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Chemical and anatomical study of *Gleditsia triacanthos* to identify opportunities for wood and non-wood uses†

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Abstract: In Uruguay and neighbouring countries, *Gleditsia triacanthos*, is an exotic tree species categorized as invasive; it produces severe ecological impact as it displaces native species, changing the structure of the native forest community. One way to mitigate its negative impact is to identify opportunities to use it by revaluating its biological products. This work studies the applicability of this species as a source of both combustible and non-wood products. The heat capacity, chemical composition and anatomical description of its wood was determined. Polyphenols extracted by way of an adhesive for timber products were finally added, partially substituting petroleum derivatives; it showed promising results.

Keywords: *Gleditsia triacanthos*; heat capacity; polyphenols; cellulose tenor; lignin tenor

1. Introduction

Known as honey-locust, *Gleditsia triacanthos* (*Gt*) is a woody species of the Fabaceae family, native to North America [1]. It is a thorny, medium-sized tree with a straight stem form, usually reaching 21-25 m, with a dbh of 60-100 cm. It appears to require warm (temperate or mediterranean) climates with moist (moist semi-arid to sub-humid) conditions to become invasive, though actual requirements are far from clear [2]. It can be considered an aggressive colonizer: a root sucker, its abundant seed production and high germination capacity [3] allows it to rapidly form dense, impenetrable stands. *Gt* is a successful invader given its competitive ability, its phenotypic plasticity and its high adaptability to different environments [4]. It forms mixed or monospecific forests [5]. This species has been introduced all around the world, spreading away from where it is planted, and becoming a naturalized or invasive species [6]. Today it is categorized as invasive in Oceania, Europe and many South American countries, such as Uruguay and Argentina. In Australia [7] and Africa [8] it is a potentially invasive species.

As any other biological invasion, *Gt* is a main cause of biodiversity loss [9] which has severe economic [10] and ecological impact, as it displaces native species, changing the structure of the native forest community and negatively affecting native fauna and flora. Given its wide distribution, it is extremely difficult to control. Chemical methods, namely drilling the trunk and applying herbicides, are commonly used; such control methods reduce its effects on the environment, visual impact and operation costs and time [1]. One way to mitigate its negative impact is to identify opportunities to use *Gt* after cutting down the bushes by reevaluating its biological products. Using its wood or non wood byproducts and residues as raw material for new biochemical products, biomaterials and biocombustibles creates added value and reduces waste. There are various examples of biorefining and valorization of *Gt*, scalable for designing cost-effective, circular bio-

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economy approaches: the galactomannans fraction from *Gt* seeds could become a food texture modifier for starch-based products [11]; the galactomannans could also be used as a foam stabilizer and thickening agent in the food industry[12]; a functional wound dressings with antioxidant and antimicrobial activity developed from the cellulose of *G. triacanthos* pods, and phenolic compounds extracted from its leaves[13].

This work aims to study the applicability and valorization of this species as a source of both combustible and non-wood products, creating sustainable value chains based on a circular economy that could be put into practice in Uruguay and the region. In order to achieve this, the calorific value, chemical composition and anatomical description of its wood was determined, as well as the suitability of its extractives for their use in wood adhesives.

2. Materials and Methods

2.1. Test specimens

27-year-old *Gleditsia triacanthos* (*Gt*) trees from Facultad de Agronomía, Udelar (32° 20'16.22 "S, 54° 26' 58.00"W) were used in the study. Sapwood and heartwood were air dried for five weeks to a stable moisture content of 12%, and then were then cut into (3,0 x 3,0 x 3,0) cm cubes.

2.2. Wood characterization

2.2.1. Microscopy

Wood samples were softened in water for 24 h, and were then sectioned with a sliding microtome Reichert-Jung xylotome (Vienna, Germany) into 10-20 mm thick slides, which were observed with fluoresce microscope, Nikon Eclipse 50i.

2.2.2. Chemical analysis

Heartwood and sapwood were finely milled in a rotary mill (Marconi Ltd, Piracicaba, Brasil), and the 40–60 mesh fraction was used for chemical analysis. A sample was taken in order to determine humidity content by weight difference before and after drying in a stove at 103 ± 2°C until constant weight. Milled samples were extracted with ethanol for 24 h in a Soxhlet apparatus. Chemical analyses were conducted in 3 replicates.

Lignin content [14]: to 300 mg of milled hardwood or sapwood, dry and free from extractives, were added 3,0 ml of 72 % sulphuric acid and then incubated in a water bath set at 30 ± 3 °C for 60 min and then diluted at 4% with purified water and placed in an autoclave at 121°C for 60 min. The mixture was finally cooled down, filtered with a filter crucible by vacuum and washed with hot deionized water. Acid soluble lignin was measured in the obtained liquid with a UV-Visible spectrophotometer at 240 nm; acid-insoluble lignin was determined by weight in the solid residue.

Holocellulose content [15]: 8ml of hot water, 0.5ml of acetic acid and 1g of sodium chlorite were added to 2.5 g of dry extractive free samples, which were then placed in a water bath at 70°C. Every hour, 0.5ml of acetic acid and 1g of sodium chlorite were added until fibers were separated. Later cooled, filtered and washed with distilled water and acetone. Solid was dried at 105° C for 24 h. Finally, for cellulose content [15]: 5g of milled wood was refluxed for 1 hour in an alcoholic solution with nitric acid, which was then filtered and left in distilled water for 30 minutes. The residue was extracted with NaOH at 4% for 40 minutes, then filtered, washed with water and acetic acid and dried at 105°C, 12 h.

2.2.3. Proximate analysis and calorific value

Ash determination was performed according to ASTM D1102 standard [16] in a muffle (ThermoScientific, Massachuset, USA) at 580°C. Volatile determination was performed according to ASTM E872-82 standard [17]. Calorific value was determined according to ASTM D2015-89(00) standard [18] using a calorimetric oxygen pump (XRY-1A +, China).

2.3. Extraction and Stiasny number

Extraction was carried out in a laboratory autoclave[19] in which the milled heartwood was placed in a 1:10 (m/m) ratio, water/wood at 120 ° C for one hour. Then, the mixture was placed on a stove at 70°C in a stainless steel tray until all water evaporated. The resulting dust was milled and used to determine the Stiasny number.

5 mL of formaldehyde 38% and 2.5 mL of HCl 37% were added to 25 mL of *Gt* hardwood extract. Mixture was refluxed for 30 minutes [19], filtered by vacuum, and the solid was washed with distilled water. Solid precipitate was dried at 105 °C until constant weight. Stiasny number (%) was determined as: (Dry mass of precipitate/ Dry mass of extract)*100

3. Results and Discussion

3.1. Chemical and anatomical analysis

Table 1 shows global chemical composition of *Gt* wood, whereas Table 2 shows the proximate analysis. Figure 1 shows pictures of tangential, radial and transversal cuts of *Gt* wood as seen through an optic microscope; porosity, multiseriate rays, as well as obstructions in heartwood vessels.

Overall, *Gt* wood has a similar composition to other wood species although its lignin content is lower than in the literature by 19-21 % [20]. As expected, more extractives were obtained with ethanol from heartwood than from sapwood; however, no differences in structural polymer content was observed between *Gt* heartwood and sapwood.

When comparing *Gt* and *Eucalyptus camaldulensis* wood, it can be observed that cellulose content is analogous to that presented in the literature - 43 – 44 % range for *E. camaldulensis* [21]. However, holocellulose content is higher than that reported for *E.camaldulensis (*65 – 79 % range) [21]. No literature could be found on *Gt*'s lignin content. *E.camaldulensis* is a very dense species, easy to work with and commonly used in the region in construction for its resistance to decay [22] and also as a combustible [23].

Table 1. Chemical composition of *G. triacanthos* sapwood and heartwood. Average values with their respective standard deviations.

Component	Sapwood	Heartwood
Extractives in ethanol (%)	4.29 ± 0.02	8.60 ± 0.02
Cellulose (%)	45.19 ± 1.42	43.41 ± 1.06
Holocellulose (%)	79.9 ± 0.97	82.88 ± 1.68
Acid soluble lignin (%)	0.54 ± 0.02	0.88 ± 0.03
Acid insoluble lignin (%)	13.30 ± 2.07	9.65 ± 0.58

Table 2. Proximate analysis and calorific value of *G. triacanthos.* Average values with their respective standard deviations.

Component	Sapwood	Heartwood
Ash (%)	0.72 ± 0.04	0.80 ± 0.03
Volatiles (%)	83.04 ± 0.62	83.18 ± 0.56
Humidity (%)	9.98 ± 0.05	10.32 ± 0.14
Calorific value (KJ8Kg)	18.24	18.61

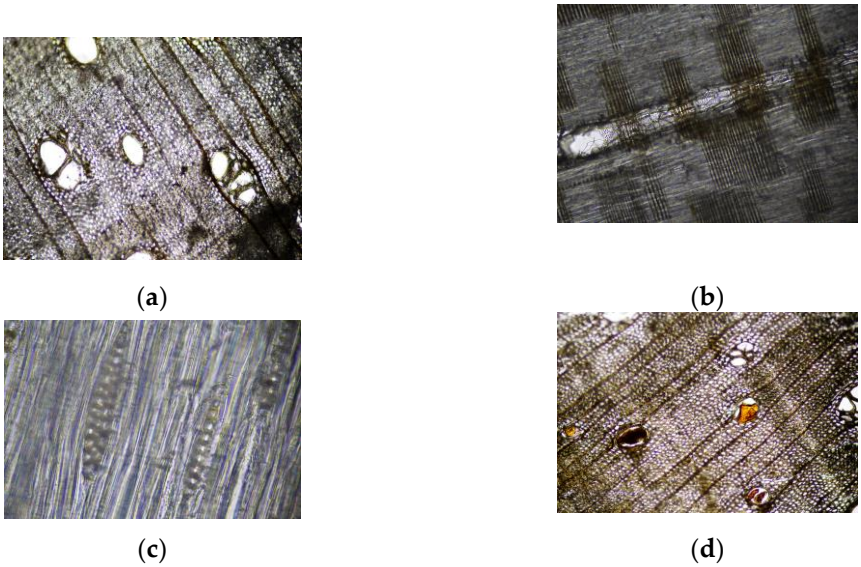

Figure 1. Optic microscope pictures of *Gt*: (**a**) Sapwood tangential cut 10X; (**b**) Sapwood radial cut 10X; (c) Sapwood transversal cut 40X; (d) Heartwood transversal cut 10X.

E.camaldulensis has a calorific value of 19.2 MJ/kg [25], higher than that of *Gt* sapwood and heartwood. Although calorific value indicates its heating potential when using wood as fuel; usually, it is the fuel value index that is used to quantify and compare wood quality as fuel [26]. Said index also takes into account basic density of the wood, humidity and ash content. *Gt* not only has a lower calorific value, but also its basic density and ash content negatively affect its fuel value index. Although using *Gt* wood as fuel does not seem to offer any advantages over wood species used today, it is still a viable option.

Finally, extractive content is lower for *Gt* than for *E. camaldulensis* (10%) [24], but it is higher than that of other *Eucalyptus* species, which present values in the 3.0-5.0% range [26]; although a determining factor for extractive type and quantity, age was not taken into account.

3.2. Extractions and Stiasny number

During the last few decades there has been an increasing interest in substituting fossil products with more natural alternatives, as evidenced by co-efficient bio-based adhesives, developed taking into account ecological and economical aspects [27]. An example of such bio.based adhesive are those in which formol-formaldehyde are partially or totally substituted with tannins. Tannins are compounds of fundamentally phenolic nature, which can be classified into hydrolyzable and condensed. The latter, are very abundant in the heartwood of some wood species, and can be used in the development of adhesives. In this work, solid/liquid extraction had a performance of 10.9 % for sapwood and 14,3 % for heartwood. The latter value coincides with that obtained by maceration with ethanol in previous studies [28] making extraction in an autoclave the most convenient method, as it uses water as a solvent, which is preferred by the industry [29].

Suitability of *Gt* tannins to be used in wood adhesives is evaluated through a simple reaction with formaldehyde, triggering the polymerization of tannins, from which Stiasny number is determined [29]. If it is above 65, tannins are considered to be suitable to be used in adhesives. *Gt* extracts presented values of 85 in heartwood and 65 in sapwood, proving to be suitable to be used in wood adhesive formulations.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. USDA. United States Department of Agriculture. Natural Resource Conservation Service. Plant Guide. Honey Locus. *Gleditsia triacanthos* L. http://plants.usda.gov/plantguide/pdf/pg_gltr.pdf. (accessed on 26 March 2021).
2. CABI, Invasive Species Compendium. Wallingford, UK: CAB International. www.cabi.org/isc. (accessed on 26 March 2021).
3. Sosa, B.; Caballero, N.; Carvajales, A.; Fernández, G.; Mello, A.; Achkar, M. Control de *Gleditsia triacanthos* en el Parque Nacional Esteros de Farrapos e Islas del Río Uruguay. *Ecol. Austral.* 2021. 25:250-254.
4. Tognetti, P. M.; Mazia, N.; Ibáñez G. Seed local adaptation and seedling plasticity account for *Gleditsia triacanthos* tree invasion across biomes. *Ann. of Bot.* 2019. 124(2):307-318
5. Ceballos, S.; Jimenez, Y.; Fernandez, R. Estructura de los bosques de *Gleditsia triacanthos* en función de la edad (valle de La Sala, Tucumán, Argentina). *Ecol. Austral* 2020. 30:251-259
6. Richardson, D.; Rejmánek, M. Trees and shrubs invasive alien species-a global review. *Divers. and Distrib.* 2011. 17:788-809.
7. Csurhes, S.; Kriticos, D. *Gleditsia triacanthos* L. (Caesalpiniaceae), another thorny, exotic fodder tree gone wild. *Plant Protect. Quarter*. 1994. 9 (3), 101–105.
8. Richardson, D.; Thuiller, W. Home away from home – objective mapping of highrisk source areas for plant introductions. *Diver. Distrib.* 2007. 13 (3), 299–312.
9. Vitousek, P.; D'Antonio, C.; Loope, L.; Westsbrooks, R. Biological invasions as global environmental change. *Amer Scient.* 1996. 84: 218 -228.
10. Pimentel, D.; Mc Nair, S.; Janecka, J.; Wightman, J.; Simmonds, C.; O'Connell, C.; Wong, E.; Russel, L.; Zern, J.; Aquino, T.; Tsomondo, T. Economic and environmental threats of alien plant, animal and microbe invasions. *Agric. Ecosyst. Environ*. 2001. 84: 1-20.
11. Loser, U.; Iturriaga, L.; Ribotta, P.D.; Barrera, G.N. Combined systems of starch and *Gleditsia triacanthos* galactomannans:

a. Thermal and gelling properties. *Food Hydrocoll.* 2021. 112 https://doi.org/10.1016/j.foodhyd.2020.106378.

12. Sciarini, L.S.; Maldonado, F.; Ribotta, P.D.; Perez, A G.; Leon T. Chemical composition and functional properties of *Gleditsia triacanthos* gum. *Food Hydrocoll.* 2009. 23: 306–313.
13. Marinas, I.C.; Oprea, E.; Geana, E.; Tutunaru, O.; Pircalabioru, G.G.; Zgura, I.; Chifiriuc, M.C. Valorization of *Gleditsia triacanthos* Invasive Plant Cellulose Microfibers and Phenolic Compounds for Obtaining Multi-Functional Wound Dressings with Antimicrobial and Antioxidant Properties. *Int. J. Mol.* Sci. 2021, 22, 33
14. Sluiter, A.; Hames, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. Determination of Structural Carbohydrates and Lignin in Biomass. National Renewable Energy Laboratory. 2008. 1-15.
15. Abreu HS.; Carvalho, AM.; Monteiro, MBO.; Pereira, RPW.; Silva, HR.; Souza, KCA.; Amparado, KF.; Chalita, DB. 2006. Métodos de análise em química da madeira. Rio de Janeiro, Brasil. Floresta e Ambiente. 20 p
16. ASTM D1102-84(2021), Standard Test Method for Ash in Wood, ASTM Int. 2021.
17. ASTM E872-82(2019), Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels, ASTM Int. 2019.
18. ASTM D2015-00, Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter, ASTM Int. 2000.
19. de Souza, JB.; de Azevêdo, TKB.; Sousa, TB.; da Silva, GGC.; Guimarães, Júnior JB.; Pimenta, AS. Plywood bonding with an adhesive based on tannins from *Acacia mangium* Wild. bark from trees grown in Northeastern Brazil. *Rev. Bras. Cienc. Agrar., Recife*, 2020. 15 (4): e8659.
20. Pereira, B.; Carneiro, A.; Carvalho, A.; Colodette, J.; Oliveira, A.; Fontes, M. Influence of chemical composition of *Eucalyptus* wood on gravimetric yield and charcoal properties. *Bioresour.* 2013. 8 (3): 4574- 4592.
21. Abdel-Aal, MA.; Shetta, N D. Extractives, cellulose, hemicellulose and ash content variation in Eucalyptus camaldulensis trees grown in Egypt. *Alexandria J. of Agric. Res.* 2007. 52 (2): 57-61.

22. Scheffer, T.; Morrell, J. Natural durability of wood: a worldwide checklist of species. Oregon, *For. Res. Lab*. 1998. 58 p.
23. Van der Broek, R.; van Wijk A. Electricidad a partir de Eucalypto y bagazo en ingenios azucareros de Nocaragua. FAO. Departamento de Montes. 1998. FOPW/99/2.
24. González, D.; Mogli, JG. Evaluación de propiedades relacionadas a la calidad de madera en *Eucalyptus camaldulensis*. *Ecoanat. y Biodiver*. 2015.
25. Cabrera, A.; Santelices, R.; Espinoza, S; Magni, C. Energy balance in the first cutting cycle of three eucalyptus species with different levels of management in the Mediterranean drylands of central Chile. *Bosque* 2019. 40(1): 49-56.
26. Deka, D.; Saikia, P.; Konwer, D. Ranking of Fuelwood Species by Fuel Value Index. *Energy Sour*. 2007. Part A. 1499-1506.
27. Pizzi, A. Recent developments in eco-efficient bio-based adhesives for wood bonding: opportunities and issues, *J of Adhesion Sci. and Tech*, 2006. 20 (8): 829-846.
28. Ibáñez, CM; Mantero, C; Raimonda, P; Pintos, X; Pereira, E. Effectiveness of Gleditsia triacanthos heartwood extractives as wood protector. Proceedings IRG *Annual Meeting* Quebec, Canada. 12-16 May 2019. IRG/WP 19-10950.
29. Fraga, M.; García, P.; Pereira, A.; Lourenço, C.; Jimenez, C.; Prieto, MA.; Simal, J. Technological Application of Tannin-Based Extracts. *Mol*. 2020, 25, 614.