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Physicochemical Characteristics of Wood Vinegars from Carbonization of *Leucaena leucocephala*, *Azadirachta indica*, *Eucalyptus camaldulensis*, *Hevea brasiliensis* and *Dendrocalamus asper*

Yongyuth Theapparat[1,*], Ausa Chandumpai[1], Wichitra Leelasuphakul[1], Nikhom Laemsak[2] and Chanita Ponglimanont[3]

ABSTRACT

The physicochemical characteristics were evaluated of eight wood vinegars from the carbonization of five wood species—*Leucaena leucocephala* (Katin), *Azadirachta indica* (Sadao), *Eucalyptus camaldulensis*, *Hevea brasiliensis* (rubber wood) and *Dendrocalamus asper* (bamboo). The vinegars were produced by heating wood samples up to 400 °C in a Thai-Iwate kiln and were compared with two commercial products. The quality assessments of all wood vinegars were determined according to criteria from the Charcoal Handbook. The results showed that all wood vinegar samples appeared to be good quality in terms of odor, color and transparency. The pH (2.9–3.5) and total soluble tar (0.325–0.963 % by weight) also met the standard criteria for the pH (around 3) and total soluble tar (not more than 3%). The values of the specific gravity of only two products, from rubber wood (1.012 g.mL^{-1}) and bamboo (1.010 g.mL^{-1}) were within the acceptance criteria of 1.010–1.050 g.mL^{-1}. Chemical compositions of wood vinegars as determined qualitatively by gas chromatography/mass spectrometry and quantitatively by gas chromatography/flame ionized detector consisted of acetic acid as the largest component (30.45–70.60 mg.mL^{-1}). A high number of phenol derivatives (16 compounds) were found and those in higher concentrations were 4-propyl-2-methoxyphenol (5–11 mg.mL^{-1}) followed by 2-methylphenol (2–4 mg.mL^{-1}). An acetic acid concentration from the eight samples whose presence was indicated by *p*Ka at 4.7 was mainly responsible for the pH values as shown in the good correlations of plots between pH and acetic acid concentrations (Correlation coefficient, R = 0.92). The total acid contents of the ten wood vinegars as determined by titration with 0.1 N sodium hydroxide showed poor correlations with pH (R = 0.65) due to the presence of a variety of organic acids and phenolic compounds which may have affected proton transition. The specific gravity showed good correlations with total soluble tar and degree Brix (R = 0.87 for both); in turn the degree Brix showed good correlation with the total soluble tar (R = 0.87). Thus, the degree Brix which was easy to determine could be used as a general indicator of total soluble tar. The amount of total soluble tar signified the presence of phenolic compounds, of which previous studies suggested antifungal activity and usefulness as wood preservatives. Phenolic compounds were also confirmed by the ultraviolet absorption maximum (λ_{max}) at 268–274 nm.

Keywords: Wood vinegar, pyroligneous acid, slow pyrolysis, physicochemical properties, quality control

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INTRODUCTION

Carbonization is a slow pyrolysis technique and wood carbonization in an oxygen-free environment leads to gaseous and liquid by-products, such as fuel gas, wood tar and wood pyrolyzates (Wada, 1997; Mohan *et al*., 2006). The Thai-Iwate kiln is a highly efficient system for wood carbonization and charcoal production in Thailand (Asian Regional Cookstove Program, 2006). Wood pyrolyzates, also called wood vinegar, pyroligneous acid or *nam som kwan mai* (Thai), are strong, smoke-flavored liquors obtained as by-products from the charcoal manufacturing process of wood (Mun *et al*., 2007; Tiilikkala *et al*., 2010). Wood vinegars have been applied for various purposes such as in agriculture and veterinary practice (Uddin *et al*., 1995; Mu *et al*., 2004; Chalermsan and Peerapan, 2009; Tiilikkala *et al*., 2010; Prasertsit *et al*., 2011). Locally produced wood vinegar has been used as a pesticide in countries where the price of other chemicals has been too high for small scale farmers (Tiilikkala *et al*., 2010). Wood vinegar can be utilized as a wood preservative against fungal degradation, as a fungicide against some plant pathogens, as a repellent and insecticide, herbicide and plant growth enhancer and as feed-stuff for pigs which will improve nutrient digestibility and reduce harmful intestinal coliforms (Tiilikkala *et al*., 2010). In addition, wood vinegar is a natural pesticide as it is a "green" chemical which can replace more harmful synthetic pesticides (Yoshimoto, 1994). In Asia, wood vinegar products listed on a commercial home page (http://www.alibaba.com) mostly come from China. The wood vinegar-based pesticide market is very progressive in Japan, Korea and in numerous other Asian countries such as Thailand, Cambodia and China (Mun *et al*., 2007; Tiilikkala *et al*., 2010). The Japan Pyroligneous Liquor Association, an industrial body set up by pyroligneous liquor traders, has set the criteria for the quality control of wood vinegar consisting of pH, specific gravity,

color, odor, transparency and dissolved tar content (Wada, 1997). Although wood vinegar has been marketed globally, the physicochemical properties of products from the carbonization of wood species grown in tropical areas like Thailand have not been widely reported. This aspect is thought to be important for product quality and its further application.

The aim of this study was to investigate the chemical composition and determine the physicochemical characteristics of eight wood vinegars from five wood species along with two commercial products. Quality assessments were determined following the Charcoal Handbook (Wada, 1997). Other related parameters were studied as well.

MATERIALS AND METHODS

Wood vinegar preparation

Eight wood vinegars from five wood species consisting of *Leucaena leucocephala* (Katin), *Azadirachta indica* (Sadao), *Eucalyptus camaldulensis*, *Hevea brasiliensis* (rubber wood) and *Dendrocalamus asper* (bamboo) were obtained from a charcoal factory in Nakhon Rachasima province, Thailand. These wood vinegars and two commercial products were studied. In order to see whether there were any differences in the wood vinegar obtained from the same wood species, wood samples were collected at different times and underwent different carbonization processes, with two wood vinegar samples being acquired from the same wood species of *L. leucocephala*, *A. indica* and *E. camaldulensi*s. All wood vinegars were prepared under the same conditions. Each wood sample was slowly heated up to 400 °C in a Thai-Iwate kiln equipped with a flame tunnel whose chimney was closed during the process of carbonization. The kiln was also equipped with a temperature gauge with sensors to indicate the smoke temperature. The vapors produced were condensed using a water-cooled condenser at an outlet temperature of 80–150 °C to give yellow or

brown bio-oil samples. Each sample was stored at room temperature in a closed polyethylene container protected from light for at least 6 mth, which resulted in a wood vinegar that was a pale yellow or brown liquid on top of heavy tar. Then, each wood vinegar sample was decanted and used for further study along with two commercial wood vinegars obtained from Japan (Super Guard, Commercial 1) and Malaysia (Tanami, Commercial 2).

Physicochemical properties evaluation

The crude wood vinegars were centrifuged at 5,000 revolutions per minute for 20 min and then filtered through a 0.45 μm × 13 mm nylon syringe filter to separate clear char particles. The acidity was measured using a pH meter (Accumet®, Fisher Scientific; Waltham, MA, USA) calibrated in standard buffer solutions (pH 4.0, 7.0 and 10.0). The specific gravity was measured using a glass hydrometer at 20 ± 0.1 °C. In the spectrophotometric evaluation, each sample was diluted with Milli-Q water and then light absorption was scanned from 600 to 200 nm (A160 ultraviolet/visible spectrophotometer; Shimadzu Corp.; Kyoto, Japan), a blank was standardized with Milli-Q water. The total acid content (TAC) and ionization characteristics were evaluated using titration with 0.1 N NaOH whose content was calculated from the volume of the titrated NaOH at pH 8.15 at the termination point of acetic acid, a major organic acid in the wood vinegar (Mun *et al.*, 2007). The NaOH concentration was standardized with 0.1 N potassium hydrogen phthalate. The total soluble tar content was evaluated by transferring a portion (0.5 g) of crude wood vinegar to a calibrated vial and heating at 105 °C overnight to remove any volatile components. The obtained residues were used for calculation of the tar content. The degree Brix was measured using a hand refractometer (N-1E, Brix range: 0–32%; Atago; Tokyo, Japan;) without dilution (Mun *et al.*, 2007).

Water content determination

A Karl Fischer titrator (Mettler DL18, Greifensee, Switzerland) was used to determine the amount of water in the wood vinegar samples. The titrator was calibrated with dry methanol. Then, 200 μL of wood vinegar was dropped in a container and titrated with the Karl Fischer reagent until reaching the end point. The results were the mean water content ± the relative standard deviation (measured as the percent milligrams of water per milliliter of sample) of three different measurements of each sample.

Qualitative and quantitative analysis of the chemical components

Qualitative analysis

A gas chromatograph (model 5890; Hewlett-Packard; Palo Alto, CA, USA) equipped with a mass spectrometer selective detector 5972 (GC/MS) was employed. The conditions for gas chromatography (GC) analysis were as follows: HP-INNOWAX capillary column (60 m × 0.5 mm internal diameter, 0.25 μm film thickness), carrier gas, helium at 2.0 mL.min^{-1} flow rate, splitless injection mode at 230 °C. The oven temperature profile was established as: initial 62 °C hold time of 6 min, 62–115 °C at 10 °C per min, 115–215 °C at 3 °C per min, with the final hold time of 15 min resulting in a total run time of 55.46 min. The volume of sample injected was approximately 1 μL. Chemstation software (Rev.A06.03[509]; Agilent Technology, Palo Alto, CA, USA) was used to control the operation of the GC system as well as for data acquisition and the analysis of the chromatograms. Mass spectra were recorded at an ionization energy of 70 eV. Components were identified by comparing their mass spectra with those in the commercial mass spectral library database (Version 275; Wiley, NY, USA).The results were accepted when the constituents with a match percentage > 90% were identified. For some components having a very low response, co-elution by standards was used to confirm these components (Guillén and Ibargoitia, 1998).

Quantitative analysis

The gas chromatograph equipped with a flame ionized detector (GC-FID) was employed for chemical analysis of the wood vinegars. The conditions for GC analysis were the same as for GC/MS mentioned above. The volume of sample injected was 2 µL. Palmitic acid methyl ester (Sigma-Aldrich; St. Louis, MS, USA) was used as an internal standard. The Chemstation software was used to control the operation of the GC system as well as for data acquisition and the analysis of the chromatograms. Components were identified by comparing the relative retention times (the ratio of component retention time versus that of the internal standard) of their peaks with those of the authentic compounds. Quantification of the components was based on the peak area ratio between the component and the internal standard compared with the standard curve plotted between the peak area ratio versus the concentration ratio between the component and the internal standard.

The 24 components identified by GC/MS and those commercially available were acquired in the highest available purity from Sigma-Aldrich (St. Louis, MS, USA), Supelco; (St. Louis, MS, USA) and J.T.Baker (Center Valley, PA, USA) and used as reference standards.

RESULTS AND DISCUSSION

The collection temperature of the smoke produced in the carbonization process is an important factor in determining the quality of wood vinegar (Mu *et al*., 2004). The vapor produced from the carbonization of the five wood species was condensed using a water-cooled condenser at an outlet temperature of 80–150 °C as recommended in the Charcoal Handbook (Wada, 1997) as smoke with a temperature of not more than 80 °C has a high water content and does not produce much wood vinegar. Conversely, when the smoke temperature exceeds 150 °C, the decomposition of the charcoal wood becomes very active, producing more sticky tar and the smoke may also contain substances which are harmful to humans. Fresh wood vinegar has as many as 200 constituents, which are prone to such complex reactions as oxidization and polymerization so the vinegar needs to be refined (Diebold, 2000). The simplest and most highly efficient method is to keep the wood vinegar standing in an acid-resistant closed container. When left standing, the unstable constituents in the raw wood vinegar are oxidized or polymerized to precipitate, suspend or adhere to the inner wall of the container. The thin oily film on the surface of the liquid must be discarded and the suspended and also precipitated matter are filtered to produce transparent wood vinegar; some 6–12 mth of standing is required to obtain such stable wood vinegar (Wada, 1997; Fagernäs *et al*., 2012). The wood vinegars in the current study were obtained after standing for 6 mth resulting in a clear solution. The colors of the solutions varied slightly, with pale yellow for *E. camaldulensis*, *L. leucocephala*, *A.indica* and the two commercial samples and bright brown for *H. brasiliensis* (rubber wood) and *D. asper*, all of which had a smoke-like odor.

The components of the wood vinegars were qualitatively identified initially by GC/MS. The identified components were all commercially available so they were acquired and further used as authentic compounds in quantitative determination by GC/FID using an internal standard to control the accuracy and precision of analysis.

Table 1 shows the 24 components of the wood vinegars which can be categorized into acids, alcohols, furfural and furan derivatives, and phenol and methoxyphenol derivatives. Many studies have reported on the characterization of wood vinegars obtained from both slow and fast pyrolysis with highly variable results depending on the wood species and experimental temperature (Maggi and Delmon, 1993; Mun *et al*., 2007; Loo *et al*., 2008; Mohan *et al*., 2008).

Table 1   Composition of wood vinegars from five wood species and two commercial samples.

Compound	Concentration (mg.mL⁻¹)									
	L. luecocephala 1	L. leucocephala 2	A. indica 1	A. indica 2	E. canmadulensis 1	E. camaldulensis 2	D. asper	H. brasiliensis	Commercial 1	Commercial 2
Organic acidic										
acetic acid	40.26±1.02	55.98±1.22	37.38±0.04	35.26±0.15	65.29±0.02	32.49±0.08	69.34±0.17	70.60±0.20	39.48±0.16	30.45±0.45
Alcohol derivatives										
methanol	3.92±0.04	8.12±0.27	3.85±0.66	3.80±0.07	3.62±0.03	6.13±0.14	4.43±0.09	4.52±0.05	3.9±0.04	0.69±0.04
n-propanol	ND	ND	ND	ND	ND	0.02±0.00	ND	ND	ND	ND
n-butanol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
∑ Alcohol derivatives	3.92	8.12	3.85	3.80	3.62	6.15	4.43	4.52	3.90	0.69
Furfural and furan derivatives										
2- furfuraldehyde	0.45±0.00	3.06±0.01	0.60±0.02	4.06±0.02	2.24±0.01	5.23±0.01	2.69±0.03	0.67±0.01	6.51±0.05	0.09±0.00
methyl-2-furoate	0.18±0.01	0.74±0.01	0.08±0.00	0.37±0.01	0.41±0.01	0.87±0.01	0.62±0.02	0.13±0.01	0.49±0.03	0.02±0.00
2- methylfuran	0.23±0.01	0.54±0.01	0.27±0.00	0.31±0.01	0.39±0.01	0.34±0.00	0.79±0.02	0.55±0.03	0.39±0.02	0.16±0.00
∑ Furfural and furan derivatives	0.86	4.34	0.95	4.74	3.04	6.44	4.10	1.35	7.39	0.27
Phenol derivative										
phenol	0.94±0.01	0.95±0.01	0.75±0.01	0.54±0.02	0.45±0.01	1.01±0.01	0.67±0.01	0.46±0.02	0.80±0.01	0.91±0.00
2 -methylphenol	3.82±0.02	2.85±0.01	2.76±0.01	1.57±0.01	2.07±0.01	3.17±0.01	2.16±0.11	4.06±0.06	2.26±0.02	3.43 ± 0.00
3-methylphenol	1.67±0.01	0.78±0.68	0.68±0.00	0.69±0.01	0.61±0.00	1.28±0.05	0.05±0.00	0.32±0.0	ND	ND
4-methylphenol	0.11±0.00	0.19±0.01	0.07±0.00	0.13±0.01	0.04±0.00	0.16±0.00	0.09±0.00	0.04±0.00	0.11±0.00	0.01±0.00
2-ethylphenol	0.03±0.00	0.03±0.00	ND	0.02±0.00	ND	0.03±0.00	0.06±0.00	0.03±0.00	0.04±0.00	ND
2,6-dimethylphenol	ND	0.03±0.00	ND	ND	ND	0.05±0.00	0.42±0.00	ND	0.02±0.00	0.03±0.00
2,5-dimethylphenol	0.29±0.01	0.10±0.00	0.17±0.01	0.07±0.00	0.13±0.01	0.24±0.00	0.20±0.00	0.12±0.00	0.46±0.02	0.06±0.00
2,4-dimethylphenol	ND	0.26±0.22	ND	0.21±0.01	ND	ND	ND	ND	0.41±0.02	0.08±0.00
2,3-dimethylphenol	0.06±0.00	0.04±0.00	ND	0.03±0.00	ND	0.04±0.00	0.05±0.00	ND	0.02±0.00	ND
∑ Phenol derivatives	6.92	5.23	4.43	3.26	3.30	5.98	3.70	5.03	4.12	4.52
Methoxyphenol derivatives										
4-propyl-2-methoxyphenol	6.90±0.05	8.92±0.03	5.88±0.03	6.43±0.03	5.54±0.02	5.54±0.02	11.56±0.04	9.56±0.01	7.29±0.20	8.12±0.00
4-methyl-2-methoxyphenol	1.51±0.01	3.09±0.01	0.24±0.00	1.51±0.02	0.89±0.01	1.27±0.01	2.59±0.06	2.23±0.01	1.12±0.04	1.18±0.00
4-ethyl-2-methoxyphenol	1.46±0.02	3.10±0.02	0.20±0.01	1.85±0.01	0.91±0.01	1.34±0.02	2.81±0.02	2.33±0.01	1.40±0.02	0.82±0.00
guaiacol	0.40±0.00	0.42±0.00	0.66±0.01	1.17±0.01	0.51±0.01	0.36±0.01	1.33±0.04	4.28±0.02	0.38±0.01	0.24±0.00
eugenol	0.27±0.01	0.21±0.02	ND	2.41±0.02	0.06±0.00	0.21±0.01	5.23±0.02	2.16±0.02	1.99±0.01	1.38±0.00
syringol	1.20±0.02	2.01±0.01	0.93±0.01	3.15±0.02	2.62±0.02	3.88 ±0.01	3.57±0.02	0.06±0.00	2.01±0.01	0.79±0.00
acetovanillone	ND	ND	ND	ND	ND	ND	0.18±0.00	ND	ND	ND
∑ Methoxyphenol derivatives	11.74	17.75	7.91	16.22	10.53	12.60	27.27	20.62	14.19	12.53
∑ Total phenol derivatives	18.66	22.98	12.34	19.48	13.83	18.58	30.97	25.65	18.31	17.05
1,2 dihydroxybenzene	ND	ND	ND	ND	0.18±0.00	ND	0.18±0.01	ND	ND	0.08±0.00

ND = Detected concentrations lower than limit of quantitative detection.

The acetic acid is believed to have originated from the acetyl groups in the hemicellulose (Kartal *et al*., 2004) and was the largest content of the wood vinegar samples obtained in the current study, with the concentration depending on the wood species and production batch. Among these, *H. brasiliensis* (70.60 mg.mL^{-1}) and *D. asper* (69.34 mg.mL^{-1}) possessed much higher concentrations of acetic acid than the others (30.45–65.29 mg.mL^{-1}). Methanol was found in all samples (0.69–8.12 mg.mL^{-1}). The amount of acetic acid may have been lessened due to esterification of the acetic acid with methanol after the long-term aging of wood vinegar (Mun and Ku, 2010). Lignocellulosic materials such as wood are mainly composed of cellulose, hemicellulose and lignin (Kartal *et al*., 2004). In the current study, many phenol derivatives (16 compounds) were found and those in higher concentrations were 4-propyl-2-methoxyphenol (5.54–11.56 mg.mL^{-1}) followed by 2-methylphenol (1.57–4.06 mg.mL^{-1}). Phenolics basically result from the thermal degradation of lignin (Mohan *et al*., 2006). Lignin is a high molecular mass, randomly cross-linked polymer, consisting of an irregular array of differently bonded hydroxy and methoxy-substituted phenylpropane units and during pyrolysis, competing thermal degradation reactions take place that generate different bond cleavages according to their bond energies providing a high number of products due to the high structural diversity of lignin (Guillén and Ibargoitia, 1998). Only three furfural and furan derivatives were detected—2-furfuraldehyde, methyl 2-furoate and 2-methyfuran.

The quality of wood vinegars varies depending on the type of charcoal kiln, type of charcoal wood and carbonization temperature (Wada, 1997. Even if the liquor is transparent and does not stain the container, it is not necessary of high quality. The criteria for judging the quality of the wood vinegar have been suggested by Wada (1997) as: pH around 3; specific gravity around 1.010–1.050 g.mL^{-1}; color (visually) pale yellow, bright brown or reddish brown; odor smoky odor; transparency visually transparent with no suspended matter; and the dissolved tar content not more than 3%.

From the current study, all wood vinegar samples appeared to be of good quality in terms of color, odor and transparency. Good wood vinegar must not have a strong and pungent odor which is a characteristic of a synthetic product containing a substance such as glacial acetic acid to adjust the pH (Wada, 1997). Table 2 shows the physicochemical properties. The pH varied slightly (2.9–3.5); nevertheless, the values met the Japanese standard of around 3 (Wada, 1997). Further experimentation determined values for *p*Ka (the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions), from which the eight samples produced the same reading of *p*Ka (4.70) while those from the two commercial products were 4.85 and 4.89, respectively. The regression analysis revealed that the pH values of the wood vinegars were in good correlation with acetic acid concentrations, (correlation coefficient, R = 0.92) as shown in Figure 1. Furthermore the *p*Ka of acetic acid is 4.70; hence, there is strong evidence to conclude that acetic acid has a major influence on the acidity level of carbonizing wood vinegars. Therefore, to improve the specificity and accuracy of the determination of acidity in wood vinegar, both the pH and *p*Ka should be simultaneously determined. The TAC of the ten wood vinegars by titration with 0.1 N sodium hydroxide used the same method as Mun *et al*. (2007). The results (Table 2) varied in the range 2.72–4.92 % by weight and showed a poor correlation with pH (R = 0.65, plot not shown), which were in agreement with a previous report by Mun *et al*. (2007). In general, wood vinegars contain a variety of organic acids and phenolics which may affect proton transition, particularly that of phenolics which can deprotonate to form phenoxide ions in the presence of strong alkalis (Mun *et al*., 2007). Most phenolics in wood vinegars have approximate *p*Ka values of

Table 2 Physicochemical properties of eight wood vinegars from carbonization of five wood species and two commercial products.

Sample	pH	SG $(g.mL^{-1})$	TAC[b] (% by weight)	pKa	Total soluble tar (% by weight)	Degree Brix	λ_{max} (nm)	A_{max}	Water content (% by weight)
L. leucocephala 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
L. leucocephala 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
A. indica 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
A. indica 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
E. camaldulensis 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
E. camaldulensis 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
H. brasiliensis	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
D. asper	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
Commercial 1	3.40	1.004±0.000	2.72±0.03	4.85	0.38±0.01	3.00±0.10	272.00	195.50±5.00	80.49 ± 0.20
Commercial 2	3.50	1.007±0.000	2.89±0.02	4.89	0.60±0.02	4.00±0.10	268.00	176.00±6.00	79.18 ± 0.95

SG = Specific gravity; TAC = Total acid content ;pKa = Equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions

Amax = Relative absorbance measured at λmax for wood vinegar at original concentration,

Water content values show water content as percentage of weight ± SD of three injections.

10, but the *p*Ka values of guaiacol and syringol skeletons with either an aldehyde or ketone group in the para position ranged from 7 to 8 (Oasmaa *et al*., 2010). The low correlation between the pH and organic acid content may imply that phenolics with values of *p*Ka in the range 7–10 can exert an influence on the organic acid content (Mun *et al*., 2007).

The specific gravity values of the ten wood vinegars were in the range 1.004–1.012 g.mL⁻¹. Only two samples from *H. brasiliensis* (1.012 g.mL⁻¹) and *D.asper* (1.010 g.mL⁻¹) met the Japanese standard of 1.010–1.050 g.mL⁻¹ (Wada, 1997) If the value exceeds this range, it signifies the presence of dissolved tar and inorganic matters which are detrimental to plant growth, requiring refining of the liquor (Wada, 1997). The Japanese standard sets a dissolved tar content of not more than 3% (Wada, 1997). All the wood vinegars studied produced total soluble tar values in the range 0.37–0.96% which were acceptable. The

total soluble tar levels of *D. asper* (0.71%) and *H. brasiliensis* (0.96%) were higher than the others (0.37–0.60%). The plot between the specific gravity and total soluble tar (Figure 2) of the ten samples shows a good correlation (R = 0.87). The results from Table 1 show that *D. asper* and *H. brasiliensis* possessed higher concentrations of total phenol than the others (30.97 and 25.65, respectively versus 12.34–22.98 mg.mL⁻¹ for the others) thus generally indicating that the high total soluble tar was associated with the high phenol content. The current method to determine total soluble tar is unconventional in practice because it is time consuming and requires some scientific equipment. The degree Brix was explored as it is commonly estimated because of the simplicity of its measurement. Data in Table 2 show the values of the degree Brix of the ten samples were in the range 3.00–6.00. The degree Brix values of *D.asper* (5.60) and *H. brasiliensis* (6.00) were higher than the others (3.00–4.60). The plot of
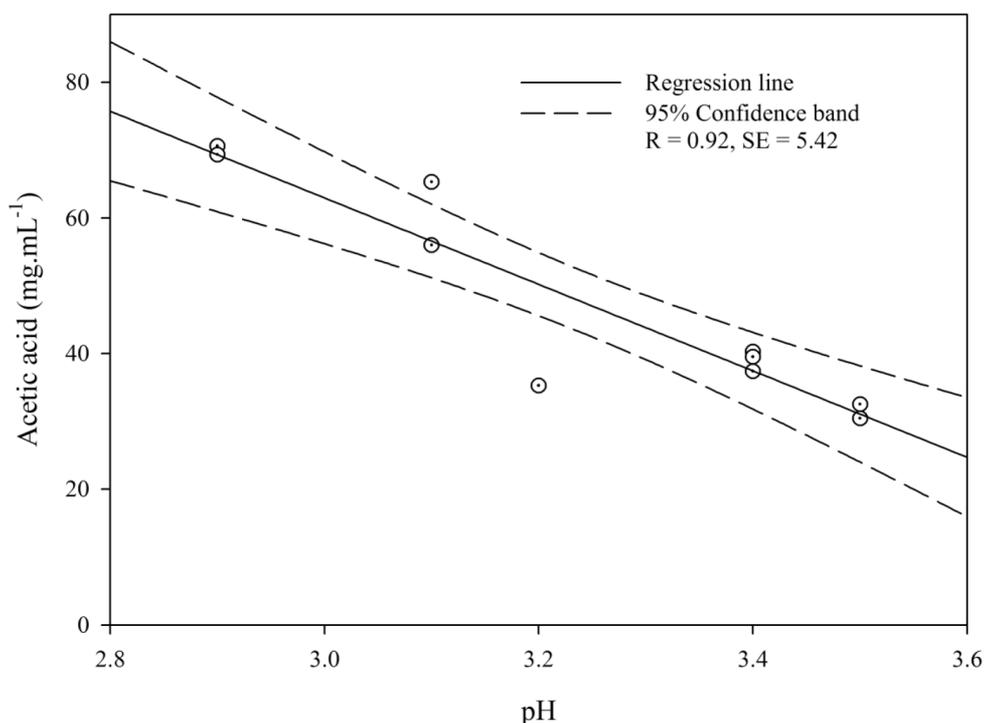
Figure 1 Correlation between pH and acetic acid concentration of ten wood vinegars (R = Correlation coefficient).

specific gravity and degree Brix (Figure 3) as well as the plot of degree Brix and total soluble tar content (Figure 4) show good correlations (R = 0.87 for both). The results suggested that the degree Brix might be useful as general indicator of the tar content which was in agreement with a report by Mun *et al.* (2007) who studied bamboo, oak wood and pine wood pyrolyzates.

From the current study and previous reports, phenolic monomers from the lignin cracking reaction under pyrolysis are a major group of compounds constituted within wood vinegars (Mohan *et al.*, 2006; Loo *et al.*, 2008). The ultraviolet absorption of all the wood vinegar samples was studied and absorption was found in the range 200 to 350 nm with similar characteristic spectra. The studied wood vinegars showed maximum absorption peaks (λ_{max}) at 268–274 nm (Table 2). The absorbance values of *H. brasiliensis* (467) and *D. asper* (470) were much higher than the rest (154–393) corresponding to the high total

phenol concentrations (Table 1) of *H. brasiliensis* (25.65 mg.mL[1]) and *D. asper* (30.97 mg.mL^{-1}). The results were in agreement with the study of Baimark and Niamsa (2009) who reported maximum absorption wavelengths of wood vinegars from the carbonization of coconut shell, bamboo and eucalypt wood in the range 268–273 nm and that of Mu *et al.* (2004) who found that Moso bamboo (*Phyllostachys pubescens*) vinegars collected over different temperature ranges from 100 to 400 °C showed a maximum absorption peak at 268–273 nm due to phenolic substances.

Previous work by Theapparat (2014) to determine the antifungal activity and efficacy as wood preservatives of wood vinegars was performed by Petri dish bioassay and a soil block test, respectively, against two white rot fungi (*Trametes versicolor* and *Rigidoporopsis amylospora*), a brown rot fungus (*Gloeophyllum trabeum*) and a sapstaining fungus (*Botryodiplodia theobromae*). The results showed that all wood
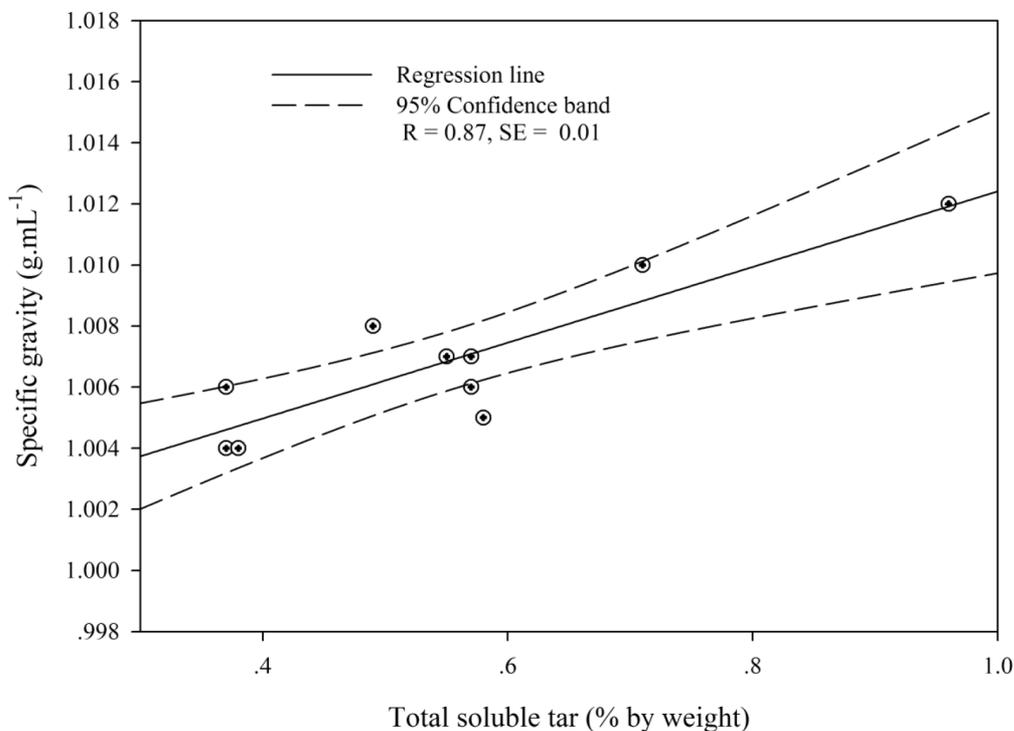
Figure 2 Correlation between average of total soluble tar and specific gravity of ten wood vinegars (R = Correlation coefficient).
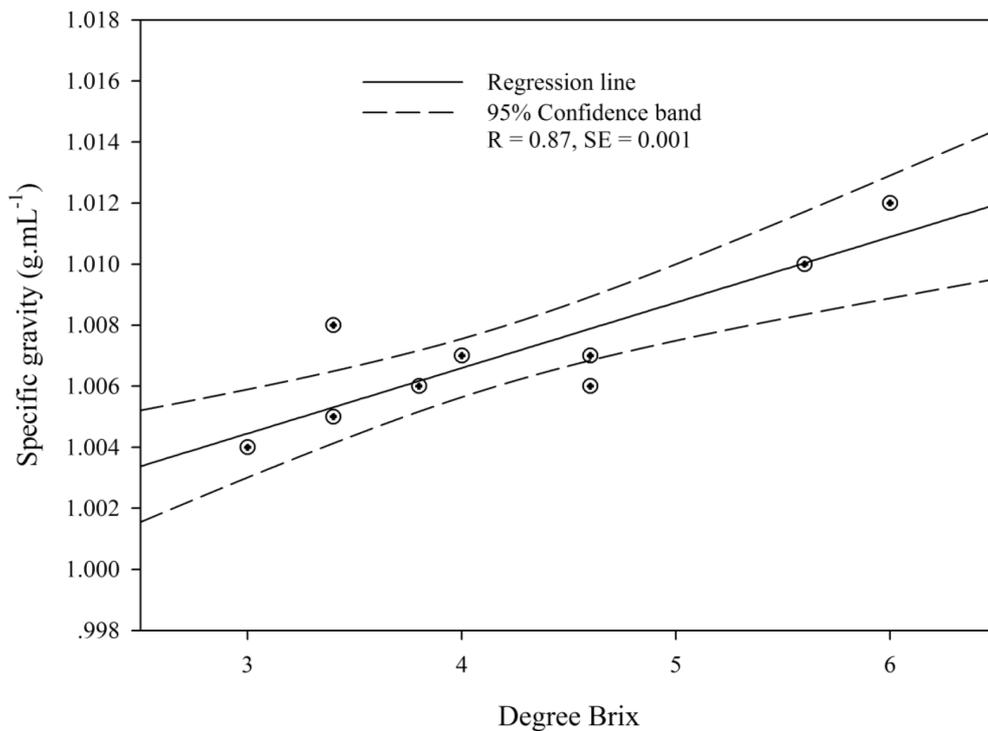
Figure 3 Correlation between average degree Brix and specific gravity of ten wood vinegars (R = Correlation coefficient).
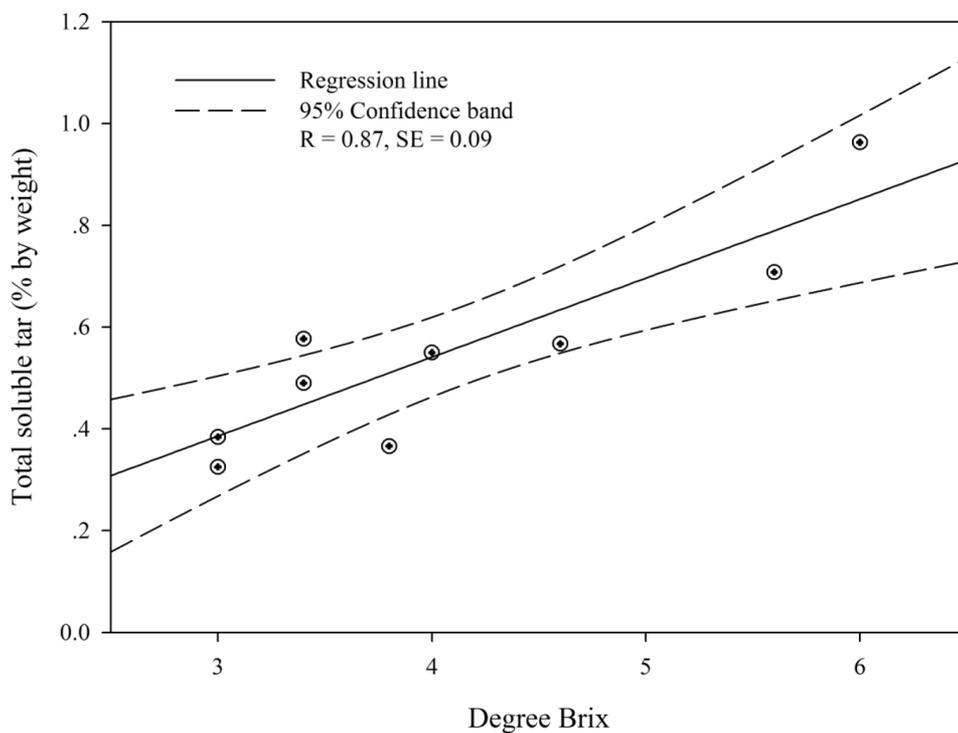
Figure 4 Correlation between degree Brix and total soluble tar content of ten wood vinegars (R = Correlation coefficient).

vinegars exhibited antifungal activity (based on the percentage growth inhibition, minimum inhibition concentration and minimum fungicidal concentration. Those from bamboo and rubber wood (whose total phenolic concentrations were higher) exhibited better antifungal activity than the others. The soil block test on rubber wood for 12 wk showed that wood vinegars from bamboo and rubber wood were more effective as wood preservatives against all fungi tested (Theapparat, 2014). Many research studies have also suggested that phenolics from lignin degradation were responsible for good antifungal activity (Kartal *et al.*, 2004; Nakai *et al.*, 2007; Mohan *et al.*, 2008; Baimark and Niamsa, 2009; Prasertsit *et al.*, 2011).

The water content (on a percent weight basis) of eight wood vinegar samples varied in the range 81%–93% while those of two commercial products possessed less water content (80.49 and 79.18%, respectively). The water content may depend on wood size, wood species and the moisture content of raw materials, as well as the collection temperature of the smoke produced in the carbonization process which should be between 80 and 150 °C. Immediately after lighting the fire, smoke with a temperature of not more than 80 °C has a high water content and does not produce much wood vinegar (Wada, 1997). In addition any moisture in the wood will extend the carbonization process thus increasing the cost of production.

Wood vinegars obtained from different batches even though coming from the same wood species possessed different chemical compositions and varied physicochemical properties. The differences may have been due to the wood size, the wood part (the branch, stem and trunk contain different compositions of cellulose, hemicellulose and lignin according to Mohan *et al.* (2006) and Bortolomeazzi *et al.* (2007), the moisture content of the wood and the collection temperature. The criteria for good wood vinegar may differ by application.

CONCLUSION

The study of eight wood vinegars, (by-products from the wood carbonization of five wood species) along with two commercial products revealed acetic acid as a major component followed by phenolic compounds. Quality assessment of the wood vinegars following the criteria of the Japanese standard from the Charcoal Handbook suggested that pH, color, odor, transparency, specific gravity and total soluble tar were important factors. The samples met all the standards except for specific gravity, with only two samples from *H. brasiliensis* (rubber wood) and *D. asper* (bamboo) just meeting the minimum standard for this parameter. The *p*Ka values of the eight wood vinegars were 4.7 while those from the two commercial products were 4.85 and 4.89, which were all similar to acetic acid (4.7). Good correlations of the plots between specific gravity and total soluble tar, between degree Brix and specific gravity and the plot between degree Brix and total soluble tar content suggested that specific gravity and degree Brix could be used as general indicators of the soluble tar content. Wood vinegars with high soluble tar contents (indicating high phenolic compounds) such as from rubber wood and bamboo, exhibited better antifungal activity than the other wood vinegar samples and were more effective as wood preservatives. The presence of phenolic compounds was also indicated by the ultraviolet absorption maximum (λ_{max}) at 268–274 nm.

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