Characterization of neutralized wood vinegar derived from durian wood (Durio zibethinus) and its prospect as pesticide in acidic soil

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Abstract. Wood vinegar is a brown liquid by-product obtained from the carbonization process. Wood vinegar could limit the usage of wood vinegar as pesticide in acidic soil because of its acidity. This study aimed to determine the main organic and inorganic components in neutralized durian wood vinegar. Wood vinegar was made by pyrolysis of durian wood in the absence of oxygen with a temperature of 350, 450, and 550 °C for 2 hours. Before being analyzed, wood vinegar was neutralized with NaOH 25% to formulate the new friendly pesticide in an agricultural field. Characterization for acidity was by pH meter; organic compounds were using GC-MS; inorganic compounds were using AAS. The result showed that both neutralized wood vinegar and acidic wood vinegar indicated groups of organic acids, phenol and carbonyl compounds, which were suspected as pesticides. The predominant component in acidic wood vinegar was guaiacol, while in neutralized wood vinegar was pyrocatechol. Both acidic and neutralized wood vinegar indicatively contained main inorganic elements such as sodium, calcium, potassium, magnesium, iron and zinc that could serve as a natural pesticide. Based on the analysis result of inorganic elements, there were significant differences between acidic and neutralized wood vinegar except for Ca.

1. Introduction

Durio zibethinus, or durian, is obtained in Southeast Asian countries such as Indonesia, Thailand, and Malaysia. According to The Indonesian Central Bureau of Statistics (BPS), the total production of durian fruit in Indonesia in 2016 was estimated to be about 995,735 ton while the rate of local forest harvested wood was estimated about 7 million m³ per year, included in 1,568,415 ha of forest coverage area. The vast amounts of wood waste are available from the logging activities (such as log end, stump, branches) and the processing of wood to produce furniture and other products (such as sawdust, chip, bark) [1]. Durian wood is classified as softwood, lightweight and is not durable durian woods which cut down from local forests have been utilized for various objectives, for example,
furniture, housing, finger joint, packaging or pulp and paper [2]. Durian wood waste contains lignocellulosic materials that could be converted to high-value products, namely wood vinegar (WV), by pyrolysis.

Wood vinegar is a liquid by-product obtained from condensing the smoke produced during the carbonization process [3,4]. In the agricultural field, wood vinegar commonly is used as environmental friendly pesticides [5,6]. Wood vinegar has been widely used to control pest only based on common traditions and knowledge both of users and local producers [7]. There is an only limited number of scientific publications that review wood vinegar as a pesticide [8]. However, recently farmers and agricultural researchers have been investigating the use of wood vinegar in improving crop yields and controlling pests as alternatives to substitute chemicals.

Crude wood vinegar contains more than 200 chemical compounds, such as acetic acid, methanol, formaldehyde, tar, etc. [9]. Each compound has specific physicochemical and ecotoxicological properties. Wood vinegar could affect the behaviour of pesticides due to the enhancement of microbial activity [6]. Because of acidic chemicals during wood destructive of hemicellulose and cellulose in the temperature range of 200-350 °C, the pH values of raw wood vinegar become acidic [4]. It could limit the utilization of wood vinegar in agriculture, especially in acidic soil, because the addition of wood vinegar to the soil could decrease soil pH [10].

The study aimed to analyze the main organic and inorganic components in neutralized wood vinegar at various pyrolysis temperature. Based on previous study, the optimum wood vinegar from pistachio shell was achieved at the temperatures between 500 and 600 °C [11]. Meanwhile, the maximum yield of wood vinegar from grape bagasse was 27.60% obtained at the final pyrolysis temperature of 550 °C [12]. On the other hand, maximum production of wood vinegar from Durio bark was obtained at a temperature of 421 °C [13]. Therefore in this study, we set three kinds of pyrolysis temperature: 350 °C, 450 °C and 550 °C.

2. Materials and methods

2.1. Location
The pyrolysis experiment was carried out on bioenergy laboratory at Tribhuvana Tunggadewi University, Malang, Indonesia from February to May 2017. Durian woods were taken from the wood waste of sawmill industry in South Kalimantan.

2.2. Experimental procedures
The first step was durian wood milling to reduce the wood chips into small particles. The durian wood were sifted by size with vibrator sieve shakers. Only particles passed through 18-mesh screens and retained on a 40-mesh screen (0.42 mm–1 mm) were selected for the sample. 500 g sample was put in a piece of stainless pyrolysis reactor which consisted of 500 mm in length and 15 cm in inside diameter. The sample was then heated externally by an electric furnace (5000 W) [14] to pyrolysis temperature of 350 °C, 450 °C and 550 °C for 2 hours. The system was set in air-closed condition and wood vinegars were collected from the cooled vapours in a condenser and left for sixty days for precipitation. Dark brown colour wood vinegar was neutralized by using NaOH 25%. Determination of pH of wood vinegar was performed by pH meter (827, Metrohm). Organic compounds were analyzed using Gas Chromatography and Mass Spectrometer (AOC-20i, Shimadzu), inorganic elements (Na, Ca, K, Mg, Fe, Zn, Mn) were measured by Atomic Absorption Spectrometer (800, Perkin Elmer).

2.3. Statistical Analysis
All experiments reported in this paper have been performed in triple. Analyzing the data was calculated by using one-way analysis of variance (one way-ANOVA). A post hoc test with Duncan’s comparison procedure was run if F achieved the necessary level of statistical significance (i.e. P < 0.05).
3. Results and discussion

3.1. Yield, pH of wood vinegar (VW)

Based on ANOVA (Table 1), there was a difference in the yield of wood vinegar at the various pyrolysis temperature (Pr<0.05). Also, Duncan’s multiple range test was applied to measure the specific difference between the yield on the pyrolysis temperature. The results of yield and pH of wood vinegar, varied with a temperature pyrolysis 350 °C, 450 °C and 550 °C, were shown in Table 2.

| Table 1. ANOVA of Yield |
|-------------------------|
| Source | Degree of freedom | Sum of squares | Mean square | F Value | Pr > F |
| Model | 2 | 123.010 | 61.505 | 282.98 | <.0001 |
| Error | 6 | 1.304 | 0.217 |
| Corrected Total | 8 | 24.314 |

| Table 2. Yield percent and acidity of wood vinegar |
|-------------------------|
| Pyrolysis temperature | Acidic WV (AWV) | Neutralized WV (NWV) |
| % Yield (w/w) | pH | pH |
|-------------------|-----------------|-----------------|
| 350 °C            | 9.81±0.30       | 3.394±0.196     | 6.938±0.107   |
| 450 °C           | 16.57±0.48      | 3.615±0.124     | 6.926±0.111   |
| 550 °C            | 18.41±0.58      | 3.621±0.090     | 7.003±0.050   |

Note: Values (mean ±SD) are average of three replicates. Different subscript letters within the same column indicate significant (p < 0.05) differences within pyrolysis temperature.

Wood vinegar yield was increased with increasing temperature. The reason for the higher liquid yield at a higher temperature may be due to the possibility that there was a secondary decomposition reaction at higher temperature [13,15]. Meanwhile, the temperature rise at the lower temperature was not enough for completing pyrolysis to take place, thus yielding a lower liquid smoke product. It was because not all of the celluloses convert into solution pirologin and gas CH₄, CO and H₂ [16].

The result showed that durian wood gives the highest yield percent of acidic wood vinegar at 550 °C pyrolysis temperature. This study was in line with the findings that stated maximum wood vinegar yield was obtained at the temperature between 500 and 600 °C [11]. The temperature was very important affected to product yields and chemical compositions [4, 15]. The amount of wood vinegar highly increased in the range of 350-450 °C and slightly increased in the range of 450-550 °C. Lignin at a temperature of 500 °C was decomposed completely. It formed a layer of aromatic and tar which will be mixed with wood vinegar resulting higher yield at a temperature of 550 °C than a temperature of 350 °C and 450 °C [16]. There were many of the smoke components being formed in secondary or tertiary reactions [17].

The pH values of crude wood vinegar were acidic with decreasing of pyrolysis temperature, as shown in Table 2. The acidity of the wood vinegar was affected by temperature because its acidic chemicals during wood destructive of hemicellulose and cellulose were formed in the 200-350 °C temperature range [4]. Decomposition of cellulose compound occurred into acetic acid and its homologues, which caused the lower pH at a lower temperature. Besides, acetic acid production was well done at temperatures higher than 280 °C [16]. 450-AWV and 550-AWV were less acidic than 350-AWV because wood decomposition at high temperature tends to form phenolic and its derivatives instead of carboxylic acid [4]. pH results in this work were in agreement with [4] and [18], in the range.
of 3.394 to 3.621. Little difference in pH was observed in the 450-WV and 550-WV. The dark brown colour of crude wood vinegar with an average pH of 3.543 was then neutralized using NaOH 25% (pH 7 ± 0.5).

3.2. Organic compound in acidic and neutralized wood vinegar
The temperature profile of durian wood that was heated at the various pyrolysis temperature was illustrated in Figure 1. The highest durian wood mass reduction was obtained at 294-386 °C. It showed that lignocellulosic degradation of durian wood occurred at the range of 300-400 °C. Based on the literature study and the temperature profile, this study used pyrolysis temperature at 350, 450, and 550 °C.

![Figure 1. Temperature profile of durian wood pyrolysis](image)

The organic compounds of both acidic and neutralized wood vinegar were carried out by GC-MS spectrum from AOC-20i Shimadzu by helium carrier gas with the flow rate 7 mL/min, injection temperature 250 °C and auto-injector used. The spectrophotometer was used a slightly polar column for separation. Based on Table 3, phenolic compounds of acidic wood vinegar at 350 °C, 450 °C and 550 °C pyrolysis temperatures were identified using Mass spectrum. 1,2,4-trimethoxybenzene was identified at all pyrolysis temperatures, while 1-(2,6-dihydroxy-4-methoxyphenyl) ethanone was detected at 350 °C pyrolysis temperature. The most chemicals compounds of 350-AWV, 450-AWV and 550-AWV, have found to be the same because of the simultaneous and consecutive pyrolysis reactions based on wood chemical compositions. Hence wood destruction of hemicellulose, cellulose and lignin occurred at the same time when wood started to carbonized. The wood destruction at high temperature tends to favour the phenolic compound and its derivatives [4]. The number of phenolic compounds was increasing with increasing temperature because of lignin destructive at a temperature of 280-500 °C. The results showed that phenolic compounds in 550-AWV were higher than 350-AWV and 450-AWV because of the chemical reaction at high temperature. The higher pyrolysis temperature, the higher the concentration of phenolic compounds.

Phenolic compounds such as phenol, guaiacol and cresol which were considered to act as biocidal agents might be responsible for antifungal properties of wood vinegar [13,19]. The results on the antifungal effect of wood vinegar derived from wood on the agriculture field were demonstrated by [20] and [21]. Wood vinegar provided some protection against fungal growth [20]. In agreement with the previous study, the major phenolic compound in this study was detected as guaiacol (2-methoxy phenol) [16] because this study used softwood as a source wood. Guaiacol had a strong antimicrobial effect against plant pathogenic microorganisms to evaluate agricultural supplement as antimicrobial chemicals [21].
Table 3. GC-MS analysis of acidic wood vinegar

| No | Compounds                                      | Relative Percentage (%) |
|----|-----------------------------------------------|-------------------------|
|    |                                               | Acidic Wood Vinegar (AWV) |
|    |                                               | 350-AWV    | 450-AWV    | 550-AWV    |
| 1  | 4-methyl-phenol (p-cresol)                     | 9.19        | 11.84      | 17.61      |
| 2  | 2-methoxy-phenol (guaiacol)                    | 37.07       | 38.31      | 40.0       |
| 3  | 2,5,dimethyl phenol (2,5 xyleneol)             | 3.08        | 4.28       | 4.04       |
| 4  | 3-ethyl-phenol                                 | -           | -          | 3.22       |
| 5  | 4-methoxy-3-methyl-phenol                     | -           | 1.48       | 1.17       |
| 6  | 2-methoxy-4-methylphenol                      | 25.25       | 23.28      | 18.62      |
| 7  | 4-ethyl-2-methoxy-phenol                      | 16.02       | 14.02      | 9.86       |
| 8  | 2,6-dimethoxy-phenol                          | 4.07        | 3.35       | 3.34       |
| 9  | 1,2,4-trimethoxybenzene                       | 3.43        | 2.85       | 2.09       |
| 10 | 1-(2,6-dihydroxy-4-methoxyphenyl) ethanone     | 1.89        | -          | -          |

On the contrary, syringol (2, 6-dimethoxy phenol) was the major phenolic component in softwood *Pinus densiflora* and hardwood *Quercus serrata* [5]. Guaiacol, cresol and 2,6-dimethoxy phenol were major polyphenolic compounds present in wood vinegar. These compounds had greater antifungal activity [22]. There only was found 3.34-4.07% syringol in this study at various pyrolysis temperature. When softwood (durian wood) used as a source, syringol was barely found in wood vinegar [23]. To sum up, the temperature of thermal lignin degradation [17] and the type of wood showed an important role in the formation of guaiacol and syringol.

Based on various pyrolysis temperature, as mentioned earlier, there were 8-9 major compounds identified in acidic wood vinegar which almost all of the compounds were phenolic elements. Meanwhile, there were 13-15 major compounds in neutralized wood vinegar, including various chemical compounds like keton, furan and pyran derivatives, aldehyde, ester, sugar derivative, phenol and derivatives. The phenol derivatives were contained at least one aromatic ring with one or more attached –OH groups. When the aromatic ring was activated with an –OH group in the ortho or para positions, its reactivity would increase [24]. The chemical compounds of neutralized wood vinegar were shown in Table 4 and Figure 2. In the neutralized wood vinegar, alkyl groups in the para position of phenolic compounds accepting the electron, which leads the decreasing in phenolic compounds ionization due to addition of NaOH into wood vinegar [5].

As seen in Figure 2, GC-MS analysis showed the presence of many phenolic compounds in neutralized wood vinegar. The number and arrangement of hydroxyl and methoxyl group determined the antioxidant ability of phenolic compound [25]. The antioxidant activity improved as the number of hydroxyl and methoxyl groups of phenolic acids increased. Neutralized wood vinegar in 2.5 and 3.0% concentration could inhibit the fungal growth in agar plates [5].

The primary compound in neutralized wood vinegar, pyrocatechol, was used in agricultural purpose to control plant diseases caused by phytopathogenic bacteria belonging to the genera Xanthomonas, Ralstonia and Acidovorax [26]. Some other compounds contained in neutralized wood vinegar might also be responsible for inhibiting fungal growth, but they were weakly to inactivate the fungal growth [5].
Table 4. GC-MS analysis of neutralized wood vinegar

| No | Compounds                                         | Relative Percentage (%) | Neutralized Wood Vinegar (NWV) | 350-NWV | 450-NWV | 550-NWV |
|----|--------------------------------------------------|-------------------------|--------------------------------|---------|---------|---------|
| 1  | pentanal                                         | 7.63                    | 10.06                          | 7.18    |         |         |
| 2  | 1,2-benzene diol (pyrocatechol)                  | 27.51                   | 31.50                          | 27.53   |         |         |
| 3  | 2-Methyl-2-propenoic acid ethyl ester            | 3.58                    | 4.49                           | 3.67    |         |         |
| 4  | 5-Hydroxymethyl-2-furancarboxaldehyde            | 3.26                    | 3.42                           | 2.94    |         |         |
| 5  | 3-methoxy-pyrocatechol                           | -                       | -                              | 1.20    |         |         |
| 6  | 3-methyl-1,2-benzenediol                         | 6.30                    | 2.11                           | 1.96    |         |         |
| 7  | 5-methyl-1,2-benzenediol                         | 3.07                    | -                              | 2.84    |         |         |
| 8  | 1,4-dione-2,5-cyclohexadiene                     | -                       | 10.11                          | -       |         |         |
| 9  | 4-ethyl-1,3-benzenediol                          | -                       | 5.08                           | -       |         |         |
| 10 | 2,6 dimethoxy phenol                             | 2.07                    | -                              | 2.07    |         |         |
| 11 | 4-ethyl-1,3-benzenediol                          | 4.96                    | -                              | 4.61    |         |         |
| 12 | 1,2,4-trimethoxybenzene                          | -                       | -                              | 1.70    |         |         |
| 13 | 2,5-dibutyl-furan                                | 6.47                    | 7.50                           | 6.43    |         |         |
| 14 | Alpha,beta,D-Ribopyranose                        | 23.4                    | 10.35                          | 20.85   |         |         |
| 15 | 4-Hydroxy-3-methoxybenzene-ave-tic acid          | 2.58                    | -                              | 2.41    |         |         |
| 16 | 1-(4-Hydroxy-3,5-dimethoxyphenyl) ethanone       | 2.53                    | -                              | 2.29    |         |         |
| 17 | 1-(2,4,6-trihydroxy-3-methylphenyl) butan-1-one  | 6.65                    | 8.51                           | 6.26    |         |         |

Figure 2. Chemical composition of neutralized wood vinegar

3.3. Inorganic elements in acidic and neutralized wood vinegar

The main inorganic components in wood vinegar consisted of K, Na, Ca, Mg, Fe, Zn, Mn, Ni, Co, and Al [27]. The inorganic compounds of acidic and neutralized wood vinegar were shown in Table 5. Based on ANOVA, the acidity of wood vinegar was a significant difference in the inorganic components contained in acidic and neutralized wood vinegar, except for Ca. Based on macro and micro elemental analysis in liquid fertilizer derived from wood vinegar [3], it showed many inorganic elements such as sodium (Na), P, K, calcium (Ca), magnesium (Mg), manganese (Mn), zinc (Zn).
Table 5. Inorganic compounds of wood vinegar

|       | Inorganic compounds (ppm) | [27] (ppm) |
|-------|---------------------------|------------|
|       | 350 °C | 450 °C | 550 °C |         |
| Na-AWV| 14.03 ± 0.76 | 14.33 ± 0.48 | 14.72 ± 0.32 | 146.15  |
| Na-NWV| 99.43 ± 0.70 | 85.86 ± 0.91 | 98.61 ± 0.79 |         |
| Ca-AWV| 14.03 ± 0.76 | 14.33 ± 0.48 | 14.72 ± 0.32 | 375.88  |
| Ca-NWV| 99.43 ± 0.70 | 85.86 ± 0.91 | 98.61 ± 0.79 |         |
| K-AWV | 11.79 ± 0.32 | 7.06 ± 0.59  | 3.63 ± 0.76  | 13.23   |
| K-NWV | 39.10 ± 0.91 | 11.65 ± 0.91 | 24.86 ± 0.73 |         |
| Mg-AWV| 10.42 ± 0.56 | 10.81 ± 0.67 | 5.92 ± 0.81  | 133.43  |
| Mg-NWV| 9.11 ± 0.20 | 11.95 ± 0.39 | 10.26 ± 0.65 |         |
| Fe-AWV| 282.02 ± 1.01 | 233.02 ± 0.17 | 255.14 ± 2.09 | 578.62  |
| Fe-NWV| 252.13 ± 1.16 | 314.67 ± 1.06 | 241.98 ± 1.05 |         |
| Zn-AWV| 42.71 ± 0.74 | 36.52 ±1.04  | 39.08 ± 0.95  | 16.71   |
| Zn-NWV| 38.81 ± 0.85 | 333.79 ± 0.87 | 38.07 ± 1.01 |         |

4. Conclusions
Wood vinegar yield was increased with increasing temperature (9.81-18.41% w/w). pH acidic wood vinegar was 3.543 on average, while neutralized wood vinegar was 6.956 on average. The predominant component in acidic wood vinegar was guaiacol which had a strong antimicrobial effect against plant pathogenic microorganisms, while in neutralized wood vinegar was pyrocatechol which used in agricultural purpose to control plant diseases. Both acidic and neutralized wood vinegar indicatively contained main inorganic elements such as sodium (Na), calcium (Ca), potassium (K), magnesium (Mg), iron (Fe) and zinc (Zn) that could serve as the natural pesticide. These neutralized wood vinegars have a prospect to be utilized in acidic soil because they have similar chemical characteristics.

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