

Review Article

Derivatives from Black Liquor as a Wood Preservant: A Review

Kelly Bossardi Dias, Ricardo Marques Barreiros

Department of Lignocellulosic Materials, School of Engineering, São Paulo State University (UNESP), Campus of Itapeva, São Paulo, Brazil

Email address:

kbossardi@gmail.com (K. B. Dias)

To cite this article:Kelly Bossardi Dias, Ricardo Marques Barreiros. Derivatives from Black Liquor as a Wood Preservant: A Review. *American Journal of Heterocyclic Chemistry*. Vol. 3, No. 6, 2017, pp. 74-77. doi: 10.11648/j.ajhc.20170306.13**Received:** November 6, 2017; **Accepted:** November 15, 2017; **Published:** December 13, 2017

Abstract: Increased concern with environmental issues, the health of operators of wood mills and the consumers of wood, and the reuse of these treated woods after their use, has generated the need to develop less aggressive wood treatments and the environment with sustainable principles. Thus, the aim of research has been to develop environmentally correct and effective products against the attack of biodeteriorating agents. One viable alternative containing interesting inhibiting properties is Tall Oil, which is a natural oil from, renewable-source. Tall Oil is a by-product of kraft pulp production. This byproduct is not a pure triglyceride compound, but a mixture of fatty acids, resin and unsaponifiable acids. The use of Tall Oil and its derivatives as a protective agent in wood has been considered promising. It can be used pure, whether crude or distilled; and also mixtures with efficient biocides, but leachable as boron. However research is still needed including the characterization of Tall Oil products, the determination of the protective agent and the environmental aspects.

Keywords: Tall Oil, Derivatives, Biodeterioration

1. Introduction

Wood is an economical, historical and sustainable material. Many species of wood are naturally resistant to the action of degrading organisms. However, species with this natural resistance can not cover the demand for wood and wood products, which has been growing year by year [1]. The shortage of species that are resistant to biological degradation has forced man to use less durable, mainly fast growing species, from reforestation, such as some species of Eucalyptus and Pinus. These species have moderate or no resistance to the attack of biological agents and require preservatives [2].

In general, in order to increase the shelf-life of these fast-growing woods by protecting them from fungi, insects and other xylophagous organisms, several preservatives (biocides) are used, these compounds being highly toxic to these xylophagous organisms.

Traditional methods of wood protection employ chemicals that are considered toxic and can harm human health and the environment [3]. The classic concept of wood preservation is

based on the principle of toxicity. The salts of arsenic, chromium, copper and tin have been used along with toxic organic chemicals, such as creosote. Wood has been treated with these chemicals at different load levels using various solvents which made them more effective in the long run against fungal attack. Unfortunately, these chemicals are also toxic to humans and other life forms [4].

For environmental reasons, both the preservation of traditional wood and the use of resistant wood species are subject to political and consumption restrictions. It is known that the effectiveness of traditional wood preservation systems is due to the biocidal effect of the products used, but, consequently, they pollute the environment. In addition to the risks involved in the use of such materials, there is a growing concern with the problems arising from the disposal of wood at the end of its commercial life [5]. Thus, there is a growing need to develop effective antifungal chemicals that are non-toxic to humans and the environment.

Efforts are being made globally to develop alternative methods of protection based on products with little or no toxicity to humans and the environment, but progress in

technology implementation has been slow because of several limitations, including laboratory and performance discrepancies in the field of natural products, variability in its exposure-related efficacy, environmental conditions, legislation and difficulties due to worldwide divergences in setting standards that define the quality of its performance and use [3].

There are several other ways to approach wood preservation without the use of toxicity as the mechanism of effectiveness. One approach is to interfere with the metabolism of aggressive organisms. There is a very close relationship between the moisture content of wood and its biodegradation [4]. For wood to be attacked by fungi and insects, four factors must be present: water, oxygen, temperature and nutrients. So, to avoid the attack of these organisms, some research has aimed at removing one of these factors, for example, water with the use of hydrophobic products [6].

The use of Tall Oil as a protective agent in wood has been considered promising because it significantly reduces sapwood capillary water absorption, removing one of the factors favoring wood being attacked by fungi and insects: water, oxygen and nutrients [7]. This repellency is due to its precursors, which are extracts found mainly in coniferous trees [5, 8].

Crude Tall Oil (CTO) can be refined to various types of Tall Oil with different chemical compositions, with CTO's main commercial products being Tall Oil (TOFA), Tall Oil Distillates (DOT) and Breu de Tall Oil (TOR). And both CTO and derivatives have potential as preservative for wood.

2. Tall Oil

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 liqueur of Kraft cooking, known as "black liquor" [9]. Tall Oil, a byproduct of the paper pulp kraft process, consists of fatty acids (typically saturated or unsaturated C16-C18), resin acids, neutral or unsaponifiable substances, and water. During this process, the fatty acids and resin acids present in the wood and main constituents of the CTO are recovered by acidifying the soaps of these acids recovered from the concentrated black

liquor [10]. This by-product was initially obtained on a laboratory scale during the alkaline pulping of coniferous wood in Europe, and the first data from its extraction and consequent commercial exploitation date back to the year 1901 in Sweden [11].

Conifer woods, especially Pinus, contain approximately 3% of a low molecular weight fraction consisting of free resin acids, long chain fatty acids, sterols, volatile terpenes and other unsaponable materials. These materials, which are the bulk of the extract from wood, make up CTO. It is a very viscous substance, darkened (yellow-black) and with a characteristic kraft odor [10].

Tall Oil is considered one of the cheapest natural oils in the world market, since it is an industrially generated product, not depending on weather and soil, but on the production of cellulose and kraft paper. The yield and composition of Tall Oil may vary, as they are influenced by the quantity of extractives, the quality and species of the wood, and the storage time before cooking [10]. It is not composed of pure triglycerides, like other vegetable oils, but a mixture of fatty acids, resin acids and unsaponifiables (eg, sterols, waxes, hydrocarbons). The amount of these components varies with age, wood species, geographical location, and also with all operations before and during the pulping process [5].

The primary organic compounds in Tall Oil are lignin, polysaccharides, carboxylic acids and extracts, while the major inorganic substances are sodium hydroxide and sodium sulfide [12].

The yield of Tall Oil in Brazil was reported in 30-40 kg / ton of cellulose produced. And statistical data provided in 2016 by the Brazilian Association of Pulp and Paper have shown annual production of 1.8 million tons of kraft pulp, indicating potential growth for this industrialization. There is a wide range of uses for Tall Oil due to availability and low cost, such as emulsifying products, drill oils, bonding and bonding materials, soap industry, enamels and paints, etc. [10]. In general, Crude Tall Oil can be refined to various types with different chemical compositions. Figure 1 lists the top commercial products and fields of application for Tall Oil distillate products. Some uses of Tall Oil are similar to TOFA and DTO, but with CTO distillation the characteristics are more uniform to the products obtained [13].

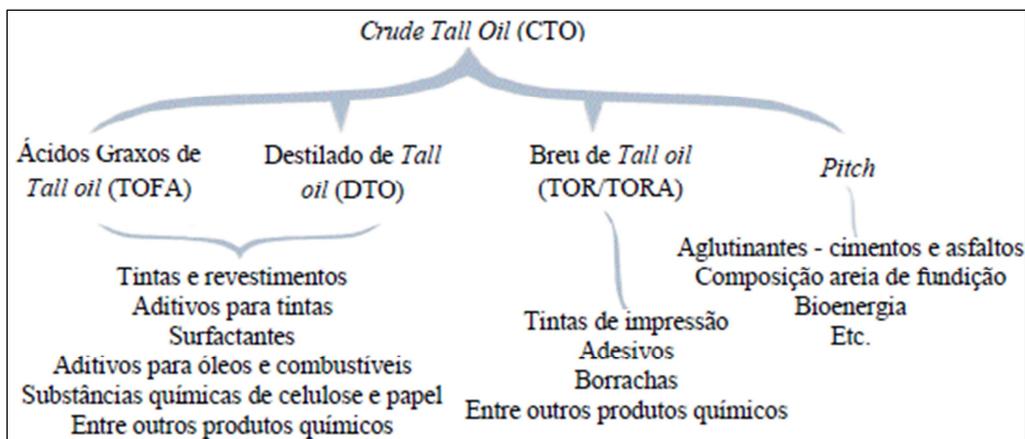


Figure 1. Distilled products obtained from Tall Oil.

3. Tall Oil as Preservative

Investigations with Tall Oil indicate their potential as a protective agent for wood. Jermer et al. (1993), Paajanen and Ritschkoff (2002), Alfredsen et al. (2004), Vähöja et al., 2005, Hyvönen et al. (2006), Temiz et al. (2008), Koski (2008), Anita et al. (2014), Durmaz et al. (2015) and Sivrikaya & Can (2016) focused their studies on developing alternatives to current preservatives using Tall Oil. In general, they indicate that the preventive effect of Tall Oil is probably related to the hydrophobic properties.

Jermer et al. (1993) tested the effect of Tall Oil derivatives against biological degradation, and compared them with preservatives in current use, such as CCA and creosote. They obtained results showing that the two derivatives of Tall Oil can be almost as effective as CCA and creosote.

Paajanen and Ritschkoff (2002) showed that the crude Tall Oil applied in varnish samples did not produce a zone of inhibition on the growth medium, thus, the inhibitory effect of Tall Oil is not caused by fungal toxicity. Most likely, the preventive effect is related to hydrophobicity. Based on the effectiveness of Tall Oil products, be mainly due to hydrophobicity, the idea is that by reducing the moisture content of the wood, fungal growth is limited.

Alfredsen et al. (2004) tested the efficacy of four Tall Oil derivatives in growth rate assays of *Coriolus versicolor* brown rot fungus and *Poria placenta* brown rot fungus on filter paper and wooden mini-blocks of *Pinus sylvestris* L. the effectiveness of the Tall Oil tested was related to the chemical composition of the oils. This was confirmed in the filter paper assay, where the increase in efficacy was relatively proportional with increasing amounts of resin acids. However, this pattern was not found for the mini-block assay. The protective effect of Tall Oil on wood, therefore, seems to be more related to its hydrophobic properties than to its fungicidal properties.

Hyvönen et al. (2006) and Koski (2008) investigated the water-repellent efficiency of raw Tall Oil and emulsified in water. Treatments with Tall Oil reduces the absorption of water in the sapwood. And, emulsion tall oil treatments showed that efficiency, compared to CTO, can be achieved. The emulsion technique is a potential method of decreasing the amount of oil needed to protect the wood from water absorption by capillarity.

The use of Tall Oil as a protective agent in wood has been considered promising because it significantly reduces sapwood capillary water absorption, removing one of the factors favoring wood being attacked by fungi and insects: water, oxygen and nutrients [7]. This repellency is due to its precursors, which are extracts found mainly in coniferous trees [5, 8].

Temiz et al. (2008) verified the potential of four commercially available Tall Oil derived products, tested separately and combined, with two concentrations of boric acid (1 and 2%) against the resistance to attack of two brown rot fungi. The results obtained showed that Tall Oil

derivatives in combination with boric acid are promising as wood preservatives, since they combine fungicidal and water repellency effects. Tests of resistance to degradation indicated that only impregnation with Tall Oil, without the presence of boric acid, was not effective to protect the wood against the fungi tested. Samples with boric acid at a concentration of 2% combined with the Tall Oil derivative consisting of 90% of acids showed the best performance in relation to two brown rot fungi, with a mass loss of less than 3%.

Vähöja et al. (2005) focused their studies on the determination of biodegradation of different products of Tall Oil and linseed oil in groundwater obtaining preliminary information about their environmental effects. They obtained promising results, showing that Tall Oil and linseed oil products are moderately biodegradable, not toxic to the assessed environment.

Anita et al. (2014) and Durmaz et al. (2015) used CTO as a protective agent for biodeterioration. Anita et al. (2014) verified that the resistance to biodeterioration of the timber Jabon (*Anthocephalus cadamba* Miq.), Improved to the attack of fungi of white and brown rot in relation to the sample of untreated wood. The results showed that the process of immersion of Soap wood in the CTO for 60 minutes showed the highest retention. The weight loss suffered by non-preserved and preserved Soap wood was 55.19% to 55.67% and from 6.64% to 12.78%, respectively. Already, Durmaz et al. (2015) found that the durability of Scottish pine saplings (*Pinus sylvestris* L.) on brown rot fungus attacks and affirmed that the products of degradation of carbohydrates, resin and extractive fatty acids, and inorganic materials in the tall oil inhibit fungal activity.

Sivrikaya and Can (2016) found that wood treated with tall oil can provide some reduction in water absorption and increase resistance to decomposition. In this research, the CTO was dissolved in ethanol at concentrations of 5, 10 and 15% in the treatment of Scotch pine. They used dyes, iron oxide and sodium ascorbate as additives in 0.5%. The best results were obtained with 10% CTO and iron oxide.

There are several other ways to approach wood preservation without the use of toxicity as the mechanism of effectiveness. There is a very close relationship between the moisture content of the wood and its biodeterioration [10]. So, to avoid the attack of these organisms, some research has aimed to limit the water with the use of hydrophobic products.

In this context, Tall Oil, which is a natural renewable source oil and exhibits hydrophobic properties, can be an alternative. Tall Oil is an industrially generated by-product of kraft pulp production. The amount of these components varies with age, wood species, geographical location, and also with all operations before and during the pulping process [5].

Tall Oil Crude can be refined to various types of Tall Oil with different chemical compositions, being the main commercial products of the CTO, TOFA, DOT and the TOR. And both CTO and derivatives have potential as a preservative for wood. In addition, in the evaluation of the properties of

various oils, resins and waxes, no single component can satisfy all the requirements for protection against bio-deterioration and the surface coatings or impregnants used for the treatment of wood must therefore be made from a blend of oils, resins and waxes. Unlike other natural oils, Tall Oil already contains all the necessary components for good protection: oils, resins and waxes [20, 21].

In general, the main protection feature for Tall Oil wood and other vegetable oils is water repellency. The progress of oils as wood protectors requires a better understanding of their distribution in the anatomical elements of wood and cell wall, as well as a better understanding of their mode of action [5, 8].

4. Conclusion

According to the investigations, Tall Oil has potential as a preservative for wood. Alternative treatments with Tall Oil have improved the resistance of several species of wood.

Studies are still needed to obtain a preservative product for wood including characterization of Tall Oil products and their derivatives, determination of the protective agent (s) and environmental aspects.

References

- [1] COSTA, F., VALE, A. T., GONZALEZ, J. C., SOUZA, F. D. M. Durabilidade de madeiras tratadas e não tratadas em campo de apodrecimento. *Floresta e Ambiente*, v. 12, n. 1, p. 07 - 14, 2005.
- [2] PAES, J. B. MORESCHI, J. C., J. G. LELLES. Avaliação do tratamento preservativo de moirões d, e *Eucalyptus viminalis* Lab. e de bracinga (*Mimosa scabrella* Benth.) pelo método de substituição de seiva. *Ciência Florestal*, v. 15, n. 1, p. 75-86. 2005.
- [3] SINGH, T., SINGH, A. P. A review on natural products as wood protectant. *Wood Science Technology*, n. 46, p. 851–870, 2012.
- [4] ROWELL, R. M. Chemical Modification: a non-toxic approach to wood preservation. In: *ECOWOOD 2006 – International Conference on Environmentally*, 2. Anais... p. 227-237, Oporto, Portugal, 2006.
- [5] KOSKI, A. Applicability of crude tall oil for wood protection. Departamento de Processos e de Engenharia Ambiental - Faculdade de Tecnologia - Universidade de Oulu, Finlândia, 2008. 104 p. Dissertação de Mestrado.
- [6] AASERUB, J.; LARNOY, E.; GLOMM, W. R. Alternative systems for wood preservation, based on treatment with silanes. In: BERGSTEDT, A. Proceedings of the 5th meeting of the Nordic-Baltic Network in Wood Material Science and Engineering. Copenhagen: Denmark, n. 43, p. 21-26, 2009.
- [7] HYVÖNEN, A., PILTONEN, P., NIINIMÄKI, J. Tall oil/water – emulsions as water repellents for scots pine sapwood. *Holz als Roh-und Werkstoff*, n. 64, p. 68-73, 2006.
- [8] TEMIZ, A., ALFREDSEN, G., EIKENES, M., TERZIEV, N. Decay resistance of Wood treated with boric acid and tall oil derivates. *Bioresource Technology*, n. 99, p. 2102-2106, 2008.
- [9] VÄHÄOJA, P., PILTONEN, P., HYVÖNEN, A. NIINIMÄRKI, J., KUOKKANEN, T. Biodegradability studies of certain wood preservatives in groundwater as determined by the respirometric bod oxiTop method. *Water, Air and Soil Pollution*, n. 165, p. 313-324, 2005.
- [10] SALES, H. J. S. Esterificação seletiva para a separação de esteróis, ácidos resínicos e ácidos graxos do resíduo oleoso de madeira (*tall oil*). Instituto de Química - Departamento de Química Orgânica, Universidade Estadual de Campinas, Campinas, 2007. 167 p. Tese de Doutorado.
- [11] TAILOR, S., KING, J. W. Fatty and resin acid analysis in tail oil products via supercritical fluid extraction-supercritical fluid reaction using enzymatic catalysis. *Journal of Chromatographic Science*, v. 39, p. 269-272, 2001.
- [12] KWON, H. S., MOON J. H., LEE U. D., YOON J. J., WALSUM G. P. V., UM B. H. Fractionation and gasification of black liquor derived from kraft pulping. *Journal of Industrial and Engineering Chemistry*, n. 34, p. 122–129, 2016.
- [13] RAMOS, L. P., GARCIA, J. N. Tall oil: uma fonte de breu ainda pouco usada no país. *Informativo ARESB*, n. 93, nov. 2007.
- [14] ALFREDSEN, G., FLAETE, P. O., TEMIZ, A., EIKENES, M., MILITZ, H. Screening of the efficacy of tall oils against Wood decaying fungi. The internacional research group on wood preservation. IRG/WP 04-30354, 2004.
- [15] ANITA, S. H., FATRIASARI, W., ZULFIANA, D. Utilization of biopulping black liquor as preservative to fungal attack on jabon wood (*Anthocephalus cadamba* Miq.). *Teknologi Indonesia*, n. 37, v. 3, p. 147-153, 2014.
- [16] AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM). ASTM D1413: Standard method for accelerated laboratory test of natural decay resistance for woods. West Conshohocken: ASTM International, 2007.
- [17] DURMAZ, S., ERISIR, E., YILDIZ, U. C., KURTULUS, O. C. Using Kraft Black Liquor as A Wood Preservative. *Procedia - Social and Behavioral Sciences*. n. 195, p. 2177 – 2180, 2015.
- [18] JERMER J., BERGMAN Ö., NILSSON T. Fungus cellar and field tests with tall oil derivatives. Final report after 11 years' testing. The international research group on wood preservation. Anais... 24th Annual Meeting in Orlando, Florida, USA, 16-21 May, 1993.
- [19] PAAJANEN, L., RITSCHKOFF, A. C. Effect of crude tall oil, linseed oil and rapeseed oil on the growth of decay fungi. The International Research Group on Wood Preservation, IRG/WP 02-30299, 2002.
- [20] PANOV, D.; TERZIEV, N.; DANIEL, G. Using plant oils as hydrophobic substances for wood protection. The International Research Group on Wood Preservation, IRG/WP 10-305550, 2010.
- [21] SCHULTZ, T. P.; NICHOLAS, D. D.; SHI, J. Water repellency and dimensional stability of wood treated with waterborne resin acids/TOR. The International Research Group on Wood Preservation, IRG/WP 07-40364, 2007.
- [22] SIVRIKAYA, H., CAN, A. Effect of weathering on wood treated with tall oil combined with some additives. *Maderas. Ciencia y tecnología* n. 18, v. 4, p. 723-732, 2016.