

Elucidating the Chemical Properties and Potential Applications of Wood vinegars Produced by Controlled Thermal Treatments

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Abstract— Wood vinegar (WV) has been used for ages as fertilizer and antimicrobial agent, but its impacts on ecosystems are not well understood. Our objective was to investigate potential uses for WVs made from biomass resources and evaluate conditions for possible agronomic, chemical/pharmaco-chemical purposes and potential impact on the environment. We studied four woods vinegars made by slow pyrolysis using: *Cambara* (WV_{Cam}), *Eucaliptus* (WV_{Euc}) at 350°C for 72 h, *Nim* (WV_{Nim}) and *Nim* mixed with fresh *Nim* leaves and branches, soaked into WV_{Nim} (WV_{Mix}) at 120°C for 40 h. WVs from WV_{Mix} , WV_{Euc} and WV_{Cam} demonstrated significant potential chemical products, while WV_{Nim} for pharmaceutical purposes. WVs can be used to partially substitute fertilizers and chemicals, most especially WV_{Mix} . Soil bacteria tests suggest a concentration of 0.8% or less for WVs application in soils. No WVs tested presented risk for environmental and human health due to absence of carcinogenic poly-aromatic hydrocarbons (PAHs).

Keywords— biomass, controlled pyrolysis, pyrolygneous acid.

I. INTRODUCTION

Large amounts of agricultural residues, such as sawdust, sugarcane straw and rice husks are produced worldwide annually, mainly in developing countries like Brazil. Current disposal methods for these residues are not usually adequate and have been responsible for a wide environmental impact¹. Thermal treatments, such as pyrolysis, could be an alternative for treatment of these residues, converting biomass into bio-products with higher added value²⁻⁴, such as wood vinegar⁵. Traditional vinegar production utilizes sugar crops that compete with food as feedstock. There are newer

processing technologies, via thermal means to produce similar wood vinegar products.

Thermal conversion technologies, such as controlled pyrolysis may be optimized to generate specific ranges of organic liquids through the condensation of the gaseous products during the thermal treatment. The ranges of chemicals and their properties vary according to operational temperature and exposure time (Capareda, 2013).

This study investigates the chemical characteristics of WVs made using different biomass resources and using controlled thermal conversion processes and conditions to generate highly valuable chemicals or pharmaco-chemicals including agronomic chemical substitutes. The study also identifies risks to the environment through its agronomic use. The overall goal is to find high value chemicals and products from materials that are considered wastes. The specific objectives are as follows:

- Evaluate wood vinegar for its agronomic fertilizer or chemical partially substitutes,
- Identify wood vinegar whose chemical components are considered beneficial and suitable high value chemical products, such as potential for pharmaco-chemicals, and
- Evaluate other properties such as various poly-aromatic hydrocarbons (PAHs) that are potential risk for environmental and human health

Review of Related Literature

1.1. Thermal Conversion Processes

Wood vinegar, also called pyrolygneous acid or wood distillate, is the water soluble organic fraction of the liquid that is produced during the pyrolysis of biomass⁶, many times treated as pyrolysis residue. The pyrolygneous acid is brown, with strong smoke smell

liquid produced by a heating biomass in oxygen-limited conditions ^{2,5,7}. When the gas generated from thermal treatment is cooled, it condenses into liquid ⁸⁻¹⁰ and generate wide range of chemicals.

The controlled pyrolysis of many different types of wood can be used to produce various wood vinegars including Eucalyptus ^{11,12}, Bamboo ^{12,13} and others. The chemical and physical properties of wood vinegar can vary, depending on the wood materials, kiln designs and reaction conditions, including heating rates and reaction temperature ^{7,14,15}.

In Brazil, the most widespread type of kiln is the hot-tail ('*rabo quente*' in Portuguese), made with clay bricks and mortar ¹⁶. In this country, WV has been used as a fertilizer and pesticide, however improperly, without any dosage control, which may cause accumulation of chemicals compounds in the soil, such as some carcinogenic poly-aromatic hydrocarbons – PAHs. Other pyrolysis systems used auger to introduce the material to the reactor or the highly advanced fluidized bed pyrolysis systems ¹⁷.

1.2. Valuable Chemical Compounds from Thermal Pyrolysis Processes

The liquid components in pyrolysis processes from various wood products contain more than 200 compounds, including phenols, poly phenols, acetic acid ¹⁸, ketones, ester, aldehydes and alcohols ¹⁹. Because of their low pH and high organic load, they cannot be disposed to the environment without treatment ²⁰. It must be properly diluted or neutralized prior to disposal.

The manufacturing conditions for the production of wood vinegar is so variable that products can differ in chemical composition and toxicity. Products can be divergent that it can pose human health risks as reported in several documents ²¹⁻²³. Thus, the same risks must be considered if these chemicals are used for animal or soil purposes. For example, some PAHs have high environmental stability and they are rapidly transported to the human through the food chain ^{24,25}.

The US Environmental Protection Agency (1993) has listed 16 PAHs as priority control pollutants, including naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benza(α)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(α)pyrene, indeno(1,2,3-cd)pyrene, dibenz(α,h) anthracene and benzo (g,h,i) perylene. Not all PAHs are carcinogen and must be used appropriately and at proper concentrations.

1.3. Beneficial Antimicrobial Properties and Soil Microbiota Improvements

Depending on the dosage, wood vinegar exhibits a high degree of antimicrobial activity against various microorganisms ^{5,26}, such as *Legionella pneumophila* ²⁷, *Escherichia coli* and *Corynebacterium agropyri* ⁹. Wood vinegar also has antioxidant activity ^{5,18,26,28}.

Wood vinegar are also considered as mosquito repellents ²⁹ and antifungal ^{18,30}. It can stimulate plant growth ^{9,19,31,32}, can be used as fertilizer ⁸ and control weeds ^{32,33}.

In addition, wood vinegar can be developed into useful sterile products for medical, aquaculture and livestock breeding applications ⁵. It has shown benefits as animal diet or feed ingredient ³⁴⁻³⁶. Finally, it has numerous dermatological purposes in humans ³⁷ and used for smoked food products ³⁸.

Wood vinegar's impact in the environment can be predicted by soil microbiota, which is easily altered by soil changes ^{39,40}. WVs can also be used as bio-indicators of high sensitivity that reflect environmental conditions ⁴¹. Among these bio-indicators, microorganisms functional groups density, such as bacteria, is one of the most effective indicator ⁴². The quantification of colony forming units (CFU) has been used to estimate the variation in bacterial density in ecotoxicology studies ⁴³.

II. MATERIAS AND METHODS

2.1. Wood Vinegar Formation

We studied four woods vinegars (WV) which were made for local farmers in Brazil, for use on their farm: (1) WV_{Cam}, made of Cambara (*Qualea* sp.) sawmill waste, in Sinop-MT, Brazil; (2) WV_{Euc}, made of Eucalyptos (*Eucalyptus* sp) in Vilhena –RO, Brazil; (3) WV_{Nim}, made of Nim (*Azadirachta indica*), in Brasnorte–MT, Brazil and (4) WV_{Mix}, made of Nim (*Azadirachta indica*), mixed with fresh Nim leaves and fine grinded branches, soaked into WV_{nim} (1:1 v/v) for 2 weeks, in Brasnorte–MT, Brazil.

The WVs were produced in hot-tail kilns on a small scale, originally for agronomic purposes. WV_{cam} and WV_{euc} were thermally treated into sealed furnace, to prevent air from entering, at around 350 °C for 72 h. WV_{nim} and WV_{mix} were thermally treated into sealed furnace, at around 120°C for 40 h. All of these thermal processes are in batch mode. WVs were obtained by condensing the pyrolysis vapors in the chimney. The pyrolysis liquids were left to sit until separated into three layers: at the top is a light oil; on the bottom is the sticky wood tar and in between lies the organic portion with the majority of refined wood vinegar.

2.2. Wood Vinegars Chemical Characterization

2.2.1 Inorganic Elemental Analysis, Total inorganic/Organic Carbon and pH

The unknown chemical composition of WV from different plants can be estimated by a comparison with the mass spectral libraries available on gas chromatography mass spectrometry (GC-MS) database^{44,45}. This technique is an easy, cost-effective and sensitive method to identify and quantify the chemical compositions of natural products.

The WVs were treated with phosphoric acid 1% to measured total carbon (TC), total inorganic carbon (TIC), total organic carbon (TOC), using TOC-Analyzer (Elementar Analysersystem GmbH). Additional WVs inorganic elemental analysis was performed⁴⁶ to determine the total Ca, Mg, Cu, Mn, K and Zn, by extraction with nitric-perchloric acid solution and determination by atomic absorption spectrometry. The total P was analyzed by colorimetry.

WVs pH titration curves were measured by incrementally adding 0.5 ml of 0.1 N NaOH to a 50 ml of WV. After each increment, the solution was stirred until the pH stabilized.

2.2.2 Organic Chemical Analysis

The organic compounds were analyzed by GC-MS, using Agilent 7890 GC apparatus (Wilmington, DE, USA) equipped with a 5975C MS detector and 7683B automatic liquid sampler with a capillary column: HP-5MS 5%-phenyl-95%-dimethylpolysiloxane (30 m, 0.25 mm i.d., film thickness 0.25 μm) (J&W Scientific, Folsom, CA, USA). The oven temperature was programmed to start at 150°C (1 min), increase to 210°C at 15°C min^{-1} (10 min), and then increase by 5°C min^{-1} to 310°C for 1 min. The injector temperature was set at 270°C in splitless mode, when 1 μl of sample was injected. The mass selective detector temperatures of the ionization chamber and MS Quad were set at 230 and 150°C, respectively. The electron ionization energy was 70 eV, and the mass range was m/z 30–500 (amu). Results (chromatographic peaks) from WV samples were used to identify the organic compounds by comparison with the experimental m/z values of the compounds from NIST data base. Only those compounds with match above 70% were considered. The relative percentage was calculated by the relation between the peak area of the compound identified and the sum of the peak areas of all majority compounds in the chromatogram.

2.2.3 Poly-aromatic Hydrocarbon (PAH) Analysis

The total PAH analysis was measured in triplicate. About 4 g of sample with 20 ml of toluene were agitated for 30 min at 50% on an Kline agitator NT151 (Novatecnica, SP, BRA). Then, the sample was sonicated for 30 min in an ultrasonic bath (Quimis, SP, BRA). After the extraction, the sample was centrifuged at 4500 rpm

for 5 minutes on a Sigma 3-16KL centrifuge (Sigma Laborzentrifugen GmbH, DE). The supernatant was collected in a glass tube. The solid residue was extracted twice. All the supernatant were cleaned up on a silica gel column (3 cm) and then eluted with heptane. The solvent was evaporated under vacuum at 60°C until a volume of 1 ml is reached. The samples were analyzed using the same apparatus used for the organic compounds analysis. However, the oven temperature was programmed to start at 50 °C (2 min), increase to 150°C at 10°C min^{-1} , then increased to 280°C at 5°C min^{-1} and held for 9 min. It is then ramped up at a rate of 40°C min^{-1} to 310°C. It is held at this temperature for 8 minutes.

The majority and main chemical and/or pharmacy usefulness of the organic compounds found by GC-MS were investigated by the SciFinder® (scifinder-cas.ez103.periodicos.capes.gov.br) and ChemSpider (<http://www.chemspider.com>) databases.

2.3. Wood Vinegar Antibacterial Tests

We assessed the antibacterial effects of wood vinegar in four types of soils: (1) crop: integrated system with a sequence of soybean and maize, this last one intercropped with pasture; (2) pasture: *Urochloa brizantha* cv. Marandu (L); (3) planted forest: *Eucalyptus urophylla* x *Eucalyptus grandis* hybrid and (4) native forest: classified as “Evergreen Seasonal Forest” soil.

Soil samples were collected in 2016 during the dry season from 0 to 10 cm using a sterile Dutch Auger. The sample was composed of twenty samples per plot.

The antibacterial study was adapted from 47. Dilution was performed starting from 10 g of soil with natural moisture in 90 ml sterile phosphate buffered saline (PBS: 1.44 g ml^{-1} Na_2HPO_4 , 0.24 g ml^{-1} KH_2PO_4 ; 0.20 g ml^{-1} KCl, 8.00 g ml^{-1} of NaCl and pH 7.4).

The dilution of about 10^{-3} was plated onto 10% Trypticase Soy Agar plates (TSA-Merk) with WV_{Cam} , WV_{Euc} , WV_{Mix} and WV_{Nim} at 0.8 and 100%. The antibacterial tests were performed with five replicates and incubated for 7 days at 28°C and related with the biological oxygen demand (BOD). The quantification of total bacteria was carried out by Colony Forming Units (CFU).

2.4. Statistical Analysis

The WVs chemical properties and antibacterial tests were compared among various treatments by performing Tukey’s test. The p-value of less than 0.05 was considered significant. Statistica Soft Version 10 was used in the statistical analysis of all the data generated from these studies.

III. RESULTS AND DISCUSSION

a. Wood Vinegar Chemical Characteristics

3.1 Chemical Fertilizer Potential

Table 1 shows the pH, complete elemental analysis important for fertilizer and nutrients as well as total organic and inorganic carbon. These properties will represent the wood vinegar's capability to partially substitute the use of chemical fertilizers. Of fertilizer importance in the concentrations of macro-nutrients (phosphorus and potassium), two of the basic inorganic chemical fertilizer component.

The other elemental components are also vital nutrient needs of plants. Among the WVs samples tested, WV_{Euc} and WV_{Mix} showed potential fertilizer P and K substitute having the highest concentrations. WV_{Euc} had reported P and K concentrations of 20.3 and 69.8 mg/ℓ, respectively. WV_{Mix} had 23.4 mg/ℓ of P and similar 69.8 mg/ℓ of elemental K. WV_{Mix} contained the highest concentrations of Mg and Ca with concentrations of 7.84 and 122.71 mg/ℓ, respectively. Hence, the elemental components of WV_{Mix} is an excellent potential supplement to other high-quality fertilizers inputs.

For example, it has been reported that WV has traditionally been applied in the growing of tea. Report showed that it increases the yield by three times the level of useable phosphoric acid. Plants roots secrete organic acids which dissolve and absorb phosphoric acid in the soil and it is thought that organic acids in WVs have the same effect⁴⁸.

Table 1 also showed the total organic carbon (TOC) data showing high values for WV_{Cam} and WV_{Euc} (258.6 – 275.6 mg/ℓ). High TOC levels indicate great material accessibility with microorganisms. This property may play the role of stimulators (or sometimes inhibitors) of plant growth and plant development because of its high carbonaceous components. This is especially true for low-molecular weight organic compounds⁴⁹.

The use of WV as fertilizer is gaining importance in many crops. It cannot act as substitute for soil fertilization, but it can supplement a sound soil fertilization program⁸. However, its utilization is generally based on local knowledge and not scientific research⁵⁰, which poses certain environmental risk for soil and water contamination, toxicity and impact on soil microbiota.

It is important to note that, because of low pH values and the high TOC values, the WVs described above will have considerable organic load. Hence, none of WVs should be disposed to the environment indiscriminately. Proper treatment or identification of recommended application rate as pesticide or chemical fertilizer in soil agriculture must be known. The beneficial

effect of WVs in soil or plant are directly related to the dosage used^{9,32,51}.

The pH of WVs can be correlated inversely with titratable acidity³⁸. Unlike strong acids that are fully dissociated, WV acids are only partially ionized. It could be attributed to differences in its buffering capacity, **Fig 1**. WV_{Nim} and WV_{Mix} contents have narrower working ranges for buffering than WV_{Cam} and WV_{Euc} do. It can positively be correlated with carbonyl and carboxyl groups content on WVs, **Fig 2**.

In addition to potential chemical fertilizer and substitutes, WVs could be recommended as co-solvents for agrochemicals. The majority of agrochemicals are dissolved most easily and their effectiveness most enhanced if they are mixed with organic acid solutions⁴⁸. The pH is a critical factor in the effectiveness of many pesticides and growth regulators, some pesticides particularly carbamate and organophosphate insecticides are broken down when combined with high pH water.

The rate and severity of the reaction is determined by how susceptible the pesticide is to hydrolysis⁵². A pH of 5.5 to 6.5 is the ideal one for mixing most pesticides. This is the primary reason that most commercial pesticides indicate in their directions the addition of a buffering or acidifying agent into the spray tank⁵³.

WV can act as a pH buffer and an acidifying agent for mixing pesticides that require low pH. This buffering and acidifying behavior will allow the plant to absorb nutrients more readily⁵⁴. Such mixture between WV and pesticides no doubt improve cost and can even increase the effectiveness of the pesticide^{55,56}.

3.2 Phenolic Compounds

WVs contains around 68 kinds of organic compounds belonging to 4 main groups, **Fig 2**. These groups include carbonyl, carboxyl, phenolics, silicates and others. The chemical composition of WVs are quite variable as shown in **Table 2**. The primary reason is that the chemical characteristics of products are so much dependent on the wood source and the thermal treatment processes. These include temperature, retention time, and even particle sizes or granulometry⁵⁷.

Phenols are the primary chemical grouping found in the WV liquid product. The relative phenolic composition ranking and of increasing order is as follows: WV_{Euc}<WV_{Cam}<WV_{Nim}<WV_{Mix}. Some phenolic compounds shown in **Table 2** are as follows:

1. Guaiacol is used as an antimicrobial agent^{58,59}, the compound reduces gastric erosions induced by classic anti-inflammatory drugs (ibuprofen)⁶⁰. It is also considered an antidiarrheal agent⁶¹ and an antioxidant⁵;

2. Creosol is used as [flavor enhancing standards, food and cosmetic component standards](#) ⁶², and an antidiarrheal agent ⁶³;
3. Eugenol is considered an antioxidant ^{64,65}, an antimicrobial agent ^{64,66} and anti-inflammatory substance ⁶⁷;
4. Kaempferol is considered an antioxidant and an anti-inflammatory agent ⁶⁸. It has been used as agent for the treatment of Alzheimer's disease ⁶⁹, and an intervertebral disc degeneration treatment compound ⁷⁰. Further, it has been used in Leishmanial chemotherapy ⁷¹ and as cancer therapeutic agent ⁷² and,
5. Syringol is used as an antioxidant ^{5,73}.

As previously cited, phenolic compounds have antibacterial properties ^{74,75}, including membrane-disrupting agents ^{76,77}. This chemical characteristic justifies the higher numbers of pharmaco-chemical compounds in this group.

Note that while those compounds are found in the liquid product, some separation techniques must be developed to recover them in pure form. This should be the subject of future research.

3.3 Carbonyl Groups

The carbonyl group appears in WV_{Cam} , WV_{Euc} , WV_{Nim} but was not found in WV_{Mix} . This results made it clear that the chemical output product of a certain biomass resource changes and can be affected by the various pyrolysis processes used, including how the material was processed (e.g. a case for Nim leaves and fine grinded branches effusion on WV_{Nim}).

The main composts derived from the carbonyl group, widely used in the chemical industry are as follows:

1. The compound 5-methylfurfural is used as a chemical for the synthesis of fine chemicals manufacture ^{78,79}. It is also used as a potential candidate for therapy of sickle cell disease ⁸⁰;
2. Acetol is an important intermediate product used to produce polyols and acrolein ⁸¹. It is being widely used as a reduced dye in the textile industry ⁸². Moreover, it is used as a skin tanning agent in the cosmetic industry and to give the unique aroma and flavor to foods ⁸³;
3. Furfural is a chemical used for the synthesis of fine chemicals manufacture ⁸⁴. It is also commonly used as sustainable intermediate for the preparation of a great variety of chemicals, pharmaceuticals and furan-based polymers ⁸⁵, and,

4. Cyclotene only appeared in WV_{Euc} and is reportedly used as anti-inflammatory agent ^{86,87}.

Likewise, techniques must be developed in the future for effective separation, isolation and purification of these valuable chemicals.

3.4 Carboxyl Groups

The main chemical compound in the carboxyl group is acetic acid. The percentage composition ranged from 8.1 to 20.74%. This is the major chemical compound in all WVs studied. This is perhaps the primary for the WVs low pH values and buffering capacity as demonstrated in **Table 1** and **Fig 1**.

Acetic acid has been widely used in chemical industries, with wide range of uses, such as the production of polymers derived from vinyl acetate production of purified terephthalic acid. This compound is used to produce polyethylene terephthalate (PET). Acetic acid may be precursor or as raw material for acetic anhydride and acetate esters production and are widely used as solvents ^{88,89}. These upgraded acids from acetic acid are commonly used in the food industry as acidity regulator ⁹⁰.

The primary industrial method for production of acetic acid is the carbonylation of methanol. The current method for commercial production of this chemical consumes fossil fuels ⁹¹. The production of these organic acid chemicals by pyrolysis of wood can be a promising approach to obtain renewable chemicals or precursors.

Likewise, there is an additional challenge to efficiently separate the organic acids from a mix of multiple diluted components. This necessary step will improve the purity of other valuable organic acids with similar properties with acetic acids ⁹². The chemical industry widely uses the distillation process to separate and purify [chemical compounds](#) based on the differences in boiling temperature of the components ^{93,94}. Other novel and cost-effective methods of separation must be studied. This should be the subject of future research.

3.5 Poly-aromatic Hydrocarbon (PAH) Group

Shown in **Table 3** are various concentrations of PAHs found in WVs. The total parent PAH concentrations ranged from 44.77 to 357.12 ng g⁻¹. One agronomic purpose of WV is to partially substitute fertilizers and pesticides. Contamination rates must be considered however as it may potentially cause cancer to humans once such chemical is spread throughout the surface of the soil. Some PAHs have lipophilic nature, that is, they are easily dissolved and transported by human cell membranes ⁹⁵.

According to one study ⁹⁶, the Danish PAH Soil Quality Criteria (SQC) limit in soil is 1000 ng g⁻¹. This

was set for the protection of the environmental and human health. This concentration is much higher than the concentrations found in WVs studied. While some PAHs compounds were found, those analyzed in WVs had no potential carcinogenic risk. The major seven carcinogenic compounds reported but were not found in this study are as follows: Benzo(a)anthracene, Chrysene, Benzo(b) fluoranthene, Benzo(k) fluoranthene, Benzo(a) pyrene, Indeno(1.2.3-cd) anthracene, Dibenz(a,h) anthracene⁹⁷. For example, naphthalene is a common compound found in most household mothballs. The other, acenaphthylene, is a compound found in coal tar and used as ligand in some organometallic processes.

Several factors, such as biomass and temperature, affect yields and distribution of PAHs formed. Thermal PAH formation can occur over a wide range of temperatures. At low temperatures, the compound distribution is governed by thermal stability and the most stable isomers are formed, while at high temperatures, PAHs of higher formation enthalpy can be generated⁹⁸.

b. Wood Vinegar Antibacterial Effects

Plating of soil onto treated plates showed that total cultured bacterial densities were significantly different among types and concentrations of WVs, **Table 4**.

The soil's bacteria were tolerant to WVs assessed at 0.8% for soils cultivated with crop, pasture and native forest. The same was not observed to the soil cultivated with Eucalyptus. This suggested a WV concentration for agronomic purposes of 0.8% or less.

Soil bacterial growth was mightily affected for WVs at the 100% rate, except for WV_{mix} in soils cultivated with crop and pasture. WVs have anti-microbial compounds that affect directly the bacterial growth as well as some organic acids and phenolic substances.

WV_{Euc} and WV_{Cam} had the highest toxicity index for soil bacteria. This behavior is due to the higher concentration of anti-microbial compounds in these two WVs. Hence, one must act with due diligence on the use of these compounds as crop soil enhancement for improved and better beneficial microbial growth. Of course, the opposite is also true, that is, WVs may be used to minimize harmful microbiota proliferation in some soils.

IV. CONCLUSION

This study has shown that the chemical composition of wood vinegars (WVs) varied with feedstock, pyrolysis temperature and exposure time. Numerous valuable chemicals were found in the liquid condensate after immediate cooling of the gaseous products produced.

This study has shown that some wood vinegars have high amounts of macronutrients P K, Mg (WV_{Euc} and

WV_{mix}) and Ca (WV_{mix}), that are partial substitute of chemical fertilizers. The high amounts of TOC in some WVs (WV_{Cam} and WV_{Euc}) showed potential as good material substrate for microbial growth that also act stimulant for plant growth.

The main constituents of the organic portion of WVs were found to include four major compounds groups in order of increasing amounts as follows: (a) phenols, (b) carboxyl groups, (c) carbonyl groups and (d) silicates. Some phenol compounds found were shown to have anti-microbial properties, as antioxidants and anti-inflammatory compounds and as food additives. The carbonyl groups showed importance in the chemical industries as pre-cursors to high value chemicals in the pharmaceutical industry. On the carboxyl group, the primary and most common organic acid compound found was acetic acid, another important chemical industry ingredient that may be used to replace fossil fuel based chemicals.

This study has further shown that WVs have potential uses as chemicals (on syntheses, adhesives and food flavoring), pharmacological (cancer treatment, antioxidant, anti-inflammatory agents) and agronomic purposes (as a partial substitute of chemical fertilizers and pesticides), with highlight to WV_{Nim} for both pharmacy and agronomic purposes.

WVs used for agronomic purposes must be diluted; based on bacterial densities in soil, we suggest dilution of 0.8% or less. This study also found that there are no significant hazardous and toxic compounds such as polyaromatic hydrocarbons (PAH) and hence, it is safe to use as chemical alternatives. More studies are warranted in the future to carefully separate, isolate and purify these valuable chemicals for their proper commercial use.

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Table 1. Wood vinegar pH, elemental analysis and inorganic/organic carbon components

Wood Vinegar	pH	Zn	Mn	Mg	Ca	K	Cu	P	TIC	TOC
----- (mg t ⁻¹) -----										
WV _{Cam}	2.68d	0.13d	5.63a	0.76c	4.87b	3.33b	-	0.49b	1,64ab	275,59a
WV _{Euc}	2.76c	1.60b	2.05b	7.12b	3.58c	69.84a	0.19	20.29a	2,29a	258,57b
WV _{Mix}	3.70a	1.13c	1.71c	7.84a	122.71a	69.84a	-	23.40a	0,95b	92,44d
WV _{Nim}	3.49b	2.23a	1.05d	0.45d	0.88d	3.48b	-	1.64b	1,02b	109,89c

Table 2. Chemical compounds of wood vinegars analyzed by CG-MS

Compounds	Relative Percentage (%)				Usefulness	References
	WV _{Cam}	WV _{Euc}	WV _{Nim}	WV _{Mix}		
5-methyl-2-Furancarboxaldehyde or 5-methylfurfural	3.84	0.89	0.24	-	Chemical for synthesis of fine chemicals ^{1,2} , potential candidate for therapy of sickle cell disease ³	¹ [53]; ² [54]; ³ [55].
1-hydroxy-2-propanone or acetol	0.43	1.78	-	-	Important intermediate used to produce polyols and acrolein ¹ ; widely used as a reduced dye in the textile industry ² and as a skin tanning agent in the cosmetic industry, to give aroma and flavor to foods ³	¹ [57]; ² [58]; ³ [56].
1-hydroxy-2-butanone		0.38	-	-		
2-Cyclopenten-1-one	0.44	0.54	-	-		
2-methyl-cyclopenten-1-one	0.32	0.31	-	-		
2-Furancarboxaldehyde or furfural	-	3.04	1.59	-	Chemical for synthesis of fine chemicals ¹ , sustainable intermediate for the preparation of a great variety of chemicals, pharmaceuticals and furan-based polymers ²	¹ [59], ² [60].
2-acetylfuran	0.5	0.4	-	-		
3-methyl-2-cyclopenten-1-one	0.39	0.6	0.29	-		
2,3-dimethyl-2-cyclopenten-1-one		0.76	0.56	-		
2-hydroxy-3-methyl-2-cyclopentene-1-one or Cyclotene		1.5	-	-	anti-inflammatory ^{1,2}	¹ [61]; ² [62].
3-Ethyl-2-hydroxy-2-cyclopenten-1-one		0.46	-	-		
Methyl 4-Hydroxy-3-methoxybenzoate	0.46	-	-	-		
Carbonyl	12.76	10.66	2.68	-		

Manly uses are in industrial chemical, for

Acetic acid	10.28	20.74	9.26	8.1	production of polymers derived from vinyl acetate production of purified terephthalic acid, which is used to produce polyethylene terephthalate (PET) raw material for acetic anhydride and acetate esters, which are, like acetic acid itself, widely used as solvents ^{1,2} . In the food industry is used as an acidity regulator ³
propionic acid	0.82	1.21	0.66	-	
ethenyl ester	0.72	-	-	-	
butanoic acid	0.36	0.43	-	-	
octanoic acid	0.28	-	-	-	
4-hydroxy-Butanoic acid	-	0.34	-	-	
Carboxyl	12.46	22.72	9.92	8.1	
3,4-Dimethoxytoluene	-	-	0.83	-	
2-methoxy-Phenol or Guaiacol	6.6	-	4.68	6.97	Antimicrobial ^{1,2} , reduce gastric erosions induced by classic anti-inflammatory drugs (ibuprofen) ³ , antidiarrheal agent ⁴ , antioxidant ⁵ .
4-methoxy-3-methyl-Phenol	0.93	-	0.78	-	
1,2-dimethoxy-4-ethylbenzene	-	-	0.48	-	
2,6-dimethyl-Phenol	0.52	-	0.25	-	
2-methoxy-5-methyl-Phenol	0.95	-	0.67	-	
2-methoxy-4-methyl-Phenol or creosol	11.70	4.76	6.64	7.00	Flavor Standards, Food and Cosmetic Component Standards ^{1,2} , antidiarrheal agent ³
2-methoxy-3-methyl-Phenol	-	0.42	-	-	
2,3,6-trimethyl-Phenol	0.55	-	0.35	-	
2-methyl-Phenol or o-cresol	2.42	5.52	1.87	2.36	
Phenol	1.75	1.64	0.98	2.67	
4-ethyl-2-methoxy-Phenol or	8.92	5.11	9.88	10.38	
4-ethyl-3-methyl-Phenol	0.77	-	-	-	
3-ethyl-2-methoxy-Phenol	-	0.5	-	-	
3-ethyl-5-methyl-Phenol	0.38	-	-	-	
2-ethyl-Phenol	0.30	-	0.61	-	

2,5-dimethyl-Phenol	0.91	-	1.12	1.15	
2,4-dimethyl-Phenol	0.49	-	1.93	1.43	
3-methyl-Phenol	-	1.32	1.92	-	
2-methoxy-4-propyl-Phenol	3.46	1.61	5.50	5.53	
2,6-dimethoxy-4-(2-propyl) Phenol	0,48	-	-	-	
2-ethyl-4-methyl-Phenol	-	-	0.31	-	
2-ethyl-5-methyl-Phenol	-	0.62	-	-	
2,3-dimethyl-Phenol	-	-	0.76	-	
Eugenol	-	0.82	1.86	1.79	Antioxidant ^{1,3} , antimicrobial ^{2,3} and anti-inflammatory ³
2(1-methylethyl)Phenol	-	-	0.90	-	¹ [72]; [73, 74]; ³ [75].
2-methoxy-4-(1-propyl-Phenol)	0.48	0.32	-	-	
2-methoxy-4-(2-propenyl) Phenol	1.16	-	-	-	
3,4-dimethyl-Phenol	0.77	0.43	2.06	1.15	
3,5-dimethyl-Phenol	-	-	-	2.10	
3,4,5-trimethyl-Phenol	0.81	-	-	-	
3-ethyl-Phenol	-	-	0.67	-	
4-ethyl-Phenol	1.44	0.39	-	-	
2,3,5-trimethyl-Phenol	-	-	1.52	-	
2-(4-methylpropyl)Phenol	-	-	0.42	-	
2,6-dimethoxy-Phenol or syringol	3.17	11.22	5.20	9.29	antioxidant ^{1,2} ¹ [4]; ² [34]
2,4,6-trimethyl-Phenol	-	-	0.54	-	
4-propyl-syringol	3.10	5.74	8.19	7.07	<i>a.</i>
4-methyl-syringol	4.48	-	-	6.24	<i>Component of wood adhesives¹</i> ¹ [76].
4-ethyl-syringol	-	-	-	11.48	
4-Allyl-2,6-dimethoxy-Phenol	-	1.22	1.60	-	
Kaempferol	-	8.26	4.64	-	Antioxidant and anti-inflammatory ^{1,6} ; Alzheimer ² ; Intervertebral disc degeneration ³ , Leishmanial chemotherapy ⁴ and uterine fibroids ⁵ treatment; Cancer therapeutic agent ^{1,7} ¹ [77, 78]; [79]; ³ [80]; [81]; [82]; [77]; ⁷ [83].
Phenol	58.26	50.22	66.30	79.46	
7,8-dimethylbenzocyclooctene	4.55	-	9.87	-	
Silicates	4.55	0.27	9.87	-	
3,4-dimethoxy-	0.82	-	0.83	1.16	

toluene					
1,2,3-trimethyl- benzene	-	-	0.42		
3,4,5-trimethoxy- toluene	-	-	1.88	3.42	
Benzenethanol or Phenylethyl alcohol	4.33	-	-	-	Chemical for synthesis ¹ , Anti- infective agent and desinfectant ²
1-ethyl-4-methoxy- benzene	-	-	0.51	-	
Others	5.62	-	3.64	4.58	

Table 3. Concentration of individual and total PAHs in the wood vinegars

Polyaromatic hydrocarbons	WV _{Cam}	WV _{Euc}	WV _{Nim}	WV _{Mix}
	(ng g ⁻¹)			
Naphthalene	18.73	1.663	-	11.34
2-Methylnaphthalene	5.25	-	-	-
1-methylnaphthalene	151.72	105.78	18.03	11.74
Acenaphthylene	134.00	45.35	22.75	8.91
Acenaphthene	31.49	47.41	-	7.20
Fluorene	10.50	0.83	-	0.80
Phenanthrene	4.81	13.06	3.99	2.81
Anthracene	0.58	6.97	-	4.10
Fluoranthene	-	-	-	-
Pyrene	-	-	-	-
Benzo(a)anthracene	-	-	-	-
Chrysene	-	-	-	-
Benzo(b)fluoranthene	-	-	-	-
Benzo(k)fluoranthene	-	-	-	-
Benzo(a)pyrene	-	-	-	-
Indeno(1.2.3-cd)anthracene	-	-	-	-
Dibenz(a,h)anthracene	-	-	-	-
Benzo(g,h,i)perylene	-	-	-	-
Total	357.12	221.08	44.77	46.90

Table 4. Bacterial densities in soils cultivated with crop, pasture, Eucalyptus and native forest under wood vinegar (WV) rates

WV (%)	Soils			
	Crop	Pasture	Eucalyptus	Native Forest
0	223.6 a	248.2 a	332.2 a	330.8 a
WV _{Mix} 0.8	183.4 a	264.6 a	235 b	301.6 a
WV _{Nim} 0.8	207.8 a	217 a	190 bc	268.2 a
WV _{Euc} 0.8	186 a	242.8 a	240.6 b	210.4 ab
WV _{Cam} 0.8	171.2 a	236.4 a	205.25 bc	272.6 ab
WV _{Mix} 100	211 a	210.8 a	141 c	151.2 b
WV _{Nim} 100	50 b	68.2 b	148 c	5.5 c
WV _{Euc} 100	12 b	16.8 b	5.6 d	6.8 c
WV _{Cam} 100	4.6 b	32.4 b	1 d	0 c

* Mean values of five plates per soil x wood vinegar assessed.

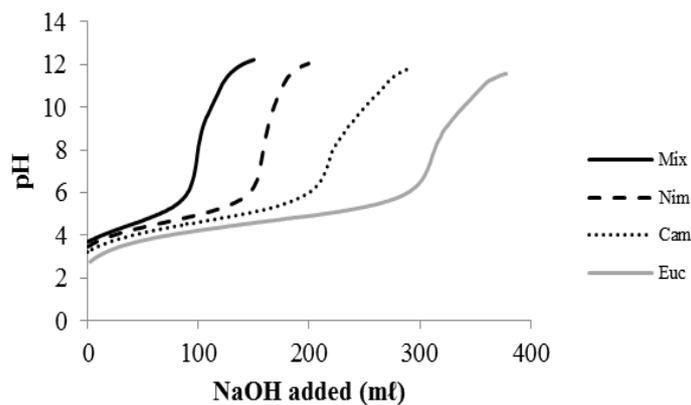


Fig.1: Titration curves for the wood vinegars made with Cambara (*Qualea sp.*), Eucaliptos (*Eucalyptus sp.*), Nim (*Azadirachta indica*) and Mix (*Azadirachta indica*) mixed with Nim leaves effusion.

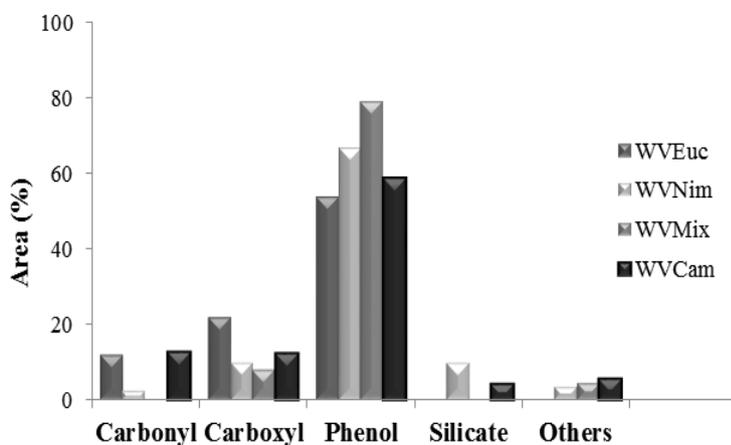


Fig.2: Wood vinegar characterization by chemical groups.