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Study of the use of organosolv lignin as bio-preservative of wood

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abstract

The service life of wood depends on the species, use and environmental conditions of exposure. The treatment of wood protects it against degradation by xylophagous agents, enhancing the durability of material up to 10 times, and reducing the deforestation around 12.5%. In this way, the use of treatments is necessary because increases the service life of material and protect against xylophagous agents who degrade the wood. The study and development of new preservative products for wood are necessary in order to substitute heavy metals-based preservatives, such as CCA (Chromated Cooper Arsenate) that entails environmental risks. Lignin is considered as a residue in pulp and paper production processes, being mainly used as fuel in the recovery boiler for energy generation. However, more valuable uses of lignin could be developed for several interesting applications such as bio-preservative activity. In this context, the present study aimed to evaluate the properties of eucalyptus organosolv lignin, obtained by using 60% (v/v) ethanol/water solution, in a solid/liquid ratio of 1:10, at 180 ◦C for 90 min. The resulting lignin samples were characterized by different analytical techniques such as FTIR, GPC, and TGA. Furthermore, the antioxidant potential of lignin by ABTS method and the fungicide potential by ASTM D 2017 – 81 were analyzed. The analyzed lignin showed neutralization and inhibition activities (antioxidant capacity). These characteristics demonstrated that lignin could be an excellent wood bio-preservative obtained from renewable sources.

**Keywords:** wood treatment, wood preservation, wood quality.

1. introduction

Wood was one of the first materials used by humanity and remains as a raw material for multiples utilizations, mainly due to availability and intrinsic characteristics.

The useful life of wood depends of species, final utilization and environmental conditions that are exposed. The treated wood is more durable, which reduces the deforestation up to 12.5%. Thus, the utilization of treatments are necessary in order to improve the useful life of wood and, consequently, to protect against biodegradation. However, the wood treatment with toxic compounds, such as CCA (Chromated Copper Arsenate) increases the environmental impacts due to the presence of arsenic. Moreover, the commercialization of products with arsenic is limited, proving the necessity of development of new products for the wood preservation.

Lignin is a chemical substance that along with cellulose forms part of vegetal cell wall and serves as an agent of cellular union. At the same time, the lignin presents a great structural diversity in trees of the same gender, same species or different morphological regions of vegetal. Considering these facts, is indispensable to investigate the lignin structural composition of wood.

The lignin is an impurity of pulp process, which is originated after the pulp bleaching. These residues are used, mainly as fuel in the ovens in order to generate energy and to recuperate inorganic reactive used in the process. In other hand, the bio-protective activity of the lignin against microorganisms and plagues was recently proved, necessitating a noble utilization for this compound.

The lignin acting as a neutralizer and inhibitor of oxidation process due to its aromatic structure and high content of reactive functional groups, which possibly demonstrates its bio-preservative action to wood. Thus, the lignin is an excellent font of new renewable materials.

2. EXPERIMENTAL METHODS

2.1 Conditioning of the raw material

*Eucalyptus paniculata* wood was used and was obtained from a homogeneous population located in the city of Charqueadas (29º57'17"south and 51º37'31" west), Rio Grande do Sul, Brazil.

2.2 Characterization of the raw material and obtained solid fractions

 The characterization of the raw material and the fiber were performed in triplicate and according to standard methods (TAPPI) and bibliographic procedures: moisture content (TAPPI T264 cm-97); holocellulose (Wise *et al*. 1946); α-cellulose and hemicellulose (Rowell 1983); ash content (TAPPI T211 om-93); solubility in hot water (TAPPI 207 om-93); aqueous 1% NaOH soluble matter (TAPPI T212 om-98); ethanol-toluene extractives (TAPPI T204 cm-97) and insoluble lignin (TAPPI T222 om-98).

**2.3 Fragmentation processes**

The raw material was treated with ethanol in a stirred reactor (4 l) equipped with a temperature control and data acquisition. The experimental conditions was 60% (v/v) ethanol-water solution in a relation liquid/solid 1:10 at 180°C for 90 min. After the reaction time, the solid fraction was separated from the liquid fraction by filtration and the residual liquor was removed (wash with water).

**2.4 Liquid fraction characterization**

The main physico-chemical properties of the liquid fraction were determined according to standard methods.

The pH was measured with a digital pH meter SELECT "pH-2005". The density was determined by measuring the weight of black liquor in a volume previously weighed and without moisture. The inorganic matter was determined by combustion of samples at 525°C (TAPPI T211 om-93). The organic matter was measured through the difference between total dissolved solids and inorganic matter.

**2.5 Lignin recovery from the liquid fraction**

The liquid fractions were treated in order to precipitate the dissolved lignin. The liquid ethanol fraction was mixed with two volumes of water and the pH of that solution was lowered to pH 2 with sulfuric acid (72% w/w). Thus, the precipitated lignin was separated by filtration, washed with acidified water and dried with vacuum at 50°C. Finally, lignin samples were characterized by different techniques: infrared spectroscopy (ATR-IR) by direct transmittance at a resolution of 4 cm-1 for 32 scans; thermogravimetric analysis (TGA) with a sample exposure between 25 and 800°C; gel permeation chromatography (GPC) and ultraviolet-visible spectrophotometry UV-VIS (Folin method and antioxidant capacity, ABTS described by García *et al*. (2010).

**2.6 Hydrothermal treatment of lignin**

The lignin obtained previously was treated at high temperatures and pressure during a fixed time (90 min) in presence of catalyst. Thus, the lignin depolymerization was realized, producing a phenolic compounds (oil) and byproducts (residual lignin).

The procedure of separation and extraction of reaction products occurred through precipitation of unconverted lignin. The reaction mix was acidified with hydrochloric acid until pH around 1 in order to precipitate the residual lignin. The solid and liquids products were separated by vacuum filtration.

The filtrated product was extracted with ethyl acetate in order to extract the phenolic monomers produced during the depolymerization of the lignin. The yield of each product was determined by gravimetric method in relation to the initial lignin content.

**2.7 Oil composition**

The composition of the oil obtained was determined by gas chromatography-mass spectroscopy (GC (7890A)-MS (5975C inert MSD with Triple-Axis Detector) Agilent) equipped with a capillary column HP-5MS ((5%-Phenyl)-methylpolysiloxane, 60 m x 0.25 mm). Moreover, the density (gravimetric method), viscosity (ostwald viscometer method) and inorganic matter (TAPPI T211 om-93) of the oil were measured.

**2.8 Wood impregnation**

The efficiency of the oil (preservative 1) and the lignin (preservative 2) both with a solution at 1% in water/ketone was measured through of impregnation in the wood samples. For this, two methods of wood impregnation were used. Before the impregnation process, the color and the odor of two preservatives were measured through sensorial techniques.

In the first method, the wood samples were impregnated in a solution of the oil at 1% by vacuum application (0.8 bar) for 90 min. In the second method (empty-cell), the wood samples was submitted a vacuum (0.8 bar) for 30 min. The application of vacuum opened the wood porous and, at the same time, the oil solution at 1% was introduced in the recipient. The oil solution remained under vacuum during 60 min for impregnation of wood samples.

The penetration of oil solution was evaluated by UNE EN351-1 rules through the difference of weight before and after the impregnation of wood samples.

**2.9 Characterization of impregnated wood**

The characterization of impregnated wood was realized through antifungal activity tests and color variation of the samples.

The antifungal activity (ASTM D2017–81) of oil solution was measured through the accelerate tests methods for evaluation wood biodegradation by *Trametes versicolor* fungus (white-rot) and *Gloeophyllum trabeum* (brown-rot). For this, samples of *Pinus* spp. sapwood with dimensions 2 x 2 x 1 cm were prepared. The weight loss was determined through the difference of samples weight before and after the action of the fungus.

The variation of color was determined with a colorimeter (CR-400 Minolta Chroma Meter) according to the *CIELab* standard. The equipment was adjusted with a D65 light source and observation angle of 2°.

For this, the parameters *L\** (lightness), *a\** (green-red chromatic coordinate), *b\** (blue-yellow chromatic coordinate). Moreover, *∆E* (color difference), *C\** (chroma) and *h\** (hue angle) were measured by Eq. 1, 2 and 3.

|  |  |
| --- | --- |
| $$ΔE= \left(ΔL^{\*2}+ Δa^{\*2}+ Δb^{\*2}\right)^{1/2}$$ | (1) |
| $$C^{\*}= \left(a^{\*2}+ b^{\*2}\right)^{1/2}$$ | (2) |
| $$h^{\*}= tang^{-1}\left(b^{\*}/a^{\*}\right)$$ | (3) |
| Where: Δ*E* = color difference; $ΔL^{\*2}, Δa^{\*2} e Δb^{\*2}$ = lightness, red-green coordinate and blue-yellow coordinate variation; $C^{\*}$ = chroma; *h*\* = hue angle; *a*\* = red (+) - green (-) color coordinate; *b*\* = yellow (+) – blue (-) color coordinate. |

3. RESULTS AND DISCUSSION

**3.1 Raw Material and fiber characterization**

Table 1 shows the chemical analysis of *Eucalyptus paniculata* wood and pulp.

Table 1: Composition of wood and pulp of *Eucalyptus paniculata.*

|  |  |  |
| --- | --- | --- |
| **Analysis (%)** | **Raw material** | **Pulp** |
| Ash | 0.23 (0.1) | 0.27 (0.02) |
| Ethanol–toluene extractives | 2.86 (0.6) | 3.88 (0.4) |
| Solubility in hot water | 6.53 (0.6) | 6.96 (0.2) |
| Aqueous 1% NaOH soluble matter | 14.97 (0.5) | 8.44 (1.2) |
| Insoluble lignin | 36.67 (0.9) | 21.23 (2.2) |
| Holocellulose | 52.19 (1.05) | 74.56 (0.96) |
| α-cellulose | 43.32 (1.25) | 63.02 (0.06) |
| Hemicellulose | 8.87 (0.21) | 11.54 (0.94) |

Values in parentheses corresponding to the standard deviation.

The lignin content of the pulp was lower than the lignin content of raw material, proving the elimination of the lignin during the delignification process. Thus, the cellulose showed an inversely proportional behaviour to the lignin. The cellulose content of the pulp was higher than the cellulose content of the raw material. This fact also was observed for Alriols (2010).

Moreover, the ash content, extractives content and solubility in hot water presented a high values for the raw material, while aqueous 1% NaOH soluble matter and hemicellulose content were high for the pulp.

**3.2 Black liquor characterization**

The results of the characterization of black liquor obtained from the organosolv process are shown in the Table 2.

Table 2: Characterization of black liquor.

|  |  |
| --- | --- |
| **Analysis** | **Average** |
| MIa (%)\* | 0.37 (0.63) |
| MOb(%)\* | 4.65 (1.11) |
| MDc (%) | 5.21 (0.56) |
| pH | 3.90 (0.03) |
| Lignin (%)\* | 19.63 (0.92) |
| Density (g/mL) | 0.90 (0.0001) |

MIa= inorganic matter; MOb= organic matter; MDc= dry matter; \*= % dry matter (w/w); Values in parentheses corresponding to the standard deviation.

The lignin concentration was 19.63%, similar to found by Serrano *et al*. (2010) and Toledano *et al*. (2010), both studies with different species. However, Cardoso *et al*. (2009) observed lignin concentration between 39 and 42% for the *Eucalyptus grandis* black liquor from Kraft industrial process. This fact could be explained due to relation dissolution/raw material because the present study was a laboratorial extraction (a lower relation dissolution/raw material than the industrial processes).

Moreover, the results of other properties (MIa, MOb, MDc, pH and density) were similar to found by Serrano *et al*. (2010). Probably, the similar results occurred due to the use of the same extraction process (organosolv), even that the species were different.

**3.3 Lignin characterization**

ATR-IR spectra of *Eucalyptus paniculata* lignin are shown in Fig. 1.

|  |
| --- |
| infra_red_lignina paniculata_4000_650.tif**A** |
| infra_red_lignina paniculata_1800_650.tif**B** |
|  |
| Figure 1: ATR-IR spectra of *Eucalyptus paniculata* lignin. (A) Spectra in the range from 750 to 4000 cm-1; (B) Spectra in the range from 750 to 1800 cm-1 |

In general, the results were similar to the reported in other study (Tejado *et al*. 2007).

A high absorption band at 3400 cm-1 and at 1030 cm-1 corresponded to the OH aromatic and aliphatic groups. The bands at 2940 and 1456 cm-1 were related to the C-H vibration of CH2 and CH3 groups. The range between 1705 and 1715 cm-1 was assigned to the unconjugated carbonyl groups.

The lignin showed the presence of bands at 1592, 1512 and 1420 cm-1 that were associated to the vibration of aromatic rings of phenylpropane skeletal. Moreover, the spectra showed bands assigned to the syringil (S) and guaiacyl (G): breathing rings of syringil with C-O stretching at 1328 cm-1, aromatic C-H of syringil type in the plane deformation at 1111 cm-1, typical syringil units at 830 cm-1 and guaiacyl units at 1268 cm-1.

Fig. 2 showed the thermograms (TG) and its derivatives thermograms (DTG) of *Eucalyptus paniculata* lignin.

|  |
| --- |
| TGA_lignina paniculata.tif |
|  |
| Figure 2: TGA (straight line) and DTG (dotted line) thermograms for the *Eucalyptus paniculata* lignin. |

The degradation process was characterized for three ranges. The first range was between 80 and 100°C, that corresponding to the moisture loss. The second range corresponding to the hemicellulose degradation and was at 220-280°C. Finally, the third range was between 280 and 300°C, that corresponding to the lignin degradation.

The lignin presented a high residual content (42.62%). According to Garcia *et al*. (2011), a high residual content means a high thermal stability and a tridimensional structure more complete. However, the high values of residues could indicate presence of inorganic matter, which was very low (1.09%) in the chemical analysis. Thus, the residues percentage could be associated to the phenolic compounds condensation during the thermal degradation.

The results of molecular weight analysis are shown in the Table 3.

Table 3: Average values of molecular weight analysis of *Eucalyptus paniculata* lignin.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Analysis** | **Mw** | **Mn** | **IP** | **EAG (%) \*** | **Inhibition****ABTS (%) \*\*** | **DTmax (ºC)** | **Lignin residue (%)** |
| Average | 10193 | 1916 | 5,32 | 46,7  | 94,8 | 358,18 | 42,62 |

Mw= molecular weight; Mn= Molecular number; IP= polydispertivity (Mw/Mn); EAG= gallic acid equivalents DTmax= maximum degradation temperature; \*Total phenolic content in the lignin expressed in percentage of content of gallic acid equivalents; \*\*Antioxidant power as a percentage of the ABTS radical reduction related to the lignin solution of 2g/l in DMSO.

The high molecular weight of *Eucalyptus paniculata* lignin could be associated to the higher concentration of contaminants due to the purity degree (75± 2%).

The molecular weight of lignin is related to the quantity of C-C. According to García *et al*. (2012), the lignin with high molecular weight has more guaiacyl units. The lignin with low molecular weight is more soluble and present more capacity to form hydrogen bonds than the lignin with high molecular weight Arantes (2007).

The total phenolic indicated by EAG (gallic acid equivalents) presented better results than observed by García *et al*. (2012) for the *Olea europea* L. specie (olive). Moreover, the antioxidant properties, based in the antioxidant power (percentage of ABTS radical reduction), of lignin sample is in agreement with the results observed in other study (García *et al*. 2010).

**3.4 Characterization of oil and lignin of** *Eucalyptus paniculata* **as a preservative product**

Table 4 shows the characterization of phenolic compounds of low molecular weight of *Eucalyptus paniculata* oil (preservative 1). This characterization did not realized for the *Eucalyptus paniculata* lignin (preservative 2) due to the conditions required for the GC-MS equipment.

Table 4: Phenolic compounds presented in the *Eucalyptus paniculata* oil.

|  |  |
| --- | --- |
| **Compound** | **Average content** |
| **ppm** | **% (W/W)\*** |
| Phenol | 38,01 | 0,39 |
| o-cresol | 5,46 | 0,05 |
| m-p-cresol | 16,61 | 0,17 |
| Guaiacol | 10,71 | 0,11 |
| Catechol | 133,28 | 1,37 |
| 4-methylcatechol | 15,03 | 0,15 |
| Syringol | 4,32 | 0,04 |

ppm= parts-per-million; \*Yield in percentage (%) of compounds corresponding to the oil weight (w/w).

The catechol and the phenol were the compounds that presented the high content in the *Eucalyptus paniculata* oil. On the other hand, the syringol and the o-cresol were the lowest compounds verified in the oil analyzed.

The physical and sensorial properties of two preservatives (oil and lignin) are shown in the Table 5.

Table 5: Physical and sensorial properties of two preservatives (oil and lignin).

|  |  |  |
| --- | --- | --- |
| **Analysis** | **Preservative 1** | **Preservative 2** |
| pH | 5.3 | 7.0 |
| Viscosity (mm2/s2) | 0.86  | - |
| Density (g/ml) | 0.98 (0.003) | 0.87 (0.005) |
| Color | Yellow | Brown |
| Odor | Characteristic | Characteristic |

Values in parentheses corresponding to the standard deviation.

The pH of preservative 1 (5.3) presented a lower value than the preservative 2 (7). Possibly, it was occurred due to the method of oil (preservative 1) extraction.

The viscosity of the preservative 1 was 0.86. The viscosity of preservative 2 was not determined because the dark color of the product thwarted the measurement by the ostwald method.

Naturally, the density of the preservative 1 (oil) was higher than the preservative 2 (lignin). The viscosity is direct proportionally to the density.

In relation to the sensorial properties, the preservative 1 presented a yellow color, while the preservative 2 showed a dark color (brown). For both preservatives, the odor was shown as characteristic.

**3.5 Characterization of impregnated wood**

Table 6 shows the results of the impregnation rates for the *Pinus* spp. wood samples.

Table 6: Impregnation rates of two preservatives in the *Pinus* spp. wood samples.

|  |  |  |
| --- | --- | --- |
| **Preservative** | **Method** | **Absorption (L/m3)** |
| 1 (oil) | Full-cell | 138.66 (25.49) |
| Empty-cell | 109.66 (16.59) |
| 2 (lignin) | Full-cell | 248.92 (30.33) |

Values in parentheses corresponding to the standard deviation.

The best impregnation of all the treatments occurred for the preservative 2 (lignin) in the full-cell process. For the preservative 1 (oil), the full-cell method showed higher impregnation rate than the empty-cell method.

The preservative 2 (lignin) presented a lower density than the preservative 1. This fact could justify its high absorption for the wood samples.

The weight losses of impregnated samples after the fungal activity are shown in the Table 7.

Table 7: Weight losses of impregnated samples after the fungal activity.

|  |  |  |
| --- | --- | --- |
| **Treatment** | **Fungus** | **Weight loss (%)**  |
| Untreated | *Trametes versicolor* | 2.83 (1.07) |
| *Gloeophyllum trabeum* | 1.35 (0.04) |
| 1 | *Trametes versicolor* | 0.42 (0.14) |
| *Gloeophyllum trabeum* | 0.81 (0.11) |
| 2 | *Trametes versicolor* | 0.36 (0.59) |
| *Gloeophyllum trabeum* | 0.88 (0.16) |
| 3 | *Trametes versicolor* | 0.66 (0.32) |
| *Gloeophyllum trabeum* | 0.24 (0.08) |

1= Preservative 1 (oil) in full-cell; 2= Preservative 1 (oil) in empty-cell; 3= Preservative 2 (lignin) in full-cell; Values in parentheses corresponding to the standard deviation.

The treatment 3 (preservative 2 in empty-cell) showed the lowest weight loss for the exposure in *Gloeophyllum trabeum* fungus, while the highest degradation occurred for the untreated samples. The treatments 1 and 2 presented similar weight loss.

In the other hand, the samples exposition to the *Trametes versicolor* demonstrated that the preservative 1 in empty-cell (treatment 2) presented the best resistance to degradation. At the same way that *Gloeophyllum trabeum*, the untreated samples showed the lowest resistance for the *Trametes versicolor* activity.

Thus, these preliminary results showed that the lignin could be used as a wood preservative.

The variations of color of impregnated samples after the fungal activity are shown in the Table 8.

Table 8: The variations of color of impregnated samples after the fungal activity.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Treatment** |  | ***L\**** | ***a\*’*** | ***b\**** | ***C\**** | ***h\**** | ***∆E*** |
| Untreated | - | 78,57 | 6,21 | 20,23 | 21,16 | 72,94 | ------ |
| *Trametes versicolor* | 62,65 | 10,9 | 33,80 | 35,52 | 72,20 | 22,14 |
| *Gloeophyllum trabeum* | 60,37 | 9,7 | 30,90 | 32,40 | 72,64 | 19,673 |
| 1 | - | 71,07 | 9,605 | 25,615 | 27,355 | 69,71 | 7,87 |
| *Trametes versicolor* | 49,91 | 12,76 | 26,71 | 29,63 | 64,45 | 21,532 |
| *Gloeophyllum trabeum* | 50,56 | 10,64 | 21,95 | 24,41 | 63,86 | 20,27 |
| 2 | - | 70,958 | 10,373 | 27,148 | 29,088 | 70,958 | 6,809 |
| *Trametes versicolor* | 48,19 | 12,82 | 25,86 | 28,88 | 63,65 | 24,18 |
| *Gloeophyllum trabeum* | 52,61 | 10,64 | 26,435 | 28,49 | 68,06 | 20,72 |
| 3 | - | 41,84 | 8,15 | 14,69 | 17,22 | 63,06 | 35,03 |
| *Trametes versicolor* | 47,65 | 9,78 | 21,305 | 25,02 | 65,09 | 13,19 |
| *Gloeophyllum trabeum* | 48,83 | 10,55 | 22,68 | 23,46 | 65,38 | 10,42 |

1= Preservative 1 (oil) in full-cell; 2= Preservative 1 (oil) in empty-cell; 3= Preservative 2 (lignin) in full-cell; L\*= lightness; a\*= red-green chromatic coordinate; b\*= blue-yellow chromatic coordinate; ∆E= color difference; C\*= chroma; h\*= hue angle.

In general, the colorimeter parameters were modified due to fungus activity.

The color of samples after the fungal activity of full-cell method was similar to the empty-cell method for the preservative 1 (oil). In general, the lightness (*L\**) decreased around 30%, while the *a\** and *b\** showed a small variation for both fungus. In the other hand, the samples impregnated with lignin solution at 1% presented a different behaviour, which its color tended to blue.

The higher value of *C\**, the better is the proximity of wood with the original color. In this context, the highest values of *C\** was verified to the untreated samples attacked by both fungus. The lowest value was observed for the treatment 3 in the samples not attacked by the fungus, probably due to the darkening of samples treated with lignin solution at 1%.

At the same way, the reduction of the *h\** was observed for all the impregnated samples in relation to the untreated samples.

A high value of ∆E\* indicates a high variation of impregnated samples color in relation to the samples untreated and not exposed to the fungus. Thus, the ∆E\* of treatment 3 (lignin solution at 1%) decreased after the fungal exposition, while the treatments 1 and 2 (oil solution at 1%) showed inversely proportional behaviour.

**4. CONCLUSIONS**

The lignin content of pulp was lower than the raw material, indicating the considerable elimination of the lignin during the organosolv delignification.

The treatment 3 (preservative 2, lignin) showed the high decay resistance to the attack of *Gloeophyllum trabeum*, while the treatment 2 (preservative 1, oil in empty-cell) presented the best decay resistance to the attack of *Trametes versicolor*. However, all the treated samples showed higher decay resistance than the untreated samples.

The colorimetric evaluation showed a high variation for the samples impregnated with lignin solution in relation to the samples impregnated with oil solution. Thus, is necessary to observe the color behaviour of each product due to the esthetic values.

Preliminary studies of the lignin as a wood preservative were possible to perform due to its chemical characteristics.

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