

Wood Vinegars: Production Processes, Properties, and Valorization

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Abstract

Pyrolysis of lignocellulosic biomass is widely used for the production of charcoal, pyroligneous liquid, and noncondensable gases. All three are value-added products that are exploited in several fields. However, this review focuses on three main areas: wood vinegar production methods, its physicochemical properties, and the use of wood vinegar or pyroligneous acid in agriculture and the environment. Wood vinegar is a liquid derived from wood by the condensation of gases and vapors released during the carbonization process, which is the transformation of wood into charcoal. It is mainly composed of aliphatic, aromatic, and naphthenic hydrocarbons and other oxygenated compounds such as alcohols, aldehydes, ketones, furans, acids, phenols, and ethers. Wood vinegar has antioxidant and free-radical-scavenging properties and is used in agriculture as an antimicrobial, antifungal, insecticide, and plant germination and growth agent. It is also used in food preservation, in medicine, and in the ecological preservation of wood. This review also examines the state of the art in pyroligneous liquid production techniques and factors that could potentially affect its quality.

About 2,400 trees are cut down every minute in the world. They are used for industrialization, energy sources, and many other things (Authentic Material 2018). According to the International Energy Agency (2014) and Madon (2017), wood energy accounts for an average of 70 percent of the total energy used in Africa (Madon 2017). In Ivory Coast, the area of natural forest has decreased from 16 million ha in 1960 to less than 2 million ha at the beginning of the 21st century, representing an annual deforestation rate of 300,000 ha (Lanly 1969, FAO 2003). Most of this logging takes place in rural areas, which generate 90 percent of the wood harvested by industry (Zobi et al. 2009). Moreover, with the growth of the Ivorian population (from 16.4 million people in 2000 to 29.3 million people in 2022; Kamgate 2022), wood is in even greater request in households, particularly as firewood and charcoal. To meet these needs, some organizations such as the Society of Forest Development, Reducing Emissions from Deforestation and Forest Degradation (REDD+ and Nitidae), the Food and Agriculture Organization (FAO), and the Center for International Cooperation in Agricultural Research for Development have taken an interest in this area of wood byproducts recovery. Their objectives are to develop improved carbonization methods to maximize the yield of charcoal (solid product). During this process, two other products are obtained by these same methods but have remained little used until now. Even if charcoal is an excellent fuel and a strong CO₂ adsorbent (Creamer et al. 2014), bio-oil (liquid product), a mixture of water and oxygenated compounds, is obtained from the condensation

of pyrolysis fumes and vapors and can be used in cosmetics, medicine, agriculture after refining, and many other fields (Kan et al. 2016). Finally, the noncondensable gases could be used for drying wood and producing electricity using thermal reactors (Creamer et al. 2014). For our part, only the use of the liquid product will be detailed.

The bio-oil, which is a raw smoke condensate obtained during pyrolysis, can be used to obtain wood vinegar after storage in a closed container for at least 3 months and then decantation of the sedimentation tar (Theapparat et al. 2018). Wood vinegar is a dark liquid made up mainly of water (80% to 90%), with more than 200 natural water-soluble compounds, the most important of which are acetic acid, methanol, phenols, and formaldehyde (Laemsak 2010). Table 1 shows a more comprehensive list of compounds obtained by gas chromatography–mass spectrometry analysis in poplar wood vinegar. This table was obtained during

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Table 1.—Main components of poplar wood vinegar.

Retention time (min)	Compounds	Relative content (%)	Formula	M (g/mol)
	Organic acids	26.97		
1.93	Formic acid	0.39	CH ₂ O ₂	46
3.16	Acetic acid	22.99	C ₂ H ₄ O ₂	60
4.76	Propanoic acid	0.38	C ₃ H ₆ O ₂	74
5.59	2-Hydroxy-2-met-propanoic acid	0.11	C ₅ H ₁₀ O ₃	118
9.93	Butyric acid	2.55	C ₄ H ₈ O ₂	88
7.21	2-Oxo- <i>n</i> -valeric acid	0.55	C ₅ H ₈ O ₃	116
	Ketones	10.53		
2.24	2-Butanone	0.37	C ₄ H ₈ O	72
3.58	Acetoin	0.30	C ₄ H ₈ O ₂	88
4.8	1-Hydroxy-2-butanone	0.28	C ₄ H ₈ O ₂	88
5.31	Cyclopentanone	0.62	C ₅ H ₈ O	84
6.15	1-Hydroxy-3-methyl-2-butanone	0.21	C ₅ H ₁₀ O ₂	102
6.5	2-Cyclopentene	1.61	C ₅ H ₆ O	82
8.81	2-Methyl-2-cyclopenten-1-one	1.44	C ₆ H ₈ O	96
12.47	2,5-Dihydro-3,5-dimeth-2-furanone	0.66	C ₆ H ₈ O ₂	112
13.8	2,3-Dimeth-2-cyclopenten-1-one	1.25	C ₇ H ₁₀ O	110
13.96	3-Methyl-1,2-cyclopentanedione	1.14	C ₆ H ₈ O ₂	112
15.85	3-Ethyl-2-methyl-2-cyclopenten-1-one	0.22	C ₇ H ₁₀ O ₂	126
20.48	2-Hydroxy-3-propyl-2-cyclopenten-1-one	0.38	C ₈ H ₁₂ O ₂	140
29.38	1-(4-Hydroxy-3-methoxyphenyl)-ethanone	0.48	C ₉ H ₁₀ O ₃	166
30.66	1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	1.29	C ₁₀ H ₁₂ O ₃	180
36.34	1-(4-Hydroxy-3-methoxyphenyl)-ethanone	0.28	C ₁₀ H ₁₂ O ₄	196
	Esters	3.85		
2.37	Ethylacetate	0.67	C ₄ H ₈ O ₂	88
9.24	Gamma-butyrolactone	2.34	C ₄ H ₆ O ₂	86
11.32	Methy-l2-furoate	0.09	C ₆ H ₆ O ₃	126
14.73	2,6-Dimethyl-1-cyclohexen-1-ylacetate	0.75	C ₁₀ H ₁₆ O ₂	168
	Furan derivatives	1.48		
5.51	Tetrahydro-2-furanol	0.41	C ₄ H ₈ O ₂	88
4.33	2-Methoxytetrahydrofuran	0.19	C ₅ H ₁₀ O ₂	102
8.98	1-(2-Furanyl)-ethanone	0.88	C ₆ H ₆ O ₂	110
	Alkane compounds	3.36		
5.79	Methoxymethyl-oxirane	0.07	C ₄ H ₈ O ₂	88
9.17	3-Bromo-pentane	0.59	C ₅ H ₁₁ Br	150
15.63	Bicyclo-[2.2.2]-octane	2.7	C ₈ H ₁₄	110
	Aldehydes	1.72		
10.85	5-Methyl-2-furancarboxaldehyde	0.19	C ₆ H ₆ O ₂	110
26.77	Vanillin	1.53	C ₈ H ₈ O ₃	152
	Phenols and derivatives	43.19		
11.95	Phenol	5.91	C ₆ H ₆ O	94
14.64	<i>O</i> -cresol	2.41	C ₇ H ₈ O	108
15.48	3-Methylphenol	3.74	C ₇ H ₈ O	108
15.73	Guaiacol	2.75	C ₇ H ₈ O ₂	124
18.03	2,4-Dimethylphenol	0.89	C ₈ H ₁₀ O	122
18.11	2,5-Dimethylphenol	0.39	C ₈ H ₁₀ O	122
18.65	4-Ethyl-phenol	0.47	C ₈ H ₁₀ O	122
18.82	3,5-Dimethylphenol	0.37	C ₈ H ₁₀ O	122
19.03	2,3-Dimethylphenol	0.22	C ₈ H ₁₀ O	122
19.5	2-Methoxy-4-methylphenol	2.04	C ₈ H ₁₀ O ₂	138
19.6	3,4-Dimethylphenol	0.27	C ₈ H ₁₀ O	122
20.01	Catechol	8.95	C ₆ H ₆ O ₂	110
22.07	4-Methyl-1,2-benzenediol	4.81	C ₇ H ₈ O ₂	124
22.51	4-Ethyl-2-methoxyphenol	1.32	C ₉ H ₁₂ O ₂	152
25.14	2,6-Dimethoxy-phenol	3.56	C ₈ H ₁₀ O ₃	154
25.23	2,5-Dimethyl-1,4-benzenediol	0.90	C ₈ H ₁₀ O ₂	138
25.37	3,4-Dimethoxy-phenol	0.29	C ₈ H ₁₀ O ₃	154
26.29	4-Ethylcatechol	1.80	C ₈ H ₁₀ O ₂	138
28.13	1,2,4-Trimethoxybenzene	1.65	C ₉ H ₁₂ O ₃	168
30.44	1,2,3-Trimethoxy-5-methyl-benzene	0.45	C ₁₀ H ₁₄ O ₃	182
	Nitrogen compounds	1.46		
21.93	Pyridine	1.46	C ₅ H ₅ N	79

the work of Zhu et al. (2021) when determining the chemical composition of poplar wood vinegar. It is a product strongly affected by the raw material as well as the carbonization technique used, as highlighted by Sutrisno et al. (2014). These authors used different particle sizes of *Macaranga* sp. wood residues, and observed differences in the yield, chemical content (pH, phenol content, total acid), and color of the wood vinegars (Sutrisno et al. 2014). Known for more than 2 decades now, wood vinegar has been the subject of research in East Asia, including Thailand, China, Japan, Korea, and Cambodia in various fields such as medicine, pharmaceuticals, food, and agriculture (Amen-Chen et al. 2001, Loo et al. 2007, Tiilikkala et al. 2010). However, wood vinegar remains little used, if at all, in our countries. Wood vinegar is a natural product used to improve soil quality, stimulate vegetable growth, reduce the odor of agricultural products, repel insects on plants, improve the quality of fruits and increase their sugar content, facilitate composting, and promote greater resistance to crops and adverse conditions (Uddin et al. 1995, Shibayama et al. 1998, Yatagai et al. 2002, Mu et al. 2006, Baimark and Niamsa 2009, Masum et al. 2013, Mungkumchao et al. 2013, Mmojieje and Hornung 2015).

This review article will focus on the different ways of obtaining wood vinegars, the physicochemical properties of wood vinegars, the parameters likely to affect composition and quality of wood vinegars, and the different areas of application to date.

Chemical Composition of Wood Vinegar

The liquid fractions from pyrolysis consist of a complex mixture of water and an organic phase containing many chemical compounds such as acids, alcohols, aldehydes, ketones, ethers, esters, phenols, sugars, alkenes, furans, and various oxygen compounds (Kan et al. 2016). The chemical composition of the pyrolysis product is highly dependent on the variation in the composition of the raw material. The water content of wood vinegar also depends on the initial water content of the biomass and the formation of water during pyrolysis, ranging from ~15 percent by weight to an upper limit ~30–50 percent (Mohan et al. 2006). It is light yellow to dark brown in color, composed mainly of water (80–90%) and more than 200 natural water-soluble compounds, the most important of which are acetic acid, methanol, phenols, and formaldehyde (Laemsak 2010). For wet wood, the water content can exceed 90 percent. The chemical composition of poplar wood vinegar presented in Table 1 shows many more compounds. These compounds are classified by respective families, namely organic acids, ketones, esters, furan derivatives, alkane compounds, aldehydes, phenols and derivatives, and nitrogen compounds. Wood vinegar can be considered a microemulsion, forming a stable single-phase mixture. The aqueous solution (especially from the decomposition of holocellulose) acts as a continuous phase that stabilizes the discontinuous phase of pyrolytic lignin macromolecules by mechanisms such as hydrogen bonding (Mohan et al. 2006, Bridgewater 2012). This liquid fraction has various nomenclatures in the literature, such as pyrolysis oil, bio-oil, liquid smoke, wood distillates, pyroligneous tar, and pyroligneous acid (Bridgewater 2003). The nature and chemical composition of wood vinegar could also depend on residence time, heating rate,

temperature, particle size, and source of raw material (Mohan et al. 2006, Mathew and Zakaria 2015).

Production Technology of Wood Vinegar

Wood vinegar is produced when the smoke from charcoal production is cooled by outside air as it passes through a chimney or flue. The cooling effect of these gases and vapors causes the condensation of a pyroligneous liquid (Chalermnan and Peerapan 2009). In accordance with Laemsak's (2010) recommendations, this liquid is refined by a simple method. This consists of letting it be sealed in a bottle where it will decant for 2 to 4 months to give wood vinegar (Burnette 2013). There are several techniques for obtaining pyroligneous liquid. The most commonly used are production by 200-liter drum ovens, by Casamance millstones, and by the hydrothermal process.

Production of wood vinegar with a 200-liter drum oven

The drum kiln generally consists of a 200-liter barrel serving as a pyrolyzer to which is connected bamboo wood acting as a smoke condenser. On this bamboo, several holes are made to recover the liquid smoke condensates and then at the outlet, the noncondensable gases (CO, CO₂, CH₄, ...) are evacuated. This process was supported in the literature by Burnette (2013). Figure 1 shows pyroligneous acid production by a 200-liter drum furnace. The first step is to place the wood inside the kiln, then ignite it, then stop feeding the flames, and then observe distinctly the changes in color of the smoke emitted (from thick white to yellow and acrid). Then extend a hollow green bamboo pole (far end elevated to 45°C) from the flue. The pyroligneous liquid can be collected using containers fixed under one or two holes, about 2 cm wide, drilled in the bamboo pole about 30 cm from the flue pipe connection. Finally, the recovered condensate is left to settle in a sealed bottle for at least 3 months, during which time the components settle in three distinct layers. The first layer at the bottom of the container is black and contains wood tar. The second layer (below the top layer of liquid) is the usable part of the wood vinegar. This component will be light yellow to reddish brown in



Figure 1.—Pyroligneous acid production process by 200-liter drum furnaces.

color. The third (top) layer is classified as light oil and will have a layer of wood tar on top. This process has been used by several authors on various biomasses. These include the work of Ratnapisit et al. (2009) with rubber wood and Nurhayati et al. (2005) on acacia wood (*Acacia mangium*). This technology was also developed by Phineath in 2018 (Keerati 2019). This same technology allowed Jain and Chavan (2013) to produce charcoal and vinegar from bamboo pieces of 15 cm split vertically. In total, 16 bamboo pieces, weight 90 kg, were used for the production of 22.30 kg of charcoal and 2.24 liters of wood vinegar. This technique shows a low performance for the production of wood vinegar, with about 2.5 percent by weight (Jain and Chavan 2013).

Production of wood vinegar with a Casamance oven

The Casamance oven is a modified traditional type of millstone. This type of millstone was first assembled in Casamance, a town in Senegal, during the years 1979 to 1980 (in the United Nations Development Programme-FAO-United Nations Sudano-Sahelian Office-Senegal project 78/002), from which it gets its name. The Casamance millstone has a chimney that allows for a reverse draught; the gases heat up inside, circulate in the wood load, preheat it, and dehydrate it. The gases then flow back down to the bottom of the grindstone and exit through the chimney, at which point the charcoal byproducts recombine with the charcoal (fixed charcoal content 80–90%). Since then, with the increase in demography in West African countries, some have taken an interest in developing this millstone locally, highlighting its performance in optimizing charcoal production. These include Benin (Akouehou et al. 2012, Issifou et al. 2020), Rwanda (Nyampeta 2004), and Côte d'Ivoire (REDD+ and Nitidae 2019). However, no specifications on the amount of pyroligneous liquid during the use of this process have been obtained in these different countries, except in Côte d'Ivoire during the training of charcoal makers in the Mé region (town of Adzopé) on the use of improved millstones with chimneys. Several advantages over the use of the Casamance millstone were listed, notably the uniform and high temperature of the remaining kiln, and a high recovery of pyroligneous liquid thanks to the presence of the chimney. Figure 2 shows a Casamance millstone created in Togo. The process of obtaining wood vinegar through such a millstone is illustrated as follows



Figure 2.—Production of pyroligneous acid by a Casamance millstone.

(REDD+ and Nitidae 2019). The assembly of the grinder consists of laying out stringers in the direction of the length of the oven, placing wood on the floor, and then positioning the chimney and covering it with earth. Then comes the lighting stage (preheating), which is carried out with small wood, twigs, or embers generally placed in the middle and then plugging the ignition well. The temperature inside can reach 600°C; the pyroligneous liquid is recovered at the base of the chimney between 80°C and 150°C. When this phase is complete, the charge is allowed to cool and the charcoal is removed from the furnace.

Production of wood vinegar by hydrothermal carbonization

During the hydrothermal treatment of biomass, two products are obtained, namely hydrochar and wood vinegar. Sztancs et al. (2020, 2021) found that hydrochar cofired with coal could reduce CO₂ greenhouse gas emissions and promote low-carbon electricity generation. Hydrothermal carbonization is carried out at high temperature (120°C to 350°C) and pressure (2 MPa to 16 MPa) in the presence of water (González et al. 2005). The carbonization temperature plays an important role in the hydrothermal treatment process. A study by Wang et al. (2020) showed the influence of temperature on the yield of wood vinegar during hydrothermal carbonization. Indeed, the yield of wood vinegar decreases from 70.6 to 68.8 percent when the treatment temperature increases from 200 to 230°C and then increases to 72.4 percent at 260°C (Wang et al. 2020). This shows that the optimum temperature for maximizing the yield of wood vinegar via the hydrothermal process was 260°C. The process of producing hydrochar and wood vinegar from hydrothermal carbonization was supported by Hernandez-Soto et al. (2019) in their studies on the production of a material with an organic carbon content suitable for use as a soil improver or as a substrate component. First is the calculation of the appropriate amounts of water and biomass for the reaction mixture. The water content of the mixture should vary between 70 and 85 percent by weight. Then comes weighing and introducing the previously calculated biomass and water into the autoclave. After this, pressurization with nitrogen at 2 MPa is carried out. The agitator is started with a temperature of 215°C for 30 minutes and maintained. The carbonization process can last from 4 hours to overnight and is then left to cool to room temperature after the heating is switched off. Finally comes the recovery of the raw hydrochar. All residual pressure is carefully released and then the autoclave is opened to recover the hydrochar, which is separated from the liquid phase by vacuum filtration through a Büchner funnel and dried in an oven at 105°C for 2 hours. The liquid phase is left to rest for months to extract the pyroligneous acid or wood vinegar.

Physical and Chemical Properties of Wood Vinegar

Quality of wood vinegar

The quality of wood vinegars depends mainly on several parameters such as pH, color, odor, dissolved tar content, ignition residue, transparency, and specific gravity (Wada, 1997). Wood vinegars have a pH between 2 and 4 because of the presence of acetic acid, formic acid, and propionic acid. The total soluble tar content is between 0.23 and 0.89

percent by weight. The specific gravity and Brix are between 1.005 and 1.016 g/mL and between 1.7 and 6.6 respectively (Mun et al. 2007). The odor of wood vinegar is smoky. Density and viscosity could also be important in the physicochemical properties of vinegar. To standardize the quality of vinegar, seven parameters have been adopted by the Japan Pyroligneous Liquor Association, which is an industrial organization for the pyroligneous liquor trade. These standards are as follows (Wada 1997):

1. pH of the vinegar should be about 3.
2. Standard specific gravity should be between 1.010 and 1.050 g/mL.
3. The product should have a pale yellow, light brown, or red-brown color.
4. The product should have a marked smoky odor.
5. The product must have a dissolved tar content of less than 3 percent.
6. The ignition residue must be less than 0.2 percent.
7. The product should have a transparency with no suspended solids.

A study by Theapparatt et al. (2014) on the physical and chemical properties of eight wood vinegars from five wood species (*Leucaena leucocephala* [katin], *Azadirachta indica* [sadao], *Eucalyptus camaldulensis*, *Hevea brasiliensis* [rubber tree], and *Dendrocalamus asper* [bamboo]) grown in Thailand, produced by heating wood samples to 400°C. Table 2 highlights the parameters for assessing the quality of these wood vinegars. Only two wood vinegars, those from rubber tree and from bamboo, unanimously met all the standards of the Japan Pyroligneous Liquor Association. Also, the pKa of 4.7 was an indicator of the major presence of acetic acid in the extracts, which was responsible for the pH values. The specific gravity showed good correlations with total soluble tar and Brix level ($R = 0.87$ for both); in turn, Brix level showed a good correlation with total soluble tar ($R = 0.87$; Theapparatt et al. 2014). Thus, the easily determined Brix degree could be used as a general indicator of total soluble tar. The amount of total soluble tar signified the presence of phenolic compounds. In addition, phenolic compounds were confirmed by the ultraviolet absorption maximum (λ_{\max} at 268 to 274 nm; Theapparatt et al. 2014).

Parameters affecting the quality of wood vinegar

Wood vinegar, being a product with a composition of several molecules with different chemical functions, is dependent on a few factors including the raw material, the carbonization process used (type of pyrolysis), and the decanting method.

Raw material.—Several biomasses are used, but generally these biomasses are lignocellulosic; they are composed mainly of three major polymers: cellulose, hemicellulose, and lignin, and other inorganic minerals as well as organic extracts such as alkaloids, resins, sugars, starches, lipids, proteins, and essential oils (Balat et al. 2009). The main high-molecular-weight structural components are cellulose and hemicellulose (65% to 75%) and lignin (18% to 35%). There are other components that are generally inorganic minerals and low-molecular-weight organic extractables in the plant biomass. The mass percentage of these chemical components varies among plant species and explains the differences in the composition of wood vinegar. In general, agricultural biomass consists of 40 to 50 percent cellulose, 20 to 30 percent hemicellulose, and 10 to 25 percent lignin (Iqbal et al. 2011). In the literature, many types of biomass are used for the production of pyroligneous acid. These include woody plants such as eucalyptus wood (*Eucalyptus globulus*; Mungkunkamchao et al. 2013), birch (*Betula* sp.; Murwanashyaka et al. 2001), oak (*Quercus acutissima*; Lee et al. 2011), beech (*Fagus* sp.; Beaumont 1985), hairy - leafy molave (*Vitex pubescens*; Oramahi and Yoshimura 2013), rubberwood (Ratanapisit et al. 2009), Japanese cedar (*Cryptomeria japonica*; Young-Hee et al. 2005), walnut twigs (*Juglans* sp.; Wei et al. 2010), East Asian cherry (*Prunus jamaskura*), Japanese chestnut (*Castanea crenata*; Kimura et al. 2002), and mangrove plant (*Rhizophora* sp.; Loo et al. 2007, Zulkarami et al. 2011). We also have agricultural biomasses that include cotton stalks (*Gossypium hirsutum*; Pütün et al. 2005), hickory hull (*Carya* sp.), and rice (*Oryza sativa*) straw (Lee et al. 2005); almond (*Prunus dulcis*; Sztancs et al. 2021), hazelnut (*Corylus avellana*), and wheat (*Triticum aestivum*; Demirbas 2004) hulls; sugarcane (*Saccharum officinarum*) and pineapple (*Ananas comosus*) wastes (Mathew and Zakaria 2015); and sugarcane bagasse (Garcia-Pérez et al. 2002), walnut hulls (Wei et al. 2010), and tea (*Camellia sinensis*) wastes (Demirbas 2007).

Type of pyrolysis.—The different pyrolysis methods are classified according to heating rates expressed in degrees Celsius per second and residence times. In general, conventional pyrolysis, which can be either slow or fast, is performed mainly for biochar and liquid and gaseous products. In contrast, fast pyrolysis is recommended to maximize the yield of liquid and gaseous products. Feedstock, heating rate, temperature, and production technology are important factors for pyrolysis products (Mathew and Zakaria 2015). High temperatures lead to the decomposition of large molecules of liquid and residual solids into small molecules enriched with fractional gases

Table 2. — Physical and chemical properties of eight wood vinegars.

Sample	pH	Specific gravity (g/mL)	Total acid content (% by weight)	pKa	Total soluble tar (% by weight)	Degree Brix	λ_{\max} (nm)	A_{\max}	Water content (% by weight)
<i>Leucaena leucocephala</i> 1	3.40	1.006 ± 0.000	4.47 ± 0.01	4.70	0.37 ± 0.02	3.80 ± 0.10	274.50	154.00 ± 5.00	91.13 ± 0.27
<i>L. leucocephala</i> 2	3.10	1.007 ± 0.000	4.61 ± 0.02	4.70	0.57 ± 0.01	4.60 ± 0.10	270.80	375.50 ± 6.20	84.54 ± 0.02
<i>Azadirachta indica</i> 1	3.40	1.004 ± 0.000	3.28 ± 0.03	4.70	0.37 ± 0.02	3.00 ± 0.10	273.40	150.50 ± 5.00	91.50 ± 0.06
<i>A. indica</i> 2	3.20	1.005 ± 0.000	3.16 ± 0.04	4.70	0.58 ± 0.03	3.40 ± 0.10	271.00	298.00 ± 6.50	93.48 ± 0.15
<i>Eucalyptus camaldulensis</i> 1	3.10	1.006 ± 0.000	4.62 ± 0.04	4.70	0.57 ± 0.02	4.60 ± 0.10	272.60	221.00 ± 5.00	89.44 ± 0.25
<i>E. camaldulensis</i> 2	3.50	1.008 ± 0.000	3.62 ± 0.03	4.70	0.49 ± 0.02	3.40 ± 0.10	270.80	393.00 ± 8.00	90.37 ± 0.20
<i>Hevea brasiliensis</i>	2.90	1.012 ± 0.000	4.92 ± 0.02	4.70	0.96 ± 0.03	6.00 ± 0.20	268.00	467.00 ± 7.00	85.30 ± 0.50
<i>Dendrocalamus asper</i>	2.90	1.010 ± 0.000	4.92 ± 0.02	4.70	0.71 ± 0.01	5.60 ± 0.20	269.20	470.00 ± 6.00	81.44 ± 0.26

(Demirbas 2007). The description of these two types of conventional pyrolysis is detailed below.

Slow pyrolysis: Traditionally, charcoal kilns, pit kilns, charcoal heaps, or earthen kilns were used, which were later replaced by permanent kilns in many places (Theapparath et al. 2018). During slow pyrolysis, the temperature for biomass decomposition is about 300°C. The vapors in slow pyrolysis are not released as quickly as in fast pyrolysis and the residence time of the vapors varies between 5 and 30 minutes (Bridgwater 2008). Plant biomass feedstocks are stacked around a central channel in the furnace and heated slowly at low temperatures to remove moisture, then exposed to higher temperatures. The openings of the kilns are partially sealed so that complete combustion of the biomass does not occur. The smoke from the kiln is piped from the main production unit to allow condensation and cooling of the smoke. Then a natural purification is carried out by sedimentation of the condensed water vapor for at least 3 months. Three layers of liquid are obtained and depending on their weight, the top layer will be light oil, the middle layer will be brown crude pyrolygneous acid, and the wood tar will be at the bottom. Slow pyrolysis yields almost identical proportions of charcoal (35 wt%), liquid (30 wt%), and gas (35 wt%; Bridgwater 2008).

Fast pyrolysis: Fast pyrolysis is a more efficient, high-temperature process in which biomass is rapidly heated and converted into biofuel. In this process, the biomass is heated to a high temperature (500°C) with a very short vapor residence time (<5 s). At the end of the process, the vapors or aerosols are rapidly cooled to produce bio-oil (Tiilikkala et al. 2010). In fast pyrolysis, a finely ground biomass feed is required because of the high temperatures and heat transfer rates (Bridgwater 2003). Fast pyrolysis produces 60 to 75 percent by weight bio-oil, 15 to 25 percent by weight biochar, and 10 to 20 percent by weight gas (Mohan et al. 2006). In the past, pyrolygneous acid was produced in charcoal kilns, but nowadays pyrolygneous acid is produced in specialized reactors. The gaseous compounds are condensed by the condenser to produce wood vinegar.

Methods of decanting wood vinegar

For the pyrolygneous liquid to be a future source of natural chemicals with consistent biological activities, an efficient separation method must be developed to generate semipurified bioactive components. To obtain more specific and consistent product properties, wood vinegar can be fractionated into a semipurified product. This could be achieved by several techniques such as sedimentation, filtration, chromatography, distillation, and solvent extraction.

Natural settling method.—This method is the most widely used to obtain wood vinegar from raw bio-oil or pyrolygneous liquid. It is the simplest and most efficient method. It consists of leaving the raw bio-oil in a sealed container. Over time, the unstable constituents of the raw wood vinegar will oxidize or polymerize to precipitate, suspend, or adhere to the inner wall of the container. A thin film of oil will form on the surface of the liquid and finally, as an intermediate phase, the wood vinegar. All suspended matter in the wood vinegar is removed to produce clear wood vinegar. When the resting and filtering processes are repeated several times, a transparent and stable wood vinegar is obtained (Fagernäs et al. 2012).

Distillation method.—Distillation is a separation technology commonly used in the chemical industry. This method successively separates components according to their different volatilities. It is mainly used for the separation of liquid mixtures. In general, there are two distillation systems: normal pressure distillation and reduced pressure distillation. In both systems, compounds are separated according to their respective boiling points. Charred wood vinegar has a water content of 80 to 90 percent, with a fairly low boiling point difference between the remaining 10 percent of organic matter. Therefore, boiling of wood vinegar starts at less than 100°C under atmospheric pressure; then distillation continues until 250 to 280°C, after which 35 to 50 percent residue remains (Czernik and Bridgwater 2004). The distillation method is quite effective in concentrating the wood vinegar and also in removing substances with low or high boiling points. However, the distillation process cannot completely remove unwanted polymers. It is more convenient to use this method after removing unwanted polymers from raw vinegar by the natural decantation method. However, care should be taken, as heating the sample to boiling may induce oxidation and polymerization, resulting in a loss of bioactivity of the components.

Liquid-liquid extraction.—The liquid-liquid extraction method involves the selective transfer of a substance from one liquid phase to another. Usually, an aqueous solution of the sample is extracted with an immiscible organic solvent. Thus, the solute is split between an aqueous solvent and an organic solvent. Liquid-liquid extraction has been introduced for the semipurification of active compounds from the wood vinegar mixture. This method is used for the separation of compounds with a different partition or relative solubility between the two solvent phases. By selecting the appropriate polarity of the solvents for extraction, such as hexane, diethyl ether, ethyl acetate, acetone, water, etc., the sample is extracted with the appropriate solvent. To obtain higher purity of bioactive compounds from wood vinegar, Oasmaa et al. (2003) suggested that step-by-step extraction on the basis of polarity order can also be used. Some reports have shown that phenolic compounds and organic acids have been extracted from wood vinegar using ethers and dichloromethane (Sipilä et al. 1998, Bedmutha et al. 2011, Fagernäs et al. 2012). However, they found that a considerable amount of volatile and high-polarity compounds were lost because of coevaporation of the compounds during the solvent drying step. In another phenomenon, the synergistic function was characterized as the mode of action of wood vinegar. It has been suggested in the literature that phenolic compounds and organic acids are active components. However, a previous report presented other unidentified components that could be active compounds (Bedmutha et al. 2011). We have caffeine, which is an alkaloid presenting, like phenol and its derivatives, natural pesticidal properties (Bedmutha et al. 2011). During the production of bio-oil, part of caffeine is degraded into a pyridine derivative that could also have pesticidal properties.

Areas of Wood Vinegar Application

Wood vinegar has been studied and continues to be studied in several fields including agriculture, medicine, wood preservation and food preservation.

Application of wood vinegar in agriculture

The use of chemical fertilizers can be quite depleting to the soil, as their long-term application has resulted in depletion of organic soil resources, poor water and nutrient conservation, and deterioration of the soil structure. Excessive chemical fertilization not only contributes to soil, water, and air pollution, but also some residues are found in the harvested fruit and vegetables. This contributes to a decrease in the quality and safety of the food supply. It was therefore important to find a natural alternative for the production of vegetables and fruit without consumption risks. Wood vinegar, which meets this required profile, is therefore suitable for use in agriculture. Over the last 2 decades, wood vinegar has been the subject of research in Southeast Asian countries, particularly in Thailand, China, and Cambodia.

Wood vinegar as a stimulator of plant growth and development.—Wood vinegar is a product that appears to stimulate cell growth and acts as a catalyst for the growth of several microbes and the activation of enzymes. The latter are essential for various physiological and biochemical processes in plants, such as photosynthesis, nutrient uptake, and cell growth, but the mechanisms involved are poorly studied. Many researchers have suggested that foliar application of wood vinegar increases the chlorophyll content and glossiness of plant leaves, which will increase photosynthesis and the synthesis of sugars and amino acids. In addition, esters such as methyl acetate and methyl formate, which accelerate plant growth and development, have been found in wood vinegar. Its application has had a significant effect on the production of rice (Tsuzuki et al. 2000), sorghum (*Sorghum bicolor*), and sweet potato (*Ipomoea batatas*; Shibayama et al. 1998). It has been reported that wood vinegar significantly increases the yield of rock melon (*Cucumis melo*), French marigold (*Tagetes erecta*), zinnia (*Zinnia elegans*), scarlet sage (*Salvia splendens*) and tomato (*Solanum lycopersicum*). In a study on tomato conducted by Mungkumchao et al. (2013), wood vinegar increased the total dry weight, the number of fruits, and the fresh and dry weights of the fruits. In addition, it effectively increased the total soluble solutes of the fruits. Masum et al. (2013) revealed that the application of wood vinegar increased the grain yield of rice. This was attributed to an increase in tillers per hill, 1,000 grain weight, and grains filled per panicle. In addition to this, wood vinegar also increased the yield of soybean (*Glycine max*; Traverro and Mihara 2016), whereas foliar spray improved the growth and yield of lettuce (*Lactuca sativa*), cucumber (*Cucumis sativus*), and cabbage (*Brassica oleracea* var. *capitata*) crops (Mu et al. 2006). In addition, wood vinegar significantly stimulated plant growth, fruit diameter, sweetness, and fruit weight in rock melon (*C. melo* var. *cantalupensis*; Zulkarami et al. 2011).

Wood vinegar as an organic fertilizer.—Many studies have demonstrated the beneficial effects of pyroligneous acid on the soil when applied as an organic fertilizer for rice (Tsuzuki et al. 2000), sugarcane (Uddin et al. 1995), and sweet potato (Shibayama et al. 1998). It was found that 20 percent of pyroligneous acids significantly increased the growth and yield of watermelon (*Citrullus lanatus*) in soilless culture (Zulkarami et al. 2011). In research on tea, it is reported that the application of pyroligneous acid increases the level of usable phosphoric acid threefold.

Root exudates in the rhizosphere include organic acids that dissolve phosphoric acid and make it more available for uptake by the roots. It has been suggested that the organic acids contained in pyroligneous acid have a similar effect in the soil.

Wood vinegar as a biopesticide.—Currently, there is pressure for sustainable agricultural practices to minimize overreliance on chemical use. The presence of phenolic compounds in pyroligneous acids allows it to have antifungal and other pest control properties (Baimark and Niamsa 2009). Pyroligneous acid also increases the permeability of agrochemicals into the leaf tissue. Generally, these agrochemicals are most effective when used in combination with other acids such as wood vinegar or pyroligneous acid at pH 4 to 5. Thus, pyroligneous acid is known to increase the effectiveness of chemical pesticides when used in combination. However, alkaline chemicals cannot be mixed with wood vinegar because of their negative reaction with acids. Mmojieje and Hornung (2015) studied the insecticidal effect of pyroligneous acid obtained from mixed wood biomass against green peach aphid (*Myzus persicae*) and red spider mite (*Tetranychus urticae*) in the United Kingdom and found mortality of over 90 percent for both pests. In Thailand, pyroligneous acid has been widely used as an insecticide in agriculture (Mmojieje and Hornung 2015). For example, birch tar oil is a good repellent against slugs (*Arion lusitanicus*) and snails (*Aranta arbustorum*; Tiilikkala et al. 2010). The application of pyroligneous acid resulted in the mortality of 95 percent of the aphid population on aubergine (*Solanum melongena*) when sprayed at a dilution of 1 percent (Regnault-Roger 1997). Yatagai et al. (2002) reported the termiticidal effect of pyroligneous acid against the Japanese termite (*Reticulitermes speratus*). In some publications, pyroligneous acid has been found to be effective against houseflies (Pangnakorn et al. 2012, 2014).

Pyroligneous acid can be used as a bioherbicide and potentially replace synthetic chemical herbicides. Phenols, organic acids, carbonyls, alcohols, and organic acids in pyroligneous acid effect its herbicidal activity (Kim et al. 2001). Acetic acid, the main component of pyroligneous acid, has been used in agriculture to control weeds. In one study, pyroligneous acid was found to be effective against underground weed propagules of freshwater plants such as *Hydrilla* spp, Sago pondweed (*Potamogeton pectinatus*), and smooth cordgrass (*Spartina alterniflora*; Spencer and Ksander 1999).

Wood vinegar as an antimicrobial agent.—Pyroligneous acids have been explored as antimicrobial agents by researchers but have not been extensively studied in this role. The presence of high concentrations of phenolic compounds and organic acids explains its antimicrobial properties (Lee et al. 2011, Mmojieje and Hornung 2015). Pyroligneous acid has been shown to have antibacterial properties on a selection of plant pathogenic bacteria by many researchers. For example, Chalermisan and Peerapan (2009) reported that pyroligneous acid inhibited *Xanthomonas campestris* pv. Citri and *Erwinia carotovora* pv. Carotovora. These pathogens can cause severe losses to horticultural crops. The agent causing bacterial wilt on many crops, *Ralstonia solanacearum*, was inhibited by phenol and pyroligneous acid guaiacols synthesized from Japanese cedar (*Cryptomeria japonica*; Young-Hee et al. 2005). Similar growth inhibition studies using 10 percent

pyroligneous acid showed an inhibitory effect on *Agrobacterium tumefaciens* and *X. campestris* (Mmojieje and Hornung 2015). Pyroligneous acid produced from pineapple solid biomass showed growth inhibition of the yellow gum disease bacterium *Corynebacterium agropyri* (Mahmud et al. 2016). As well as antibacterial properties, pyroligneous acids have also shown an inhibitory effect on phytopathogenic fungi. The higher content of organic acids and phenols in pyroligneous acids from various sources has shown inhibition of a wide range of plant pathogens (Mourant et al. 2005, Chalermisan and Peerapan 2009, Tiilikkala et al. 2010, Wei et al. 2010). Wei et al. (2010) reported antipathogenic effects of pyroligneous acid on plant pathogenic fungi such as *Helminthosporium sativum*, *Cochliobolus sativus*, *Valsa mali*, and *Colletotrichum orbiculare*. Pyroligneous acids produced at lower temperatures have a lower degree of antimicrobial activity compared with those produced at higher temperatures. Pyroligneous acids are effective in a wide range of dilutions. Jung (2007) showed that pyroligneous acid at a dilution of 1:32 inhibited *Alternaria mali*, the causal agent of alternaria leaf spot on apple. It was assumed that the presence of furaldehydes and phenols in pyroligneous acid are the main cause of the antifungal activity. A primary report by Tiilikkala and Setälä (2009) indicates that birch tar oil can be used effectively to control *Phthophthora infestans*. All these functional activities and applications suggest that pyroligneous acid could be an alternative to synthetic chemicals for use as antimicrobial agents.

Application of wood vinegar in medicine

Wood vinegar from charring has been used in the preparation of the detoxification pad available in Japan, the United States, Korea, and China. The method of using the detoxification pad is to place it under both feet before going to bed. The detoxification cushion is attached directly to the reflex points on the feet. It is believed to promote balance and healing in the body. It is a source of short-chain fatty acids that help promote acidity in the large intestine, resulting in the inhibition of the growth of bad bacteria, enteropathogenic bacteria (Nakai and Siebert 2003), and protozoa (*Cryptosporidium parvum*; Kniel et al. 2003), and stimulates the growth of prebiotics, *Enterococcus faecium* and *Bifidobacterium thermophilum* (Tana et al. 2003). In addition, wood vinegar also reduces the absorption of alkaline carcinogens, improves the absorption of calcium and magnesium, and increases blood circulation. Distilled wood vinegar could inhibit allergic reactions, especially type I allergic reactions by oral administration. This solution was indicated to prevent allergic rhinitis, hay fever, allergic conjunctivitis, atopic dermatitis, allergic asthma, urticaria, and food allergy (Imamura and Watanabe 2007).

Application of wood vinegar in food preservation

Underreporting of foodborne diseases is a common and sometimes fatal problem for millions of people worldwide (Vattem et al. 2004). Food additives are used to preserve foods, improve nutritional value, add or replace color, add or replace flavor, improve texture, or provide processing aids (Brannen et al. 2002). However, in recent times, a decrease in demand for synthetic food additives has been recorded worldwide because of increased consumer aware-

ness. Consequently, natural food additives have become popular (Deba et al. 2008). Several natural additives and preservatives have been widely used in foods, such as spices, herbs, essential oils from plants, and wood vinegar. Wood vinegar could be an excellent additive as it is obtained from natural biomass and by natural processes. It can be used in processed foods to inhibit microbial growth because of the phenols and short-chain organic acids contained in the vinegar (Kahl and Kappus 1993). In addition, smoke flavors extracted from wood vinegar have been used in foods as a safety product (Mohan et al. 2006). In addition, the US Food and Drug Administration permits the use of pyroligneous acid for smoke flavoring and preserving foods such as ham, bacon, sausages, fish, and cheese.

Application of wood vinegar in wood preservation

Recently, some researchers have reported that bio-oil and wood vinegar obtained from fast pyrolysis have a strong potential to be used as wood preservatives, and they have suggested that phenolic compounds, which permeate the wood matrix, seem to play an important role in fungal growth inhibition and decay resistance tests (Kartal et al. 2004, Mohan et al. 2006, Nakai et al. 2007). Furthermore, wood blocks treated with filtrates obtained from the fuel slurry of several woods such as sugi (*Cryptomeria japonica*) and acacia (*Acacia mangium*) showed resistance to the brown rot fungus (*Fomitopsis palustris*) and white rot fungus (*Trametes versicolor*). However, the filtrates did not increase the durability of the wood blocks against subterranean termites (*Coptotermes formosanus*; Kartal et al. 2004).

Conclusion

The carbonization of lignocellulosic biomass is an important process in the valorization of residues from agriculture and forestry. This pyrolysis allows the formation of three exploitable compounds, namely biochar as an amendment, gases for thermal drying, and pyroligneous acid, which is used in several fields thanks to its impressive composition. Pyroligneous acid has antioxidant and antimicrobial properties, making it suitable for use as a biopesticide, organic fertilizer, plant growth stimulator, food preservative, wood preservative, and even in medicine. As such, pyroligneous acid could be an ecological and sustainable tool for farmers and, in turn, for consumers. Because it is obtained without potentially harmful chemical additives in the long term, the more global use of wood vinegar could contribute to a healthier environment and ecological system, as well as increased socioeconomic and health benefits.

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