forests

MDPI

Article

Wood Vinegar from Slow Pyrolysis of Eucalyptus Wood: Assessment of Removing Contaminants by Sequential Vacuum Distillation

Alexandre Santos Pimenta [1,*], Gil Sander Próspero Gama [2], Francisco Marlon Carneiro Feijó [3], Renata Martins Braga [1], Tatiane Kelly Barbosa de Azevedo [1], Rafael Rodolfo de Melo [4], Neyton de Oliveira Miranda [4] and Gabriel Siqueira de Andrade [1]

[1] Graduate Program in Forest Sciences—PPGCFL, Universidade Federal do Rio Grande do Norte (UFRN), Rodovia RN 160, km 03 s/n, Distrito de Jundiaí, Macaíba CEP 59280-000, RN, Brazil; renata.braga@ufrn.br (R.M.B.); tatianekellyengenheira@hotmail.com (T.K.B.d.A.); gabrielsiqueira96@gmail.com (G.S.d.A.)
[2] Graduate Program in Development and Environment—PRODEMA, Universidade Federal do Rio Grande do Norte (UFRN), Campus de Lagoa Nova, Natal P.O. Box 1524, RN, Brazil; gilsander.pgama@gmail.com
[3] Graduate Program in Environment, Technology, and Society—PPGATS, Laboratory of Veterinary Microbiology, Universidade Federal Rural do Semiárido (UFERSA), Av. Francisco Mota, 572—Bairro Costa e Silva, Mossoró CEP 59625-900, RN, Brazil; marlon@ufersa.edu.br
[4] Centro de Ciências Agrárias, Department of Agronomy and Forest Engineering, Universidade Federal do Semiárido (UFERSA), Av. Prof. Francisco Mota, 572, Costa e Silva, Mossoró CEP 59625-900, RN, Brazil; rafael.melo@ufersa.edu.br (R.R.d.M.); neyton.miranda@ufersa.edu.br (N.d.O.M.)
* Correspondence: alexandre.pimenta@ufrn.br; Tel./Fax: +55-84-3342-2297

Abstract: Eucalyptus wood vinegar (WV) is a versatile natural product employed in several areas such as for agriculture, zootechnics, and veterinary applications. However, the product may contain contaminants such as polycyclic aromatic hydrocarbons, methanol, metals, and so on in its raw form. Thus, refining is required to remove them. Only after reaching a high-purity grade can WV be applied as a basis for pharmaceuticals, antimicrobials, and additives for animal husbandry. This work aimed to assess the effect of refining on the contaminant content of a WV produced on an industrial scale and traded as agricultural input in the Brazilian market. WV was refined by sequential vacuum distillations and had its contaminant contents assessed before and after refining. The following chemical classes were investigated: metals and other elements, insecticides, fungicides, and herbicides (carbamates, organochlorines, organophosphates, pyrethroids, and others), mycotoxins, polychlorinated dioxins and furans, polycyclic aromatic hydrocarbons, and volatile organic compounds, encompassing more than 100 chemical species. Also, the WV physical–chemical properties before and after refining were determined. Gas chromatography and mass spectrometry (GC/MS) were employed to attain the WV's chemical profile. The main chemical components, such as phenolic compounds, furans, ketones, pyrans, etc., were annotated in the WV chemical profile. No traces of insecticides, fungicides, herbicides, heavy metals, mycotoxins, polychlorinated dioxins, or polychlorinated furans were found in raw WV or refined versions. However, several other undes/irable chemicals were determined in the raw product, such as PAHs and volatile organic compounds (acetaldehyde, acetone, ethylene glycol, and methanol). Nevertheless, all of them were effectively removed from the raw WV after the first or second sequential refining steps, resulting in a pure product. Therefore, only one refining step can be applied to raw WV to yield a high-quality product for pharmaceutical and animal husbandry applications.

Keywords: eucalyptus wood; slow pyrolysis; carbonization; wood vinegar; organic and inorganic contaminants; contaminant removal

Citation: Pimenta, A.S.; Gama, G.S.P.; Feijó, F.M.C.; Braga, R.M.; de Azevedo, T.K.B.; de Melo, R.R.; de Oliveira Miranda, N.; de Andrade, G.S. Wood Vinegar from Slow Pyrolysis of Eucalyptus Wood: Assessment of Removing Contaminants by Sequential Vacuum Distillation. *Forests* **2023**, *14*, 2414. https://doi.org/10.3390/f14122414

Academic Editor: Antonios Papadopoulos

Received: 21 November 2023
Revised: 5 December 2023
Accepted: 8 December 2023
Published: 11 December 2023

1. Introduction

The carbonization smoke is composed of gases and vapors emitted during the thermal decomposition of the wood in a poor-oxygen environment from the breakdown of molecules such as hemicelluloses, celluloses, and lignins [1–3]. Carbonization liquids are obtained by driving the smoke gases through a condensation device. Part of the smoke gases condense and are collected by a recipient. After a settling process taking weeks to months, two phases separate: an oily fraction at the bottom of the recipient, called wood tar, and a supernatant aqueous one, the raw wood vinegar (WV). WV has an acidic character with a pH of 2.3–3.2 [4–6]. Around 85%–90% of the product is water, and the remaining 15%–10% is an organic fraction composed of several chemical compounds, such as aldehydes, organic acids, furans, ketones, phenolic compounds, pyrans, etc. [7–9].

WV, known as pyroligneous acid or liquid smoke, comes from wood or woody biomass carbonization. The expression 'liquid smoke' refers to when the product is directed to impart a smoked flavor to meat products, sauces, and other foods [10,11]. In the first approach, WV is essentially a safety additive with a strong odor of smoke employed worldwide in the food industry and used by 8 out of 10 manufacturers of smoked products, providing them with characteristic flavor and aroma [12]. In addition to its use as a smoked flavor, WV can also be applied when the objective is to preserve food (fish, meat, and sausages) by extending its shelf life [13]. Like this, WV is a natural chemical product with properties recognized and certified by several renowned international bodies with respective register numbers, such as Chemical Abstracts Service (CAS 8030 97-5), Flavor and Extract Manufacturers Association (FEMA 2967), European Inventory of Existing Chemical Substances (EINECS 232-450-0), Harmonized Commodity Description and Coding Systems (HS 2915.50.5000), and Food and Drug Administration (FDA-21-CFR compliance 172.515) [14].

Especially in the last two decades, WV has been standing out and drawing the attention of several researchers worldwide. WV is a versatile product that has been increasingly assessed in several application fields, such as animal husbandry [15], agriculture [4,16], food industry [12,13,17], and veterinary uses [18]. Practical uses for the product as herbicide [3], insect repellent or insecticide [8,19,20], antifungal [9,21], antimicrobial [22–24], antioxidant [25,26], antiseptic [27], and antiviral [2], among others, have been reported. However, reports of the use of WV date back centuries, with the product being applied in embalming, boat caulking, the treatment of diseases, dyeing of linen fabrics, and as an alternative for preserving meat during the American Civil War, among many other uses [28–30]. The versatility of using WV is attributed to its rich and varied chemical constitution and its acidic character [31,32].

WV production in Brazil is significant but incipient, considering it is the largest charcoal producer in the world, with 4.5 million metric tons a year [33]. Roughly 95% of this overall charcoal is consumed by companies from the metalwork sector. In the so-called Brazilian 'green metallurgy', 70% of the pig iron, 40% of the steel, 100% of silicon, and iron alloys are produced having charcoal as a reducer. An important characteristic to be pointed out is that over 95% of the charcoal consumed by the metalwork industries comes from the wood of their eucalyptus-planted forests. Otherwise, the production of WV is incipient and carried out only by some companies. Until recently, small charcoal makers or farmers produced most of the WV available for sale in Brazil, an emplacement also prevailing worldwide. With the escalation of the prices of conventional pesticides in the world market in recent years and the need to bring sustainable practices to agricultural activities, WV is increasingly gaining market share in Brazil and the world market. This way, the WV production has drawn the attention of the larger charcoal producers from the metalwork sector, and slowly, some of them decided to invest in this type of business. However, we observed that WV produced by those companies is only filtered, so the product is clarified from a dark brown color to a yellow-reddish one. The filtration aims to eliminate tar bubbles in the product that can clog the nozzles of the spraying types of equipment traditionally employed in everyday agriculture practice. The industrial WV is directed only to agricultural uses as an insect repellent, fungicide, or adjuvant in herbicide solutions, and so on.

WV originating from the carbonization of different types of woody biomass is recognized and effectively used worldwide as a safe food additive for human consumption per the regulations of the agencies cited previously [10,12]. However, protocols require refining to achieve this so that the WV reaches food and pharmaceutical grade, depending on the product type generated with this input. Polycyclic aromatic hydrocarbons (PAHs) and other contaminants should be removed in the refining or purification phase, along with tar residues and remaining soluble tar [26,34–36]. Several processes are cited as effective in removing contaminants from WV, with decantation and filtration being the most common. However, despite one or another method applied, traces of tar may remain in the final product, carrying contaminants in their structure. Other options for refining include combining filtration with ultrafiltration, centrifugation, and distillation. Vacuum refining is the most reliable and efficient process to refine WV and pyrolysis oils for food uses as liquid smoke, for example, generating a high-quality final product [1,4,29,37]. Even for agriculture, refining WV is recommended to remove soluble and insoluble tar [27]. Despite being a significant matter, no information on the presence or absence of contaminants is usually provided in the WV packaging sold in the Brazilian market or other countries.

The WV must undergo a more pronounced refinement for more restrictive applications, such as research in health areas. To achieve this, it must be subjected, at least, to the double distillation process, where the product is distilled twice consecutively for higher purity assurance [2,6,38]. After refining, the WV is usually profiled to determine its main components, which are more representative in biological effect according to their final use. When studying the chemical composition of WV from Eucalyptus wood, ref. [1] found 63 components, with the methoxyphenol group having the highest representation. The more abundant components were 2,6-dimethoxy-phenol (syringol), 1,2,3-trimethoxybenzene, 2-methoxy-4-methylphenol, guaiacol and 5-tert-butylpyrogallol. Ref. [31] reported the same chemical profile for WV from *Litchi chinensis* wood. Other studies identified more compounds in WV from different forest species [4,39].

Except for use as a food additive, the removal of contaminants from WVs and pyrolysis liquids by any purification process, in general, is scarcely or not reported at all. Not even the presence of contaminants is referred to in most research works dealing with the employment of WV as an agricultural input and for its applications as an antimicrobial agent. Regarding studies dealing with applications of WV, one significant shortcoming identified in most of the articles cited in the specialized literature is the lack of information about the chemical profile of the types of WV used to perform the assessments. Another issue concerns the absence of a description of properties (density, color, pH, refractive index, water and acetic acid content, titratable acidity, phenolic content, and so on). Most works do not report the woody biomass from where the WV was produced. Additionally, the types of carbonization kilns and production process parameters are other missing pieces of information. Most importantly, as commented above, the presence or absence of contaminants in the types of WV are additional features not referred to. This way, many questions remain unanswered after a careful reading, and another one is whether the WVs employed by the peers were refined before the cited uses. This deficiency of information is problematic because it makes it harder to establish solid comparisons among experimental results and relate them with WVs' composition and properties. This way, besides the presence or absence of contaminants and the refining methods employed to achieve a clean WV, more information such as those listed above should be included in research works so the reader can assess and compare results from one experiment to another. The refining strategies should be applied on a larger scale and systematically as long as WV properties and quality can be standardized and kept constant so the product can be used as any other chemical input for veterinary uses or animal management.

In the context discussed above, firstly this work presents the industrial charcoal and WV production chain belonging to one of the largest pig iron producers in Minas Gerais

State, Brazil. In such a production chain, all the steps were parametrized and described, starting with the firewood from planted eucalyptus forests, the kilns, the carbonization process description, the WV recovery and filtering, and finishing with the refining of the product to remove contaminants. This way, the production chain became traceable, and a standard refined WV could be obtained. In turn, this work also aimed to evaluate the presence or absence of contaminants in the industrial-grade WV and the outcome of a sequential vacuum distillation on eliminating the contaminants if detected in the original industrial WV.

2. Material and Methods

2.1. WV Production

Eucalyptus WV is produced on an industrial scale by one of the largest companies in the metalwork sector in Minas Gerais State, Brazil. The monthly WV production is over 300 tons in a carbonization unit of 110 masonry kilns. The carbonization equipment is a classic circular masonry kiln, each with a capacity for 55 m^3 (or 35 m^3 solid) of firewood 1.90–2.00 m long and 8–22 cm in diameter. The firewood comes from 7-year-old eucalyptus-clonal plantations. The carbonization cycle totals eight days: four days for carbonizing and four days for cooling. On the sixth day of the cycle, the charcoal is unloaded, the firewood is loaded upright into the kiln up to the height of the wall, and the dome is filled with wood positioned horizontally. The charcoal unloading takes 1 to 2 hours, while firewood loading takes 2 to 3 hours. Usually, carbonization runs performed in these kilns yield 32% charcoal and 0.7 to 0.8 tons of raw WV, which corresponds to roughly 4%–5% based on the initial weight of bone-dry wood. This way, each kiln can produce over 3 tons of raw WV per month.

The recovery device comprises a mobile set of four stainless-steel tubes (Braspirol Ltd., Campinas, SP, Brazil) coupled to the kilns (Figure 1A). The pipes are naturally air-cooled. No other cooling agent exists, but air and the uncondensed gases are released into the surrounding atmosphere. The carbonization liquid collection starts when the carbonization gases reach 60–70 °C (temperature measured at the chimney basis). After condensation, the liquids are collected inside plastic containers (Figure 1B) and placed on the recovery apparatus's basis. The recovery process evolves, and when the smoke temperature becomes 150 °C, the device recovery is disconnected so the carbonization can continue and be finished one or two days later. The interruption of the recovery at this final temperature is intended to minimize the amount of wood tar in the final liquid product.

Figure 1. Carbonization liquids recovery devices (**A**); recovery apparatus basis (**B**).

After each carbonization is concluded, the resulting liquid is taken to settling tanks with 30,000 L capacity and left standing for 3–4 months until any remaining amount of heavy wood tar settles at the bottom can be separated and properly discarded. Even after decantation, some amount of dissolved wood tar is present in the raw WV, enough to make its color dark brownish and form tiny bubbles. To make the product more transparent and reach the industrial grade, it is filtered so the wood tar bubbles are removed, and the product becomes dark orange. This final quality enables the product to be commercialized as an industrial-grade product for agricultural uses. For the present work, 22 samples of 100 L were collected randomly from several settling tanks in the industrial facility. The samples were mixed to compose one of 2200 L, which provided the material for further experimental steps. Each sample had its quality checked to ensure the same pH, density, and color, but no variations were detected.

2.2. *Industrial-Grade WV Refining and Contaminant Analysis*

After several preliminary tests, which consisted of distillation runs under vacuum to establish the primary operational conditions of the distillation equipment, the following refining conditions were adopted as a standard procedure and strictly kept on. The raw WV was distilled in the 90–103 °C range under a 20 mmHg vacuum employing a stainless-steel device (Linax, São Paulo, SP, Brazil) with a capacity of 300 L per batch. Figure 2 displays a diagram of the vacuum distillation set. See that the diagram in Figure 2 is merely schematic and the components are not fully scaled.

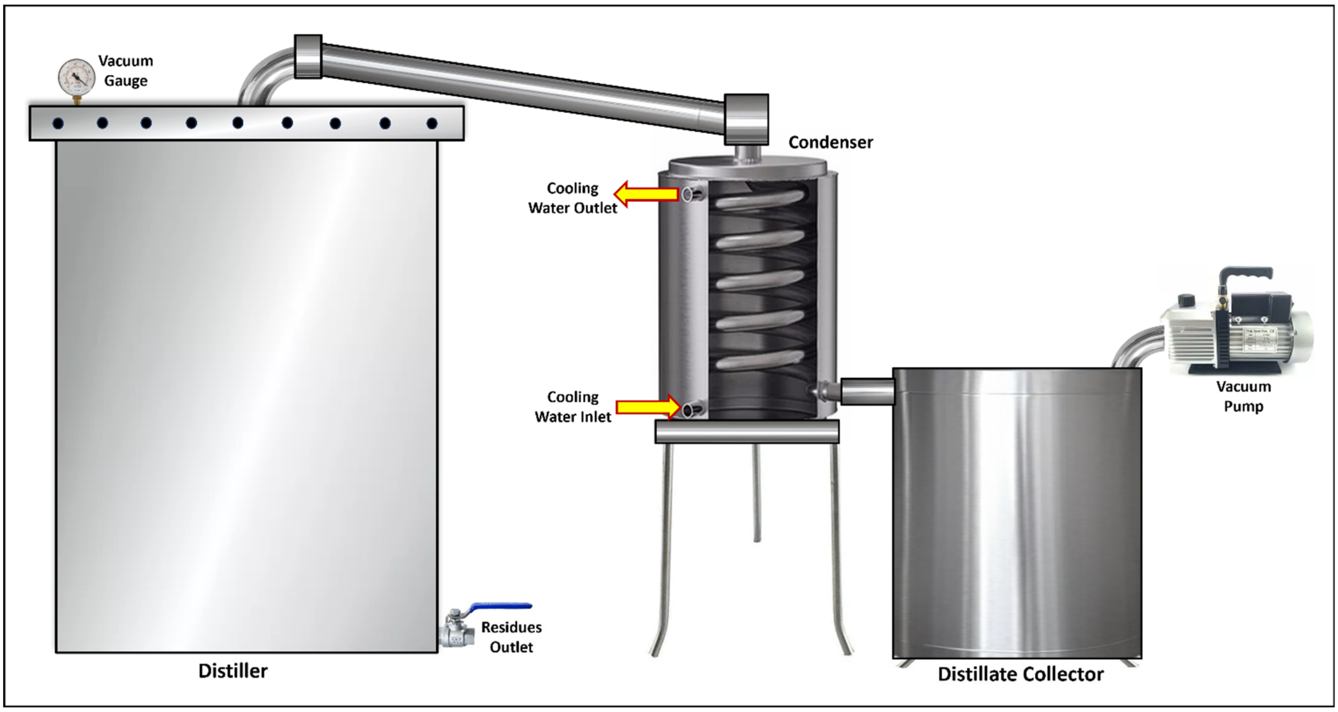

Figure 2. Schematic diagram of the vacuum distillation set.

Eight distillation runs totaled a processed initial volume equal to 2400 L (refining step 1). After processing, the yields from the step 1 were determined. The distilled volumes from all runs were put together inside a container and homogenized. The total volume was divided into batches of 300 L, re-distilled, and the final yields were obtained (refining step 2). This way, the refining process consisted of two distillation steps under vacuum at the same temperature range. Aliquots of 1000 mL were collected from each batch before and after the first distillation run and after the second one to provide the samples in which the presence or absence of contaminants could be determined. So, three samples were obtained: original industrial-grade (raw) WV and WV after refining steps 1 and 2. The following WV properties were determined using standard analytical methods: density at 25 °C (ASTM D5057-90) [40], electrical conductivity at 25 °C (ASTM D1125-23) [40], and pH (EPA 9045D:2004) [41]. The chemical classes and the respective chemical species belonging to each of them and searched in the WV samples (before and after refining) are listed in Table 1.

Table 1. Chemical classes and species searched in Eucalyptus WV.

Classes	Chemical Species
Heavy metals and other elements	Aluminum, boron, cadmium, calcium, cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, phosphorous, potassium, sodium, sulfur, and zinc
Insecticides, fungicides, and herbicides (carbamates, organochlorines, organophosphates, pyrethroids, and others)	4,4-DDD (p,p′-DDD ou p,p′-TDE), 4,4-DDE (p,p′-DDE), 4,4-DDT (p,p′-DDT), (aldicarb + aldicarb sulfone + aldicarb sulfoxide), aldrin, aminocarb, atrazine, carbaryl, carbofuran, cis-permethrin, cyanazine, cypermethrin, chlordane (sum of cis-, trans-, and oxychlordane), chlorfenvinphos, chlorobenzylate, chloroneb, chlorothalonil, chlorpyrifos (dursban), coumaphos, deltamethrin, demeton-O, demeton-S, dieldrin, disulfoton, dihydrodicyclopentadienyl acrylate (DCPA), diuron, drins sum (aldrin + dieldrin + endrin), endosulfan I, endosulfan I (a + b + sulfate), endosulfan, endosulfan sulfate, endrin, etoprofos, fenchlorfós (fenchlorphos + fenchlorphos-oxan), fenitrothion (metation), fensulfothion, fenthion, phentoate, phorate, fosalone, phosmet, heptachlor (heptachlor epoxide cis + trans), hexachlorobenzene (HCB), hexachloroethane, iprovalicarb, L-cyhalothrin, linuron, malathion, mancozeb, merphos, methamidophos, methidathion, metolachlor, methoxychlor, mevinphos, molinate, oxamyl, permethrin, pirimicarb, propenofos, propaphos, propachlor, propanil, quinalphos, simazine, tebuconazole, terbufos, tetrachlorvinphos (stirophos), tokuthion, trans-nonachlor, triazophos, and trichloronate
Mycotoxins	Aflatoxins B1, B2, G1, and G2, deoxynivalenol, fumonisins, ochratoxin A, patulin, and zearalenone
Polychlorinated dioxins and furans	1,2,3,4,6,7,8-heptachlorodibenzofuran, 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin, 1,2,3,4,7,8,9-heptachlorodibenzofuran, 1,2,3,4,7,8-hexachlorodibenzofuran, 1,2,3,4,7-pentachlorodibenzo-p-dioxin, 1,2,3,4- tetrachlorodibenzo-p-dioxin, 1,2,3,6,7,8-hexachlorodibenzofuran, 1,2,3,7,8,9-hexachlorodibenzofuran, 1,2,3,7,8,9-hexachlorodibenzo- p-dioxin, 1,2,3,7,8-pentachlorodibenzofuran, 1,2,3,7,8-pentachlorodibenzo-p-dioxin, 2,3,4,7,8-pentachlorodibenzofuran, 2,3,7,8-tetrachlorodibenzofuran, 2,3,7,8-tetrachlorodibenzo-p-dioxin, octachlorodibenzofuran, and octachlorodibenzo-p-dioxin
Polycyclic aromatic hydrocarbons	Acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, phenanthrene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene; and total PAHs
Volatile organic compounds	Acetone, acetaldehyde, acetic acid, ethylene glycol, and methanol

All the chemical classes were determined by following standard analytical methods as follows: metals and other elements (SW 846 6010D:2018/3050B:1996/3052:1996—EPA) [41]; insecticides, fungicides, and herbicides (CR 0104, CR-0118, CR-0120—AOAC 2019) [42]; mycotoxins (CR-0059, CR-0104, CR 121 01, CR 0123 01, CR 0124-00, CR 0125 02—AOAC 2019) [42]; polychlorinated dioxins and furans (CR-0109—AOAC 2019) [42]; polycyclic aromatic hydrocarbons (EPA 3500C:2007; EPA 8270E:2018—APHA 2023) [41,43]; and volatile organic compounds (EPA 5021A:2014/EPA 8260D:2017—APHA 2023, CR-0094—AOAC 2019) [41–43].

2.3. Gas Chromatography/Mass Spectrometry (GC/MS) Analyses

The GC/MS analysis protocols reported by [4] were employed to determine the WV chemical profile after refining. Three aliquots (5 mL) of the bi-distilled WV were taken, and 1.5 mL of ammonium hydroxide (Caledon, Ammonia Solution UN 2672, Canada) was added. After this addition, the organic fraction of each sample was subjected to liquid–liquid extraction with 1 mL of ethyl acetate (HPLC grade, Merck, São Paulo, SP, Brazil). The organic fraction was separated, and the samples were immediately analyzed. The GC/MS analyses were performed in a SHIMADZU QP 2010 gas chromatography/mass spectrometer equipped with a DB-Wax 52 CB (Agilent, distributed by Hexis Científica, São Paulo, SP, Brazil) measuring 30 m length, 0.25 mm diameter, 0.25 µm film thickness) filled with a cross-linked and high-polarity polyethylene glycol (PEG) stationary phase. The injector temperature was kept at 250 °C. One µL of each sample was injected with a 1:10 split ratio. The oven was programmed to start at an initial temperature of 50 °C and was held for 2 min. After this, a heating rate of 2 °C min^{-1} was employed until a final temperature of 240 °C was reached, keeping it for 2 min. Helium was the carrier gas with a flow rate of 3 mL min^{-1}. The total time for each chromatography run was equal to 99 min. The acquisition of the mass spectra was carried out from *m/z* 50 to 650 Da. The electronic ion source (EI) and the MS interface were kept at 250 °C. The solvent cut-off time was adjusted for 3 min. Major (>1.5% area) and minor (~0.2%) compounds were detected and annotated based on their characteristic electron ionization mass spectra (EI 70 eV) compared to those from the NIST library. All reported chemical compounds had a mass spectral similarity of at least 85%.

3. Results and Discussion

Figure 3 depicts the production chain steps at Brazil's largest pig iron producer. Initially, seven-year clonal eucalyptus forests (1) provide the firewood (2) which is taken to the carbonization kilns (3) and processed. The resulting charcoal (4) goes to the blast furnaces (5) where the pig iron (6) is produced and exported or converted into steel. Recovery apparatuses (7) collect the WV. After collection, WV is transferred to settling tanks (8). After 3–4 months of settling time, the wood tar at the bottom of the tanks is separated, and the aqueous phase is filtered (9), yielding the raw WV (10) that goes to agricultural uses (11) as a pesticide among other applications. As it is proposed here, a new line of products can be generated by refining (12) to remove contaminants from the raw product to obtain the refined WV (13) which would be directed to formulating new products for animal husbandry, veterinary purposes, and other uses (14).

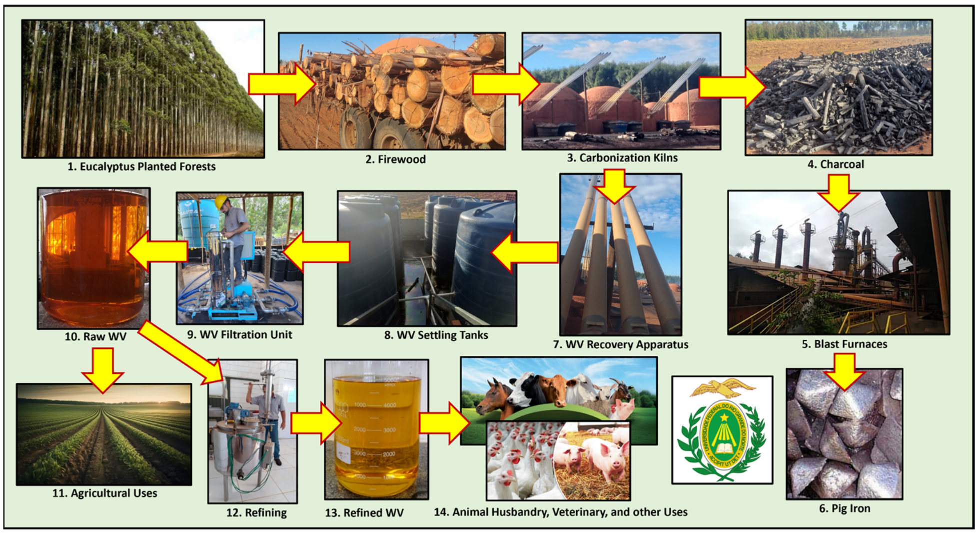

Figure 3. Charcoal and WV production chain at Brazil's largest pig iron producers with a proposed additional step of WV refining.

Yields in distilled liquid after refining steps 1 and 2 are shown in Table 2. After refining steps 1 and 2, the residual fractions remaining at the bottom of the distillation device reached values around 3%–4% of the initial volume of liquid.

Table 2. Yields in distilled liquid after refining steps 1 and 2.

Refining Step	Initial Volume (L)	Final Volume (L)	Yield (%)
1	2400	2304	96.0
2	2304	2234.9	97.0

Table 3 displays the WV properties before and after the two refining steps. After refining steps 1 and 2, the pH decreased from 2.90 to 2.60, which was not expected since the acid content was reduced (see Table 4) from 3.8 in the raw WV to 2.6% in the refined versions. WV's density decreased from 1.01 to 1.00 g cm^{-3}, remaining constant from one refining step to another. In turn, the conductivity was reduced from 1260 to 980 µS cm^{-1}, most likely due to decreased concentrations of cations and other products with residual electric charge after refining.

Table 3. Eucalyptus WV properties.

Properties (Units)	LQ or LD	Raw WV	Step 1	Step 2
Conductivity (µS cm^{-1})	LQ = 0.1 µS cm^{-1}	1290	980	864
Density at 25 °C (g cm^{-3})	LQ = 0.14 g cm^{-3}	1.01	1.00	1.00
pH at 25 °C	LQ = 1.00	2.90	2.60	2.60

Table 4. Concentrations of the chemical species searched in the Eucalyptus WV before and after refining steps 1 and 2.

Chemical Classes and Analytical Methods	Chemical Species	LQ or LD	Raw WV	Step 1	Step 2
Heavy metals and other elements (mg kg^{-1})	Aluminum	LQ = 5.0	152	<LQ	<LQ
	Boron	LQ = 50	<1	<LQ	<LQ
	Cadmium	LQ = 0.080	<LQ	<LQ	<LQ
	Calcium	LQ = 50	14	<LQ	<LQ
	Cobalt	LQ = 5.0	<2	<LQ	<LD
	Copper	LQ = 1.0	<2	1.0	<LQ
	Iron	LQ = 0.20	18	1.90	1.80
	Lead	LQ = 0.40	<LQ	<LQ	<LQ
	Magnesium	LQ = 50	2.8	<LQ	<LQ
	Manganese	LQ = 1.0	3.9	<LQ	<LQ
	Mercury	LQ = 0.80	<LQ	<LQ	<LQ
	Molibdenum	LD = 0.12	<2	<LD	<LD
	Nickel	LQ = 0.20	<2	<LQ	1,1
	Phosphorous	LQ = 50.0	<30	17.0	16.2
	Potassium	LQ = 1.0	<2	<LQ	<LQ
	Sodium	LQ = 50	<2	<LQ	<LQ
	Sulfur	LQ = 3.0	36	9.0	8.0
	Zinc	LQ = 1.0	<2.0	1.0	1.0
Insecticides, fungicides, and herbicides (mg L^{-1})	All species	LD = 0.006	<LD	<LD	<LD

Table 4. *Cont.*

Chemical Classes and Analytical Methods	Chemical Species	LQ or LD	Raw WV	Step 1	Step 2
Mycotoxins (µg L^{-1})	Aflatoxin B1	LD = 0.2	<LD	<LD	<LD
	Aflatoxin B2	LD = 0.06	<LD	<LD	<LD
	Aflatoxin G1	LD = 0.2	<LD	<LD	<LD
	Aflatoxin G2	LD = 0.06	<LD	<LD	<LD
	Deoxynivalenol	LD = 10	<LD	<LD	<LD
	Fumonisin B1 and B2	LD = 20	<LD	<LD	<LD
	Ochratoxin A	LD = 1.0	<LD	<LD	<LD
	Patulin	LD = 3.0	<LD	<LD	<LD
	Zearalenone	LD = 10	<LD	<LD	<LD
Polychlorinated dioxins and furans (µg kg^{-1})	All species	LD = 0.5	<LD	<LD	<LD
Polycyclic aromatic hydrocarbons (µg kg^{-1})	Acenaphthylene	LD = 2.0	2110	<LD	<LD
	Acenaphthene	LD = 2.0	73	<LD	<LD
	Fluorene	LD = 2.0	330	<LD	<LD
	Fenanthrene + anthracene	LD = 2.0	50	<LD	<LD
	Fluoranthene	LD = 2.0	32	<LD	<LD
	Pyrene	LD = 2.0	38	<LD	<LD
	Benzo[a]anthracene + crysene	LD = 2.0	56	<LD	<LD
	Benzo[b] + benzo[k]fluoranthene	LD = 2.0	59	<LD	<LD
	Benzo[a]pyrene	LD = 2.0	31	<LD	<LD
	Indeno[1,2,3 cd]pyrene	LD = 2.0	79	<LD	<LD
	Dibenzo[a,h]anthracene	LD = 2.0	33	<LD	<LD
	Benzo[g,h,i]perylene	LD = 2.0	37	<LD	<LD
	Naphtalene	LD = 2.0	881	<LD	<LD
Volatile organic compounds	Acetic acid (% m/m)	LD = 0.003 mg kg^{-1}	3.8	2.8	2.8
	Acetaldehyde (mg kg^{-1})	LD = 0.01 mg kg^{-1}	2100	<LD	<LD
	Acetone (µg kg^{-1})	LD = 10 µg kg^{-1}	15,300	<LD	<LD
	Ethylene glycol (% m/m)	LD = 0.05 µg kg^{-1}	90	<LD	<LD
	Methanol (% m/m)	LD = 1.0 µg kg^{-1}	3400	<LD	<LD

The concentration of the chemical species searched in the raw WV and steps 1 and 2 of refining are presented in Table 4, followed by concentrations and the respective limits of quantification or determination. It is essential to highlight that the polychlorinated dioxins and furans, mycotoxins, and pesticides (fungicides, insecticides, and herbicides) were not detected in the eucalyptus WV before or after refining. These types of contaminants are not expected to exist in WV samples whatsoever. Yet, they were searched to ensure its absence and give information for possible future uses of WV as a basis for veterinary products or additives for animal husbandry and the treatment of agricultural seeds. This way, the WV purity should not be questioned regarding the possible presence of these contaminants for further applications.

Still, the heavy metals cadmium, lead, and mercury were also not detected in any eucalyptus WV samples assessed in this work, which is reassuring. The other elements seen in the raw WV were boron, calcium, cobalt, copper, iron, magnesium, manganese, molybdenum, nickel, phosphorous, potassium, sodium, sulfur, and zinc. Except for aluminum, cobalt, nickel, and sodium, they all participate in the essential macro- (phosphorous and potassium) microelements (boron, calcium, copper, iron, magnesium, molybdenum, sulfur, and zinc) required for the satisfactory growth of several crops [44,45]. The high aluminum concentration is one point to consider in the raw WV composition. This element has a density no higher than 5 g cm^{-3}, so it is not dense enough to be called heavy. However, due to its toxicity, it is included in the category of heavy metals. Aluminum can be beneficial or toxic to plants depending on the soil and plant tissue concentration [46]. Attention should be given to whether the continuous use of raw WV assessed here as agricultural input can increase the concentration of this element in soils. At some point, it can become toxic to crops. WV is usually employed alone as a pesticide and for other finalities or combined with other agricultural products [4,16], so the risk of possible aluminum toxicity from soil accumulation cannot be ruled out. However, all metals and other elements were successfully removed without significant problems during the first or second distillation, except sulfur and zinc, whose traces remained in the refined product (Table 4).

Concerning volatile organic compounds (VOCs), their presence in the raw WV is a point to be carefully evaluated: acetaldehyde (2100 µg kg^{-1}), acetone (15,300 µg kg^{-1}), methanol (3400 µg kg^{-1}), and ethylene glycol (90 µg kg^{-1}) were found in the raw WV. Although they are not in very high concentrations in the raw WV since they are harmful products, some digression about them should be made because inhalation of vapors or microdroplets during crop application might be a possible source of contamination to humans after long-term exposure. Acetaldehyde, for instance, is a highly reactive and toxic compound. With a 4 h LC50 of acetaldehyde in rats 13,300 ppm (24.0 g m^{-3} air), this chemical is considered a Class 1 toxin (human carcinogen), and the primary source of it is alcohol consumption [47]. Still, there are many other sources of acetaldehyde. Also, inhalation is another way of contamination to be seriously considered [48]. Increased intake of acetaldehyde in the human organism is associated with neurological pathologies such as stroke, Wernicke encephalopathy, and Alzheimer's disease, as well as alcohol-induced impairment of brain structure and function [47].

Among all VOCs, acetone was determined to have the highest concentration in the raw WV. If ingested in specific amounts, it may cause cardiac arrest and death. Studies of acute inhalation exposures to acetone in animals indicate that high concentrations are required to result in death. Signs of narcosis usually precede death in animals from high exposure levels [49]. An 8 h lethal dose (LD50) value of 21,091 ppm and a 4 h LD50 value of 31,994 ppm were found for female rats [49]. Inhalation exposure to acetone for a few hours has resulted in death in rats at concentrations ranging from 16,000 to 50,600 ppm. Methanol is another proven toxic chemical to humans and animals due to its harmful metabolic effects after ingestion or inhalation. Among other effects, the by-products of methanol metabolism cause an accumulation of acid in the blood called metabolic acidosis, blindness, and death with a median lethal dose of 1–2 mL kg^{-1} body weight [50]. Finally, ethylene glycol in the raw WV should also be alluded to since exposure to it can be extremely dangerous, with significant morbidity and mortality if left untreated, with acute toxicity of the vapor (LC50) > 200 mg m^{-3}, for 4 h in rats [51]. Excepting acetic acid, the toxic effects of the VOCs in raw WV composition constitute a firm matter to justify the product's purification to remove them. See that after the first round of refining (Table 4), all of them were utterly removed, maintaining their levels below the limits of detection, which is significantly low.

A vital chemical class of contaminants in the raw WV are the polycyclic aromatic hydrocarbons. Several of them have been proven to be carcinogenic and harmful to human health [52,53]. Although PAHs can exist in over 100 combinations, according to [41], only 21 are classified as critical pollutants. PAHs are a significant concern because they are persistent and can remain in the environment for extended periods [52]. Among PAHs, benzo(a)pyrene stands out, for example, because it may cause fetal malformation and several other damages to human health. Maximum limits of 10 ppb for this chemical and 20 ppb for benzo(a)anthracene are tolerated in smoked flavorings for the food industry [53]. Seven PAHs are named individually on the EPA's Priority Chemical list: acenaphthene, acenaphthylene, anthracene, benzo(g,h,i)perylene, fluorene, phenanthrene, and pyrene [41]. All of them were determined in the raw WV assessed in this work (Table 4), two in relatively high concentrations, acenaphthylene and fluorene, 2110 and 330 μg kg^{-1}, respectively.

As shown in Table 4, all PAHs were removed entirely from the WV after the first distillation step. It was pretty par for the course since PAHs are combined with wood tar and heavy oils in the raw WV composition [35]. These fractions are heavy and not volatilized or drafted during distillation. Hence, after raw WV was distilled (step 1), they remained composed of the residual portion and could be discarded appropriately. These results corroborate the statement of Ayvaz and Atar (2016) [54], who commented that once properly purified, pyrolysis condensates did not present any traces of benzo(a)pyrene, for instance. Also, ref. [55] highlighted the importance of purification processes to give pyrolysis liquids free of PAHs, especially for food industry use. Usually, the concentrations of raw WV in most pesticide sprays for agricultural uses are low [3,5,16], around 1%–5%, so one could reason that the possibility of human contamination by VOCs and PAHs from it is remote due to their dilutions. Nevertheless, the concern about the presence of contaminants must be a priority, not only considering applications of the product as a basis for pharmaceuticals and food additives for animal husbandry but also for agriculture uses when used as a pesticide or growth stimulator in edible leaves, fruits, grains, and tubers, for instance. Still, contaminants in raw WV used for agriculture become more severe if organic-brand crops are accounted for. With all being said, if WV is intended to be employed as an input for pharmaceuticals and as an additive for animal feeding, those contaminants cannot be tolerated at any level since these end-uses require strict quality control.

The chemical profile with the main compounds in the composition of the WV after refining step 2 is shown in Table 5. The chemical profile was determined after steps 1 and 2, but no appreciable differences in the chemical composition were observed. As reported in previous studies [4,6], the main components in the eucalyptus WV are furfural and phenols, followed by several others in minor proportions. Therefore, the refining process could efficiently remove the contaminants without significantly changing the contents of the compounds that have biological effects. It is a critical point because if the refining process alters the main compounds' content to any extent, the efficiency of the product as antimicrobial, antifungal, antiviral, and so on would be negatively affected as well.

Table 5. Annotated compounds in the refined eucalyptus WV after refining.

Compound	Area (%)
2-Cyclopenten-1-one	1.9
2-Cyclopenten-1-one, 2-methyl-	1.5
1-Hydroxy-2-butanone	1.0
2-Furanmethanol, tetrahydro-	1.0
Furfural	17.2
Ethanone, 1-(2-furanyl)-	1.5
2-Cyclopenten-1-one, 3-methyl-	2.4
2-Cyclopenten-1-one, 2,3-dimethyl-	1.4
2-Furancarboxaldehyde, 5-methyl-	4.4
Butyrolactone	0.8
2-Furanone, 2,5-dihydro-3,5-dimethyl	1.0
1,2-Cyclopentanedione, 3-methyl-	3.3
Phenol, 2-methoxy-	9.4
Phenol, 2-methoxy-4-methyl-	0.4
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	1.0
Phenol, 2-methoxy-4-methyl-	4.4
Phenol	8.5

Table 5. *Cont.*

Compound	Area (%)
Phenol, 4-ethyl-2-methoxy-	1.8
Phenol, 2,3-dimethyl-	0.5
Phenol, 4-methyl-	2.3
Phenol, 3-methyl-	3.3
Phenol, 2-methoxy-4-propyl-	0.3
Phenol, 3,4-dimethyl-	0.8
Phenol, 2,6-dimethoxy-	10.7
1,2,3-Trimethoxybenzene	3.5
Benzene, 1,2,3-trimethoxy-5-methyl-	1.9
Total	69.3
Others	30.7

4. Conclusions

The results presented herein indicated that after only one refining step by vacuum distillation, all undesirable components were removed from the raw WV, which reached a quality that enabled it to be applied as a basis for pharmaceuticals, antimicrobials, and additives for animal husbandry. The main chemical components, such as phenolic compounds, furans, ketones, pyrans, etc., were annotated in the WV chemical profile as typical compounds. No traces of insecticides, fungicides, herbicides, heavy metals, mycotoxins, polychlorinated dioxins, or polychlorinated furans were found in raw WV or refined versions. However, several other undesirable chemicals were determined in the raw product, such as volatile organic compounds and PAHs. Nevertheless, all of them were effectively removed from the raw WV, yielding a pure product. Therefore, depending on the type of contaminant, only one refining step can be applied to raw WV to deliver a high-quality product for pharmaceuticals and animal husbandry applications.

Author Contributions: Conceptualization, R.M.B.; methodology, A.S.P., G.S.P.G., F.M.C.F., R.M.B., T.K.B.d.A., N.d.O.M. and G.S.d.A.; software, G.S.d.A.; validation, F.M.C.F., T.K.B.d.A. and R.R.d.M.; formal analysis, F.M.C.F.; investigation, F.M.C.F.; resources, A.S.P., G.S.P.G., T.K.B.d.A. and R.R.d.M.; data curation, G.S.P.G., R.M.B., N.d.O.M. and G.S.d.A.; writing—original draft, A.S.P., G.S.P.G. and N.d.O.M.; supervision, A.S.P.; project administration, A.S.P. and R.R.d.M.; funding acquisition, F.M.C.F., R.M.B., T.K.B.d.A. and R.R.d.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by the National Council for Scientific and Technological Development (grant number 101) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (grant number 103).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors would like to thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and the National Council of Research Development (CNPq) for supporting this work.

Conflicts of Interest: All authors agree with the submission and declare no conflict of interest regarding the manuscript's content, ethical procedures, and funding agencies.

References

1. Souza, J.B.G.; Ré-Popii, N.; Raposo, J.L., Jr. Characterization of pyroligneous acid used in agriculture by gas chromatography-mass spectrometry. *J. Braz. Chem. Soc.* **2012**, *23*, 610–617. [CrossRef]
2. Li, R.; Narita, R.; Nishimura, H.; Marumoto, S.; Yamamoto, S.P.; Ouda, R.; Yatagai, M.; Fujita, T.; Watanabe, T. Antiviral activity of phenolic derivatives in pyroligneous acid from hardwood, softwood, and bamboo. *Sustain. Chem. Eng.* **2017**, *6*, 119–126. [CrossRef]
3. Aguirre, J.L.; Baena, J.; Martín, M.T.; Nozal, L.; González, S.; Manjón, J.L.; Peinado, M. Composition, aging and herbicidal properties of wood vinegar obtained through fast biomass pyrolysis. *Energies* **2020**, *13*, 2418. [CrossRef]

4. Pimenta, A.S.; Fasciotti, M.; Monteiro, T.V.C.; Lima, K.M.G. Chemical composition of pyroligneous acid obtained from Eucalyptus GG100 Clone. *Molecules* **2018**, *23*, 426. [CrossRef] [PubMed]
5. Theapparat, Y.; Chandumpai, A.; Leelasuphakul, W.; Faroongsarng, D. *Physicochemistry and Utilization of Wood Vinegar from Carbonization of Tropical Biomass Waste*; IntechOpen: London, UK, 2018; Chapter 8.
6. Gama, G.S.P.; Pimenta, A.S.; Feijó, F.M.C.; Santos, C.S.; Fernandes, B.C.C.; Oliveira, M.F.; Souza, E.C.; Monteiro, T.V.C.; Fasciotti, M.; Azevedo, T.K.B.; et al. Antimicrobial activity and chemical profile of wood vinegar from eucalyptus (*Eucalyptus urophylla x Eucalyptus grandis*—clone I144) and bamboo (*Bambusa vulgaris*). *World J. Microbiol. Biotechnol.* **2023**, *39*, 186. [CrossRef]
7. Chukeatirote, E.; Jenajai, N. Antimicrobial activity of wood vinegar from Dimocarpus longan. *Environment. Asia* **2018**, *11*, 161–169. [CrossRef]
8. Akkus, M.; Akçay, C.; Alçim, N. Antifungal and larvicidal effects of wood vinegar on wood-destroying fungi and insects. *Maderas Cienc. Tecnol.* **2022**, *37*, 1–10. [CrossRef]
9. Bouket, A.C.; Narmani, A.; Sharifi, K.; Naeimi, S.; Mogaddam, M.R.A.; Hamidi, A.A.; Luptakova, L.; Alenezi, F.N.; Belbahri, L. Semi-VOCs of wood vinegar display strong antifungal activities against oomycete species *Globisporangium ultimum* and *Pythium aphanidermatum*. *Microbiol. Res.* **2023**, *14*, 371–389. [CrossRef]
10. Burdock, G.A. *Fenaroli's Handbook of Flavor Ingredients*, 6th ed.; CRC Press: Boca Raton, FL, USA, 2010.
11. Budaraga, I.K.; Arnim, Y.M.; Bulanin, U. Analysis of liquid smoke chemical components with GC/MS from different raw materials: Variation, production and pyrolysis temperature level. *Int. J. ChemTech Res.* **2016**, *9*, 694–708.
12. Montazeri, N.; Oliveira, A.C.M.; Himelbloom, B.H.; Leigh, M.B.; Crapo, C.A. Chemical characterization of commercial liquid smoke products. *Food Sci. Nutr.* **2013**, *1*, 102–115. [CrossRef] [PubMed]
13. Achmadi, S.S.; Mubarik, N.R.; Nursyamsi, R.; Septiaji, P. Characterization of redistilled liquid smoke of oil-palm shells and its application as fish preservatives. *J. Appl. Sci.* **2013**, *13*, 401–408. [CrossRef]
14. Food and Drug Administration (FDA). Elemental Analysis Manual. Section 4.4: Inductively Coupled Plasma-Atomic Emission Spectrometric Determination of Elements in Food Using Microwave-Assisted Digestion. US Department of Health and Human Services, August, USA. 2010. Available online: http://www.fda.gov/Food/FoodScienceResearch/LaboratoryMethods/ucm2006954.htm (accessed on 10 October 2023).
15. Hanchai, K.; Trairatapiwan, T.; Lertpatarakomol, R. Drinking water supplemented with wood vinegar on growth performance, intestinal morphology, and gut microbial of broiler chickens. *Vet. World* **2021**, *14*, 92–96. [CrossRef] [PubMed]
16. Tiilikkala, K.; Fagernas, L.; Tiilikkala, J. History and Use of Wood Pyrolysis Liquids as Biocide and Plant Protection Product. *Open Agric. J.* **2010**, *4*, 111–118. [CrossRef]
17. Ramakrishnan, S.; Moeller, P.E. Liquid smoke: Product of hardwood pyrolysis. *Fuel Chem. Div. Prepr.* **2002**, *47*, 366.
18. Feijó, F.M.C.; Pimenta, A.S.; Pereira, A.F.; Soares, W.N.C.; Benício, L.D.M.; Silva Júnior, E.C.; Ribeiro, Y.S.R.; Santos, C.S.; Praxedes, D.A.E.; Sousa, E.M.M.; et al. Use of eucalyptus wood vinegar as antiseptic in goats; In *Goat Science*; Kukovics, S., Ed.; IntechOpen: London, UK, 2023. [CrossRef]
19. Yatagai, M.; Nishimoto, M.; Hori, K.; Ohira, T.; Shibata, A. Termiticidal activity of wood vinegar, its components and their homologues. *J. Wood Sci.* **2002**, *4*, 338–342. [CrossRef]
20. Rahmat, B.; Pangesti, D.; Natawijaya, D.; Sufyadi, D. Generation of wood-waste vinegar and Its effectiveness as a plant growth regulator and pest insect repellent. *Bioresources* **2014**, *9*, 6350–6360. Available online: https://ojs.cnr.ncsu.edu/index.php/BioRes/article/download/BioRes_09_4_6350_Rahmat_Generation_Wood_Waste_Vinegar/3030 (accessed on 10 October 2023) [CrossRef]
21. Ibrahim, D.; Kassim, J.; Sheh-Hong, L.; Rusli, W. Efficacy of pyroligneous acid from Rhizophora apiculata on pathogenic *Candida albicans*. *J. Appl. Pharm. Sci.* **2013**, *3*, 7–13.
22. Hwang, Y.H.; Matsushita, Y.; Sugamoto, K.; Matsui, T. Antimicrobial effect of the wood vinegar from *Cryptomeria japonica* sapwood on plant pathogenic microorganisms. *J. Microbiol. Biotechnol.* **2005**, *15*, 1106–1109.
23. Suresh, G.; Pakdel, H.; Roussi, T.; Brar, S.K.; Fliss, I.; Roy, C. In vitro evaluation of antimicrobial efficacy of pyroligneous acid from softwood mixture. *Biotechenol. Res. E Innov.* **2019**, *3*, 47–53. [CrossRef]
24. Desvita, H.; Faisal, M.; Mahidin, S. Antimicrobial potential of wood vinegar from cocoa pod shells (*Theobroma cacao* L.) against *Candida albicans* and *Aspergillus niger*. *Mater. Today Proc.* **2022**, *63*, S210–S213. [CrossRef]
25. Xue, R.; Cui, E.R.; Hu, G.Q.; Zhu, M.Q. The composition, physicochemical properties, antimicrobial and antioxidant activity of wood vinegar prepared by pyrolysis of *Eucommia ulmoides* Oliver branches under different refining methods and storage conditions. *Ind. Crops Prod.* **2022**, *178*, 114586. [CrossRef]
26. Feng, T.H.; Xue, R.; Zhu, L.; Zhu, Y.H. Comparison of antioxidant and antibacterial effects of the *Eucommia* wood vinegar under the refining methods of atmospheric distillation and vacuum distillation. *Ind. Crops Prod.* **2023**, *192*, 116013. [CrossRef]
27. Silva, B.A.; Feijó, F.M.C.; Alves, N.D.; Pimenta, A.S.; Benicio, L.D.M.; Silva, E.C., Jr.; Santos, C.S.; Pereira, A.F.; Mora, Y.B.F.; Gama, G.S.P.; et al. Use of a product based on wood vinegar of Eucalyptus clone I144 used in the control of bovine mastites. *Vet. Microbiol.* **2023**, *279*, 109670. [CrossRef] [PubMed]
28. Kurlansky, M. *Salt: A World History*, 1st ed.; Penguin Books: Los Angeles, CA, USA, 2002.
29. Campos, A.D. *Técnicas Para Produção De Extrato Pirolenhoso Para Uso Agricola*; Embrapa Clima Temperado, Circular Técnica: Pelotas, Brazil, 2007; Volume 65, 8p, Available online: https://ainfo.cnptia.embrapa.br/digital/bitstream/item/30826/1/Circular-65.pdf (accessed on 10 October 2023).

30. Balat, M.; Balat, M.; Kirtay, E.; Balat, H. Main routes for the thermoconversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. *Energy Convers. Manag.* **2009**, *50*, 3147–3157. [CrossRef]
31. Yang, J.F.; Yang, C.H.; Liang, M.T.; Gao, Z.J.; Wu, Y.W.; Chuang, L.Y. Chemical composition, antioxidant, and antibacterial activity of wood vinegar from *Litchi chinensis*. *Molecules* **2016**, *21*, 1150. [CrossRef] [PubMed]
32. Hou, X.; Qiu, L.; Luo, S.; Kang, K.; Zhu, M.; Yao, Y. Chemical constituents and antimicrobial activity of wood vinegars at different pyrolysis temperature ranges obtained from *Eucommia ulmoides* Olivers branches. *RSC Adv.* **2018**, *8*, 40941–40949. [CrossRef]
33. Indústria Brasileira de Árvores (IBÁ). *Relatório Anual 2021*; IBÁ: Brasilia, Brazil, 2022; Available online: https://iba.org/publicacoes/relatorios (accessed on 10 October 2023).
34. Pakdel, H.; Roy, C. Hydrocarbon content of liquid products and tar from pyrolysis and gasification of wood. *Energy Fuels* **1991**, *5*, 427–436. [CrossRef]
35. Pimenta, A.S.; Bayona, J.M.; García, M.T.; Solanas, A.M. Evaluation of acute toxicity and genotoxicity of liquid products from pyrolysis of *Eucalyptus grandis* wood. *Arch. Environ. Contam. Toxicol.* **2000**, *38*, 169–175. [CrossRef]
36. Barbosa, J.M.S.; Ré-Poppi, N.; Santiago-Silva, M. Polycyclic aromatic hydrocarbons from wood pyrolysis in charcoal production furnaces. *Environ. Res.* **2006**, *101*, 304–311. [CrossRef] [PubMed]
37. Higashino, T.; Shibata, A. Basic study for establishing specifications for wood vinegar by distillation. *Mokuzai Gakkaishi* **2005**, *51*, 180–188. [CrossRef]
38. Araújo, E.S.; Pimenta, A.S.; Feijó, F.M.C.; Castro, R.V.O.; Fasciotti, M.; Monteiro, T.V.C.; Lima, K.M.G. Antibacterial and antifungal activities of pyroligneous acid from wood of Eucalyptus urograndis and Mimosa tenuiflora. *J. Appl. Microbiol.* **2017**, *124*, 85–96. [CrossRef]
39. Furtado, C.M.; Stols, A.S.; Pinto, F.L.; Moura, A.B.D.; Morisso, F.D.P.; Pitarelo, A.P.; Ramos, L.P.; Mühlen, C.V.; Riegel-Vidotti, I.C. Pyroligneous liquor produced from Acacia mearnsii de wild wood under controlled conditions as a renewable source of chemicals. *Química Nova* **2015**, *38*, 1068–1074. [CrossRef]
40. *D4940*; Standard Test Method for Conductimetric Analysis of Water-Soluble Ionic Contamination of Blasting Abrasives. American Society for Testing and Materials (ASTM): West Conshohocken, PA, USA, 2020.
41. Environmental Protection Agency (EPA). *EPA Archives—Polycyclic Aromatic Hydrocarbons—PAHs*; EPA: Washington, DC, USA, 2018. Available online: https://www.epa.gov (accessed on 10 October 2023).
42. AOAC International—Association of Official Agricultural Chemists. *Official Methods of Analysis*, 21st ed.; AOAC International: Baltimore, MD, USA, 2019.
43. American Public Health Association (APHA); American Works Association, Water Environment Federation. *Standard Methods for the Examination of Water and Wastewater*, 24th ed.; American Public Health Association: Washington, DC, USA, 2023.
44. Merchant, S.S. The elements of plant micronutrients. *Plant Physiol.* **2010**, *154*, 512–515. [CrossRef] [PubMed]
45. Kumar, S.; Kumar, S.; Mohapatra, T. Interaction between macro- and micro-nutrients in plants. *Front. Plant Sci. Sec. Plant Nutr.* **2021**, *12*, e665583. [CrossRef] [PubMed]
46. Ofoe, R.; Thomas, R.H.; Asiedu1, S.K.; Gefu Wang-Pruski, G.; Fofana, B.; Abbey, L. Aluminum in plant: Benefits, toxicity and tolerance mechanisms. *Front. Plant Sci.* **2023**, *13*, e1085998. [CrossRef] [PubMed]
47. Rajendram, R.; Rajendram, R.; Preedy, V.R. Chapter 51—Acetaldehyde: A reactive metabolite. In *Neuropathology of Drug Addictions and Substance Misuse*; Victor, R.P., Ed.; Academic Press: Cambridge, MA, USA, 2016; pp. 552–562. [CrossRef]
48. National Research Council (US). Committee on Emergency and Continuous Exposure Guidance Levels for Selected Submarine Contaminants. In *Acetaldehyde: Emergency and Continuous Exposure Guidance Levels for Selected Submarine Contaminants*; Academies Press: Washington, DC, USA, 2009; Volume 3. Available online: https://www.ncbi.nlm.nih.gov/books/NBK219914/ (accessed on 10 October 2023).
49. *Toxicological Profile for Acetone*; Chapter 2; Agency for Toxic Substances and Disease Registry (US): Atlanta, GA, USA, 2022. Available online: https://www.ncbi.nlm.nih.gov/books/NBK590387/ (accessed on 10 October 2023).
50. Ashurst, J.V.; Nappe, T.M. Methanol Toxicity. In *StatPearls [Internet]*; StatPearls Publishing: Treasure Island, FL, USA, 2023. Available online: https://www.ncbi.nlm.nih.gov/books/NBK482121/ (accessed on 10 October 2023).
51. Iqbal, A.; Glagola, J.J.; Nappe, T.M. Ethylene Glycol Toxicity. In *StatPearls [Internet]*; StatPearls Publishing: Treasure Island, FL, USA, 2023. Available online: https://www.ncbi.nlm.nih.gov/books/NBK537009/ (accessed on 10 October 2023).
52. Abdel-Shafy, H.I.; Mansour, M.S.M. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Pet.* **2015**, *25*, 107–123. [CrossRef]
53. Duedahl-Olesen, L. Polycyclic aromatic hydrocarbons (PAHs) in foods. In *Persistent Organic Pollutants and Toxic Metals in Foods*; Woodhead Publishing: Cambridge, UK, 2013; pp. 308–333.
54. Ayvaz, Z.; Atar, M.H.e. The use of liquid smoke condensate in foods and its effects on health. In Proceedings of the World Congress on Public Health and Nutrition OMICS International Conference Series.com, Madrid, Spain, 10–12 March 2016.
55. Cadwallader, K.R. Wood Smoke Flavor Handbook of Meat, Poultry and Seafood Quality. Nollet, L.M.L., Ed.; Blackwell Publishing: Ames, IA, USA, 2007; 705p.