre-hydrolysis promoted a significant decrease in the amount of hemicelluloses present in the depithed bagasse with a consequent proportional increase in the content of cellulose.The hemicelluloses are dissolved as oligomers after acid hydrolysis of the polymeric structures (Chen et al., 2010). Subsequently, a fraction of the hemicellulose oligomers in solution are further hydrolyzed to monomer sugars and sugar degradation products. Sugar degradation products include hydroxymethylfurfural (HMF) formed from hexose sugars and furfural formed from pentoses and uronic acids (Chen et al., 2010).

A fraction of the lignin removed in the pre-hydrolysis treatment (38.5%) was caused by partial depolymerization by the acidic conditions of the pretreatment; complete delignification is not possible using hot water alone, because of the re-condensation of soluble components originated from lignin (Alvira et al., 2010). The loss of acetyl groups was 69.9% but it could have been higher if the bagasse contained more acetyl groups; it has been reported that acetyl groups removal increases with decreasing pre-hydrolysis pH and this pH is closely related to the amount of acetyl groups originally present in the biomass (Batalha et al, 2012). The removal of uronic acid groups (85.8%) is important for production of dissolving pulps because they may cause pulp brightness instability after being converted into hexenuronic acids during alkaline pulping (Sixta, 2006). The glucans increase occurs as a consequence of lignin, xylan, mineral, uronic acid, and acetyl group removal, which in turn negatively affects the process yield.

The mineral removal is also very important for dissolving pulp production, because the minerals may cause corrosion and deposits in the digester and bleaching equipment, decrease pulp bleachability, viscosity and brightness stability. An effective way of decreasing pulp silica content is by effective washing of the biomass prior to processing in order to remove sand (Sixta, 2006). The extractives removed (11.5%) during the pre-hydrolysis are mainly comprised of hot water soluble substances such as tannins, sugars, gums, pigments and starches (Li, 2004).

3.3. Soda Pulping

The pre-hydrolyzed depithed bagasse was cooked by the soda process according to conditions previously optimized in our laboratories. The screened yields and overall yields, including pre-hydrolysis and soda pulping, were higher for the pulp with high kappa number. The brightness and viscosities values varied significantly between the two pulps. The reject contents were very low in both cases. Both the cellulose and hemicelluloses remaining in the bagasse after the pre-hydrolysis pretreatment presents lower molecular weight than those in the original material and tend to solubilize in larger extent during the alkaline cooking than the untreated material (Colodette, et al., 2011). This results in lower pulp yield if compared with pulps produced by alkaline pulping processes, without the pre-hydrolysis treatment (Table 4).

Table 4. Soda pulping* results for pre-hydrolyzed depithed bagasse chips

Kappa Number	Alkali (%)	Rejects (%)	Soda Pulping Screened Yield - (%)	Pre-hydrolysis + Soda Pulping Screened Yield - (%)	Brightness (%ISO)	Viscosity (dm^3/kg)
16.9	12.5	0.1^a	49.5^a	35.1^a	34.4^a	809^a
9.2	15.0	0.1^a	47.6^b	33.8^b	41.1^b	716^b

*Soda pulping conditions: liquor/biomass: 8:1 l/kg, maximum temperature: 180°C, time to maximum temperature: 60 min, time at maximum temperature: 20 min.

Note: The averages marked with the same the letters in each column, are not significantly difference by Tukey's test at a 5% significance level.

According to Colodette, et al., 2011, the xylan removal by pre-hydrolyses prior to alkaline pulping decreases pulping yield significantly and the low stability of the carbohydrates remaining in the chips after the pre-hydrolysis treatment toward alkaline (Kraft or Soda) cooking may be explained by two factors: (1) the xylans remaining in the auto-hydrolyzed (pre-hydrolyzed) chips are very sensitive to alkaline cooking conditions because they are severely degraded, possessing very low molecular weight and being largely soluble in alkali; (2) the cellulose chains become more susceptible to alkaline cooking because the xylan layer existing over the cellulose fibrils is partially removed, exposing the cellulose to alkali attack with consequent decrease in molecular weight and increased polydispersity.

Conventional soda pulping, without pre-hydrolysis, removes about half of the bagasse xylans. For example, in the work of Rainey, (2012), it was found 23.3% of xylans in the pulp derived from a soda cook that yielded 54.6%. If we consider that the original sugar cane bagasse contains about this same amount of xylans (22.1% in our study), it can be inferred that the xylan loss across de conventional soda cook was about 45.4%. On the other hand, in the pre-hydrolysis-soda pulping, the total yield including pre-hydrolysis and soda pulping were 35.1% and 33.8% for the pulps produced at kappa 16.9 and 9.2, respectively. The xylan content of the final pulp was 4.8% for both pulps. Thus, the xylan loss across the pre-hydrolysis-soda pulping was 92.4% and 92.7%, respectively. This indicates that the pre-hydrolysis treatment has a very large effect on the pulp xylan content, but it is obvious the soda pulping also causes xylan losses.

The carbohydrate composition of the depithed bagasse pulps with kappa 16.9 and 9.2 were somewhat similar with 92.4% and 93.7% glucans and 4.8% and 4.8% xylans, respectively. The amount of minerals and silica were also very similar for both pulps (~0.4% ash and 0.2% SiO_2). The xylan retention in the soda pulps derived from pre-hydrolysis (4.8%) were very low in relation to the non-hydrolyzed (22.1%) and only pre-hydrolyzed (10.5%) depithed chips. The xylans losses across cooking were 77.4 and 78.2% for the pre-hydrolyzed pulps with kappa 16.9 and 9.2, respectively. The mineral content decreased by 72.2% and 74.4% during soda cooking to kappa 16.9 and 9.2 pulps, respectively (Table 5).

Table 5. Pre-hydrolyzed depithed bagasse and pre-hydrolysis soda pulp chemical composition, in percentage of biomass dry weight, and material loss across soda pulping.

Analyses , %	**Pre-hydrolyzed Depithed Bagasse***	**Pre-hydrolysis Soda Pulp at kappa 16.9****	**Pre-hydrolysis Soda Pulp at kappa 9.2****	**Material Loss Across Soda Pulping at kappa 16.9**	**Material Loss Across Soda Pulping at kappa 9.2**
Klason lignin	18.0	-	-	-	-
Acid soluble lignin	0.7	-	-	-	-
Total lignin	18.7	-	-	-	-
Lignin H:G:S	1.0 : 1.9 : 1.7	-	-	-	-
Glucans	61.0	92.4	93.7	25.0	26.9
Xylans	10.5	4.8	4.8	77.4	78.2
Galactans	0.0	-	-	-	-
Mannans	0.0	-	-	-	-
Arabinans	0.2	-	-	-	-
Uronic acids	0.2	-	-	-	-
Acetyl	1.1	-	-	-	-
Total Sugars***	72.9	97.2	98.5	34.0	35.7
Ash	0.8	0.45	0.43	72.2	74.4
Silica	0.5	0.22	0.25	78.2	76.2
Extractives	7.6	-	-	-	-
Grand Total, %****	100	98.0	99.2	-	-
Yield, %	71	-	-	-	-

*pre-hydrolysis pretreatment: water/biomass: 8:1 l/kg, temperature: 180°C, time to temperature: 60 min, time at temperature: 15 min.

**Soda pulping conditions: liquor/biomass: 8:1 l/kg, maximum temperature: 180°C, time to maximum temperature: 60 min, time at maximum temperature: 20 min, 12.5% and 15% active alkali for kappa 16.9 and 9.2, respectively.

***includes glucans, xylans, galactans, mannans, arabinans, uronic acids and acetyl groups.

****include total lignin, total sugars, ash and extractives.

3.4. ECF Bleaching

The pre-hydrolysis soda pulps were bleached by the O-D-(EP)-D-P sequence to a target brightness of 88% ISO. The oxygen delignification (O) efficiencies, compared at fixed conditions and similar final reaction pH (10.9-11.2) was higher for the kappa 16.9 pulp (76.3%) in relation to that of the kappa 9.2 pulp (67.4%) with the pulps achieving 59.1 and 62.0% ISO brightness values, respectively, after the O-stage. The oxygen delignification efficiency is calculated on the basis of kappa number before and after the oxygen stage. The behavior of brightness, kappa number and viscosity across the O-D-(EP)-D-P sequence are shown in Figure 2.

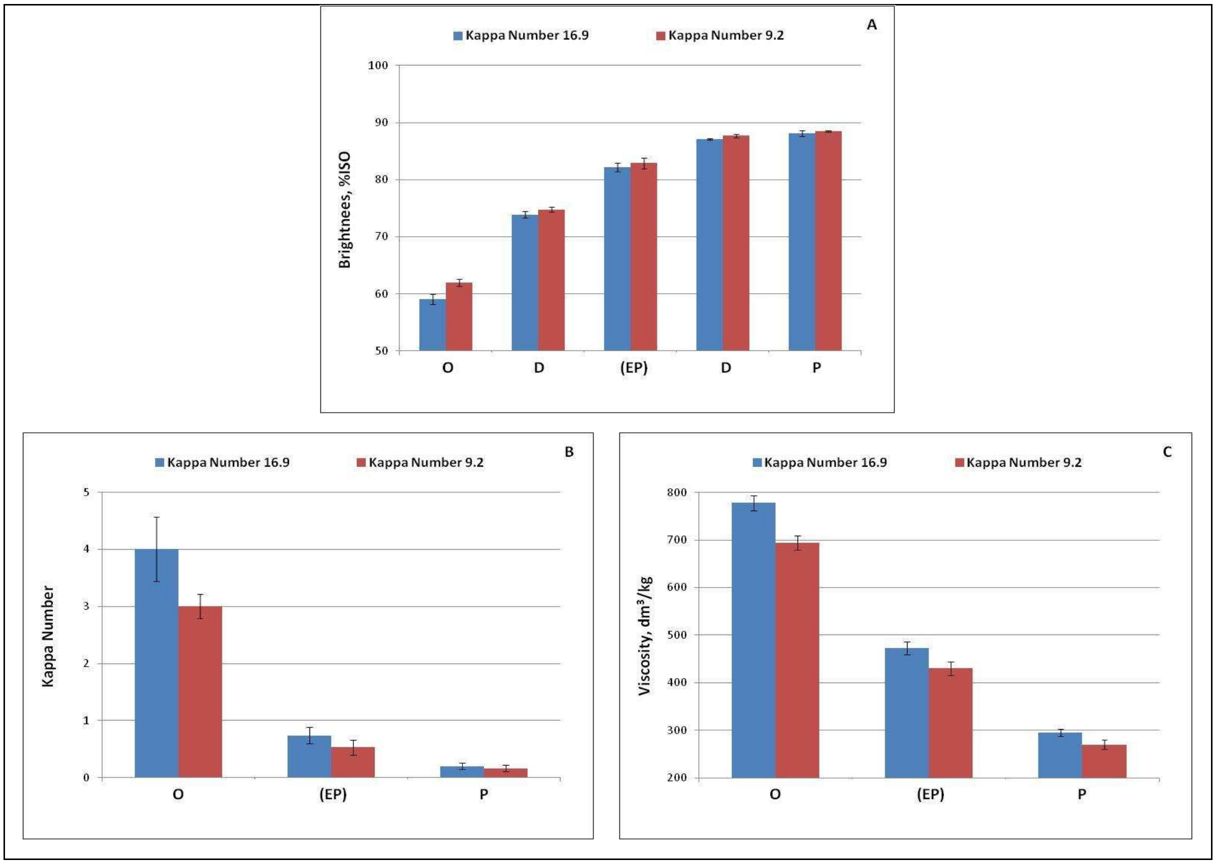

Figure 2. Brightness (A), Kappa number (B) and Viscosity (C) profile across the O-D-(EP)-D-P sequence for pulps of kappa number 16.9 and 9.2.

No significant brightness changes were observed between the pulps of kappa number 16.9 and 9.2. Except for the oxygen delignification stage, where the difference in brightness values is significantly higher than the next stages of bleaching, due to the initial difference in kappa number values after cooking. The last bleaching stage did not provide a significant brightness increase; hence, it could be deleted from the sequence without major consequences on pulp quality but with reduced reagent consumption. The reinforcing an extraction stage with H_2O_2 (EP) increase the amount of lignin removed, resulting in substantial reduction in kappa number after this stage, values of 0.7 and 0.5 were found for the pulps of kappa number 16.9 and 9.2, respectively. Despite the low final kappa number values of the samples (~0.20 for both pulps), the brightness values were practically unchanged in the final stages of bleaching. The more severe cooking conditions used to obtain the 9.2 kappa pulp caused a decrease in pulp carbohydrates contents with negative reflex on viscosity, this profile is observed in all stages of bleaching. The viscosity drop after stage (EP) are explained by the high demand of chlorine dioxide in the initial D_0 stage and by the hydrogen peroxide used in stage (EP). The decomposition of hydrogen peroxide in the alkaline conditions generates free radicals which attack the cellulose fibers, thus reducing the viscosity of the pulp. The bleached pulp final viscosities were 295 and 270 dm^3/kg for the kappa 16.9 and 9.2 pulps, respectively.

The overall bleaching chemical consumptions by the 16.9 and 9.2 kappa pulps, measured as total active chlorine, were 54.8 and 52.7 kg/odt pulp, respectively, to achieve an ISO brightness of about 88% (Table 6). The post color numbers values were in the range of 0.11-0.13 for both bleached pulps, indicating high brightness stability. The summary results of the bleaching by O-D-(EP)-D-P sequence is showed in Table 6.

Table 6. Summary results of the bleaching by O-D-(EP)-D-P sequence.

Bleaching Parameter	Kappa Number 16.9	Kappa Number 9.2
Total Active Chlorine[*],	54.8^a	52.7^b
Brightness, % ISO	88.1^a	88.5^a
Post Color Number	0.11^a	0.13^a
Viscosity, dm^3/kg	295^a	270^b
Kappa Number	0.20^a	0.16^a

[*] Total Active Chlorine (kg/odt) = ClO_2 (kg/odt)*2.63 + H_2O_2 (kg/odt)*2.09.

Note: The averages marked with the same letters in each line, are not significantly difference by Tukey's test at a 5% significance level.

3.5. Dissolving pulp characteristics

The pre-hydrolyzed bleached pulps showed similar glucans (~94.5%), xylans (~4.7%), ash (~0.4%), silica (~0.15%) and α-cellulose content (~91.5%) regardless of initial kappa number (Table 7).

Table 7. Characteristics of the dissolving pulps derived from pre-hydrolysis soda pulping of depithed bagasse to kappa number 16.9 and 9.2.

Brown pulp kappa number	% Glu	% Xyl	% Ash	% Silica	% α-Cellulose
16.9	94.4^a	4.6^b	0.42^c	0.14^d	91.8^e
9.2	94.7^a	4.7^b	0.43^c	0.16^d	91.3^e

Note: The averages marked with the same the letters in each column, are not significantly difference by Tukey's test at a 5% significance level.

The efficiency of conversion of cellulose into specific derivatives is dependent upon hemicelluloses content of the dissolving pulp (Christov et al., 1998). Hemicelluloses are undesirable impurities in dissolving pulps, affecting the cellulose processability, e.g. the filterability and the xanthanation in the viscose production process, and end product properties such as viscose strength. In this study, a bagasse bleached pulp containing 4.6% and 4.7% xylan was achieved (Table 7), values that are acceptable for viscose grade dissolving pulp applications (Chistov et al., 1998).

The mineral content of the bleached bagasse pulp were within acceptable levels. Barba et al., (2002) showed that carboxymethhylcellulose (CMC) can be produced from non-woody dissolving pulps, with an ash content of about 0.7%.

The α-cellulose content is in agreement with the values (>90%) reported in the literature for viscose grade pulps (Christov et al., 1998; Behim and Zeyghami, 2009).

The low viscosity of the bleached bagasse pulp, 295 and 270 dm^3/kg for the kappa 16.9 and 9.2 pulps, respectively, somewhat limits its uses for certain dissolving grades applications such as acetate and nitrate; but it could be useful for production of viscose rayon and carboxymethhylcellulose (CMC) derivatives. According to Henriksson et al., 2005 and Kvarnlof et al., 2006 during the viscose process, it is necessary to decrease pulp viscosity to values in the range of 200-300 dm^3/kg via a pre-aging stage, since a high viscosity affects the cellulose process ability. The viscosity reduction in pulps increasing the accessibility and reactivity of cellulose. According to Ibarra et al. (2010), high reactivity cellulose could improve the homogeneity and quality of cellulose-end products and decrease the demands of reactants, e.g. use of carbon disulfide in the viscose manufacture, reducing production costs and the environmental impact. The same author reported that the low charges of certain monocomponent endoglucanases, preferably with cellulose-binding domain and inverting glycosidic hydrolysis mechanism, could be efficiently used prior to viscose production to enhance the reactivity and reduce the viscosity of pulps.

4. Conclusions

- The pre-hydrolysis soda pulping followed by ECF bleaching with the sequence O-D-(EP)-D-P sequence is adequate for producing dissolving pulp from depithed bagasse, regardless of kappa number (16.9 and 9.2). However, terminating the cook at a higher kappa number is more cost effective due to higher pulping yield.

- The bagasse pre-hydrolysis soda process applied to dissolving pulp improves the xylan removal but decreases pulp yield.
- The low viscosity limits the uses of the bagasse pulps for certain dissolving grades applications such as acetate and nitrate; but it is useful for production of viscose rayon and CMC derivatives.

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CAPÍTULO 4

Production of Printing and Writing Paper Grade Pulp of Sugar Cane Bagasse

Abstract

The main goal of this study was evaluating the potential of the depithed bagasse for the production of printing and writing paper. Industrial whole bagasse was separated into two fractions: pith and depithed bagasse. The depithed bagasse was cooked by the soda process to two different degrees of delignification. The resulting pulps were fully bleached by the O-D*-(EP)-D sequence and characterized for their beatability, drainability and physical-mechanical properties. The bleached soda pulps cooked to 17.5 and 10.8 kappa numbers showed similar refinability, resistance to drainage, and the strength properties (tensile, burst and tear). It was concluded that both 10.8 and 17.5 kappa pulps from depithed sugar cane bagasse are suitable for the production of printing and writing paper grade pulps, but the higher kappa pulp is more economically attractive given its higher pulping yield, without significantly increasing the bleaching chemical demand.

Keywords

Sugar cane bagasse, printing and writing paper, soda pulping.

1. Introduction

In recent years, there has been an increasing trend towards more efficient utilization of agro-industrial residues, including sugar cane bagasse. Several processes and products have been reported that utilize sugar cane bagasse as a raw material. Among the many agricultural fibers used for pulp manufacture, sugar cane bagasse is the one with most promise. The sugar cane (*Saccharum officinarum*) is a perennial grass, originated from Asia, but well adapted in most tropical and subtropical climates. Brazil is the largest producer of sugar cane in the world.

In 2011/12, Brazil produced 571 million tons of sugar cane on 8.4 million ha of land, with an average productivity of 68 tons/ha [1]. Wastes from sugar cane agro-industry are produced in large quantities. Each processed sugar cane ton generates about 140 kg of bagasse on a dry weight basis [2]. Approximately 80 million tons of bagasse are generated per year on 8.4 million hectares of land [1]. This wasted material can potentially be used for producing high-added value pulp, such as the production of printing and writing pulp grades. Brazil is predominant in the production of significant volumes of packaging, printing and writing, and paperboard grades of paper. In 2011, Brazil was positioned as the 9th world producer of paper, and in 2012, it produced 10.1 million ton of paper [3].

Sugar cane bagasse is a lignocellulosic material with potential for printing and writing papers production, especially when integrated into biorefinery processes [4, 5]. Bagasse is a low cost raw material and has high carbohydrate content (51%-78%), which is suitable for papermaking [4, 5, 6, 7, and 8]. In addition, it provides longer fiber than straw, low refining energy consumption, and good sheet formation, as well as paper smoothness [9]. These are relevant raw material traits for pulp production and other industrial uses. The bagasse pulp is generally comparable to hardwood pulps [10].

The soda pulping process is widely applied for non-wood material all over the world [11, 12]. The cooking chemical is sodium hydroxide and the amount needed depends on the particular fiber raw material. The cooking temperature also depends on the cooking time and alkali charge. Typical NaOH charge is around 16% and typical cooking temperature is 140 to 170°C [13-16]. Its main advantage in relation to the traditional kraft process is the non-use of sulfur-based chemicals, which minimizes air emissions and facilitates the recovery of pulping chemicals. But the soda process produces lower pulp yield in relation to the kraft process [17].

According to Foelkel [18], the required properties for printing and writing papers are: smoothness, opacity, formation, bulk, porosity, printability, strength and dimensional stability. They may be obtained with short and small diameter fibers, such as eucalyptus and bagasse fibers.

The main goal of this study was evaluating the potential of the depithed bagasse for the production of printing and writing paper pulp at two levels of delignification (kappa 17.5 and 10.8).

2. Experimental

2.1. Working plan

Figure 1 depicts the working plan. The two fractions of the sugar cane bagasse (pith and fibers) were separated in a hammer mill. The depithed bagasse fraction (fibers) was soda pulped to two different levels of delignification (kappa 17.5 and 10.8). The resulting brownstock pulps were fully bleached by the O-D*-(EP)-D sequence, and subsequently, characterized for their beatability, drainability and physical-mechanical properties.

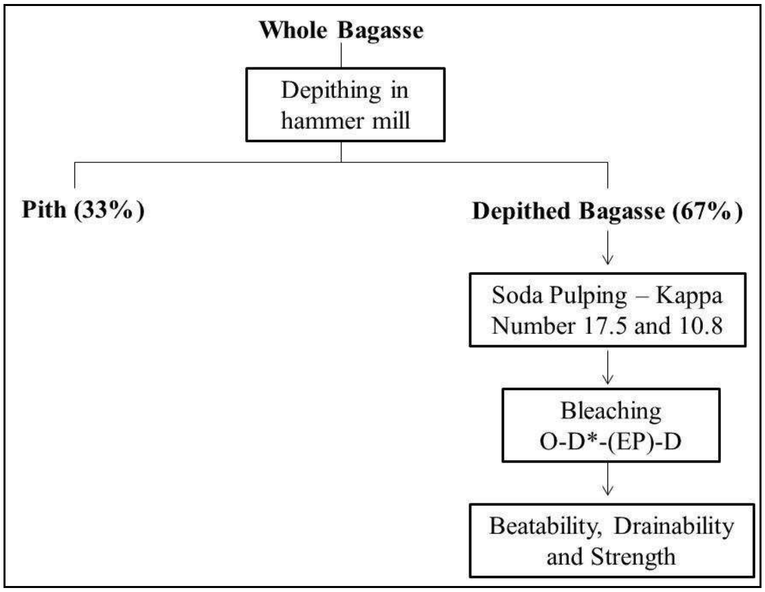

Figure 1. Working plan for bagasse fractionation.

2.2. Material

About 150 kg of industrial whole bagasse was provided by a Brazilian pulp mill. About 100 kg of the whole bagasse was separated into two fractions (pith and depithed bagasse) by a hammer mill. The pith fraction represented 33%, while the other 67% remained as the depithed bagasse. The pith, depithed bagasse and whole bagasse were dried to about 85% dryness in a conditioning room (23.0 ± 1.0°C and 50.0 ± 2.0% humidity) and stored in polyethylene bags for further use. The air-dried samples were ground in a Wiley mill and sieved, and the fraction that passed through a 40 mesh screen but was retained by a 60 mesh screen was collected.

2.3. Methods

2.3.1. Soda pulping

The soda pulping of the depithed bagasse was performed with a M/K laboratory digester (Systems Inc., Massachusetts - USA) with a capacity of 7 liters, equipped with forced circulation and heat exchanger. Pulping conditions were altered to produce pulps with two different levels of delignification (17.5 and 10.8 kappa number). Soda pulping was conducted using the following parameters: ratio of liquor/biomass = 8 L/1 kg; maximum temperature 180°C; time to maximum temperature of 60 min.; time at maximum temperature of 20 min.; and 12.5% or 15.0% alkali charge (as % NaOH) to obtain kappa number 17.5 or 10.8, respectively.

After cooking, the pulped chips were placed into a stainless steel box with a 150 mesh screen and were washed thoroughly with running water. The washed chips were defiberized utilizing a laboratory "hydropulper" with a 25 L capacity. The pulp was classified in a "Voith" laboratory screener equipped with 0.20 mm slotted screen; accepts were centrifuged to a consistency of about 30%, and the resulting dewatered pulp was stored in polythene bags. The following procedures were used for soda pulping analysis: brightness (TAPPI T452 om-08), kappa number (TAPPI T236 om-06) and viscosity (TAPPI T230 om-08).

2.3.2. ECF Bleaching

The 17.5 and 10.8 kappa number brownstocks were fully bleached by the O-D*-(EP)-D_1 sequence, where: O = simple stage oxygen delignification; D* = hot chlorine dioxide stage; (EP) = alkaline extraction with hydrogen peroxide; and D_1 = chlorine dioxide bleaching stage. Table 1 lists the conditions used in each bleaching stage. The O stage was carried out in a Teflon-lined Mark V (Quantum Technologies Inc.) mixer/reactor, with samples of 300 g bone-dry pulp. The desired charges of $MgSO_4$, NaOH and O_2 were added to the reactor, in this order, after the desired temperature was reached. After the total reaction time had elapsed, the system was depressurized and the pulp discharged. The D* and D_1 stages were carried out in polyethylene bags. The bleaching liquor containing ClO_2, H_2O, and NaOH or H_2SO_4 was added to the pulp at room temperature. The application of NaOH or H_2SO_4 was to control the ClO_2 reaction pH, and the amount was determined in previous experiments with mini-samples of the pulp. After hand mixing the chemicals with the pulp in polyethylene bags, the material was heated in a microwave oven to the desired temperature and transferred to a water bath set to the desired reaction temperature and was maintained for the predetermined time. The same aforementioned procedure was used for the (EP) stage, except for the bleaching liquor was comprised of H_2O, NaOH, and H_2O_2, which was added in this order to the pulp. After each bleaching stage, the residual liquor was extracted for pertinent chemical analysis, and the pulp samples were washed with an equivalent of 9 m^3 of distilled warm water per ton of dry pulp. All experiments were run in duplicate.

Table 1. Conditions in each bleaching stage of bagasse pulps from soda pulping

Parameters	**Kappa Number 17.5**				**Kappa Number 10.8**			
	O	**D***	**(EP)**	**D**	**O**	**D***	**(EP)**	**D**
Consistency, %	10	10	10	10	10	10	10	10
Temperature, °C	105	95	80	80	105	95	80	80
Time, min	70	120	90	120	70	120	90	120
Pressure, kPa	600	-	-	-	600	-	-	-
O_2, kg/odt	20.0	-	-	-	20.0	-	-	-
ClO_2, as active Cl_2, kg/odt	-	20.4	-	13.2	-	17.7	-	13.2
H_2O_2, kg/odt	-	-	5.0	-	-	-	5.0	-
NaOH, kg/odt	20.0	-	9.0	1.0	15.0	-	9.0	1.0
H_2SO_4, kg/odt	-	4.0	-	-	-	4.5	-	-
$MgSO_4$, kg/odt	1.5	-	-	-	1.5	-	-	-

After bleaching the pulps were characterized for their beatability, drainability and physical-mechanical properties.

2.3.3. Physico-mechanical tests

The pulps were beaten in a PFI mill, capable of measure energy consumption (Wh), at different energy inputs (0, 300, 600 and 1000 revolutions), made into handsheets and tested for physico-mechanical properties according to TAPPI standards listed in Table 2. The tests related to the tensile stresses were carried out by an Instron instrument, and the tear, burst and air resistance tests were carried out utilizing an Eldendorf, a Müllen and a Gurley porosimeter tester, respectively. Opacity and scattering measurements of the sheets were performed with a Datacolor spectrophotometer, Elrepho 2000 Model, while brightness ISO measurements were performed with a Datacolor spectrophotometer, Elrepho 450X Model.

Table 2. TAPPI standard methods used for PFI pulp beating, handsheet formation, and phyico-mechanical handsheet testing

Parameters	TAPPI Standard Methods
Grammage	TAPPI T410 om-08
Thickness	TAPPI T551 om-06
Tear Index	TAPPI T414 om-04
Burst Index	TAPPI T403 om-02
Tensile Index	TAPPI T494 om-06
Modulus of Elasticity - MOE	TAPPI T494 om-06
Tensile Energy Absorption - TEA	TAPPI T494 om-06
Apparent Specific Volume - *bulk*	TAPPI T220 sp-06
Apparent Specific Weight	TAPPI T220 sp-06
PFI Beating	TAPPI T248 sp-08
Forming Handsheets for Physical Tests	TAPPI T205 sp-06
Air Resistance	TAPPI T460 om-02
Opacity	TAPPI T1214 sp-07
Scattering Coefficient	TAPPI T1214 sp-07
Brightness	TAPPI T452 om-08
Drainage Resistance - Schopper Riegler	TAPPI T423 cm-07

2.3.4. Data analysis

The pulp physico-mechanical properties obtained at different beating levels were analyzed using Excel 5.0, calculating the mean and standard deviation for each level.

3. Results and Discussion

3.1. Soda Pulping

Table 3 shows the results of soda pulping of the depithed bagasse. The brownstock with a kappa of 17.5 afforded a 49.5% screened yield and a pulp viscosity of 947 dm^3/kg when compared to a 47.6% yield and a pulp viscosity of 805 dm^3/kg for the 10.8 kappa brownstock. The reject contents were very low in both cases (< 1%). The lower kappa number pulp achieved higher unbleached brightness values than the higher kappa number pulp, which can be explained by the higher amount of lignin in higher kappa pulp. The majority of pulp chromophores are from the lignin [19], whereas a small amount arises from the decomposition of the carbohydrates [20]. The lower pulp viscosity of the low kappa pulp is explained by the higher alkali charge used during soda pulping. The alkali degrades the carbohydrates by cleaving the chains of cellulose and hemicelluloses, thus affecting the pulp's viscosity.

Table 3. Results of soda pulping of the depithed bagasse*

Kappa Number	Alkali (%)	Rejects (%)	Screened Yield (%)	Total Yield (%)	Brightness (%ISO)	Viscosity (dm^3/kg)
17.5	12.5	0.9	49.5	50.4	35.0	947
10.8	15.0	0.4	47.6	48.0	42.5	805

*Soda pulping conditions: liquor/biomass: 8L/1kg, maximum temperature: 180°C, time to maximum temperature: 60 min, time at maximum temperature: 20 min.

The results obtained in this study for the kappa 17.5 pulp were somewhat similar to those reported by Hamzeh et al. [21] that carried out soda pulping on depithed bagasse to kappa 17.1; the authors reported values of 15.0% NaOH, 52.5%, 1.1% and 36.0% ISO, for the alkali demand, screened yield, rejects and brightness, respectively. Compared to eucalypt, the depithed bagasse is easier to cook to kappa numbers of 17 to 18. Values of 25% NaOH, 49.8%, 0.1%, 33.4% ISO, and 862 cm^3/g, have been reported for the alkali charge, screened yield, rejects, brightness and viscosity, respectively, for the soda pulping of eucalypt [22].

3.2. ECF Bleaching

The depithed bagasse pulps were bleached by the O-D*-(EP)-D sequence to a target brightness of 88% ISO. The oxygen delignification (O) efficiencies, compared at fixed conditions and similar final reaction pH (10.6-10.8) was higher for the 17.5 kappa pulp (61.1%) versus 10.8 kappa pulp (45.4%); the post-O brightness values of the pulps were 50.6 and 52.6% ISO, respectively. The oxygen delignification efficiency is calculated on the basis of kappa number before and after the oxygen stage. The brightness, kappa number and viscosity of the pulps when treated with the O-D*-(EP)-D sequence are shown in Figure 2.

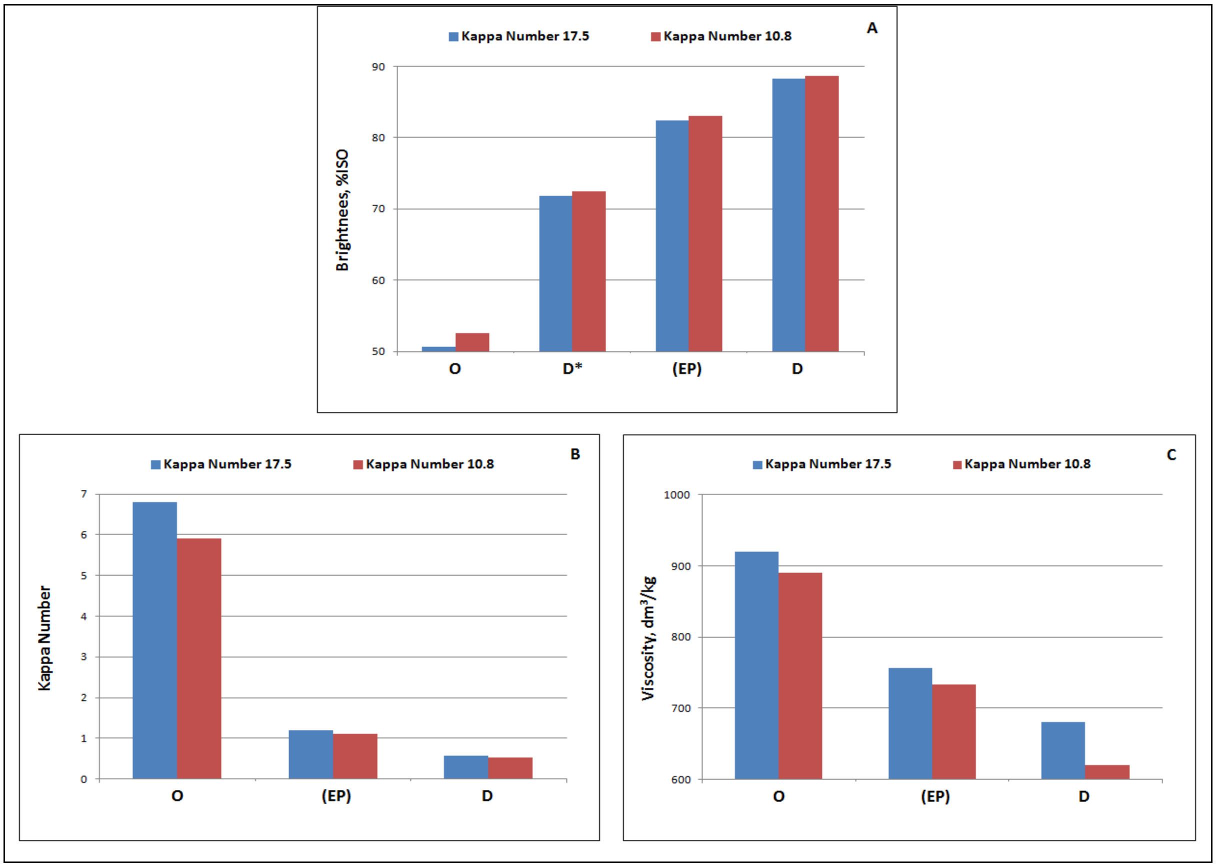

Figure 2. Brightness (A), kappa number (B) and viscosity (C) profile across the O-D*-(EP)-D sequence for pulps of kappa number 17.5 and 10.8.

No significant brightness changes were observed between the pulps of kappa number 17.5 and 10.8, with the exception for the oxygen delignification stage, where the difference in brightness values is significantly higher than the next stages of bleaching, this occurred due to the initial difference in kappa number values after cooking. The positive effect in the brightness values of the pulps after stage D* is probably due to higher kappa factor used in this study (0.30, for both pulps). The main goal of reinforcing an extraction stage with H_2O_2 (EP) is to increase the amount of lignin removed [23], which resulted in substantial reduction in kappa number after this stage; post-extracted kappa numbers of 1.2 and 1.1 were obtained for the 17.5 and 10.8 kappa pulps, respectively. The final bleached kappa number values were similar for both pulps studied. The viscosity values decreased over the bleaching stages. The more severe cooking conditions used to obtain pulps with low kappa number, caused a decrease in carbohydrates contents with a negative influence on viscosity. The significant viscosity losses after the (EP) stage for both pulps were more likely to be caused by to the high temperature used in D* coupled with the low pH (acid hydrolysis of the glycosidic linkages), and by the hydrogen peroxide used in the (EP) stage. The decomposition of hydrogen peroxide in the alkaline conditions generates free radicals which attack the cellulose fibers, thus reducing the viscosity of the pulp. According to Ventorim, et al. [24], pulps exposed to hot acid hydrolysis stage (e.g., D*) may experience some carbohydrate degradation, which is dependent upon reaction conditions. The bleached pulp final viscosities were 680 and 620 dm^3/kg for the 17.5 kappa and 10.8 kappa pulps, respectively.

The overall bleaching chemical consumptions by the 17.5 kappa and 10.8 kappa pulps, measured as total active chlorine, were 44.05 and 41.35 kg/odt pulp, respectively, to achieve a brightness of about 88% ISO (Table 4). The post color numbers values were in the range of 0.24-0.27 for both bleached pulps, which indicated high brightness stability. The summary results of the bleaching by O-D*-(EP)-D sequence is showed in Table 4.

Table 4. Summary results of the bleaching by O-D*-(EP)-D sequence.

Bleaching Parameter	**Kappa Number 17.5**	**Kappa Number 10.8**
Total Active Chlorine*,	44.05^a	41.35^b
Brightness, % ISO	88.3^a	88.6^a
Post Color Number	0.24^a	0.27^a
Viscosity, dm^3/kg	680^a	620^b
Kappa Number	0.58^a	0.53^a

* Total Active Chlorine (kg/odt) = ClO_2 (kg/odt)*2.63 + H_2O_2 (kg/odt)*2.09.

Note: The averages marked with the same letters in each line, are not significantly difference by Tukey's test at a 5% significance level.

3.3. Physico-mechanical tests

The bleached pulps were beaten using different revolutions in the PFI mill (0, 300, 600, and 1000 revolutions) and subjected to physical and mechanical tests in order to evaluate their potential for the production of printing and writing paper grades. All the properties were expressed in relation to the energy consumed during beating given its contribution to paper production cost. For the development of required pulp properties, beating refining require substantial energy, about 18% of the total electrical energy required for producing paper from wood [25]. Each graph shows the experimental data and the curves, represented through mean values and standard deviation.

3.3.1. Drainage Resistance and Beatability

Pulp drainability can be loosely defined as the capacity of the pulp to drain the water from the mat. Since ^{o}SR is a drainage resistance measure, gives a conception of pulp drainability. Therefore, once ^{o}SR increases, so does the tensile index. Pulp beatability can be loosely defined as the amount of pulp beating energy required to achieve a certain drainage degree. Therefore, the relationship between ^{o}SR and energy consumption, for example, gives a direct indication of pulp beatability. The higher the amount of beating energy required to achieve a given ^{o}SR, the lower is the pulp's beatability. Figure 3 shows the relations between °SR and tensile index (A) and °SR and energy consumption (B) for the bleached pulps with initial brownstock kappa numbers of 17.5 and 10.8. As anticipated, the resistance to drainage increased with increasing tensile index and the ^{o}SR increased with increasing energy consumption. As observed, through the curves tendency, the drainage resistance and beatability seems not to be influenced by the degree of pulping delignification.

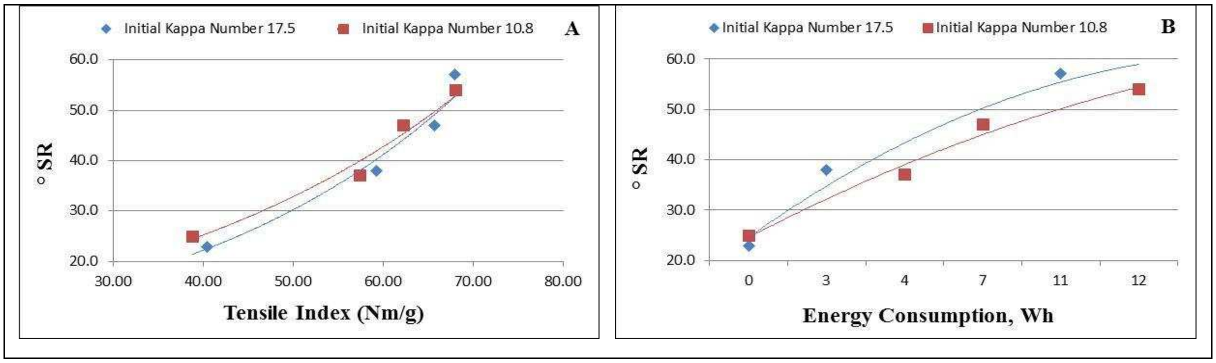

Figure 3. Drainage resistance (A): Schopper-Riegler versus tensile index; beatability (B): Schopper-Riegler versus energy consumption for bleached pulps cooked to two different degrees of delignification (kappa numbers of 17.5 and 10.8).

3.3.2. Tensile Index, Burst Index and Tear Index

In papermaking, the strength properties, due to the fiber strength, bonding, and length, indicate the paper's resistance to web breaking during printing and converting [26].

Figure 4 shows the relations between tensile, burst and tear index versus energy consumption for the bleached pulps with initial brownstock kappa numbers 17.5 and 10.8.

It is observed that tensile and burst index increases with energy consumption. The 17.5 kappa pulp exhibited a slightly higher tensile, burst and tear index than the 10.8 kappa pulp over the beating energy range examined, especially for tensile index. The more severe cooking conditions used to obtain the 10.8 kappa pulp probably caused a decrease in pulp's xylan content, which resulted in a negative impact on tensile.

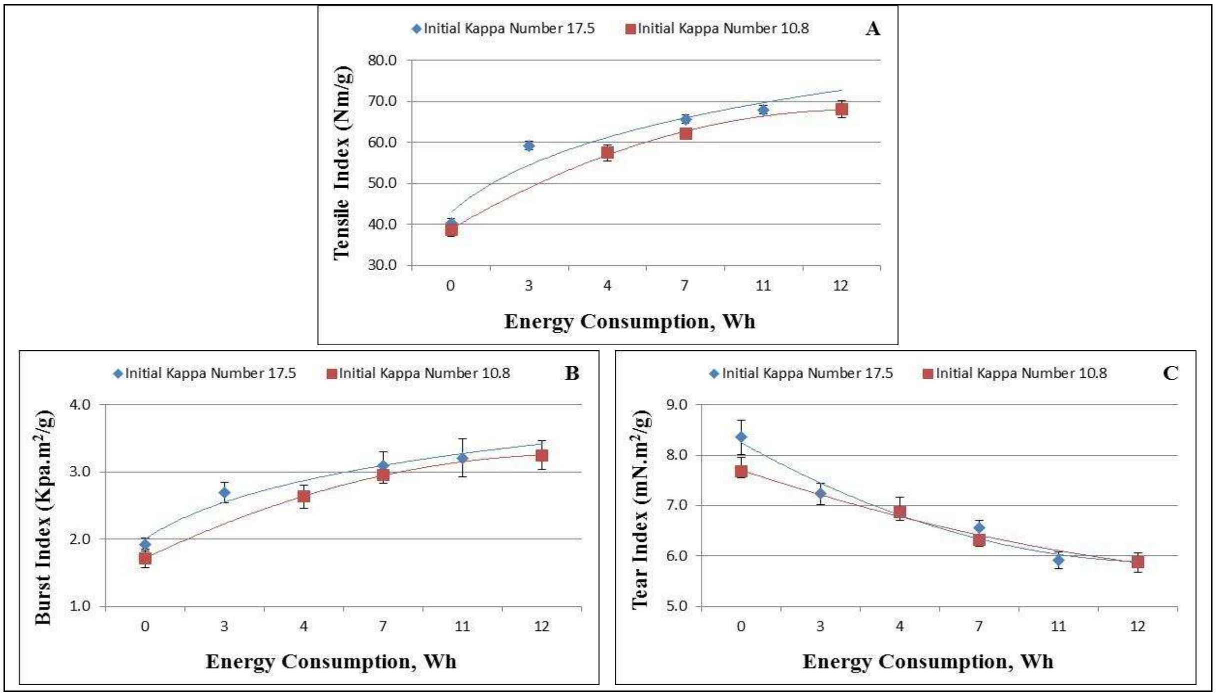

Figure 4. Tensile Index (A); Burst Index (B) and Tear Index (C) versus Energy Consumption for bleached pulps cooked to two different degrees of delignification (kappa 17.5 and 10.8).

3.3.3. Specific Elastic Modulus (MOE) and Tensile Energy Absorption (TEA)

Modulus of elasticity (MOE), also known as specific elastic modulus, is an important property because it represents the capacity of the material to absorb a tensile force without suffering substantial deformation. Higher MOE values provide greater capacity of the material to absorb a certain load without undergoing large deformations. The tensile energy absorption (TEA) represents the durability of the paper when subjected to repetitive use when subjected to tensile or impact forces. Figure 5 shows the relations of MOE and TEA with energy consumption for the two bleached pulps. As observed, through the curves tendency, the cooking conditions employed to obtain different delignification degrees did not have any significant effect on MOE and TEA values at the various beating energy levels.

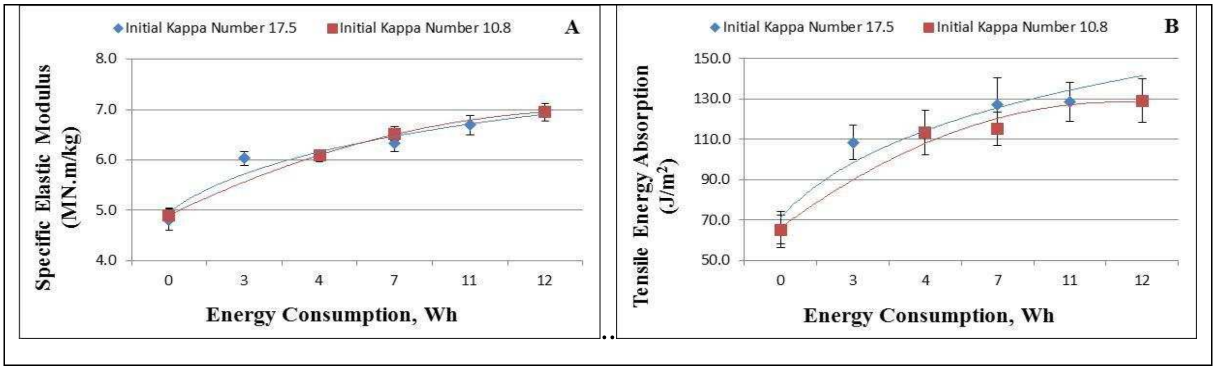

Figure 5. Specific elastic modulus (A) and tensile energy absorption (B) versus energy consumption for bleached pulps cooked to two different degrees of delignification (kappa numbers of 17.5 and 10.8).

3.3.4. Resistance to air passage, Apparent Specific Weight and Apparent Specific Volume

Air resistance has an inverse relationship with paper porosity. This property is highly and positively influenced by the amount of pulp refining. Its behavior as a function of beating energy consumption is presented in Figure 6 for the two bleached pulps. The paper sheet resistance to air passage increases with increasing energy consumption due to decreased porosity. The pulp of kappa 10.8 showed slightly higher air resistance than that of kappa 17.5. The 10.8 kappa pulp possessed more collapsible fibers and produced more fines during refining, with consequent increase in the amount of fines and reduced empty spaces, thus decreasing porosity.

The apparent specific weight and volume are very important properties for printing and writing paper grade as they influence the porosity and opacity of paper. For a given raw material, an increase in apparent specific volume or a decrease in apparent specific weight means an increase in paper opacity and porosity. The apparent specific volume is also known as *bulk*. The structural characteristics of the fibers also influence the determination of this property. Less collapsible fibers contribute to increased specific volume of papers because their low conformation capacity. Figure 6 show the relations of apparent specific weight and apparent specific volume with energy consumption for the two bleached pulps. From Figure 6, it could be seen that apparent specific weight increased and apparent specific volume decreased with refining energy consumption. Both specific weight and volume were not significantly affected by the degree of delignification during soda pulping.

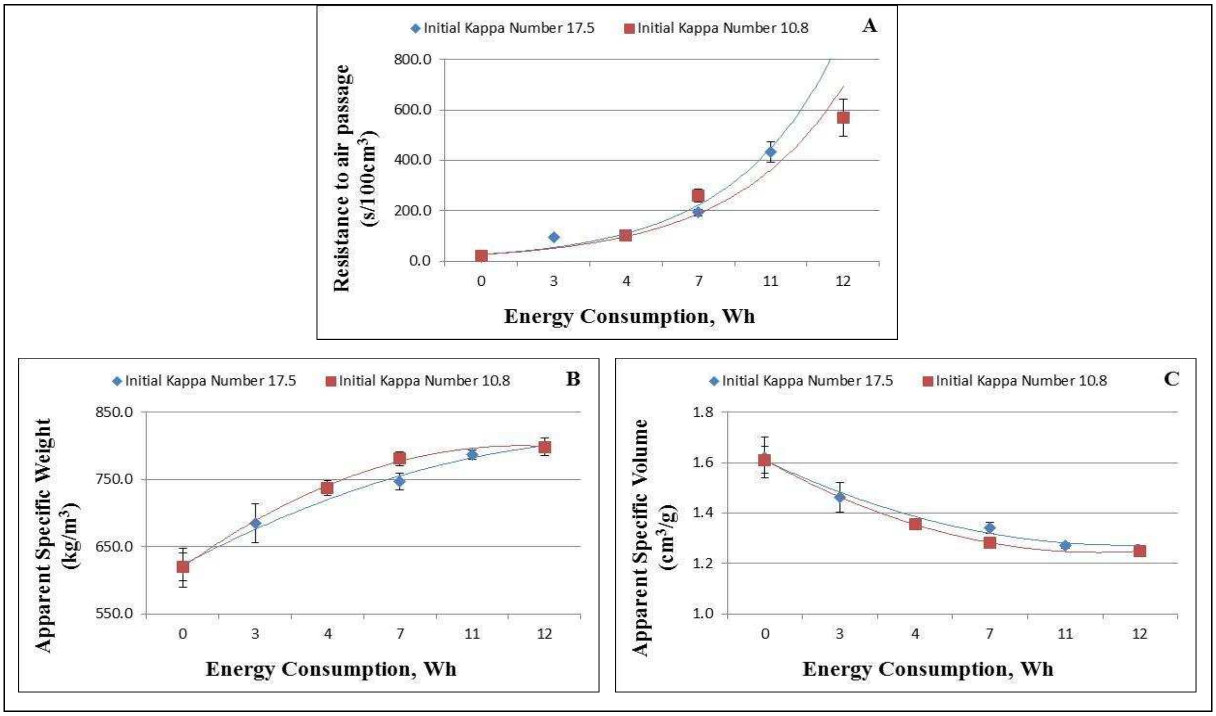

Figure 6. Resistance to air passage (A); apparent specific weight (B) and apparent specific volume (C) versus energy consumption for bleached pulps cooked to two different degrees of delignification (kappa 17.5 and 10.8).

3.3.5. Opacity and Scattering Coefficient

Opacity is defined as the ability of light to pass through a paper sheet. The extent of beating affects opacity. Opacity is important in printing and writing paper grade pulps in order to prevent the printed images or text from the opposite side from being seen from the other side of the sheet. Opacity is a function of paper thickness, amount of filler(s), pulp brightness, and beating degree. Beating makes the paper denser, but excessive beating results in lower opacity [27]. The scattering coefficient is a measure of the ability of the sheet to scatter light. Figure 7 shows the relations between opacity and scattering coefficient versus energy consumption during refining for the two bleached pulps. The opacity and scattering coefficient decreases with increasing refiner energy consumption. The opacity and scattering were not influenced by the degree of pulping delignification.

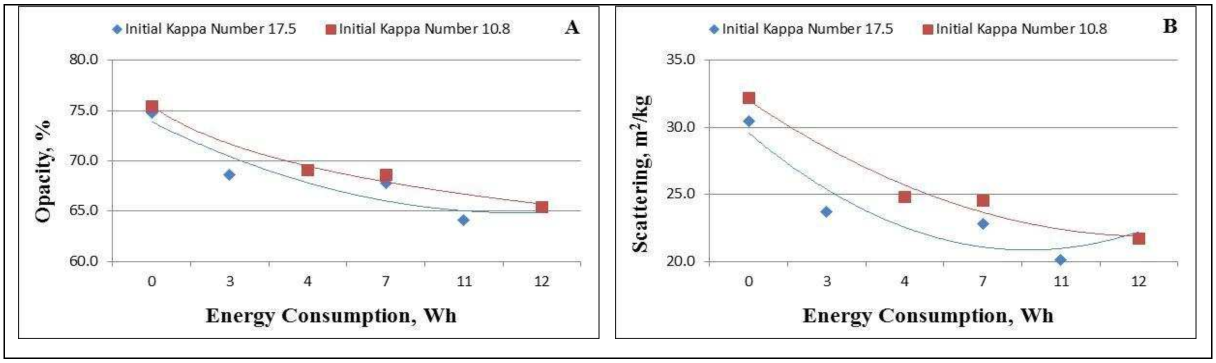

Figure 7. Opacity (A) and Scattering (B) versus Energy Consumption for bleached pulps cooked to two different degrees of delignification (kappa 17.5 and 10.8).

3.4. Potential of bleached depithed bagasse soda pulp for production of printing and writing paper grade

In order to determine the potential of the pulps produced in this study for the production of printing and writing (P&W) paper grade, these pulps were compared with eucalypt pulps that are traditionally used for this application. According to Foelkel [18], tensile and tear indexes are important for P&W paper grades. However, other very important properties of P&W paper grade pulps are opacity, bulk and porosity. Table 5 shows a list of relevant properties for the pulps of this study and of commercial eucalypt P&W paper grade kraft pulps. In general, the bleached pulps derived from depithed bagasse presented acceptable properties; however, they did not measure up to those of traditional eucalypt kraft pulps. Considering opacity as one of the most important properties for this paper grade, it was chosen as standard property to comparison between sugarcane bagasse and eucalypt pulps properties.

The strength properties of the eucalypt kraft pulps, as tensile index, burst index and tear index, were generally higher than those of the depithed bagasse soda pulps (Table 5).

Although both the eucalypt and depihted bagasse raw materials had similar fiber morphology, the fiber viscosities of the eucalypt kraft pulps were higher than those of the bagasse soda pulp. However, the values of bulk (~1.5 cm^3/g) and opacity (~70%), which are very important properties for printing and writing paper grades, were similar for eucalypt kraft and bagasse soda pulps. Yet, when comparing the depithed bagasse pulps with eucalypt pulps (*Eucalyptus grandis*), the variations between the physico-mechanical properties values were small. Values of bulk, tensile index, burst index and opacity were 1.5 cm^3/g, 56.5 N•m/g, 3.6 kPa•m^2/g, and 71.9%, respectively for the *Eucalyptus grandis* pulps.

Table 5. Selected printing and writing paper grade properties for the depithed bagasse soda pulp of this study (initial kappa 17.5 and 10.8) and of commercial eucalypt kraft pulps and of *Eucalyptus grandis.*

Sample	Opacity %	Mill Revo-lutions	°SR	Bulk cm^3/g	Tensile Index N•m/g	Burst Index kPa•m^2/g	Tear Index mN•m^2/g	Air Resistance s/100cm^3
Depithed Bagasse KN:17.5	68.7	300	38	1.5	59.2	2.7	7.2	86.8
Depithed Bagasse KN:10.8	69.1	300	37	1.4	57.4	2.6	6.9	85.5
Eucalyptus Hybrid [28]	70.8	1793	34	1.4	78.0	5.4	10.5	4.6
Eucalyptus Hybrid [28]	74.1	1184	34	1.6	66.2	4.6	8.6	3.8
Eucalyptus Hybrid [29]	70.7	3000	40	1.2	77.0	4.8	9.0	31.3
***Eucalyptus Grandis* [30]**	72.9	1000	33	1.5	56.5	3.6	9.8	8.9

4. Conclusions

- The bleached soda pulps cooked to 17.5 and 10.8 kappa numbers showed similar refinability, resistance to drainage, and the strength properties (tensile, burst and tear).

- Both brownstock pulps obtained from depithed sugar cane bagasse were suitable for the production of printing and writing paper grades; however, the higher kappa brownstock was more economically attractive given its higher pulping yield.
- In general, the bleached pulps derived from depithed bagasse presented acceptable properties; however, these pulps did not measure up against those of traditional eucalypt kraft pulps.

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CAPÍTULO 5

Production of Printing and Writing Paper Grade Pulp from Elephant Grass

Abstract

The main goal of this study was characterizing chemically and morphologically the elephant grass, and evaluating the potential of the fibers for production of printing and writing paper grade pulp. The elephant grass was chemically and morphologically characterized and cooked by the soda process to two different degrees of delignification (kappa 17.5 and 10.6). The resulting pulps were fully bleached by the O-D*-(EP)-D sequence and characterized for their beatability, drainability and physical-mechanical properties. The lignin content (20.2%) was low indicating that this grass should be easier to pulp. The morphological analyses of the elephant grass indicated a short fibered material, similar to hardwoods. The soda pulp from elephant grass cooked to kappa number 17.5 presented higher screened yield than 10.6 kappa pulp, with alkali demands of 15.0% and 20.0%, respectively. The total active chlorine required by the 17.5 and 10.6 kappa pulps, were 42.1 and 35.1 kg/odt pulp, respectively, to achieve an ISO brightness of about 90.0%. The bleached soda pulps cooked to 17.5 and 10.6 kappa number showed similar refinability and resistance to drainage, but the tensile and burst index were higher for the 17.5 kappa pulp at beating energy consumptions in the range of 0-6 Wh. It was concluded that both 10.6 and 17.5 kappa pulps from elephant grass are suitable for the production of printing and writing paper grade pulps, but the higher kappa 17.5 pulp is more economically attractive given its higher pulping yield, despite the significantly increased of chemical demand for bleaching.

Keywords

Elephant grass, printing and writing paper, soda pulping, bleaching

1. Introduction

Biomass from grasses is the largest renewable source for the production of bioproducts and biofuels, it is available in high amounts (as forest, agricultural or industrial lignocellulosic wastes and crops) at relatively low cost. Elephant grass (*Pennisetum purpureum*) is originated from Africa and now introduced into most tropical and subtropical countries. It has a large genetic variability and is considered a species of fast growth and high production of plant biomass.

The renewed interest in non-wood fiber sources stems from the fact that they offer several advantages in the pulp and paper industry. Non-wood fibers can be used in most paper grades including board, fiberboard [1; 2] and composite materials [3]. According to Mazzarella [4], the comparative advantages of elephant grass in relation to other biomass sources are: increased productivity (45 ton per ha per year), smaller cultivated areas for a particular production, lower production cycle (two harvests per year), better cash flow, mechanization, renewable energy and greater carbon assimilation. However, compared to wood, non-wood fibers sources present challenges with their seasonal (and not year-round) availability; handling, given their high volume, low density; and the large volumes of silica that have to be removed during processing [5].

Elephant grass is therefore considered to be an excellent feedstock to provide abundant and sustainable resources of lignocellulosic biomass for the production of energy, industrial chemicals, and/or pulp and paper [6; 7]. Elephant grass has beneficial characteristics for pulp production, such as high fibers production and its chemical composition [8; 9; 10]. According to Madakadze et al., [7] the elephant grass contents of cellulose, hemicelluloses, and lignin are 40, 30, and 18.0%, respectively. These values are suitable for pulp production, especially the low lignin content, suggesting high pulpability of this material in cooking processes.

The aforementioned studies indicate that elephant grass has potential for paper production, but a more thorough investigation is required, particularly comparing its potential with that of the well-known eucalyptus wood. The main goal of this study was characterizing chemically and morphologically the elephant grass, and evaluating its potential of the fibers for production of printing and writing paper grade pulp.

2. Experimental

2.1. Working plan

Figure 1 depicts the working plan. The elephant grass was characterized chemically and morphologically, and converted into brown pulp of two different delignification degrees (kappa 17.5 and 10.6) by the soda pulping. The resulting pulps were fully bleached by the O-D*-(EP)-D sequence and characterized for their beatability, drainability and physical-mechanical properties.

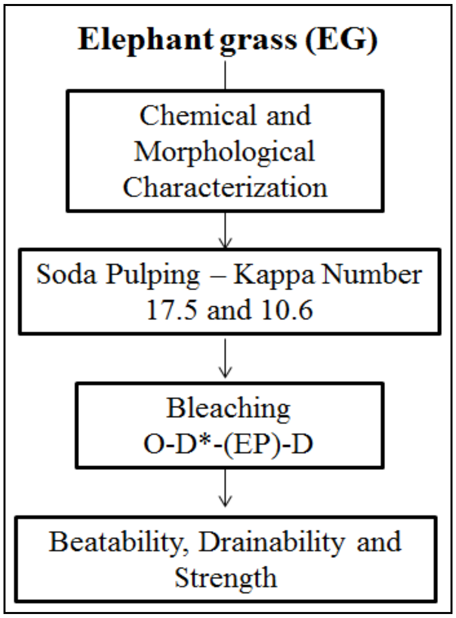

Figure 1. Working plan for EG fractionation, characterization and bleached pulp production using the soda process and respectively physical-mechanical tests.

2.2. Material

About 100 kg of elephant grass (*Pennisetun purpureum*) was collected at an age of 150 days old, from the experimental station of the University of Viçosa (Brazil). The sample was dried to about 85% dryness in an acclimated room (23.0 ± 1.0^{o}C and 50.0 ± 2.0% moisture) and stored in polyethylene bags for further use. The air-dried sample was ground in a Wiley mill, sieved, and the fraction that passed through a 40 mesh screen and was retained in the 60 mesh screen was collected, air dried and stored in wide mouth sealed flasks.

2.3. Methods

2.3.1. Chemical characterization of elephant grass biomass

The following procedures were used for chemical analysis: moisture content (TAPPI T 264 om-88), total extractives content (TAPPI T 264 cm-97), acid soluble lignin [11], Klason lignin [12], lignin syringyl/guaiacyl ratio [13], preparation of biomass for sugar analysis (TAPPI T 249 cm-85), sugar analysis [14], acetyl groups [15], uronic acids [16], silica (TAPPI T245 cm-98) and ash (TAPPI 211 om 93).

2.3.2. Morphological characterization of elephant grass biomass

Elephant grass biomass was investigated for fiber dimensions. For the implementation of the morphological analysis, the sample was fragmented and 1g o.d. of each sample was macerated using 5 parts of acetic acid and 1 part of nitric during a time of 4 to 6 hours at chapel (time variable, dependent on the total dispersion of the fiber material used in the solution). Subsequently, the sample was washed in running water diluted with distilled water to favor the dispersion of the fibers. The analysis was performed in the sample after hydration and soft agitation for complete fiber individualization.

Microscopic blades were prepared and images were captured in a video microscope equipped with image analysis software (model SZ - STS, Olympus, Japan). Small amount of colorant (Astra blue) was added for better visualization of the fibers and about 100 whole fibers were measured. The following fiber biometric traits were measured: length, width, lumen diameter and cell wall thickness. Fiber length was measured with a 70X magnification whereas the other traits were measured with 1000X magnification. The variation coefficient was taken at every 25 measurements. The data obtained by measurements were transferred to the *Office Excel* 2007, which determined the averages, standard deviations, and variation coefficients.

From the fiber biometry measurements mathematical inferences were done to determine other fiber properties, namely: (1) Felting Index (FI) = relation between fiber length (FL) and fiber width (FW), (FL/FW)*1000, where, 1000 is a conversion factor of µm to mm. (2) Flexibility Coefficient (FC) = relation between lumen diameter (LD) and fiber width (FW), (LD/FW)*100, where, 100 is a conversion factor for percentage. (3) Wall Fraction (WF), relation between wall thickness (WT) and fiber width (FW), (2*WT/FW)*100, where, 100 is a conversion factor for percentage. (4) Ratio length/thickness (L/T) = relation between fiber length (FL) and wall thickness (WT): (FL/WT)*1000. Where, 1000 is a conversion factor of µm to mm. (5) Runkel Index (RI) = relation between wall thickness (WT) and lumen diameter (LD), (2*WT/LD).

2.3.3. Soda pulping

The soda pulping of the elephant grass was carried out n a M/K digester (Systems Inc., Massachusetts - USA) with a capacity of 7 liters, equipped with forced circulation and heat exchanger devices, aiming at producing pulps with two different delignification degrees. It was conducted using the following parameters: ratio of liquor/biomass 8L/1kg, maximum temperature 180°C, time to maximum temperature of 60 min, time at maximum temperature of 20 min, and 15.0% and 20.0% alkali charges, to reach kappa number 17.5 and 10.6, respectively.

After cooking, the chips were placed in stainless steel screen box of 150 mesh and were washed thoroughly with running water. The individualization of the fibers was performed in a laboratorial "hidrapulper" of 25 liters of capacity. The pulp was classified in a "Voith" laboratorial screener equipped with 0.20 mm slotted plate, centrifuged to a consistency of about 30% and then stored in polythene bags. The following procedures were used for soda pulping analysis: Brightness (TAPPI T452 om-08), kappa number (TAPPI T236 om-06) and viscosity (TAPPI T230 om-08).

2.3.4. ECF Bleaching

The two pulps resulting from the soda pulping at kappa 17.5 and 10.6 were fully bleached by the O-D*-(EP)-D_1 sequence, where: O = simple stage oxygen delignification; D* = hot chlorine dioxide stage; (EP) = alkaline extraction with hydrogen peroxide; D_1 = chlorine dioxide bleaching stage. Table 1 describes the conditions used in each bleaching stage. The O stage was carried out in a Teflon-lined Mark V (Quantum Technologies Inc.) mixer/reactor, with samples of 300g absolutely dry pulp. The desired charges of $MgSO_4$, NaOH and O_2 were added to the reactor, in this order, after the desired temperature was reached. After the total reaction time elapsed, the system was depressurized and the pulp discharged. The D* and D_1 stages were carried out in polyethylene bags. The bleaching liquor containing ClO_2, H_2O, NaOH or H_2SO_4 was added to the pulp at room temperature. The application of sulfuric acid or sodium hydroxide to control the pH was determined in previous experiments with mini-samples of pulp. After hand mixing in polyethylene bags, the material was heated in a microwave oven to the desired temperature and transferred to a steam bath with temperature control and was maintained for the time predetermined. The same procedure aforementioned was used in the (EP) stage, except for the bleaching liquor that in this case was comprised of H_2O, NaOH, H_2O_2 added to the pulp in this order. After each bleaching stage, the residual liquor was extracted for pertinent analysis and the pulp samples were washed with an equivalent of $9m^3$ of distilled warm water per ton of dry pulp. All experiments were run in duplicate.

Table 1. Conditions in each bleaching stage of elephant grass pulps from soda pulping

Parameters	**Kappa Number 17.5**				**Kappa Number 10.6**			
	O	**D***	**(EP)**	**D**	**O**	**D***	**(EP)**	**D**
Consistency, %	10	10	10	10	10	10	10	10
Temperature, °C	105	95	80	80	105	95	80	80
Time, min	70	120	90	120	70	120	90	120
Pressure, kPa	600	-	-	-	600	-	-	-
O_2, kg/odt	20.0	-	-	-	20.0	-	-	-
ClO_2, as Cl_2, kg/odt	-	10.8	-	25.0	-	8.8	-	20.0
H_2O_2, kg/odt	-	-	3.0	-	-	-	3.0	-
NaOH, kg/odt	20.0	-	8.0	3.0	15.0	-	8.0	2.0
H_2SO_4, kg/odt	-	5.0	-	-	-	5.0	-	-
$MgSO_4$, kg/odt	1.5	-	-	-	1.5	-	-	-

After bleaching the pulps were characterized for their beatability, drainability and physical-mechanical properties.

2.3.5. Physical-mechanical tests

The pulps were beaten in a PFI mill at different energy inputs, made into hand sheets and tested for physical-mechanical properties according to TAPPI standards (Table 2). The tests related to the tensile stresses were carried out by an Instron instrument, and the tear, burst and air resistance tests were carried out in Eldendorf, Müllen and Gurley porosimeter, respectively. Opacity and Scattering of the sheets were measured in Datacolor spectrophotometer, Elrepho 2000X Model.

Table 2. TAPPI standard methods used for PFI beating, hand sheet making and physical and mechanical properties

Parameters	TAPPI Standard Methods
Grammage	TAPPI T410 om-08
Thickness	TAPPI T551 om-06
Tear Index	TAPPI T414 om-04
Burst Index	TAPPI T403 om-02
Tensile Index	TAPPI T494 om-06
Modulus of elasticity – MOE	TAPPI T494 om-96
Tensile energy absorption – TEA	TAPPI T494 om-96
Apparent Specific Volume – *bulk*	TAPPI T220 sp-01
Apparent Specific density	TAPPI T220 sp-96
PFI Beating	TAPPI T248 sp-08
Forming Handsheets for physical tests	TAPPI T205 sp-95
Air resistance	TAPPI T460 om-02
Drainage resistance - Schopper Riegler	TAPPI T423 cm-07

2.3.6. Statistical analysis

The pulp physical-mechanical properties obtained at different beating levels were statically analyzed using the Curve Expert software. The adjusted equations were compared by F test, using the identity test models and adopting a significance level of up to 5%

probability, according to the methodology described by Regazzi [17] for linear models and Regazzi and Silva [18] for nonlinear models.

3. Results and Discussion

3.1. Chemical characterization of elephant grass

The contents of cell wall structural constituents (cellulose, hemicelluloses and lignin) in the elephant grass biomass are show in Table 3. Xylans (14.0%) are the main hemicelluloses of elephant grass, with the contents of galactans, mannans and arabinans of this material being rather low.

The contents of glucans (39.9%) and uronic acids (1.3%) in elephant grass were similar to content of others non woody materials, such as sugar cane bagasse [19], but lower than eucalyptus woods [20; 21]. The low content of uronic acids can be negative, since the uronic acids act protecting the xylans during the alkaline pulping [22]. The acetyl group content in the elephant grass (2.1%) was similar to content of the others woody and non woody materials [19; 20; 23].

The elephant grass biomass presented much larger amounts of non-structural constituents (extractives and minerals) in relation to woody biomass, such as eucalyptus [21; 23]. The amount of ethanol/toluene extractives and minerals in the elephant grass were 14.8% and 6.0%, respectively. These values are so high when compared with eucalyptus woods. The silica was responsible for 25.0% of the elephant grass mineral contents.

Table 3. Chemical composition of elephant grass in percentage of biomass dry weight

Analyses , %	Elephant grass
Klason lignin	18.1
Acid soluble lignin	2.1
Total lignin	20.2
Lignin S/G	1.1
Glucans	39.9
Xylans	14.0
Galactans	0.5
Mannans	0.0
Arabinans	1.1
Uronic acids	1.3
Acetyl	2.1
Total Sugars*	58.9
Ash	6.0
Silica	1.5
Extractives	14.8
Grand Total, %**	100

*include glucans, xylans, galactans, mannans, arabinans, uronic acids and acetyl groups.

**include total lignin, total sugars, ash and extractives.

The lignin contents of elephant grass (20.2%) was low indicating that this grass should be easier to pulp than wood with a lignin content of 26 - 30% [24]. The lignin content of the elephant grass was similar to values reported in the literature. Values in the range of 18%-21% were reported by Gomes et al., [21]; Del Rio et al., [9] and Madakadze et al., [7]. High ash, silica and extractives contents on elephant grass have been reported by the same workers. The high extractive and mineral contents are quite challengeable for pulp production. Besides causing a variety of operational problems (scaling, corrosion, pitch deposition, chemical degradation during bleaching, recovery boiler plugging, etc), minerals and extractives may cause severe difficulties during the bleaching, if not properly removed during the process.

3.2. Morphological characterization of elephant grass

The determination of pulp fibers biometry is quite relevant in the production of printing and writing paper grade pulp since they affect paper beatability, drainability and properties rather significantly. Table 4 shows the average biometry of the elephant grass fibers.

Table 4. Elephant grass fiber dimensions

Dimension	Statistic	Elephant Grass Biomass
Fiber length, mm	Average	1.1
	Standard Deviation	0.2
	C.V., %	16.2
Fiber width, µm	Average	14.7
	Standard Deviation	3.5
	C.V., %	23.8
Lumen diameter, µm	Average	7.9
	Standard Deviation	3.0
	C.V., %	37.8
Wall thickness, µm	Average	3.4
	Standard Deviation	0.8
	C.V., %	22.1

The average fiber length, fiber width, lumen diameter and wall thickness of the elephant grass was 1.1 mm, 14.7 µm, 7.9 µm and 3.4 µm, respectively. In general, the fiber morphology of elephant grass is somewhat similar to those of many hardwoods, thus being qualified as short fibered materials. Other significant information can be obtained from biometry data through correlations among the various fiber dimensions. Table 5 shows the relations calculated based on the average value of each morphological parameter evaluated. These relations help understanding the influence of fiber morphology on paper formation and properties [25]. Fibers with a high Runkel index and wall fraction, and low flexibility coefficient are more rigid and present high tear resistance, which is a property dependent on the intrinsic strength of the fiber, but low tensile and burst indexes, which are properties that depend on fiber bonding [25].

The elephant grass fibers showed Runkel index (0.86) and wall fraction (46.3%) values lower than those reported for eucalypt woods, which were 1.1-2.67 and 52-73%, respectively [25]. The elephant grass flexibility coefficient value (53.7%) was higher than that reported for eucalypt woods (28-47%). Pulps of high flexibility coefficient produce more inter-fiber bonding during beating, increasing tensile and burst strengths. The felting index in elephant grass (74.8) was similar to that of other grasses, such as bagasse (~70.0) reported by Carvalho, [26] and higher than that of eucalypt wood fibers (48-59) [25]. The length/thickness ratio of the depithed bagasse soda pulp was higher (323.5) than that of eucalyptus wood fibers (145-196) [25] and similar to values of others grasses [26].

Table 5. Relations of morphological properties

Relationship	**Elephant Grass Biomass**	**Eucalyptus Hybrids**[*]
Felting index	74.8	48.0 - 59.0
Flexibility coefficient, %	53.7	28.0 - 47.0
Wall fraction, %	46.3	52.0 - 73.0
Ratio length/thickness	323.5	145.0 - 196.0
Runkel index	0.86	1.10 - 2.67

[*] Foelkel, et al., 1975

3.3. Soda Pulping

Table 6 shows the results of soda pulping of elephant grass to kappa numbers 17.5 and 10.6. The soda pulp of kappa 17.5 presented 46.1% screened yield (pulp viscosity of 1279 dm^3/kg) against 44.6% yield (pulp viscosity of 1146 dm^3/kg) for the 10.6 kappa pulp, with alkali demands of 15.0% and 20.0%, respectively. It is conceivable that the higher pulp yield in elephant grass is attributable to its low lignin content and high alkali solubility. The reject contents were low in both cases (< 2%); this indicated that the soda pulping provided adequate defibering. Pulps originated from kappa numbers 10.6 achieved brightness values higher than pulps from kappa numbers 17.5, which is explained by the higher amount of lignin in the kappa 17.5 pulp. The largest fraction of pulp chromophores originates from lignin [27] and only a small fraction from the decomposition of carbohydrates [28]. The lower pulp viscosity of the low kappa pulp is explained by the higher alkali charge used during the soda cooking. The soda acts degrading carbohydrates and breaking the chains of cellulose and hemicelluloses, thus affecting the viscosity.

Table 6. Results of Soda Pulping*

Sample	Kappa Number	Alkali (%)	Rejects (%)	Screened Yield (%)	Total Yield (%)	Brightness (%ISO)	Viscosity (dm^3/kg)
Elephant grass	17.5	15.0	1.5	46.1	47.6	38.9	1279
Elephant grass	10.6	20.0	0.3	44.6	44.9	45.3	1146

*Soda pulping conditions: liquor/biomass: 8L/1kg, maximum temperature: 180°C, time to maximum temperature: 60 min, time at maximum temperature: 20 min.

Compared to eucalypt, the elephant grass is easier to cook aiming at a kappa number about 17-18. Values of 25% NaOH, 49.8%, 0.1%, 33.4% ISO, and 862 cm^3/g, have been reported for alkali charge, screened yield, rejects, brightness and viscosity, respectively, in the soda pulping of eucalypt [29].

3.4. ECF Bleaching

The elephant grass pulps were bleached by the O-D*-(EP)-D sequence to a target brightness of 90% ISO. The oxygen delignification (O) efficiencies, compared at fixed conditions and similar final reaction pH (10.6-10.8) was higher for the 17.5 kappa pulp (69.4%) versus 10.6 kappa pulp (58.5%); the post-O brightness values of the pulps were 48.5 and 54.6% ISO, respectively. The oxygen delignification efficiency is calculated on the basis of kappa number before and after the oxygen stage. The behavior of brightness, kappa number and viscosity across the O-D*-(EP)-D sequence are shown in Figure 2.

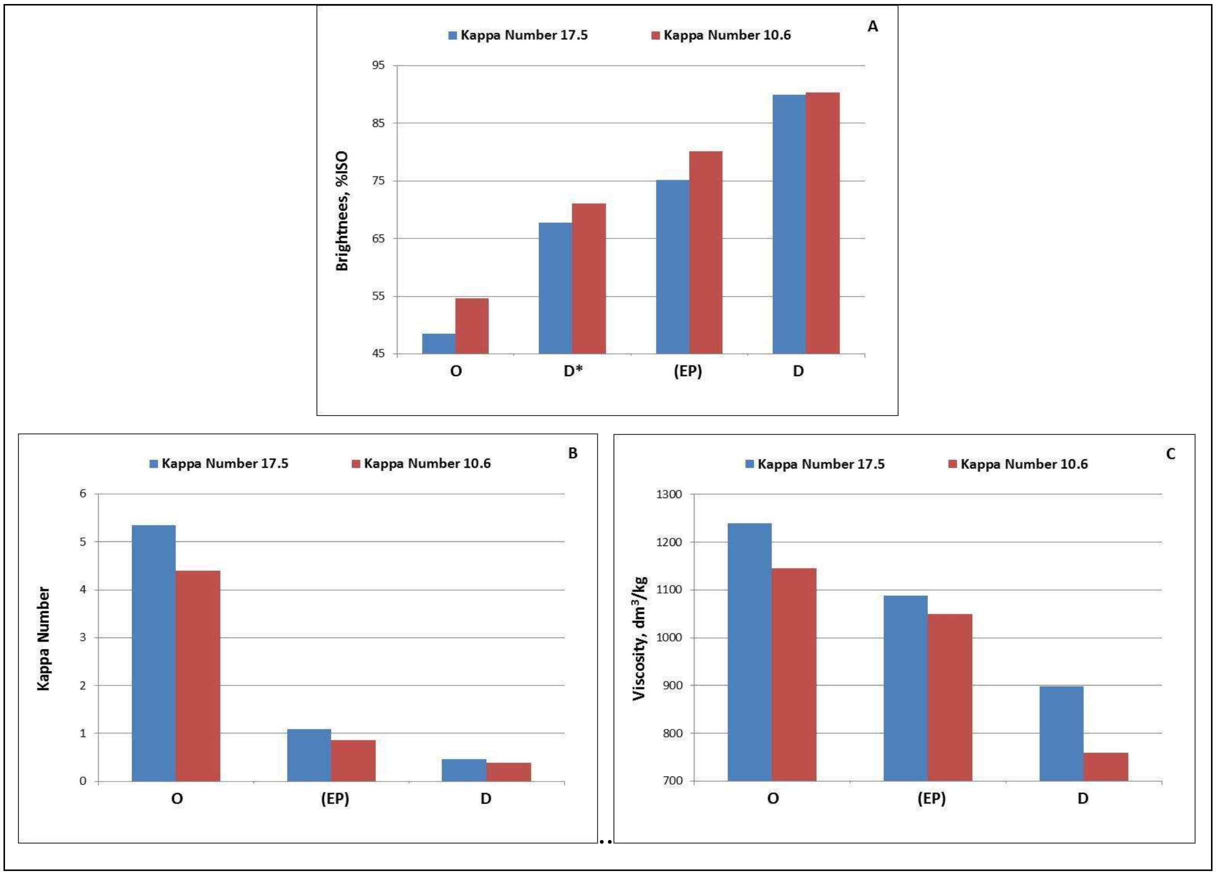

Figure 2. Brightness (A), Kappa number (B) and Viscosity (C) profile across the O-D*-(EP)-D sequence for pulps of kappa number 17.5 and 10.6.

The brightness values across the sequence of bleaching were higher for pulps with kappa number 10.6 than pulps with kappa number 17.5. The except for the last stage of the bleaching sequence, where the difference in brightness values were similar for the two pulps (~ 90.0% ISO), due to the higher charge of chlorine dioxide used in the pulp from kappa number 17.5 for achieved the desired brightness value. The higher reduction in kappa number in D* treatment, is explained by the higher HexA removal in the D* stage, under higher temperature and longer reaction time conditions [30]. Furthermore, the main goal of reinforcing an extraction stage with H_2O_2 (EP) is to increase the amount of lignin removed [31], resulting in substantial reduction in kappa number after this stage, values of 1.1 and 0.9 were found for the pulps of kappa number 17.5 and 10.6, respectively. The final kappa number values were similar for both pulps studied. The viscosity values decreased over the bleaching stages. The more severe cooking conditions used to obtain pulps with low kappa number, caused a decrease in carbohydrates contents with a negative influence on viscosity, this profile is observed in all stages of bleaching. The significant viscosity losses after the (EP) stage for both pulps were more likely to be caused by to the high temperature used in D* coupled with the low pH (acid hydrolysis of the glycolsidic linkages), and by the hydrogen peroxide used in the (EP) stage. The decomposition of hydrogen peroxide in the alkaline conditions generates free radicals which attack the cellulose fibers, thus reducing the viscosity of the pulp. According to Ventorim, et al., [32], pulps exposed to hot acid hydrolysis stage (e.g., D*) may experience some carbohydrate degradation, which is dependent upon reaction conditions. The bleached pulp final viscosities were 899 and 760 dm^3/kg for the 17.5 kappa and 10.6 kappa pulps, respectively.

The overall bleaching chemical consumptions by the kappa 17.5 and 10.6 pulps, measured as total active chlorine, were 42.1 and 35.1 kg/odt pulp, respectively, to achieve an ISO brightness of about 90.0%. The post color numbers values were in the range of 0.37-0.51 for both bleached pulps, indicating high brightness stability. The summary results of the bleaching by O-D*-(EP)-D sequence is showed in Table 7.

Table 7. Summary results of the bleaching by O-D*-(EP)-D sequence.

Bleaching Parameter	Kappa Number 17.5	Kappa Number 10.6
Total Active Chlorine[*], kg/odt	42.1^a	35.1^b
Brightness, % ISO	89.9^a	90.4^a
Post Color Number	0.51^a	0.37^a
Viscosity, dm^3/kg	899^a	760^b
Kappa Number	0.47^a	0.38^a

[*] Total Active Chlorine (kg/odt) = ClO_2 (kg/odt)*2.63 + H_2O_2 (kg/odt)*2.09.

Note: The averages marked with the same letters in each line, are not significantly difference by Tukey's test at a 5% significance level.

3.3. Physico-mechanical tests

The bleached pulps were beaten using different revolutions in the PFI mill (0, 500, 1000,1500 and 0, 1000, 1500, 2000 revolutions for pulps originated from soda pulping with final kappa number 17.5 and 10.6, respectively) and subjected to physical and mechanical tests in order to evaluate their potential for the production of printing and writing paper grades. All the proprieties were expressed in relation to the energy consumed during beating given its contribution to paper production cost. For the mass production the consumption of energy during refining can represent up to 30% of the cost. Each graph shows the experimental data and the curves that describe the fitted models.

3.3.1. Drainage Resistance and Beatability

Pulp drainability can be loosely defined as the capacity of the pulp to drain the water from the mat. As this parameter increases, so does the tensile index. Pulp beatability can be loosely defined as the amount of pulp beating energy required to achieve a certain drainage degree. Therefore, the relationship between ^{o}SR and energy consumption, for example, gives a direct indication of pulp beatability. The higher the amount of beating energy required to achieve a given ^{o}SR, the lower is the pulp's beatability. Figure 3 shows the relations between °SR and tensile index (A) and °SR and energy consumption (B) for the bleached pulps with initial brownstock kappa numbers of 17.5 and 10.6. As anticipated, the resistance to drainage increased with increasing tensile index and the ^{o}SR increased with increasing energy consumption. The drainage resistance and beatability were not influenced by the degree of pulping delignification. Thus, such properties of the two pulps are represented by common curve.

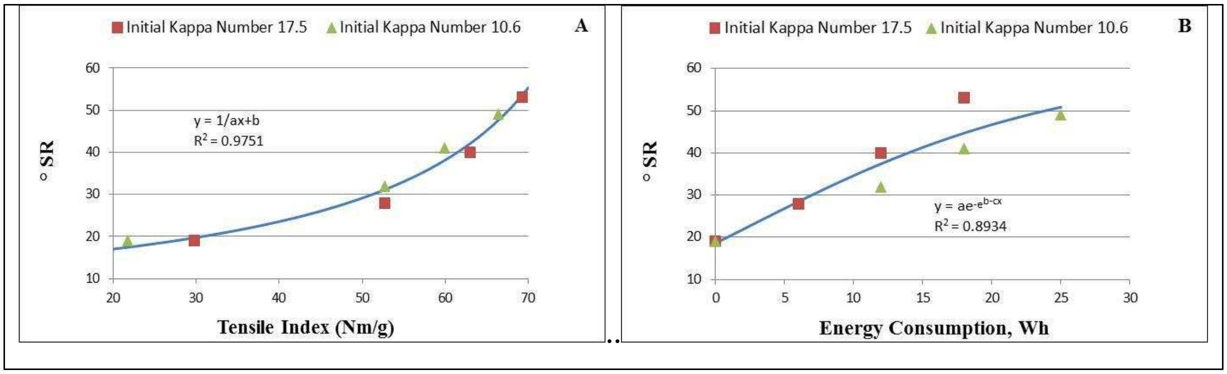

Figure 3. Drainage resistance (A): Schopper-Riegler versus tensile index; beatability (B): Schopper-Riegler versus energy consumption for bleached pulps cooked to two different degrees of delignification (kappa numbers of 17.5 and 10.6).

3.3.2. Tensile Index, Burst Index and Tear Index

The tensile index is a representation of the fiber strength, bonding and length and is an indicator of the paper's resistance to web breaking during printing and converting [33]. The burst index measures the amount of hydrostatic pressure necessary to rupture a piece of paper and is expressed in kPa•m^2/g [34]. The tearing resistance of paper depends on the fiber individual strength, but is also affected by fiber orientation, fiber strength, fiber length, bonding and fiber flexibility [35]. Figure 4 shows the relations between tensile, burst and tear index versus energy consumption for the bleached pulps with initial kappa numbers 17.5 and 10.6.

It is observed that tensile and burst index increases with energy consumption. The 17.5 kappa pulp exhibited a higher tensile and burst index than the 10.6 kappa pulp over the beating energy range examined. This difference was significant since the identity models fitted two different curves for the two pulps. The more severe cooking conditions used to obtain the 10.6 kappa pulp probably caused a decrease in pulp's xylan content, which resulted in a negative impact on tensile.

Regarding the tear index, the tendencies of the curves are different. Tear index increases in the initial phase and then decreases. This behavior is similar to eucalyptus pulps [36; 37]. The pulps studied were statistically different. The pulp with kappa number 17.5 showed higher values of tear index in the initial phase than pulp with kappa number 10.6. Throughout the refining this tendency was reversed.

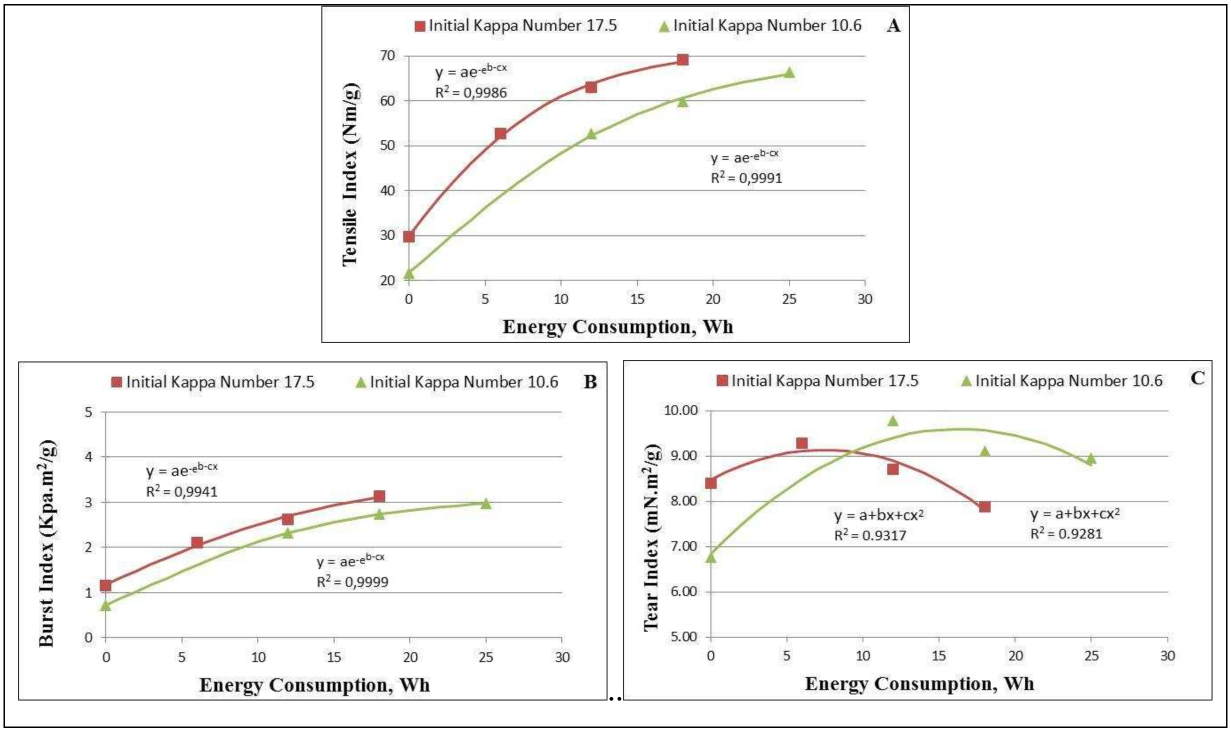

Figure 4. Tensile Index (A); Burst Index (B) and Tear Index (C) versus Energy Consumption for bleached pulps cooked to two different degrees of delignification (kappa 17.5 and 10.6).

3.3.3. Specific Elastic Modulus (MOE) and Tensile Energy Absorption (TEA)

Modulus of elasticity (MOE), also known as specific elastic modulus, is an important property because it represents the capacity of the material to absorb a tensile force without suffering substantial deformation. Higher MOE values provide greater capacity of the material to absorb a certain load without undergoing large deformations. The tensile energy absorption (TEA) represents the durability of the paper when subjected to repetitive use when subjected to tensile or impact forces. Figure 5 shows the relations of MOE and TEA with energy consumption for the two bleached pulps.

Both MOE values as those of TEA values showed higher for the pulps with kappa number 17.5 than pulps with kappa number 10.6. Probably due to drastic cooking that the pulp of lower kappa number was submitted.

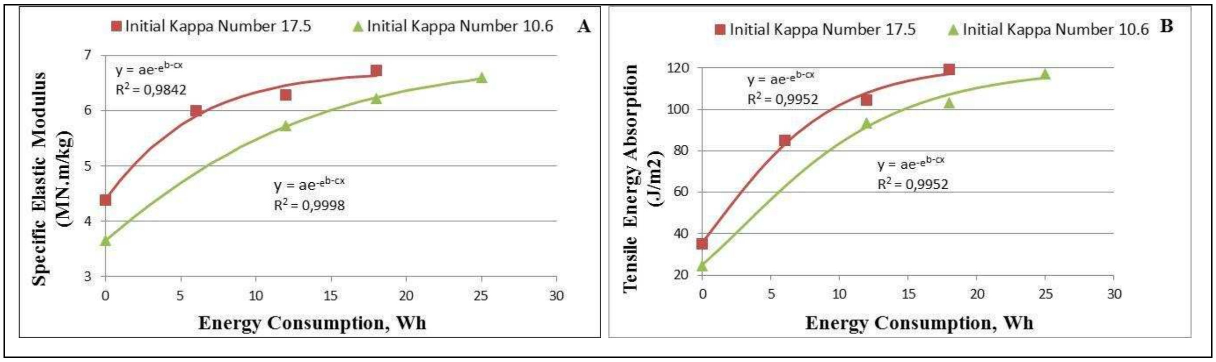

Figure 5. Specific elastic modulus (A) and tensile energy absorption (B) versus energy consumption for bleached pulps cooked to two different degrees of delignification (kappa numbers of 17.5 and 10.6).

3.3.4. Resistance to air passage, Apparent Specific Weight and Apparent Specific Volume

Air resistance has an inverse relationship with paper porosity. This property is highly and positively influenced by the amount of pulp refining. Its behavior as a function of beating energy consumption is presented in Figure 6 for the two bleached pulps. The paper sheet resistance to air passage increases with increasing energy consumption due to decreased porosity. The pulp of kappa 17.5 showed higher air resistance than that of kappa 10.6 (Figure 6). This difference was significant since the identity models fitted two different curves for the two pulps.

The apparent specific weight and volume are very important properties for printing and writing paper grade papers as they influence the porosity and opacity of paper. For a given raw material, an increase in apparent specific volume or a decrease in apparent specific weight means an increase in paper opacity and porosity. The apparent specific volume is also known as *bulk*. The structural characteristics of the fibers also influence the determination of this property. Less collapsible fibers contribute to increased specific volume of papers because their low conformation capacity. Figure 6 show the relations of apparent specific weight and apparent specific volume with energy consumption for the two bleached pulps. From Figure 6, it could be seen that apparent specific weight increased and apparent specific volume decreased with refining energy consumption. Both specific weight and volume were not significantly affected by the degree of delignification during soda pulping. Thus, such properties of the two pulps are represented by common curve.

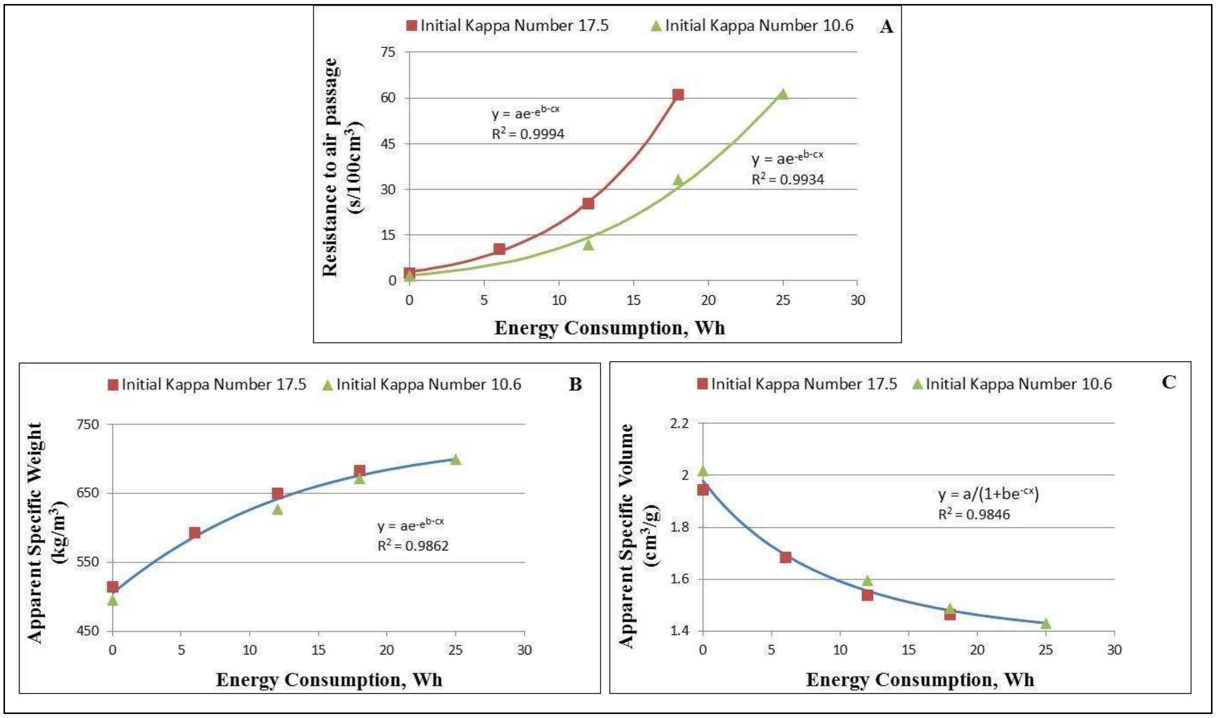

Figure 6. Resistance to air passage (A); apparent specific weight (B) and apparent specific volume (C) versus energy consumption for bleached pulps cooked to two different degrees of delignification (kappa 17.5 and 10.6).

3.3.5. Opacity and Scattering Coefficient

Opacity is defined as the ability of light to pass through a paper sheet. The extent of beating affects opacity. Opacity is important in printing and writing paper grade pulps in order to prevent the printed images or text from the opposite side from being seen from the other side of the sheet. Opacity is a function of paper thickness, amount of filler(s), pulp brightness, and beating degree. Beating makes the paper denser, but excessive beating results in lower opacity [38]. The scattering coefficient is a measure of the ability of the sheet to scatter light. Figure 7 shows the relations between opacity and scattering coefficient versus energy consumption during refining for the two bleached pulps. The opacity and scattering coefficient decreases with increasing refiner energy consumption.

The opacity and scattering were not influenced by the degree of pulping delignification. Thus the opacity and scattering of the two pulps is represented by common curve.

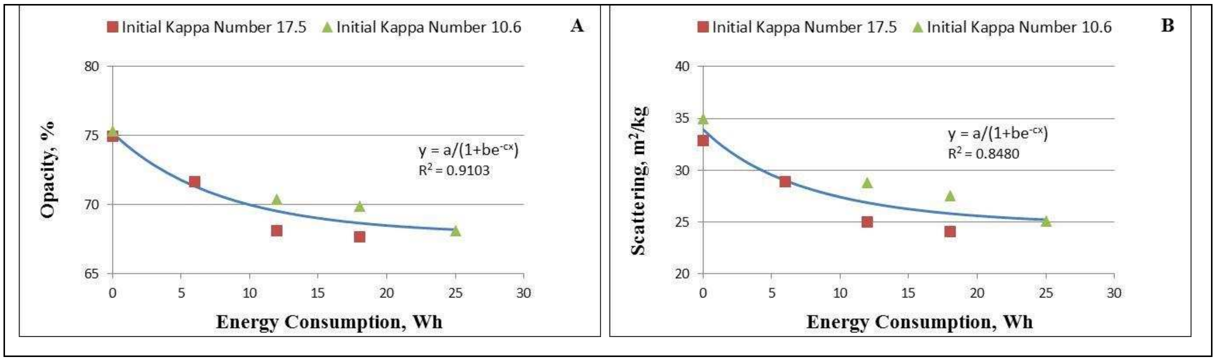

Figure 7. Opacity (A) and Scattering (B) versus Energy Consumption for bleached pulps cooked to two different degrees of delignification (kappa 17.5 and 10.6).

3.4. Potential of bleached elephant grass soda pulp for production of printing and writing paper grade

In order to determine the potential of the pulps produced in this study for the production of printing and writing (P&W) paper grade, the elephant grass pulps were compared with eucalypt pulps that are traditionally used for this application. According to Foelkel [39], tensile and tear indexes are important for P&W paper grades. However, other very important properties of P&W paper grade pulps are opacity, bulk and porosity. Table 8 shows a list of relevant properties for the pulps of this study and of commercial eucalypt P&W paper grade kraft pulps. In general, the bleached pulps derived from elephant grass presented acceptable properties and presented similar properties with those of traditional eucalypt kraft pulps. Considering opacity as one of the most important properties for this paper grade, opacity was chosen as property to be standard for comparison between elephant grass and eucalypt pulps properties.

The strength properties of the eucalypt kraft pulps, such as tensile and burst index, were generally higher than those of the elephant grass soda pulps. But tear index showed similar values for elephant grass and eucalyptus pulps. Due both the eucalypt and elephant grass raw materials had similar fiber morphology; the fiber viscosities of the eucalypt kraft pulps were similar to the elephant grass pulp. However, the values from eucalypt kraft pulps were slightly higher than those of the elephant grass pulp. The values of bulk (~1.5 cm^3/g) and opacity (~70%), which are very important properties for printing and writing paper grades, were similar for eucalypt kraft and elephant grass pulps. Yet, when comparing the elephant grass pulps with eucalypt pulps (*Eucalyptus grandis*), the variations between the physico-mechanical properties values were small. Values of bulk, tensile index, burst index and opacity were 1.5 cm^3/g, 56.5 N•m/g, 3.6 kPa•m^2/g, and 71.9%, respectively for the *Eucalyptus grandis* pulps.

Table 8. Selected printing and writing paper grade properties for the elephant grass soda pulp of this study (initial kappa 17.5 and 10.6) and of commercial eucalypt kraft pulps and of *Eucalyptus grandis.*

Sample	Opacity %	Mill Revo-lutions	°SR	Bulk cm^3/g	Tensile Index N•m/g	Burst Index kPa•m^2/g	Tear Index mN•m^2/g	Air Resistance s/100cm^3
EG KN:17.5	71.6	500	28	1.7	52.7	2.1	9.3	10.5
EG KN:10.6	70.4	1000	32	1.6	52.7	2.3	9.8	11.8
Eucalyptus Hybrid [*]	70.8	1793	34	1.4	78.0	5.4	10.5	4.6
Eucalyptus Hybrid [*]	74.1	1184	34	1.6	66.2	4.6	8.6	3.8
Eucalyptus Hybrid [**]	70.7	3000	40	1.2	77.0	4.8	9.0	31.3
Eucalyptus Grandis [***]	72.9	1000	33	1.5	56.5	3.6	9.8	8.9

[*] Bassa et. al., 2005.

[**] Andrade, 2010.

[***] Pedrazzi, 2009.

4. Conclusions

- The morphological analyses of the elephant grass indicated a short fibered material, similar to hardwoods.
- The bleached soda pulps cooked to 17.5 and 10.6 kappa numbers showed similar refinability and resistance to drainage, but the tensile and burst index were higher for the 17.5 kappa pulp.
- Both bleached pulps (17.5 and 10.6 kappa) obtained from elephant grass were suitable for production of printing and writing paper grades; however, the higher

kappa pulp was more economically attractive given its higher pulping yield, despite the significantly increased bleaching chemical demand.

- In general, the bleached pulps derived from elephant grass presented acceptable properties and presented similar properties when compared to those of traditional eucalypt kraft pulps.

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Conclusões Gerais

- O conteúdo de celulose, hemiceluloses e lignina das frações córtex e medula do bagaço variaram significativamente entre si, com o córtex apresentando mais celulose e hemiceluloses e menos lignina, minerais e extrativos. A lignina da fração córtex apresentou elevados teores de PCAs (ácidos cinâmicos) e estrutura similar à de madeiras de folhosas. A análise morfológica da fração córtex do bagaço indicou ser um material composto por fibras curtas, semelhante às de madeiras de folhosas.

- O rendimento do isolamento da lignina da preparação CEL96 foi muito maior do que o da preparação MWLc. O conteúdo de ácido *p*-coumárico presente no extrato alcalino foi maior que o conteúdo de ácido ferúlico. O pico de correlação da ligação β-O-4 ' foi o sinal de ligação entre unidades mais importante encontrado em todas as frações da lignina isolada. Foi verificado que ambas as preparações, MWLc e CEL96, do córtex e da medula contêm elevadas quantidades de ácidos *p*-hidroxicinâmicos (*p*HCAs).

- A produção de polpa solúvel foi possível pelo processo de pré-hidrólise seguido de polpação soda (PHS) independente do número kappa inicial, sendo o kappa 16,9 mais desejável, pelo maior rendimento de polpa solúvel. A polpa solúvel do córtex de bagaço, produzida pelo processo PHS em qualquer dos dois níveis de kappa, apresenta baixa viscosidade e teor relativamente alto de cinzas, o que limita seu uso para certas aplicações de polpa solúvel; algum sistema de desmineralização da polpa no final do branqueamento é requerido.

- As polpas branqueadas e cozidas pelo processo soda com números kappas 17,5 e 10,8 apresentaram similares valores de refinabilidade, resistência à drenagem e propriedades de resistência (tração, arrebentamento e rasgo). Ambas as polpas marrons obtidas a partir do córtex do bagaço de cana-de-açúcar foram apropriadas para a produção de papéis de imprimir e escrever, no entanto, a polpa marrom de maior número kappa foi economicamente mais atraente dado o seu rendimento de polpação superior.

- O capim elefante se caracterizou pelo baixo teor de lignina e relativamente alto teor de minerais e extrativos, em relação à madeira de eucalipto, por exemplo. A análise morfológica do capim elefante indicou ser um material de fibra curta, semelhante a madeiras de folhosas. As polpas cozidas pelo processo soda até números kappa 17,5 e 10,6 e branqueadas apresentaram valores similares de refinabilidade e resistência à drenagem, mas o índice de tração e arrebentamento foram maiores para a polpa com número kappa 17,5. Porém, ambas as polpas são apropriadas para a produção de papéis de imprimir e escrever, sendo a de maior número kappa economicamente mais atraente dado o seu rendimento de polpação superior, sem significativo aumento da demanda de reagentes químicos de branqueamento.