FERNANDO JOSÉ BORGES GOMES

ESTUDOS DE CARACTERIZAÇÃO E DESCONSTRUÇÃO DE BIOMASSAS DE EUCALIPTO E CAPIM ELEFANTE PARA APLICAÇÕES EM BIORREFINARIA INTEGRADA A INDÚSTRIA DE CELULOSE

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

Fernando José Borges Gomes, filho de Josefina Borges Gomes e Odilon Justino Gomes, nasceu em 25 de abril de 1983, em Teixeiras, estado de Minas Gerais.

Cursou o ensino fundamental do pré-escolar à quarta série na Escola Estadual Professor Carlos Trivellato, em Ponte Nova, MG, e o ensino fundamental da quinta à oitava série e o ensino médio, na Escola Estadual Professor Antônio Gonçalves Lanna, também em Ponte Nova, MG.

Em 2004, ingressou no curso de Engenharia Florestal na Universidade Federal de Viçosa. Foi bolsista da FAPEMIG por dois anos no projeto “Avaliação não destrutiva da madeira visando à produção de celulose Kraft”. Foi estagiário por quatro anos no Laboratório de Celulose e Papel na área de química da madeira e branqueamento de polpa celulósica, sob a orientação do professor Jorge Luiz Colodette. Concluiu a graduação em Engenharia Florestal em janeiro de 2009.

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Em março de 2010 ingressou no Programa de Pós-graduação em Ciência Florestal em nível de doutorado.

SUMÁRIO

LISTA DE ABREVIATURAS

AFEX – ammonia fiber expansion

AHQ – anthrahydroquinone

AQ – anthraquinone

ARP – Ammonia recycle percolation

C – carbon

Ca – calcium

CCD - charge-coupled device

Cl^- - chloride

Cu – cooper

DMAC – dimethylacetamide

DP – degree polymerization

ECF – elemental chlorine free

Fe – iron

GPC – gel permeation chromatography

H – hydrogen

HPLC – high performance liquid chromatographic

K – potassium

LGF – lignofiber

LiCl – lithium chloride

MAI – medium annual increase

Mg – magnesium

Mn – manganese

N – nitrogen

Na_2S – sodium sulphide

NaOH – sodium hydroxide

NMR – nuclear magnetic resonance

O-stage – oxygen delignification stage

RID – refractive index detector

S/G – syringyl / guaiacyl

SiO_2 – silicon dioxide (silica)

Soda-AQ – soda anthraquinone

Soda-Aq-O_2 – soda anthraquinone oxygen

Soda-O_2 – soda oxygen

TAC – total active chlorine

RESUMO

GOMES, Fernando José Borges, D.Sc., Universidade Federal de Viçosa, Dezembro, 2013. **Estudos de caracterização e desconstrução de biomassas de eucalipto e capim elefante para aplicações em biorrefinarias integradas à indústria de celulose.** Orientador: Jorge Luiz Colodette. Coorientadores: José Lívio Gomide e Rubens Chaves de Oliveira.

O grande desafio da civilização moderna é se tornar uma sociedade mais sustentável, baseada no uso racional dos recursos naturais. Nesse contexto, surgiu o conceito de biorrefinaria, que prevê a conversão de materiais lignocelulósicos em bioprodutos (materiais, produtos químicos, etc) e bioenergia (biocombustíveis, energia, etc) com baixo desperdício e mínimas emissões. O conceito de biorrefinaria esta alicerçado em biomassas variadas como, por exemplo, resíduos agrícolas e florestais, madeira, gramíneas em geral, etc. A indústria de celulose e papel tem boa condição para colocar em prática esse conceito, pois já possui infraestrutura adequada para a colheita, transporte, armazenamento e manuseio de grandes volumes de biomassa, para desconstrução da biomassa, para queima de resíduos do processo, para geração de energia, para tratamento de resíduos, sólidos, líquidos e gasosos, etc. Um dos grandes desafios às biorrefinarias é a variada gama de matérias primas a serem processadas, que apresentam características e comportamentos distintos nos processos de desconstrução. O objetivo desse estudo foi investigar a biorrefinagem de uma nova geração de clones de eucalipto e de capim elefante com vistas à produção de polpa e etanol celulósico. A tese foi dividida em cinco capítulos, a saber: (1) uma revisão bibliográfica sobre processos de biorrefinaria integrados à indústria de polpa celulósica; (2) caracterização completa da nova geração de clones de eucalipto brasileiros e capim elefante; (3) avaliação de processos alcalinos de desconstrução da nova geração de clones de eucalipto brasileiros; (4) desconstrução alcalina de um clone de eucalipto brasileiro visando à produção de bioetanol; e (5) potencial do capim elefante para a produção de polpa celulósica. No Capítulo 1 foi feito uma revisão de literatura sobre a integração dos processos de biorrefinaria com a indústria de polpa celulósica, com ênfase na produção de etanol celulósico como subproduto, focalizando as tecnologias de pré-tratamentos ácidos, neutros e alcalinos, de sacarificação enzimática e de fermentação de açúcares C6 e C5 em processos separados e

simultâneos. No Capítulo 2, foi avaliada a qualidade de 18 clones de eucalipto e de 2 espécies de capim elefante considerando os parâmetros mais relevantes para processos de biorrefinaria, incluindo produtividade de biomassa, densidade, teor de umidade, e morfologia e composição química das fibras; desse estudo foram selecionados os quatro mais promissores clones de eucalipto, e uma espécie de capim elefante para os estudos posteriores. No Capítulo 3, investigaram-se os comportamentos dos materiais selecionados no Capítulo 2, quanto aos seus comportamentos frente a vários métodos de desconstrução alcalinos (Kraft, soda-AQ, soda-AQ-O_2 e soda-O_2), que foram avaliados quanto ao rendimento gravimétrico, demanda de reagentes químicos e grau de polimerização dos polissacarídeos em níveis variados de deslignificação; os dois processos mais promissores (soda-AQ e Kraft) para a produção de polpas foram estudados minuciosamente, através da avaliação de polpas de kappa 15 e 20 quanto a suas composições e estrutura (conteúdos de carboidratos, ácidos urônicos, ácidos hexenurônicos, peso molecular dos carboidratos e estrutura da lignina residual), e dos respectivos licores negros (poder calorifico, teor de sólidos, análise elementar, e estrutura da lignina). No Capítulo 4, foram investigados os dois processos de desconstrução alcalinos (soda-AQ e soda-O_2) mais promissores para a produção de bioetanol, a partir do clone de eucalipto G1xUGL, após desconstrução até os números de kappa 15, 35, 50 e 70, sacarificação e fermentação. No Capítulo 5, o potencial do capim elefante para a produção de polpa celulósica foi avaliado em relação ao eucalipto, comparando-se os processos alcalinos kraft e soda-AQ nos níveis de número kappa 15 e 20, através da análise de rendimento gravimétrico, demanda de reagentes químicos, propriedades químicas da polpa, e branqueabilidade da polpa. As principais conclusões desse estudo foram: Capítulo 1: paralelamente ao aprimoramento dos processos de desconstrução da biomassa, a conversão enzimática de polissacarídeos da biomassa lignocelulósica pode ser apontada como a tecnologia mais promissora para a consolidação das biorrefinarias. Capítulo 2: a madeira de eucalipto apresenta maior potencial para biorrefinaria que o capim elefante pelos seus maiores valores de produtividade de massa seca/ha e densidade, e menores teores de umidade e de minerais que o capim elefante, com destaque para os clones (U1xU2; G1xUGL; DGxU2, e IP); dentre os capins elefantes, destaque para a amostra EG1 (*Pennisetum purpureum*) pela sua maior

produtividade (32 t/ha/ano) e densidade (216 kg/m^3). Capítulo 3: os processos soda-AQ e Kraft são os mais indicados para a desconstrução alcalina da biomassa para a produção de polpa celulósica. Os processos alcalinos que utilizam oxigênio como aditivo (soda-AQ-O_2 e soda-O_2) são mais indicados para desconstrução da biomassa com vistas ao etanol celulósico. Capítulo 4: a desconstrução da madeira de eucalipto pelo processo soda-O_2 terminado em número kappa na faixa de 35-50 apresentou bom potencial para produção de etanol celulósico, resultando níveis de sacarificação (73%). Esses rendimentos garantem um rendimento teórico de etanol acima de 370 L/t de madeira seca. Capítulo 5: Apesar de o capim elefante apresentar um alto conteúdo de extrativos e minerais, ele tem potencial para produção de polpa celulósica, sendo que a sua desconstrução deve ser realizada pelo processo kraft em kappa 20 ou processo soda-AQ em kappa 15.

ABSTRACT

GOMES, Fernando José Borges, D.Sc., Universidade Federal de Viçosa, December, 2013. **Studies of the characterization and deconstruction of eucalypt and elephant grass for biorefinery applications integrated to the pulp industry.** Adviser: Jorge Luiz Colodette. Co-advisers: José Lívio Gomide e Rubens Chaves de Oliveira.

The great challenge of modern civilization is becoming a sustainable society based on rational utilization of natural resources. In this scenery, the biorefinery concept came up, which refers to the conversion of lignocellulosic materials into bioproducts (pulp, chemicals, etc.) and bioenergy (ethanol, energy, etc.) with minimal emissions and low waste. The biorefinery concept is based on many different kinds of biomass such as agricultural and forest wastes, wood, and grasses in general, etc. For applying this concept, the pulp and paper industries are an ideal place, since they have all infrastructures for the harvesting, transportation, storage, and handling of large volumes of biomass, for partial biomass deconstruction, burning of the process wastes, aiming energy generation, and for the treatment of the solids and gas wastes, etc. One of the great challenges to the biorefineries is the wide range of raw materials to be processed, which presents different characteristics and behaviors during the deconstruction processes. This work aimed to investigate the biorefinery processes of a new generation eucalypt clones and elephant grass aiming pulp and cellulosic ethanol production. This thesis is divided in five chapters, namely: (1) literature review on biorefinery processes integrated to the pulp industry, (2) thorough characterization of Brazilian new generation eucalypt clones and elephant grass, (3) evaluation of alkaline deconstruction processes for Brazilian new generation of eucalypt clones, (4) evaluation of Brazilian new generation of eucalypt clone for biofuel production, (5) potential of elephant grass for pulp production. In Chapter 1, it was made a literature review on the integration of biorefinery processes associated with the pulp industry, with emphasis on the cellulosic ethanol production as a byproduct, focusing on technologies acids, neutral and alkaline pretreatment, enzymatic saccharification and fermentation of C6 and C5 sugars in separate and simultaneous processes. In Chapter 2, it was evaluated the quality of 18 eucalypt clones and 2 species of elephant grass for the production and pulp and biorefinery processes. The goal of this chapter was to select the four most promising clones of eucalypts and one species of elephant grass for subsequent studies. For this, a

thorough investigation of the samples, which contemplated analyses of forestry productivity, density, moisture content, morphology and chemical composition, was performed. In Chapter 3, it was investigated for the four eucalypt clones chosen previously in Chapter 2, regarding their behavior when submitted to the alkaline deconstruction processes (soda-AQ, soda-AQ-O_2, soda-O_2, and Kraft), which were evaluated considering their screening yield, alkali charge and viscosity for different kappa number levels. The two most promising processes for producing pulp (kraft and soda-AQ) were studied in details through the pulp production aiming kappa numbers 15 and 20 regarding their composition and structure (content of carbohydrates, uronic acid, hexenuronic acid, carbohydrate molecular weight, structure of residual lignin), as well as for their respective black liquors (heating value, solid content, elemental analysis, and lignin structure). In Chapter 4, it was investigated two kinds of alkaline deconstruction processes (soda-AQ and soda-O_2), which are most promising for bioethanol production, being used as a raw material the eucalypt clone G1xUGL. The processes of deconstruction were conducted aiming different levels of kappa number (15, 35, 50 and 70). After this step, a stage of saccharification followed by another of fermentation of the samples was performed. In Chapter 5, the potential of elephant grass for pulp production was evaluated in comparison with a eucalypt clone by using alkaline processes (kraft and soda-AQ) terminated at kappa numbers 15 and 20, through the screened yield, alkali charge, viscosity and bleachability. The main findings of this work were: (Chapter 1) besides the biomass pretreatments improvement and processes for biomass deconstruction, enzymatic conversion of polysaccharides in the lignocellulosic biomass will be a key technology in future biorefineries; (Chapter 2) the eucalypt clones showed a higher potential for biorefinery applications than the elephant grass due to their high dry biomass production per hectare, high density and contain fewer minerals and extraneous materials, highlighting the eucalypt clones U1xU2, G1xUGL, DGxU2, and IP; between the elephant grass, the EG1 (*Pennisetum purpureum*) sample was chosen due to its highest productivity (32 ton/ha/yr) and density (216 kg/m^3); (Chapter 3) soda-AQ and Kraft showed to be the best processes for producing pulp. The alkaline processes using oxygen (soda-AQ-O_2 and soda-O_2) are more indicated for working as alkaline pretreatment method to be used in lignocellulose biorefineries; (Chapter 4) the soda-O_2 process at kappa number levels of 35-50 provided the best potential for cellulosic ethanol production, with the best rate of saccharification (73%).

These levels of sugar released are high and warrant efficient production of ethanol with yield above 370 L/t of dry wood; (Chapter 5) although the elephant grass showed a high extractive and minerals content, it proved as a potential raw material for pulp production, being the ideal cooking processes the Kraft at kappa number 20 or soda-AQ at kappa number 15.

INTRODUÇÃO GERAL

Em razão da grande disponibilidade de áreas de alta produtividade agrícola e florestal, o Brasil é considerado um grande centro para o desenvolvimento, aperfeiçoamento e implementação de tecnologias que visem converter biomassa lignocelulósica em energia, bioprodutos (biomateriais, bioquímicos, etc.) e biocombustíveis (etanol, butanol, biogás, etc), utilizando-se o conceito de biorrefinaria. O termo biorrefinaria se refere à conversão da biomassa em uma gama de produtos, com baixo desperdício e mínimas emissões. É aplicado à indústria que transforma materiais brutos de fonte renovável (bagaço-de-cana, bambu, palha de cereais, resíduos florestais, madeira, licor negro kraft, etc.) em produtos de maior valor agregado. Fabricando produtos múltiplos, a biorrefinaria permite maximizar o valor derivado da matéria prima, através de sua utilização mais racional e sustentável. O conceito de biorrefinaria está em grande evidência no setor de celulose e papel, onde duas principais estratégias têm sido consideradas: (1) processamento completo da biomassa com geração de produtos de alto valor agregado, espelhando-se nas refinarias petroquímicas; e (2) conversão eficiente de algumas frações da biomassa em combustíveis, energia, materiais e/ou produtos químicos, sendo as demais utilizadas para fabricação de polpa celulósica.

Para utilização da biomassa em processos de biorrefinaria é necessária a sua desconstrução, para isolar seus componentes e torna-los acessíveis ao processamento químico, bioquímico, térmico, etc. Por isso, a indústria de celulose é altamente cogitada para funcionar como uma plataforma de biorrefinaria, já que essa indústria tem experiência na desconstrução parcial da biomassa visando à produção de polpa celulósica. Os processos de desconstrução mais utilizados pelas indústrias de celulose são os chamados processos alcalinos, sendo o Kraft o mais difundido, e muito bem consolidado. O processo kraft apresenta severas desvantagens em processos de biorrefinaria por utilizar compostos de enxofre. O enxofre dificulta a recuperação racional dos componentes da madeira dissolvidos durante o processo de desconstrução. Existe uma série de processos alcalinos alternativos ao Kraft, tais como soda-AQ, soda-AQ-O_2 e soda-O_2 que podem

utilizar as mesmas instalações usadas no processo kraft com vantagens ambientais e operacionais.

Existe preocupação constante com a disponibilidade e qualidade da matéria-prima que abastece a indústria de celulose, pois ela representa o maior custo de fabricação. Na América do Sul, a principal matéria para fabricação de celulose é a madeira, que representa 50% do custo de produção dessa *commodity*, sendo o item mais relevante na composição de custos, e com tendência de aumento. Por se tratar de um material biológico, a madeira é grandemente heterogênea, e programas de melhoramento genético vêm sendo realizados no intuito de se obterem clones mais bem adaptados aos interesses do setor.

Paralelamente, há uma constante busca, por matérias primas alternativas de alta produtividade e que apresentem custos competitivos e composição físico-química adequada. Dentre estas se destacam o bagaço-de-cana, bambu, palhas de cereais, capim elefante, etc. O capim elefante tem sido plantado em grande escala no Brasil, como uma forrageira para atender o setor de produção animal. Essa gramínea apresenta grande potencial como matéria-prima alternativa para processos de biorrefinaria integrados a indústria de celulose, porque o seu cultivo tem sinergia silvo-agro-pastoril com as florestas de eucalipto, além de a mesma apresentar características físico-químicas desejáveis.

Estudos na área de biorrefinaria requerem conhecimento profundo da matéria-prima lignocelulósica bem como dos processos para desconstruí-la de forma a se desenhar processos eficientes, sustentáveis e ambientalmente compatíveis. O objetivo desse estudo foi investigar a biorrefinagem de uma nova geração de clones de eucalipto e de capim elefante com vistas à produção de polpa e etanol celulósico. A tese está dividida em cinco capítulos, a saber: (1) uma revisão bibliográfica sobre processos de biorrefinaria integrados à indústria de polpa celulósica; (2) caracterização completa da nova geração de clones de eucalipto brasileiros e capim elefante; (3) avaliação de processos alcalinos de desconstrução da nova geração de clones de eucalipto brasileiros; (4) desconstrução alcalina de um clone de eucalipto brasileiro visando à produção de bioetanol; e (5) potencial do capim elefante para a produção de polpa celulósica.

CAPITULO 1

LITERATURE REVIEW ON BIOREFINERY PROCESSES INTEGRATED TO THE PULP INDUSTRY

Abstract

Biorefinery is a new term to designate two main subjects, bioproducts and bioenergy, which play important roles towards a more bio-based society. This paper reviews the current biorefineries model as well as its future importance focusing on pulp mill opportunities. There are currently several different levels of integration in biorefineries which adds to their sustainability, both economically and environmentally. Enzymatic pretreatment for biomass deconstruction aiming to release the polysaccharides is a key technology in future biorefineries and it is currently the subject of intensive research.

1. Introduction

A great challenge for the modern civilization is becoming a sustainable society based on more realistic needs and rational utilization of the natural resources. In this context, energy is one of the most important issues. Currently, the fossil fuels (oil, coal, and natural gas) are the main energy sources worldwide but their exploitation is neither sustainable nor environmental unfriendly.

The scientific community believes that in the near future large volumes of biomass will be processed to produce biofuels together with valuable co-products, which will be increasingly used to make other bioproducts (DEMIRBAS, 2008; BALAT, 2009; DEMIRBAS, 2009; BÖRJESSON, 2009; SANTOS et al, 2012; GUPTA et. al., 2013). In this scenario, certain bio based industries such as the pulp and the sugar cane could take enormous advantage of their current know how in order to make intelligent use of their biomass feedstocks, by operating their facilities as biorefineries. Biorefinery is a new term that is related to two main subjects, value-added bioproducts (chemical building blocks, materials, pulps), and bioenergy (biofuels, power, and heat) from biomass, considering sustainability assessment and life cycle (ARESTA et al. 2012)

Many recent studies have pointed out the pulp industry as an interesting platform to deploy the biorefinery concept (AXEGARD, 2006; LARSON, 2007; SLANGARD et. al., 2013). This industry applies partial biomass deconstruction processes for

producing pulp and other products, such as paper, viscose, acetate, nitrates, lignosulphonates, vanillin, ethanol, acetic acid, etc, in addition to steam and power. The processes currently used are efficient to separate the lignin and extractives fractions from the polysaccharides; this cracking is very suitable and necessary for biorefinery applications. This paper reviews the current biorefineries model as well as its future importance focusing on cellulosic pulp mill opportunities.

2. Biorefineries

The emerging bio-based economy is a very promising sector with notable future potential and many business opportunities (LUOMA et al., 2011); in this scenario it is includes the biorefinery concept. There are many different definitions for biorefinery, but in general the term is applied for using renewable raw materials (e.g. biomass) to produce energy together with a wide range of everyday commodities in an economic and sustainable manner (ZHANG, 2008; HIMMEL, 2008; DEMIRBAS, 2009, ARESTA et al. 2012). The fossil fuels (oil, coal, and natural gas) are the main energy source worldwide; however, one of the most important challenges of the modern society is in decreasing our dependency on fossil fuel reserves and boosting rural development. The biorefinery concept attempts to apply to biomass conversion, the methods that have been applied to the refining of petroleum (DEMIRBAS, 2009). Biorefineries would simultaneously produce biofuels as well as bio-based chemicals, heat, and power. Biorefineries are seen as a very promising route to meeting our aims for sustained prosperity and preserving the environment. Unlike oil refineries, which are units of large industrial size, biorefineries should include facilities of various sizes (RODRIGUES, 2011).

Renewable sources of energy are required for sustainable development of our society in the near future (DEWULF and VAN LANGENHOVEN, 2006). Plant biomass is the main source of renewable materials on earth and represents a potential source of renewable energy. However, the main source of bioethanol currently used (starch from cereal seeds) is too expensive and of limited availability. By contrast, cellulose is available in high amounts at very low cost (as forest, agricultural or industrial lignocellulosic wastes and cultures) and, after overcoming some current barriers, could be a widely available and inexpensive bioethanol source

in the future (GRAY et al., 2006; U.S.DOE, 2006; ARESTA et al. 2012, OHASI, 2013).

3. Biomass sources

Hardwoods and softwoods have been the world's main raw materials for pulp production and they deliver suitable product quality. However, the cost of these raw materials has greatly increased in the last decade due to many factors, including the newly created demand for biorefinery applications. Therefore, the establishment of new raw materials that can compensate the lack of low cost wood has been largely sought. In this way, each one should be able to identify the ideal biomass source which should be used for biorefinery application. High productivity plants such as grasses can potentially supply biomass of low cost to meet the current demand (VILELA et al. 1997, 2001a,b, 2002a,b, 2003a,b; PAULINO et al.,2007; MAZZARELLA et al., 2007). Currently, the biomass sources are divided in two groups: woody and nonwoody.

Forest and agricultural residues have been the main target in Europe, North America and other places of temperate climate. In tropical climates like in Brazil there is great opportunity to use rapid growth and high productivity woody and nonwoody biomass to practice the Biorefinery concept. In fact, it is possible harvesting eucalypt plantations at one year of age, resembling agricultural crops, with fairly high biomass production. This has been possible due to the great improvements achieved in eucalypt biomass productivity through intensive breeding programs in the last 50 years. There exist clonal plantations in Brazil that delivers productivities of 40 ton/ha/year of bone dry wood at the age of 7 years (BRACELPA, 2013). Planted forests are very productive and homogeneous, delivering outstanding wood quality. Another relevant point is that these breeding programs have been focused on pulp and paper production and the wood quality has been tailor-made for that. When the focus is Biorefinery, there is much more to be done in regard to the understanding of the wood chemical characteristics required for this new purpose.

Regarding woody raw materials some countries and species have been highlighted, e.g. in Brazil has a forest vocation spurred by its large territorial area and tropical climate. The forested area covers more than half of the Brazilian territory (forest per capita: 2.56 ha/person), but only 7 million ha (0.7%) is made of planted forests (SBS,

2012). The Brazilian planted forests (6.7 million ha) are dominated by eucalypts (over 5.1 million ha) and *Pinus* spp (over 1.6 million ha).

Some of the Brazilian planted forests are highly productive, particularly those of *Eucalyptus* spp (Table 1). In some areas of the Brazilian southeast and northeast *Eucalyptus* spp productivity can reach 80 m^3/ha/year (GOMES et al., 2013). The very high productivity of Brazilian eucalypt forests stems from the good adaptation of the species to the climate but also from the breakthrough scientific and technological advances made by Brazilian scientists and forest companies throughout the years. For example, the average productivity of the Brazilian eucalypt forests increased from 24 m^3/ha/yr in 1980 to 41 m^3/ha/yr in 2012, representing an 83% increase in productivity of planted forests in Brazil. It is expected that this productivity will reach 70 m^3/ha/year in the near future (BRACELPA, 2013).

Table 1. Annual productivity of main Brazilian planted forests (SBS, 2012)

Species	Productivity, m^3/ha/year
Acacia (*Acacia* spp)	15-25
Araucaria (*Araucaria angustifolia*)	10-25
Aspen (*Populus deltoides*)	20-30
Eucalypt (Eucalyptus spp)	30-40
Pine (*Pinus* spp)	25-30
Teak (*Tectona grandis*)	15-20

Regarding nonwoody raw materials, there are many possibilities. Sugar cane is one of the most important biomass sources in the world, since it can be used as a food resource (e.g. sugar) or raw material to produce renewable fuels (e.g. ethanol). The sugar cane (*Saccharum spp*) is an interesting raw material for biorefinery since it can provide the following materials: (1) sugars (sucrose, glucose, and xylose); (2) natural polymers (cellulose, hemicellulose, and lignin present in the bagasse and straw); (3) stillage rich in organic raw material; and (4) other compounds, such as alcohols and carbon dioxide (CO_2).

Currently, the biorefinery concept applied to sugar cane has focused on the production of first generation ethanol (from extracted sugar cane juice), and second

generation ethanol (from cellulose). There are three new plants planned for the year 2014 for producing second generation ethanol in Brazil using a biorefinery model (BATISTA, 2013). The second generation ethanol will largely enhance the total ethanol that can actually be produced from sugar cane. . For example, the average sugar cane productivity in Brazil is 85 tons per hectare, and for each ton of sugar cane processed about 140 kg dry-matter of bagasse and 140 kg dry-matter of straw are generated, i.e, 12 tons of straw and 12 tons of bagasse per hectare (SANTOS et al., 2012). The estimated current total global production of first generation ethanol from sugar cane is 20 billion liters a year (Renewable Fuels Association, 2012). When using the sugar cane bagasse and straw in a biorefinery model, the theoretical ethanol yield (considering that all glucose will be converted to ethanol) would be improved by approximately 98.4%, i.e., the current production could be increased to 49.7 billion liters a year (SANTOS et al, 2012).

The use of the sugar cane bagasse residue after sugar extraction to produce second-generation biofuel (e.g. ethanol) has been extensively studied due to its wide availability and low cost (PATEL et. al., 2005; SANTOS et al., 2012). However, the process of using sugarcane bagasse residues to produce ethanol is not cost-effective due to high energy consumption required for a harsh pretreatment process, a complicated detoxification process and the use of expensive enzymes for polysaccharide hydrolysis (WANG et. al., 2013).

Another potential nonwoody raw material is the elephant grass (*Pennisetum* spp) which is highly effective in the CO_2 fixation during the photosynthesis process for biomass production. Vilela *et al.* (1997, 2001a,b, 2002a,b, 2003a,b) and Paulino *et al.* (2007) obtained different results of biomass production from elephant grass (cultivar “Paraíso”) due to the various treatments in their research works. The total production of biomass with 85% of dry matter is 27 ton/ha and may be stored for an indefinite period of time. In accordance with Mazzarella (2007), the advantages of elephant grass as biomass source in relation to other sources are: greater productivity (45 t dry-matter/ha/year), shorter productive cycle (two cuts per year), better cash flow, possibility of total mechanization, and greater assimilation of carbon. Some characteristics of elephant grass compared with sugar cane bagasse are reported by Seye *et al.* (2000). Elephant grass has special potential for biorefinery applications because of its high fiber production of adequate chemical composition,

similar to sugar cane bagasse in many senses (QUESADA et al., 2004; SEYE et al. 2000). Some studies on elephant grass have shown a content of 40, 30 and 17.7% for cellulose, hemicelluloses and lignin, respectively (MADAKADZE et al, 2010). These values are adequate for biorefinery applications, in special the low lignin content that indicate an easier fractionation of this material in deconstruction processes.

Another characteristic of elephant grass is that in the stalks, the fiber content is frequently higher than in leaves (53 and 45-46%, respectively), as well as lignin (11 and 9%, respectively) and cellulose (40-41 and 29-30%, respectively) (VILELA *et al.*, 2003a,b; QUESADA *et al.*, 2004). Another important parameter to take into account is the amount of energy produced per hectare per year. In average, elephant grass can produce 190,000 Mcal/ha/year whereas eucalypt produces about 100,000 and sugar cane bagasse only 30,000.

4. The pulp mills as biorefineries platform

The major components of all lignocellulosic materials are cellulose, hemicelluloses, and lignin, which have the structural formulae $CH_{1.67}O_{0.83}$, $CH_{1.64}O_{0.78}$, and $C_{10}H_{11}O_{3.5}$, respectively (SIXTA, 2006; BERMIDAS, 2009). There are also other compounds in minor proportion such as proteins, lipids, pectin, soluble sugars and minerals (PAULY and KEEGSTRA, 2008; GOMES, 2010). In its native state, lignocellulosic material is recalcitrant to efficient hydrolysis of its cellulose fraction into glucose monomer due to the physicochemical and structural composition of the material (HIMMEL et al., 2007). The most important carbohydrates present in the biomass plant are shown in the Figure 1. Partial deconstruction of biomass to make paper pulp is a quite well known and established technology and aimed to separate cellulose and hemicelluloses fractions from the lignin, extractives and minerals. However, deconstruction aimed at production of biofuels and biomaterials other than paper pulp is still a great challenge (RAGAUSKAS *et al.*, 2006; KADAM *et al*., 2008, BERMIDAS, 2009). Although lignocellulosic biomass is a very promising biofuel and bioproducts source, it cannot be currently commercially exploited mainly due to limitations for chemical or enzymatic hydrolysis caused by the presence of lignin. If this drawback is solved, low cost wood materials can be the source of choice to obtain renewable energy in the near future.

Thus, the optimization of pretreatment methods for deconstructing biomass into their cellulose, hemicelluloses and lignin fractions is of great importance for the pulp and paper, biofuel and bioproducts industry (HENDRIKS and ZEEMAN, 2009; CHANDRA et al., 2008; TAHERZADEH and KARIMI, 2008). Such optimization requires a particular emphasis on the development of analytical methods for the characterization of the structural (cellulose, hemicelluloses, lignin) and non-structural (lipids, minerals, etc.) biomass constituents and the study of their fate during the pretreatment and deconstruction process. This is particularly true when dealing with unknown faster growing feedstocks such as elephant grass.

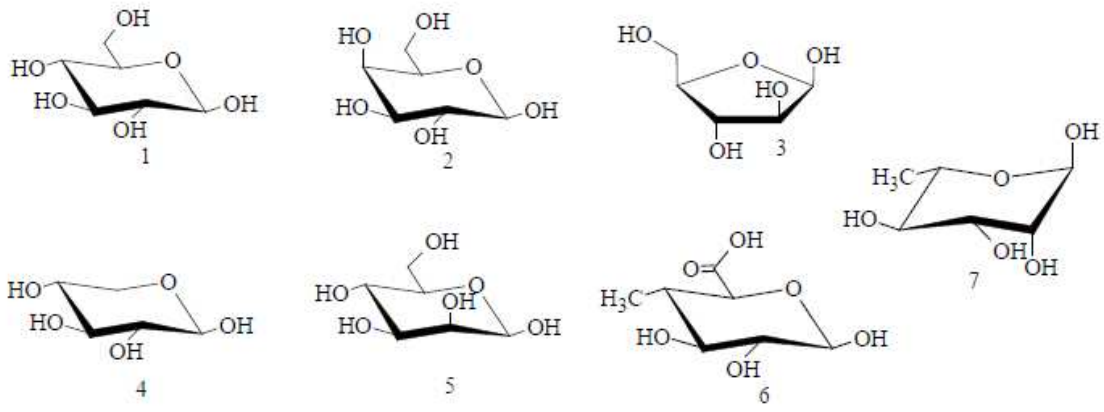

Figure 1. Important plant carbohydrates: (1) D-glucose, (2) D-galactose, (3) L-arabinose, (4) D-xilose (5) D-mannose, (6) 4-O-metil-D-glicuronic e (7) L-Rhamnose (SJÖSTROM, 1992).

Partial deconstruction of lignocellulosic biomass to make paper pulp is currently done with the secular kraft process, which delivers a high quality product. This process is efficient to separate the lignin and extractives fractions from the polysaccharides, but the lignin fraction becomes contaminated with sulfur, which hinders its utilization in many applications and creates air pollution problems. If lignin were free from sulfur, they could potentially be more easily recovered for producing energy and as a phenol source for many applications such as carbon fiber, activated carbon and other aromatic added-value chemicals (GLASSER ET AL., 2000; BELGACEM AND GANDINI, 2008). Among the non-sulfur partial deconstructing biomass processes currently known, the soda-anthraquinone (AQ) and organosolv processes are included (FRANCIS, 2008). Partial deconstruction by these methods have been

largely studied in the past and proven non-competitive with the kraft process mainly due to the low paper pulp product quality.

Nevertheless, in the context of operating a pulp mill as a Biorefinery, where wood is not the unique feedstock and paper pulp is not the only product within the value added product chain, such processes may become more interesting than the kraft (Figure 2). For example, the quality of the paper pulps derived from these processes may be improved by incorporating to them some fractions of the deconstruction process such as hemicelluloses (MUGUET et al., 2010). Other paper products less demanding in regard to strength can be made from these pulps without penalty (MUGUET, 2010). A significant part of the pulp produced can be actually directed towards biofuel and biomaterials production, and in this case strength is not an issue. Furthermore, in all these alternative pulping methods the black liquor derived from biomass deconstruction is much more amenable for recovery than that of the kraft process, both for energy and lignin separation and conversion into biomaterials.

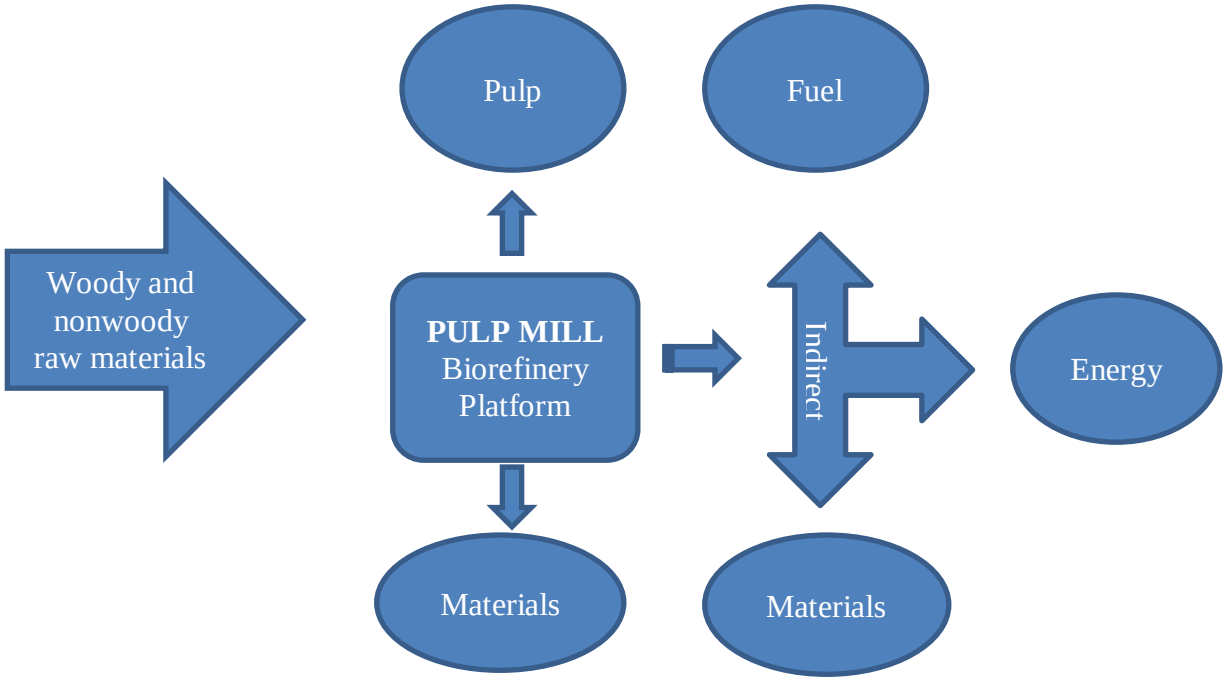

Figure 2. Pulp mill working as a biorefinery platform for producing chemicals, energy, fuels, and materials

5. The biochemical platform in lignocellulose biofuels

Another option that a biorefinery should contemplate is the complete biomass deconstruction without going through paper pulp production. This can be done by two different routes, the biochemical and the thermo-chemical conversions. In both cases biochemical intermediates and residues are produced with the first being used for fuels, chemicals and materials production, and the residues used for combined heat and power generation. Although both routes are promising, the biochemical platform integrates better with a paper pulp manufacturing facility.

The biochemical platform converts the carbohydrate fraction into fermentable sugars, leaving lignin and other fractions as a residue**.** There are several approaches to this, including: (1) separate hydrolysis and fermentation, (2) simultaneous saccharification and fermentation, (3) simultaneous saccharification and co-fermentation and (4) consolidated bioprocessing (SANTA ANNA, 2008; SANTOS et al., 2012). In the first approach the C5 sugars are firstly hydrolyzed under acidic conditions and the solids remaining are treated with cellulases to produce C6 fermentable sugars, leaving lignin and other materials as residues. In the second case the C5 sugars are firstly hydrolyzed under acidic conditions and the solids remaining are scarified / fermented simultaneously to produce bioethanol, leaving lignin and other materials as residues. In both cases, the C5 and C6 sugars are fermented separately. The third scenery suggests a similar route as the second, except that C5 and C6 sugars are fermented together. The fourth route is still a theory, but may become reality in the future, and suggests the acid hydrolysis of C5 sugars followed by cellulases production, hydrolysis of C6 and co-fermentation of C5 and C6 in a single reactor, leaving lignin and other materials as residues.

In the biochemical platform, acid hydrolysis is the conventional method for the liberation of simple sugars for fermentation; however, it is not the ideal method, since compounds such as furfural and hydroxymethylfurfural are formed as side products, which are toxic for the yeasts, and thus lower the fermentation yield (SANTOS et al., 2012). To avoid the formation of toxic compounds, it would be desirable to accomplish the saccharification step enzymatically using a combination of hydrolytic enzymes. However, the complex structure of the fiber wall, being composed of a matrix of entangled polymers of cellulose, hemicellulose, lignin and protein, depending on the plant material, complicates the enzymatic hydrolysis. In practice, a

pretreatment stage is required to loosen the cell wall structure and/or remove lignin and other non-carbohydrate components in order to expose cellulose and the hemicelluloses (CHANDRA *et al.*, 2007; GALBE and ZACCHI, 2007; HENDRIKS and ZEEMAN, 2009; TAHERZADEH and KARIMI, 2008; YOSHIDA *et al.*, 2008).

5.1 Pre-treatments based on the most usual pulping technologies

Pretreatment refers to the mechanical, physical, chemical, and/or biological treatments to reduce the particle size of the material and disrupt its cell structure to make it more accessible to chemical or enzymatic hydrolysis treatments (SANTOS et al, 2012; KAUTTO et al., 2013). More specifically, the aims of pretreatment are typically the hydrolysis of hemicelluloses and reduction of crystallinity and degree of polymerization of cellulose, to facilitate the subsequent enzymatic hydrolysis of cellulose (KAUTTO et al., 2013).

The most used pretreatments include: (1) *Ball mill*, which is based on a type of grinder used to grind biomass into extremely fine powder, being effective for a decrease in the cellulose crystallinity and improve the enzyme digestibility (TERAMOTO et.al. 2008); (2) *Diluted acid*, which is based on the use of diluted acids such as sulfuric and phosphoric acid at high temperature (140-200˚C) for up to 1 hour, aiming the hydrolyzes of the hemicelluloses fraction of the biomass to soluble sugars while the lignin condenses and precipitates (HSU, 1996; BALAT et al., 2008; GALBE and ZACCHI, 2007; HENDRIKS and ZEEMAN 2009); (3) *Ammonia Recycle Percolation – ARP*, which is a pretreatment method based on aqueous ammonia, aiming the enzymatic digestibility and also achieves high degree of delignification (IYER et al., 1996; KIM and LEE, 1996; KIM et al., 2003); (4) Alkaline pretreatments: *sodium hydroxide* and *calcium hydroxide*, they causes the lignocellulose to swell, thereby increasing the surface area while reducing the degree of polymerization and crystallinity of the material, these processes can be performed at ambient temperatures and pressures, although longer reaction times may be needed in this case (BALAT et al., 2008; GALBE and ZACCHI, 2007; HENDRIKS and ZEEMAN, 2009); (5) Ozonolysis, which is based on biomass ozone application, this pretreatment has shown its efficacy essentially degrading the lignin polymer but also slightly solubilizing hemicellulose content of lignocellulosic biomass (QUESADA et al., 1999; SUN and CHENG, 2002); (6) *Organosolv*, which is based on the organic

solvents or their aqueous solution for extracting lignin from lignocellulosic raw materials at high temperatures; the main difference between organosolv pretreatment and organosolv pulping process is the delignification degree, which is not demanded to be as high as that for pulping (ZHAO et al., 2009); (7) *Biological*, which is based on the use of microorganisms and their enzymatic machineries to break down lignin and alter lignocellulose structures (ISROI et al., 2011); (8) *Steam explosion*, which is based on the use of water at high temperature in a pressurized reactor prior a rapid decompression, providing an explosion, which effectively breaks bonds between the lignin and hemicellulose fractions, allowing the material to expand and expose the cellulose (JORGENSEN et al., 2007); (9) *Ammonia fiber expansion – AFEX*, is similar to that of steam explosion, except the biomass soaks in liquid ammonia instead of water in a pressurized reactor prior to rapid decompression; in this process the recycle of the ammonia would be required to make this option economically feasible *(*JORGENSEN et al., 2007; BALAT et al. 2008). In Table 2 the effects of various pretreatments are presented.

Table 2. Effect of different pretreatments in lignocellulosic biomass (SANTOS et al., 2012).

Pretreatment		Biomass changes			Advantages	Disadvantages
		Cellulose	Hemicellulose	Lignin		
Physical	Ball Mill	High crystallinity decrease	Not changed	Not changed	Crystallinity decrease	High energy consumption
Chemical	Diluted acid	Mild depolymerization	80-100% removal	Mild removal	High xylans production	Hard acid recovery, corrosive, andhigh cost
	Sodium hydroxide	Significant swelling	High solubility, >50%	High solubility, >50%	Effectiveestersremoval	High cost
	ARP	Low depolymerization	High solubility, >50%	High solubility, ≈70%	Effectivedelignification	High cost
	Calcium hydroxide	Mild depolymerization	Significant solubility	Partialsolubilization (≈40%)	Effective ligninand acetilremoval; low cost	Lowsolubulity
	Ozonolysis	No depolymerization	Lowsolubilization	High solubility, >70%	Effectivedelignification	High cost, and requires ozone
	Organosolve	Significant swelling	80-100% removal	80-100% removal	High xylans production, and Effective delignification	High cost for solvent recovery
Biological	Biological	20-30% of depolymerization	High solubility, >80%	Partial solubilization (≈40%)	Low energy consumption, and effective delignification	Loss cellulose, low hydrolysis rate
Combined	Steam explosion	Mild depolymerization	80-100% removal	Mild removal, however the lignin structure is modified	Low energy consumption, and no recovery costs	Xylans degradation working as inhibitor compound
	AFEX	Decrease in the crystallinity degree	High solubility, >60%	Partial solubilization (10 to 20%)	Loss xylans, and no inhibitor formation	Recovery of ammonia, is not effective for high lignin concentrations

5.1.2 Kraft and Soda-AQ pulping of fast growth feedstocks

Biomass deconstructions through the alkaline process are quite well known and are the most used processes for converting the wood into pulp. Currently, the main pulping process used worldwide is the kraft one, which uses sodium hydroxide and sodium sulphide as reagents; its hegemony in the world comes from the fact that it produces pulp of high strength, uses any type of biomass, possesses a highly developed chemical recovery technology and is the most selective of all chemical processes known (CARDOSO et. al, 2009; GOMES et al. 2013; PIERRE et al., 2013).

Concerning the alkaline processes, these are well established technologies for pulping, however targeting a new pulp industry working as a biorefinery, some characteristics of the processes should be considered, such as sulfur free technologies, since compounds containing this element are responsible for decreasing the black liquor heating value, for example (CARDOSO et al., 2009). Additionally, benefits of using sulfur free processes may be also interesting for decreasing environmental pressures, since the elimination of sulfur from the processes will greatly decrease aerial emissions of the reduced sulfur compounds usually produced by the kraft process (FRANCIS et al., 2008). Soda process also appears as an interesting alternative, since the mill structure is compatible with the kraft process. The interest in sulfur free pulping has centered on soda pulping with anthraquinone (AQ) additions, since its presence accelerates delignification during soda pulping and produces pulps with strength properties which approach kraft levels (FRANCIS et al, 2008, PIERRE et al., 2013).

Regarding the pulping process characteristics, selectivity is a significant parameter when the pulp strength properties are relevant. In this case the kraft process is the ideal choice, since it is well known to deliver the best fibers. Although selectivity is still important in the deconstruction for biofuel and bioproducts (yield) it play a less important role since the fiber integrity is no longer important. In this way, the resulting black liquor free of sulfur offers more opportunities for lignin use than the kraft one.

Most modifications of the kraft process have been aimed at improving yield and the properties of the pulp produced. AQ has been used as an additive to the soda and kraft pulping processes due to improved delignification rate and protection of cellulose and hemicelluloses chains against peeling reactions. The benefits of using AQ in eucalypt kraft pulping have been proven by many authors (GOMIDE and OLIVEIRA, 1980, SILVA JÚNIOR and BARRICHELLO, 1995; FRANCIS et al, 2008; PIERRE et al., 2013).

Emissions of total reduced sulfur compounds (TRS) in a kraft pulp mill have been an environmental concern. They are corrosive and responsible for the bad odor of the kraft process. TRS compounds are generated during pulping and are liberated mainly from digester together with steam. TRS formation during pulping depends on sulphidity level, pulping time and pulping temperature. Some decrease in TRS compounds emissions have been obtained by reducing pulping sulphidity (SARKANEN *et al.*, 1970; D'ALMEIDA, 1985; CHAI *et al.*, 2000; FRANCIS et al., 2008). Use of low or zero sulfidity and addition of AQ can be an alternative to reduce pollutant emission without decreasing delignification efficiency (SILVA *et al.*, 2002; FRANCIS et al., 2008). One alternative that can be used is the Soda-AQ process. The use of Soda process catalyzed by AQ would have additional benefits by reducing mill odors, simplifying the recovery process, and allowing gasification technology to be utilized for recovery. On the other hand, the Soda-AQ process has well-known drawbacks, including the high AQ cost and the production of pulp with lower tear strength (MacLEOD *et al.*, 1980). These drawbacks account for the limited implementation of Soda-AQ pulping to a few hardwood pulp mills. On the other hand, if the Soda-AQ pulp is used to produce biofuel rather than paper pulp, the strength problem is not a problem. The financial considerations for AQ pulping technologies have been improved over the past decade. First, the cost of AQ has decreased substantially over the past few years, as the AQ pulping patents have lapsed, new inexpensive off-shore AQ production facilities have been established, and several new AQ derivatives have been reported in the literature that exhibit improved activity (DIMMEL, 2000).

5.1.3 Organosolv pre-treatment

With that focus, organosolv pulping processes have very few advantages compared to the traditional kraft process. However, organosolv processes may turn out to be potential as pre-treatment technologies for bioethanol production, aiming at delignification and opening of the cell wall matrix (KAUTTO et al., 2013).

According to Muurinen (2000), a successful organosolv process for the replacement of the kraft process has the following characteristics (even if some of them are specific to paper grade pulp, most are relevant also in case of bioethanol as the target product): i) totally sulfur free; ii) solubilization of most of the lignin with little loss of cellulose and hemicelluloses; iii) moderate temperature, pressure and pulping times; iv) efficient and simple chemical recovery system; v) no environmental problems; vi) the optimal size of the process smaller than that of the kraft process; vii) applicable to broad selection of raw materials; viii) recovery of valuable by-products; ix) high pulp quality; x) good bleachability without chlorine chemicals; xi) high pulp yield; xii) low energy consumption of the process; and **xiii)** closed chemical cycle of the process.

The search for pulping processes that could fulfill the requirements listed above has led to the development of several organosolv methods capable of producing pulp with properties near those of kraft pulp. The Organocell (methanol), ASAM (methanol), Acetosolv (acetic acid) and Milox (peroxyformic acid) processes were tested either in pilot or full scale, but none of them led to continued production (LORA and AZIZ 1985, YOUNG and BAIERL 1985, POPPIUS *et al.* 1986, DAHLMANN and SCHROETER 1990, FUNAOKA and ABE 1989, GOTTLIEB *et al.* 1992; HAMELINCK et. al., 2005; ZHENG et. al., 2009; KAUTTO et al., 2013).

Nonwoody raw materials differ from wood in their chemical composition, especially concerning their high silica content which is problematic in kraft or soda cooking; during the delignification process, the silica present in the raw material dissolves into the cooking liquor, which has led to difficulties in the recovery chemicals system. Organosolv processes are therefore especially interesting for nonwoody

raw materials, and at least the formic acid process has been commercialized (Rousu *et al.* 2002). The Lignofiber (LGF) process is a novel versatile organosolv method that fulfills most of the requirements listed previously, being applicable for annual plants as well as wood raw materials (LIITIA et al, 2011).

5.1.4 Enzymes as potential cell-wall deconstructing biocatalysts

Several enzyme types are involved in natural biomass degradation (PÉREZ *et al.*, 2002; SWEENY et al., 2012). Many lignocellulose degrading enzymes work in a hydrolytic reactions system (mainly acting on hemicelluloses), while others works as oxidoreductive ones (mainly acting on lignin) (SWEENY et al., 2012). Cell wall decay is a sequential process where lignin removal is generally the first and rate limiting step. When the cell wall protection due to the recalcitrant lignin is removed, the polysaccharides are susceptible towards attack by hydrolytic enzymes; however, an initial degradation of lignin-polysaccharide linkages can be produced in some cases (CHANDRA et al., 2007; RATANAKHANOKCHAI et al., 2013).

5.1.4.1 Lignin-degrading enzymes

Lignin is an aromatic heteropolymer consisting of three monolignols, methoxylated to various degrees: coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. These monolignols are incorporated into lignin in the form of guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H), respectively (RENCORET et. al., 2010). Lignin are natural glues that bind tightly to polysaccharides, complicating our understanding of its native structure; the lignin-polysaccharide presents covalent and other linkage types, whose nature varies in different plants (KOSHIJIMA and WATANABE, 2003; ACHYUTAHN et al., 2010) resulting in different susceptibilities towards enzymatic deconstruction. Whereas direct linkages between polysaccharide and lignin exist in wood, this association in most nonwoody angiosperms involves *p*-hydroxycinnamic acids forming lignin-polysaccharide bonds (IIYAMA *et al.*, 1994). In first studies on enzymatic degradation of lignin during the 1970' the involvement of a variety of enzymes was considered (EGGELING, 1983). This was because of the structural complexity of the lignin

polymer (formed by different units and inter-unit linkages) that, according to the classic concept of enzyme-substrate specificity, suggested different enzyme types acting on the different substrate substructures. However, the main lignin degrading organisms (the so-called white-rot fungi because of the whitish color of the cellulose enriched substrate after lignin removal) have solved the problem of lignin heterogeneity just in the opposite way (SALVACHÚA et. al, 2013). The current evidence indicates that they have developed a unique degradation mechanism based on high redox-potential oxidoreductases, which often act in combination with redox mediators increasing their oxidative power (RUIZ-DUEÑAS and MARTÍNEZ, 2009). These enzymes include laccases (fungal phenoloxidases) and ligninolytic peroxidases, the so-called lignin peroxidase (LiP), manganese peroxidase (MnP) and versatile peroxidase (VP), acting in synergy with H_2O_2-producing oxidases, among other enzymes (KERSTEN and CULLEN, 2007; MARTÍNEZ *et al.*, 2005; MACIEL et al., 2010).

Lignin degradation by the above oxidoreductases has been defined as an "enzymatic combustion" (KIRK and FARRELL, 1987) because of the unspecific enzymatic attack, which is directed towards the benzenic ring of the lignin substructures. This results in a variety of subsequent side-reactions of the aromatic cation radical formed resulting in ether and side-chain breakdown (leading to depolymerization), demethoxylation, and even aromatic-ring opening. Because of the bulky nature of lignin, the lignin-degrading peroxidases have developed a noteworthy mechanism enabling oxidation of the polymer at the enzyme surface by an exposed protein radical, and subsequent long-range electron transfer to the peroxide-activated heme cofactor (that is located in a central pocket) (PÉREZ-BOADA *et al.*, 2005; RUIZ-DUEÑAS and MARTÍNEZ, 2009). An alternative is the use of redox mediators, simple compounds that form diffusible stable radicals once oxidized by the enzyme, acting at distance and even when the access to the lignin polymer is limited by steric hindrances (such as the compact structure of the plant cell-wall in undecayed materials). These mediators have been largely investigated for their use in combination with laccases in different industrial applications

including paper pulp delignification in totally chlorine free industrial-type bleaching sequences (IBARRA *et al.*, 2006).

5.1.4.2 Hemicellulose-degrading enzymes

Hemicelluloses vary in their constitutive monosaccharide units, as well as in their branching and acetylation degrees. Therefore, a variety of glycosidases and esterases are involved in hemicellulose degradation (GHATORA *et al.*, 2006). The former are often 1,4-β-glycosidases, since 1,4-linkages predominate among hemicellulose units, whereas the latter mainly include acetyl-esterases releasing acetic acid from acetylated units, but also feruloyl esterases breaking down the lignin-polysaccharide bridges mentioned above. Hemicellulose deacetylation can affect the substrate specificity of glycosidases involved in subsequent depolymerization (ACHYUTHAN et al., 2010), and is also of technological interest in biomass pre-treatment since the acetic acid released can contribute to lignin depolymerization by solvolysis reactions (as occurs in the organosolv processes). Pectinases are important for cell-wall deconstruction in non-fully lignified tissues, where pectin in primary wall acts as the intercellular gluing agent. Since hemicelluloses occupy an intermediate position in the lignocellulosic matrix, being covalently-linked to lignin (directly or via cinnamic bound) and establishing hydrogen bond interactions with cellulose, its degradation often results in cell-wall deconstruction and separation of its two main constituents, cellulose and lignin. In a similar way, xylanases are used for years in the industrial bleaching of paper pulp (MACIEL et al., 2010), since xylan hydrolysis facilitates the removal of the residual lignin remaining in the paper pulp.

5.1.4.3 Cellulose-degrading enzymes

Although cellulose is a simple polymer formed by cellobiose units, several enzymes (different 1,4-β-glucosidases) are involved in its hydrolytic breakdown (LYND *et al.*, 2002). These include the so-called endoglucanases breaking down internal glycosidic bonds in the cellulose polymer, a process that results in a decrease of molecular mass (polymerization degree). On the contrary, 1,4-

cellobiohydrolases (exocellulases) release the cellobiose units from cellulose chain-ends, which are hydrolyzed by cellobiases (β-glucosidases) yielding free glucose. The action of the latter enzymes is facilitated by the depolymerizing action of the above endoglucanases that increase the number of chain-ends susceptible of attack by exocellulases. The action of cellulases is facilitated by the existence of conserved cellulose-binding domains in their molecular structure. The bacterial cellulosomes are suggestive examples of complex multienzymatic systems including different carbohydrate hydrolases and carbohydrate-binding modules on a common scaffold for their concerted action on a lignocellulosic substrate (BAYER *et al.*, 2004). Crystallinity is a main bottleneck for cellulose hydrolysis by cellulase complexes and some proteins lowering the crystallinity degree have been also described in cellulolytic organisms, such as fungal swollenins (SALOHEIMO *et al.*, 2002). Moreover, an extended attack on crystalline cellulose, without the previous removal of lignin, is produced by brown-rot fungi.

In the same way that the unique ligninolytic oxidoreductases produced by white-rot fungi are of enzymes of interest as industrial biocatalysts, the so-called brown-rot fungi have developed a noteworthy mechanism for the selective removal of wood carbohydrates leaving a lignin-enriched residue (BALDRIAN and VALASKOVA, 2008) that could be applied in lignocellulose biorefineries. Recent studies, including the complete sequencing of the first genome of a brown-rot fungus at the DOE Joint Genome Institute (www.jgi.doe.gov) have shown that their ability to use lignin, without a previous removal of the lignin barrier, is based on the enzymatic generation of hydroxyl radical in the so-called Fenton reaction (consisting of peroxide reduction by ferrous iron). The hydroxyl free radical is one of the strongest oxidizers involved in biological reactions, depolymerizing cellulose even in its crystalline state. These findings suggest the feasibility of a biomimetic approach based on Fenton chemistry to improve polysaccharide hydrolysis for the subsequent production of bioethanol and other products from the lignocellulosic biomass.

5.1.4.4 Other enzymes

In addition to the above enzymes, other enzymes with a potential interest in cell-wall deconstruction participate in the natural decay of lignocellulosic biomass. These include, among others, lipases hydrolyzing triglycerides representing a significant percentage of lipophilic extractives, and esterase and glycosidase hydrolyzing sterol esters and glycosides also present in this fraction (GUTIÉRREZ *et al.*, 2001; CALERO *et al.*, 2002; McCANN and CARPITA, 2008; GILBERT, 2010). Proteins also represent a minor fraction in lignocellulosic materials (together with the water-soluble material containing free sugars), and proteases (peptidases) hydrolyzing the amide type peptidic bonds can be of interest in the isolation of cell wall constituents (GILBERT, 2010).

6. Conclusions

Biofuels e.g. bioethanol, are important to the future because they replace petroleum based fuels, and they can be obtained from renewable sources such as sugar cane, corn, straw, grasses and wood. There are currently several different levels of system integration of for biofuel production which add to their sustainability, both economically and environmentally. The pulp industry appear as a very interesting opportunity, since they already have efficient process to separate the lignin and extractives fractions from the polysaccharides; this cracking is very suitable and necessary for biorefinery applications. Efficient enzymatic conversion of lignocellulosic polysaccharides into sugars is a key technology in future biorefineries and is currently the subject of intensive research.

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8. References

ABRAF: Associação Brasileira de Produtores de Florestas Plantadas (2012). www.abraflor.org.br/

ACHYUTHAN, K. E.; ACHYUTHAN, A. M.; ADAMS, P.D.; DIRK, S. M.; HARPER, J. C.; SIMMONS, B.A.; and. SINGH, A. K. (2010). Supramolecular self-assembled chaos: polyphenolic lignin's barrier to cost-effective lignocellulosic biofuels. Molecules, 15, 8641-8688.

ARESTA, M.; DIBENEDETTO, A. AND DUMEIGNIL, F.. (2012) Biorefinery: from biomass to chemicals and fuels. Green Process Synth 2013; 2: 87–88.

ASSOCIAÇÃO DOS FABRICANTES DE CELULOSE E PAPEL – BRACELPA. Disponível em: <http://www.bracelpa.com.br>. Access on: 22 April, 2013.

AXEGARD, P. (2006). Status of the Bio-refinery Development in Scandinavia Forum on Energy: Immediate Solutions, Emerging Technologies. May 15-17 Appleton, WI.

BALAT M, BALAT H, OZ C. (2008) Progress in bioethanol processing. Progress in Energy and Combustion Science 34(5):551-573.

BALAT M. (2009) New biofuel production technologies. Energy Educ Sci Technol Part A; 22:147–61.

BALDRIAN, P., V. VALASKOVA. (2008) Degradation of cellulose by basidiomycetous fungi. FEMS Microbiol. Rev. 32:501-521.

BATISTA, F. (2013) Brasil terá 3 usinas de etanol celulósico até 2015. Jornal Valor Economico, 20 de setembro.

BAYER EA, BELAICH JP, SHOHAM Y, and LAMED R. (2004) The cellulosomes: multienzyme machines for degradation of plant cell wall polysaccharides. Annual Review of Microbiology,58:521-54.

BELGACEM, M. N., A. GANDINI. 2008. Monomers, polymers and composites from renewable resources. Elsevier, Amsterdam. Cosmochim. Acta 43: 1803–1807

BÖRJESSON P. (2009) Good or bad bioethanol from a greenhouse gas perspective – what determines this? Appl Energy;86:589–94.

CALERO-RUEDA, O., F.J. PLOU, A. BALLESTEROS, A.T. MARTÍNEZ, M.J. MARTÍNEZ (2002) Production, isolation and characterization of a sterol esterase from Ophiostoma piceae. BBA Proteins Proteomics 1599: 28-35.

CARDOSO, M.; OLIVEIRA, E.D.; PASSOS, M.L. (2009): Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills. Fuel. Volume 88, p. 756-763.

CHAI, X.-S., LIU, P.-H. and ZHU, J.Y. (2000) Analysis of volatile organic sulphur compounds in kraft liquors by full evaporation headspace gas chromatography. Journal of Pulp and Paper Science, v.26, n.5, p.167-172.

CHANDRA, R.P., R. BURA, W. E. MABEE, A. BERLIN, X. PAN, J. N. SADDLER. (2007) Substrate pretreatment: The key to effective enzymatic hydrolysis of lignocellulosics? Adv. Biochem. Engineer. Biotechnol. 108: 69-73.

D'ALMEIDA, M.L.O. (1985) Formação de compostos malcheirosos durante o processo de polpação sulfato. O Papel, v.46, n.8, p.65-68.

DAHLMANN G., SCHROETER, M.C. (1990) Pulping of spruce and pine with alcohol and alkali by the Organocell process. Tappi Pulping Conference, Toronto, Canada, 2: 657-661.

SALVACHÚA, D.; MARTÍNEZ, A. T.; TIEN, M.; LÓPEZ-LUCENDO, M. F.; GARCÍA, F.; RÍOS, V.; MARTÍNEZ, M. J.; and PRIETO, A. (2013) Differential proteomic analysis of the secretome of Irpex lacteus and other white-rot fungi during wheat straw pretreatment. Biotechnology for Biofuels, 6:115

DEMIRBAS A. (2008) Economic and environmental impacts of the liquid biofuels. Energy Educ Sci Technol; 22:37–58.

DERMIBAS, M. F. (2009) Biorefineries for biofuel upgrading: A critical review. Applied Energy 86 S151–S161

DEWULF, J., H. VAN LANGENHOVEN. (2006) . Renewables-based technology. Sustainability assessment. John Wiley & sons, Chichester, UK.

DIMMEL, D.R., (2000) Method for the Delignification of Lignocellulosic Material by Adding a Dialkyl Substituted Octahydroanthraquinone, U.S. Patent 6,156,155.

EGGELING, L. (1983) Lignin-an exceptional biopolymer...and a rich resource? Trends Biotechnol. 1:123-127.

FRANCIS, R. C., BOLTON, T. S., ABDOULMOUMINE, N., LAVRYKOVA, N., & BOSE, S. K. (2008). Positive and negative aspects of soda/anthraquinone pulping of hardwoods. Bioresource technology, 99(17), 8453-8457.

FUNAOKA, M., ABE, I. (1989) Rapid separation of wood into carbohydrate and lignin with concentrated acid-phenol system. Tappi J 72(8): 145-149.

GALBE M, ZACCHI G. (2007). Pretreatment of lignocellulosic materials for efficient bioethanol production. Biofuels 108:41-65.

GHATORA, S. K., B. S. CHADHA, H. S. SAINI, M. K. BHAT,, C. B. FAULDS. (2006) Diversity of plant cell wall esterases in thermophilic and thermotolerant fungi. J. Biotechnol. 125:434-445.

GILBERT, H. J. (2010). The biochemistryand strucutural biology of plant cell wall deconstruction. Plant Physiology153 (2): 444-455.

GLASSER, W. G., R. A. NORTHEY,, T. P. SCHULTZ. (2000) Lignin: Historical, biological, and materials perspectives. American Chemical Society.

GOMES, F. J. B. (2010) Bleaching improvement of kraft pulp in wood mixture of *Pinus spp.* and *Eucalyptus spp.* by the sequence OQD* (PO) and OQD*(PO)DP. Master Dissertation presented to Federal University of Viçosa.

GOMES, F. J. B. ; COLODETTE, J. L. ; BURNET, A. ; BATALHA, L. AP. R. ; BARBOSA, B. M. (2013). Potential of elephant grass for pulp production. Bioresources (Raleigh, N.C), v. 8, p. 4359-4379.

GOMIDE, J. L. & OLIVEIRA, R. C. (1980) Eficiência da antraquinona na polpação alcalina do eucalipto. O Papel, São Paulo, 41:67-72,.

GOTTLIEB, K., PREUSS, A.W., MECKEL, J., BERG, A. (1992) Acetocell pulping of spruce and chlorine-free bleaching. 1992 Solvent Pulping Symposium Notes, Boston, MA, p 35-39.

GRAY, K.A., L.S. ZHAO, M. EMPTAGE. (2006) Bioethanol. Curr.Opin.Chem.Biol. 10:141-146,.

GUPTA; K. V.; TUOHY, M G. (2013) Biofuel Technologies: Recent Developments. Book published by Springer, XVII, 534 p.

GUTIÉRREZ, A.; DEL RÍO, J. C.; MARTÍNEZ, M. J.; MARTÍNEZ, A. T. (2001). The biotechnological control of pitch in paper pulp manufacturing. Trends Biotechnol. 19:340-348.

HAMELINCK CN, VAN HOOIJDONK G, FAAIJ APC (2005) Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long term. Biomass Bioenergy 28:384–410.

HAMELINCK, C. N. (2005) Etanol from lignocellulosic biomass: technoeconomic performance in short, middle and long term. Biomass and Bioenergy, v. 28, p. 384-410.

HENDRIKS, A. T., G. ZEEMAN. (2009). Pre-treatments to enhance the digestibility of lignocellulosic biomass. Bioresour. Technol. 100:10-18.

HIMMEL ME, DING S-H, JOHNSON DK, ADNEY WS, NIMLOS MR, BRADY JW, FOUST TD (2007) Biomass recalcitrance: engineering plants and enzymes for biofuels production. Science 315:804–807

HIMMEL, M. E. (2008). Biomass recalcitrance. Deconstructing the plant cell wall or bioenergy. Blackwell, Oxford.

HSU, T. (1996), in Handbook on Bioethanol: Production and Utilization, Wyman, C., ed., Taylor & Francis, Washington, DC, pp. 179–212.

IBARRA, D., S. CAMARERO, J. ROMERO, M. J. MARTÍNEZ,, A. T. MARTÍNEZ. (2006). Integrating laccase-mediator treatment into an industrial-type sequence for totally chlorine free bleaching eucalypt kraft pulp. J. Chem. Technol. Biotechnol. 81:1159-1165.

IIYAMA, K., T. B. T. LAM,, B. A. STONE. (1994). Covalent cross-links in the cell wall. Plant Physiol. 104:315-320.

ISROI; MILLATI, R.; SYAMSIAH, S.; NIKLASSON, C.; CAHYANTO, M. N.; LUNDQUIST, K.; AND TAHERZADEH, M. J. (2011) Biological pretreatment of lignocelluloses with white-rot fungi and its applications: a review. BioResources 6(4), 5224-5259.

IYER, P.V., WU, Z., KIM, S.B., and Y.Y. (1996) Ammonia Recycled percolation Process for Pretreatment of Herbaceous Biomass. Applied Biochem. Biotechnol. 57/58: 121– 132.

RALPH, J.; MARTÍNEZ, A. T.; and RÍO, J. C. (2011) Lignin Composition and Structure in Young versus Adult Eucalyptus globulus Plants. Plant Physiology vol. 155 no. 2 667-682.

KADAM, K. L., C. Y. CHIN,, L. W. BROWN. (2008). Flexible biorefinery for producing fermentation sugars, lignin and pulp from corn stover. J. Ind. Microbiol. Biotechnol. 35:331-341.

KAUTTO J.; REALFF M. J.; RAGAUSKAS A. J. (2013) Design and simulation of an organosolv process for bioethanol production. Biomass Conv. Bioref. 3:199–212.

KERSTEN, P., D. CULLEN. (2007). Extracellular oxidative systems of the lignin-degrading Basidiomycete *Phanerochaete chrysosporium*. Fungal Genet. Biol. 44:77-87.

KIM, T.H., KIM, J.S., SUNWOO, C., and LEE, Y.Y. (2003) Pretreatment of corn stover by aqueous ammonia. Bioresource Technol. 90: 39–47.

KIRK, T. K., R. L. FARRELL. (1987). Enzymatic "combustion": The microbial degradation of lignin. Annu. Rev. Microbiol. 41:465-505.

KOSHIJIMA, T., T. WATANABE. 2003. Association between lignin and carbohydrates in wood and other plant tissues. Springer, Berlin.

LARSON, E. (2007) Pulp Mill Integrated Gasification-Based Liquid Biofuels Production. International Renewable Energy Conference, 10-11 May 2007

LIITIÄ, T.; MIKKONEN, H.; UUSITALO, J.; TAMMINEN, T.; COLODETTE, J. L.(2011) Organosolv pretreatment of lignocellulosics for bioethanol production. 5th International Colloquium on Eucalyptus Pulp, Porto Seguro – BA, Brazil, May 09-12.

LORA, J.H., AZIZ, S. (1985) Organosolv pulping: a versatile approach to wood refining. Tappi J 68(8): 94-97.

LUOMA, P., VANHANEN, J. AND TOMMILA, P. (2011). Distributed Bio-Based Economy – Driving Sustainable Growth, Sitra, September 2011 Available at http://www.sitra.fi/julkaisu/2011/distributed-bio-based-economy. Accessed 16.11.2013.

LYND, L. R., P. J. WEIMER, W. H. VAN ZYL,, I. S. PRETORIUS. (2002) Microbial cellulose utilization: Fundamentals and biotechnology. Microbiol. Mol. Biol. Rev. 66:506.

MACIEL, M. J. M.; SILVA, A. C.; RIBEIRO, H.C.T. (2010). Industrial and biotechnological applications of ligninolytic enzymes of the basidiomycota: A review. Electronic Journal of Biotechnology, vol. 13, no. 6. http://dx.doi.org/10.2225/vol13-issue5-fulltext-1

MACLEOD, J.M., FLEMING, B.I., KUBES, G.J.,, BOLKER, H.I. (1980). Strengths of Kraft-AQ (Anthraquinone) and Soda-AQ Pulps. (1). Bleachable-Grade Pulps, Tappi, 63(1), 57.

MADAKADZE, I. C.; MASAMVU, T. M.; RADIOTIS, T. J. LI and SMITH, D. L. (2010). Evaluation of pulp and paper making characteristics of elephant grass (Pennisetum purpureum Schum) and switchgrass (Panicum virgatum L.). African Journal of Environmental Science and Technology Vol. 4(7), pp. 465-470.

MARTÍNEZ, A.T.; SPERANZA, M.; RUIZ-DUEÑAS, F.J.; FERREIRA, P.; CAMARERO, S.; GUILLÉN, F.; MARTÍNEZ, M.J.; GUTIÉRREZ, A. and DEL RIO, J.C. (2005). Biodegradation of lignocellulosics: microbial, chemical and enzymatic aspects of fungal attack to lignin. International Microbiology, vol. 8, no. 3, p. 195-204.

MAZZARELLA, V.N.G., (2007). Jornada Madeira Energética-Capim Elefante com Fonte de Energia no Brasil: Realidade Atual e Expectativas. IPT-BNDS - Rio de Janeiro, maio de 2007. P.Point.

MCCANN, M. C., and CARPITA, N. C (2008). Designing the deconstruction of plant cell walls. Current Opinion in Plant Biology , 11:314–320.

MOSIER N, WYMAN C, DALE B, ELANDER R, LEE YY, HOLTZAPPLE M, LADISCH M (2005) Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour Technol 96:673–686

MUGUET, M. C. S.; PEDRAZZI, C.; AND COLODETTE, J. L.(2010) Xylan deposition onto eucalypt pulp fibers during oxygen delignification. Holzforschung. Volume 65, Issue 4, Pages 605–612.

MUURINEN, E. (2000) Organosolv pulping, A review and distillation study related to peroxyacid pulping, ISBN 951-42-5661-1, Dissertation, University of Oulu, 314 p.

PATEL MA, OU MS, INGRAM LO, SHANMUGAM KT (2005) Biotechnol Prog 21:1453.

PAULINO, V.T. DE LUCENAS, T.L., POSSENTI, R.A., 2007. Capim elefante cv. Paraíso (Pennisetum hybridum): produção de matéria seca, composição química e biológica em diferentes alturas de corte. http://www.iz.sp.gov.br/artigos.php?ano=2007

Pauly M, Keegstra K. (2008) Cell-wall carbohydrates and their modification as a resource for biofuels. Plant Journal, 54:559-568.

PAULY, M. and KEEGSTRA K. (2008). Cell-wall carbohydrates and their modification as a resource for biofuels. Plant Journal 2008 May;54(4):559-68.

PÉREZ, J., J. MUÑOZ-DORADO, R. T. DE LA,, J. MARTÍNEZ. 2002. Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview. Int. Microbiol. 5:53-63.

PÉREZ-BOADA, M., F. J. RUIZ-DUEÑAS, R. POGNI, R. BASOSI, T. CHOINOWSKI, M. J. MARTÍNEZ, K. PIONTEK,, A. T. MARTÍNEZ. 2005. Versatile peroxidase oxidation of high redox potential aromatic compounds: Site-directed mutagenesis, spectroscopic and crystallographic investigations of three long-range electron transfer pathways. J. Mol. Biol. 354:385-402.

PIERRE, D. A. and GOMIDE, J. L. (2013). Anthraquinone and surfactant effect on soda pulping. O PAPEL vol. 74, num. 7, pp. 53 – 56.

POPPIUS, K., LAAMANEN, L., SUNDQUIST, J., WARTIOVAARA, I., KAULIOMÄKI, S. (1986) Bleached pulp by peroxyacid/alkaline peroxide delignification. Paperi ja Puu 68(2): 87-92.

QUESADA, D. M., BODDEY, R.M., MASSENA REIS, V., URQUIAGA, S. 2004. Parâmetros Qualitativos de Genótipos de Capim Elefante (Pennisetum purpureum Schum.) estudados para a produção de energia através da Biomassa. CIRCULAR TÈCNICA 8. Seropédica, RJ, Novembro.

QUESADA, J., RUBIO, M., GÓMEZ, D., 1999. Ozonation of lignin rich solid fractions from corn stalks. J. Wood Chem. Tech. 19, 115–137.

RAGAUSKAS, A. J., M. NAGY, D. H. KIM, C. A. ECKERT, J. P. HALLET,, C. L. LIOTTA. 2006. From wood to fuels. Integrating biofuels and pulp production. Industr. Biotechnol. 2:55-65.

RATANAKHANOKCHAI, K.; WAEONUKUL, R.; PASON, P.; AACHAAPAIKOON, C.; KYU, K. L.; SAKKA, K.; KOSUGI, A.; and MORI, Y.. (2013) Paenibacillus curdlanolyticus Strain B-6 Multienzyme Complex: A Novel System for Biomass Utilization. Biomass Now – Cultivation and Utilization (http://dx.doi.org/10.5772/51820).

RENEWABLE FUELS ASSOCIATION, (2012) The paradox of rising USethanol exports: increased market opportunities at the expense of enhanced nationalenergy security? Renewable Fuels Association, Washington, DC.

RODRIGUES, J. A. R. (2011) From the mill to a biorefinery: the sugar factory as an industrial enterprise for the generation of biochemicals and biofuels. *Química Nova*, *34*(7), 1242-1254.

ROUSU, P., ROUSU, P., ANTTILA, J. (2002) Sustainable pulp production from agricultural waste. Resources, Conservation and Recycling (35): 85-103.

RUIZ-DUEÑAS, F.J., MARTÍNEZ, A.T. (2009) Microbial degradation of lignin: How a bulky recalcitrant polymer is efficiently recycled in nature and how we can take advantage of this. *Microbial Biotechnol.*: doi:10.1111/j.1751-7915.2008.00078.x.

SALOHEIMO, M., M. PALOHEIMO, S. HAKOLA, J. PERE, B. SWANSON, E. NYYSSONEN, A. BHATIA, M. WARD,, M. PENTTILA. (2002) Swollenin, a *Trichoderma reesei* protein with sequence similarity to the plant expansins, exhibits disruption activity on cellulosic materials. Eur. J. Biochem. 269:4202-4211.

SANGLARD, M.; CHIRAT, C.; JARMAN, B.; LACHENAL, D. (2013) Biorefinery in a pulp mill: simultaneous production of cellulosic fibers from *Eucalyptus globulus* by soda-anthraquinone cooking and surface-active agents. Holzforschung. Volume 67, Issue 5, Pages 481–488.

SANTA ANNA, L.M. M., (2008) III Seminar on pulp and paper: Biorefinery & biopulping and their impact on the pulp industry. Viçosa, MG, Brazil. April 11,).

SANTOS, F. A., QUEIRÓZ, JOSÉ H. DE, COLODETTE, JORGE L., FERNANDES, SERGIO A., GUIMARÃES, VALÉRIA M., & REZENDE, SEBASTIÃO T.. (2012).

Potencial da palha de cana-de-açúcar para produção de etanol. Química Nova, 35(5), 1004-1010.

SARKANEN, K.V., HRUTFIORD, B.F., JOHANSON, L.N and GARDNER, H.S. (1970) Kraft odor. Tappi Journal, v.53, n.5, p.766-783,.

SBS : SOCIEDADE BRASILEIRA DE SILVICULTURA. (2007). www.sbs.org.br.

SEYE, OMAR, CORTEZ, LUÍS AUGUSTO BORBOSA, GÓMEZ, EDGARDO OLIVARES *(*2000) Queima direta de gramínea. Projeto Integrado de Biomassa - PIB. In: Encontro de Energia no Meio Rural, 3., , Campinas.

SILVA JÚNIOR, F. G. & BARRICHELO, L. E. G. (1995) Conversion of the kraft process in soda-DDA (disodium salt of 1,4-dihydro-9,10-dihydroxy anthracene) for eucalypt. In: Proceedings of the 1995 Pulping Conference, Vol. 2, 757, Chicago.

SILVA, F. J.; GOMIDE, J. L.; COLODETTE, J. L. (2002) Effects of Sulfidity Reduction and Anthraquinone Addition on Pollutant Emission and Quality of Eucalyptus Kraft Pulp. Tappi Journal, v. 1, p. 1-9.

SJÖSTROM, E. (1992) Wood chemistry, fundamentals and applications. 2. ED. California, USA, Academic Press,.

SUN, Y., CHENG, J., (2002). Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour. Technol. 83, 1–11.

SWEENEY M. D. and XU F. (2012). Biomass converting enzymes as industrial biocatalysts for fuels and chemicals: recent developments. Catalysts 2012, 2, 244-263

TAHERZADEH, M., KARIMI, K. (2008). Pre-treatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review, Int. J. Mol. Sci. 9:1621-1651.

TERAMOTO Y., TANAKA N., LEE S. H. AND ENDO T. (2008) Pretreatment of Eucalyptus Wood Chips for Enzymatic Saccharification Using Combined Sulfuric Acid-Free Ethanol Cooking and Ball Milling. Biotechnology and Bioengineering, 99: 75-85, 2008.

U.S.DOE. (2006) Breaking the biological barriers to cellulosic ethanol. A Joint Research Agenda (DOE/SC-0095)).

VILELA, H., BARBOSA, F.A, RODRIGUEZ, N. (2001a). Qualidade das silagens de capim elefante Paraíso submetidas a três tempos de emurchecimento. Anais: XXXVIII Reunião Anual da Sociedade Brasileira de Zootecnia. julho de 2001. Piracicaba/SP. 323 a 324 p. 2001. ISBN: 63600981.

VILELA, H., BARBOSA, F.A., RODRIGUEZ, N. E BENEDETTI, E. (2001b) Efeito da idade planta sobre a produção e valor nutritivo do capim elefante Paraíso

(Pennisetum hybridum). Anais: XXXVIII Reunião Anual da Sociedade Brasileira de Zootecnia. Julho de 2001. Piracicaba/SP. 320 a 321, p. 2001. ISBN: 63600981.

VILELA, H., BARBOSA, F.A., RODRIGUEZ, N., BENEDETTI, E., NOGUEIRA, A.C. (2002a) Produção e composição química do capim elefante Paraíso submetida a três alturas de corte. Anais da XXXIX Reunião Anual da Sociedade Brasileira de Zootecnia. Julho de 2002. URPE. Recife/PE, CD, 2002.

VILELA, H., RODRIGUEZ, N. & DIAS TEIXEIRA, E. (1997) Produções de forragem de um híbrido hexaplóide (Pennisetum glaucum X Pennisetum purpureum) e seu valor nutritivo. In: Anais da XXXIV Reunião da SBZ, julho de 1997, Juiz de Fora/MG.

VILELA, H., VILELA, D., BARBOSA F.A., BENEDETTI, E. (2003a) Quantidade de água suplementar para o capim elefante Paraíso. Veterinária Notícias, ISSN 0104-3463. 2003.

VILELA, H., VILELA, D., BARBOSA, F.A., BENEDETTI, E. (2003b) Análise de crescimento do capim elefante Paraíso. Veterinária Notícias, ISSN 0104-3463.

VILELA, H., VILELA, D., BARBOSA, F.A., BENEDETTI, E. (2002b) Irrigação do capim elefante Paraíso. Anais da XXXIX Reunião Anual da Sociedade Brasileira de Zootecnia. URPE-Recife/PE.

WACLAWOVSKY, A.J.; SATO, P.M.; LEMBKE, C.G.; MOORE, P.H.; SOUZA G.M. (2010). Sugarcane for Bioenergy Production: an assessment of yield and regulation of sucrose content. Plant Biotechnology J 8:263

WANG, L.; TONG, Z.; INGRAM , L. O.; CHENG, Q.; MATTHEWS, S. (2013) Green Composites of Poly (Lactic Acid) and Sugarcane Bagasse Residues from Bio-refinery Processes. Journal Polymer and the Environment 21:780–788

YOSHIDA, M., Y. LIU, S. UCHIDA, K. KAWARADA, Y. UKAGAMI, H. ICHINOSE, S. KANEKO,, K. FUKUDA. (2008) Effects of cellulose crystallinity, hemicellulose, and lignin on the enzymatic hydrolysis of *Miscanthus sinensis* to monosaccharides. Biosci. Biotechnol. Biochem. 72:805-810.

YOUNG, R.A., Baierl, K.W. (1985) Ester pulping of wood: A revolutionary process. Southern Pulp Paper 48(12): 15-17.

ZHANG, Y. H. P. (2008) Reviving the carbohydrate economy *via* multi-product lignocellulose biorefineries. J. Ind. Microbiol. Biotechnol. 35:367-375.

Zhao, X.; Cheng, K.; Liu, D.. (2009) Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. Appl Microbiol Biotechnol 82:815–827.

ZHENG Y, PAN Z, ZHANG R (2009) Overview of biomass pretreatment for cellulosic ethanol production. Int J Agric Biol Eng 2:5.

CAPÍTULO 2

THOROUGH CARACTERIZATION OF BRAZILIAN NEW GENERATION OF EUCALYPT CLONES AND ELEPHANT GRASS

Abstract

Eucalypt wood is the most important raw material for the pulp industries in South America; it also appears as a promising material for biorefinery applications. However, due to the high wood cost in comparison to other raw material sources, nonwoody materials are being investigated for these purposes as well. This study aimed at the evaluation of eighteen eucalypt clones obtained from the Brazilian Genolyptus project and two elephant grasses regarding their potential for biorefinery applications. The selection of the most suitable materials was carried out on the basis of the following traits: forestry productivity, moisture, density, fiber morphology, and fiber organic and inorganic chemistry. Four eucalypt clones and one elephant grass species were indicated for pulp production and biorefinery applications. Among the eucalypt clones, the four most suitable for the subsequent pulp production and biorefinery studies were (*Eucalyptus urophylla* x *Eucalyptus urophylla* (U1xU2); *Eucalyptus grandis* x (*Eucalyptus urophylla* x *Eucalyptus globulus*) (G1xUGL); (*Eucalyptus dunnii* x *Eucalyptus grandis*) x *Eucalyptus urophylla* (DGxU2); and a commercial elite clone (IP)). Concerning the elephant grass, the EG1 (*Pennisetum purpureum*) sample was chosen due to its highest productivity (32 ton/ha/yr) and density (216 kg/m^3). An interesting finding obtained through the chemical composition analysis was that the lignin containing high S/G ratio, condenses less during the acid hydrolysis procedure and produce more soluble lignin in the filtrates; thus, a good positive correlation was established between lignin S/G ratio and acid soluble lignin.

1. Introduction

Biorefinery is a new term that is related to two main subjects, value-added bioproducts (chemical building blocks, materials, pulps), and bioenergy (biofuels, power, and heat) from biomass, considering sustainability assessment and life

cycle (ARESTA et al. 2013). The use of adequate biomass sources appears as a prerequisite for the development of the sustainable biorefineries, considering technical, economical, social and environmental aspects. The most investigated a biomass source has been lignocellulose, which is commonly found as wood, agricultural products and wastes, municipal wastes, fast rotation crops, etc.

Hardwoods and softwoods are important raw materials for biorefinery application, since they deliver biomass with suitable characteristics to the final products with competitive costs. In this context, eucalypt is becoming the most important raw material. The major interest in eucalypt wood comes from its relative low production cost in certain regions, e.g. in South America, due mainly to high forest productivity and high conversion yields into products.

It is very well known that wood quality is a factor of extreme importance when the goal is the pulp production with high industrial yield, low cost and high quality. Wood characteristics like fiber anatomy and chemical composition are expected to affect its processability, i.e., ease of delignification and the quality of the pulp products (FOELKEL, 2007; Mokfienski et al, 2008). Chemical structures may vary among different wood species and even among different wood clones of a given species. The effect of forest cloning and hybridization on wood productivity and quality has been extensively studied in the last 50 years (ASSIS, 2001; BISON, 2004). The turnout of this significant investment in research has been quite positive with the average productivity of the Brazilian eucalypt forests increasing from 24 m^3/ha/yr in 1980 to 41 m^3/ha/yr in 2010, representing a 71% growth (BRACELPA, 2013).

Although wood is a well fit and consolidated raw material for the pulp industry and biorefinery applications, it is definitely an expensive source of biomass. Thus, alternative sources of biomass have been investigated such as, for example, grasses. High productivity plants such as elephant grass (30-45 bone dry t/ha/yr) can potentially supply biomass of low cost to meet the current demand imposed by the biorefinery applications (VILELA et al. 1997, 2001a,b, 2002a,b, 2003a,b; PAULINO et al.,2007; MAZZARELLA et al., 2007). However, the quality of such

raw material aiming at pulp production is not yet fully known. Elephant grass presents high fiber productivity (fiber/ha) and the chemical composition of its fibers is potentially adequate for pulp production, since they are somewhat similar to those of sugar cane (QUESADA et al., 2004; SEYE et al. 2000). Some studies have shown contents of 40, 30 and 17.7% of cellulose, hemicelluloses and lignin, respectively, for elephant grass fibers (Madakadze 2010).

In this study, eighteen eucalypt clones obtained from the Brazilian Genolyptus project and two elephant grasses were investigated regarding their potential characteristics for biorefinery applications. The raw materials were analyzed for their forestry productivity, moisture, density, fiber morphology, and fiber organic and inorganic chemistry.

2. Materials and Methods

2.1. Materials

Eighteen eucalypt clone samples in commercial harvesting age (7 years) were collected from an experimental station of the *GENOLYTPUS* project, located in Minas Gerais State (Belo Oriente). Two species of elephant grass (150-days old) were also collected in Minas Gerais State, one from Embrapa Gado de Leite experimental station (Coronel Pacheco) and the other from UFV Animal Science Department (Viçosa). The complete list of samples used in this study is presented in the Table 1.

Table 1. Codification of the eucalypt clones and elephant grass species.

	Sample Code	**BiomassType**
1	U1xU2	*E. urophylla (Flores IP) x E. urophylla (Timor)*
2	U2xC1	*E. urophylla (Timor) x E. camaldulensis (VM1)*
3	G1xUGL	*E. grandis (Coffs Harbour) x [E. urophylla (R) x E. globulus (R)]*
4	U1xUGL	*E. urophylla (Flores IP) X [E. urophylla (R) x E. globulus (R)]*
5	U1xC2	*E. urophylla (Flores IP) x E. camaldulensis(VM2)*
6	C1xC2	*E. camaldulensis (VM1) x E. camaldulensis (VM1)*
7	DGxUGL1	*[E. dunnii* (R) x *E. grandis (R)] x [E. urophylla (R) x E. globulus (R)]*
8	DGxU2	*[E. dunnii* (R) x *E. grandis (R)] x E. urophylla (Timor)*
9	C1xUGL	*E. camaldulensis (VM1) x [E. urophylla (R) x E. globulus (R)]*
10	G1xGL2	*E. grandis (Coffs Harbour)x E. globulus (R)*
11	DGxC1	*[E. dunnii* (R) x *E. grandis (R)] x E. camaldulensis (VM1)*
12	U2xGL1	*E. urophylla (Timor) x E. globulus (R)*
13	DGxGL2	*[E. dunnii* (R) x *E. grandis (R)] x E. globulus (R)*
14	U1xD2	*E. urophylla (Flores IP) x E. dunnii (R)*
15	U1xG2	*E. urophylla (Flores IP) x E. grandis*
16	IP	*E. urophylla (IP) x E. grandis (IP)* commercial clone
17	VC	*E. urophylla x E. grandis* commercial clone
18	CC	*E. urophylla x E. grandis* commercial clone
19	EG1	*Pennisetum purpureum*
20	EG2	*Pennisetum americanum*

Five representative trees of the population with average diameter at breast height and height were selected. They were harvested and from each tree it was extracted five 1m-long bolts at 0, 25, 50, 75, and 100% of the tree heights; and a 100 kg sample of each elephant grass species were harvested at a Federal University of Viçosa experimental station. The samples were evaluated for their moisture content at the moment of harvesting according to Tappi T264 cm-97 standard procedure. The eucalypt clones samples were chipped in a laboratory chipper, a Chogokukikai model, equipped with 3 knives and 2 screens (40 & 13mm). Both eucalypt clones and elephant grass chips were well mixed (260m3 rotary mixer) and the eucalypt clones samples were screened according to SCAN-CN 40:94 procedure. For eucalypt clones samples, the chips retained in the 3 mm and 7 mm screens were collected and mixed again, air dried to about 15% moisture and stored in large plastic bags. The elephant grass samples were manually chipped, producing wet chips about 5 mm long. The chip thickness was quite variable since it depended on the grass thickness, which varies from 1 cm

diameter to 4 cm diameter. The grass chips were air dried to a moisture content of about 15% and stored in large plastic bags.

2.2. Methods

Sampling for physical, chemical and morphological analyses was done using the so-called quartering technique which is trivial for those skilled in the art. Chips were used to measure chips bulk and basic density according to SCAN CN-49:92 and SCAN CM-46:92 standard procedures, respectively.

2.2.1. Biomass productivity

The biomass productivity was calculated using the medium annual increase (MAI) and basic density, by the following equation:

$$\text{Biomass productivity } (\text{ton/ha/yr}) = \text{MAI } (\text{m}^3/\text{ha/yr}) \times \text{basic density } (\text{ton/m}^3)$$

2.2.2. Samples preparation for morphological analysis

About 200 grams of each biomass sample were sliced into toothpick type material and macerated using nitro-acetic acid solution in order to prepare individual fibers for morphological analyses. To make the maceration, a solution of five parts of acetic acid and one part of nitric acid were mixed, added to the biomass material until they were completely immersed and let stand for 6 hours at 100 ˚C under a hood. The reaction was stopped by washing the material, which was dispersed in distilled water. Following, the material was gently mixed in a magnetic stirrer (slowly and steadily) for 60 min. so that all the fiber bundles were separated. Morphological characterization of fibers, vessels and fines was carried out on a pulp suspension passing through a specific cell illuminated by a laser beam and connected to a high-resolution camera (CCD - charge-coupled device). This analysis allowed reliable statistical measurement of thousands of fiber, vessels and fines to determine the main morphological and dimensional characteristics of the pulp components.

2.2.3. Samples preparation for chemical analysis

For the chemical analyses, about 1 kg of each biomass were sampled and ground in a Wiley type mill to produce sawdust of variable size. This sawdust was screened according to Tappi Standard T257-cm85. The sawdust that passed the 40 mesh screen and was retained in the 60 mesh screen was selected for the chemical analyses. The sawdust was air dried and conditioned in a temperature and humidity controlled room (23±1˚C, 50±2% RH) until an equilibrium moisture was achieved (~10%). This sawdust (raw sawdust) was used for the chemical analyses. The analyses of ash, silica, chloride, iron, copper, manganese, potassium, calcium and magnesium were carried out directly on the raw sawdust, according to the Standard Methods for the Examination of Water and Wastewater (2000), except for chloride, which was determined according to Tappi T256 cm-97 standard procedure. The biomass extractives contents in acetone, ethanol/toluene(1:2) and ethanol/toluene(1:2) →ethanol →hot water solvent series was also determined in the raw sawdust using the TAPPI T280 pm-99, T204 cm-97 and TAPPI T264 cm-97 standard procedures, respectively. In order to determine biomass main cell wall components, a 200g sample of extractives freed was prepared using TAPPI T264 cm-97 standard procedure. This extracted sample (extractive free sawdust) was conditioned in a temperature and humidity controlled room (23±1˚C, 50±2% RH) until an equilibrium moisture was achieved (~10%). The contents of uronic acids, acetyl groups and sugars (glucans, mannans, galactans, xylans and arabinans) in the extractive free biomass were determined according to Scott (1979), Solar et al. (1987) and Wallis et al. (1996). The acid insoluble lignin, acid soluble lignin and lignin syringyl/guaiacyl (S/G) ratio were determined according to TAPPI T 222 om-97 standard procedure, Goldschmid (1971) and Lin & Dence (1992), respectively.

3. Discussion and results

3.1. Forestry characteristics

Two very important factors regarding biomass use for pulp production are moisture content and density since they affect harvesting, transportation and utilization costs. The eucalypt clones analyzed in this study show average moisture and density of 55 % and 502 kg/m^3. These values are considered satisfactory for pulp production (DIAS and CLÁUDIO-DA-SILVA, 1991; SILVA JR. et al., 1996, GOMIDE et al., 2010). The average annual increment (AAI) varied in the range of 16-101.6 m3/ha/yr. The lowest AAI extreme occurred for the C1xC2 woody raw material. This may be explained due to the fact that eucalypt hybrid is poorly adapted to Minas Gerais State climate conditions and did not develop satisfactorily. Among the woody raw materials, the highest growth (101.6 m^3/ha/yr) was obtained with sample DGxU2, which is a triple hybrid of (*Eucalyptus dunnii x Eucalyptus grandis*) x *Eucalyptus urophylla* (Table 2). This productivity is much above the average MAI obtained in commercial plantations in the Brazilian Territory (~40-60 m^3/ha/yr) (BRACELPA, 2013).

Table 2. Forestry and physical characteristics of the eucalypt clones and elephant grass species evaluated.

Sample #	Sample Code	Moisture, %	Average Annual Increment, m^3/ha/yr*	Biomass basic density, kg/m^3	Biomass Productivity, bone dry ton/ha/yr	Chip bulk density, kg/m^3
1	U1xU2	54	86.0	504	43.3	209
2	U2xC1	55	54.1	547	29.6	220
3	G1xUGL	53	46.2	500	23.1	202
4	U1xUGL	54	46.9	496	23.3	193
5	U1xC2	53	52.9	517	27.4	203
6	C1xC2	54	16.0	533	8.5	207
7	DGxUGL1	55	57.7	449	25.9	193
8	DGxU2	56	101.6	496	50.4	203
9	C1xUGL	53	19.9	519	10.3	220
10	G1xGL2	54	39.3	530	20.8	211
11	DGxC1	53	72.6	500	36.3	213
12	U2xGL1	52	40.1	506	20.3	208
13	DGxGL2	55	28.5	489	13.9	197
14	U1xD2	54	42.6	441	18.8	178
15	U1xG2	56	63.4	518	32.8	228
16	IP	55	80.9	480	38.8	183
17	VC	54	80.3	473	38	179
18	CC	55	40.2	472	19	183
19	EG1	73	148.1	216	32	54
20	EG2	75	140.0	200	28	75

3.2. Morphological characteristics

Another important aspect of the raw material for pulp production is the *morphological* characteristics of its fibers. The strength and morphology of fibers have a strong influence on the physical properties of paper (SETH et al., 1988; FOELKEL, 2007; MOKFIENSKI et al, 2008). The morphological characterizations of all the evaluated samples are presented in Table 3.

It was observed that the fiber content depends on the fiber coarseness; the lower coarseness, the higher fiber content. The fiber coarseness is lower for samples

U2xGL1, C1xC2, DGxUGL1 and C1xUGL and higher for samples DGxGL2, IP and U1xUGL. This fiber coarseness measurement gives indication on the number of fiber required to reach a given basic weight and therefore affects the runnability of the paper machine, for example. The longest mean area-weighted fiber length is obtained for hybrid eucalypt clone U2xC1, followed by samples DGxC1, UG, DGxU2, G1xUGL, U1xUGL and C1xUGL. The eucalypt clones DGxGL2 and CC have the shortest fiber. The length of the fiber has a positive influence on the mechanical properties of the final paper (NASCIMENTO, 2009). Curl index is higher for samples UxGL1, CC, C1xC2 and C1xUGL. This characteristic indicates that the fibers of these samples are less flexible than those of other eucalypt clone fibers. Macrofibrillation index and broken fiber content give information on the state of the fiber before deconstruction pretreatment or pulping. The CC and DGxUGL1 clones presented more broken fiber and the corresponding fiber is more fibrillated than the other clones. The Clones DGxGL2, IP and CC contain a higher amount of broken fiber which can explain the higher amount of fines on these eucalypt clones.

For the pulping process, the vessel elements are desirable, since they facilitate penetration of cooking liquors. However, for the production of special kinds of paper, such as printing papers, they are considered undesirable, because the vessel on the surface of the paper sheet tend to be pulled thereby causing printing failures; this is known as “vessels picking” (LINDSTRÖN et al, 2012). Eucalypt clones DGxC1, U1xU2, U1xD2, U1xG2, G1xUGL and CC have higher vessels content than the other samples. This vessels content can be correlated to the growth rate of the tree, as for example the higher wood production, the higher vessels content. It is apparent that fiber length and vessels content are the most important characteristics to help in the choice of the clones that should be used for pulp and paper manufacture. The hybrid eucalypt clones C1xUGL, U1xUGL, DGxUGL1 seem interesting because some characteristics, such as vessels content, fiber length, broken fiber and fines content are adequate for quality of papers.

Regarding the elephant grass samples, it was observed a lower fiber content per gram in EG1 and EG2 samples compared to wood samples. The width, length, coarseness, fine content, macro fibrillation index may be considered close to the eucalypt samples. However, the EG1 and EG2 showed a high vessel content. Vessels are recognized to generate problems during printing as explained previously (LINDSTRÖN et al, 2012). But in general it is possible to say that the fibers have potential for paper production, since the characteristics desired for paper quality are observed.

Table 3. Fiber and vessels characterization of the eucalypt clones and elephant grass species evaluated.

	Sample Code	Fiber content, millions/ g of pulp	Mean fiber arithmetic length, µm	Mean length-weighted fiber length, µm	Mean area-weighted length , µm	Mean fiber width, µm	Mean fiber coarseness, mg/m	Mean fiber curl index, %	Macro--Fibrillation index, %	Broken fiber content, %	Fine content, % in area	Mean fine area, µm2	Mean fine length ,µm	Vessel content, nb/g of pulp	Mean area-weighted length, mm	Mean vessel width, µm
1	**U1xU2**	29.8	617.5	746.5	742.5	16.0	0.05	4.5	0.48	14.6	7.8	1707	65.5	8132	0.41	186.5
2	**U2xC1**	26.2	692.5	843.5	847.0	15.2	0.05	4.3	0.42	14.1	7.2	1666	64.5	3730	0.31	181.2
3	**G1xUGL**	27.9	635.0	779.5	775.0	16.5	0.05	5.0	0.45	15.0	8.0	1661	66.0	10795	0.44	185.0
4	**U1xUGL**	26.5	637.0	788.0	786.5	17.0	0.06	4.0	0.43	16.0	9.0	1590	64.0	3699	0.45	189.0
5	**U1xC2**	32.1	579.0	732.0	729.5	16.1	0.05	5.0	0.55	16.0	11.0	1537	63.0	3523	0.33	185.0
6	**C1xC2**	33.5	601.0	753.0	749.0	15.2	0.04	5.5	0.51	14.6	7.5	1594	64.0	3232	0.41	182.0
7	**DGxUGL1**	36.6	584.0	729.0	731.5	18.8	0.04	5.0	0.56	18.4	8.8	1512	61.0	1580	0.34	178.1
8	**DGxU2**	31.6	622.5	763.0	768.0	17.6	0.05	4.2	0.49	16.4	8.0	1574	61.5	1774	0.32	182.8
9	**C1xUGL**	35.8	631.5	791.0	789.5	15.0	0.04	6.1	0.50	14.3	6.8	1499	61.5	2756	0.30	181.4
10	**G1xGL2**	30.5	621.0	755.0	752.0	15.9	0.05	4.9	0.47	14.7	8.0	1534	61.5	3502	0.36	188.7
11	**DGxC1**	26.1	655.0	790.5	789.5	16.1	0.05	4.4	0.39	15.3	8.0	1663	63.0	7857	0.35	188.1
12	**U2xGL1**	37.5	589.0	717.5	719.5	15.7	0.04	5.4	0.58	15.0	7.4	1479	60.5	2891	0.43	183.5
13	**DGxGL2**	29.4	567.0	703.0	705.5	18.2	0.06	5.0	0.53	19.4	12.2	1462	58.5	2942	0.37	182.7
14	**U1xD2**	31.2	591.5	736.0	740.5	18.8	0.05	4.4	0.54	18.4	9.0	1469	59.0	8484	0.44	183.3
15	**U1xG2**	27.8	629.5	766.5	767.0	17.3	0.05	4.4	0.48	15.3	8.9	1751	64.5	10434	0.35	189.3
16	**IP**	28.1	562.0	733.0	733.5	16.4	0.06	4.5	0.54	17.7	12.4	1647	64.5	6771	0.43	194.3
17	**VC**	30.0	579.0	729.5	733.0	17.3	0.05	4.6	0.52	17.9	9.0	1578	63.5	3101	0.47	186.6
18	**CC**	33.8	551.5	692.5	695.5	18.3	0.05	5.1	0.57	18.1	11.6	1633	64.5	7546	0.45	190.2
19	**EG1**	14.9	695.5	1131	1114	21.5	0.09	6.8	0.42	26.1	11.9	1987	62	11628	0.45	191.1
20	**EG2**	21.7	686.0	1113	1059	19.1	0.06	6.0	0.45	20.6	11.1	2748	73	12023	0.61	205.6

3.3. Chemical characteristics

Table 4 shows the extractive quantity of the eucalypt and elephant grass samples extracted with the ethanol/toluene→ethanol→hot water solvent series, with ethanol/toluene 1:2 only and with acetone only. In order to measure the biomass cell wall components, it is relevant to remove all extractives present in the material. The Tappi T204 CM 97 standard procedure (ethanol/toluene 1:2 → ethanol → hot water) was efficient for removing all polar and lipophilic extractive fractions. Although this procedure is intended to free the wood from extractives, it serves also to quantify the total amount of extractives present in the biomass, since the main cell wall components (cellulose, hemicelluloses and lignin) are not soluble in any of the solvents comprising the series. Extraction with ethanol/toluene only extracts substances as waxes, fats, resins, phytosterols and non-volatile hydrocarbons. Extraction in acetone (Tappi 280 PM99) serves to quantify those extractives that are more relevant to the pulping operation and pitch formation in the pulp. The acetone extractable content of wood is a measure of such substances as fatty acids, resin acids, sterols, waxes and non-volatile hydrocarbons. Because acetone is both more polar and water-miscible than dichloromethane or benzene-ethanol, the quantity of acetone extractable material, especially in wood, may be higher than that found with the other solvents. This procedure will not give the same results as ethanol-toluene or dichloromethane extractions. In his work, Barbosa et. al. (2005) showed that acetone is the best solvent for the evaluation of the wood lipophilic extractive content.

Biomass extractives are quite troublesome since they cause many difficulties in operating the industrial facilities, causing unexpected lost time in the operation for cleaning of equipment and instruments due to their stickiness and tackiness. In addition the deposition of these substances in the pulp may occur, which are called pitch (BARBOSA et. al., 2005), decreasing the pulp value or even its rejection by market. Cruz et. al. (2006) showed that pitch is comprised of waxes, fats and long chain alcohols, with these being the main compounds associated with pitch formation (Karlsson et al, 2001).

For the biorefinery and pulp production aim, among the eucalypt clones it was observed acceptable total extractive contents (1.9 to 4.9%) were observed for all

clones. Pitch formation and pulp dirtiness are much more likely on raw materials containing extractive levels higher than the values found. (SIXTA, 2006). On the other hand, elephant grass showed high total, acetone and ethanol/toluene extractive contents, in general above the desired value for pulp manufacture. The the EG1 and EG2 presented total extractive contents of 14.8 and 17.6%, respectively; this certainly has significant negative impact on elephant grass conversion yields since extractives are largely lost in biomass deconstruction procedures. .

Table 4. Extractive content of the eucalypt clones and elephant grass species evaluated.

	Sample Code	Acetone Extractives, %	Ethanol/Toluene (1:2) Extractives, %	Total Extractives, %
1	U1xU2	1.7	1.9	3.6
2	U2xC1	1.1	1.4	3.4
3	G1xUGL	2.5	2.5	4.9
4	U1xUGL	1.9	1.3	3.6
5	U1xC2	1.2	1.2	2.8
6	C1xC2	1.2	1.3	3.0
7	DGxUGL1	1.2	2.7	2.8
8	DGxU2	1.2	2.2	2.7
9	C1xUGL	0.9	1.6	2.1
10	G1xGL2	1.2	1.9	2.8
11	DGxC1	0.9	1.2	1.9
12	U2xGL1	1.0	1.4	2.5
13	DGxGL2	1.1	1.7	1.9
14	U1xD2	2.3	2.3	3.0
15	U1xG2	2.1	1.6	2.8
16	IP	0.8	1.5	2.3
17	VC	1.6	2.6	3.7
18	CC	1.1	2.6	3.5
19	EG1	3.9	6.8	14.8
20	EG2	9.9	1.8	17.6

Biomass minerals are detrimental for industrial utilization, since they cause corrosion and deposits on equipment, reduce biomass heating value and decrease mill throughput. The results of biomass mineral content presented in Table 5 show generally low amounts of inorganics in the eucalypt woods (MOREIRA, 2006; FOELKEL, 1977). For the eucalypt clones, the total inorganics measured by complete biomass combustion (ash content) varied in the range of 950-2,510 mg/kg biomass. For the EG1 and EG2, they reached 60,100 and 37,900 mg/kg, respectively. The very high mineral content in the grass is explained by its fast metabolism at the young age when it needs plenty of minerals to produce the biomass. Another interesting fact about the contents of minerals in biomass is that

they tend to decrease with aging due to decreased biomass deposition rate as a function of time (MORAIS, 2008). The same trend observed for total inorganics (ash content) is also verified for the individual components such as silica, chloride, calcium, potassium and magnesium, with the elephant grass samples always presenting higher values than the eucalypt clone samples. Calcium, magnesium and silica are very undesirable in most industrial processes because of their ability to cause deposits in equipment during evaporation of liquid streams and combustion of solid streams. On the other hand, potassium and chloride are particularly dangerous for their ability to decrease the ash melting point during combustion, thus causing sticky ash problems in recovery boiler systems (WESSEL et al., 2002). In addition, chlorides are highly corrosive and troublesome for most equipment regardless of metallurgy. In regard to transition metals (Fe, Cu and Mn), there were also significant differences among the eucalypt clones and elephant grass materials, again always presenting the same trend, higher content in elephant grass samples.

Table 5. Ash and metal content of the eucalypt clones evaluated.

	Sample Code	**Inorganics, mg/kg biomass**							
		Ash	**Cu**	**Fe**	**Ca**	**Mn**	**Mg**	**K**	**Cl^-**
1	U1xU2	950.0	0.8	15.5	307.0	9.5	81.0	194.0	260.0
2	U2xC1	1850.0	0.7	12.3	384.0	16.0	146.0	265.0	328.0
3	G1xUGL	1950.0	0.5	13.1	452.0	14.0	112.0	188.0	629.0
4	U1xUGL	1200.0	1.2	14.6	394.0	9.8	148.0	185.0	454.0
5	U1xC2	1250.0	0.7	10.3	328.0	9.7	144.0	340.0	594.0
6	C1xC2	2510.0	1.1	8.2	518.0	19.8	156.0	404.0	413.0
7	DGxUGL1	1950.0	0.8	18.2	532.0	16.3	118.0	358.0	500.0
8	DGxU2	2280.0	1.2	13.5	531.0	13.2	123.0	218.0	427.0
9	C1xUGL	2160.0	0.6	10.6	627.0	23.6	166.0	435.0	523.0
10	G1xGL2	1790.0	0.6	19.5	525.0	18.9	129.0	450.0	446.0
11	DGxC1	1400.0	0.9	10.6	263.0	11.2	128.0	252.0	701.0
12	U2xGL1	1800.0	0.7	13.5	475.0	14.3	136.0	152.0	519.0
13	DGxGL2	1750.0	1.0	11.3	462.0	15.0	123.0	202.0	600.0
14	U1xD2	1400.0	0.8	14.8	264.0	10.9	115.0	222.0	689.0
15	U1xG2	1850.0	1.1	20.4	296.0	11.2	92.0	384.0	477.0
16	IP	1550.0	1.1	9.3	378.0	18.2	104.0	369.0	434.0
17	VC	1800.0	1.4	9.9	491.0	2.2	123.0	469.0	488.0
18	CC	1700.0	1.2	8.5	356.0	13.9	183.0	370.0	399.0
19	EG1	60100	8.8	11.2	423	11.1	490	21194	15167
20	EG2	37900	3.8	67.5	352	56.5	1201	16055	2335

In Table 6 the biomass organic composition is presented. There were significant variations among the results of contents of sugars, acetyl group, uronic acids, lignin, and syringyl / guaiacyl ratio of lignin. Among the eucalypt clones, the total lignin contents varied in the range of 27.1 to 31.3%. The maximum value was obtained for the double crossing U1xC2 hybrid and the minimum for the G1xGL2 one. However, these values are considered acceptable for eucalypt clones, but for pulp production a lower lignin content and high S / G ratio are desired due to the increase of the pulpability of the wood (GOMES, 2008). About the carbohydrate content, the eucalypt clones presented values considered satisfactory for eucalypts aiming at pulp production (GOMIDE, 2005).

Regarding elephant grass, the lignin contents for EG1 and EG2 biomass were 18 and 16.5%, respectively. The low lignin content of the elephant grass samples is advantageous for potentially improving pulping easiness and yield. However, its low lignin S/G ratio and low sugar content work in the opposite direction (GOMES et al., 2008). The low sugars content of the elephant grass samples reflected their very high extractive and mineral contents.

Table 6. Chemical composition of the eucalypt clones and elephant grass species evaluated (all percentages based on extractive free biomass)

Sample	Sample Code	Sugar Composition, %					Acid Soluble Lignin %	Total lignin,%	Lignin S/G ratio	Acetyl Group, %	Uronic Acid Group %
		Glucan	Xylans	Galactans	Mannans	Arabinans					
1	U1xU2	46.1	11.8	0.8	0.8	0.2	4.3	30.3	2.8	2.1	3.7
2	U2xC1	45.5	10.7	1.2	1.0	0.2	4.6	30.8	2.7	1.9	4
3	G1xUGL	43.9	13	0.8	0.9	0.2	4.7	28.9	2.9	2.7	3.8
4	U1xUGL	44.9	11.7	1.1	0.8	0.2	5	29.7	3.1	2.4	4
5	U1xC2	45.6	10	1.4	1.1	0.2	4.5	31.3	3	1.8	3.8
6	C1xC2	45.6	9.7	1.6	0.9	0.3	5.1	31.1	3	1.6	4.1
7	DGxUGL1	45.5	13	0.9	0.8	0.3	5.3	29.2	3.2	2.6	4
8	DGxU2	45.3	12.6	0.9	1.0	0.3	4.4	29.8	2.6	2.5	4
9	C1xUGL	46	11.9	1.1	0.9	0.3	5	30.7	3.2	2.2	4
10	G1xGL2	46.4	14.1	1.0	0.8	0.3	5	27.1	3.5	3	3.9
11	DGxC1	47.2	10.8	1.2	0.9	0.3	4.7	31	2.8	1.8	4
12	U2xGL1	45.5	13.4	1.2	0.8	0.3	5.6	29.3	3.8	2.6	4
13	DGxGL2	45.8	12.9	1.1	1.0	0.3	4.4	28.2	2.9	2.5	3.8
14	U1xD2	48.1	11.4	1.0	0.9	0.3	4.4	28.6	2.6	2	3.9
15	U1xG2	46.8	11.8	1.0	0.8	0.3	4.4	30.2	2.6	2	4
16	IP	49.4	12	1.2	0.9	0.3	4.2	27.2	2.7	1.9	4
17	VC	46.9	11.4	0.8	1.1	0.2	4.6	28.4	2.9	2.1	3.8
18	CC	47.4	11.2	1.0	1.1	0.2	4.1	28.4	2.4	1.9	3.9
19	EG1	38.2	9.6	0.8	0.6	0.2	2.2	18.0	0.8	1.9	1.2
20	EG2	35.6	16.1	0.5	ND	1.6	1.6	16.5	0.7	1.8	1.4

3.4. Some Relations among cell wall components

In order to determine lignin content, it is necessary to treat biomass with strong acids so that the carbohydrate fraction is hydrolyzed, leaving lignin as a residue. This acid hydrolysis procedure leads to severe lignin condensation and precipitation so that it is easily collected from the solution through simple filtration. Some of the lignin, particularly in hardwoods, seemingly condenses insufficiently in the acid media, becomes soluble and sieves through the filtration system. This lignin is the so-called acid soluble lignin. Although acid soluble lignin is negligible for softwood biomass, it is quite important for hardwoods. The amount of acid soluble lignin in the woody biomass investigated varied in the range of 4.1-5.6% of the wood dry weight (Table 5). Although not commonly investigated, the amount of acid soluble lignin seems to be related to the lignin S/G ratio. Lignin containing larger amounts of syringyl monomers will condense less during the strong acid hydrolysis treatment, since the

C5 position in the aromatic ring is blocked in the syringyl units. These blocked C5 positions prevent C5 condensation. Therefore, lignin containing high S/G ratio, i.e., high number of syringyl units will condense less during the acid hydrolysis procedure and produce more soluble lignin in the filtrates. Figure 1 shows that there is very good correlation between lignin S/G ratio and acid soluble lignin content for the various woody and nonwoody biomass, in agreement with the proposed theory.

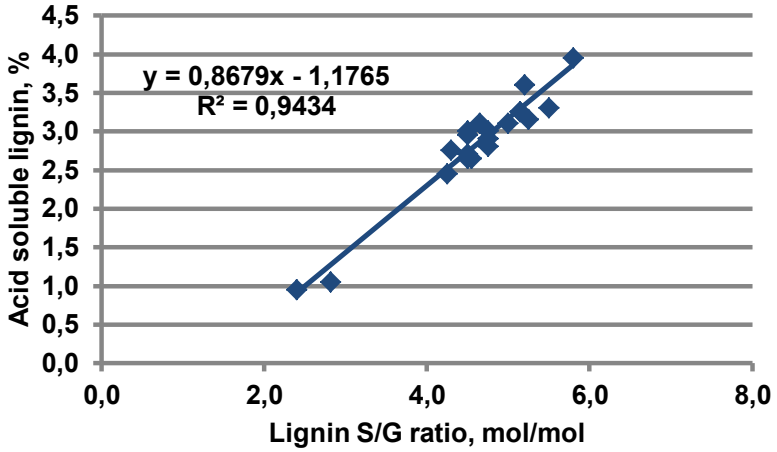

Figure 1. Correlation between biomass acid soluble lignin and lignin S/G ratio.

3.5. Raw material selection for biorefinery application

Based on the results previously discussed, it was selected four eucalypt clones and one elephant grass considered the most suitable for the subsequent pulp production and biorefinery studies, namely:

(1) a double crossing hybrid of *Eucalyptus urophylla* x *Eucalyptus urophylla* (U1 x U2), that was selected on the basis of its very high annual growth (83 m^3/ha/yr), high wood density, excellent morphological traits, very high forest yield (43 ton/ha/yr) and low xylan and uronic acid contents;

(2) a triple crossing hybrid of *Eucalyptus grandis* x (*Eucalyptus urophylla* x *Eucalyptus globulus*) (G1 x UGL), which presented a high xylan content and possessed *Eucalyptus globulus* in its genotype, which is of interest for its high S/G ratio, although it is quite challenging for its high content of extractives (4.9%);

(3) a triple crossing of (*Eucalyptus dunnii* x *Eucalyptus grandis*) x *Eucalyptus urophylla* (DG x U2), that was selected due to its highest annual growth (101 m^3/ha/yr) among all eucalypts evaluated, good density, outstanding morphological traits, and the highest forest yield (~50 ton/ha/yr);

(4) a commercial elite clone (IP) was obtained from a large Brazilian forest company, which is a double crossing of *Eucalyptus urophylla* x *Eucalyptus grandis*, for its excellent forest productivity (38.5 ton/ha/yr), good density, the highest cellulose content and lowest lignin content among all; also for being a very good reference since it is commercially planted by a large pulp company in Brazil;

(5) regarding the elephant grass, it was selected the EG1 (*Pennisetum purpureum*); it presented the highest productivity (32 ton/ha/yr) and density (216 kg/m^3) at harvesting age (mature material), highest glucan content and uronic acid contents among the grasses evaluated.

4. Conclusions

- All eucalyptus wood clones evaluated show high technological quality and suitability for pulp production and biorefinery applications, but the most suitable were *Eucalyptus urophylla* x *Eucalyptus urophylla* (U1 x U2), *Eucalyptus grandis* x (*Eucalyptus urophylla* x *Eucalyptus globulus*) (G1 x UGL), (*Eucalyptus dunnii* x *Eucalyptus grandis*) x *Eucalyptus urophylla* (DG x U2), and a commercial elite clone (IP);
- Eucalypt wood clones are less moist, denser and contains fewer minerals and extraneous materials than the elephant grass species;
- Both elephant grasses investigated presented aceptable characteristics for biorefinery studies, with the sample EG1 (*Pennisetum purpureum*) being the most attractive due to its highest productivity (32 ton/ha/yr) and density (216 kg/m^3);
- A good positive correlation was established between lignin S/G ratio and acid soluble lignin, for the pool of lignocellulosic raw materials investigated.

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6. References

ALVES, E. F., (2005) Interação de fibras e elementos de vasos de polpa kraft de eucalipto com tintas de impressão offset. Master's Thesis, Federal University of Viçosa, Viçosa, Brazil.

ARESTA, M.; DIBENEDETTO, A. AND DUMEIGNIL, F.. (2013) Biorefinery: from biomass to chemicals and fuels. Green Process Synth; 2: 87–88.
Assis, T. F., 2001. Melhoramento para Produtividade e Qualidade de Celulose de Fibra Curta. Workshop sobre Melhoramento de Espécies Florestais e Palmáceas no Brasil. Embrapa Florestas, p. 193-214.

ASSOCIAÇÃO DOS FABRICANTES DE CELULOSE E PAPEL – BRACELPA. Disponível em: <http://www.bracelpa.com.br>. Access on: 22 April, 2013.

BARBOSA, L. C. A., MALTHA, C. R. A., AND CRUZ M. P., (2005) Chemical composition of lipophilic and polar extractives of *Eucalyptus grandis*, Science & Engineering Journal 15(2), 13-20.

BISON, O., (2004) Melhoramento de eucalipto visando à obtenção de clones para a indústria de celulose. 169 p. Tese (Doutorado em Genética e Melhoramento de Plantas) – Universidade Federal de Lavras, Lavras, MG.

BRACELPA, (2013) Brazilian Pulp and Paper Association, (http://www.bracelpa.com.br). Access on: 22 April, 2013.

COLODETTE, J. L., GOMIDE, J. L., JÚNIOR, D. L., and PEDRAZZI, C., (2007). Effect of pulp delignification degree on fiber line performance and bleaching effluent load, BioResources 2(2), 223-234.

DIAS, V. R. L.; CLÁUDIO-DA-SILVA, JR. E. (1991)"Pulp and paper properties as influence by wood density - same species and age of Eucalyptus." In: INTERNATIONAL PAPER PHYSICS CONFERENCE, 1., Kailua Kona, Hawai.

EIRAS, K. M. M., and COLODETTE, J. L., (2001). Influência das condições de operação no estágio DHT na branqueabilidade e nas características físico-químicas da polpa e do filtrado. 34º Congresso Anual de Celulose e Papel, São Paulo.

EIRAS, K. M., MOUNTEER, A. H., VENTURIM, G., COLODETTE, J. L., and GOMIDE, J. L. (2003). “Effect of pulp leachable lignin and hexenuronic acids contents on O2-stage,” El Papel, Palafrugell, 106(1), 32-36.

FOELKEL, C. E. B., (1977). Qualidade da madeira de eucalipto para atendimento das exigências do mercado de celulose e papel. In: Conferência IUFRO sobre silvicultura e melhoramento de eucalipto, 1997, Salvador. Anais... Salvador: IUFRO, v.1, p.1.

FOELKEL, C., (2007). As fibras dos eucaliptos e as qualidades requeridas na celulose kraft para a fabricação de papel. Eucalyptus Online Book e Newsletter, 48p. <http://www.eucalyptus.com.br/capitulos/PT03_fibras.pdf>.

GOMES, F. J. B., GOMES, A. F., COLODETTE, J. L., GOMIDE, J. L., CARVALHO, A. M. M. L., TRUGILHO, P. F., GOMES, C. M., and ROSADO, A. M., (2008). Influence of content and S/G relation of the wood lignin on kraft pulping performance, O Papel 12, 95-105.

GOMIDE, J. L., COLODETTE, J. L., OLIVEIRA, R. C., and SILVA, C. M., (2005). Technological characterization of the new generation of Eucalyptus clones in brazil for kraft pulp production, Revista Árvore (Impresso) 29(1), 129-137.

GOMIDE, J. L., FANTUZZI, N. H., and REGAZZI, A. J., (2010). Analysis of wood quality criteria of eucalyptus wood for kraft pulp production, Revista Árvore 34(2), 339-344.

KARLSSON, S., HOLMBOM, B., SPETZ, P., MUSTRANTA, A., & BUCHERT, J. (2001). Reactivity of “Trametes laccases with fatty and resin acids”. Applied microbiology and biotechnology, 55(3), 317-320.

KLEEN, M., SJÖBERG, J., DAHLMAN, O., JOHANSSON, L.-S., KOLJONEN, K., and STENIUS, P., (2002). The effect of ECF and TCF bleaching on the chemical composition of soda-anthraquinone and kraft pulp surfaces, Nordic Pulp and Paper Research Journal 17(3), 357-363.

LEITE, F. P., GOMES, F. J. B., SOUZA, E., ROSADO, A. M., and AMARAL, L. S., (2010). Investigation of drying time in the humidity content and on physical and chemical characteristics of wood for the production of pulp, 42nd Pulp and Paper International Congress and Exhibition - ABTCP, São Paulo, Brazil.

LINDSTRÖN, N., and FARDIM, P., (2012). Chemistry and surface chemistry of vessels in eucalyptus kraft pulps, O Papel 73(9), 65-72.

MADAKADZE, I. C.; MASAMVU, T. M.; RADIOTIS, T. J. LI and SMITH, D. L. (2010). Evaluation of pulp and paper making characteristics of elephant grass (Pennisetum purpureum Schum) and switchgrass (Panicum virgatum L.). African Journal of Environmental Science and Technology Vol. 4(7), pp. 465-470.

MAZZARELLA, V.N.G., (2007). Jornada Madeira Energética-Capim Elefante com Fonte de Energia no Brasil: Realidade Atual e Expectativas. IPT-BNDS - Rio de Janeiro, maio de 2007. P.Point.

MOKFIENSKI, A., COLODETTE, J. L., GOMIDE, J. L., & CARVALHO, A. M. M. L. (2008) Relative importance of wood density and carbohydrate content on pulping yield and product quality. Ciência Florestal, Vol. 18, No. 3,pp. 401-413.

MORAIS, P. H. D. (2008). Effect of age of the wood of eucalyptus in its chemical and pulpability, and bleachability and properties of the pulp, Master's Thesis, Federal University of Viçosa, Viçosa, Brazil.

MOREIRA, E. (2006). Effects of acid leaching of wood chips on the kraft process, Master's Thesis, Federal University of Viçosa, Viçosa, Brazil.

NASCIMENTO, A. C., MOREIRA, J. V., (2009). Influence of recycled fiber on the physical and mechanical paper properties. Revista de Engenharia e Tecnologia, ISSN 2176-7270, 1(1), 63-71.

PAULINO, V.T. DE LUCENAS, T.L., POSSENTI, R.A., (2007). Capim elefante cv. Paraíso (Pennisetum hybridum): produção de matéria seca, composição química e biológica em diferentes alturas de corte. http://www.iz.sp.gov.br/artigos.php?ano=2007

QUESADA, D. M., BODDEY, R.M., MASSENA REIS, V., URQUIAGA, S. (2004). Parâmetros Qualitativos de Genótipos de Capim Elefante (Pennisetum purpureum Schum.) estudados para a produção de energia através da Biomassa. CIRCULAR TÈCNICA 8. Seropédica, RJ, Novembro.

Rabelo, M. S.. (2006) Tecnologias avançadas para o pré-branqueamento de polpa kraft de eucalipto. Teses de doutorado apresentada a Universidade Federal de Viçosa,.

SCANDINAVIAN STANDARD, (1992). SCAN-CM 46:92, Bulk density.

SCANDINAVIAN STANDARD, (1994). SCAN-CM 40:94, Size distribution.

SCANDINAVIAN STANDARD, (1995). SCAN-CM 43:95, Basic density.

SCOTT, R. W., (1979). Colometric determination of hexuronic acids in plant materials, Analytical Chemistry 7, 936-941.

SETH, R. S., and PAGE, D. H., (1988). Fiber properties and tearing resistance, Tappi Journal 71(2), 103-107.

SEYE, O.; CORTEZ, L. A. B.; GÓMEZ, E. O. (2000).Queima direta de gramínea. Projeto Integrado de Biomassa - PIB. In: Encontro de Energia no Meio Rural, 3., , Campinas.

SILVA JR., F. G.; DO VALLE, C. F.; MUNER, J. C. G. (1996) Programa de qualidade da madeira da Votorantim Celulose e Papel – VCP". O Papel, p. 35-43.

SOLAR, R., KACIK, F., AND MELCER, I., (1987). Simple semimicro method for the determination of O-acetyl groups in wood and related materials, Nordic Pulp and Paper Research Journal 2(4), 139-141.

TAPPI standard, (2006). T280 wd-06, Acetone extractives of wood and pulp.

TAPPI standard, (2007). T204 cm-07, Solvent extractives of wood and pulp.

TAPPI standard, (2007). T256 cm-07, Water-soluble chlorides in pulp and paper.

TAPPI standard, (2007). T264 cm-07, Preparation of wood for chemical analysis.

TAPPI standard, (2010). TIS 017-10, Post color number.

TAPPI standard, (2011). T222 om-11, Acid-insoluble lignin in wood and pulp.

TAPPI standard, (2011). T684 om-11, Gross heating value of black liquor.

TAPPI standard, (2012). T257cm-12, Sampling and preparing wood for analysis.

VILELA, H., BARBOSA, F.A., RODRIGUEZ, N., BENEDETTI, E., NOGUEIRA, A.C. (2002a). Produção e composição química do capim elefante Paraíso submetida a três alturas de corte. Anais da XXXIX Reunião Anual da Sociedade Brasileira de Zootecnia. Julho de 2002. URPE. Recife/PE, CD, 2002.

VILELA, H., RODRIGUEZ, N. & DIAS TEIXEIRA, E. (1997) Produções de forragem de um híbrido hexaplóide (Pennisetum glaucum X Pennisetum purpureum) e seu valor nutritivo. In: Anais da XXXIV Reunião da SBZ, julho de 1997, Juiz de Fora/MG.

VILELA, H., VILELA, D., BARBOSA F.A., BENEDETTI, E. (2003a).Quantidade de água suplementar para o capim elefante Paraíso. Veterinária Notícias, ISSN 0104-3463. 2003.

VILELA, H., VILELA, D., BARBOSA, F.A., BENEDETTI, E. (2003b).Análise de crescimento do capim elefante Paraíso. Veterinária Notícias, ISSN 0104-3463.

VILELA, H., VILELA, D., BARBOSA, F.A., BENEDETTI, E. (2002b). Irrigação do capim elefante Paraíso. Anais da XXXIX Reunião Anual da Sociedade Brasileira de Zootecnia. Julho de 2002.URPE-Recife/PE, CD, 2002.

VUORINEN, T., BUCHERT, J., TELEMAN, A., TENKANEN, M., AND FAGERSTRÖM, P., (1996). Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps, In International Pulp Bleaching Conference, 43-51, Tappi Press, Atlanta, USA.

WALLIS, A. F. A., WEARNE, R. H., and WRIGHT, P. J., (1996). Chemical analysis of polysaccharides in plantation eucalypt woods and pulps, Appita Journal 49(4), 258-262.

WERH, T. R.; BARRICHELO, L. E. G. (1993) “Cozimento Kraft com madeiras de Eucalyptus grandis de diferentes densidades básicas e dimensões de cavacos”. O Papel, V.54, n.5, p. 33-41.

WESSEL, R. A., TRAN, H., MAHINPEY, N., KUHN, D., (2002). Effect of particle composition on carryover deposition in recovery boilers. TAPPI Fall Conference & Trade Fair.

ZONG LAI, Y., 1999. The influence of alkaline pulping conditions on the efficiency of oxygen delignification. (1999). Access on: 22 April, 2013. http://www.TAPPI.org/Downloads/unsorted.

CAPITULO 3

EVALUATION OF ALKALINE DECONSTRUCTION PROCESSES FOR BRAZILIAN NEW GENERATION OF EUCALYPT CLONES

Abstract

Wood utilization for pulp and paper and biorefinery applications requires some kind of mechanical and/or physical-chemical pretreatment. Among the chemical treatments the alkaline ones are the most used worldwide, although acid and solvent treatments have also being used. This paper deals with eucalypt wood deconstruction with alkaline processes including soda-AQ, soda-AQ-O_2, soda-O_2, and kraft. The kraft process is largely used by the pulp industry and is evaluated here only to serve as a reference. The behavior of the four eucalypt clones selected in chapter 2 were investigated when submitted to the aforementioned processes regarding their screened yield, chemical demands and pulp quality at different kappa number levels (15, 35, 50, and 70). The two most promising processes (kraft and Soda-AQ) were chosen for producing pulps (kappa 15 and 20) which were studied in depth (content of carbohydrates, uronic acid, hexenuronic acid, polysaccharide molecular weight, residual lignin structure, etc), as well as their respective black liquors (heating value, solid content, elemental analysis, and lignin structure). The main findings of this work were: (1) the wood of the four different hybrid eucalypt clones behave similarly in the various alkaline deconstruction treatments; (2) the soda-AQ and Kraft were considered the most suitable processes for producing pulp on the basis of yield, chemical demands and pulp fiber integrity; (3) the soda-AQ process can potentially replace the kraft for a high degree of wood delignification (kappa number 15); (4) the alkaline processes using oxygen (soda-AQ-O_2 and soda-O_2) are more suitable for wood deconstruction aimed at biofuels; and (5) the soda-AQ process resulted black liquor of more suitable burning characteristics than the kraft.

1. Introduction

The most common processes for pulping are the alkaline ones, with especial emphasis to the kraft process, which uses sodium hydroxide and sodium sulphide as main reagents. When targeting a new pulp industry working as a biorefinery, some

processes changes such as sulphur free technologies shall be considered, since compounds containing this element are responsible for decreasing the black liquor heating value (CARDOSO et al., 2009). Moreover, sulphur is known to poison many catalytic reactions and would be negative to any high value application of the lignin extracted from black liquor (VISHTAL and KRASLAWSKI, 2011). Furthermore, sulfur free processes are interesting for decreasing environmental pressures, since the elimination of sulfur from the processes avoid TRS emissions that are typical of the kraft process.(ALISSON, 1983; FRANCIS et al. 2009).

The soda based processes are interesting because they are compatible with the existing kraft pulping technology. The interest in sulfur-free pulping has centered on soda-anthraquinone (AQ) process, since AQ accelerates delignification and produces pulps with strength properties which approach that of kraft pulps (FRANCIS et al, 2009, GOMIDE et al., 1980; SILVA JÚNIOR et al., 1996). Sulfur free pulping technologies such as soda-anthraquinone-oxygen (Soda-AQ-O_2) and soda-oxygen (Soda-O_2) have not been largely studied for eucalyptus wood (KHRISTOVA et al, 2006; FRANCIS et al, 2009).

This paper deals with eucalypt wood deconstruction with alkaline process including soda-AQ, soda-AQ-O_2, soda-O_2, and kraft aiming pulp production. The kraft process is largely used by the pulp industry and is evaluated here only to serve as a reference.

2. Material and methods

For this study, 4 eucalypt wood clone samples in commercial harvesting age were investigated, provided by *GENOLYTPUS* project, located in Minas Gerais State – Brazil. The complete list of samples used in this study is presented in the Table 1.
Five representative trees of the population with average diameter at breast height and height were selected. They were harvested and from each tree it was extracted five 1m-long bolts at 0, 25, 50, 75, and 100% of the tree heights. The samples were evaluated for their moisture content at the moment of harvesting according to Tappi T264 cm-97 standard procedure. The eucalypt clone samples were chipped in a laboratory chipper, a Chogokukikai model, equipped with 3 knives and 2 screens (40 & 13mm); in the sequence, they were well mixed (260m^3 rotary mixer) and screened

according to SCAN-CN 40:94 procedure. The chips retained in the 3 mm and 7 mm screens were collected and mixed again, air dried to about 15% moisture and stored in large plastic bags.

Table 1. Codification of the eucalypt clones species.

Sample Code	BiomassType
U1xU2	*E. urophylla (Flores IP) x E. urophylla (Timor)*
G1xUGL	*E. grandis (Coffs Harbour) x [E. urophylla (R) x E. globulus (R)]*
DGxU2	*[E. dunnii* (R) x *E. grandis (R)] x E. urophylla (Timor)*
IP	*E. urophylla (IP) x E. grandis (IP)* commercial clone

Methods

Sampling for physical, chemical and morphological analyses was done by using the so-called quartering technique, which is trivial for those skilled in the art. Chips were used to measure chip bulk and basic density according to SCAN CN-49:92 and SCAN CM-46:92 standard procedures, respectively.

Biomass productivity

Biomass productivity was calculated by using the medium annual increase (MAI) and basic density, by the following equation:

$$\text{Biomass productivity (ton/ha/yr)} = \text{MAI } (\text{m}^3/\text{ha/yr}) \times \text{basic density } (\text{ton/m}^3)$$

Sample preparation for morphological analysis

About 200 grams of each eucalypt clone sample were sliced into toothpick type material and macerated by using nitro-acetic acid solution in order to prepare individual fibers for morphological analyses. To make the maceration, a solution of five parts of acetic acid and one part of nitric acid were mixed, added to the biomass material until they were completely immersed and let stand for 6 hours at 100 ˚C under a hood. The reaction was stopped by washing the material, which was dispersed in distilled water. Following, the material was gently mixed in a magnetic stirrer (slowly and steadily) for 60 min. so that all the fiber bundles were separated. Morphological characterization of fibers, vessels and fines was carried out on a pulp

suspension passing through a specific cell illuminated by a laser beam and connected to a high-resolution camera (CCD). This analysis allowed reliable statistical measurement of thousands of fiber, vessels and fines to determine the main morphological and dimensional characteristics of the pulp components.

Sample preparation for chemical analysis

For the chemical analyses, about 1 kg of each eucalypt clone were sampled and ground in a Wiley type mill to produce sawdust of variable size. This sawdust was screened according to Tappi Standard T257-cm85. The sawdust that passed the 40 mesh screen and was retained in the 60 mesh screen was selected for the chemical analyses. The sawdust was air dried and conditioned in a temperature and humidity controlled room (23±1˚C, 50±2% RH) until an equilibrium moisture was achieved (≈10%). This sawdust (raw sawdust) was used for the chemical analyses. The analyses of ash, silica, chloride, iron, copper, manganese, potassium, calcium and magnesium were carried out directly on the raw sawdust, according to the Standard Methods for the Examination of Water and Wastewater (2000), except for chloride, which was determined according to Tappi T256 cm-97 standard procedure. The biomass extractive contents in acetone, ethanol/toluene(1:2) and ethanol/toluene(1:2) →ethanol →hot water solvent series were also determined in the raw sawdust by using the TAPPI T280 pm-99, T204 cm-97 and TAPPI T264 cm-97 standard procedures, respectively. In order to determine biomass main cell wall components, a 200g sample of extractives freed was prepared by using TAPPI T264 cm-97 standard procedure. This extracted sample (extractive free sawdust) was conditioned in a temperature and humidity controlled room (23±1˚C, 50±2% RH) until an equilibrium moisture was achieved (~10%). The contents of uronic acids, acetyl groups and sugars (glucans, mannans, galactans, xylans and arabinans) in the extractive free biomass were determined according to Scott (1979), Solar et al. (1987) and Wallis et al. (1996). The acid insoluble lignin, acid soluble lignin and lignin syringyl/guaiacyl (S/G) ratio were determined according to TAPPI T 222 om-97 standard procedure, Goldschmid (1971) and Lin & Dence (1992), respectively.

Pulping: processes and conditions

Four deconstruction processes were used to convert the eucalypt clones into pulps, namely: Soda-AQ, soda-AQ-O_2, soda-O_2, and kraft. For analyzing the deconstruction processes five levels of kappa numbers were investigated: 15, 20, 35, 50 and 70. The cooking trials of the eucalypt clones were done in an M&K digester, with 2 individual reactors of 10 liters each, equipped with a forced liquor circulation system and electrically heated with temperature and pressure control. The digester was coupled to a cooling system (Coil System with residual liquor, involved with water at room temperature), to ensure the cooling of the liquor after the cooking simulation. . With the exception of the alkaline charge, the other deconstruction conditions were kept constant as shown in Table 1. Eight cooking experiments were performed for each sample and process, using different active alkali charge to establish the delignification curves.

Table 2. Conditions for pulping processes.

Parameter	***Soda-AQ process***	***Soda-AQ-O_2 process***	***Soda-O_2 process***	***Kraft process***
Chips, kg o.d.	1	1	1	1
Active alkali as NaOH, % on o.d. chips*	Variable	Variable	Variable	Variable
Sulfidity as NaOH, % on o.d. chips	-	-	-	26
Anthraquinone charge, % on o.d. chips	0.05	0.05	-	-
Oxygen charge, % on wood chips**	-	6	6	-
Liquor to chips ratio, L/kg	4/1	4/1	4/1	4/1
Maximum temperature, ˚C	170	170	170	170
Time to maximum temperature, min.	90	90	90	90
Time at maximum temperature, min.	50	50	50	50

* The active alkali charge was investigated in various levels in order to reach kappa numbers 15, 20, 35, 50 and 70

** In the Soda-AQ-O_2 and Soda-O_2 processes, the oxygen dosage (6% on chip o.d. weight) was split into three parts and applied after 50 minutes, 70 minutes and 110 minutes reaction time from the beginning of cooking, thereby ensuring that the pressure limit (20kgf/cm²) of the digester was not exceeded.

Fiber individualization was achieved in a "hydrapulper" (15 liters capacity), followed by fine screening (*Voith laboratory cleaner*) equipped with perforated plates with 0.2 mm openings. The material retained on the sieve (rejects) was dried and weighed. The clean pulp was dewatered in centrifuge to a consistency of about 30%, weighed and stored in polyethylene bags for further analysis. With the known weights of the sieved and retained materials, the reject content and the screened yield were determined. Pulp viscosity and brightness were measured in the screened material.

Detailed pulp and black liquor characterization

Detailed pulp and black liquor characterization were carried out only for the soda-AQ and kraft cooks terminated at kappa 15 and 20. These kappa numbers were chosen since they are most common values used by the eucalypt pulp industry worldwide. The pulps were evaluated regarding their carbohydrate molecular weight distribution, carbohydrate content, uronic acid, and hexenuronic acid content. For the determination of the molecular weight distribution Gel Permeation Chromatography (GPC) was used, in which the pulps were activated with dimethylacetamide before the GPC analysis through solvent exchange. The activated pulp samples were dissolved in DMAC/LiCl 9.0 % (w/v) at 80˚C for 2 hours. Then, the solution was centrifuged at 4000 rev/min to remove undissolved components; thereafter the supernatant solution was analyzed. The calibration of the GPC columns was made with Pullulan reference materials (Agilent) in the range 0.18 to 778 kDa. The Data analysis was performed with LC Solution GPC software. The GPC analysis was performed on four serially connected columns PLgel Mixed A 300 x 7.5 mm columns protected by a PLgel 20 mm pre-column (Polymer Laboratories Ltd, UK). The temperatures of the pre-column and columns, the injector, and the detector (RI) were kept constant at 80˚C. DMAC with 0.5% of LiCl (w/v) was used as the eluent at a rate of 0.8 $mL.min^{-1}$, and the injection volume was 100 µL. The contents of uronic acids, acetyl groups, sugars (glucans and xylans), and hexenuronic acid were determined according to Scott (1979), Wallis et al. (1996), and Vuorinen et. al (1996).

The residual lignin isolated from soda-AQ and k raft pulps cooked to kappa number 15 and 20 of the clone G1xUGL (isolated from the pulps by acidolysis) as well as the lignin precipitated from their respective black liquors were analyzed by two-dimensional nuclear magnetic resonance (2D-NMR). The isolation of MWL and their structural characteristics were compared to those of the milled wood lignin (MWL) isolated from the initial raw material, a lignin preparation that is still considered to be the representative of the native lignin in the plant, despite its limitations (GUERRA et al., 2006; RENCORET et al., 2009). The isolation of MWL from wood of the eucalypt clone G1xUGL was previously described by Prinsem et al. (2012). MWL was extracted from finely ball-milled (15 h) wood, free of extractives and hot water-soluble material, using dioxane−water (9:1, v/v), followed by evaporation of the solvent, and

purified as described by Björkman (1956). The final yield ranged from 15% to 20% of the original Klason lignin content. For the isolation of residual lignin, first, all pulp samples were air-dried at 37−40 °C. Extractives were eliminated by Soxhlet extraction for 9 h with acetone and subsequent extraction with water at 100 °C (three steps). Then, 15 g of dry pulp was subjected to acidolysis, according to the method previously described by Evtuguin et al. (2001), using a two-step extraction with 0.1 M HCl in a 1,4-dioxane:water mixture (82:18 v/v) under an inert (argon) atmosphere at 88− 92 °C. The solid:liquid ratio for the first and second extraction step was, respectively, 13.3 and 10.0 mL per gram of dry pulp. After the extractions, the pulp was washed with the same 1,4-dioxane:water mixture, but without HCl. In order to avoid high acid concentration, the washing liquor was added equally to both extracts, which were evaporated separately under reduced pressure until a volume reduction of ∼70% was obtained. Both concentrated extracts were added together in 1.5 L of cold distilled water under strong stirring. The lignin was precipitated overnight at 4°C and then centrifuged (25 min, 9000 rpm, 4˚C). A washing step with cold distilled water was included, and after recovery (30 min, 9000 rpm, 4 °C) the samples were freeze dried. The extraction yields of the residual lignins ranged from 60% to 82%, based on the theoretical lignin content of pulp (% lignin = 0.15 × kappa number), except for the residual lignins from the pulps with kappa 15, which were in the range of 26%− 30%. The residual lignins were submitted to Soxhlet extraction with n-pentane during 8 h. After drying with nitrogen, the residual lignin was ready for analysis. The lignins from the collected black liquors were precipitated at pH 4.0 and the obtained slurries were air-dried at 40 °C. The homogenized samples were stored in a desiccator until stable humidity was attained. All analytical techniques ($^{1}H–^{13}C$ 2D-NMR, and ^{31}P NMR) were performed on these samples according previously methodologie which was described by Prinsem et al. (2012).

The two-dimensional nuclear magnetic resonance (2D-NMR) spectra were recorded at 25 ˚C in a Bruker AVANCE 600 MHz spectrometer, equipped with a cryogenically cooled z-gradient triple resonance probe. Forty milligrams (40 mg) of lignin sample were dissolved in 0.75 mL of dimethylsulfoxide (DMSO)-d6, and $^{1}H–^{13}C$ HSQC (heteronuclear single quantum correlation) spectra were recorded. The spectral widths were 5000 and 13200 Hz for the ^{1}H and ^{13}C dimensions, respectively. The number of collected complex points was 2048 for the ^{1}H dimension, with a recycle

delay of 1s. The number of transients was 64, and 256 time increments were recorded in the ^{13}C dimension. The $^{1}J_{CH}$ constant was set to 140 Hz. The J-coupling evolution delay was set to 3.2 ms. Squared cosine-bell apodization function was applied in both dimensions. Prior to Fourier transformation, the data matrices were zero-filled up to 1024 points in the ^{13}C dimension. The central solvent peak was used as an internal reference (*δC 39.5 ppm*; *δH 2.49 ppm*). HSQC cross-signals were assigned by comparing with the literature.23,29,35−40 In the aromatic region, C2,6-H2,6 correlations from S units and C2−H2 correlations from G units were used to estimate the S/G lignin ratios. The abundances of the different inter unit linkages were referred to the number of aromatic units (per 100 aromatic units), to obtain a comparative estimation of their removal during pulping.

Concerning the black liquor heating value, solids, sodium, silicate, and chloride were determined according to Tappi T684 om-11, CPPA H1, Tappi T25 cm-85, Tappi T244, and Tappi T699 om-87. The elemental analysis (including C, H, N, S, and O), and potassium were determined by using elemental analyzer equipment and atomic absorption spectrometer, respectively.

3. Results and Discussion

3.1. Wood productivity, morphology and physical-chemical characteristics

3.1.1 Wood productivity and physical properties

The average annual increment (AAI) varied in the range of 46.2-101.6 m^3/ha/yr. The lowest AAI occurred for the G1xUGL clone and the highest for for the DGxU2 clone. However, even the one with lowest AAI may be considered satisfactory given that the average for Brazilian commercial plantations is 40-60 m^3/ha/yr (BRACELPA, 2013).

Two very important factors regarding biomass use in industrial processes are moisture content and density, since they affect harvesting, transportation and utilization costs. The eucalypt clones analyzed in this study showed similar values of moisture (minimum 53% and maximum 56%) and density varying from 480 to 504 kg/m^3. These values are considered satisfactory for pulp production (DIAS and CLÁUDIO-DA-SILVA, 1991; WEHR-BARRICHELO,1993; SILVA JR. et al., 1996, GOMIDE et al., 2005).

Table 3. Wood productivity and physical characteristics of the eucalypt clones evaluated.

Sample Code	Moisture, %	Average Annual Increment, m^3/ha/yr*	Biomass basic density, kg/m^3	Biomass Productivity, bone dry ton/ha/yr	Chip bulk density, kg/m^3
U1xU2	54	86.0	504	43.3	209
G1xUGL	53	46.2	500	23.1	202
DGxU2	56	101.6	496	50.4	203
IP	55	80.9	480	38.8	183

3.1.2. Wood morphological characteristics

The strength and morphology of fibers have a strong influence on the physical properties of paper (SETH et al., 1988; FOELKEL, 2007; MOKFIENSKI et al, 2008). In Table 4, the morphological characterizations of the eucalypt clones are presented. The values of width, length, coarseness, macro fibrillation index were somewhat similar for the four eucalypt samples. Concerning fine contents, the values were also similar among the samples, except for the IP clone, which presented a highest fine content. Due to a high surface area, and high swelling, fines affect paper sheet structure and properties in several ways, including increased sheet wetness for given dewatering conditions and increased fiber interaction by increasing the fiber water-air interfaces where the surface tension forces act during sheet drying (SETH, 2003).

The vessel contents were different among the eucalypt clones, the low value was observed for the DGxU2 clone, and the high value was observed to G1xUGL one. For the pulping process, the vessel elements are desirable, since they facilitate penetration of cooking liquors. However, for the production of special kinds of paper, such as the printing papers, they are considered undesirable, because the vessel on the surface of the paper sheet tend to be pulled, thereby causing printing failures known as “vessels picking” (LINDSTRÖN et al, 2012).

Table 4. Fiber and vessels characterization of the eucalypt clones evaluated.

	Eucalypt clones			
Sample Code	**U1xU2**	**G1xUGL**	**DGxU2**	**IP**
Fiber content, millions/g of pulp	29.8	27.9	31.6	28.1
Mean fiber arithmetic length, µm	617.5	635.0	622.5	562.0
Mean length-weighted fiber length, µm	746.5	779.5	763.0	733.0
Mean area-weighted length , µm	742.5	775.0	768.0	733.5
Mean fiber width, µm	16.0	16.5	17.6	16.4
Mean fiber coarseness, mg/m	0.05	0.05	0.05	0.06
Mean fiber curl index, %	4.5	5.0	4.2	4.5
Macro-Fibrillation index, %	0.48	0.45	0.49	0.54
Broken fiber content, %	14.6	15.0	16.4	17.7
Fine content, % in area	7.8	8.0	8.0	12.4
Mean fine area, µm2	1707	1661	1574	1647
Mean fine length ,µm	65.5	66.0	61.5	64.5
Vessel content, nb/g of pulp	8132	10795	1774	6771
Mean area-weighted length, mm	0.41	0.44	0.32	0.43
Mean vessel width, µm	186.5	185.0	182.8	194.3

3.1.3. Wood chemical properties

Table 4 shows the extractive quantity of the eucalypt clones samples extracted with the ethanol/toluene→ethanol→hot water solvent series, with ethanol/toluene 1:2 only and with acetone. In order to measure the biomass cell wall components, it is relevant to remove all extractives present in the material. The Tappi T204 CM 97 standard procedure (ethanol/toluene 1:2 → ethanol → hot water) was efficient for removing all polar and apolar extractive fractions. Although this procedure is intended to free the wood from extractives, it serves also to quantify the total amount of extractives present in the biomass, since the main cell wall components (cellulose, hemicelluloses and lignins) are not soluble in none of the solvents comprising the series. Extraction with ethanol/toluene only extracts substances as waxes, fats, resins, phytosterols and non-volatile hydrocarbons. Extraction in acetone (Tappi 280 PM99) serves to quantify those extractives that are more relevant to the pulping operation and pitch formation in the pulp. The acetone extractable content of wood is a measure of such substances as fatty acids, resin acids, sterols, waxes and non-volatile hydrocarbons. Because acetone is both more polar and water-miscible than dichloromethane or benzene-ethanol, the quantity of acetone extractable material,

especially in wood, may be higher than that found with the other solvents. This procedure will not give the same results as ethanol-toluene or dichloromethane extractions. In his work, Barbosa et. al. (2005) showed that acetone is the best solvent for the evaluation of the wood lipophilic extract content.

Biomass extractives are quite troublesome since they cause many difficulties in operating the industrial facilities, causing unexpected lost time in the operation for cleaning of equipment and instruments due to their stickiness and tackiness. In addition may occur the deposition of these substances in the pulp, which are called pitch (BARBOSA et. al., 2005), decreasing the pulp value or even its rejection by market. In her study Cruz et. al. (2006) showed that in pitch composition are present waxes, fats, long chain alcohols, being these main compounds associated with pitch formation (Karlsson et al, 2001).

The evaluated eucalypt clones showed acceptable acetone extractives, Ethanol/Toluene (1:2) extractives and total extractive contents for the pulp mills (GOMIDE et al., 2010). The highest value was observed to G1xUGL clone. In addition, pitch formation and pulp dirtiness are much more likely on raw materials containing high content of these extractives (BARBOSA et al., 2005), another negative aspect of materials with high extractive content is that they are likely to result low yield during cooking process.

Table 5. Extractive content of the eucalypt clones evaluated.

Sample Code	Acetone Extractives, %	Ethanol/Toluene (1:2) Extractives, %	Total Extractives, %
U1xU2	1.7	1.9	3.6
G1xUGL	2.5	2.5	4.9
DGxU2	1.2	2.2	2.7
IP	0.8	1.5	2.3

Table 6. Ash and metal content of the eucalypt clones evaluated.

Sample Code	Inorganics, mg/kg biomass							
	Ash	Cu	Fe	Ca	Mn	Mg	K	Cl^-
U1xU2	950.0	0.8	15.5	307.0	9.5	81.0	194.0	260.0
G1xUGL	1950.0	0.5	13.1	452.0	14.0	112.0	188.0	629.0
DGxU2	2280.0	1.2	13.5	531.0	13.2	123.0	218.0	427.0
IP	1550.0	1.1	9.3	378.0	18.2	104.0	369.0	434.0

In Table 7, the results of the analysis of content of sugar, acetyl group, uronic acids, lignin and syringyl / guaiacyl ratio from lignin are presented. Among the woody biomass, there were significant variations among the total lignin contents, in the range of 27.2-30.3%; the maximum value was obtained for the U1xC2 hybrid and the minimum for the G1xGL2 one. However, these values are considered acceptable for eucalypt clones, but for pulp production a lower lignin content and high S/G ratio are desired due to the increase of the pulpability of the wood (GOMES, 2008). About the carbohydrate content, the eucalypt clones presented values considered satisfactory for eucalypts for pulp production (GOMIDE, 2005).

Table 7. Chemical composition of the eucalypt clones evaluated.

Sample Code		**U1xU2**	**G1xUGL**	**DGxU2**	**IP**
Total Extractives, %		3.6	4.9	2.7	2.3
Total Ash, %		0.1	0.2	0.23	0.16
Sugar Composition, %	Glucans	46.1	43.9	45.3	49.4
	Xylans	11.8	13.0	12.6	12.0
	Galactans	0.8	0.8	0.9	1.2
	Mannans	0.8	0.9	1	0.9
	Arabinans	0.2	0.2	0.3	0.3
Acid Soluble Lignin %		4.3	4.7	4.4	4.2
Total lignin,%		30.3	28.9	29.8	27.2
Lignin S/G ratio		2.8	2.9	2.6	2.7
Acetyl Group, %		2.1	2.7	2.5	1.9
Uronic Acid Group %		3.7	3.8	4.0	4.0

3.2. Wood Pulpability

The chemistry and efficiency of alkaline pulping technologies are influenced by several process parameters, alkali charge and the possible addition of tother cooking chemicals e.g. sulphide or anthraquinone (LETHO et al., 2013). Currently, Kraft pulping is the dominant process for the delignification of wood into pulp. The key to the kraft process is the kraft recovery cycle that is quite efficient at recovering the pulping chemicals, NaOH and Na_2S (VAKILAINEN, 2000). However, energy efficiency is becoming more important each passing year and there is a sense of inevitability that gasification of the pulping effluent or black liquor will replace the kraft recovery cycle for chemical and energy recovery (BOSE et al., 2009). The technical feasibility of black liquor gasification would improve significantly if a non-sulfur

pulping process were used to replace kraft (FRANCIS et al., 2008). In this context, soda pulping which is traditionally the most employed chemical pulping process for various different types of raw materials (KHRISTOVA et al. 2006; ENAYATI et al. 2009) appears as an interesting alternative. However, the soda pulping produces a low yield and highly colored pulp, consuming a large amount of bleaching chemicals (FRANCIS et al. 2006; LABID et al. 2008). Some these disadvantages of soda pulping could be overcome by the using of pulping additives. The addition of anthraquinone (AQ) to soda pulping liquor is known as an effective and simple approach that increases delignification selectivity, carbohydrate protection, and pulp yield (HAMZEH et. al., 2009). A study conducted by Pierre (2013) shown that the anthraquinone addition increases the soda pulping screened yield level and, for some dosages, this yield turns out higher than the Kraft yield; indicating that this process seems to be the ideal for replacing the kraft. The cooking results for all materials and processes evaluated are presented in Table 8. Among the eucalypt clones, it was possible to observe slightly high and slightly low alkali demand for the materials U1xU2 and IP, respectively, when aiming to low kappa numbers, a result that can be traced to their high and low lignin contents, respectively. The other eucalypt clones showed similar chemical consumptions

Additionally, alternative processes can also be used when it is desired to obtain other products besides pulp, such as soda-AQ-O_2 and soda-O_2. The oxygen addition in the pulping processes greatly improves the delignification rate, which is very suitable for pulping processes (ROVIO et. al., 2011). On the other hand, the oxidative conditions affect the fiber ultrastructure in a deconstructive manner (CHANG et al., 2001; ROVIO et. al., 2011). Since that these processes have a more drastic consequence for the mechanical fiber properties, they can be considered a promising alternative for replacing the kraft and soda-AQ as pretreatment for biorefinery processes. In contrast to paper grade pulps, when aiming some biorefinery applications such as bioethanol, the pulp strength is not important. In these cases, the deconstruction of the lignocellulosic matrix is aimed at the removal and/or modifications of the lignin in order to improve substrate digestibility (CHEN et al, 2013).

A comparison of the different deconstruction methods indicate the Soda-AQ-O_2 and Soda-O_2, as the most drastic since they presented high alkali demand to achieve a

given degree of delignification (Table 1). As expected, the kraft process consumed the lowest amount of alkali to achieve the desired kappa number among all alkaline processes.

Table 8. Pulping results of the eucalypt clones evaluated by soda-AQ, soda-AQ-O_2, soda-O_2 and Kraft processes.

E. clones	Parameter	Soda-AQ				Soda-AQ-O_2				Soda-O_2				Kraft			
U1xU2	Alkaline Charge, %	35.0	16.2	14.5	13.0	34.5	24.0	22.0	20.5	40.0	28.0	23.0	22.0	27.5	15.1	13.1	12.5
	Kappa Number	15.2	35.5	53.6	73.8	15.5	36.3	47.3	68.7	16.2	32.1	52.2	75.6	14.9	37.7	53.1	72.4
	Yield Screened, %	47.3	47.3	42.0	32.7	49.0	48.0	44.5	35.0	46.3	49.2	43.7	25.7	49.5	49.4	43.2	36.2
	Reject Content, %	0.1	9.9	19.1	33.3	0.1	2.6	5.7	27.3	0.0	1.5	11.1	31.1	0.1	8.7	13.2	31.4
G1xUGL	Alkaline Charge, %	31.0	16.2	15.1	13.0	33.5	25.0	22.5	20.8	40.0	28.5	25.0	24.0	27.5	15.0	13.8	13.0
	Kappa Number	15.2	35.0	51.5	69.1	15.8	35.2	53.4	70.0	15.5	39.3	54.4	74.4	15.4	35.0	50.9	68.1
	Yield Screened, %	48.8	47.0	40.0	28.0	50.6	49.9	42.9	30.3	50.1	46.5	40.1	25.1	49.6	49.5	45.4	34.1
	Reject Content, %	0.1	7.8	20.0	32.5	0.2	5.3	17.2	31.3	0.0	4.9	18.6	36.2	0.1	10.7	18.2	29.5
DGxU2	Alkaline Charge, %	29.5	16.3	14.5	13.0	33.0	24.0	22.0	20.0	39.0	28.0	26.0	24.5	28.0	15.5	13.9	12.8
	Kappa Number	15.9	36.9	50.7	70.2	15.3	36.9	52.7	69.3	15.4	33.9	52.5	71.3	14.5	35.7	50.2	71.4
	Yield Screened, %	48.1	45.7	40.9	29.4	49.2	46.9	42.2	27.8	44.7	49.8	45.1	30.6	49.6	49.5	42.0	29.9
	Reject Content, %	0.1	9.4	20.0	28.6	0.2	6.1	16.1	32.0	0.0	1.2	12.6	29.3	0.1	8.2	20.1	35.1
IP	Alkaline Charge, %	29.5	16.5	14.4	13.0	32.5	24.2	23.0	21.2	40.0	27.0	25.0	23.0	26.0	15.0	13.3	12.7
	Kappa Number	15.3	35.6	50.7	70.1	15.4	35.0	50.0	70.0	16.1	39.2	54.8	71.5	15.7	36.0	55.8	71.9
	Yield Screened, %	49.6	48.2	39.9	30.0	50.8	48.7	44.0	32.8	43.7	49.7	47.0	35.6	50.4	50.4	43.0	32.0
	Reject Content, %	0.1	9.9	19.1	33.3	0.1	2.6	5.7	27.3	0.0	1.5	11.1	31.1	0.1	8.7	13.2	31.4

On the other hand, although all processes could be considered satisfactory regarding their viscosity values, soda–AQ and kraft presented the highest values for this parameter, indicating less carbohydrate degradation. It can be explained due to selectivity effect of the AQ (KHRISTOVA et al., 2006), and low alkaline charge applied in the kraft process.

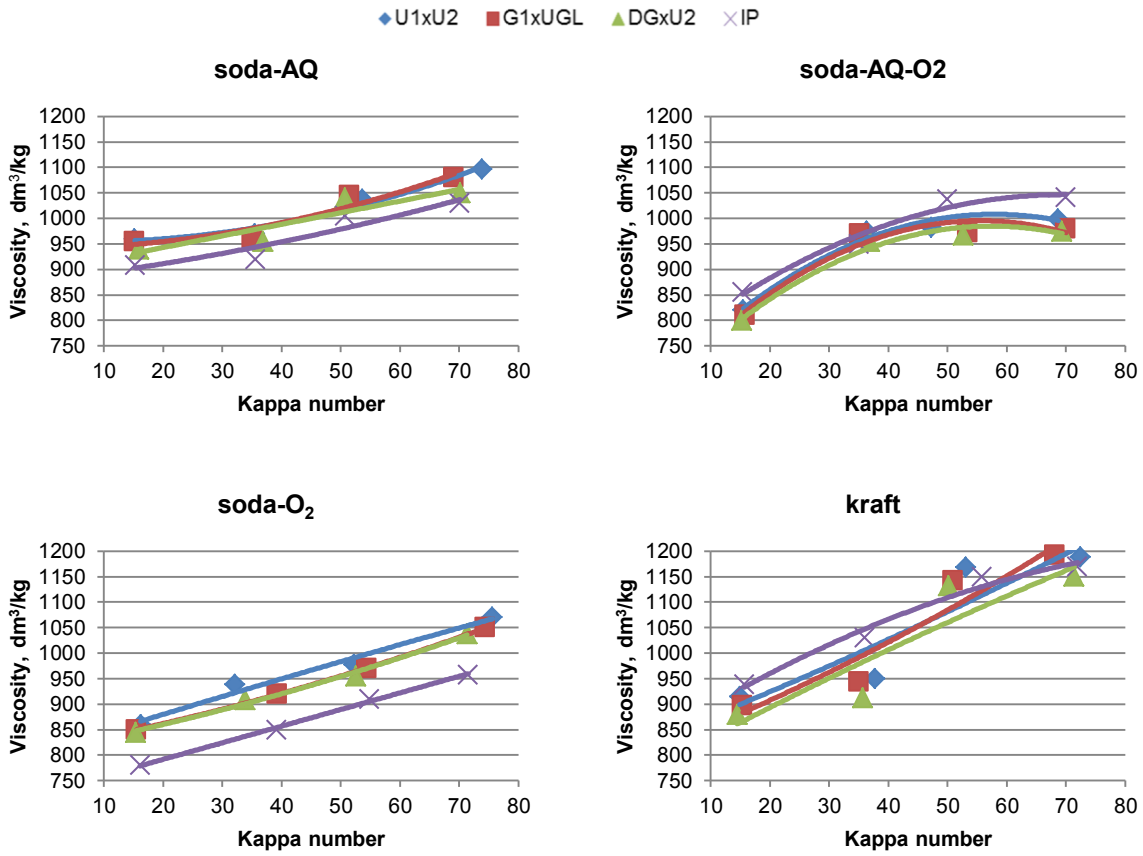

Figure 1. Viscosity *versus* kappa number for the processes and raw materials evaluated.

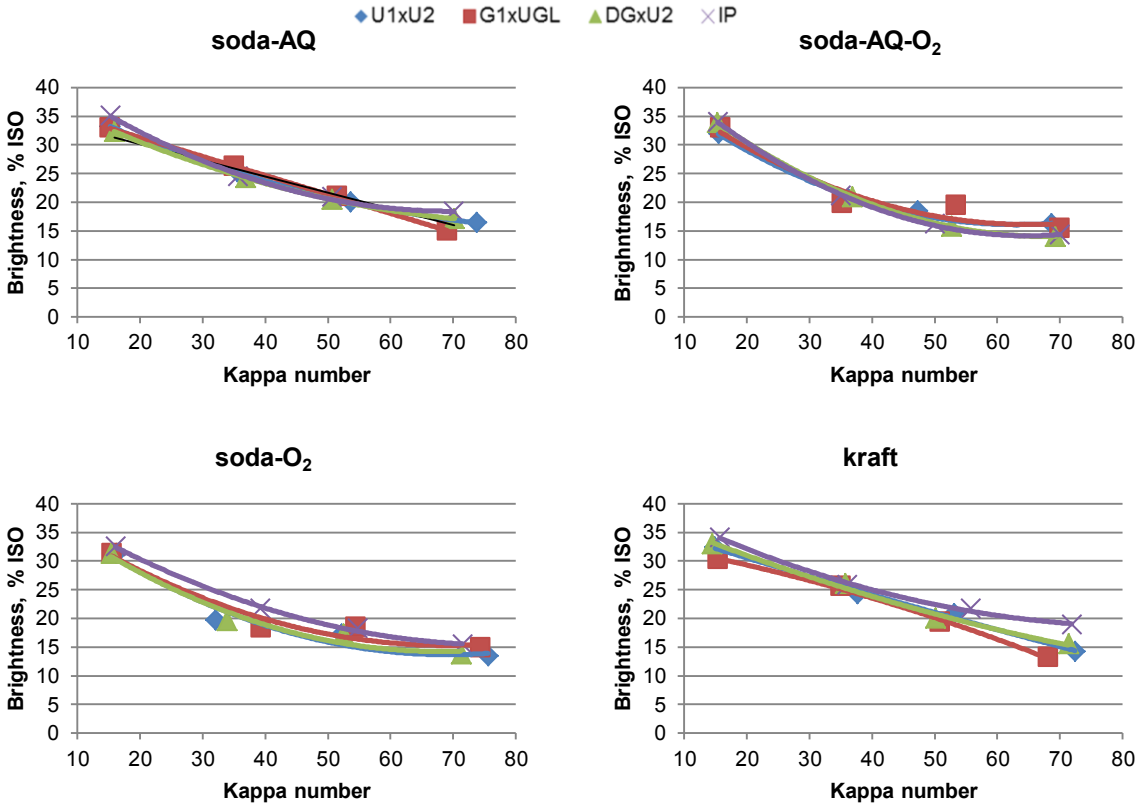

Figure 2. Brightness *versus* kappa number for the processes and raw materials evaluated.

Regarding the yield, soda-O_2 showed the worst performance among the studied processes. The soda-AQ-O_2 showed a slightly better yield performance than Soda-AQ, in spite of the high alkali demand, but the pulp presented low viscosity. In general, the kraft process presented the best performance when all parameters are considered.

In this way, the two chosen processes were: soda-AQ and Kraft, and as previously described in the methodology pulps were produced by these processes at kappa number 15 and 20, using the established conditions curves obtained in the pulpability study; the results of these pulping processes are presented in Table 9.

Table 9. Pulping results for the soda-AQ and Kraft processes at kappa number 15 and 20.

Eucalypt clones	Parameter	Soda-AQ		Kraft	
		kappa 15	Kappa 20	Kappa 15	kappa 20
U1xU2	Alkali Charge, % NaOH	35.0	24.0	27.5	22.0
	Screened yield, %	47.3	50.0	49.5	51.2
	Reject Content, %	0.1	1.1	0.1	0.3
	Viscosity, dm^3/kg	875	919	1032	1073
	Brightness, % ISO	33.3	30.8	33.5	31.9
G1xUGL	Alkali Charge, % NaOH	31.0	23.0	27.5	21.0
	Yield Screened, %	47.0	51.0	49.6	50.4
	Reject Content, %	0.1	0.2	0.1	0.5
	Viscosity, dm^3/kg	748	917	1144	1193
	Brightness, % ISO	34.0	32.1	32.3	30.6
DGxU2	Alkali Charge, %	29.5	22.0	28.0	22.0
	Screened yield, %	48.1	51.1	49.6	52.0
	Reject Content, %	0.1	0.4	0.1	0.4
	Viscosity, dm^3/kg	951	1020	892	1054
	Brightness, % ISO	34.0	30.8	34.3	31.8
IP	Alkali Charge, %	29.5	22.0	26.0	20.0
	Yield Screened, %	49.6	51.6	50.4	52.0
	Reject Content, %	0.2	0.6	0.1	0.4
	Viscosity, dm^3/kg	972	1028	939	1100
	Brightness, % ISO	34.0	29.6	33.3	31.1

3.3 Pulp characterization

The soda-AQ and kraft pulps of kappa number 15 and 20 were evaluated regarding their contents of carbohydrate, uronic acids and hexenuronic acids (Table 10). Regarding the carbohydrate content, the soda-AQ presented the highest glucans content, which can be explained due to AQ effect preserving these polymers against the peeling reactions during the pulping process (KHRISTOVA et al., 2006). On the

other hand, concerning the xylans content, the kraft pulps showed highest contents, which reflected on the highest uronic acid and hexenuronic acids contents in these pulps. In addition, more xylans were also found in the kappa 20 kraft pulp in relation to the kappa 15 one. Concerning the pulp chemical composition among the eucalypts studied, considering each evaluated process, it was observed the same trend among them. In general, the pulps cooked at kappa 15 showed lower xylan contents than those cooked to kappa 20, indicating that these carbohydrates are penalized when the pulping process is conducted aiming lower kappa number.

Table 10. Results of glucan, xylans, uronic acid, and hexenuronic acid content of pulps obtained by the Soda-AQ and Kraft processes at kappa numbers 15 and 20.

		Kappa 15				**Kappa 20**			
		Glucans, %	Xylans, %	Uronic Acids, %	HexA, mmol/kg	Glucans, %	Xylans, %	Uronic Acids, %	HexA, mmol/kg
soda-AQ	U1 x U2	88.1	8.5	0.2	15.8	84.9	11.3	0.5	40.3
	G1 x UGL	86.2	10.4	0.3	21.2	83.9	12.2	0.7	48.2
	DG x U2	88.0	8.8	0.3	15.9	84.2	11.8	0.6	43.4
	IP	87.1	9.6	0.3	21.8	84.5	11.2	0.6	45.7
Kraft	U1 x U2	82.0	13.9	0.6	39.8	81.2	14.2	1.3	48.8
	G1 x UGL	81.6	15.4	0.7	41.8	80.8	15.8	1.2	48.6
	DG x U2	82.2	13.4	0.7	39.1	81.2	14.0	1.3	48.9
	IP	81.9	14.0	0.6	39.5	80.6	14.9	1.3	46.4

Regarding the hexenuronic acid content, a positive point of the soda-AQ process is its low generation of this acid, e.g. a bleachability of theses pulps are positively impacted; it has been documented in the literature that pulps with lower hexenuronic acid content have a greater performance in the O-stage, since small amounts of hexenuronic acid are removed during oxygen delignification (EIRAS, 2003). Another relevant point for bleaching processes which may be also attractive in Soda-AQ pulps of the pulp obtained by the Soda-AQ process is that they present higher content of free phenolic hydroxyl groups (FRANCIS et al, 2005; BOSE et al., 2009), which are the main sites for oxygen reactions (COLODETTE et al., 2007). It is known that in soda-AQ pulping, AQ oxidizes the reducing end groups of carbohydrates, thus stabilizing them towards peeling reactions in alkaline media. The reduced form, AQ, cleaves part of the β-aryl ether linkages in lignin. Thus, the molecular mass of the residual lignin is reduced and new phenolic hydroxyl groups are formed. Both effects render the lignin more soluble (KLEEN et al., 2002). Since phenolic hydroxyl groups

are essential to lignin dissolution in alkali, a higher content of this functional group in the residual lignin may be partly related to the residual lignin being more condensed. In his work, ZONG LAI (2011) showed that the tendency of alkaline lignin condensation reactions would increase in the order of: high sulfidity < kraft < Soda-AQ < soda cooks.

The soda-AQ pulps at kappa number 20 presented satisfactory values to DP, which were similar to those found for kraft pulps at kappa number 15 (Table 11). Concerning the pulp viscosities, they presented an expected behavior, decreasing with the DP decrease. Another interesting finding is that in spite of low xylans content. The polydispersity of xylans is lower than that of glucans regardless of the pulp sample (Table 12). Among the eucalypts studied, the U1xU2 pulp presented the highest DP among all pulps.

Table 11. Degree of polymerization (DP) and intrinsic viscosity of eucalyptus kraft and soda-AQ pulps cooked to kappa 15 and 20

		Kappa 15			Kappa 20		
		Glucans DP	Xylans DP	Pulp Visc., dm^3/kg	Glucans DP	Xylans DP	Pulp Visc., dm^3/kg
Soda-AQ	U1 x U2	4986	296	875	6416	313	919
	G1 x UGL	4745	266	748	6310	281	917
	DG x U2	4603	180	951	5951	256	1020
	IP	5007	277	972	6218	297	1028
Kraft	U1 x U2	6939	199	1032	7340	265	1073
	G1 x UGL	6030	233	1144	8114	244	1193
	DG x U2	5672	222	892	6965	269	1054
	IP	5376	257	939	6935	254	1100

Table 12. Polydispersity of eucalyptus kraft and soda-AQ pulps cooked to kappa number 15 and 20.

		Kappa 15		Kappa 20	
		Glucans DP	Xylans DP	Glucans DP	Xylans DP
Soda-AQ	U1 x U2	2.46	1.14	2.04	1.17
	G1 x UGL	2.29	1.12	2.09	1.29
	DG x U2	2.79	1.61	2.31	1.50
	IP	2.33	1.17	2.19	1.26
Kraft	U1 x U2	1.91	1.71	2.26	1.35
	G1 x UGL	2.42	1.52	2.37	1.37
	DG x U2	2.19	1.65	2.21	1.33
	IP	2.31	1.37	2.14	1.29

Table 13 present results of 2D-NMR analysis of lignin isolated from kraft and soda-AQ pulps of kappa 15 and 20, derived from the G1XUGL eucalypt clone, which is a

triple crossing hybrid of Eucalyptus grandis x (Eucalyptus urophylla x Eucalyptus globulus); it was selected due to its high xylan content and for possessing *Eucalyptus globulus* in its genotype, which is of interest for its high S/G ratio, although it is quite challenging for its high content of extractives (4.9%), being an interesting raw material for a detailed study. A quantitation of the abundance of the main lignin inter-unit linkages present in the different residual lignin, as well as the abundance of the G and S lignin units was performed by integration of the volume contours of their cross-signals and was referred to as per 100 aromatic units (Table 13). The main linkages observed in the residual lignin from G1xUGL were β-O-4' aryl ether, β-β' resinol and β-5' phenylcoumaran structures, in both the soda-AQ and kraft pulps. No oxidized lignin moieties were observed by 2D-NMR in this residual lignin.

The distributions of the different inter-unit linkages in the pulp residual lignin is similar to that observed in the native lignin in wood, with a predominance of β-O-4 alkyl-aryl ether linkages, followed by lower amounts of resinols and phenylcoumaran, although with a drastic reduction in their content. This reduction in the content of linkages was more evident in the pulps with lower kappa number (kappa 15) than in pulps with higher kappa number (kappa 20) due to the more drastic pulping conditions at lower kappa numbers. Moreover, at similar kappa number, the content of β-O-4' aryl ether linkages in the residual lignin were lower for the soda-AQ process that for the kraft process, indicating a higher efficiency of the soda-AQ process for delignifying the G1xUGL eucalypt wood.

Table 13. Main lignin characteristics (linkages per 100 aromatic units, and S/G ratio) of the residual lignins isolated from the pulps produced from eucalypt G1xUGL after kraft and soda-AQ processes at kappa 20 and 15. The composition of the MWL isolated from G1xUGL is shown for comparison.

Linkages *(per 100 aromatic units)*		Soda-AQ		Kraft	
	MWL	Kappa 20	Kappa 15	Kappa 20	Kappa 15
β-O-4 alkyl-aryl ether	75.1	11.0	8.7	15.5	10.1
β-β resinols	13.4	7.6	6.2	6.4	5.6
β-5 phenylcoumarans	6.2	1.5	1.4	1.1	1.0
S/G ratio	2.8	2.8	2.8	3.0	3.0

3.4 Black liquor characterization

The material dissolved in the black liquor consists mainly of lignin and degraded carbohydrates (hemicelluloses and cellulose), while the minor part are extractives, proteins and inorganic constituents (CARDOSO et al., 2009). Table 14 presented the results of black liquor heating value, total solids, inorganic solids, and organic solids. Results of inorganic/organic mass demonstrate that the eucalypt clones as processed by Soda-AQ and kraft processes possess an average of 46.5% (44.1-49.8%) inorganic and 53.2% (50.2-56.3%) organic materials.

The Soda-AQ process would be an excellent solution compared to kraft process, since the black liquor from this process presents a higher heating value than the kraft black liquor and it is a sulfur free process. The absence of sulfur compounds in the Soda-AQ black liquor enormously facilitates its further fractionation into valuable components (FRANCIS et al, 2009).

Chemically, black liquor is a mixture of several basic elements. The results of Na, S, K, Cl, SiO_2, C, H, O and N are presented in the Table 15 and are expressed in terms of the percentage of the element mass to the total mass of dry solids existing in the liquor. Potassium and chloride are particularly dangerous for their ability to decrease the ash melting point during combustion, thus causing sticky ash problems in recovery boiler systems (KAHN et al., 2009). In addition, chlorides are highly corrosive and troublesome for most equipment regardless of metallurgy (PFROMM, 1997). The amounts of Cl, SiO_2, C, N, H and O contents were very close among the eucalypt black liquors.

Table 14. Heating value, total solids, inorganic solids, and organic solids of the black liquor obtained by Soda-AQ and Kraft processes ending in kappa number 15 and 20.

		Kappa 15				Kappa 20			
		Heating value, cal/g	Total Solids,%	Inorganic Solids,%	Organic Solids, %	Heating value, cal/g	Total Solids,%	Inorganic Solids,%	Organic Solids, %
Soda-AQ	U1 x U2	3442.5	13.4	45.4	54.6	4000.2	13	45.2	54.8
	G1 x UGL	3705.1	13.5	49.7	50.3	4049.1	11.2	47.6	52.4
	DG x U2	3691.3	15.7	46.9	53.1	4071.3	12.4	43.7	56.3
	IP	3602.3	13	49.8	50.2	4072.6	11.3	46.1	53.9
Kraft	U1 x U2	3963.1	13	46.5	53.5	3949.6	10.9	45.4	54.6
	G1 x UGL	3591.7	13.4	44.1	55.9	3970.6	12.8	49.4	50.6
	DG x U2	3669	12.7	46.3	53.7	4028.8	11.2	41.4	53.7
	IP	3657	12.5	46.8	53.2	3920.3	11	49.4	50.6

Table 15. Elemental analyses of the black liquor obtained by Soda-AQ and Kraft processes ending in kappa number 15 and 20

		Kappa 15									Kappa 20								
Element, %		**Na**	**SiO_2**	**Cl**	**K**	**C**	**H**	**N**	**S**	**O**	**Na**	**SiO_2**	**Cl**	**K**	**C**	**H**	**N**	**S**	**O**
Soda-AQ	U1 x U2	18.3	1.4	0.06	0.06	40.2	3.9	ND	ND	35.2	14.9	1.9	0.07	0.09	44.4	4.0	ND	ND	34.3
	G1 x UGL	17.8	1	0.09	0.1	40.5	3.8	ND	ND	35	15.3	0.7	0.08	0.07	44.1	4.0	ND	ND	34.9
	DG x U2	17.8	1.4	0.07	0.06	41.9	3.8	ND	ND	35.4	15.6	1.7	0.07	0.06	44.4	3.9	ND	ND	34.5
	IP	17.9	1.2	0.08	0.09	40.4	3.9	0.1	ND	34.7	14.7	1.5	0.76	0.08	44.4	4.0	0.1	ND	34.7
Kraft	U1 x U2	18.1	1.6	0.08	0.08	41.1	3.7	0.1	3.5	33.7	20.7	1.3	0.07	0.08	43	3.9	0.1	2.8	34.1
	G1 x UGL	17.8	1.1	0.1	0.07	39.2	3.7	ND	4.5	34.7	17.4	1.4	0.1	0.08	42	3.8	0.1	3.6	34.7
	DG x U2	22.3	1.1	0.06	0.09	41.2	3.8	0.1	3.9	34.3	14.6	1.2	0.06	0.07	43	3.9	ND	3.3	34.4
	IP	20.5	1.4	0.05	0.06	40.6	3.8	0.1	3.4	34.8	17.9	1.4	0.12	0.07	44.7	4.0	0.1	2.9	34

ND: not detected

Regarding the lignin structure, they were precipitated from the black liquors of eucalypt wood G1xUGL from the Soda-AQ and kraft processes, at kappa 20 and kappa 15, and were also analyzed by 2D-NMR. The quantitation of the main inter-unit linkages and lignin units is shown in Table 16. It is clear from the NMR spectra that these precipitated lignin are enriched in β-β resinol structures, while the other linkages (β-O-4 alkyl-aryl ether and β-5 phenylcoumarans), if present, are in much lower amounts. An increase of the S/G ratio is observed, indicating that S-lignin units, which are predominantly forming β-O-4 alkyl-aryl ether structures, are preferentially removed from the eucalypt during pulping and are being enriched in the black liquors. It is interesting to notice that the lignin from Soda-AQ process is more enriched in S-

lignin units than the lignin from kraft process. In addition, while minor amounts of β-O-4 alkyl-aryl ether structures are still present in the lignins from kraft process, they were completely absent in the lignin from Soda-AQ process. Therefore and as already observed in the analysis of the residual lignins, a comparison between the Soda-AQ and kraft processes indicates that the former seems to be more efficient to depolymerize the lignin than the latter.

Table 16. Main lignin characteristics (linkages per 100 aromatic units, and S/G ratio) of the lignins precipitated from the black liquors produced from G1xUGL after kraft and soda-AQ processes at kappa 20 and 15. The composition of the MWL isolated from G1xUGL is shown for comparison.

Linkages *(per 100 aromatic units)*		**Soda-AQ**		**Kraft**	
	MWL	**Kappa 20**	**Kappa 15**	**Kappa 20**	**Kappa 15**
β-O-4 alkyl-aryl ether	75.1	0.0	0.0	2.6	0.8
β-β resinols	13.4	2.8	4.8	6.2	6.5
β-5 phenylcoumarans	6.2	0.0	0.0	0.6	0.0
S/G ratio	2.8	8.9	12.0	6.2	6.0

4. Conclusions

- Soda-AQ and Kraft were the most adequate processes for producing pulp.
- The Soda-AQ process can potentially replace the kraft one for a high degree of wood delignification (kappa number 15), without significant yield penalty
- The soda-AQ pulp presented low xylan content in relation to kraft;
- More xylans were retained in kraft and soda-AQ pulps of kappa 20 in relation to kappa 15;
- Xylans from both kraft and soda-AQ pulps are less polydisperse than cellulose;
- The alkaline processes using oxygen (soda-AQ-O_2 and soda-O_2) are more suitable for biofuel production.
- The main linkages observed in the kraft and soda-AQ pulp lignins from G1xUGL eucalypt were β-O-4' aryl ether, β-β' resinol and β-5' phenylcoumaran structures;
- The presence of sulphur in kraft black liquor decreases its heating value in relation for soda-AQ black liquor.

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6. References

ALVES, E. F. (2005) Interação de fibras e elementos de vasos de plpa kraft de eucalipto com tintas de impressão offset. Dissertação de mestrado apresentada a Universidade Federal de Viçosa,

ASSOCIAÇÃO DOS FABRICANTES DE CELULOSE E PAPEL – BRACELPA. Disponível em: <http://www.bracelpa.com.br>. Access on: 22 April, 2013.

Barbosa, L. C. A., Maltha, C. R. A., and Cruz M. P. (2005) Chemical composition of lipophilic and polar extractives of Eucalyptus grandis, Science & Engineering Journal 15(2), 13-20.

BJÖRKMAN, A. (1956) Studies on finely divided wood. Part I. Extraction of lignin with neutral solvents. Sven. apperstidn., 13, 477−485.

BOSE, S. K.; OMORI S.; KANUNGO D. ;FRANCIS, R. C .; SHIN, N.H. (2009) Mechanistic Differences Between Kraft and Soda/AQ Pulping. Part 1: Results from Wood Chips and Pulps. Journal of Wood Chemistry and Technology, 29:3, 214-226,.

Cardoso, M.; Oliveira, E.D.; Passos, M.L. (2009): Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills. Fuel. Volume 88, p. 756-763.

CHANG, V. S.; NAGWANI, M.; KIM, C. -H.; Holtzapple, M. T. (2001) Oxidative lime pretreatment of high-lignin biomass. Appl. Biochem. Biotechnol., 94, 1−28.

CHEN, Y.; STEVENS, M. A.; ZHU, Y.; HOLMES, J.; XU, H. (2013) Understanding of alkaline pretreatment parameters for corn stover enzymatic saccharification. Biotechnol. Biofuels, 6, 8.

COLODETTE, J. L.; GOMIDE, J. L.; LONGUE JÚNIOR, D.; PEDRAZZI, C. (2007) Effect of pulp delignification degree on fiber line performance and bleaching effluent load. BioResources, v. 2, p. 223-234,.

CRUZ, MARILUZE P. et al . (2006) Caracterização química do "pitch" em indústria de celulose e papel de Eucalyptus. Quím. Nova, São Paulo, v. 29, n. 3, June.

DIAS, V. R. L.; CLÁUDIO-DA-SILVA, JR. E. (1991) “Pulp and paper properties as influence by wood density - same species and age of Eucalyptus.” In: INTERNATIONAL PAPER PHYSICS CONFERENCE, 1., Kailua Kona, Hawai.

EIRAS, K. M. M.; COLODETTE, J. L. (2001) Influência das condições de operação no estágio DHT na branqueabilidade e nas características físico-químicas da polpa e do filtrado. 34º Congresso Anual de Celulose e Papel, São Paulo.

EIRAS, K.M.; MOUNTEER, A.H.; VENTURIM, G.; COLODETTE, J.L.; GOMIDE, J.L. (2003) Efeito do conteúdo de lignina lixiviável e de ácidos hexenurônicos da polpa na performance da deslignificação com oxigênio. International Coloquium on Eucalyptus Pulp,. 01 pp. Acesso em 20/01/2012, disponível em: http://www.eucalyptus.com.br/icep01/katia_eiras2.pdf.

ENAYATI, A. A., HAMZEH, Y., MIRSHOKRAIEI, S. A., and Molaii, M. (2009) “Papermaking potential of canola stalks,” BioRes. 4(1), 245-256,.

FOELKEL, C. “As fibras dos eucaliptos e as qualidades requeridas na celulose kraft para a fabricação de papel.” Eucalyptus Online Book e Newsletter, (2007). 48p. Disponivel em: <http://www.eucalyptus.com.br/capitulos/PT03_fibras.pdf>

FOELKEL, C. E. B. (1997) Qualidade da madeira de eucalipto para atendimento das exigências do mercado de celulose e papel. In: Conferência IUFRO sobre silvicultura e melhoramento de eucalipto, , Salvador. Anais. Salvador: IUFRO, 1977, v.1, p.1.

FRANCIS, R. C., BOLTON, T. S., ABDOULMOUMINE, N., LAVRYKOVA, N., & Bose, S. K. (2009) Positive and negative aspects of soda/anthraquinone pulping of hardwoods. Bioresource technology, 99(17), 8453-8457.

FRANCIS, R. C., SHIN, S.-J., OMORI, S., AMIDON, T. E., and BLAIN, T. J. (2006) Soda pulping of hardwoods catalyzed by AQ and methyl substituted AQs, J. Wood Chem. Technol. 26(2), 141-152.

GOMES, F. J. B.; GOMES, A. F.; COLODETTE, J.L.; GOMES, C. M.; SOUZA, E.; MACEDO, A. M. L. (2008) Influência do teor e da relação S/G da ligninada madeira no desenpenho da polpaçao Kraft. O Papel (São Paulo), v. 12, p. 95-105.

GOMIDE, J. L. & OLIVEIRA, R. C. (1980) Eficiência da antraquinona na polpação alcalina do eucalipto. O Papel, São Paulo, 41:67-72.

GOMIDE, J. L.; COLODETTE, J. L.; OLIVEIRA, R. C.; SILVA, C. M. (2005) Caracterização tecnológica, para produção de celulose, da nova geração de clones de eucalyptus do Brasil. Revista Árvore, Viçosa-MG, v.29, n.1, p.129-137.

GOMIDE, J. L.; FANTUZZI, N. H.; REGAZZI, A. J. (2010) Análise de critérios de qualidade da madeira de eucalipto para produção de celulose kraft. Rev. Árvore, Viçosa, v.34, n.2, Apr. .

GUERRA, A.; FILPPONEN, I.; LUCIA, L.; SAQUING, C.; BAUMBERGER, S.; ARGYROPOULOS, D. S. (2006) Toward a better understanding of the lignin isolation process from wood. J. Agric. Food Chem., 54, 5939− 5947.

HAMZEH, YAHYA; ABYAZ, A.; NIARAKI, M.O-S. M.; and ABDULKHANI, A. (2009) Application of surfactants as pulping additives in soda pulping of bagasse. BioResources 4(4), 1267-1275.

KARLSSON, S., HOLMBOM, B., SPETZ, P., MUSTRANTA, A., & BUCHERT, J. (2001). Reactivity of “Trametes laccases with fatty and resin acids”. Applied microbiology and biotechnology, 55(3), 317-320.

KHAN, A. A., DE JONG, W., JANSENS, P. J., & SPLIETHOFF, H. (2009). Biomass combustion in fluidized bed boilers: Potential problems and remedies. Fuel processing technology, 90(1), 21-50.

KHRISTOVA, P.; KORDSACHIA, O.; PATT, R.; DAFAALLA, S. (2006) Alkaline pulping of some eucalypts from Sudan. Bioresource Technology vol. 97 issue 4 March,. p. 535-544.

KLEEN, M.; SJÖBERG, J; DAHLMAN, O. (2002) The effect of ECF and TCF bleaching on the chemical composition of soda-anthraquinone and kraft pulp surfaces. Nordic Pulp and Paper Research Journal Vol 17 no. 3.

LABID, J., TEJADO, A., GARCÍA, A., and JIMÉNEZ, L. (2008) Simulation of tagasaste pulping using soda-anthraquinone, Biores. Technol. 99(15), 7270-7277.

LEHTO, J.; ALÉN, R. (2013) Alkaline Pre-treatment of Hardwood Chips Prior to Delignification. J. Wood Chem. Technol, 33, 77−91.

LEITE, F. P.; GOMES, F. J. B.; SOUZA, E.; ROSADO, A. M.; AMARAL, L. S. (2010) Investigação do tempo de secagem no teor de umidade e nas características físicas e químicas da madeira para produção de celulose. 42o Congresso e Exposiçao Internacional de Celulose e Papel- ABTCP, São Paulo.

LINDSTRÖN, N., and FARDIM, P., (2012). Chemistry and surface chemistry of vessels in eucalyptus kraft pulps, O Papel 73(9), 65-72.

MOKFIENSKI, A., COLODETTE, J. L., GOMIDE, J. L., & CARVALHO, A. M. M. L. (2008) Relative importance of wood density and carbohydrate content on pulping yield and product quality. Ciência Florestal, Vol. 18, No. 3, pp. 401-413.

MORAIS, P. H. D. (2008) Influência da idade de clones de eucalipto na composição química e polpabilidade da madeira e na branqueabilidade e propriedades das polpas. Dissertação de mestrado apresentada a Universidade Federal de Viçosa,.

MOREIRA, E. (2006) Efeito da lixiviação ácida de cavacos de eucalipto no processo Kraft. Dissertação apresentada à Universidade federal de Viçosa.

NASCIMENTO, A. C.; MOREIRA, J. V. (2009) Influência de fibras recicladas nas propriedades físico-mecânicas do papel. Revista de Engenharia e Tecnologia, V. 1, No. 1, p. 63-71.

P. Khristova, O. Kordsachia, R. Patt , S. Dafaalla. (2006). Alkaline pulping of some eucalypts from Sudan. Bioresource Technology 97 (2006) 535–544.

PFROMM, P. H. (1997). Low effluent processing in the pulp and paper industry: Electrodialysis for continuous selective chloride removal. Separation science and technology, 32(18), 2913-2926.

PRINSEN, P.; GUTIÉRREZ, A.; RENCORET, J.; NIETO, L.; JIMÉNEZ- BARBERO, J.; BURNET, A.; PETIT-CONIL, M.; COLODETTE, J. L.; MARTÍNEZ, A. T.; DEL RÍO, J. C. (2012) Morphological characteristics and composition of lipophilic extractives and lignin in Brazilian woods from different eucalypt hybrids. Ind. Crop. Prod. ,36, 572−583.

RABELO, M. S.. (2006) Tecnologias avançadas para o pré-branqueamento de polpa kraft de eucalipto. Teses de doutorado apresentada a Universidade Federal de Viçosa.

RENCORET, J.; MARQUES, G.; GUTIÉRREZ, A.; NIETO, L.; SANTOS, J. I.; JIMÉNEZ-BARBERO, J.; MARTÍNEZ, A. T.; DEL RÍO, J. C. HSQC-NMR analysis of lignin in woody (Eucalyptus globulus and Picea abies) and non-woody (Agave sisalana) ball-milled plant materials at the gel state. (2009) Holzforschung, 63, 691−698.

ROVIO, S.; KUITUNEN, S.; OHRA-AHO, T.; ALAKURTTI, S.; KALLIOLA, A.; TAMMINEN, T. (2011) Lignin oxidation mechanisms under oxygen delignification conditions. Part 2: Advanced methods for the detailed characterization of lignin oxidation mechanisms. Holzforschung, 65, 575−585.

SCANDINAVIAN PULP, PAPER AND BOARD TESTING COMMITTEE. (1993) Scan Test Methods,.

SCOTT, E. W.; ABBOTT, J. C. (1995) Properties of paper – an introduction. Atlanta: TAPPI Press,. 136p.

SETH, R. S.; Page, D.H.. (1988) Fiber properties and tearing resistance. TAPPI Journal p. 103-107, February.

SETH, R. S. (2003) The measurement and significance of fines. Pulp & Paper Canada. p. 104:2, v. 47.

SILVA JR., F. G.; DO VALLE, C. F.; MUNER, J. C. G. (1996) Programa de qualidade da madeira da Votorantim Celulose e Papel – VCP". O Papel, p. 35-43.

Solar, R.; Kacik, F.; Melcer, I. (1987) Simple semimicro method for the Determination of O-Acetyl Groups in Wood and Related Materials. Nordic Pulp and Paper Research Journal, n. 4, p. 139-141.

Technical association of the pulp and paper industry (2000). TAPPI standard methods. Atlanta: TAPPI.

VAKILAINEN, E. (2000) "Chemical Recovery". Papermaking Science and Technology 6b. Published in Cooperation with the Finish paper Engineering's Association and TAPPI.

VISHTAL, A. and KRASLAWSKI, A. **(**2011) Challenges in industrial pplications of technical lignins. *BioResources* 6(3), 3547-3568.

VUORINEN, T.; TELEMAN, A.; FAGERSTRÖM, P.; BUCHERT, J.; TENKANEN, M. (1996) Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. In: INTERNATIONAL PULP BLEACHING CONFERENCE, Washington. Proceedings… Washington, p. 43-51.

WALLIS, A. F. A.; WEARNE, R. H.; WRIGHT, P. J. (1996) Chemical analysis of polysaccharides in plantation eucalypt woods and pulps. Appita Journal, v.49, n.4, p.258-262.

WERH, T. R.; Barrichelo, L. E. G. (1993)"Cozimento Kraft com madeiras de Eucalyptus grandis de diferentes densidades básicas e dimensões de cavacos". O Papel, V.54, n.5, p. 33-41,

WESSEL, R. A.; TRAN, H.; MAHINPEY, N.; KUHN, D. (2002) Effect of particle composition on carryover deposition in recovery boilers. TAPPI Fall Conference & Trade Fair.

ZONG LAI, Y. (1999) The influence of alkaline pulping conditions on the efficiency of oxygen delignification. Acesso em 22/01/2012. Disponível em: http://www.TAPPI.org/Downloads/unsorted.

CAPITULO 4

EVALUATION OF BRAZILIAN NEW GENERATION OF EUCALYPT CLONE FOR BIOETHANOL PRODUCTION

Abstract

Wood structure is rather complex, thus requiring severe deconstruction treatments in order to make available its carbohydrate fraction for biofuel production. Partial wood deconstruction has been practiced for a long time by the pulp and paper industry in order to produce fibers. However, deconstruction processes targeting production of biofuels require fiber disassembling as well, and that is more challengeable. In this study, the soda-AQ and soda-O_2 deconstruction processes were evaluated for the hybrid clone of *Eucalyptus grandis* x [*Eucalyptus urophylla* x *Eucalyptus globulus*] (G1xUGL) aiming at bioethanol production. In order to achieve the optimum point for stopping the deconstruction process and proceeding with the saccharification, various kappa numbers were evaluated after the alkaline deconstruction. The results of this study showed that the selected wood clone productivity and physical-chemical characteristics are suitable for bioethanol production. The soda-O_2 process proved more suitable for bioethanol production than soda-AQ process. For the soda-AQ processes, the optimum hydrolysability during saccharification was achieved by the pulp delignified at kappa number 15, whereas for the soda-O_2 process, this optimum value occurred at kappa number 35-50. Levels of sugar release in the range of 64 and 73% were achieved with the optimized soda-AQ and soda-O_2 process, respectively. These levels of sugar release are high and warrant efficient production of bioethanol with yields in the range of 326.4 and 372.3L/t of dry wood, respectively, considering a fermentation yield of 0.51 g of ethanol per g of glucose.

1. Introduction

It is anticipated that large volumes of biomass will be used for producing biofuels along with valuable co-products in the near future. Wood and forest residues will certainly play a role in the biofuel and bio products industry, particularly if they are processed integrated with pulp production. This integration could be loosely defined as the pulp mill biorefinery (DEMIRBAS, 2008; BALAT, 2009; DEMIRBAS, 2009; BÖRJESSON, 2009; GUPTA et. al., 2013). Biorefinery is a new term that is related to two main subjects, value-added bioproducts (chemical building blocks, materials,

pulps), and bioenergy (biofuels, power, and heat) from biomass, considering sustainability assessment and life cycle (ARESTA et al. 2012).

Eucalypt wood can be highlighted as one of the main raw materials for biorefinery application in South America due to its high forest productivity and relative low wood cost. In order to use wood for bioethanol production, for example, it is necessary a pretreatment to induce cell wall deconstruction that will be followed by enzymatic saccharification, fermentation and distillation. The most accepted pretreatments for wood deconstruction aiming at bioethanol are the steam explosion and auto-hydrolysis (hydrothermal), which occur under acidic conditions. Despite the many advantages of these acidic treatments such as low cost, simplicity, no chemicals to recover, etc, they both suffer from the problem of creating fermentation inhibitors such as furfural, hidroxymethyl furfural, formic acid, acetic acid and levulinic acid, which greatly reduce the ethanol yields (SANTOS et al., 2012). On the other hand, alkaline deconstruction pretreatments usually do not produce inhibitors and, potentially, result in much higher ethanol yields. A number of alkaline pretreatments have been studied, with the most successful being the ones based on the use of ammonia solution (FOSTER et al, 2001), and ammonia hydroxide (PRIOR et al., 2008). The alkaline pretreatment is believed to cleave hydrolysable linkages in lignin and glycosidic bonds of polysaccharides, which causes a reduction in the degree of polymerization and crystallinity, swelling of the fibers, as well as disruption of the lignin structure (CHEN, 2013). Additionally, ammonia has the effect of decrystallizing the highly ordered cellulose strands found in lignocellulosic materials, allowing the cellulose to be more easily degraded during enzyme hydrolysis (FOSTER et al., 2001).

Most of the pulp mills use alkaline chemistry for wood deconstruction, with the Kraft process being dominant. The presence of sulfur compounds in kraft black liquor is a major hindrance to the successful use of the dissolved lignin and other wood components for biorefinery purposes (FRANCIS, et al., 2009; CARDOSO et al., 2009). For example, the regeneration of Na_2S from kraft black liquor would be tedious for all gasification processes. Some of the sulfur in the BL will be converted to H_2S in the fuel gases. This H_2S has to be selectively removed by adsorption onto a solid sorbent or absorption into a solvent. The H_2S would have to be desorbed from

the solid sorbent and the surface reconditioned for another sulfidation cycle. If the H_2S is absorbed into a solvent then desorption into a non-reactive gas followed by re-absorption into NaOH or Na_2CO_3 would be required (FRANCIS et. al., 2009). The technical feasibility of black liquor gasification would improve significantly if a non-sulfur pulping process were to replace kraft (FRANCIS et al., 2006; FRANCIS et al., 2009).

Therefore, sulfur free processes, such as soda are more indicated for biomass deconstruction aiming at biorefinery applications. On the other hand, the soda process presents as disadvantage its low yield (FRANCIS et al., 2009; PIERRE et al., 2013). In order to make the soda process attractive the use of additives for improving the yield is necessary (PIERRE et al., 2013). The use of anthraquinone has been proposed by many authors (FRANCIS et. al., 2006; FRANCIS et. al., 2009; BOSE et al., 2009; HAMZEH et al., 2009; ROVIO et al., 2011; LEHTO et. al., 2013; PIERRE et. al, 2013; CHEN et al., 2013). It has been shown that AQ can bring the soda process to the same yield efficiency as compared to kraft (PIERRE et al., 2013).

The soda processes with or without additives are interesting alternatives to retrofit into existing kraft pulp mills giving their technological similarities with the kraft process. Thus, the conversion of kraft mills into biorefineries with production of bioethanol and other bio products will be best served, if the kraft technology is converted into the soda technology in order to avoid sulfur handling issues (FRANCIS et al., 2009).

Additionally, alternative processes such as soda-AQ-O_2 and soda-O_2 can also be used when it is desired to obtain other products besides pulp. . The oxygen addition in the pulping processes greatly improves the delignification rate, which is very suitable for pulping processes (ROVIO et. al., 2011). On the other hand, the oxidative conditions affect the fiber ultrastructure in a deconstructive manner (CHANG et al., 2001; ROVIO et. al., 2011). Since these processes have more drastic consequence for the mechanical fiber properties, they can be considered promising alternatives for replacing the kraft and soda-AQ as pretreatment for biorefinery processes. In contrast to paper grade pulps, when aiming some biorefinery applications such as bioethanol, the pulp strength is not important. In these cases, the deconstruction of

the lignocellulosic matrix is aimed at the removal and/or modifications of the lignin in order to improve substrate digestibility (CHEN et al, 2013).

This study focused on the development of the soda-AQ and soda-O_2 processes for deconstruction of eucalypt wood aiming at the production of bioethanol.

2. Material and Methods

Materials

For this study, one eucalypt wood clone sample in commercial harvesting age was investigated, provided by *GENOLYTPUS* project, located in Minas Gerais State – Brazil. The eucalypt clone used is called G1XUGL, it is a triple crossing hybrid of *Eucalyptus grandis* x (*Eucalyptus urophylla* x *Eucalyptus globulus*).

Methods

The sampling for physical, chemical and morphological analyses was done using the so-called quartering technique which is trivial for those skilled in the art. Chips were used to measure chips bulk and basic density according to SCAN CN-49:92 and SCAN CM-46:92 standard procedures, respectively.

Biomass productivity

The biomass productivity was calculated using the medium annual increase (MAI) and basic density, by the following equation:

$$\text{Biomass productivity } (\text{ton/ha/yr}) = \text{MAI } (\text{m}^3/\text{ha/yr}) \times \text{basic density } (\text{ton/m}^3)$$

Samples preparation for chemical analysis

For the chemical analyses, about 1 kg of each biomass were sampled and ground in a Wiley type mill to produce sawdust of variable size. This sawdust was screened according to Tappi Standard T257-cm85. The sawdust that passed the 40 mesh screen and was retained in the 60 mesh screen was selected for the chemical analyses. The sawdust was air dried and conditioned in a temperature and humidity controlled room (23±1˚C, 50±2% RH) until an equilibrium moisture was achieved (~10%). This sawdust (raw sawdust) was used for the chemical analyses. The

analyses of ash, silica, chloride, iron, copper, manganese, potassium, calcium and magnesium were carried out directly on the raw sawdust, according to the Standard Methods for the Examination of Water and Wastewater (2000), except for chloride, which was determined according to Tappi T256 cm-97 standard procedure. The biomass extractives contents in acetone, ethanol/toluene(1:2) and ethanol/toluene(1:2) →ethanol →hot water solvent series was also determined in the raw sawdust using the TAPPI T280 pm-99, T204 cm-97 and TAPPI T264 cm-97 standard procedures, respectively. In order to determine biomass main cell wall components, a 200g sample of extractives freed was prepared using TAPPI T264 cm-97 standard procedure. This extracted sample (extractive free sawdust) was conditioned in a temperature and humidity controlled room (23±1˚C, 50±2% RH) until an equilibrium moisture was achieved (~10%). The contents of uronic acids, acetyl groups and sugars (glucans, mannans, galactans, xylans and arabinans) in the extractive free biomass were determined according to Scott (1979), Solar et al. (1987) and Wallis et al. (1996). The acid insoluble lignin, acid soluble lignin and lignin syringyl/guaiacyl (S/G) ratio were determined according to TAPPI T 222 om-97 standard procedure, Goldschmid (1971) and Lin & Dence (1992), respectively.

Pulping: processes and conditions

Four pulping processes were used to convert the eucalypt clones into pulps, namely: Soda-AQ and Soda-O_2. For analyzing the deconstruction processes were investigated three level of kappa: 15, 35, and 50 The cooking trials of the eucalypt clones were done in a M&K digester, with 2 individual reactors of 10 liters each, equipped with a forced liquor circulation system and electrically heated with temperature and pressure control. The digester is coupled to a cooling system (Coil System with residual liquor, involved with water at room temperature), to ensure the cooling of the liquor after the cooking simulation. The experimental conditions used in the cooking process were established based on technical knowledge of the Pulp and Paper Laboratory of the Federal University of Viçosa - Brazil. With the exception of the alkaline charge, the other cooking conditions were kept constant for all cooking and are showed in the Table 1. Eight cooking experiments were performed for each sample and process, using different active alkali charge to establish the delignification curves.

Table 1. Conditions for pulping processes.

Parameter	***Soda-AQ***	***Soda-O_2***
Biomass, kg	1	1
Active alkali as NaOH, % on o.d. chips*	Variable	Variable
Anthraquinone charge, % on o.d. chips	0.05	-
Oxygen charge, % on wood chips**	-	6
Liquor to chips ratio, L/kg	4/1	4/1
Maximum temperature, ˚C	170	170
Time to maximum temperature, min.	90	90
Time at maximum temperature, min.	50	50
* The active alkali charge was investigated in various levels aiming to reach kappa number 15, 35, and 50. ** In the Soda-O_2 process the oxygen dosage (6% on chip o.d. weight) was split into three parts and applied after 50 minutes, 70 minutes and 110 minutes reaction time from the beginning of cooking, thereby ensuring that the pressure limit (20kgf/cm²) of the digester was not exceeded.		

Enzymatic hydrolysis and fermentation

The effect of pretreatment process on enzymatic hydrolysis was screened at constant conditions. The washed pulp samples were suspended into 100 mM sodium citrate buffer at pH 5, 45˚C temperature and 1% consistency. Enzymatic hydrolysis was started by adding commercial Novozyme's cellulase mixture (Celluclast 1.5 FPU) at the dosage of 10 FPU/g dry weight and β-glucosidase (Novozymes 188) at the dosage of 500 nkat/g dry weight. The suspensions were incubated at 45ºC with magnetic stirring for 72 hours, and the content of released sugars was followed. The 3,5-dinitrosalicylic acid (DNS) assay was used for the determination of reducing sugars. The DNS method employing glucose as the standard; DNS reacts with free carbonyl group of the reducing sugars under alkaline condition, forming 3-amino-5-nitrosalicylic acid, an aromatic compound with maximum absorption at 540 nm, allowing a quantitative spectrophotometer measurement of the amount of reducing sugars present in the sample.

Fermentation was carried out anaerobically in Erlenmeyer flask (25 ml) in an incubator at 10% consistency. The same relative enzyme loading was used as in hydrolysis experiments (10 FPU/g Celluclast 1.5L and 500 nkat/g Novozyme 188). After 6h prehydrolysis at 45˚C, the yeast (Red Star, Fermentis; a *Saccharomyces serevisiae* strain) was added with an OD_{600} of 3.5 (being ~1g cell dry weight/l) to the flask to start the simultaneous saccharification and fermentation (SSF), and the

temperature was lowered to 30°C with slow shaking (100 rpm). The ethanol yield was measured by High Performance Liquid Chromatographic (HPLC), being collected approximately 1 ml of each sample, centrifuged and the supernatant removed for determining of the ethanol production. The HPLC was coupled to a refractive index detector Shimadzu (RID-10A) equipped with a BIO-RAD Aminex HPX-87H (300 x 7.8 mm) analytical column and 134 kgf of pressure. The samples were analyzed under the following conditions: column temperature of 60 °C, 5 mmol/L^{-1} of sulfuric acid as eluent, flow rate of 0.6 mL/min^{-1}, and the sample injected volume of 20 µl, with a retention time of 30 minutes.

3. Results and Discussion

3.1 Biomass characterization

Concerning wood feasibility as raw material for bioethanol production two very important factors are moisture content and density since they affect harvesting, transportation and utilization costs. The productivity and physical-chemical characteristics of the eucalypt clone used in this study are presented in Table 2. The productivity of the G1xUGL eucalypt clone is within of the average MAI obtained in commercial plantations in the Brazilian Territory (≈40-60 m^3/ha/yr) (BRACELPA, 2013). Regarding moisture and density, these values are considered satisfactory for pulp production (DIAS and CLÁUDIO-DA-SILVA, 1991; WEHR-BARRICHELO,1993; SILVA JR. et al., 1996, GOMIDE et al., 2005).

Table 2. Forestry and physical characteristics of the eucalypt clone evaluated.

Moisture, %	**Average Annual Increment, m^3/ha/yr***	**Biomass basic density, kg/m^3**	**Biomass Productivity, bone dry ton/ha/yr**	**Chip bulk density, kg/m^3**
53	46.2	500	23.1	202

The raw material minerals are detrimental for their industrial utilization, since they cause corrosion and deposits on equipment, reduce biomass heating value and decrease mill throughput (HAZLEWOOD et al., 2006). In Table 4 the results of biomass mineral content are presented. In general the amounts of inorganics present

in the eucalypt clone were very low and quite acceptable for most applications (FOELKEL, 1977; EVTUGUIN et al., 2003; MOREIRA, 2006).

Table 4. Ash, metal, and chloride content of the eucalypt clones evaluated.

Inorganics, mg/kg biomass							
Ash	Cu	Fe	Ca	Mn	Mg	K	Cl^-
1950.0	0.5	13.1	452.0	14.0	112.0	188.0	629.0

Concerning biomass organic chemical composition, it was observed a acceptable carbohydrate composition for bioethanol production . The extractives are quite troublesome since they cause many difficulties in operating the industrial facilities, causing unexpected lost time in the operation for cleaning of equipment and instruments due to their stickiness and tackiness (HAZLEWOOD et al., 2006). For the biorefinery, it was observed a high but acceptable total extractive content (4.9%) (RESQUIM et. al., 2006). It was observed also an acceptable carbohydrate composition (EVTUGUIN et al., 2003; RESQUIM et. al., 2006).

Another interesting relation in its chemical composition was the S/G ratio (2.9), which could be considered slightly above the average when compared to most common Eucalypt planted for pulp and bioethanol production, e.g. *Eucalyptus grandis* which presents in average S/G ratio of 2.0 (BARBOSA et. al. 2008; NUNES et al., 2010). This result can be explained as a consequence of possessed *Eucalyptus globulus* in its genotype, which is of interest for high S/G ratio (RENCORET et al., 2007). A high S/G ratio is desired since it increases the pulpability of the wood (GOMES, 2008).

Table 5. Chemical composition of the eucalypt clone.

Sugar Composition, % on extractive free wood weight	Glucan	43.9
	Xylans	13
	Galactans	0.8
	Mannans	0.9
	Arabinans	0.2
Acid Soluble Lignin % on extractive free wood		4.7
Total lignin,%		28.9
Lignin S/G ratio		2.9
Acetyl Group, %		2.7
Uronic Acid Group, %		3.8
Acetone Extractives, %		2.5
Ethanol/Toluene (1:2) Extractives, %		2.5
Total Extractives, %		4.9

3.2 Pulping processes

The evaluation of deconstruction technologies aimed at ethanol production differs somewhat from that when aiming at pulp production. While producing a high yield is desirable in both cases, the maintenance of fiber integrity is not interesting for bioethanol production. The subsequent steps in the ethanol production (saccharification and fermentation) are facilitated when fiber integrity is decreased. However, very aggressive treatments tend to destroy the sugars present in the wood resulting in very low product yield. Therefore, a balance between process yield and fiber integrity must be found. In this study the deconstruction was terminated at variable kappa numbers in order to find the best compromise between yield and the efficiency of the subsequent treatment (saccharification and fermentation) in the ethanol production.

The cooking results for the two processes evaluated are presented in Table 6. It is observed that the soda-O_2 process consumes large quantities of alkali when delignification terminates at low kappa number. This result is explained by the oxidation of lignin by oxygen resulting in ring opening and formation of carboxylic acids that consume the alkali (ASGARIS and ARGYROPULOS, 1999). Regarding the screened yield and reject content, the increase in kappa number led to a decrease in pulp screened yield and increase in the reject content due to fiber release difficulties.

It is possible to observe by the pulp viscosities that the soda-O_2 process showed higher fiber damage when compared to soda-AQ, which were caused by two facts: (1) the AQ was used as a pulping additive in the soda-AQ process to decrease the carbohydrate degradation (KHRISTOVA et al., 2006); (2) the oxidative conditions caused by the oxygen addition, which affect the fiber ultrastructure (CHANG et al., 2001; ROVIO et. al., 2011). Concerning the pulp brightness, it was possible to observe a trend of highest values for the soda-O_2 process, indicating that the lignin was modified in this process and probably is less condensed than in soda-AQ process (AHVAZI et. al., 1998).

Concerning the black liquor properties, as expected the residual alkaline increased with increasing of delignification degree, it can be explained due to a high alkaline demand for achieving the aimed kappa numbers. As consequence, the black liquor inorganic fraction followed the same trend, increased with increasing of the alkaline charge, and the black liquor organic fraction followed the opposite direction. Between the two evaluated processes, the soda-O_2 showed the highest black liquor solids, and inorganic content, mainly due to a higher alkaline charge required by this process. However, presented the lowest residual alkali content, reinforcing the theory of carboxylic acids during the alkaline processes using oxygen as additive, which is responsible for the alkaline consumption (ASGARIS and AGYROPOLUS, 1999).

The goal biofuels production such as ethanol, carbohydrate preservation during the pulping process is desirable, since it will be converted in to fermentable sugars. In this way the highest viscosity values and lowest solid organic content in the black liquor obtained to Soda–AQ are preferable, indicating less carbohydrate degradation; which can be explained due to selectivity effect of the AQ (KHRISTOVA et al., 2006), and low alkaline charge applied in the Soda-AQ process.

Table 6. Pulping results of G1XUGL by Soda-AQ and Soda-O_2 processes aiming kappa number 15, 30, and 50.

Parameter	Soda-AQ			Soda-O_2		
Alkaline Charge, %	31.0	16.2	15.1	40.0	28.5	25.0
Kappa Number	15.2	35	51.5	15.5	39.3	54.4
Yield Screened, %	48.8	47.0	40.0	50.1	46.5	40.1
Reject Content, %	0.1	7.8	20.0	0.1	4.9	18.6
Viscosity, dm^3/kg	748	1130	1148	827	995	1068
Brightness, % ISO	34.0	20.9	18.1	35.1	27.0	22.5
Black Liquor Residual AA, g/L	18	6.8	5.9	20.1	5.3	2.1
Black Liquor solids, %	10.7	10.1	9.3	13	11.9	10.8
Black Liquor organics, %	50.3	59	60.1	43.3	47.9	49.8
Black Liquor inorganics, %	49.7	41.0	39.9	56.7	52.1	50.2

3.3 Comparison of pretreatment methods for bioethanol production

The pulps produced at kappa number 15, 35, and 50 by Soda-O_2 and Soda-AQ processes were tested regarding their potential for bioethanol production. Concerning the reducing sugar release, the degree of conversion rate was increased with increase in duration of treatment. In general, the highest reduced sugar release was obtained for at 72 hours of reaction for all samples, except for the pulp soda-AQ at kappa number 15, which presented its higher hydrolysability at 68 hours of reaction.

Between the processes, the best hydrolysability was achieved by the pulp soda-AQ delignified at kappa number 15, achieving 64% of the reducing sugar released. On the other hand, for the soda-O_2 process, the kappa number levels of 35-50 provided the best range of hydrolysable pulp for fermentation, achieving 73% of the reducing sugar released. Considering the theoretical yield of 0.51 g of ethanol per g of glucose (SANTOS et al., 2012), these levels of sugar release are high and warrant efficient production of bioethanol with yields in the range of 326.4 and 372.3 L/ton of dry wood for soda-AQ and soda-O_2, respectively.

In this way, the Soda-O_2 pretreatment was more suitable for bioethanol production. The Soda-O_2 treatment probably opens up the fiber ultrastructure better at the same

lignin content, and even at high kappa number levels; also the rejects can be hydrolyzed more efficiently. It can be explained by oxygen action, which works to enhance carbohydrate and cellulose degradation (RAY and KARANDHIKAR, 2009), improving the enzymatic accessibility.

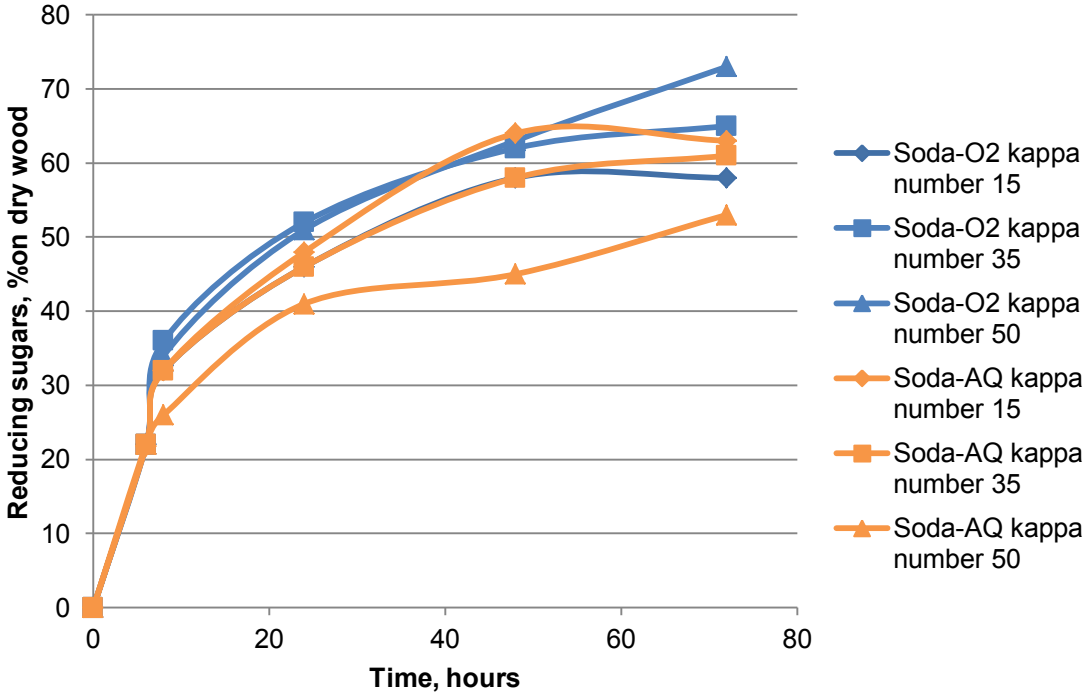

Figure 1. Effect of alkaline pretreatments (Soda-O_2, Soda-AQ) on enzymatic hydrolysis. The results are corrected with pulp yields and shown as percentage on original wood raw material.

The bioethanol yields of the pulps were first determined using the standard hydrolysis protocol as described in the methodology. In Figure 2, it is possible to observe the ethanol yield; the soda-O_2 pulp at kappa 15 (240.8 liters per ton of dry wood) and kappa 35 (228.7 liters per ton of dry wood) gave the highest yields on wood. Based on the saccharification tests, soda-O_2 pulp at kappa number 15 showed the best of the alkaline pulps when aiming ethanol production.

It is obvious that the soda-AQ process would require low kappa number (15) in order to produce a very good saccharification and fermentations yields, whereas the soda-O_2 process is efficient even at kappa 50. Therefore, the soda-O_2 technology is more appropriate for bioethanol production than the soda-AQ. This trend is exactly the

opposite of that found in Chapter 3 when deconstructing the wood for pulp production.

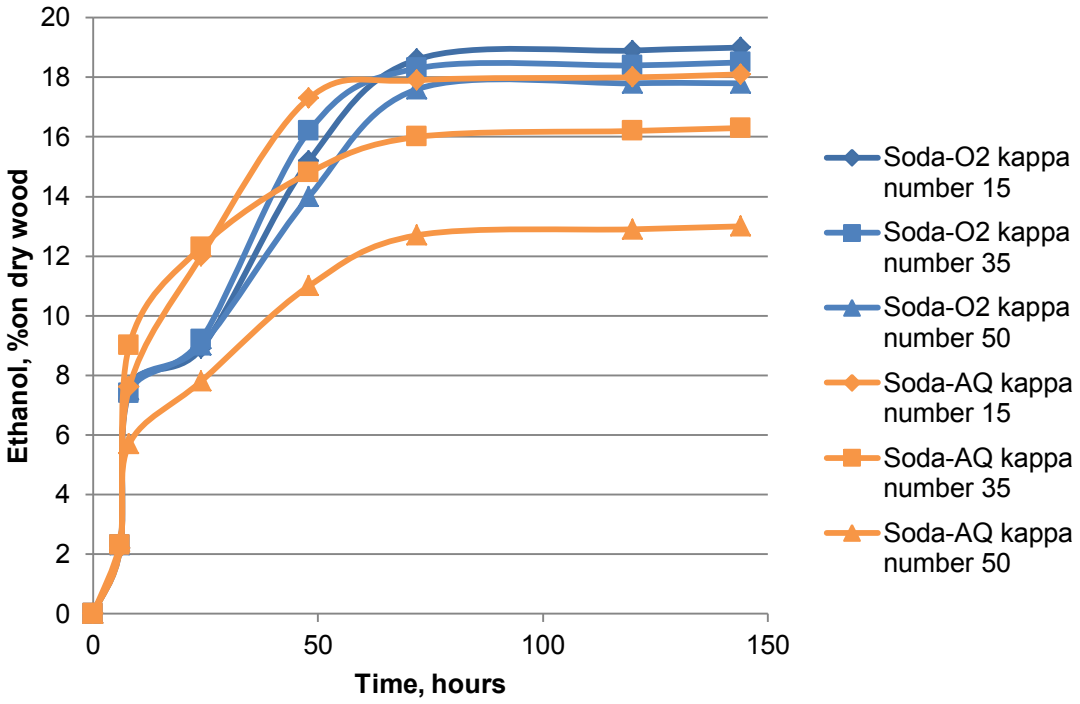

Figure 2. Comparison of the Soda-O_2 and Soda-AQ processes at various kappa number levels as pretreatments for the production of bioethanol using G1xUGL hybrid as raw material: ethanol yield on dry wood.

4. Conclusions

- The Soda-O_2 is more suitable for bioethanol production than the Soda-AQ process;
- Adequate hydrolysability was achieved at kappa 15 for the soda-AQ process and at kappa 35-50 for the soda-O_2 process;
- The levels of sugar release were high and warrant theoretical production of bioethanol with yields in the range of 326.4 and 372.3 L/ton of dry wood for soda-AQ and soda-O_2 processes, respectively.

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6. References

AHVAZI, B. C.; PAGEAU, G.; and ARGYROPOULOS, D S.. (1998) On the formation of diphenylmethane structures in lignin under kraft, MCC7, and soda pulping conditions. Can. J. Chem. 76: 506.512,.

ARESTA, M.; DIBENEDETTO, A. AND DUMEIGNIL, F.. (2012) Biorefinery: from biomass to chemicals and fuels. Green Process Synth 2013; 2: 87–88.
ASGARI, F. and ARGYROPOULOS, D.S.. Fundamentals of oxygen delignification. Part II. Functional group formation/elimination inresidual kraft lignina. Can. J. Chem. 76: 1606–1615 1998.

BALAT M. (2009) New biofuel production technologies. Energy Educ Sci Technol Part A; 22:147–61.

BARBOSA, L. C. A., MALTHA, C. R. A., and CRUZ M. P., (2005). Chemical composition of lipophilic and polar extractives of *Eucalyptus grandis*, Science & Engineering Journal 15(2), 13-20.

BARBOSA, LUIZ C. A., MALTHA, CÉLIA R. A., SILVA, VANESSA LOPES, & COLODETTE, JORGE LUIZ. (2008). Determination of the siringyl/guaiacyl ratio in eucalyptus wood by pyrolysis-gas chromatography/mass spectrometry (PY - GC/MS). Química Nova, 31(8), 2035-2041.

BÖRJESSON P. (2009) Good or bad bioethanol from a greenhouse gas perspective – what determines this? Appl Energy;86:589–94.

BOSE, S. K.; OMORI S.; KANUNGO D. ;FRANCIS, R. C .; SHIN, N.H. (2009) Mechanistic Differences Between Kraft and Soda/AQ Pulping. Part 1: Results from Wood Chips and Pulps. Journal of Wood Chemistry and Technology, 29:3, 214-226,.

BRACELPA, (2013). Brazilian Pulp and Paper Association, (http://www.bracelpa.com.br). Access on: 22 April, 2013.
CHANG, V. S.; NAGWANI, M.; KIM, C. -H.; Holtzapple, M. T. Oxidative lime pretreatment of high-lignin biomass. Appl. Biochem. Biotechnol. 2001, 94, 1−28.

CHEN, Y.; STEVENS, M. A.; ZHU, Y.; HOLMES, J.; XU, H. (2013) Understanding of alkaline pretreatment parameters for corn stover enzymatic saccharification. Biotechnol. Biofuels, 6, 8.

DEMIRBAS A. (2008) Recent progress in biorenewable feedstocks. Energy Educ Sci Technol;22:69–95.

DEMIRBAS T. (2009) Overview of bioethanol from biorenewable feedstocks: technology, economics, policy and impacts. Energy Educ Sci Technol Part A ;22:163–77.

EVTUGUIN D. V. AND NETO C. P. (2003). Recent advances in eucalyptus wood chemistry: structural features through the prism of technological response.
FOELKEL, C. E. B., 1977. Qualidade da madeira de eucalipto para atendimento das exigências do mercado de celulose e papel. In: Conferência IUFRO sobre silvicultura e melhoramento de eucalipto, 1997, Salvador. Anais... Salvador: IUFRO, v.1, p.1.

FOSTER B.L.; DALE B.E.; DORAN-PETERSON J.B.: (2001) Enzymatic hydrolysis of ammonia-treated sugar beet pulp. Appl Biochem Biotechnol, 91/93:269-82

FRANCIS, R. C., BOLTON, T. S., Abdoulmoumine, N., Lavrykova, N., and Bose S. K. (2009) Positive and negative aspects of soda/anthraquinone pulping of hardwoods, *Biores. Technol.* 99(17), 8453-8457,.

FRANCIS, R. C., SHIN, S.-J., OMORI, S., AMIDON, T. E., and BLAIN, T. J. (2006) Soda pulping of hardwoods catalyzed by AQ and methyl substituted AQs, *J. Wood Chem. Technol.* 26(2), 141-152.

GOMES, F. J. B., GOMES, A. F., COLODETTE, J. L., GOMIDE, J. L., CARVALHO, A. M. M. L., TRUGILHO, P. F., GOMES, C. M., and ROSADO, A. M., (2008). Influence of content and S/G relation of the wood lignin on kraft pulping performance, O Papel 12, 95-105.

GOMIDE, J. L. & OLIVEIRA, R. C. (1980) Eficiência da antraquinona na polpação alcalina do eucalipto. O Papel, São Paulo, 41:67-72,.

GOMIDE, J. L., COLODETTE, J. L., OLIVEIRA, R. C., and SILVA, C. M., (2005). Technological characterization of the new generation of Eucalyptus clones in brazil for kraft pulp production, Revista Árvore (Impresso) 29(1), 129-137.

GOMIDE, J. L., FANTUZZI, N. H., and REGAZZI, A. J., (2010). Analysis of wood quality criteria of eucalyptus wood for kraft pulp production, Revista Árvore 34(2), 339-344.

GUPTA; K. V.; TUOHY, M G. (2013) Biofuel Technologies: Recent Developments. Book published by Springer, XVII, 534 p.

HAMZEH, YAHYA; ABYAZ, A.; NIARAKI, M.O-S. M.; and ABDULKHANI, A.. (2009) Application of surfactants as pulping additives in soda pulping of bagasse. BioResources 4(4), 1267-1275,

HAZLEWOOD, P. E.; SINGH, P. M.; HSIH, J. S. (2006) Pulp mill corrosion and wood chip extractives. Engineering, Pulping, & Environmental Conference -TAPPI
HSU TA, In Handbook on bioethanol, production and utilization: Pretreatment of biomass. Washington DC: Taylor and Francis: Edited by Wyman, CE,179-212, 1996.

KHRISTOVA, P.; KORDSACHIA, O.; PATT, R.; DAFAALLA, S. (2006) Alkaline pulping of some eucalypts from Sudan. Bioresource Technology vol. 97 issue 4 March,. p. 535-544.

LEHTO, J.; ALÉN, R. (2013) Alkaline Pre-treatment of Hardwood Chips Prior to Delignification. J. Wood Chem. Technol, 33, 77−91,.

LEITE, F. P., GOMES, F. J. B., SOUZA, E., ROSADO, A. M., and AMARAL, L. S., (2010). Investigation of drying time in the humidity content and on physical and chemical characteristics of wood for the production of pulp, 42nd Pulp and Paper International Congress and Exhibition - ABTCP, São Paulo, Brazil.

LIN, S. Y.; DENCE, C. W. (1992) Methods in lignin chemistry. Berlin: Springer-Verlag,. 578p.

MOREIRA, E. (2006). Efeito da lixiviação ácida de cavacos de eucalipto no processo Kraft. Dissertação apresentada à Universidade federal de Viçosa.

NUNES, CLEITON A. ; LIMA, CLÁUDIO F. ; BARBOSA, LUIZ C.A. ; COLODETTE, JORGE LUIZ ; GOUVEIA, A.F.G. ; SILVÉRIO, FLAVIANO O. (2010) Determination of Eucalyptus spp lignin S/G ratio: A comparison between methods. Bioresource Technology, v. 101, p. 4056-4061,.

PRIOR BA, DAY DF: (2008) Hydrolysis of ammonia-pretreated sugar cane bagasse with cellulase, beta-glucosidase, and hemicellulase preparations. Appl Biochem Biotechnol, 146:151-64.

RAY, A. K. and KARANDHIKAR, G. (2009) Delignification of bagasse by soda-oxygen process. Engineering, Pulping, Environmental Conference. Proceedings of a meeting held 11-14 October 2009, Memphis, Tennessee,USA.

RENCORET, J.; GUTIERREZ, A; and DEL RIO, J. C. (2007) Lipid and lignin composition of woods from different eucalypt species. Holzforschung, Vol. 61, pp. 165–174.

RESQUIN, F; BARRICHELO L E G, JÚNIOR F G S, BRITO, J. O. E SANSIGOLO, C. A.. (2006) Wood quality for kraft pulping of Eucalyptus globulus origins planted in Uruguay. Scientia Florestali n. 72, p. 57-66, December 2006.

ROVIO, S.; KUITUNEN, S.; OHRA-AHO, T.; ALAKURTTI, S.; KALLIOLA, A.; TAMMINEN, T. (2011) Lignin oxidation mechanisms under oxygen delignification conditions. Part 2: Advanced methods for the detailed characterization of lignin oxidation mechanisms. Holzforschung, 65, 575−585.

SCANDINAVIAN STANDARD, (1992). SCAN-CM 46:92, Bulk density.

SCANDINAVIAN STANDARD, (1994). SCAN-CM 40:94, Size distribution.

SCANDINAVIAN STANDARD, (1995). SCAN-CM 43:95, Basic density.

SCOTT, R. W., (1979). Colometric determination of hexuronic acids in plant materials, Analytical Chemistry 7, 936-941.

SILVA JR., F. G.; DO VALLE, C. F.; MUNER, J. C. G. (1996) Programa de qualidade da madeira da Votorantim Celulose e Papel – VCP". O Papel, p. 35-43,.

Solar, R., Kacik, F., and Melcer, I., (1987). Simple semi micro method for the determination of O-acetyl groups in wood and related materials, Nordic Pulp and Paper Research Journal 2(4), 139-141.

TAPPI standard, (2006). T280 wd-06, Acetone extractives of wood and pulp.

TAPPI standard, (2007). T204 cm-07, Solvent extractives of wood and pulp.

TAPPI standard, (2007). T256 cm-07, Water-soluble chlorides in pulp and paper.

TAPPI standard, (2007). T264 cm-07, Preparation of wood for chemical analysis.

TAPPI standard, (2010). TIS 017-10, Post color number.

TAPPI standard, (2011). T222 om-11, Acid-insoluble lignin in wood and pulp.

TAPPI standard, (2011). T684 om-11, Gross heating value of black liquor.

TAPPI standard, (2012). T257cm-12, Sampling and preparing wood for analysis.

WALLIS, A. F. A., WEARNE, R. H., AND WRIGHT, P. J., (1996). Chemical analysis of polysaccharides in plantation eucalypt woods and pulps, Appita Journal 49(4), 258-262.

WERH, T. R.; BARRICHELO, L. E. G. (1993) "Cozimento Kraft com madeiras de Eucalyptus grandis de diferentes densidades básicas e dimensões de cavacos". O Papel, V.54, n.5, p. 33-41,

WESSEL, R. A., TRAN, H., MAHINPEY, N., KUHN, D., (2002). Effect of particle composition on carryover deposition in recovery boilers. TAPPI Fall Conference & Trade Fair.

CAPITULO 5

Potential of Elephant Grass for Pulp Production

Abstract

Elephant grass (Pennisetum *purpureum*) (EG) is a fast growing plant, with high biomass productivity in the range of 30-45 bone dry t/ha/yr. This high productivity qualifies EG as a potential raw material for paper and dissolving pulp production as well as biorefinery applications. This study aimed at evaluating elephant grass as a raw material for paper pulp production through its full chemical and morphological characterization, pulpability at kappa 15 and 20 via the Kraft and Soda-AQ processes and its pulp bleachability at 90% ISO brightness. The results were compared with those of a commercial hybrid eucalyptus wood clone (*Eucalyptus urophylla* x *Eucalyptus grandis*) (EUCA) highly planted in Brazil. About its chemical composition, the elephant grass presents a high ash (60,100 mg/kg) and total extractive content (14.8%). However, the elephant grass showed a good potential for pulp production, being the ideal cooking process the Kraft at kappa number 20 with the highest screened yield (47.9%), bleachability (0.163 Δkappa/TAC) and good viscosity (812 dm^3/kg). For the EUCA the ideal cooking process also was the Kraft at kappa number 20 with the highest screened yield (52%), bleachability (0.217 Δkappa/TAC) and final viscosity (886 dm^3/kg).

1. INTRODUCTION

Hardwoods and softwoods have been the world's main raw materials for pulp production and they deliver suitable product quality. However, the cost of these raw materials has greatly increased in the last decade due to many factors, including the newly created demand for biorefinery applications. Therefore, the establishment of new raw materials that can compensate the lack of low cost wood has been largely sought.

The biomass quality is of extreme importance for pulp production with high yield, low cost and high quality. It is certainly difficult to find raw materials that can beat wood

as source of fiber for pulp production. High productivity plants such as elephant grass (30-45 bone dry t/ha/yr) can potentially supply biomass of low cost to meet the current demand (VILELA et al. 1997, 2001a,b, 2002a,b, 2003a,b; PAULINO et al.,2007; MAZZARELLA et al., 2007). However, the quality of such raw material for pulp production is not yet fully known.

Among the many nonwoody raw materials used to make pulp, which represents a market of about 8-10% of the world's pulp production, there is no reference to the commercial use of elephant grass (GONZALEZ et al., 2008; ALAEJOS et al., 2004; HAMMETT et al., 2001; JIMÉNEZ et al., 2006; JOHNSON et al., 1999; REZAYATI-CHARANI et. al., 2006). Elephant grass has special characteristics for the pulp production, which are the high fibers production, similar to sugar cane (QUESADA et al., 2004; SEYE et al. 2000), and its chemical composition. Some works have showed a content of 40%, 30% and 17.7% for cellulose, hemicelluloses and lignin, respectively (MADAKADZE et al, 2010). These values are good for pulp production, in special the low lignin content, indicating a high pulpability of this material in cooking processes. The few studies aforementioned indicate that EG has some potential for paper production, but a more thorough investigation is required, in special comparing its potential with that of the well-known eucalypt wood, which is largely planted in Brazil and many other parts of the world.

This study aimed at evaluating elephant grass as a raw material for paper pulp production through its full chemical and morphological characterization, pulpability at kappa 15 and 20 *via* the Kraft and Soda-AQ processes and its pulp bleachability at 90% ISO brightness. The results were compared with those of a commercial hybrid eucalyptus wood clone (*Eucalyptus urophylla* x *Eucalyptus grandis*) highly planted in Brazil.

2. EXPERIMENTAL

Materials

A 500 kg sample of 150-days old elephant grass (*Pennisetum purpureum*) (EG) harvested at a Federal University of Viçosa experimental station and a 500 kg sample of eucalypt (*Eucalyptus urophylla* x *Eucalyptus grandis*) (EUCA) wood

supplied by a Brazilian Forest Company were used throughout the study. The samples were evaluated for their moisture content at the moment of harvesting according to Tappi T264 cm-97 standard procedure. The EG sample was manually chipped, producing wet chips about 5 mm long. The chip thickness was quite variable since it depended on the grass thickness, which varies from 1 cm diameter to 4 cm diameter. The grass chips were air dried to a moisture content of about 15% and stored in large plastic bags. The eucalypt sample was chipped in a laboratory chipper, a Chogokukikai model, equipped with 3 knives and 2 screens (40 & 13mm). Both EG and EUCA chips were well mixed (260m^3 rotary mixer) and the EUCA sample was screened according to SCAN-CN 40:94 procedure. For EUCA sample, the chips retained in the 3 mm and 7 mm screens were collected and mixed again, air dried to about 15% moisture and stored in large plastic bags.

Methods

The sampling for physical, chemical and morphological analyses was done using the so-called quartering technique which is trivial for those skilled in the art. Chips were used to measure chips bulk and basic density according to SCAN CN-49:92 and SCAN CM-46:92 standard procedures, respectively.

Biomass productivity

The biomass productivity was calculated using the medium annual increase (MAI) and basic density, by the following equation:

$$\textbf{Biomass productivity}\ (\textbf{ton/ha/yr}) = \textbf{MAI}\ (\textbf{m}^3\textbf{/ha/yr}) \times \textbf{basic density}\ (\textbf{ton/m}^3)$$

Samples preparation for morphological analysis

About 200 grams of biomass were sliced into toothpick type material and macerated using nitro-acetic acid solution in order to prepare individual fibers for morphological analyses. To make the maceration, a solution of five parts of acetic acid and one part of nitric acid were mixed, added to the biomass material until they were completely immersed and let stand for 6 hours at 100 ^oC under a hood. The reaction was stopped by washing the material, which was dispersed in distilled water. Following, the material was gently mixed in a magnetic stirrer (slowly and steadily) for 60 min so

that all the fiber bundles were separated. Morphological characterization of fibers, vessels and fines was carried out on a pulp suspension passing through a specific cell illuminated by a laser beam and connected to a high-resolution camera (CCD). This analysis allowed reliable statistical measurement of thousands of fiber, vessels and fines to determine the main morphological and dimensional characteristics of the pulp components.

Samples preparation for chemical analysis

For the chemical analyses, about 1 kg of EG and EUCA biomass were sampled and ground in a Wiley type mill to produce sawdust of variable size. This sawdust was screened according to Tappi Standard T257-cm85. The sawdust that passed the 40 mesh screen and was retained in the 60 mesh screen was selected for the chemical analyses. The sawdust was air dried and conditioned in a temperature and humidity controlled room (23±1^{o}C, 50±2% RH) until an equilibrium moisture was achieved (~10%). This sawdust (raw sawdust) was used for the chemical analyses. The analyses of ash, silica, chloride, iron, copper, manganese, potassium, calcium and magnesium were carried out directly on the raw sawdust, according to the Standard Methods for the Examination of Water and Wastewater (2000), except for chloride, which was determined according to Tappi T256 cm-97 standard procedure. The biomass extractives contents in acetone, ethanol/toluene(1:2) and ethanol/toluene(1:2) →ethanol →hot water solvent series was also determined in the raw sawdust using the TAPPI T280 pm-99, T204 cm-97 and TAPPI T264 cm-97 standard procedures, respectively. In order to determine biomass main cell wall components, a 200g sample of extractives freed was prepared using TAPPI T264 cm-97 standard procedure. This extracted sample (extractive free sawdust) was conditioned in a temperature and humidity controlled room (23±1^{o}C, 50±2% RH) until an equilibrium moisture was achieved (~10%). The contents of uronic acids, acetyl groups and sugars (glucans, mannans, galactans, xylans and arabinans) in the extractive free biomass were determined according to Scott (1979), Solar et al. (1987) and Wallis et al. (1996). The acid insoluble lignin, acid soluble lignin and lignin syringyl/guaiacyl (S/G) ratio were determined according to TAPPI T 222 om-97 standard procedure, Goldschmid (1971) and Lin & Dence (1992), respectively.

Pulping: processes and conditions

Two pulping processes were used to convert EG and EUCA into pulps, namely: Kraft and Soda-AQ processes. The cooking trials of the EG and EUCA were done in a M&K digester, with 2 individual reactors of 10 liters each, equipped with a forced liquor circulation system and electrically heated with temperature and pressure control. The digester is coupled to a cooling system (Coil System with residual liquor, involved with water at room temperature), to ensure the cooling of the liquor after the cooking simulation. The experimental conditions used in the cooking process were established based on technical knowledge of the Pulp and Paper Laboratory of the Federal University of Viçosa - Brazil. With the exception of the alkaline charge, the other cooking conditions were kept constant for all cooking and are showed in the Table 1. Eight cooking experiments were performed for each sample, using different active alkali charge to establish the delignification curves for each sample. Eight cook trials were performed for each sample to establish the delignification curve. After determination of the delignification curve, four samples of pulp were prepared for each raw material, from two processes and two kappa numbers per process, 15 and 20.

Table 1. Conditions for pulping processes of EG and EUCA to kappa 15 and 20.

Parameter	Kraft process	Soda-AQ process
Biomass, kg	1	1
Active alkali as NaOH, % on o.d. chips*	Variable	Variable
Sulfidity as NaOH, % on o.d. chips	26	26
Anthraquinone charge, % on o.d. chips	-	0.05
Liquor to chips ratio, L/kg	4/1	4/1
Maximum temperature, ^{o}C	170	170
Time to maximum temperature, minutes	90	90
Time at maximum temperature, minutes	50	50
*The optimum AA for achieving kappa 15 and 20 were determined by varying the AA charge from 15.5-23.1% and 13.8-27.7% for the Kraft and Soda-AQ processes.		

Fiber individualization was achieved in a "hydrapulper" (15 liters capacity), followed by fine screening (Voith laboratory cleaner) equipped with perforated plates with 0.2 mm openings. The material retained on the sieve (rejects) was dried and weighed. The clean pulp was dewatered in centrifuge to a consistency of about 30%, weighed and stored in polyethylene bags for further analysis. With the known weights of the sieved and retained materials, the reject content and the screened cooking yield

were determined. The hexenuronic acid content, heating value and solids content were determined according Vuorinen et. al (1996), Tappi T684 om-97 and CPPA H1, respectively.

Bleaching: sequence and conditions

The pulps derived from the pulps cooked at kappa number 15 and 20 were bleached by the elemental chlorine free sequence (ECF) O-D-P-D to 90% ISO brightness. The oxygen delignification (O-stage) was run at 10% consistency, 100^{o}C, 60 min, 700 kPa pressure, 20 kg NaOH/odt pulp and 20 kg O2/odt pulp. The first chlorine dioxide stages (D) were carried out at 10% consistency, end pH 3.5, 85ºC, 120 min, with kappa factor of 0.20 for pulps with kappa number 15 and 0.24 for pulps with kappa number 20, respectively. The P stages were run at 10% consistency, end pH 10.5, 85ºC, 120 min, with hydrogen peroxide doses of 0.5 on pulp weight. The second chlorine dioxide stages (D) were carried out at 10% consistency, end pH 5.5, 70ºC, 120 min. with chlorine dioxide variable to achieve the desired brightness. The bleached pulps were evaluated for their brightness, brightness stability and viscosity. The brightness stability expressed as post color number was calculated according the Tappi TIS 017-10.

3. RESULTS AND DISCUSSION

3.1 Biomass productivity, morphological and chemical characteristics of EG and EUCA

Biomass productivity

Two very important factors regarding biomass use for pulp production are moisture content and density since they affect harvesting, transportation and utilization costs (LEITE, 2010). In the Table 2 are presented the biomass productivity results of the EG and EUCA. The samples analyzed in this study showed average moisture of 73 and 55%, density 216 and 480kg/m3, for EG and EUCA respectively. This value for eucalypt is considered satisfactory for pulp production (GOMIDE et al., 2005; GOMIDE et al., 2010), since a high density is always favorable in pulp production because it increases pulp mill throughput, but may penalize pulping yield due to poor white liquor penetration when conditions are not properly optimized (BATALHA et al., 2012).

This result points out to the great difficulty in industrially processing the EG materials and to the need for developing methods for compacting such materials in order to increase their density before utilization. The MAI for EG sample was 148.1 m^3/ha/yr, but its low density (216 kg/m^3) resulted a biomass productivity of only 32 tons of material per ha/yr, which is much lower than that for the EUCA sample. The MAI for EUCA sample was 80.9 m^3/ha/yr, which works out to a productivity of 38.8 ton s of wood per ha/yr. This productivity is much above the average obtained in commercial plantations in the Brazilian Territory (~20-30 t/ha/yr) (BRACELPA, 2013). However, the EG biomass productivity is quite satisfactory when compared for example with the Brazilian average for eucalyptus.

Table 2. Biomass productivity for EG and EUCA.

Sample Code	Average Annual Increment, m^3/ha/yr	Biomass basic density, kg/m^3	Biomass Productivity, bone dry ton/ha/yr	Chip bulk density, kg/m^3
EG	148.1	216	32.0	85
EUCA	80.9	480	38.8	183

Morphological characteristics

Another important aspect of the raw material for pulp production is its morphological characteristics. The strength and morphology of fibers have a strong influence on the physical properties of paper (SETH et al., 1988). In the Table 3 are presented the morphological characterizations of EG and EUCA. It was observed a lower fiber content per gram of pulp in EG sample. The width, length, coarseness, fine content, macro fibrillation index may be considered close to the eucalypt sample. However, the EG showed a high vessel content. For the pulping process, the vessel elements are desirable, since the penetration of cooking liquors is easier. However, for the production of special kinds of paper, such as the printing papers, they are considered undesirable, because the vessel on the surface of the paper sheet tend to be pulled thereby causing printing failures this is known as “vessels picking” (LINDSTRÖN et al, 2012). But in general it is possible to say that the fibers have potential for paper production, since the characteristics desired for paper quality are observed.

Table 3. Morphological characterization of EG and EUCA materials.

Sample	EG	EUCA
Fibre content, millions/g of pulp	14.9	28.1
Mean fibre arithmetic length, μm	695.5	562

Mean length-weighted fibre length, µm	1131	733
Mean area-weighted length, µm	1114	733.5
Mean fibre width, µm	21.5	16.4
Mean fibre coarseness, mg/m	0.09	0.06
Mean fibre curl index, %	6.8	4.5
Macro--Fibrillation index, %	0.42	0.54
Broken fibre content, %	26.1	17.7
Fine content, % in area	11.9	12.4
Mean fine area, μm^2	1987	1647
Mean fine length ,µm	62	64.5
Vessel content, nb/g of pulp	11628	6771
Mean area-weighted length, mm	0.45	0.43
Mean vessel width, µm	191.1	194.3

Chemical characteristics

Table 4 shows the extractive quantity of the EG and EUCA samples extracted with the ethanol/toluene→ethanol→hot water solvent series, with ethanol/toluene 1:2 only and with acetone. In order to measure the biomass cell wall components, it is relevant to remove all extractives present in the material. The Tappi T204 CM 97 standard procedure (ethanol/toluene 1:2 → ethanol → hot water) was efficient for removing all polar and apolar extractive fractions. Although this procedure is intended to free the wood from extractives, it serves also to quantify the total amount of extractives present in the biomass, since the main cell wall components (cellulose, hemicelluloses and lignins) are not soluble in none of the solvents comprising the series. Extraction with ethanol/toluene only extracts substances as waxes, fats, resins, phytosterols and non-volatile hydrocarbons. Extraction in acetone (Tappi 280 PM99) serves to quantify those extractives that are more relevant to the pulping operation and pitch formation in the pulp. The acetone extractable content of wood is a measure of such substances as fatty acids, resin acids, sterols, waxes and non-volatile hydrocarbons. Because acetone is both more polar and water-miscible than dichloromethane or benzene-ethanol, the quantity of acetone extractable material, especially in wood, may be higher than that found with the other solvents. This procedure will not give the same results as ethanol-toluene or dichloromethane extractions. In his work, Barbosa et. al. (2005) showed that acetone is the best solvent for the evaluation of the wood lipophilic extract content.

Biomass extractives are quite troublesome since they cause many difficulties in operating the industrial facilities, causing unexpected lost time in the operation for cleaning of equipment and instruments due to their stickiness and tackiness. In addition may occur the deposition of these substances in the pulp, which are called pitch (BARBOSA et. al., 2005), decreasing the pulp value or even its rejection by market. In her study Cruz et. al. (2006) showed that in pitch composition are present waxes, fats, long chain alcohols, being these main compounds associated with pitch formation.

The evaluated EUCA material showed acceptable acetone extractives, Ethanol/Toluene (1:2) extractives and total extractive contents for the pulp mills (GOMIDE et al., 2010). For the pulp production aim, the EG showed a high of acetone extractives and ethanol/toluene extractives. In addition, pitch formation and pulp dirtiness are much more likely on raw materials containing high content of these extractives. As a consequence, the EG also presented a high total extractive content (14.8%) since such materials are likely to result low yield during cooking process.

Table 4. Extractives content of EG and EUCA materials.

Sample Code	Acetone Extractives, %	Ethanol/Toluene (1:2) Extractives, %	Total Extractives, %
EG	3.9	6.8	14.8
EUCA	0.8	1.5	2.3

The raw material minerals are detrimental for their industrial utilization since they cause corrosion and deposits on equipment, reduce biomass heating value and decrease mill throughput. In general the amount of inorganics present in the eucalyptus woods was very low and quite acceptable for most applications (MOREIRA, 2006). The total inorganics measured by complete biomass combustion (ash content) for the EUCA was 1550 mg/kg biomass (Table 5). For the EG it reached 60,100 mg/kg. The very high mineral content in the grass is explained by its fast metabolism at the young age when it needs plenty of minerals to produce the biomass. The mineral contents in biomass tend to decrease with aging due to decreased biomass deposition rate as a function of time (MORAIS, 2005). The same trend observed for total inorganics (ash content) is also verified for the individual components such as silica, chloride, calcium, potassium and magnesium, with the EG always presenting higher values than the EUCA sample. Calcium, magnesium

and silica are very undesirable in most industrial processes because of their ability to cause deposits in equipment during evaporation of liquid streams and combustion of solid streams. On the other hand, potassium and chloride are particularly dangerous for their ability to decrease the ash melting point during combustion, thus causing sticky ash problems in recovery boiler systems (WESSEL et al., 2002). In addition, chlorides are highly corrosive and troublesome for most equipment regardless of metallurgy. In regard to transition metals (Fe, Cu and Mn), there were also significant differences between the EH and EUCA materials. For the EG ones these levels were 8.8, 11.2 and 11.1 mg/kg for copper, iron and manganese, respectively. For the EUCA materials copper, iron and manganese were 1.1, 9.3 and 18.2 mg/kg, respectively. Transition metals are particularly important in operating systems where oxygen derived chemicals are used for processing biomass. These metals are aggressive to oxygen-oxygen bonds thus degrading any peroxide form with subsequent formation of highly reactive free radical intermediates that negatively affect the integrity of carbohydrate chains.

Table 5. Metal contents, Cl^- and SiO_2 of EG and EUCA materials.

Sample Code	Inorganics, mg/kg biomass								
	Ash	Cu	Fe	Ca	Mn	Mg	K	Cl^-	SiO_2
EG	60,100	8.8	11.2	423	11.1	490	21194	6631	15167
EUCA	1,550	1.1	9.3	378	18.2	104	369	434	-

Table 6 presents results of contents of sugars, acetyl group, uronic acids and, lignin, and syringyl / guaiacyl ratio of lignin. The lignin contents for EG and EUCA biomasses were 18 and 27.2%, respectively, with these values being acceptable for pulp production. The low lignin content of the EG is advantageous for potentially improving pulping easiness and yield (GOMES et al., 2008). However, its low lignin S/G ratio and low sugar content work in the opposite direction. The low sugar content of the EG reflected its very high extractive and mineral contents.

Table 6. Chemical composition of EG and EUCA materials.

Sample Code	*Sugar Composition, %					Acid Soluble Lignin, %	Total lignin,%	Lignin S/G ratio	Acetyl Group, %	Uronic Acid Group, %
	Gluc.	Xyl.	Galac.	Man.	Arab.					
EG	38.2	9.6	0.8	0.6	0.2	2.2	18	0.8	1.9	1.2
EUCA	49.4	12	1.2	0.9	0.3	4.2	27.2	2.7	1.9	4.0
*Sugar composition: Gluc.= Glucans; Xyl. = Xylans; Galac. = Galactans; Man. = Mannans ; Arab. = Arabinans.										

In general, both the EG and EUCA hemicelluloses were largely comprised of xylans with the minor components (mannans, galactans and arabinans) being of little importance. The EG showed lower uronic acids than the EUCA, which can be negative for this raw material, since the uronic acids protect the xylans, preserving them during alkali pulping process (MAGATON et al., 2008).

3.2 Pulpability of EG and EUCA by the Kraft and Soda-AQ processes

The pulpabilities of EG and EUCA were compared at kappa number 20 and 15, with the Kraft and Soda-AQ processes. The 15 and 20 kappa targets were chosen because they are largely used for production of bleachable grade hardwood pulps. The kappa 15 is more conventional and the kappa 20 is desirable for fiber line yield improvements but more challengeable in the mill screening and bleaching areas. The Kraft process is conventional and the Soda-AQ process is highly desirable when the use of black liquor for biorefinery purposes is at stake. The absence of sulfur compounds in the Soda-AQ black liquor enormously facilitates its further fractionation into valuable components.

In order to achieve these kappa number targets for both processes, the raw materials were cooked at various active alkali doses and a delignification curve was determined whereby kappa number was plotted against active alkali charge (Figures 1 and 2 for EG and EUCA, respectively) and yield (Figures 3 and 4, for EG and EUCA, respectively). For both processes (Soda-AQ and Kraft), increasing the alkali charge decreased kappa number and increased screened yield.

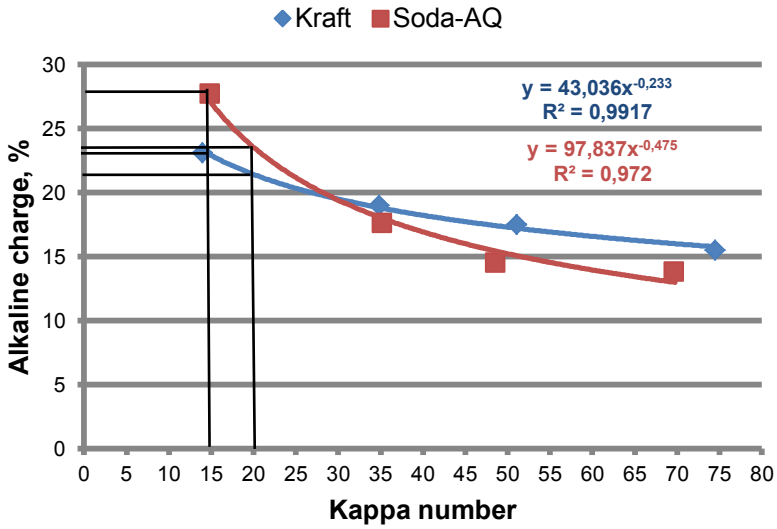

Figure 1. Delignification curve by Kraft and Soda-AQ processes for EG.

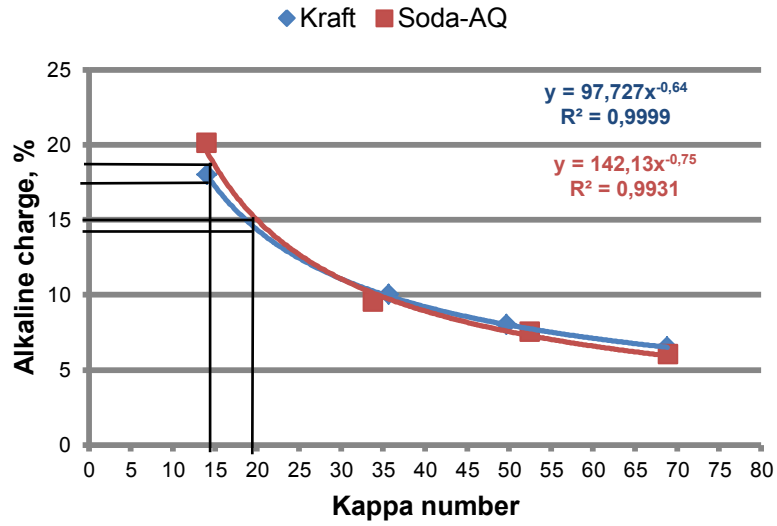

Figure 2. Delignification curve by Kraft and Soda-AQ processes for EUCA.

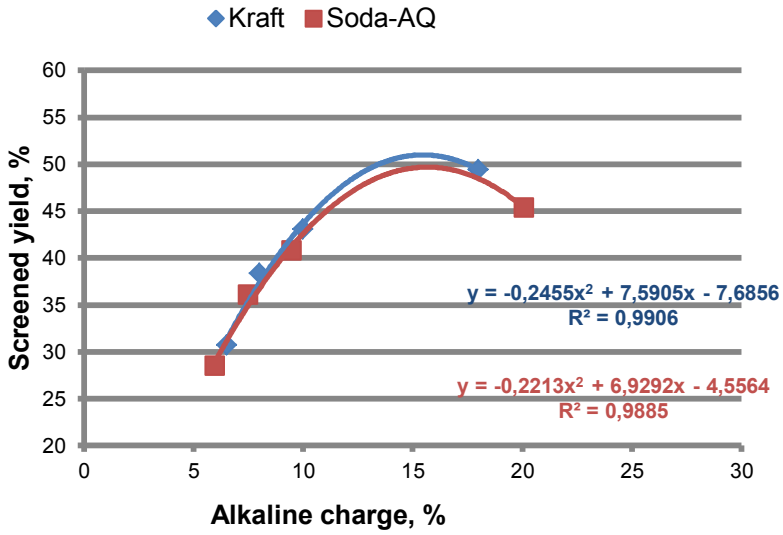

Figure 3. Alkaline charge *versus* screened yield by Kraft and Soda-AQ processes for EG.

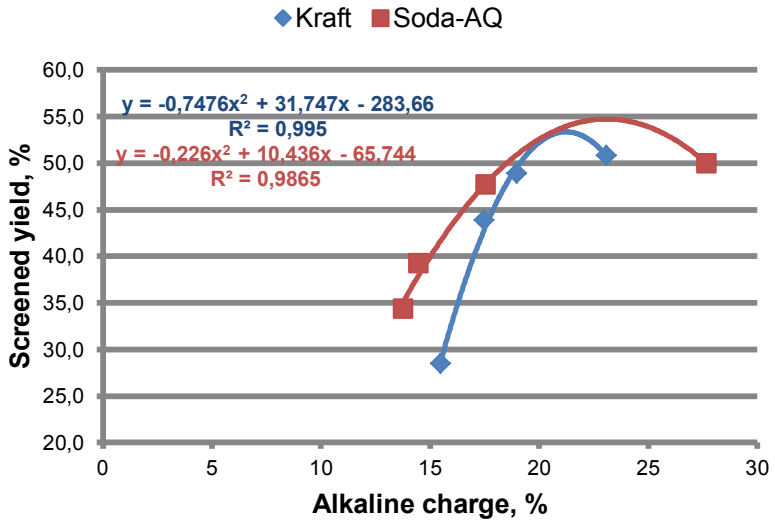

Figure 4. Alkaline charge *versus* screened yield by Kraft and Soda-AQ processes for EUCA.

Kraft pulping of EG and EUCA

The key to the Kraft process is the recovery furnace that is quite efficient at recovering the pulping chemicals, NaOH and Na_2S, currently it is the most used process for pulp production (BOSE et al., 2009). Table 7 presents the results for EG and EUCA by Kraft process for the two kappa numbers. For the Kraft process, increasing the alkali charge resulted in the expected behavior, in general: lower total yield, higher yield of screened accepts, lower rejects, lower Kappa number, lower viscosity, and higher alkali residual. The EG samples showed a lower alkali charge demand than EUCA samples. High consumption of alkali charges is a characteristic highly unfavorable, since it penalizes: the yield, carbohydrate chains, recovery boiler

and increasing the production cost (GOMIDE et al., 2004). Overall, for EG the low values screened yield confirmed the significant presence of extraneous and non-cellulosic materials, as indicated by the analytical data. The screened yield values of EG were in close agreement to those found in the literature for Kraft process (MADAKADZE et al, 2010). For eucalypt the values screened yield were also in close agreement to those found in the literature in cooking process by Kraft process (GOMIDE et. al., 2005).

About the brightness values, the results of EG and EUCA were similar between each kappa number evaluated, as expected, being the high values obtained for kappa number 15. Another parameter evaluated was the hexenuronic acid content, and a lower content for EG pulps than EUCA was observed. This fact can be explained due to the low uronic acid content in EG material. In addition this pulp characteristic also helps explain the low screened yield during pulping process for the EG, since the uronic acids work as a protection for xylan preserving it during the pulping process (MAGATON et al., 2008).

Another parameter evaluated was the heating values of black liquor, and it has been associated with lignin content, being increased with increasing of lignin content (BIERMANN et al., 1996). It was observed for both raw materials that the kappa number 20 showed a high value. It may be explained due to a less carbohydrate loss in pulps with high kappa number. Another parameter that confirmed this fact is that the black liquor solids and organic solids were always high in the process ending in kappa number 15 for both raw materials.

Table 7. Cooking results of EG and EUCA by Kraft process for kappa number 15 and 20.

Parameters	EG kappa 15	EG kappa 20	EUCA kappa 15	EUCA kappa 20
Alkaline Charge, %	18	15	26	20
Screened Yield, %	47.4	47.9	50.4	52.0
Rejects, %	1.1	5.6	0.1	0.4
Viscosity, dm^3/kg	1100	1359	939	1100
Brightness, % ISO	32.9	31.1	33.3	31.1
HexA, mmol/kg	13.2	11.1	39.5	46.4
Black Liquor Residual AA, g/L	4.1	8.0	16.1	15.8
Black Liquor solids, %	11.3	7.4	13.1	10.1
Black Liquor organics, %	54.0	52.5	54.2	49.4
Black Liquor inorganics, %	46.0	47.5	46.8	51.6
Black Liquor heating value, cal/g	3395.0	3554.0	3657.0	3920.3

Soda-AQ pulping of EG and EUCA

Soda pulping is a chemical process for making wood pulp with sodium hydroxide as cooking chemical. In the Soda-AQ process, anthraquinone (AQ) may be used as a pulping additive to decrease the carbohydrate degradation (GOMIDE et al., 1980; BOSE et al., 2009). Table 8 presents the results of EG and EUCA cooked by Soda-AQ process ending in kappa number 15 and 20. For the Soda-AQ process increasing the alkali charge resulted in the expected behavior, in general: lower total yield, higher yield of screened accepts, lower rejects, lower Kappa number, lower viscosity, and higher alkali residual. As well as for the Kraft process, the pulp yield in Soda-AQ process was quite satisfactory for both EG and EUCA among all the kappa numbers evaluated (KHRISTOVA et al., 1998; JERONIMO et al., 2000), with a lower value for the EG, reflecting again its high extractive and mineral content.

About the brightness values in Soda-AQ process, the results for EG and EUCA followed the same tendency of Kraft process, the values were similar between each kappa number evaluated, and also being the high values obtained for kappa number 15. Similar to Kraft process, the hexenuronic acid content for EG pulps was lower than EUCA pulps. This can be again explained due to the low uronic acid content in EG material. As well as to the Kraft process, this pulp characteristic of elephant grass also helps explain the low screened yield during Soda-AQ pulping for the EG, since the uronic acids help to preserve xylan during the pulping (MAGATON et al., 2008).

As for the Kraft process, the heating values of black liquor obtained by Soda-AQ processes were evaluated. For EG and EUCA again the same tendency was observed, in kappa number 20 the pulps showed a high value. Similarly to Kraft process, these results indicating less carbohydrate loss in pulps with high kappa number by Soda-AQ process, which was also confirmed by black liquor solids and organic solids, which were always high in process ending in kappa number 15 for both raw materials.

Table 8. Cooking results of EG and EUCA by Soda-AQ process for kappa number 15 and 20.

Parameters	EG kappa 15	EG kappa 20	EUCA kappa 15	EUCA kappa 20
Alkaline Charge, %	19.5	15	29.5	22
Screened Yield, %	46.0	47.5	49.6	51.6
Rejects, %	1.4	3.8	0.2	0.6
Viscosity, dm^3/kg	875	883	972	1028
Brightness, % ISO	31.6	28.5	33.0	29.6
HexA, mmol/kg	15.2	16.3	21.8	45.7
Black Liquor Residual AA, g/L	10.4	7.7	24.7	19.7
Black Liquor solids, %	11	9.3	12.5	11.7
Black Liquor organics, %	53.4	56.1	50.2	56.4
Black Liquor inorganics, %	46.6	43.9	49.8	43.6
Black Liquor heating value, cal/g	3510.5	3696.0	3602.3	4072.6

Kraft versus Soda-AQ pulping of EG and EUCA

Comparing the Kraft and Soda-AQ processes for EG and EUCA (Table 7 and 8, respectively), it was possible to observe that the screened yield and viscosity were higher in Kraft than Soda-AQ. It may also be attributed to the high alkaline charge required in Soda-AQ process to achieve the desired kappa number. Another interesting point about the viscosity is to observe a positive effect of anthraquinone in preserving the carbohydrates, since viscosity values were close between the kappa number 15 and 20 for each raw material evaluated.

It was also possible to observe a highest heating value of black liquor and lowest brightness for the Soda-AQ process. In his work, Bosa (2009) analyzing pulps by periodate and permanganate oxidations suggested that the residual lignin from the non-sulfur processes contained more condensed structures than Kraft residual lignin. The low reactivity of these structures is believed to be responsible for the lower

brightness of Soda-AQ pulps than Kraft pulps. Likewise the highest result for heating value of black liquor may be explained, as stated previously. The heating value has been associated with lignin content, and being the most condensed lignin which is rich in carbon-carbon bonds, so more energy may be provided from this black liquor.

For pulping processes of EG and EUCA pulps the Soda-AQ process has the disadvantage of lower yields and worse pulp quality than Kraft process. However, Soda-AQ process would be an excellent solution to replace the Kraft process if it gets improvements in pulp quality, yield and delignification rate, since the black liquor from Soda-AQ process may present a high heating value and great potential for applications in biorefinery, because the absence of sulfur compounds in the Soda-AQ black liquor enormously facilitates its further fractionation into valuable components.

3.3 Oxygen delignification stage of EG and EUCA pulps

The pulps produced by two processes and two kappa numbers were submitted to oxygen delignification process as described in methodology. In the Table 9 are shown the results of the oxygen delignification stage (O-stage). The overall oxygen delignification stage performance was measured by the kappa drop and brightness gain across the O-stage. It was observed that the kappa drop decreased with increasing kappa number, a result likely explained by the decreased content of lignin containing free phenolic hydroxyl groups and increased HexA content with increasing kappa (COLODETTE et al., 2007).

The EG sample showed the best performance in kappa drop. It was possible also to observe that the kappa drop was higher in the Soda-AQ process. This fact may be explained due to a lower hexenuronic acid content in the EG pulp (Table 7). It has been documented in the literature that the oxygen stage is more efficient on pulps with lower hexenuronic acid content since only small amounts of hexenuronic acids are removed in the oxygen delignification (VENTORIM et al, 2006; EIRAS, 2003). Another relevant point that helps to explain the higher efficiency of the pulp obtained by the Soda-AQ process is a possible higher content of free phenolic hydroxyl groups (ZONG LAI, 1999), which are the main sites for oxygen reactions (COLODETTE et al., 2007). It is known that in Soda-AQ pulping, AQ oxidizes the reducing end groups of carbohydrates, thus stabilizing them towards peeling reactions in alkaline media.

The reduced form, AHQ, cleaves part of the β-aryl ether linkages in lignin. Thus, the molecular mass of the residual lignin is reduced and new phenolic hydroxyl groups are formed. Both effects render the lignin more soluble (KLEEN et al., 2002). Since phenolic hydroxyl groups are essential to lignin dissolution in alkali, a higher content of this functional group in the residual lignin may be partly related to the residual lignin being more condensed. For woody samples, in his work Zong Lai et al. (1999) showed that the tendency of alkaline lignin condensation reactions would increase in the order of: high sulfidity < Kraft < Soda-AQ < soda cooks.

Table 9. Oxygen delignification performance of EG and EUCA pulps.

		Kappa 15		**Kappa 20**	
		Kappa drop, %	**Brightness gain, % ISO**	**Kappa drop, %**	**Brightness gain, % ISO**
Kraft	EG	61.9	12.0	50.9	7.5
	EUCA	47.4	20.1	43.8	16.2
Soda-AQ	EG	73.7	14.5	69.4	14.7
	EUCA	54.0	18.3	47.3	16.6

3.4 Bleachability of EG and EUCA pulps

The pulps were bleached aiming brightness of 90% ISO as described in the methodology. For a fair analysis of all pulps, it was used the bleachability of each pulp studied. In this work bleachability has been defined as the ratio between kappa number entering the bleach process and total active chlorine (TAC) required for attaining the target brightness of 90% ISO. Total active chlorine was defined by the following equation:

$$\mathbf{TAC=[(ClO_2\times 2.63)+(H_2O_2\times 2.09)]}$$

In the equation above, the factors 2.63 and 2.09 are simple conversions of ClO_2 and H_2O_2 into active Cl_2 based on their oxidation equivalents. The EG pulp showed a lower bleachability when compared to EUCA, this was probably due to its high content of metals (Figure 5). About the bleachability of the EUCA, it was possible to observe that they were influenced by the type of process used in producing the pulp. The best performance was observed for the pulps from the Kraft process at kappa

number 20. The worst performance was observed for the pulps from the Soda-AQ process at kappa number 15.

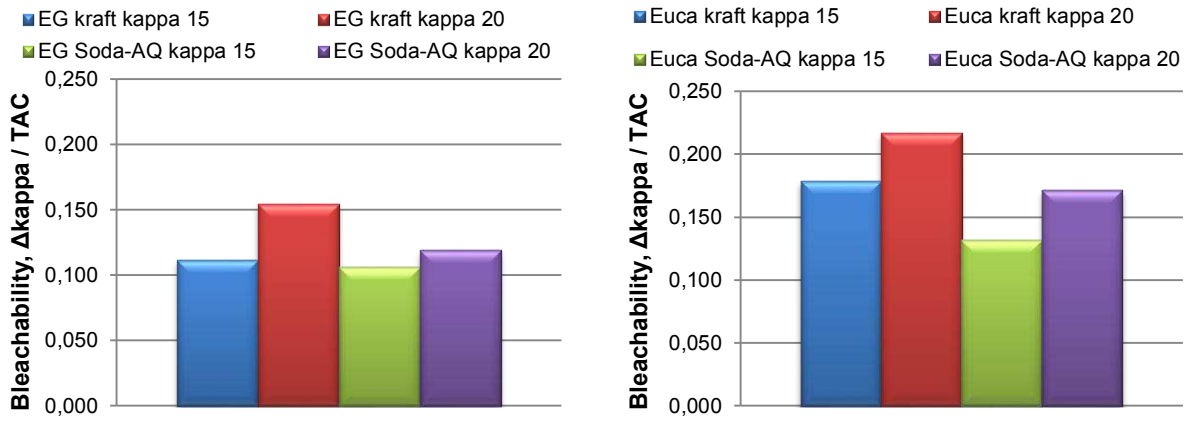

Figure 5. Bleachability of EG and EUCA pulps in each process studied.

Among the EUCA pulps, the best bleachability was found for the Kraft process at kappa number 20 (44.1 TAC kg/odt). For the EG, the best bleachability was found also for the Kraft process at kappa number 20 (50.6 TAC, kg/odt). It is important to remember that the EG used in this study do not have any improvement process aiming at the pulp production, so the values of TAC found may be better if the raw material used has a lower metal content, for example. The total active chlorine (TAC) demands to bleach the pulps to 90% ISO are shown in Figure 6. Although the bleachability of the Kraft kappa 20 for the EG and EUCA pulps were the highest, their TAC was not the lowest due to the effect of the kappa number value. Actually the lowest TAC was achieved for the EUCA pulp at Kraft kappa 15. In general the highest values of TAC were seen for the Soda-AQ pulps of kappa 20, especially for the EUCA sample.

Figure 7 shows results of viscosity for EG and EUCA bleached pulp. In regard to viscosity among all samples studied, the EG bleached pulp showed the highest value (886 dm^3/kg). For EUCA only the Kraft process at kappa number 20 achieved satisfactory viscosity for most pulp applications (GOMIDE et al., 2005). On the other hand, the EG bleached pulp presented viscosity values satisfactory for most pulp applications by the two processes and all kappa numbers evaluated (GOMIDE et al., 2005). Figure 8 shows the results of brightness stability expressed as post color number. The brightness stability increased with increasing kappa number (increasing

TAC) as previously reported (EIRAS et al., 2001). However, no effect of pulping process and biomass raw material were observed on brightness stability.

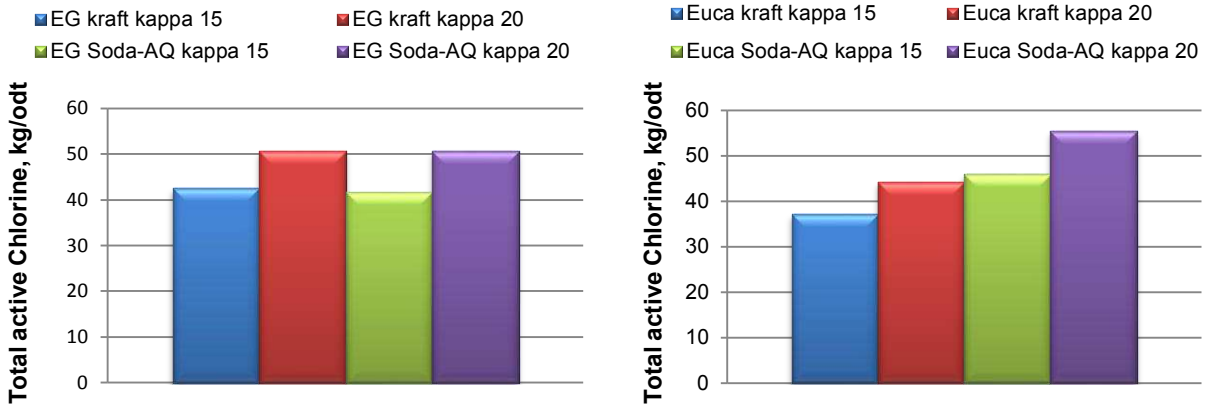

Figure 6. Total active chlorine of EG and EUCA pulps during the bleaching process.

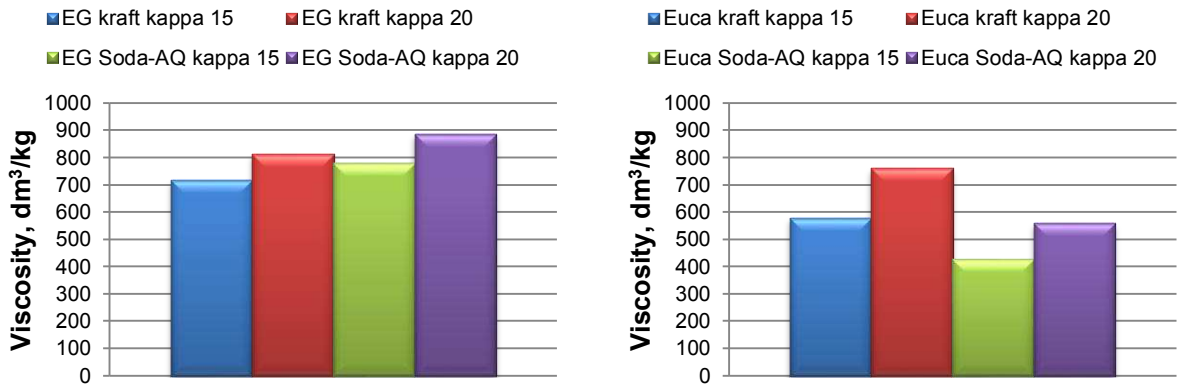

Figure 7. Viscosity for of EG and EUCA pulps during the bleaching process.

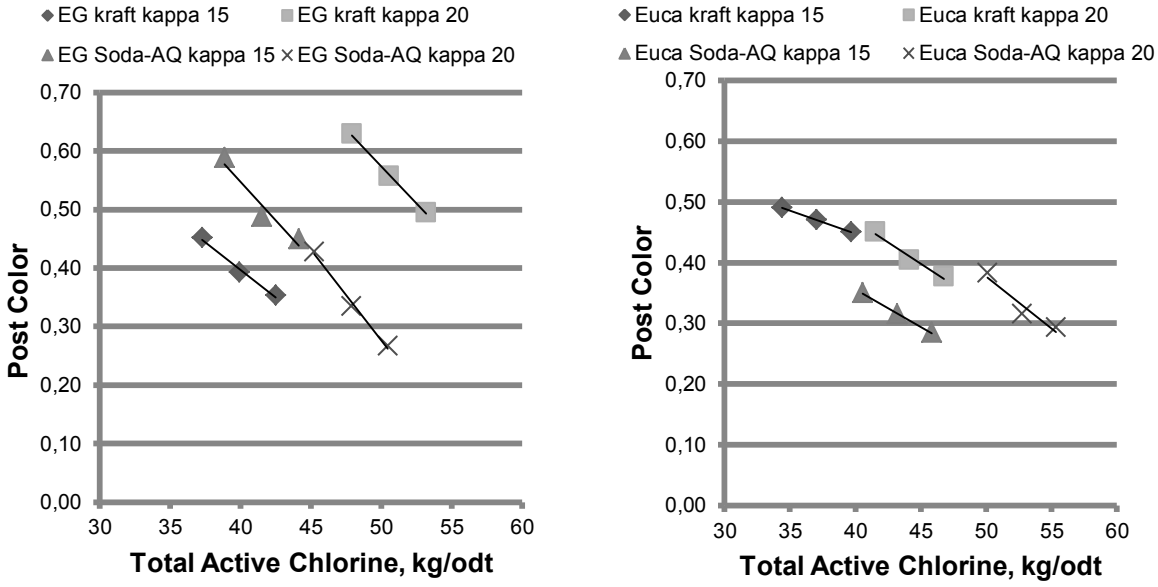

Figure 8. Post color number of EG and EUCA pulps during the bleaching process.

4. CONCLUSIONS

- The Soda-AQ process presented the worst screened yield and bleachability among all samples.
- The EG showed a good potential for pulp production, being the ideal cooking process the Kraft at kappa number 20 with the highest: screened yield (47.9%), bleachability (0.163 Δkappa/TAC) and good viscosity (812 dm^3/kg).
- For the EUCA the ideal cooking process also was the Kraft at kappa number 20 with the highest: screened yield (52%), bleachability (0.217 Δkappa/TAC) and final viscosity (886 dm^3/kg).
- The EG showed a high vessel content (11,628 vessels/g of pulp) which is negative for some specific paper productions.
- The EG presents a high ash (60,100 mg/kg) and total extractive content (14.8%), which are negative and need to be improved for this raw material aiming for pulp production.

5. ACKNOWLEDGMENTS

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6. REFERENCES

Associação dos Fabricantes de Celulose E Papel – BRACELPA (2013). http://www.bracelpa.com.br)

Barbosa, L. C. A.; Maltha, C. R. A. and Cruz M. P. (2005).Chemical composition of lipophilic and polar extractives of Eucalyptus grandis. Science & Engineering Journal,15 (2): 13 - 20.

Batalha, L. A. R.; Colodette, J. L.; Gomide, J. L.; Barbosa, L. C. A.;. Maltha, C. R. A. and Gomes, F. J. B. (2012). Dissolving pulp production from bamboo. BioResources p. 640-651.

Biermann, C.J. (1996). Handbook of Pulping and Papermaking (2nd edition). Academic Press, San Diego, California p.21.

Bose, S. K.; Omori, S.; Kanungo, D.; Francis, R.C. and Shin, N.-H. (2009). Mechanistic differences between kraft and Soda/AQ pulping. Part 1: Results from Wood Chips and Pulps. Journal of Wood Chemistry and Technology, 29: 214–226,.

Canadian Pulp & Paper Technical Association – CPPA. (1984) Standard Methods.

Colodette, Jorge Luiz ; Gomide, José Lívio ; Longue Júnior, Dalton ; Pedrazzi, Cristiane. (2007) Effect of pulp delignification degree on fiber line performance and bleaching effluent load. BioResources, v. 2, p. 223-234.

Cruz, Mariluze P. et al . (2006) Caracterização química do "pitch" em indústria de celulose e papel de Eucalyptus. Quím. Nova, São Paulo, v. 29, n. 3, June.

Eiras, K.M.; Mounteer, A.H.; Venturim, G.; Colodette, J.L.; Gomide, J.L..Efeito do conteúdo de lignina lixiviável e de ácidos hexenurônicos da polpa na performance da deslignificação com oxigênio. International Coloquium on Eucalyptus Pulp, 2003. 01 pp. Acesso em 20/01/2012, (http://www.eucalyptus.com.br/icep01/katia_eiras2.pdf)

Gomide, J. L. (1980). Soda-AQ: Um Novo Processo para Produção de Polpa Celulósica de Eucalipto. Revista Árvore (Impresso), Viçosa - MG, v. 4, n. 1, p. 75-90.

Gomide, J. L.; Fantuzzi, N. H.; Regazzi, A. J. (2010). Análise de critérios de qualidade da madeira de eucalipto para produção de celulose Kraft. Rev. Árvore, Viçosa, v.34, n.2.

Jeronimo, L. H.; Foelckel, C. E. B.; Frizzo, S. M. B. Adição de antraquinona na polpação de Eucalyptus saligna. Ciência Florestal, p.31-37, vol 10, 2000.

Khristova, P.; Gabir S.; Bentcheva S.; Dafalla, S. (1998). Soda-anthraquinone pulping of sunflower stalks. Industrial Crops and Products 9–17.

Lindström, N.; Fardim, P. Chemistry and surface chemistry of vessels in eucalyptus Kraft pulps. O PAPEL vol. 73, number 9, pp. 65 – 72, September 2012.

Leite, F. P.; Gomes, F. J. B.; Souza, E.; Rosado, A. M.; Amaral, L. S. (2010). Investigação do tempo de secagem no teor de umidade e nas características físicas e químicas da madeira para produção de celulose. 42o Congresso e Exposiçao Internacional de Celulose e Papel- ABTCP, São Paulo.

Madakadze, I. C.; Masamvu, T. M.; Radiotis, T. J. Li And Smith, D. L. (2010). Evaluation of pulp and paper making characteristics of elephant grass (Pennisetum purpureum Schum) and switchgrass (Panicum virgatum L.). African Journal of Environmental Science and Technology Vol. 4(7), pp. 465-470.

Magaton, A. S.; Pilo-Veloso, D.; Colodette, J. L. (2008). Caracterização das O-acetil-(4-O-metilglicurono)xilanas isoladas da madeira de Eucalyptus urograndis. Quím. Nova, São Paulo, v. 31, n. 5.

Mazzarella, V.N.G. (2007). Jornada Madeira Energética-Capim Elefante com Fonte de Energia no Brasil: Realidade Atual e Expectativas. IPT-BNDS - Rio de Janeiro, maio de 2007. P.Point.

Morais, P. H. D. (2008). Influência da idade de clones de eucalipto na composição química e polpabilidade da madeira e na branqueabilidade e propriedades das polpas. Dissertação de mestrado apresentada a Universidade Federal de Viçosa.

Moreira, E. (2006). Efeito da lixiviação ácida de cavacos de eucalipto no processo Kraft. Dissertação apresentada à Universidade federal de Viçosa.

Quesada, D. M.; Bodey, R. M.; Reis, V. M.; Urquiaga, S.(2004). Parâmetros Qualitativos de Genótipos de Capim Elefante (Pennisetum purpureum Schum.) estudados para a produção de energia através da Biomassa. Circular Técnica 8 – EMBRAPA. Seropédica, Rio de Janeiro- Brasil.

Scandinavian Pulp, Paper And Board Testing Committee.(1993). Scan Test Methods.

Scott, E. W.; Abbott, J. C. Properties of paper – an introduction. Atlanta: Tappi Press, 1995. 136p.

Seth, R. S.; Page, D.H. (1988). Fiber properties and tearing resistance. Tappi Journal p. 103-107, February.

Seye, O.; Cortez; L. A. B.; Gómez, E. O. (2000). Queima direta de gramínea. Projeto Integrado de Biomassa - PIB. In: Encontro de Energia no Meio Rural, 3..

Solar, R.; Kacik, F.; Melcer, I.(1987). Simple semimicro method for the Determination of O-Acetyl Groups in Wood and Related Materials. Nordic Pulp and Paper Research Journal, n. 4, p. 139-141.

Technical association of the pulp and paper industry. (2000). Tappi standard methods. Atlanta.

Vilela, H., Barbosa, F.A, Rodriguez, N. (2001a). Qualidade das silagens de capim elefante Paraíso submetidas a três tempos de emurchecimento. Anais: XXXVIII Reunião Anual da Sociedade Brasileira de Zootecnia. julho de 2001. Piracicaba/SP. 323 a 324 p.

Vilela, H., Barbosa, F.A., Rodriguez, N. E Benedetti, E. (2001b). Efeito da idade planta sobre a produção e valor nutritivo do capim elefante Paraíso (Pennisetum hybridum). Anais: XXXVIII Reunião Anual da Sociedade Brasileira de Zootecnia. 320 a 321p.

Vilela, H., Barbosa, F.A., Rodriguez, N., Benedetti, E., Nogueira, A.C. (2002a). Produção e composição química do capim elefante Paraíso submetida a três alturas

de corte. Anais da XXXIX Reunião Anual da Sociedade Brasileira de Zootecnia, CD, 2002.

Vilela, H., Rodriguez, N. & Dias Teixeira, E. (1997) Produções de forragem de um híbrido hexaplóide (Pennisetum glaucum X Pennisetum purpureum) e seu valor nutritivo. In: Anais da XXXIV Reunião da SBZ.

Vilela, H., Vilela, D., Barbosa F.A., Benedetti, E.(2003a). Quantidade de água suplementar para o capim elefante Paraíso. Veterinária Notícias, ISSN 0104-3463. 2003.

Vilela, H., Vilela, D., Barbosa, F.A., Benedetti, E. 2003b. Análise de crescimento do capim elefante Paraíso. Veterinária Notícias, ISSN 0104-3463.

Vilela, H., Vilela, D., Barbosa, F.A., Benedetti, E. (2002b). Irrigação do capim elefante Paraíso. Anais da XXXIX Reunião Anual da Sociedade Brasileira de Zootecnia. Julho de 2002.URPE-Recife/PE, CD.

Vuorinen, T.; Teleman, A.; Fagerström, P.; Buchert, J.; Tenkanen, M. Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of Kraft pulps. In: International Pulp Bleaching Conference, (1996). Washington. Proceedings. Washington, 1996, p. 43-51.

Wallis, A. F. A.; Wearne, R. H.; Wright, P. J. (1996). Chemical analysis of polysaccharides in plantation eucalypt woods and pulps. Appita Journal, v.49, n.4, p.258-262.

Wessel, R. A.; Tran, H.; Mahinpey, N.; Kuhn, D. (2002). Effect of particle composition on carryover deposition in recovery boilers. TAPPI Fall Conference & Trade Fair.

Zong Lai, Y. (1999).The influence of alkaline pulping conditions on the efficiency of oxygen delignification. (http://www.tappi.org/Downloads/unsorted).

CONCLUSÕES GERAIS

Através dos resultados obtidos nesse trabalho, foi possível observar que há grandes oportunidades para a produção de biocombustíveis em substituição aos combustíveis fosseis por meio de diversas rotas tecnológicas, por exemplo, por meio de pré-tratamentos alcalinos da biomassa seguidos de sacarificação e fermentação. Destacando-se nesse cenário, a indústria de celulose e papel, uma vez que a sua integração em uma plataforma de biorrefinaria seria grandemente facilitada por esta já possuir o conhecimento, e parte da infraestrutura necessária para fracionar os componentes da biomassa. Paralelamente ao aprimoramento dos pré-tratamentos, a conversão enzimática de polissacarídeos da biomassa lignocelulósica pode ser apontada como a tecnologia mais promissora para a consolidação da biorrefinarias (Capítulo 1).

Os estudos da investigação de 18 clones de eucalipto de ultima geração permitiu atestar a alta qualidade tecnológica dos mesmos. Uma análise mais criteriosa dos principais parâmetros de qualidade requeridos, quando se objetiva a produção de polpa celulósica e aplicações de biorrefinaria, permitiu a escolha dos quatro clones de eucalipto mais promissores, sendo estes: (1) *Eucalyptus urophylla* x *Eucalyptus urophylla* (U1 x U2); (2) *Eucalyptus grandis* x (*Eucalyptus urophylla* x *Eucalyptus globulus*) (G1 x UGL); (3) (*Eucalyptus dunnii* x *Eucalyptus grandis*) x *Eucalyptus urophylla* (DG x U2); e um clone comercial elite (IP). Ainda no que diz respeito a analises de potenciais matérias primas, foi possível observar que os clones de eucalipto apresentam uma maior densidade e possuem menores teores de umidade e de minerais em comparação ao capim elefante. Adicionalmente, também foi observado no material estudado uma alta correlação entre lignina solúvel e a relação S/G da lignina (Capítulo 2).

Os diferentes clones de eucalipto possuem comportamento similar quando submetidos a processos de desconstrução alcalinos. Os processos soda-AQ e kraft se mostraram mais promissores para a produção de polpa celulósica com relação ao rendimento depurado, consumo de reagentes e qualidade da fibra. O processo soda-AQ (kappa 20) pode ser utilizado para substituir o kraft (kappa 15), mantendo-se o rendimento. Os processos alcalinos que utilizam oxigênio como aditivo (soda-AQ-O_2

e soda-O_2) são mais indicados para atuarem como pré-tratamentos alcalinos visando-se processos de biorrefinaria. Analises do peso molecular dos carboidratos presentes na polpa indicaram que as xilanas são menos polidispersas que a celulose. O processo soda-AQ produziu licor negro de maior poder calorífico que o processo kraft (Capítulo 3).

Quanto ao potencial de produção de bioetanol, o processo Soda-O_2 com número kappa na faixa de 35-50 apresentou os melhores resultados de sacarificação atingindo valores superiores a 70 %. As taxas de açúcares liberados seriam suficientes para garantir um rendimento teórico de bioetanol superior a 370 L por tonelada de madeira para o processo soda-O_2. O processo soda-AQ é mais indicado para produção de polpa para papeis, por exemplo, enquanto o soda-O_2 é mais indicado como pré-tratamento para produção de etanol da biomassa lignocelulósica (Capítulo 4).

O capim elefante mostrou potencial para fabricar polpa celulósica. A sua composição química apresentou um alto conteúdo de extrativos e minerais, indicando potenciais riscos operacionais. O processo kraft foi o mais adequado para cozinhar o capim elefante até número kappa 20, produzindo rendimento de 47,9%, viscosidade de 812 dm^3/kg e boa branqueabilidade (0,217 Δkappa/cloro ativo total) (Capítulo 5).