Furfural production from lignocellulosics

Bianca M. Barbosa: PhD student, UFV, Brazil, bianca.barbosa@ufv.br
Jorge L. Colodette: Full Professor, UFV, Brazil, colodett@ufv.br
Carla P. T. Cabral: Full Professor, UEAP, Brazil, lcajir@yahoo.com.br
Juliana C.da Silva: PhD student, UFV, Brazil, jcsfloresta@yahoo.com.br
Fernando B. Gomes: PhD, UFV, Brazil, fernando.gomes@ufv.br
Flávia N. Oliveira: Master, UFV, Brazil, flavianatalino@yahoo.com.br

Abstract
This study focused on the production of furfural from agricultural and industrial biomass residues by a hydrodistillation process. Corncobs, sugarcane bagasse, and eucalypt wood were treated with sulfuric, hydrochloric, and phosphoric acids as catalysts, with different acid concentrations (1.5 to 5.2 mol.L$^{-1}$). In addition, the eucalypt liquor from the 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$^{-1}$). Furfural yields of 30.2, 25.8, and 13.9% were achieved for corncob, sugarcane bagasse, and eucalypt wood, respectively, on the basis of biomass dry weight. The efficiency of conversion from pentose to furfural using eucalypt liquor from the pre-hydrolysis kraft process was 71.5% using HCl 3.9 mol.L$^{-1}$. Due to the presence of a high amount of pentose, corncob produced the highest amount of furfural, followed by sugarcane bagasse and then eucalypt wood.

Keywords: Furfural, mineral acids, auto-hydrolysis, hemicelluloses, dissolving pulp production.

Introduction
Interest in chemical production based on renewable sources has increased in the last decade due to 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 as an inexpensive source for polymeric materials, energy, or chemicals [1–3].

Agricultural and agro-industrial residues are mainly constituted of 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 a raw material for furfural production; however, furfural industrial production requires a minimum pentosans content of around 15 to 20% [4]. Only about one third of the pentosans in raw materials can be converted into furfural through the 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 considered the major market for furfural [5]. 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 corncobs, cotton stalks, sunflower stalks, sugarcane bagasse, etc.) [5–7].

There are two main types of technologies to produce furfural. The first is a one-stage technology where the pentosans’ depolymerization in xylose and dehydration to furfural occur simultaneously [1,8]. The second is a two-stage technology where the dissolution and depolymerization of pentosans occur under mild conditions, followed by dehydration of xylose to furfural [9]. 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.

Several researchers have investigated the production of furfural by hydrolysis of lignocellulosic residue materials in the presence of a mineral acid as catalyst, such as hydrochloric acid (HCl) [10–12], nitric acid (HNO$_3$) [13], sulfuric acid (H$_2$SO$_4$) [6,14,15] and phosphoric acid (H$_3$PO$_4$) [5,16,17]. Among these acids, HCl, H$_2$SO$_4$, and H$_3$PO$_4$ produce high furfural yield whereas HNO$_3$ is not so effective. Raw materials used for furfural production reported in the literature included sugarcane.
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. 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.

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% H₂SO₄ followed by hydrolysis with 3% H₂SO₄ 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 [29]. The solid residue after hydrolysis was considered as Klasson lignin according to T222 cm-11 standard procedure. Ashes were determined by calcination according to TAPPI standard T211 om-12. Acid soluble lignin was determined by measuring the UV-absorbance of the filtrate at 205 nm according to Goldschmid [30]. Total uronic acids in raw materials hydrolysates were measured by the colorimetric method involving 3,5-dimethylphenol addition according to Scott [31]. The acetyl group content in samples wood was determined according to Solar et al. [32]. 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 (m³/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, according to a previous study [25].
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. 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 (H₂SO₄) and phosphoric acid (H₃PO₄) 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 H₂SO₄ the following conditions were used: temperature 170°C, 0.9 mol.L⁻¹, 3 hours reaction time and 3/1 liquid/solid ratio [33]. 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. [34]. 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:

\[
\% \text{ Furfural productivity} = \frac{w_0}{w_1} \times 100\% \quad (1)
\]

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:

\[
\% \text{ Furfural yield} = \frac{w_0}{w_2} \times 100\% \quad (2)
\]

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 [35].

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 fufural production [20]. Because of the current importance of lignin as a raw material for the production of bioproducts and biofuels [36], 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 [19, 37, 38], 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 [19, 37] for similar samples.

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

<table>
<thead>
<tr>
<th>Component, %</th>
<th>Corn cob (CC)</th>
<th>Sugarcane bagasse (SCB)</th>
<th>Eucalypt (EUCA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Results</td>
<td>Van Dongen et al.</td>
<td>Lili et al.</td>
</tr>
<tr>
<td>Glucose</td>
<td>47.1</td>
<td>34</td>
<td>34.6</td>
</tr>
<tr>
<td>Xylose</td>
<td>28.0</td>
<td>28</td>
<td>27.0</td>
</tr>
<tr>
<td>Arabinose</td>
<td>5.4</td>
<td>2.4</td>
<td>3.6</td>
</tr>
<tr>
<td>Galactose</td>
<td>2.2</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>Mannose</td>
<td>0.2</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Acetyl groups</td>
<td>2.9</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>Uronic acids</td>
<td>2.2</td>
<td>1.8</td>
<td>-</td>
</tr>
<tr>
<td>Lignin(c)</td>
<td>17.8</td>
<td>18.3</td>
<td>9.4(b)</td>
</tr>
<tr>
<td>Ash</td>
<td>1.2</td>
<td>-</td>
<td>2.5</td>
</tr>
<tr>
<td>Glucose</td>
<td>46.4</td>
<td>40.5(d)</td>
<td>43.1</td>
</tr>
<tr>
<td>Xylose</td>
<td>28.2</td>
<td>14.5</td>
<td>23.8</td>
</tr>
<tr>
<td>Arabinose</td>
<td>2.6</td>
<td>2.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Galactose</td>
<td>1.0</td>
<td>2.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Mannose</td>
<td>1.0</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>Acetyl groups</td>
<td>3.0</td>
<td>-</td>
<td>3.0(e)</td>
</tr>
<tr>
<td>Uronic acids</td>
<td>1.5</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>Lignin(c)</td>
<td>21.4</td>
<td>28.2</td>
<td>23.2</td>
</tr>
<tr>
<td>Ash</td>
<td>2.3</td>
<td>4.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Glucose</td>
<td>53.1</td>
<td>42.8</td>
<td>47.9(a)</td>
</tr>
<tr>
<td>Xylose</td>
<td>12.3</td>
<td>17.1</td>
<td>11.2(a)</td>
</tr>
<tr>
<td>Arabinose</td>
<td>0.3</td>
<td>0.4</td>
<td>0.1(a)</td>
</tr>
<tr>
<td>Galactose</td>
<td>2.1</td>
<td>-</td>
<td>0.9(a)</td>
</tr>
<tr>
<td>Mannose</td>
<td>1.4</td>
<td>-</td>
<td>0.9(a)</td>
</tr>
<tr>
<td>Acetyl groups</td>
<td>2.8</td>
<td>3.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Uronic acids</td>
<td>3.1</td>
<td>-</td>
<td>5.9</td>
</tr>
<tr>
<td>Lignin(c)</td>
<td>30.1</td>
<td>21.2</td>
<td>26.6</td>
</tr>
<tr>
<td>Ash</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\(a\) 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.
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 [39-41]. It is well known that pentoses and hexoses, respectively, are the precursors for furfural and HMF formed during the conversion of lignocellulosic biomass [7]. 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 [25,39], 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 [42].

### 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 [43, 44].

<table>
<thead>
<tr>
<th>PH Result</th>
<th>Yield, %</th>
<th>Xylans, % on wt.</th>
<th>Xylans Removal, %</th>
<th>Spent liquor pH</th>
<th>Hydrolyzate solids, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EUCA</td>
<td>88.6</td>
<td>7.1</td>
<td>48.9</td>
<td>2.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

### 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\(_2\)SO\(_4\) 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\(_3\)PO\(_4\), 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 [7] 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. [45] reported that the furfural productivity was higher in high concentration of H\(_2\)SO\(_4\) systems compared to that in low concentration and the highest furfural conversion efficiency (75%) was achieved with 10% (w/w) H\(_2\)SO\(_4\), but the conversion efficiency decreased to 51% when the concentration of H\(_2\)SO\(_4\) 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 [7] comparing the effect of four strong mineral acids (hydrochloric, sulfuric, nitric, and phosphoric acids) and two organic acids - acetic (CH\(_3\)COOH) and formic acids (HCOOH) on furfural yield. The furfural productivities obtained from xylose in the presence of HCl, H\(_2\)SO\(_4\), HNO\(_3\) (nitric acid), H\(_3\)PO\(_4\), CH\(_3\)COOH and HCOOH were 37.5%, 31.9%, 3.5%, 27.6%, 15.8%, and 23.8% at pH 1.12, respectively.
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.

According to Figure 3, the furfural conversion yield was higher for EUCA in relation to CC and SCB, when HCl and H$_2$SO$_4$ 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$_2$SO$_4$ 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$_3$PO$_4$ 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. [46] 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 Burket [47], 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, condensation of the furfural with pentose-to-furfural intermediates.

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.

The mass balance of the furfural production from CC, SCB and EUCA.

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 H₂SO₄ 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

<table>
<thead>
<tr>
<th>Material</th>
<th>Acid</th>
<th>Concentration (mol.L⁻¹)</th>
<th>Productivity (%)</th>
<th>Yield (%)</th>
<th>g furfural/g acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC</td>
<td>HCl</td>
<td>5.2</td>
<td>30.2</td>
<td>90.5</td>
<td>0.40</td>
</tr>
<tr>
<td>SCB</td>
<td>HCl</td>
<td>5.2</td>
<td>25.8</td>
<td>83.6</td>
<td>0.34</td>
</tr>
<tr>
<td>EUCA</td>
<td>HCl</td>
<td>3.9</td>
<td>13.9</td>
<td>110.6</td>
<td>0.24</td>
</tr>
<tr>
<td>EUCA liquor PH</td>
<td>HCl</td>
<td>3.9</td>
<td>8.8</td>
<td>71.5</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Conclusions

The maximum productivity and furfural yield were found when HCl was used as catalyst in the hydrodistillation process, in relation to H₂SO₄ and H₃PO₄.

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.

References

7. Yemis, O.; Mazza, G. Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction. Bioresource Technology 2011, 102(15), 7371–7378.
42. Mokfienski, A.D.S. Importância Relativa da Densidade Básica e da Constituição Química de Madeira de Eucalyptus spp no Rendimento, Branqueabilidade e Qualidade da Polpa Kraft; UFV: Vic¸osa. 2008.

ACKNOWLEDGMENTS
Funding provided by the Minas Gerais State Research Foundation (FAPEMIG), from the Brazilian National Council for Science and Technology Development (CNPq), and from the Coordination for the Improvement of Higher Education Personnel (CAPES) is greatly appreciated.