

# **Valorization of waste generated in the kraft paper manufacturing industry: Sustainable alternative to chemical treatments of wood**

IEMS

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### **ABSTRACT**

Wood is an attractive material due to its low energy demand for processing, contribution to the reduction of the greenhouse effect during its formation and insulating properties when dry. While many woods are naturally resistant to spoilage agents, some fast-growing species require preservative treatment. In Brazil, about 70% of the wood consumed by the industry comes from reforestation, with Pinus sp. and Eucalyptus sp. widely used in building construction. Political and environmental constraints are driving the search for more sustainable alternatives, both in the preservation of wood and in the choice of resistant species. The effectiveness of traditional preservation methods is undermined by the environmental impacts of the products used. There is a growing need to develop antifungal chemicals that are effective and safe for the environment and humans.

**Keywords:** Wood, Thermal insulation, Environmental impact.

### **INTRODUCTION**

Wood has characteristics that make it attractive compared to other materials. It is a material that consumes little energy for its processing, helps to reduce the greenhouse effect during its formation and has good thermal and electrical insulation characteristics when it dries (SOUZA; DEMENIGHI, 2017).

Most of the woods are naturally resistant to the action of xylophagous agents, however, some of fast-growing species, from planted forests, are not resistant and need preservative treatments. About 70% of the wood consumed by the Brazilian industry comes from reforestation. In Brazilian civil construction, specifically in the production of wooden housing, Pinus sp. and Eucalyptus sp., among the fast-growing species from planted forests, in the form of sawn wood, agglomerated boards, plywood and round pieces (SOUZA; DEMENIGHI, 2017).

For environmental reasons, both the preservation of traditional wood and the use of hardwood species are subject to political and consumer restrictions. It is known that the effectiveness of traditional wood preservation systems is due to the biocidal effect of the products used, however, consequently, they pollute the environment. In addition to the risks involved in the use of such materials, there is a growing concern about the problems arising from the flow of wood at the end of its commercial life (KOSKI,

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2008). Thus, there is a growing need to develop effective antifungal chemicals that are non-toxic to humans and the environment.

The search for alternatives to current condoms has been efficient, but not effective, that is, a viable alternative to existing products has not yet been found. Based on several studies, the search for a wood preservative can be divided into:

- Plant extractives with natural resistance to biodeterioration.
- By-products of processes.

In general, obtaining extractives from plants with natural resistance to biodeterioration adds cost to the product, as it has the need for reforestation areas in addition to an extraction and processing process.

So, focusing on the Cost x Benefit x Environment relationship, the most viable alternative was established to develop a preservative that contemplates most of the desirable properties, and that is effective in protecting Pine and Eucalyptus wood. Therefore, the sustainable alternative chosen for the development of this study was based on by-products of processes.

In the literature, the alternatives of by-products under study with interesting characteristics as a preservative for wood are:

- Chitosan By-product of the crustacean processing industries such as shrimp, crab and lobster (MAOZ; MORREL, 2004; EIKENES et al., 2005; TORR et al., 2006; SINGH et al., 2008; TREU et al., 2009; SATTOLO et al., 2010;
- GORGIJ et al., 2014);
- Okara Organic waste produced from the manufacture of soybean bedding and tofu (AHN et al., 2008 and AHN et al. 2010);
- Konjac Powder Ethanolic Extract (Amorphophallus konjac K. Koch) By-product produced during the mechanical processing of ethane extract (BI et al., 2019):
- Crude Tall Oil (CTO) e seus derivados Subproduto da polpação Kraft (JEMER etal., 1993; PAAJANEN; RITSCHKOFF, 2002; ALFREDSEN et al., 2004; VÄHÄOJA et al., 2005; HYVÖNEN et al., 2006; TEMIZ et al., 2008; KOSKI, 2008; ANITA et al., 2014; DURMAZ et al., 2015; SIVRIKAYA; CAN, 2016).

Among the alternatives of process by-products, Tall Oil was chosen for this investigation, because Brazil has several kraft pulp and paper industries. In addition, in evaluating the properties of various oils, resins and waxes, no single component can meet all the requirements regarding protection from biodeterioration and the surface coatings or impregnating used for wood treatment must therefore be made from a mixture of oils, resins and waxes. According to Temiz et al. (2008) and Koski et al. (2008), unlike

other natural oils, Tall Oil already contains all the necessary components for good natural protection: oils, resins and waxes.

According to Singh et al. (2019), wood extractives from coniferous species, which include resinous acids, fatty acids, and triglycerides, have useful properties making them valuable as natural products. Their water repellency, adhesive properties, and biological activity make them useful in manufacturing, agriculture, and medicine with wider applications, which are expected to be developed in the future with a shift towards renewable resources, and Tall Oil has these extractives.

Tall Oil Crude (CTO), Tall Oil or Talol or resin oil is the generic name for products derived from residual, smelly, gummy and black liquor. It is found and extracted from the residual liquor of Kraft cooking from the production of pulp and paper, known as "black liquor" (VÄHÄOJA et al., 2005), and considered one of the cheapest natural oils, from a renewable source, on the world market, as it is an industrially generated product, not depending on weather and soil, but on the production of pulp and kraft paper. (HYVÖNEN et al., 2006).

The use of Tall Oil as a protective agent in wood has been considered promising for significantly reducing the absorption of capillary water from the sapwood, removing one of the factors that favor wood being attacked by fungi and insects: water, oxygen and nutrients (HYVÖNEN et al., 2006). This repellency is due to its precursors, which are extracts found mainly in coniferous trees (KOSKI, 2008; TEMIZ et al., 2008).

Tall Oil is considered one of the cheapest natural oils from renewable sources in the world market, as it is an industrially generated product, not depending on weather and soil, but on the production of pulp and kraft paper. The yield and composition of Tall Oil can vary, as they are influenced by the amount of extractives, the quality and species of the wood, and the storage time before cooking (SALES, 2007).

It is not composed of pure triglycerides, like other vegetable oils, but rather a mixture of fatty acids, resinous and unsaponifiable acids, e.g. sterols, waxes, hydrocarbons. The amount of these components varies with age, wood species, geographic location, and also with all operations before and during the pulping process (KOSKI, 2008).

According to KWON et al. (2016), the primary organic compounds in Tall Oil are lignin, polysaccharides, carboxylic acids, and extracts, while the main inorganic substances are sodium hydroxide and sodium sulfide. Studies on the use of Tall Oil as a preservative for wood are scarce, and it is necessary to leverage research in this area. In addition, the few studies found only take into account CTO, Tall Oil Fatty Acid (TOFA) fatty acids and Tall Oil (DOT) distillates, and there is no research considering the byproducts of Tall Oil fractionation. In addition, investigations on the corrosive effect of Tall Oil and its derivatives are necessary to establish the optimal condition of protection of wood against biodeteriorating agents and the durability of the metal fasteners used in wood. It should be noted that the corrosion



products of the metallic elements embedded in the wood can, among other factors, stimulate the development of xylophagous fungi through the release of nutrients or the alteration of pH, and thus increase the rate of biodeterioration of the wood.

In general, raw Tall Oil can be refined to various types with different chemical compositions, namely: Tall Oil Fatty Acid (TOFA), Tall Oil Distillate (DTO), Tall Oil Rosin (TOR/TORA), and Pitch. In addition to the commercial products already mentioned, fractionation by-products are Ejector Oil (OE) and Light Oil (LO), which do not yet have commercial application. And, among the by-products of fractionation, the EO has interesting characteristics such as preservatives for wood.

#### **OBJECTIVE**

The objective of this study is to develop a preservative for fast-growing woods using by-products of processes. Two viable alternatives that contain interesting inhibition properties are ejector oil, which is a derivative of Tall Oil, which is a byproduct of Kraft pulping; and the silver skin of the coffee that is separated from the bean during the coffee roasting process and considered waste by the coffee industry. Thus, obtaining a sustainable alternative in the management of waste generated in the *kraft paper* and coffee industries, adding value to the by-products.

#### **METHODOLOGY**

**Samples of wood species:** Two fast-growing wood species were sampled in this study: Pinus elliotti and Eucalyptus grandis. Wood samples were taken on 18-year-old Pinus and 8-year-old Eucalyptus. For both pine and eucalyptus, the samplings were of sapwood wood. The 60 specimens, 30 of Pine and 30 of Eucalyptus, were packed at  $25 + 3$  °C, relative humidity at 65% and equilibrium humidity at 12%. Specimens of 2.5 x 2.5 x 5.0 cm were used for the tests, respectively in the radial longitudinal, tangential longitudinal and transverse sections.

**Tall Oil Samples:** The samples used for this study were Crude Tall Oil (CTO), Tall Oil Distillate (DTO) and Ejector Oil (OE), with the EO being a by-product of CTO fractionation.

The current technology for CTO refining is based on vacuum distillation, whereby its acid fraction is separated by means of distillation columns. Normally, a first distillation column is used to separate the most volatile fraction (fatty acids and resinsic) from the heavier one, called Pitch, which contains sterols, hydrocarbons, long-chain alcohols and high molar mass waxes. A second column is usually used in the volatile fraction to separate the Tall Oil Fatty Acid (TOFA) from the resin acids (rosin or rosin), these two fractions being the ones with the highest commercial value. The CTO fractionation process condition data has not been released by the vendor.

So, in addition to the known products of commercial interest, a by-product of the fractionation of the CTO, namely, the State Budget. The CTO, and the derivatives (DTO and OE) were obtained from the company Resitec Indústria Química Ltda.

Figure 1 shows the CTO, DTO and OE samples in natura. The three samples are viscous liquids, dark in color (yellow-black) and with a strong odor characteristic of the Kraft pulping process.

Figure 1. Physical aspect of the CTO, DTO and OE in natura samples.



**Physical characterization of the Tall Oil samples:** The physical characterization of the three Tall Oil samples was carried out according to the current standards, as described in Table 1.



**Chemical characterization - Chromatographic analysis:** The chemical characterization of the CTO, DTO and OE samples was carried out at Resitol Indústria Química Ltda. The equipment used for characterization was a gas chromatograph coupled to a mass spectrometer (GG-EM), HP 5890 series II mass chromatograph, equipped with an Ultra HP-5 capillary column (30 m, 0.25 mm internal diameter). An HP 5970 mass detector was used. The conditions of analysis were not released by the company.

**Application of preservative systems to specimens:** In the present study, the effects of three samples of Tall Oil with variable chemical composition were tested separately in two wood species – Pinus elliotti and Eucalyptus grandis. The Tall Oil samples were applied in natura and dissolved in isopropanol at concentrations of 25%, 50% and 75%. The condom treatment systems under study were applied to the specimens at room temperature  $(27 + 4 °C)$ , as described in Table 2.



Sistemas preservativos	<b>Etapas</b>	Processo aplicação dos sistemas nos Corpos de Prova
CTO (25%, 50% e 75%)		Vácuo inicial de 600 mmHg por 30 minutos.
DTO (25%, 50% e 75%)	$\overline{2}$	Aplicação do produto (CTO, DTO ou OE) sob vácuo.
OE (25%, 50% e 75%)	3	Vácuo de 600 mmHg por 30 minutos com o produto aplicado.
	4	Amostras retiradas do cilindro e secas ao ar.

Table 2. Stages of the application processes of preservative treatment systems

The Tall Oil samples were prepared by dissolving each of them in isopropanol. The bibliographic references on the use of Tall Oil as a preservative for wood showed trials with the use in natura (KOSKI, 2008) and dissolved in isopropanol (TEMIZ et al., 2008). It was decided to develop the study with samples in 25%, 50% and 75% isopropyl solution. The equipment used to apply the condom systems to the specimens consisted of a vacuum pump, a stainless steel cylinder with a capacity of 1.5 liters.

**Accelerated rot test:** The specimens were subjected to accelerated rot tests in the laboratory with white rot rotting fungi, *Trametes versicolor* (L.; Fr.) Pilát., using the methodology adapted from ASTM D2017 (2005). White rot fungi are considered to be important commercial wood rot fungi as they can cause serious damage within a short period of time (TEMIZ *et al.*, 2008).

The inoculums of the white rot fungus were previously prepared in liquid medium (malt and distilled water) and later deposited in the earth as a substrate. The samples were placed in containers with soil contaminated with the rotting fungus of white rot. The fungus was inoculated into the soil without prior sterilization. Three replicates for each treatment and for each wood species were used; and samples of untreated wood were included to measure the viability of the fungus strain, totaling 63 samples. Thus, the treatments were established in the combination of the two wood species and the 9 preservative systems.

The incubation time in an acclimatized chamber was 12 weeks at  $27 + 2$  °C and 75% relative humidity. After the incubation period, the fungal mycelium was removed from the samples, and the specimens were dried in an oven at  $40 + 2$  °C to 12% humidity. To verify whether the humidity reached the desired value of 12%, humidity measurements were taken every 24 hours with a portable Instrutherm meter model UM-626.

**Contact angle measurement – Goniometry:** Goniometry is a macroscopic measurement that allows the determination of the surface energy of a given material. To do this, a drop of a given solution is pipetted over a given sample under study. The contact angle is a quantitative measure of the wettability of a solid by a liquid. The greater the contact angle, the lower the wettability, that is, the greater the hydrophobicity of the substrate (BURKARTER, 2010). The contact angle  $(\theta)$  used in the study is illustrated in Figure 2. The surfaces were classified according to their contact angle, as shown in Table 3.



Figure 2. Wettability conditions of a surface: (a) superhydrophilic surface,  $θ = 0^\circ$ ; (b) surface with partial wettability,  $140^\circ > θ$  $> 0^{\circ}$ ; and (c) superhydrophobic surface,  $\theta > 140^{\circ}$ . (Burkarter, 2010).



Table 3. Classification of surfaces according to contact angle (Adapted from Burkarter, 2010).



As it is an anisotropic material, wood has distinct properties in the three planes (transverse, radial longitudinal and tangential longitudinal). The contact angle measurements were performed in these three directions for the two wood samples analyzed, as shown in Figure 3.



Figure 3. Transverse, tangential longitudinal and radial longitudinal planes of a wood sample (Barnices, 2010).

The treated sample was placed on the goniometer, a drop of deionized water was then placed on the sample and the angle of contact between the droplet and the treated surface was measured. The analysis was carried out under the conditions of ambient temperature and humidity, respectively,  $25 + 2$ °C and 60%. Figure 4 (a) and (b) shows the goniometer used to measure the contact angles.





## **RESULTS AND DISCUSSIONS**

**Physical characterization of the Tall Oil samples:** The results of the physical characterization tests of the three Tall Oil samples can be seen in Table 4.

Table 4. Results of the tests carried out for the physical characterization of the Tall Oil samples

	Amostras de Tall Oil										
<b>Características Físicas</b>	<b>CTO</b>	<b>DTO</b>	<b>OE</b>								
Indice de Acidez (mg KOH g <sup>-1</sup> )	155,00	182,00	90,00								
Viscosidade (Cts)	80,00	50,00	45,00								
Flash Point (°C)	190	210	160								
Insaponificáveis (%)	8,00	4,00	30,00								
Indice de Saponificação (mg KOH g-1)	164,00	184,00	90,00								

The EO sample was the one that presented the lowest incidence of acidity, and lowest viscosity, the lowest Flash Point and lowest saponification index, and consequently the highest percentage of unsaponifiables. These characteristics are very important for the stability of a wood preservative product. According to Dias (2015), the high concentration of unsaponifiables is capable of delaying the appearance of degradation products, partially preventing the deterioration of the bioactive compounds present.

**Chemical composition of the Tall Oil samples –** Chromatography: Bibliographic references were found regarding the composition of the CTO of other countries, being very restricted as to the composition of the national CTO. Table 5 shows the results of the typical composition of the CTO of Scandinavia, the United States, France and Canada presented by Sales (2007), showing that the composition of the national CTO of Resitol Indústria Química Ltda, presents a very particular composition, being different from that found in the world literature . Compared to the data obtained in the literature, the CTO sample analyzed has a higher amount of fatty acids and a lower amount of resinous acids.



. . Característica	Escandinávia	<b>Estados Unidos</b>	Canadá	Franca	<b>Brasil</b>
Acidos Graxos, %	45,0	45,0	42,0	40,0	55,0
<b>Ácidos Resínicos, %</b>	30,0	42,0	30.0	46,0	30,0
Insaponificáveis, %	25,0	13,0	28,0	14,0	15,0

Table 5. Typical Composition for the worldwide CTO compared to the analyzed sample

Figure 5 shows the result of the chromatographic analysis of the CTO, DTO and EO samples. It is possible to observe that DTO contains more fatty acids. The EO contains a greater amount of unsaponifiables, which include sterols, alcohols and hydrocarbons. According to Koski (2008) and Sales (2007), the amounts of fatty acids, resinous and unsaponifiable acids in the CTO vary, respectively,  $40 -$ 60%,  $30 - 55%$  and  $1 - 10%$ ; and, in this study, the data obtained for the CTO were 55% fatty acids, 30% resinous acids and 15% unsaponifiables, showing that the amounts of fatty and resin acids are within the limits of the literature.



The composition of the products, DTO and OE, of the fractionation of the CTO, have a concentrated composition of fatty acids and unsaponifiables, as they are two currents composed of the lighter components of the CTO. DTO has 64.8% fatty acids, 30% resinous acids and 5.2% unsaponifiables. Comparing the CTO samples with the DTO samples, a decrease in the concentration of unsaponifiables and an increase in the concentration of fatty acids were observed. And as for the increase in the concentration of unsaponifiables in the EO sample to 47.1%, it was already expected due to the thermal degradation of fatty and resinous acids during the thermal fractionation process. And, it is still possible to observe that resinous acids have suffered greater thermal degradation than fatty acids. This result is in line with what was obtained. Table 6 and Figure 6 show the types and amounts of fatty acids and resinic acids in the CTO, DTO and EO samples.

The fatty acids found in the samples were palmitic, palmitoleic, stearic, oleic, linolenic and linoleic; and the resin acids were palustric, abiotic, dehydroabietic and neoabietic. In the three samples, the fatty acid in greater quantity is oleic acid (C18H34O2).

In the DTO sample, an increase in the concentration of fatty acids is observed. In the EO samples, an increase in the concentrations of oleic and palmitoleic fatty acids was observed. This result shows that the fatty and resinous acids that have been reduced, have undergone thermal degradation.







Figure 6. Result of chromatographic analysis of resinous acids and fatty acids of CTO, DTO and OE

Accelerated rot assay: The specimens were evaluated weekly to monitor the growth of the fungal mycelia. Table 7 shows the week in which white rot mycelia began to appear in treated and untreated specimens.

	<b>SEMANA</b>																							
<b>SISTEMAS PRESERVATIVOS</b>	1 <sup>a</sup>			2 <sup>a</sup>		3 <sup>2</sup>		4 <sup>3</sup>		5 <sup>2</sup>		6 <sup>3</sup>		7 <sup>2</sup>	8 <sup>3</sup>		9 <sup>3</sup>		10 <sup>3</sup>		11 <sup>3</sup>		12 <sup>a</sup>	
	P	E	P	E	P	Е	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E
<b>Sem Tratamento</b>	X	$\times$	X	X	X	X	$\times$	$\times$	$\times$	$\mathsf{X}$	$\times$	X	$\mathsf{X}$	$\mathsf{X}$	$\times$	$\times$	X	$\times$	X	X	X	$\mathsf{X}$	X	$\mathsf{X}$
CTO(25%)																							x x x x x x x x x x x x x x x x x	
CTO (50%)							X	$\times$	X	$\times$		X X X X				X X	X		$X$ $X$ $X$		$\mathsf{X}$		$X$ $X$ $X$	
CTO (75%)								$X$ $X$ $X$		$\mathsf{X}$											X X X X X X X X X X X		$X$ X	
DTO (25%)												$X$ $X$ $X$		X		X X	X	$\mathsf{X}$	X	$\times$			$X$ $X$ $X$ $X$	
DTO (50%)																							X X X X X X X X X X X X X	
DTO (75%)																							X X X X X X X X X X X X X	
OE (25%)												$X$ $X$	$\mathsf{X}$	X							X X X X X X X X		X X	
OE (50%)													X	X	$\times$	$\times$	$\times$	$\times$	X	$\times$		x x	X X	
OE (75%)															X								X X X X X X X X X	
Legenda: P – Pinus elliottii; E – Eucalyptus grandis; X – Presença do micélio.																								

Table 7. Visual monitoring of the accelerated approval test

White mycelia in the Eucalyptus and Pinus samples were observed in the 1st week of inoculation in the untreated samples and increased until the end of the trial. In the samples treated with CTO, changes were observed in the 4th week in the three concentrations studied. It is shown that increasing the concentration from 25% to 75% did not alter the protection mechanism. The same behavior was observed in the samples treated with DTO, but the mycelia appeared in the 6th week. For the samples treated with EO, the mycelia appeared in the 6th week. And, the results showed that the higher the concentration of LE, the greater the resistance to biodegradation, because for every 25% increase in concentration, resistance increased in 1 week. For all systems, there was no difference in the treatments regarding the wood species. Both Eucalyptus and Pinus showed similar results for the same treatment.

The results obtained in the accelerated rot assay showed that CTO and its derivatives are suitable as a preservative for fast-growing woods, as they increase the resistance to white rot, but with some observations that will be pointed out below. The samples that showed the best result of resistance to attack of the white rot fungus were those treated with DTO and with LE in which the mycelia only appeared in the 6th week. And the increase in the concentration of EO increases resistance to biodegradation. This increase in resistance may be due to the high concentration of oleic acid and unsaponifiables of the OE, as suggested by some researchers such as Davidson et al. (1999), Walter et al. (2004), Hashim et al. (2009), Clausen et al. (2010), Dias (2015), Rabello et al. (2017) and Godoy et al. (2018).

Research is still needed to identify the unsaponifiable substances present in the Tall Oil samples.

**Measurement of the contact angle – Goniometry:** Table 8 shows the images obtained in the goniometric test and the measurements of the contact angles. The results showed that the specimens

treated with CTO, DTO and EO samples improve the water repellency action. Regarding the direction of the plane (transverse, longitudinal radial and longitudinal tangential), the results did not show significant variations, showing that the impermeability offered by the condom product is the same in all planes.

The untreated Pinus samples showed a contact angle close to 0 (zero), showing to be superhydrophilic; and the Eucalyptus samples, under the same conditions, showed variations in the contact angle between 23° and 26°, showing to be hydrophilic.

All samples, both pine and eucalyptus, submitted to treatments with CTO, DTO and OE, showed intermediate behavior between hydrophilicity and hydrophobicity with contact angle varying between 56° and 70°, regardless of the concentration of the condom systems. This result shows that the systems under study decrease hydrophilicity.

Even maintaining an intermediate behavior between hydrophilicity and hydrophobicity with contact angle, the variation in the contact angle of the sample treated with EO is smaller than that of samples treated with CTO and DTO. This result may be due to the high concentration of unsaponifiables in the EO sample.

According to Koski (2008), non-biocidal treatments act in a hydrophobic way, delaying or preventing colonization by fungi; Therefore, the tested preservative systems have potential as preservatives for wood.



### **FINAL CONSIDERATIONS**

From the accelerated rot assay, it was observed that the condom systems with CTO, DTO and OE improve the white rot resistance class.

The literature describes that the resistance to biodegradation of the various Tall Oil's is due only to hydrophobicity. This information is not supported by the results of the tests carried out in this study. The three samples showed similar degree of hydrophobicity, but the systems that showed greater resistance to the white rot fungus were with EO and DTO.

It was found that the increase in the concentration of fatty acids increases hydrophobicity and this increase is not proportional to the resistance to rot, showing that the presence of unsaponifiables also contributes to the increase of this resistance. And, this increase contradicts Koski (2008), where he states that the resistance to rot is due only to hydrophobicity.

So, it is not only hydrophobicity that inhibits the action of microorganisms. The high concentration of oleic acid, the presence of unsaponifiables and the stability of the acidity index and saponification index may be indicative of better resistance to biodegradation. According to the literature, oleic acid and unsaponifiables may be the precursors of this resistance.

The substance that presented the most satisfactory results for potential use as a preservative for wood was OE, a by-product of CTO fractionation.

This research should be extended to other characterization analyses of unsaponifiable substances, helping to understand the composition of the Tall Oil samples, relating to the resistance to biodeterioration on wood, and this is being provided to support possible conclusions to be made in the publications organized in the future.



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