BIANCA MOREIRA BARBOSA

ASSESSMENT OF LIGNOCELLULOSIC MATERIALS QUALITY AND FURFURAL PRODUCTION FROM CORN COBS, SUGARCANE BAGASSE, EUCALYPTUS WOOD AND DISSOLVING PULP PRE-HYDROLYZATE

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

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Fábio de Ávila Rodrigues

Carolina Marangon Jardim

Jorge Luiz Colodette
(Orientador)
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SUMÁRIO

RESUMO

BARBOSA, Bianca Moreira, M.Sc., Universidade Federal de Viçosa, julho de 2013. **Avaliação da qualidade de materiais lignocelulósicos e produção de furfural a partir do sabugo de milho, bagaço da cana-de-açúcar, madeira de eucalipto e pré-hidrolisado da produção de polpa para dissolução.** Orientador: Jorge Luiz Colodette.

Esse trabalho está apresentado em duas partes distintas, sendo a primeira focalizada na qualidade da madeira de eucalipto cultivada sob diferentes regimes de ferti-irrigação para produção de celulose (Capítulo 1) e a segunda na avaliação preliminar da qualidade da madeira de eucalipto e de outras matérias-primas, tais como bagaço da cana-de-açúcar, sabugo de milho e licor de eucalipto do processo pré-hidrólise Kraft de produção de polpa solúvel, para a produção de furfural (Capítulo 2). O grande interesse em madeira de eucalipto vem de seu baixo custo de produção em regiões tropicais, principalmente devido à alta produtividade florestal. O melhoramento genético associado ao adequado manejo florestal (fertilização, irrigação) se destaca como ferramenta importante na produção de madeira de alta qualidade e de baixo custo. O objetivo do Capítulo 1 foi avaliar o efeito do regime de ferti-irrigação na composição química e massa específica básica da madeira de clones do *Eucalyptus* spp. e suas possíveis consequências na produção de polpa celulósica. Quatro clones foram avaliados, sendo dois da espécie *Eucalyptus grandis* e os outros dois provenientes dos híbridos de *Eucalyptus grandis* x *Eucalyptus urophylla*, com a idade de 72 meses. Os tratamentos avaliados foram 2 níveis de adubação, o Tradicional não irrigado (T/NI) e o Ferti-irrigado (F/I), além do tratamento Controle (C/NI), onde não foi utilizado nenhum tipo de adubo ou irrigação, tendo cada tratamento 3 repetições, totalizando 36 amostras. Os resultados indicaram diferença estatística significativa para massa específica básica, teor de manganês, relação siringila/guaiacila da lignina e teor de grupos acetila das madeiras, e similaridade para teor de carboidratos, lignina total, ácidos urônicos, extrativos, cinzas, Fe, Ca e Mg. Conclui-se que a técnica de ferti-irrigação, apresentou alguns aspectos negativos no que tange à qualidade da madeira de certos clones de eucalipto, sendo relevante considerar os seus impactos no processo produtivo de fabricação de polpa celulósica. No Capítulo 2, considerando o conceito de biorrefinaria é possível a integração dos processos de produção de celulose aos de materiais, produtos químicos e combustíveis, a partir de biomassa lignocelulósica. Por exemplo, derivados de furano, tais como o 5-hidroximetilfurfural (HMF) e furfural originários de biomassa, têm potencial para substituir derivados do petróleo na fabricação de químicos finos e de plásticos. Foi estudado o efeito de diferentes concentrações

($1{,}5$-$5{,}2$ mol.L^{-1}) dos ácidos minerais, ácido clorídrico (HCl), ácido sulfúrico (H_2SO_4) e ácido fosfórico (H_3PO_4) na produção de furfural por hidrodestilação do sabugo de milho, bagaço da cana-de-açúcar e madeira de eucalipto. Foi também avaliado o licor pré-hidrolisado da madeira de eucalipto, proveniente do processo pré-hidrólise Kraft de fabricação de polpa solúvel para a produção de furfural, utilizando ácido sulfúrico e ácido clorídrico como catalisadores. Os resultados mostraram que a produção de furfural foi fortemente influenciada pela concentração e tipo de ácido mineral e pela matéria-prima. As maiores produtividades de furfural, com base no peso seco da biomassa, foram de 30,2% para o sabugo de milho e 25,8% para o bagaço da cana-de-açúcar, ambos utilizando HCl 5,2 mol.L^{-1}, para a madeira de eucalipto, a produtividade foi de 13,9% usando HCl 3,9 mol.L^{-1}. O rendimento de conversão de pentoses para furfural usando o licor pré-hidrolisado do eucalipto foi de 71,5%, utilizando HCl 3,9 mol.L^{-1}. Foi concluído que o uso de ácidos minerais como catalisadores por hidrodestilação é adequado para a produção de furfural a partir de resíduos lignocelulósicos oriundos de processos industriais.

ABSTRACT

BARBOSA, Bianca Moreira, M.Sc., Universidade Federal de Viçosa, July, 2013**. Assessment of lignocellulosic materials quality and furfural production from corn cobs, sugarcane bagasse, eucalyptus wood and dissolving pulp pre-hydrolyzate.** Adviser: Jorge Luiz Colodette.

This work is presented in two distinct parts, the first focused on the quality of eucalyptus wood grown for pulp production under different ferti-irrigation systems (Chapter 1) and the second on the preliminary assessment of the quality of eucalyptus wood and other materials for the production of furfural such as sugarcane bagasse, corn cobs and pre-hydrolyzed eucalyptus from the pre-hydrolysis Kraft process for dissolving pulp production (Chapter 2). The great interest in eucalyptus wood comes from its low cost of production in some regions, mainly due to high forest productivity. Genetic improvements associated with appropriate forest management (fertilization, irrigation, etc.) stand out as important tools in the production of wood of high quality and low cost. The goal of Chapter 1 was to evaluate the effect of the ferti-irrigation regime on the chemical composition and specific basic mass of wood from clones of the *Eucalyptus* spp. and possible consequences on the production of cellulose pulp. Four clones were evaluated, two being from the species *Eucalyptus grandis* and the other two coming from hybrids of Eucalyptus grandis x *Eucalyptus urophylla*, with age of 72 months. The treatments were evaluated with two levels of fertilization, the Traditional no irrigated (T/NI) and Ferti-irrigation (F/I), and a treatment Control no irrigated (C/NI), which was to not use any fertilizer or irrigation, with each treatment having three replicates, totaling 36 samples. The results indicated statistically significant differences for specific basic mass , manganese, lignin syringyl/guaiacyl ratio and acetyl group content of the woods, and similarity in carbohydrate, total lignin, uronic acids, extractives, ash, Fe, Ca and Mg. We conclude that the technique of ferti-irrigation presented some negative aspects regarding the quality of the wood of certain eucalyptus clones, it being relevant to consider their impacts on the production process for manufacturing cellulose pulp. In Chapter 2, considering the biorefinery concept it is possible to integrate the processes of pulp production to those of materials, chemicals and fuels from lignocellulosic biomass. For example, furan derivatives, such as 5-hydroxymethylfurfural (HMF) and furfural originating from biomass have the potential to replace petroleum in the manufacture of fine chemicals and plastics. The effect was studied of different concentrations (1.5 to 5.2 mol.L^{-1}) of mineral acids, hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4) on the production of furfural by hydro distillation of corn cob, sugarcane bagasse and eucalyptus wood. The liquor from the pre-hydrolysis Kraft process for dissolving pulp production was also assessed for furfural production, using sulfuric acid and hydrochloric acid as catalysts. The results showed that the production of furfural was strongly influenced by the concentration and type of mineral acid and the raw material. The highest productivity of furfural, based on the dry weight biomass were 30.2% for corn cobs and 25.8% for the sugarcane bagasse, both using HCl 5.2 mol.L^{-1}, for eucalyptus wood, the yield was 13.9% using 3.9 mol.L^{-1} HCl. The yield of conversion of pentose to furfural using the eucalyptus pre-hydrolysis liquor was 71.5% using HCl 3.9 mol.L^{-1}. It was concluded that using mineral acids as catalysts for hydro distillation is suitable for the production of furfural from lignocellulosic wastes originating from industrial processes.

INTRODUCTION

The world economy is currently undergoing major changes that have been increasingly influenced by climate change that the planet is passing through. The current need to seek renewable and alternative energy has led to the development of various technologies. Processing industries correspond to the main targets of these technologies, which in addition to seeking cleaner energy sources, have also invested efforts in search of the better use of natural resources, increasing process efficiency while reducing pressure on planted areas. Studies to correlate the use of a cleaner energy matrix and the increase in the use efficiency of natural resources have yet to relate these two factors to the quality assurance of the final product, which makes this new vision of development included in the production sectors even more challenging.

In virtue of adequate climate, large areas available for cultivation technologies for advanced agricultural and forest production and an excellent adaptation of certain crops under the tropical climate, the costs of biomass in Brazil are quite low compared with other parts of the world. Various clones of the genus *Eucalyptus* are continuously improved and cultivated in order to provide the most suitable raw material for production, according to the evaluation criteria of quality wood.

The wood quality is the factor that determines its market value and its applications in various industrial segments. For the cellulose and paper sector, wood quality has been described primarily through its physical properties such as specific basic mass and chemical composition. Thus, there is a need to study how these factors are affected throughout the growth of the tree. In general, it is found that the properties of wood are dependent on genetics, growth conditions and the age of the tree. Fertilization techniques can be used during tree growth to improve its development, but the effect of fertilization on the chemical composition of the wood has not yet been fully elucidated.

Chapter 1 discusses the effects of ferti-irrigation on the chemical composition of the wood and its specific basic mass in clones of the genus *Eucalyptus* spp., assessing its possible consequences on cellulose production. The evaluation of these factors helps in understanding the properties required for cellulose production and biomaterials production, its constitution being relevant for determining its final destination.

Lignocellulosic biomass is a renewable and available resource, which needs to be further explored, and the manufacture of products with high added value from biomass, is an important option to be pursued. Decreased dependence on fossil fuel reserves, through the intensive use of renewable materials, boosts rural development, and heads towards a modern sustainable society.

The possibility of cellulose production process integration with those of biomaterials came about from the concept of biorefineries. This new line of worldwide research seeks more rational use of fibrous materials, favoring the extraction of the various components of natural resources, minimizing waste generation and contemplating the use of the multiproducts generated.

The use of eucalyptus in the cellulose and paper industry is well established. However, the possibility of using grasses to add value to that industry, using the new biorefinery concept, has been widely studied. Fibrous materials such as bagasse and straw (composed of the sugarcane leaf and apical portion of the stem) of sugarcane, bamboo and corn cobs have good hemicellulose values in their constitution. These residues materials, being available from agricultural biomass and forestry processing, constitute a potential source for the production of chemicals such as ethanol, sugars and furfural, using enzymes or by acid-catalyzed hydrolysis.

The interest in the production of chemicals from renewable resources has increased in the last decade in direct relation to the declining reserves and rising prices of fossil fuels. The use of renewable raw materials, biomass in particular, is a good option as a new economic and environmental alternative. In this regard, furan derivatives, such as furfural and 5-hydroxymethylfurfural (HMF) can be produced from the acid catalyzed dehydration of pentoses and hexoses, respectively, contained in lignocellulosic biomass (such as corn cobs and cotton). These compounds have the potential to be sustainable substitutes for petrochemicals used in the production of fine chemicals and plastics.

Chapter 2 addresses the use of different mineral acids for the conversion of pentose, from lignocellulosic materials, into furfural. Among the lignocellulosic materials used, there is the corn cob, sugarcane bagasse and eucalypt wood, which are wastes from agroindustrial processes, besides trying to produce furfural from the eucalyptus liquor from pre-hydrolysis Kraft dissolving pulp production, which is rich in pentoses.

This study aimed to: assess the quality of *Eucalyptus* spp. under the influence of ferti-irrigation treatments to produce cellulose, in addition to a review of the effect of hydrochloric, sulfuric and phosphoric acid as a catalyst for the production of furfural associated with different lignocellulosic raw materials.

CHAPTER 1

QUALITY OF *EUCALYPTUS* SPP.WOOD CULTIVATED UNDER DIFFERENT FERTI-IRRIGATION SCHEMES FOR CELLULOSE PRODUCTION

ABSTRACT

This current paper has the objective of evaluating the effect of two levels of fertilization (NPK) on the chemical composition and on the specific basic mass of the wood of clones from the *Eucalyptus* spp., assessing its possible consequences in the production of cellulosic pulp. Four clones were evaluated, two of those being of the *Eucalyptus grandis* species and the other two proceeding from hybrids of *Eucalyptus grandis* x *Eucalyptus urophylla*, at the age of 72 months. The treatments were evaluated with two levels of fertilization, the Traditional no irrigated (T/NI) and Ferti-irrigation (F/I), and a treatment Control no irrigated (C/NI), which was to not use any fertilizer or irrigation, with each treatment having three replicates, totaling 36 samples. The analyzed chemical features were associated with the level of fertilization and the type of genetic material at stake. For the statistical analysis one used the STATISTICA 7.0 software, where one made the analysis of variation and, in the case of significant interaction, there was decomposition through the Tukey test, at the level of 5% probability. There was significant difference for the following properties: specific basic mass, manganese, lignin syringyl/guaiacyl ratio (S/G) and acetyl group content. For the remaining analyzed properties such as carbohydrate content, total lignin, uronic acids, extractives, ashes, Fe, Ca and Mg, no statistical difference was noticed. We conclude that the technique of ferti-irrigation presented some negative aspects regarding the quality of the wood of certain eucalyptus clones, it being relevant to consider their impacts on the production process for manufacturing cellulose pulp.

Keywords: fertilization, chemistry of wood, eucalyptus and specific basic mass.

INTRODUCTION

The genus *Eucalyptus* has, as representatives, the most commonly grown species in the world, with over 4.75 million hectares in Brazil (Bracelpa, 2013). It is widely employed to produce wood for various purposes, due to its rapid growth, good ecological adaptation and high versatility. *Eucalyptus grandis*, along with others such as *Eucalyptus urophylla*, is one of the most studied species. These species generally have satisfactory characteristics to be employed for various purposes, particularly for the cellulose and paper industries, hardboard and energy use, according to the quality of the wood (Berger, 2002).

For the cellulose and paper sector, wood quality has been described primarily through its physical, chemical and anatomical parameters which are considered as good evaluation parameters of its characteristics and of great use in forestry breeding programs. Thus, there is a need to study how these factors are affected throughout the growth of the tree. In general, it appears that the wood properties depend on genetics, growth conditions and the age of the tree (Mellerowicz and Sundberg, 2008; Cooke *et al*., 2005). Ferti-irrigation techniques may be used during tree growth to improve its development, because the formation of wood is highly sensitive to environmental changes.

The natural soil characteristics, as well as fertilizer and moisture content, are factors that can influence the wood quality. Changes in growth conditions, due to the application of fertilizers and the use of irrigation techniques, are often associated with significant changes in the quality of the wood. This importance refers to the physical, chemical and anatomical attributes (Pitre *et al*., 2010). However, the effects of ferti-irrigation are difficult to predict; some studies indicate an increase, others, to the contrary, show a decline in wood quality (Barreiros *et al*., 2007; Punches and Country, 2004).

The recommendations for mineral fertilizers used always refer to the elements Nitrogen, Phosphorus and Potassium, but very rarely to Boron and Zinc, which are recommended for application at planting or as top dressing applied 90 days after planting (Barros, 2012). Currently, most commercial plantations are fertilized using virtually the same N-P-K (6-30-6), regardless of species, soil type and planting time.

Nitrogen fertilization is one of the practices that has been most employed to achieve increased productivity (Macdonald and Hubert, 2002). Nitrogen is often a limiting factor for the growth of terrestrial plants, therefore, the addition of nitrogen-rich fertilizers can have profound effects on the physiology of the tree and biomass accumulation (Cooke *et al*., 2005; Gessler *et al*., 2004.) Changes at the anatomical and compositional levels have often been described in relation to N-P-K fertilization, water stress and mechanical stimuli. However, the effects of fertilization on wood quality are difficult to predict.

For the cellulose and paper industry, a proper assessment of specific basic mass provides very precise indications about the chip impregnation and process yield and is usually associated with quality traits and pulp physical-mechanical resistance. There are few studies that directly relate the interference of soil attributes on the quality of forest species (Rigatto *et al*., 2005). In this context, this study aimed to evaluate the effect of ferti-irrigation on the chemical composition and specific basic mass of *Eucalyptus* spp.

MATERIAL AND METHODS

This study evaluated two fertilization levels, the Traditional no irrigated (T/NI) and Ferti-irrigation (F/I), besides the Control (C/NI) treatment, in which fertilization or irrigation was not used. Fertilizer applications were made by topdressing applied in three doses per year for the first three years. Irrigation was tested only for the F/I treatment in which irrigation was conducted, in order to maintain an average soil humidity around 15-30 mm. This procedure was performed twice every seven days, in order to maintain moisture from precipitation and compensate for evapotranspiration.

Table 1 shows the types of treatments and their respective amounts of chemicals per hectare. The C/NI treatment was not added in the table, since there was no fertilization and irrigation.

Table 1. Nutritional conditions in kg/ha, used for the treatments, where fertilization took place.

Treatments	**Fertilization**					
	Nitrogen	**Phosphorus**	**Potassium**	**Calcium**	**Magnesium**	**Boron**
T/NI	86	40	171	705	120	3
F/I	732	145	570	918	180	8

*T/NI - Traditional no irrigated; F/I – Ferti-irrigation.

The eucalyptus species used were: *Eucalyptus grandis* (Clones A and B) and hybrids of *Eucalyptus grandis* x *Eucalyptus urophylla* (Clones A and B), originating from the city of Guanhães in the state of Minas Gerais. The trees used were 72 months old and were taken from the same 30 x 30 m planting parcel, with row spacing of 3.0 x 3.0 m cultivated in a Oxisol. We sampled three trees for each clone, considering each fertilization level and C/NI treatment, totaling 36 samples.

The wood samples for chemical analyzes were collected after their reduction into sawdust in a Wiley laboratory mill, and subsequently classified into sieves of 40 and 60 mesh. The samples were air conditioned and packed in airtight containers and their moisture content determined. All chemical analyzes were performed in duplicate.

After preparation of the samples, the following analyzes were performed: carbohydrate content (Wallis *et al.*, 1996), uronic acids (Scott, 1979), acetyl groups (Solar *et al.*, 1987), acid-insoluble lignin TAPPI T222 om-11 (Tappi, 2011a), acid-soluble lignin (Goldschimid, 1971), total lignin (insoluble lignin + acid-soluble lignin), lignin syringyl/guaiacyl (S/G) ratio (Lin and Dence, 1992), ash content TAPPI T211 om-12 (Tappi, 2012), wood extractives TAPPI T264 cm-07 (Tappi, 2007), specific basic mass of the wood TAPPI T258 om-11 (Tappi, 2011b) and metal content - Ca, Mg, Mn and Fe TAPPI T266 om-11 (Tappi, 2011c).

Experimental design

The experiment was arranged in a completely randomized design in a 3 x 4 factorial outline; three fertilization levels (C/NI, T/I and F/I) and four clones, 2 of *Eucalyptus grandis* and two hybrids of *Eucalyptus grandis* x *Eucalyptus urophylla* with 3 replications, totaling 12 treatments and 36 samples.

The results were analyzed by analysis of variance, upon noting the presence of significant interaction, the results were compared by the Tukey test at 5% level of significance. Statistical analyzes were performed using STATISTICA 7.0 software and the 3D graphs elaborated in the software MATLAB R2011b.

RESULTS AND DISCUSSION

The effect of fertilization on the four clones studied at 72 months of age was evaluated based on the specific basic mass and chemical composition of wood (glucans, xylans, galactans, mannans, arabinans, acetyl groups, uronic acids, total lignin, syringyl/guaiacyl (S/G) ratio, ash, extractives, and Ca, Mg, Fe and Mn). The average of all analyzes of the chemical composition for both clones: *Eucalyptus grandis* (Clones A and B) and hybrids of *Eucalyptus grandis* x *Eucalyptus urophylla* (Clones A and B) are shown in **Table 2**. The averages of the metal content for the four clones are shown in **Table 3**.

Table 2. Mean values of wood chemical composition, functioning as silvicultural treatment, from the clones and the 2 species of the *Eucalyptus* genre.

Species	Treatments	Glucans (%)	Xylans (%)	Galactans (%)	Mannans (%)	Arabinans (%)	Uronic acids (%)	Acetyl groups (%)	Total lignin (%)	S/G ratio	Ash (%)	Extractive (%)
Eucalyptus Grandis (Clone A)	C/NI	47.7 (a)	10.8 (a)	1.9 (a)	1.2 (a)	0.3 (a)	3.1 (a)	2.8 (ab)	30.1 (a)	2.8 (abc)	0.1 (a)	1.6 (a)
	T/NI	48.6 (a)	11.2 (a)	1.7 (a)	1.4 (a)	0.3 (a)	3.2 (a)	2.9 (a)	28.8 (a)	3.1 (a)	0.2 (a)	1.7 (a)
	F/I	49.7 (a)	10.8 (a)	1.7 (a)	1.4 (a)	0.3 (a)	3.2 (a)	2.9 (a)	29.1 (a)	2.8 (abc)	0.2 (a)	1.9 (a)
Eucalyptus Grandis (Clone B)	C/NI	49.7 (a)	11.4 (a)	1.9 (a)	1.3 (a)	0.3 (a)	3.4 (a)	2.6 (bc)	28.5 (a)	2.3 (e)	0.2 (a)	1.7 (a)
	T/NI	49.0 (a)	11.1(a)	1.8 (a)	1.4 (a)	0.2 (a)	3.2 (a)	2.6 (bc)	28.9 (a)	2.3 (e)	0.2 (a)	1.5 (a)
	F/I	50.1 (a)	11.0 (a)	1.8 (a)	1.3 (a)	0.3 (a)	3.1 (a)	2.6 (bc)	28.2 (a)	2.4 (de)	0.3 (a)	1.6 (a)
Hybrids of *Eucalyptus grandis* X *Eucalyptus urophylla* (Clone A)	C/NI	49.0 (a)	11.3 (a)	1.9 (a)	1.3 (a)	0.3 (a)	3.4 (a)	2.6 (bc)	28.8 (a)	2.7 (bcd)	0.2 (a)	1.6 (a)
	T/NI	50.0 (a)	10.7 (a)	1.8 (a)	1.2 (a)	0.3 (a)	2.7 (a)	2.5 (c)	28.3 (a)	2.8 (abc)	0.1 (a)	1.5 (a)
	F/I	48.8 (a)	11.1 (a)	1.8 (a)	1.4 (a)	0.3 (a)	2.9 (a)	2.6 (bc)	29.7 (a)	3.0 (ab)	0.2 (a)	1.6 (a)
Hybrids of *Eucalyptus grandis* X *Eucalyptus urophylla* (Clone B)	C/NI	49.2 (a)	10.6 (a)	1.8 (a)	1.2 (a)	0.2 (a)	3.2 (a)	2.5 (c)	29.1 (a)	2.6 (cde)	0.1 (a)	2.6 (a)
	T/NI	49.9 (a)	11.2 (a)	1.8 (a)	1.3 (a)	0.3 (a)	3.0 (a)	2.4 (c)	28.5 (a)	2.8 (abc)	0.2 (a)	2.4 (a)
	F/I	50.6 (a)	10.9 (a)	1.9 (a)	1.2 (a)	0.2 (a)	2.9 (a)	2.6 (bc)	27.6 (a)	2.8 (abc)	0.2 (a)	2.0 (a)

*Slashes followed by the same small letter don't differ among themselves at 5% probability (Tukey, p>0.05).

******C/NI- Control no irrigated; T/NI - Traditional no irrigated; F/I – Ferti-irrigation.

Table 3. Mean values of metal content, functioning as silvicultural treatment, from the clones and the 2 species of the *Eucalyptus* genre.

Species	Treatments	Ca (mg/kg)	Mg (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
Eucalyptus Grandis (Clone A)	C/NI	752.2 $^{(a)}$	167.7 $^{(a)}$	11.6 $^{(a)}$	7.5 $^{(ab)}$
	T/NI	618.2 $^{(ab)}$	167.0 $^{(a)}$	14.4 $^{(a)}$	7.9 $^{(ab)}$
	F/I	583.7 $^{(ab)}$	109.9 $^{(a)}$	20.3 $^{(a)}$	13.7 $^{(bcd)}$
Eucalyptus Grandis (Clone B)	C/NI	800.0 $^{(a)}$	167.5 $^{(a)}$	11.1 $^{(a)}$	10.8 $^{(abcd)}$
	T/NI	882.7 $^{(a)}$	179.4 $^{(a)}$	16.4 $^{(a)}$	12.1 $^{(abcd)}$
	F/I	750.2 $^{(a)}$	162.4 $^{(a)}$	22.5 $^{(a)}$	16.2 $^{(d)}$
Hybrids of *Eucalyptus grandis* X *Eucalyptus urophylla* (Clone A)	C/NI	465.0 $^{(ab)}$	105.9 $^{(a)}$	27.7 $^{(a)}$	9.3 $^{(abc)}$
	T/NI	522.5 $^{(ab)}$	124.6 $^{(a)}$	9.2 $^{(a)}$	7.4 $^{(a)}$
	F/I	536.7 $^{(ab)}$	91.1 $^{(a)}$	13.2 $^{(a)}$	12.1 $^{(abcd)}$
Hybrids of *Eucalyptus grandis* X *Eucalyptus urophylla* (Clone B)	C/NI	665.7 $^{(ab)}$	164.3 $^{(a)}$	13.6 $^{(a)}$	14.6 $^{(cd)}$
	T/NI	716.3 $^{(ab)}$	147.9 $^{(a)}$	13.0 $^{(a)}$	6.6 $^{(a)}$
	F/I	610.0 $^{(ab)}$	128.0 $^{(a)}$	17.7 $^{(a)}$	11.2 $^{(abcd)}$

*Slashes followed by the same small letter don’t differ among themselves at 5% probability (Tukey, $p>0.05$).

******C/NI- Control no irrigated; T/NI - Traditional no irrigated; F/I – Ferti-irrigation.

Wood polysaccharides

The glycans, which are the main carbohydrates present in the wood, maintained their levels statistically similar for all evaluated treatments (**Table 2**), as in Jian Ju *et al*. (1998) who studied the effect of 5 fertilization treatments of *Eucalyptus urophylla* with 108 months of age, and noted that fertilization did not significantly influence the carbohydrate content. Similarly, Miranda and Pereira (2002) studied the quality of *Eucalyptus globulus* with 24, 36 and 72 months of age, and verified no significant differences between the control and the treatment that received fertilization. The content of uronic acids and xylan in the wood also showed no significant differences between treatments. In the case of acetyl groups, side chains of the hemicelluloses, there was no effect of ferti-irrigation, but significant difference was observed between the clones, showing that there is influence of the genetic material on the content of acetyl groups. Among the clones tested, clone A of *Eucalyptus grandis* showed the highest levels of acetyl groups in relation to the others. The results of acetyl groups are slightly below the reference range in the literature of 2.5 to 4% (Mokfienski *et al*., 2004), however, in the work done by Gomide *et al*. (2005) results were obtained that are consistent with the data presented in the present study, with mean values ranging from 2.6% to 3.1%.

Lignin

Lignin, the second largest wood quantitative constituent, had its content determined by summing the values of the acid soluble and insoluble fractions. There were no significant differences among treatments for total lignin content (**Table 2**). The results of this study are consistent with Miranda and Pereira (2002), Jian Ju *et al*. (1998), and Andrade *et al*. (1994) who studied the effect of fertilizer on *Eucalyptus* spp. observed no influence on the total lignin content.

S/G Ratio

From a structural standpoint, lignins can be divided into two main classes, namely: guaiacyl lignin (predominant in softwoods) and syringyl/guaiacyl lignin (prevalent in hardwoods).

The S/G ratio is the amount of units derived from sinapyl alcohol (syringyl monomers) in reference to the content of coniferyl alcohol (guaiacyl monomers) of the lignin (Sixta, 2006). The syringyl lignin structure is more reactive, so it is believed that wood with a high S/G ratio are easier to delignify.

In this work, there was a statistically significant differences among clones for the lignin S/G ratio (**Table 2**), indicating no influence of the genetic material. In the work of Magaton *et al*. (2006) a mean value of 2.0 for the S/G ratio in *Eucalyptus grandis* x *Eucalyptus urophylla* was found. The *Eucalyptus grandis* clone B showed the lowest S/G values, which is unfavorable for the process of wood conversion into cellulose, because it hinders the wood delignification process, since the lignin is more condensed (Gomes, 2008).

The ferti-irrigation had no effect on the treatments for the lignin S/G ratio from a statistical point of view. However, numerically, the Ferti-irrigation treatment showed higher values than the Control non-irrigated treatment.

Ash

The principal mineral components of wood are Ca, K and Mg, Ca being the element in larger amounts, representing up to 50%, followed by K, Mg, Mn, N and P, respectively, among others (Cutter and Murphy, 1978).

Some forest species have, as reserve material, oxalate, phosphate and silicate crystals, and others, in their makeup, forming bonds with the carboxylic acids of the chemical components of the cell wall. These crystals are often present in parenchyma cells occupying the lumen as reserve material (Sjöström, 1993). The shape and the amount of these crystals will depend on genetic and environmental factors.

In *Eucalyptus* species, these crystalline formations are rare, however, in these forest species oxalates formations, especially calcium, may be a result of various factors, including mineral deficiency. In soils with high acidity, high rainfall, low amount of available nutrients and cation leaching, the plant resorts to storing this mineral, in order to maintain its normal development during seasonal growth periods (Gonzales *et al*., 2009; Cumming *et al*. 2001).

For species assessed in this study, the ash content was not significantly different for all treatments (**Table 2**). The ash contents were found in the range of 0.1 to 1.0% based on dry wood, these values being in agreement with those found by other authors, such as Oliveira *et al*. (2012), Neves *et al*. (2011).

Extractives

The wood extractives, that comprise a large number of components, which, unlike most of the lignin and polysaccharides, can be extracted by means of organic solvents, showed statistically significant for all clones (**Table 2**). The results indicate that there is significant influence of the genetic material, but there was no effect of ferti-irrigation on the content of extractives for the clones, as in Miranda and Pereira (2002), who also observed in their studies no effect of fertilization on the content of extractives.

Metal Content

The highest amount of minerals was found in the bark, which may amount to more than 10 times the amount present in the wood. Among the minerals occurring in greater quantities we can cite calcium, potassium and magnesium, followed respectively by Mn, Na, Cl and P (Andrade, 2011).

Regarding the metal content for the four clones in this study, Ca, Mg, and Fe content showed no statistical difference. Only for the element Mn were statistical differences observed between the clones, a fact that shows the influence of the genetic material, as shown in **Table 3**. There was a trend of increasing Mn content in the Ferti-irrigation treatments compared to the non-irrigated control. This is an undesirable result because transition metals can cause encrustation, besides catalyzing the decomposition of peroxides during the cellulose production process. The decomposition of peroxide leads to the production of free radicals such as hydroxyl and hydroperoxide that degrade the carbohydrate chains, lowering the viscosity of the cellulose (Colodette *et al*., 1993; Thakore *et al*., 2005).

Interaction of metal contents versus specific basic mass

Generally woods of *Eucalyptus* species have low metal content, but if we analyze the wood of younger individuals aged close to two years, we will see that there is a higher metal content, this fact can be related to a more accelerated plant growth due to a greater absorption of nutrients from the soil, caused by higher cell metabolism during this development phase. Associated with nutrient availability, irrigation influences the mobility of nutrients in the soil, favoring their absorption by the plant.

Trees older than two years may also exhibit greater amount of mineral elements in the wood constitution, this fact can be related to fertilization techniques, for example, the use of intensive soil fertilization associated to irrigation, which may result in faster growth and a possible reduction in its specific basic mass .

Among the minerals absorbed by most plants we can cite manganese, magnesium, iron and calcium.

The main form of manganese absorption by plants is as Mn^{2+}, being absorbed by the roots and translocated through the xylem, along with other mineral elements dissolved in the sap. In tropical acid soils its availability is higher, and this characteristic decreases with increasing pH of the soil (Bertolazi *et al*., 2010).

Figure 1 shows the relationship between specific basic mass and concentration of manganese (Mn) and magnesium (Mg), where the clones for C/NI treatment, which are devoid of fertilization and irrigation, are represented.

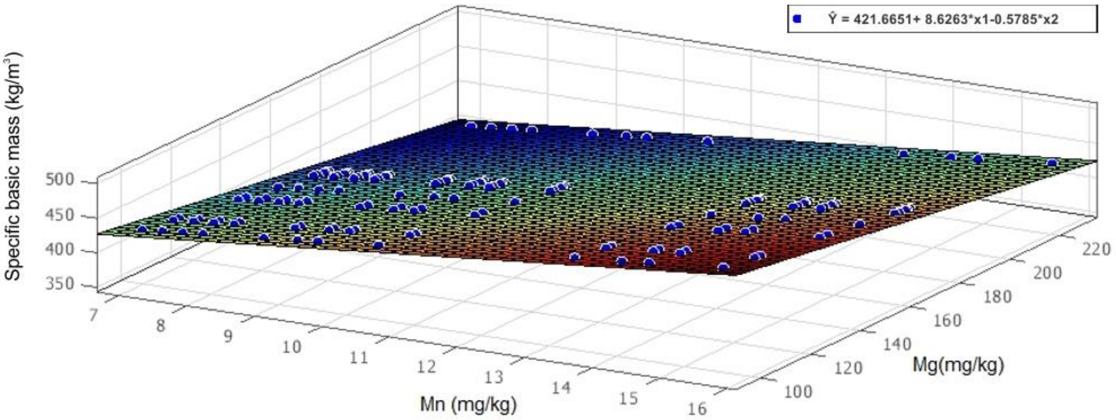

Figure 1. Graph of the relation between the values of specific mass (kg/m^3), manganese concentration (mg/kg) and magnesium (mg/kg) in the wood of two tested species, for the C/NI treatment.

In **Figure 1**, we see that as the specific basic mass of the clone in the C/NI treatments increases, we note the Mn increases and the Mg decreases. This fact may be related to a possible competition between the elements Mn and Mg, the first of which inhibits the absorption of certain nutrients by plants, including the Mg (Correia and Durigan, 2009; Mukhopadhyay and Sharma, 1991).

Figure 2 graphically shows the values for the relationship between the specific basic mass and concentration of manganese (Mn) and magnesium (Mg) in the wood of ther 4 clones of the F/I treatment.

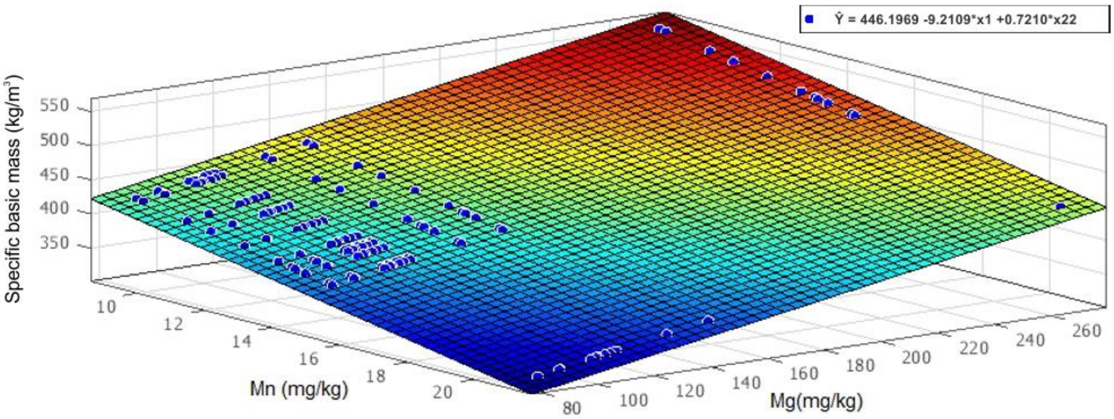

Figure 2. Graph of the relation between specific mass values (kg/m^3), manganese concentration (mg/kg) and magnesium (mg/kg) in the wood of two tested species, for the F/I treatment.

In **Figure 2** it can be seen that there was a decrease in the specific basic mass of the element associated with an increase of Mn and a decrease of Mg. The trees with more growth tend to have a lower specific basic mass associated to greater absorption of nutrients. Mn, as it is an element with lower mobility in the plant, tends to be absorbed in higher quantities and accumulate in certain parts of the wood, consequently also causing a reduction in the absorption of magnesium, since they compete (Bertolazi *et al*., 2010; Correia and Durigan, 2009; Mukhopadhyay and Sharma, 1991). According Bertolazi *et al*. (2010) one of the ways to increase the availability of manganese in the soil is associated with fertilizer application.

Figure 3 graphically presents the values for the relationship between the specific basic mass and the concentration of iron (Fe) and calcium (Ca) in the wood of the 4 clones of the C/NI treatment.

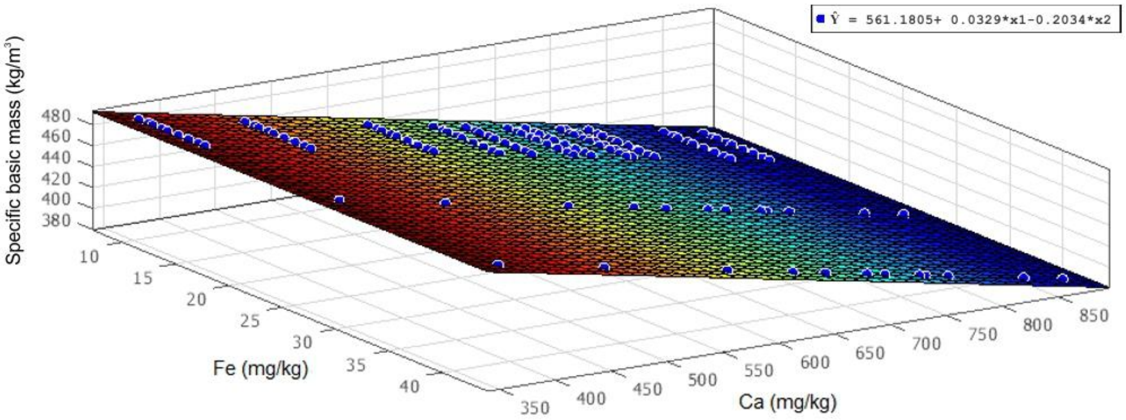

Figure 3. Graph of the relation between the specific mass (kg/m^3), concentration of Fe (mg/kg) and Ca (mg/kg) in the wood of two tested species, for the C/NI treatment.

Analyzing **Figure 3,** it can be seen that there was an increase in specific basic mass accompanied by an increase in the amount of iron, and a reduction of the amount of calcium, considering the values for the two species.

The soils of origin of the species studied was the oxisol, which has a low pH, combined with a high amount of aluminum, which increases its toxicity to plants. Calcium absorption by trees in soils with low nutrient availability, in addition to low pH, favors its storage by the plant, as a reserve nutrient, so that it can complete its development during inhospitable times (Gonzales *et al*., 2009) .

One possible explanation for the high iron content is in the content of manganese. Woods with high density, present lower amounts of manganese in relation to the low specific basic mass , the Mn being a competitor of the Fe

In **Figure 4** graphically showns the values for the relationship between the density and the concentration of iron (Fe) and calcium (Ca) in the wood of the 4 clones of the F/I treatment.

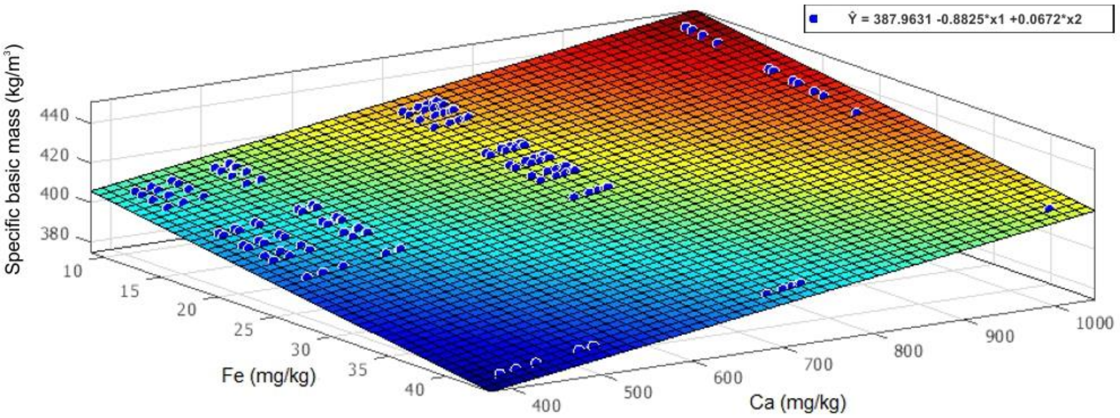

Figure 4. Graph of the relation between specific mass values (kg/m^3), concentration of Fe (mg/Kg) and Ca (mg/Kg) in the wood of two tested species, for the F/I treatment.

In the **Figure 4** graph of it can be seen that with the decreasing values of specific basic mass, there is an increase of iron content and a reduction in the calcium content of the wood of the clones for both species.

With irrigation associated to fertilization the availability and mobility of the soil nutrients increases, favoring their higher absorption by the plant and thus, greater development. Trees with rapid development, in general, show a reduction in their specific basic mass and low calcium accumulation (Gonzales *et al*., 2009).

It can be seen in **Figure 4** that the iron content increased with decreasing specific basic mass , which probably can be associated with the competition of manganese with iron and also the occurrence of a larger amount of Fe^{2+} in the soil, which is soluble and can be absorbed by the plant in greater amounts, especially in irrigated crops (Mendonça *et al*., 2005).

Other factors, such as genetic characteristics and environmental conditions, may also influence the concentration of elements in different plant tissues, causing changes in nutrient use efficiency (Silva, 2011).

Specific basic mass

One of the most important properties of wood for cellulose production is its specific basic mass, because it is directly related to the specific consumption of the wood, i.e. the volume of wood needed to produce a given mass of cellulose. The higher the specific basic mass, the lower the wood consumption. This characteristic is strongly associated with the wood anatomy, with those less dense overall, having a higher pore diameter, which facilitates the penetration of the reagents during the wood chemical deconstruction process.

In **Figure 5**, presents the specific basic mass values for the four clones and their treatments.

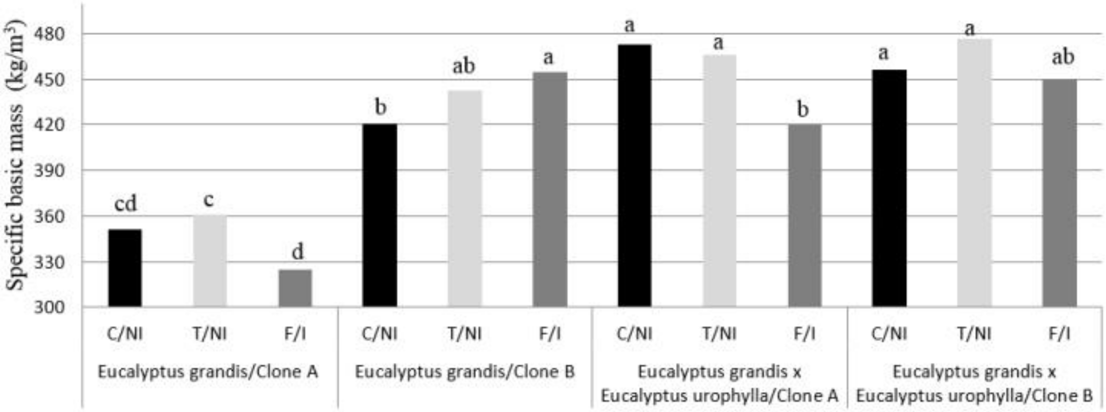

Figure 5. Mean values of specific basic mass of kg/cm^3 clones, functioning as treatments, being: C/NI - Control no irrigated**;** T/NI - Traditional no irrigated; F/I - Ferti-irrigation. Slashes followed by the same small letter don't differ among themselves at 5% probability (Tukey, p>0,05).

Through the analysis of **Figure 5**, one can see that the means for the specific basic mass variable of the F/I treatments were lower in comparison with the other two treatments, (C/NI and T/NI). This fact can be explained by greater tree growth, when subjected to a stimulus caused by the increased availability of nutrients in the soil.

The variation of the specific basic mass is not only linked to the fertilization factor, other factors, such as genetic variation, water and light availability, the location of the tree in the stand and spacing between individuals, also affect the specific basic mass . In previous studies, the effect of fertilization on specific basic mass was also observed, where it decreased with the use of fertilizer (Berger, 2000).

Figure 5 shows that for clone A of the *Eucalyptus grandis* species, the variation in specific basic mass between treatments C/NI and F/I was 8%, and for clones A and B of the hybrid *Eucalyptus grandis* x *Eucalyptus urophylla* it was 11.2 and 1.3%, respectively, values that are close to those found in the works cited by Berger (2000).

In Clone B of *Eucalyptus grandis* a decrease in the specific basic mass was not observed; there was an increase. This fact may be related to the type of genetic material in the individuals of this clone. Vital (1990) in his work, cites conflicting results, from the decrease to the increase of this property, caused by fertilization.

CONCLUSIONS

Overall, the ferti-irrigation caused a reduction in the specific basic mass of the wood , except for the clone B of *Eucalyptus grandis* which had its specific basic mass increased because of ferti-irrigation. The syringyl/guaiacyl ratio, manganese content and acetyl group contents were influenced by the type of genetic material, with no effect of ferti-irrigation on such properties.

The ferti-irrigation technique, showed some negative aspects regarding the quality of the wood of certain eucalyptus clones, it being relevant to consider the impact if this technique on the cellulose manufacturing production process.

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CHAPTER 2

PRELIMINARY STUDIES ON FURFURAL PRODUCTION FROM LIGNOCELLULOSICS

ABSTRACT

This study focused on the production of furfural from agricultural and industrial biomass residues by the hydrodistillation process. Corn cobs, sugarcane bagasse and eucalypt wood were treated with sulfuric, hydrochloric and phosphoric acids as catalysts, with different acids concentrations (1.5 to 5.2 mol.L^{-1}). In addition the eucalyptus liquor from pre-hydrolysis Kraft dissolving pulp production process was also investigated as a source of furfural, using sulfuric and hydrochloric acids as a catalyst (0.9 and 3.9 mol.L^{-1}). It was shown that furfural production is strongly influenced by the acid catalyst concentration, the source of mineral acid and the raw material. Furfural productivity of 30.2, 25.8 and 13.9% were achieved for corn cob, sugarcane bagasse and eucalypt wood, respectively, on the basis of biomass dry weight. Conversion yield of pentose into furfural were 90.5, 83.6, 110.6% for corn cob, sugarcane bagasse and eucalypt wood, respectively The HCl requirements were 5.2 mol.L^{-1} for both corn cob and sugarcane bagasse and 3.9 mol.L^{-1} for eucalypt wood. The yield of conversion from pentose to furfural using eucalypt liquor from the pre-hydrolysis Kraft process was 71.5% using HCl 3.9 mol.L^{-1}. So, it can be concluded that the use of hydro distillation process was a very effective method for the furfural production from lignocellulosic residues by mineral acid catalysis. The most attractive raw material was corn cobs which resulted in the highest furfural production (ex: 302 kg furfural/ dry ton of biomass), with sugarcane bagasse coming second.

Keywords: Furfural, mineral acids, pre-hydrolysis, lignocellulosic material.

INTRODUCTION

The interest for chemical production based on renewable source has increased in the last decade due the declining reserves and increasing prices of fossil materials. Among the different types of available biomass, agricultural crops, non-woody materials, annual plants or grasses present a special interest due to their abundance, renewability and inexpensive source to obtain polymeric materials, energy or chemicals (Egüés *et al.*, 2012a; Egüés *et al.*, 2012b; Serrano *et al.*, 2010).

Agricultural and agro-industrial residues are mainly constituted by three structural components (lignin, cellulose and hemicellulose) and each compound has specific properties destined for different uses for chemical production. Biomass residues available from agricultural and forest processing constitute a potential source for chemical production such as ethanol, reducing sugars and furfural, using enzyme or acid-catalyzed hydrolysis. All pentosans containing fibrous material could in theory be used as raw material for furfural production; however, the furfural industrial production requires minimum pentosans content around 15 to 20% (Yahyazadeh, 2011). Only about one third of the pentosans in the raw materials can be converted into furfural by means of existing production processes.

Furfural is an important chemical because it is a selective solvent for separating saturated and unsaturated compounds in petroleum refining, gas, oil and diesel fuel and for the high demand of its derivatives, especially furfuryl alcohol, used mainly in the production of furan resins for foundry sand binders, which is consider the major market for furfural (Vázquez *et al.*, 2007). So far, there is no synthetic route available for furfural production in the chemical industry, consequently it is exclusively produced by acid hydrolysis and dehydration of pentoses (mainly xylose) contained in lignocellulosic biomass (like corn cobs, cotton stalk, sunflower stalk, sugarcane bagasse, etc.) (Riansa-ngawong and Prasertsan, 2011; Vázquez *et al.*, 2007; Yemiş and Mazza, 2011).

There are two main types of technologies to produce furfural. First one it is an one-stage technology, when the pentosans depolymerization in xylose and dehydration to furfural occur simultaneously (Perego and Bianchi, 2010; Serrano *et al.*, 2010). The second one is the two-stage technology, when the dissolution and depolymerization of pentosans occur under mild conditions, followed by dehydration of xylose to furfural (Sánchez *et al.*, 2013). The advantage of the two-stage technology is that the residual lignocellulose is less degraded and can be used for conversion to other chemicals (glucose, ethanol, phenols, etc.) in a subsequent step. The scheme of reactions for furfural production is given in **Figure 1** (Ribeiro *et al.*, 2012).

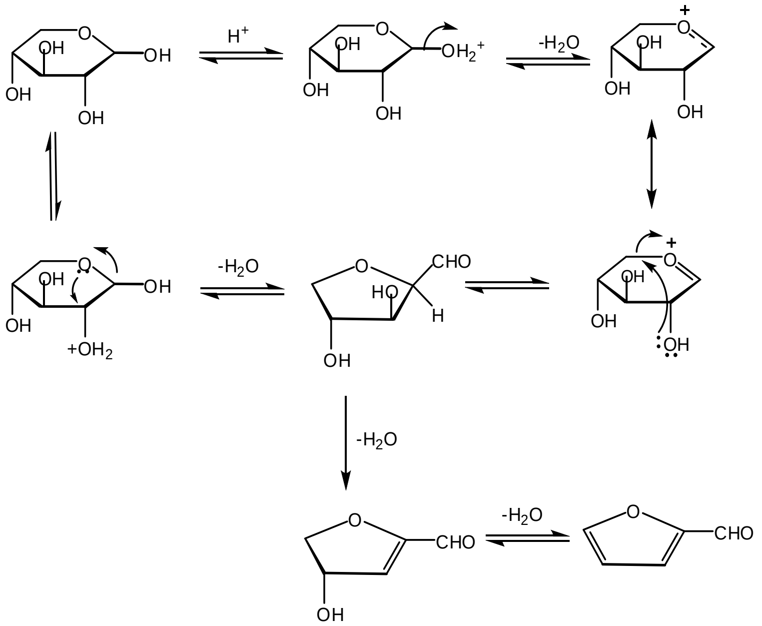

Figure 1. Dehydration of xylose to form furfural (Ribeiro *et al.*, 2012).

Several researchers investigated the production of furfural by hydrolysis of lignocellulosic residue materials in the presence of mineral acid as catalyst, such as hydrochloric acid - HCl (Herrera *et al.*, 2004; Lavarack *et al.*, 2002; Yemiş and Mazza, 2012), nitric acid - HNO_3 (Rodríguez-Chong *et al*., 2004), sulfuric acid - H_2SO_4 (Bamufleh *et al*., 2013; Riansa-ngawong and Prasertsan, 2011; Yat *et al*., 2008) and phosphoric acid - H_3PO_4 (Gámez *et al*., 2006; Lenihan *et al*., 2010; Vázquez *et al*., 2007). Raw materials used to furfural production reported in the literature included sugarcane bagasse (Gámez *et al*., 2006; Rodríguez-Chong *et al*., 2004), timber (Yat *et al*., 2008), date-palm trees (Bamufleh *et al*., 2013), sorghum straw (Herrera *et al*., 2004; Vázquez *et al*., 2007), eucalypt (García-Domínguez *et al*., 2013), corn cobs (Garrote *et al*., 2007; Sánchez *et al.*, 2013), rice hull (Mansilla *et al.*, 1998) and rice straw (Amiri *et al.*, 2010).

Currently, many studies have been developed for using lignocellulosic materials as feedstock for chemicals production, such as furfural, for example (Sánchez *et al.*, 2013; Liu *et al.*, 2013). In this context, are applied the biorefinery concept, which use pretreatments for an organized deconstruction of the biomass aiming bioproducts and chemicals production. Among the pre-treatments for lignocellulosic biomass, the pre-hydrolysis treatment recovers high quantities of hemicelluloses, converting them into soluble saccharides, while both cellulose and lignin are largely retained in the solid phase (Liu *et al.*, 2010). The solid fraction obtained from the pre-hydrolysis treatments can be used for bioethanol production or some biobased added-value products (Batalha *et al.*, 2012; Behin and Zeyghami, 2009). The liquid hemicellulose-rich stream, can be used as raw material for furfural, hydroxymethylfurfural and alcohol production and to extract phenols from the dissolved lignin fractions (Garrote *et al.*, 2006; Carvalheiro *et al.*, 2008; Alvarado-Morales *et al.*, 2009; Garrote *et al.*, 2004).

The aim of this study was investigating furfural production from corn cob, sugarcane bagasse and eucalypt wood using different concentrations of mineral acids (hydrochloric, sulfuric and phosphoric acids) through the acid-catalyzed hydrolysis process. In addition, the eucalypt liquor from the pre-hydrolysis Kraft process was investigated for furfural production, using hydrochloric and sulfuric acid as catalysts.

MATERIALS AND METHODS

Materials

Corn cob (CC) and sugarcane bagasse (SCB) harvested at Federal University of Viçosa, a Brazilian experimental station, and also, the *Eucalyptus urophylla* x *Eucalyptus grandis* chips (EUCA) supplied by a Brazilian forest company were used in this study. The raw materials were dried at room temperature and grinded in a laboratory mill, then sieved and classified according to T257 cm-12 standard procedure (Tappi, 2012a). All samples were extracted with ethanol/toluene 1:2, ethanol 95% and hot water and subjected to moisture determination in accordance with T264 cm-07 (Tappi, 2007).

Quantitative Chemical Characterization

The carbohydrate composition of raw materials was determined by High Performance Anion Exchange Chromatography with Pulse Amperometric Detection (HPAEC-PAD) after pre-treatment (30°C, 1 h) of the materials with aqueous 72% H_2SO_4 followed by hydrolysis with 3% H_2SO_4 in an autoclave (100°C, 3 h). HPAEC-PAD was carried out in a Dionex ICS-3000 system equipped with a CarboPac PA1 (250 x 4mm) analytical column. The monosaccharides were separated isocratically with 0.001 M NaOH (45 min, flowrate 1 mL/min) according to (Wallis *et al.*, 1996). The solid residue after hydrolysis was considered as Klason lignin according to T222 cm-11 standard procedure (Tappi, 2011). Ashes were determined by calcination according to TAPPI standard T211 om-12 (Tappi, 2012b). Acid soluble lignin was determined by measuring the UV-absorbance of the filtrate at 205 nm according (Goldschimid, 1971). Total uronic acids in raw materials hydrolysates were measured by the colorimetric method involving 3,5-dimethylphenol addition according to Scott (1979). The acetyl group content in samples wood was determined according to Solar *et al.* (1987). All results were calculated from two replicate determinations.

Pre-hydrolysis (PH)

The pre-hydrolysis treatment for EUCA chips was carried out in 7 liter M/K digester equipped with a heat exchanger, circulating pump, and computer-controlled time and temperature, under the following fixed conditions: 1000 g oven-dry (OD) of chips, 4/1 (m^3/t) liquid/material ratio, 170°C maximum temperature, 90 minutes to maximum temperature, 15 minutes at maximum temperature, and 2.5 to 3.0 final pH.

Hydro distillation

Furfural production in the two-stage process was carried out initially with a pre-hydrolysis of 1 g OD sample in a boiling flask with 100 mL of mineral acids at different concentration and reflux times (time was recorded immediately after initiation of boiling). The flask was connected to the simple distillation apparatus, so it was added 300 mL of mineral acids into separatory funnel, previously assembled as in T223 cm-10 (Tappi, 2010). During the boiling time, furfural was recovered by steam distillation. In the next step, the hydrolysate was heated and the distillate was collected in a 500 mL erlenmeyer flask immersed in an ice bath. For each 30 mL of hydrolysate obtained in the distillation, it was added 30 mL acid until reached 300 mL of hydrolysate. Results were calculated from two replicate determinations.

Furfural production

The raw materials (CC, SBC and EUCA) were used for furfural production by hydro distillation, while the hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) were used as catalysts to improve the reaction. The experimental parameters of the acid catalysts concentrations used, for each raw material was following concentrations: 1.5; 2.3; 2.6; 3.0; 3.9 and 5.2 mol.L^{-1}.

From the hemicelluloses present in the EUCA pre-hydrolysate, furfural was obtained by two different experimental designs. In the experimental design with H_2SO_4 the following conditions were used: temperature 170°C, 0.9 mol.L^{-1}, 3 hours reaction time and 3/1 liquid/solid ratio (Mamman *et al.*, 2008). The experimental design with HCl (3.9 mol.L^{-1}) used to determine the maximum production of furfural was by hydro distillation transformations of pentoses into furfural.

Furfural quantification

Furfural was determined using a spectrophotometric method developed by Nascimento *et al.* (1998). The analysis is based on the reaction of furfural with aniline in acetic acid and ethanol 95% to stabilize the colour. The test was conducted in the dark and under stirring for 15 minutes. Spectral analyses were done at 510 nm (Varian Cary 50 Probe UV-visible, U.S.A.) and compared with a calibration curve for pure furfural, and the furfural productivity was calculated by according to Equation 1:

$$\%\ \text{Furfural productivity} = \frac{w_0}{w_1} \text{ x } 100\ \% \qquad (1)$$

where: w_0= furfural mass concentration of total distillate; w_1= the total mass of raw material.

The furfural conversion yield was calculated according to Equation 2:

$$\%\ \text{Furfural yield} = \frac{w_0}{w_2} \text{ x } 100\ \% \qquad (2)$$

where: w_0= furfural mass concentration of total distillate; w_2= the mass of pentose (xylose and arabinose) in raw material.

RESULTS AND DISCUSSION

Chemical composition of raw materials

The chemical compositions of CC, SCB and EUCA (percentage on oven-dry weight basis) are showed in **Table 1**, based on two replicate determinations. The raw materials are defined by their content of glucose, xylose, arabinose, galactose, mannose, acetyl groups, lignin, ash and uronic acid. Due to the presence of ash, acid insoluble lignin analysis gave an overestimation to lignin content; therefore, the lignin values were corrected by their ash content (Anglés *et al.*, 1997).

Table 1. Chemical composition results of CC, SCB, EUCA and reported by other authors.

Component,%	**Corn cob (CC)**			
	Results	**Van Dongen *et al.*, 2011**	**Lili *et al.*, 2011**	**Garrote *et al.*, 2007**
Glucose	47.1	34	34.6	34.3[a]
Xylose	28.0	28	27.0	31.1[a]
Arabinose	5.4	2.4	3.6	3.01[a]
Galactose	2.2	0.8	-	-
Mannose	0.2	0.1	-	-
Acetyl groups	2.9	-	0.3	3.07
Uronic acids	2.2	1.8	-	3.45
Lignin[c]	17.8	18.3	9.4[b]	18.8
Ash	1.2	-	2.5	1.3
Component,%	**Sugarcane bagasse (SCB)**			
	Results	**Hamzeh *et al.*, 2013**	**Alves *et al.*, 2010**	**Canilha *et al.*, 2007**
Glucose	46.4	40.5[d]	43.1	48.2
Xylose	28.2	14.5	23.8	24.8
Arabinose	2.6	2.2	1.5	1.66
Galactose	1.0	2.6	0.4	-
Mannose	1.0	-	0.3	-
Acetyl groups	3.0	-	3.0[e]	2.83
Uronic acids	1.5	-	1.2	-
Lignin[c]	21.4	28.2	23.2	24.1
Ash	2.3	4.8	2.5	-

Component,%	Eucalypt (EUCA)			
	Results	**García-Domínguez *et al.*, 2013**	**Batalha *et al.*, 2012**	**Alves *et al.*, 2010**
Glucose	53.1	42.8	47.9[a]	46.5
Xylose	12.3	17.1	11.2[a]	12.1
Arabinose	0.3	0.4	0.1[a]	0.5
Galactose	2.1	-	0.9[a]	1.2
Mannose	1.4	-	0.9[a]	1.0
Acetyl groups	2.8	3.5	2.0	2.8[e]
Uronic acids	3.1	-	5.9	2.2
Lignin[c]	30.1	21.2	26.6	29.2
Ash	0.2	0.2	0.3	0.3

[a] All sugars expressed as anhydro-units in polymers;
[b] Lignin values were measured as acid insoluble lignin contents;
[c] Lignin values were measured as acid insoluble lignin contents and acid soluble;
[d] Glucose values measured were α-cellulose contents;
[e] Acetyl groups values were measured by NMR.

Also, the data showed that the pentose content (xylose + arabinose) were 33.4% for CC, 30.8% for SCB and 12.6% for EUCA, which constitute an adequate content comparable to that found in wheat hulls, cotton seeds, and nut shells commonly used for furfural production. Because of the current importance of lignin as a raw material for the production of bioproducts and biofuels (Buranov and Mazza, 2008), samples were also analyzed for their acid insoluble lignin and acid soluble lignin.

The chemical composition of CC showed that total lignin was 17.8%, while their uronic acid and ash contents were 2.2% and 1.2%, respectively. In relation to glucose content (47.1%), the experimental result was higher than reported by other authors (Van Dongen *et al.*, 2011; Lili *et al.*, 2011; Garrote *et al.*, 2007), fact which can be explained by the method used by each author for quantification of carbohydrates. Values of xylose, 28.0%; arabinose, 5.4%; mannose, 0.2%; and acetyl groups, 2.9%; for samples determined in this study are closely comparable to those reported by them (Van Dongen *et al.*, 2011; Garrote *et al.*, 2007) for similar samples.

The structural carbohydrates (glucose and xylose) which are the major substrates for furan production, accounted for approximately 74.6% of the SCB (**Table 1**). These values are in the range found by other workers for this kind of materials (Alves *et al.*, 2010; Canilha *et al.*, 2007; Hamzeh *et al.*, 2013). It is well known that pentoses and hexoses, respectively, are the precursors for furfural and HMF formed during the conversion of lignocellulosic biomass (Yemis and Mazza, 2011). Determination of the initial quantity of the main constituents available in biomass allowed for the calculation of the yields and theoretical conversion rates of furfural from raw material for calculation of efficiency of furfural production.

The chemical composition of the *Eucalyptus urophylla* x *Eucalyptus grandis* hybrid was similar to reported for other eucalyptus reported by other authors (Batalha *et al.*, 2012; Alves *et al.*, 2010), except in relation to glucose content (53.1%) as showed in **Table 1**. However, glucose values similar to the one observed in this work has been previously reported (Mokfienski *et al.*, 2008).

Pre-hydrolysis

The pre-hydrolysis (PH) has the advantage or removing significant amounts of xylans. In comparison to acid hydrolysis, autohydrolysis generates lower quantities of byproduct, minimizes equipment corrosion, and decrease operational costs. The eucalypt xylan content decreased 48.9%, from 12.3% in the original material to 7.1% in the PH chips. The yield loss in the pre-hydrolysis treatment was 11.4%, (**Table 2**). According to a literature, the liquor derived from the PH treatment contains a mixture of sugar oligomers mostly xylo-oligosaccharides (XOS), monosaccharides (xylose and arabinose), acetic acid (from acetyl groups) and sugar decomposition products. Moreover, it was found that the formation rate of these compounds depends on the autohydrolysis conditions, e.g. temperature and reaction time, in agreement with previous reports (Pu *et al*., 2011; Garrote *et al.*, 1999).

Table 2. Eucalypt chip Pre-hydrolysis (PH) result.

PH Result	Yield, %	Xylans, % on wt.	Xylans Removal, %	Spent liquor pH	Hydrolyzate solids, %
EUCA	88.6	7.1	48.9	2.5	2.2

Furfural production

Sulfuric, hydrochloric and phosphoric acids are widely used as catalysts in industrial furfural production. The results of **Figure 2** indicate the productivities of the furfural production with different acids for CC, SCB and CC. The furfural productivity increases with increasing acid concentration regardless of raw material and acid type. The highest furfural productivities were achieved with HCl as catalyst. Based on the biomass dry weight, productivities of 30.2, 25.8 and 13.9% were obtained for CC, SCB and EUCA, respectively.

This productivity was achieved with 5.2 mol.L^{-1} HCl for CC and SCB and 3.9 mol.L^{-1} HCl for EUCA. When H_2SO_4 was used as catalyst, the maximum productivities attained were 27.3, 21.0 and 11.4% for CC, SCB and EUCA, respectively, under the same acid molar concentrations previously reported for HCl. In the case of H_3PO_4, the highest furfural productivities were 26.0, 18.2, 7.6 for CC, SCB and EUCA, respectively, under the same acid molar concentrations previously reported for HCl.

Yemis and Mazza (2010) reported an increase in furfural productivity from xylose from 9.3 to 36.1 g/100 g when the HCl concentration increased from 0.01 to 0.1 mol.L^{-1}. Recently, Rong *et al.* (2012) reported that the furfural productivity was higher in high concentration of H_2SO_4 systems compared to that in low concentration and the highest furfural conversion efficiency (75%) was achieved with 10% (w/w) H_2SO_4, but the conversion efficiency decreased to 51% when the concentration of H_2SO_4 was raised to 12.5% (w/w).

The fact that the highest furfural productivity obtained in this study was with HCl can be explained by the greater availability of H^+ ions in HCl solutions compared to phosphoric and sulfuric acid solutions at a given molar concentration. Similar results have been reported by (Yemiş and Mazza, 2011) comparing the effect of four strong mineral acids (hydrochloric, sulfuric, nitric, and phosphoric acids) and two organic acids - acetic (CH_3COOH) and formic acids (HCOOH) on furfural yield. The furfural productivities obtained from xylose in the presence of HCl, H_2SO_4, HNO_3 (nitric acid), H_3PO_4, CH_3COOH and HCOOH were 37.5%, 31.9%, 3.5%, 27.6%, 15.8%, and 23.8% at pH 1.12, respectively.

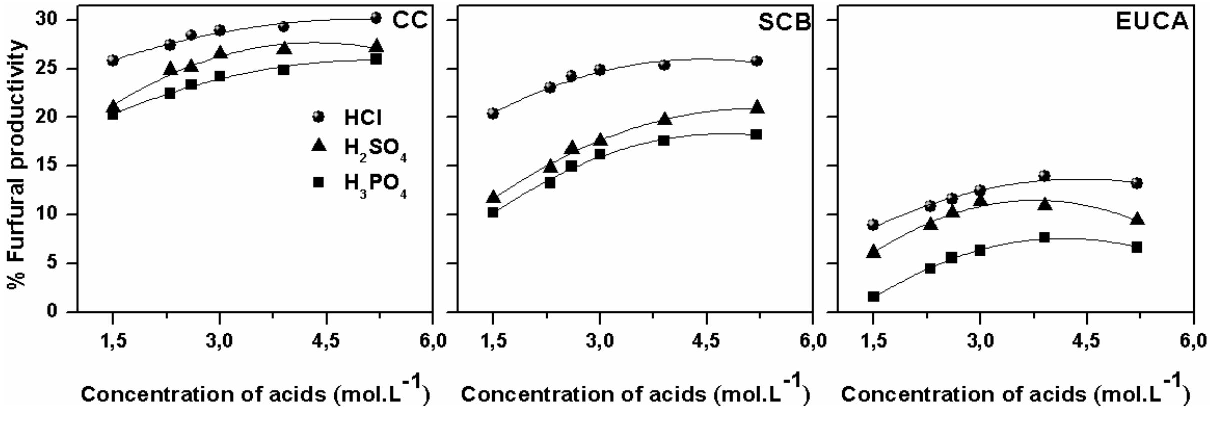

Figure 2. Furfural productivities on the basis of CC, SCB, and EUCA dry weight for various mineral acid catalysts concentrations.

The gradual decrease in furfural concentration beyond the maximum value achieved indicates that beyond certain achieved furfural concentration the rate of furfural loss to decomposition products becomes higher than the rate of furfural production. Moreover, the nature of the solvent chosen and the biomass type were the major factors influencing conversion of pentose to furfural. So, the furfural conversion yield is an important parameter, for each raw material used in this study, in order to know the rate of pentose conversion into furfural. The results for furfural conversion yield are shown in **Figure 3**.

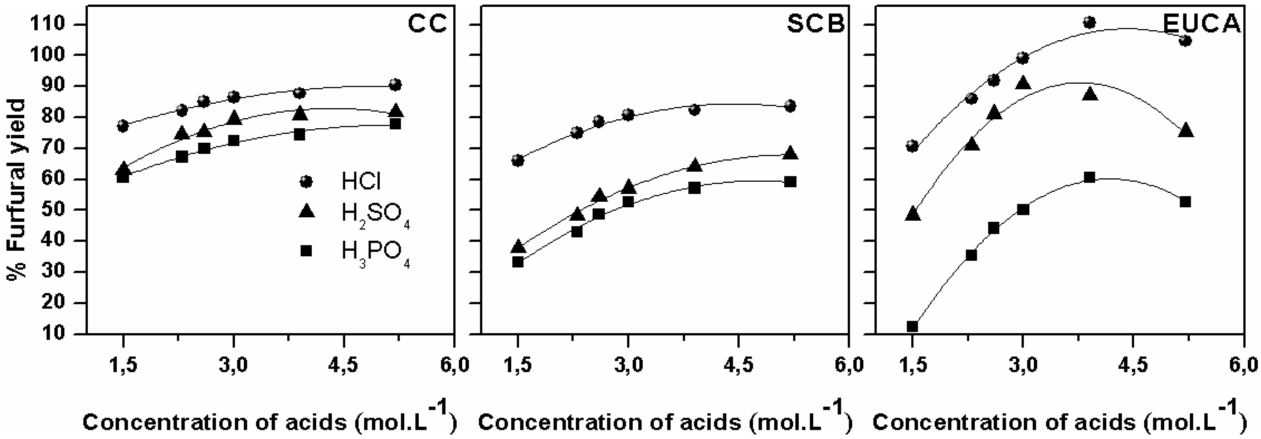

Figure 3. Furfural conversion yield on the basis of CC, SCB, and EUCA pentose contents for various mineral acid catalysts concentrations.

According to **Figure 3**, the furfural conversion yield was higher for EUCA in relation to CC and SCB, when HCl and H_2SO_4 were used as catalysts. The highest furfural conversion yield was found when HCl was used as catalyst reaching 90.5% for CC (5.2 mol.L^{-1}) 83.6% for SCB (5.2 mol.L^{-1}) and 110.6% for EUCA (3.9 mol.L^{-1}). The highest furfural conversion yields for H_2SO_4 were 81.6 (5.2 mol.L^{-1}), 68.1 (5.2 mol.L^{-1}) and 90.6 (3.0 mol.L^{-1}) for CC, SCB and EUCA, respectively. Finally, the highest conversion yields for H_3PO_4 were 77.8 (5.2 mol.L^{-1}), 59.2 (5.2 mol.L^{-1}) and 60.6% (3.9 mol.L^{-1}) for CC, SCB and EUCA, respectively. These results indicate that the initial pentose concentration is a very important parameter for furfural conversion yield. Yang *et al.* (2012) reported that furfural conversion yield decreased from 70 to 60% when the xylose concentration increased from 40 to 120 g/L. It could be concluded that furfural conversion yield decreases with increasing pentose concentration.

This fact may be explained considering that furfural formation is followed by side reactions, such as resinification of the furfural formed, condensation of furfural with pentose-to-furfural intermediates and fragmentation of pentose, all of which decrease the furfural conversion yield. According to Dunlop (1951), the initial pentose concentration greatly affects the maximum obtainable furfural conversion yield in an aqueous solution. The dilute pentose concentrations helps reducing the undesirable side reactions between furfural and its precursors, such as the resinification of the furfural produced (**Figure 4**), condensation of the furfural with pentose-to-furfural intermediates.

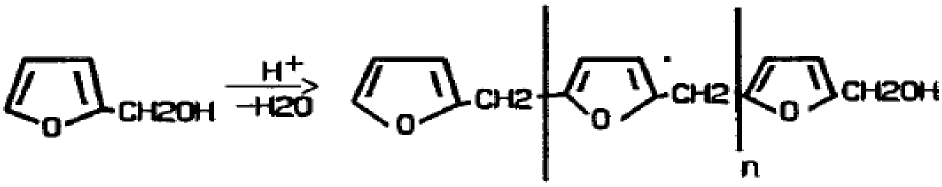

Figure 4. Reaction resinification of the furfural.

However, in commercial processes, low initial pentose concentrations are undesirable since they require larger reactors and more heat to produce the furfural. So, for economical reasons, initial pentose concentration should not be too low. The optimal initial pentose concentration is also decided by furfural yield, operating costs, and the pentose concentration in the hydrolysate.

A low initial concentration of pentoses showed high furfural conversion yield, however the overall cost per gallon of furfural produced is a much better criterion for a process design than the achievement of high furfural productivities.

The mass balance of total furfural production is shown in **Figure 5**. Among the raw materials, CC was one with high furfural productivity in relation of SCB and EUCA, but EUCA was one with higher furfural conversion yield than the others raw materials used in this study. Overall, the best raw material for furfural production was corn cobs, and HCl was the best catalyst.

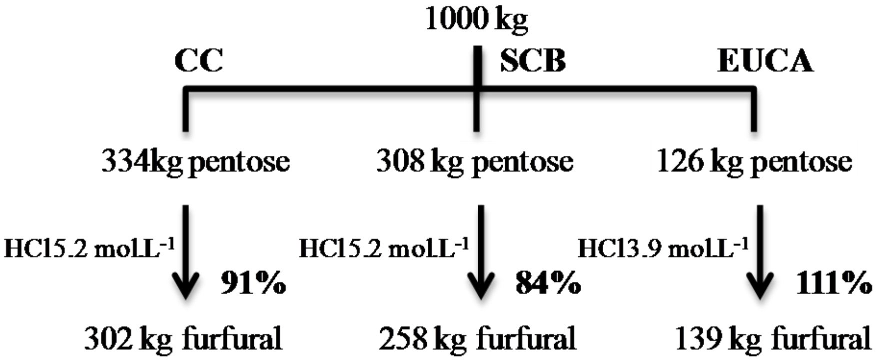

Figure 5. Mass balance of the furfural production from CC, SCB and EUCA.

Furfural production from EUCA pre-hydrolysis liquor

The highest furfural concentration obtained from EUCA pre-hydrolysis liquor using 3.9 mol.L^{-1} of HCl as catalyst, by hydro distillation, was 9.3 g/L. This furfural concentration corresponds to a furfural productivity of 8.8% and conversion yield of 71.5% respect to total pentoses present in the EUCA liquor PH. A 9.2 g/L of furfural concentration was obtained using 0.9 mol.L^{-1} H_2SO_4 as catalyst for 3 hours at 170° C; this concentration corresponds to a furfural productivity of 8.8%, conversion yield of 70.8% respect to pentoses in the EUCA liquor PH.

From the xylans obtained from EUCA pre-hydrolysis high concentration of furfural can be produced. It is a way of consuming renewable agro-industrial residues of dissolving pulp production. From 1 Ton of dissolving pulp, it is possible to produce 100 kg of furfural, consuming 1537 kg of HCl. The process must be improved giving its poor economics.

Furfural production from CC, SCB, EUCA, and EUCA liquor PH (liquors rich in xylans) can be achieved using high concentration mineral acid catalyst. Thus, it is relevant to considerer the amount of acid spent in the processes (g produced furfural/g spent acid). A summary of optimum conditions for furfural production on the basis of the results of this study are show in **Table 3**.

Table 3. Optimum conditions of furfural production

Material	Acid	Concentration (mol.L^{-1})	Productivity (%)	Yield (%)	g furfural/ g acid
CC	HCl	5.2	30.2	90.5	0.40
SCB	HCl	5.2	25.8	83.6	0.34
EUCA	HCl	3.9	13.9	110.6	0.24
EUCA liquor PH	HCl	3.9	8.8	71.5	0.07

CONCLUSIONS

The maximum productivity and furfural yield were found when HCl was used as catalyst in the hydro distillation process, in relation to H_2SO_4 and H_3PO_4.

The most attractive raw material was corn cobs which resulted in the highest furfural production (ex: 302 kg furfural/ dry ton of biomass), with sugarcane bagasse coming second.

Furfural productivity increased with increasing raw material pentosan content, but furfural conversion yield from pentose increased with decreasing pentose concentration.

The eucalyptus liquor from pre-hydrolysis Kraft dissolving pulp production, proved to be technically feasible for the furfural production, the process must be improved giving its poor economics.

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OVERALL CONCLUSIONS

In the first part of this study that evaluated the effect of ferti-irrigation on the quality of eucalyptus wood it was concluded that the ferti-irrigation caused a reduction in the wood specific basic mass, except for the clone B of *Eucalyptus grandis*, in which its specific basic mass increased. The syringyl/guaiacyl ratio, manganese content and acetyl group content were influenced by the type of genetic material, with no effect of ferti-irrigation on such properties.

The ferti-irrigation technique decreased the specific basic mass of certain eucalyptus clones, making it relevant to consider the negative aspects regarding the quality of the wood, in the cellulose manufacturing production process.

In the second part of this paper we present a preliminary study on the production of furfural from different lignocellulosic materials. We concluded that the maximum performance, productivity and yield of furfural were found when HCl was used as a catalyst in the steam distillation process compared to H_2SO_4 and H_3PO_4. The raw material with the highest furfural production was the corn cob, sugarcane bagasse being second best. The furfural productivity was directly proportional to the pentoses content in the raw material, but the yield proceeded inversely, increasing with the decreasing concentrations of pentoses.

The eucalyptus liquor from pre-hydrolysis Kraft dissolving pulp production, proved to be technically feasible for the production of furfural, but should be improved so that it becomes economically viable.

APPENDIX

Species	Treatments	Glucans (%)	Xylans (%)	Galactans (%)	Mannans (%)	Arabinans (%)	Uronic acids (%)	Acetyl groups (%)	Total lignin (%)	S/G ratio	Ash (%)	Extractive (%)
Eucalyptus Grandis (Clone A)	C/NI	49.3	10.7	1.7	1.3	0.3	3.2	2.8	28.9	2.8	0.2	1.5
	C/NI	47.1	10.8	1.9	1.4	0.3	3.3	2.9	30.7	2.7	0.1	1.6
	C/NI	47.0	11.0	2.0	1.1	0.3	2.9	2.8	30.7	2.9	0.2	2.6
	T/NI	47.4	11.1	1.7	1.6	0.2	3.4	3.0	29.9	3.2	0.2	2.6
	T/NI	50.0	11.7	1.9	1.1	0.3	2.6	2.8	27.7	3.1	0.2	1.7
	T/NI	48.6	10.9	1.7	1.5	0.3	3.6	2.8	28.8	3.0	0.2	1.4
	F/I	48.2	11.2	1.7	1.3	0.3	3.5	2.8	29.6	2.9	0.2	1.9
	F/I	50.9	10.5	1.6	1.5	0.3	2.9	2.9	28.1	2.7	0.2	1.6
	F/I	49.9	10.8	1.9	1.4	0.2	3.1	2.9	29.6	2.7	0.2	2.1
Eucalyptus Grandis (Clone B)	C/NI	50.0	11.5	1.7	1.4	0.3	3.2	2.6	28.4	2.3	0.2	1.6
	C/NI	50.2	10.9	2.1	1.3	0.3	3.4	2.6	28.6	2.2	0.2	1.7
	C/NI	48.8	11.8	1.8	1.4	0.3	3.6	2.7	28.5	2.4	0.2	1.6
	T/NI	49.8	11.4	1.9	1.2	0.3	2.9	2.6	28.8	2.2	0.3	1.7

	T/NI	49.7	10.5	2.0	1.3	0.2	3.5	2.7	28.6	2.3	0.2	1.7
	T/NI	47.7	11.3	1.7	1.4	0.3	3.4	2.6	29.5	2.4	0.2	1.9
	F/I	50.5	11.4	1.7	1.5	0.2	2.9	2.5	27.9	2.3	0.2	1.3
	F/I	51.1	10.8	1.8	1.3	0.3	2.8	2.7	28.1	2.7	0.2	2.4
	F/I	48.7	11.0	1.9	1.6	0.3	3.5	2.5	28.7	2.3	0.2	1.5
Hybrids of *Eucalyptus grandis* X *Eucalyptus urophylla* (Clone A)	C/NI	49.6	11.0	1.9	1.4	0.3	3.3	2.6	28.3	2.6	0.1	1.6
	C/NI	47.2	11.8	2.1	1.4	0.3	3.6	2.6	29.4	2.8	0.2	2.1
	C/NI	50.2	11.0	1.8	1.2	0.3	3.4	2.6	28.8	2.6	0.2	1.2
	T/NI	50.5	10.8	2.0	1.1	0.3	2.8	2.5	28.3	2.7	0.2	1.7
	T/NI	51.6	11.1	1.6	1.3	0.3	2.5	2.5	26.1	2.9	0.2	1.3
	T/NI	48.0	10.4	1.8	1.1	0.2	2.9	2.5	30.5	2.9	0.1	1.5
	F/I	47.9	11.6	2.0	1.4	0.3	2.6	2.6	30.3	2.9	0.2	1.7
	F/I	49.7	10.3	1.9	1.3	0.2	3.2	2.6	28.9	3.1	0.2	1.6
	F/I	48.9	11.4	1.6	1.4	0.3	2.7	2.6	30.0	2.9	0.2	1.5
Hybrids of *Eucalyptus grandis* X *Eucalyptus*	C/NI	50.0	11.5	1.7	1.4	0.3	3.2	2.6	28.4	2.3	0.2	1.6
	C/NI	50.2	10.9	2.1	1.3	0.3	3.4	2.6	28.6	2.2	0.2	1.7

urophylla (Clone B)	C/NI	48.8	11.8	1.8	1.4	0.3	3.6	2.7	28.5	2.4	0.3	1.6
	T/NI	49.1	11.6	1.9	1.3	0.3	3.0	2.4	28.7	2.8	0.2	3.1
	T/NI	49.8	11.3	1.8	1.3	0.3	3.1	2.5	28.5	2.8	0.2	2.4
	T/NI	50.7	10.7	1.8	1.4	0.3	2.9	2.5	28.4	2.8	0.2	2.0
	F/I	50.9	11.1	1.8	1.3	0.2	3.0	2.8	27.7	2.8	0.2	1.8
	F/I	49.8	10.8	2.0	1.0	0.2	2.8	2.6	28.9	2.8	0.2	2.0
	F/I	51.1	10.9	1.9	1.2	0.3	3.0	2.6	26.3	2.8	0.2	2.6

Species	Treatments	Ca (mg/kg)	Mg (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Species	Treatments	Ca (mg/kg)	Mg (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
Eucalyptus Grandis (Clone A)	C/NI	742.0	170.5	10.2	8.0	*Eucalyptus Grandis* (Clone B)	C/NI	835.0	135.3	9.8	14.2
	C/NI	747.1	167.1	11.6	7.4		C/NI	695.0	138.5	11.1	9.4
	C/NI	767.5	165.6	12.6	7.1		C/NI	870.0	228.8	14.5	8.9
	T/NI	499.6	119.9	14.4	7.5		T/NI	727.5	110.3	16.4	11.3
	T/NI	475.0	120.2	16.5	7.5		T/NI	920.0	170.1	15.2	14.3
	T/NI	880.0	260.9	13.8	8.7		T/NI	1000.2	257.9	20.5	10.6
	F/I	510.0	104.6	25.4	13.9		F/I	495.0	107.1	22.5	15.0
	F/I	511.0	113.6	19.8	13.8		F/I	740.0	109.6	10.4	12.4
	F/I	730.0	111.4	20.3	13.4		F/I	1015.0	270.4	42.3	21.1

Species	Treatments	Ca (mg/kg)	Mg (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Species	Treatments	Ca (mg/kg)	Mg (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
Hybrids of *Eucalyptus grandis* X *Eucalyptus urophylla* (Clone A)	C/NI	365.0	109.3	27.7	9.7	Hybrids of *Eucalyptus grandis* X *Eucalyptus urophylla* (Clone B)	C/NI	710.9	151.5	15.1	13.5
	C/NI	460.0	96.8	42.6	10.6		C/NI	628.7	171.6	13.5	15.7
	C/NI	570.0	111.6	8.9	7.7		C/NI	657.5	169.9	13.6	14.6
	T/NI	470.0	114.2	4.8	8.3		T/NI	710.4	146.9	9.7	6.5
	T/NI	410.0	104.3	9.2	6.0		T/NI	713.5	149.8	13.1	6.9
	T/NI	687.5	155.4	18.6	8.0		T/NI	725.0	147.1	13.0	6.4
	F/I	447.5	93.6	11.0	11.4		F/I	720.0	131.5	17.7	14.9
	F/I	425.0	86.0	21.7	10.7		F/I	702.5	146.1	11.9	9.4
	F/I	737.5	93.8	13.2	14.2		F/I	407.5	106.5	18.1	9.2