Chemical characterization of wood vinegar from acacia barks

A H Prianto¹,², Budiawan¹, Y Yulizar¹ and P Simanjuntak³,⁴

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok16424; Indonesia
²Research Center for Biomaterial-LIPI, Cibinong, Bogor 16911, Indonesia
³Research Center for Biotechnology-LIPI, Cibinong, Bogor 16911, Indonesia
⁴Faculty of Pharmacy, Universitas Pancasila, Jagakarsa, Jakarta, Indonesia

E-mail: arie009@lipi.go.id

Abstract. The pyrolysis process was conducted into a low heating rate of 400 °C using a pyrolysis reactor. It was made of stainless steel, covered by fire clay bricks, and used electrical heating. Acacia barks were pyrolyzed for six hours. The chemical characteristics of wood vinegar produced from *Acacia mangium* bark were done by means of titration method, UV-VIS spectrophotometer, gas chromatography-mass spectrometry (GC-MS) analysis. The organic acid and phenol were analyzed to determine the quality of wood vinegar. The chemical components of wood vinegar were identified by GC-MS. The carbonation process produced charcoal, wood vinegar, gas, and tar, i.e., 66.33; 21.45; 12.16, and 0.06%, respectively. Wood vinegar has a brown color, a specific gravity of 1.0064, and a viscosity of 12-49 1 mPa·s at 60 rpm of the spindle. The major components of wood vinegar were acetic acid (47.36%) and phenolic compounds (18.96%), while tar was dominated by pentanoic acid (90.29%).

1. Introduction

Indonesia is the largest exporter of charcoal in Southeast Asia. Charcoal production potential is still open on a larger scale because there is still a lot of untapped biomass waste from the agriculture and forestry industry. Production of charcoal uses a pyrolytic process that produces condensable and non-condensable gas as a byproduct. Currently, smoke products from the pyrolysis process have not been widely used and are wasted in the air. According to Nurhayati et al. [1], the charcoal industries in Indonesia have not utilized the smoke fraction from the carbonation process, only using charcoal as the main product. The utilization of wood in the charcoal process is not efficient because it removes 80% of the smoke potential. The use of wood vinegar will also benefit the environment because it reduces air pollution. Utilization of gas products from the pyrolysis process into wood vinegar is a challenge to add value [2].

The carbonation process is the decomposition of wood components, namely cellulose, hemicellulose, and lignin. Decomposition produces charcoal, gas, which can be condensed into wood vinegar, and non-condensable gas. Wood vinegar has a diverse chemical component, with organic acids and phenols as the main components. The use of wood vinegar is extensive. It can be used as a coagulant, fertilizer, antimicrobial, antifeedant, repellent, anti-termite, fertilizer [3,4] The composition of wood vinegar depends on the raw material [4].

*Acacia mangium* Willd. is one of the fast-growing species that is widely planted by industrial plantation companies. Industrial plantations only use wood as raw material for pulp, while the bark is...
discarded. Acacia bark are one of the wood fiber industry wastes that has not been utilized by the industry [5]. The potential abundant as a source of lignocelluloses so that it can be used as a source of wood vinegar. The barks contain additives and secondary metabolism up to 20% and show family or genus characteristics [6]. Based on literature surveys, there is little information about the chemical characteristics of wood vinegar produced from the bark of *acacia*. Therefore, this study utilized acacia barks to produce wood vinegar by steel pyrolysis reactor and characterize its chemical properties.

2. Material and methods

2.1. Design of pyrolysis reactor
Figure 1 shows the steel pyrolysis reactor with the condenser. A steel sheet with a thickness of 1.0 mm covered the kiln body. The size of the pyrolysis reactor was 0.58 m in diameter and 0.92 m in height. Fire clay brick with maximum service temperature 1050 °C was used as an insulator. The burning reactor used an electric heater that is spread around fire clay brick. To control the temperature in the reactor, we used and connected a thermocouple to a temperature control panel. In the combustion chamber, there is smoke ventilation to the condenser unit. The condenser processed smoke to wood vinegar.

![Figure 1. Steel pyrolysis reactor. a) Temperature controller, b) Sample bracket, c) Thermocouple, d) Electric heater, e) Condensable-gas collector, f) Non-condensable-gas, g) water, h) Condensor, i) Fire clay brick.](image)

2.2. Wood vinegar production
In this research, acacia bark was used as raw material to produce wood vinegar. The carbonations process was carried out using a metal kiln. The bark was weighed and then put into a sample bracket (11,304 cm³). It was then placed in a pyrolysis reactor and closed tightly. The resulting wood vinegar was accommodated in the storage tube.

2.3. Characterization of wood vinegar
The phenolic content of wood vinegar was analyzed by the Folin-Ciocalteu method [7]. One mL of wood vinegar was diluted with distilled water to 500 mL. One mL solution was put into the test tube
and added 5 mL of 15% sodium carbonate. The sample was allowed to stand at room temperature for 10 min. About 0.5 mL Folin-Ciocalteau reagent was then added. The solution was shaken with vortex shaker and incubated at room temperature for 30 min. The absorbance of the solution was measured by UV-VIS spectrophotometer (Shimadzu 1800) against the blank solution at a wavelength of 750 nm. The phenolic concentration of the sample solution was calculated based on a standard curve obtained from pure phenol solution.

Acid content was analyzed by titration method [8]. One mL of wood vinegar was weighed carefully and then was added 100 mL of distilled water. Three drops of phenoptaline (pp) indicator was then added and homogenized. The solution was then titrated with 0.1 N NaOH. This process was carried out until the color changed from clear yellow to yellowish-brown color. The titrated acid total is expressed as percent acetic acid.

\[
\text{Total acid (\%)} = \left( \frac{V \times N \times M}{W \times 1000} \right) \times 10
\]

where:

- \( V \) : volume (mL)
- \( N \) : normality of NaOH (N)
- \( M \) : molecular weight of acetic acid (g/mol)
- \( W \) : the weight of the sample (g)

2.4. GC-MS analysis

GC-MS analysis was performed using the Shimadzu GC-MS-QP 2010 Ultra Instrument with a stationary phase Rtx-1MS (100% dimethyl polysiloxane) column length of 30 m and diameter of 0.25 mm. The carrier gas used ultra-high purity helium with a pressure of 50.4 kPa, a flow rate of 0.85 mL/min, an injection volume of 1µl, a split of 1: 200. Injection was carried out at 280°C, ion source 200°C, and interface 300°C. The column was programmed from 75°C for 5 minutes, then raised to 130°C for 3 minutes at a rate of increase of 8 °C /min. The final column temperature was 290°C with a rate of increase of 10°C /min for three minutes.

3. Results and discussion

Acacia barks were inserted into the sample bracket until they are full and solid, so there was very little air in the pyrolysis reactor (Figure 1). Electric heaters did not come into direct contact with the sample. Heating occurred through the transfer of heat from an electric heater to the reactor tube and then arrived at the sample bracket. The reactor tube was tightly closed so that the formed gas could only pass through the condenser. Heating took place until the condensed-gas (CG) and non-condensed gas (NCG) were no longer formed (6 hours). The formed charcoal was left inside the sample bracket. The pyrolysis reactor temperature was set at a maximum temperature of 400°C. According to Souza et al. [9] wood vinegar obtained at temperatures up to 400°C is reddish-brown. In contrast, those obtained above 400°C are darker because the decomposition of lignocellulosic material at higher temperatures tends to increase tar formation.

| Temp Max. (°C) | Wood Vinegar (%) | Charcoal (%) | Tar (%) | NCG (%) |
|---------------|-----------------|--------------|---------|---------|
| 400           | 21.45           | 66.33        | 0.06    | 12.16   |

Table 1 shows the gravimetric yields of acacia barks carbonation. The maximum temperature of pyrolysis was conducted at 400°C. Wood vinegar begins to form at a temperature of pyrolysis below 120 °C. This is following the results of Nurhayati et al. [1] study, which obtained acacia wood vinegar...
at a temperature of 100-130°C. At this temperature range, the wood begins to lose water before decomposition of the wood components. Pyrolysis at the temperature (120-280°C), the condensable gas rises rapidly to produce large amounts of wood vinegar. According to Loo [10], water vaporization occurred in the sample of pyrolyzed material at a temperature of 100-280°C. At temperatures between 280 and 400°C, CG and NCG both were produced in large quantities. This phenomenon was indicated by the formation of wood vinegar and gas in a more rich color. At the end of the carbonation process (400-500°C), lignin and cellulose were decomposed to form a solid mass called charcoal.

Table 2 presents the property of wood vinegar. Phenol determination was conducted using a UV Vis spectrophotometer at \( \lambda_{\text{max}} \) 750 nm. The phenol content of wood vinegar of acacia barks was 2.27%. It is following the results of Oramahi et al. [11], where the phenolic content of wood vinegar of Acacia and Laban wood mixture ranged between 2.17-6.30. Phenol and its derivatives are essential components in wood vinegar. Phenolic compounds in wood vinegar can be in the form of guaiacol, phenol, cresols, and catechol [2]. Wood vinegar had a viscosity value of 12 at 60 rpm from the spindle, at different speeds, wood vinegar showed changes in viscosity. This character shows that wood vinegar is classified as the non-Newtonian liquid. The specific gravity of wood vinegar in acacia barks is 1.0064, and this value is smaller than in acacia wood (1.0080) [1]. Lower temperatures tend to produce wood vinegar, which is more acidic; it supports the formation of carboxylic acids rather than phenolics and their derivatives. The degree of heating does not have a significant effect on pH and specific gravity [9].

| No. | Property of wood vinegar |
|-----|--------------------------|
| 1   | pH                       | 2.86                           |
| 2   | Color                    | Brown                          |
| 3   | Specific gravity         | 1.0064                         |
| 4   | Viscosity                | 12 cp at 60 rpm                |
| 5   | Odor                     | Pleasant-smoky aroma           |
| 6   | Titratable acidity       | 0.0108 g NaOH/g sample         |
| 7   | Phenol content           | 2.27%                          |

Table 3 displays the components of wood vinegar of acacia barks with GC-MS. The results of the GC-MS analysis showed that there were 20 components of wood vinegar. Wood vinegar contains more than 200 species of organic compounds, but some bamboo extract compounds break down thermally before reaching retention time [12]. The largest component was acetic acid (47.36%), phenol (3.27%), and its derivatives (28.85%). The content of acetic acid and other organic acids predominantly affects the pH value of wood vinegar. The content of wood vinegar components was influenced by the constituents of acacia barks. Darmadji [13] stated that cellulose is decomposed into acetic acid, hemicellulose produced acetic acid, furan, and furfural, while lignin generated phenol and its derivatives. The high content of acetic acid and phenol showed that acacia bark contained high cellulose, hemicellulose, and lignin. Acacia barks contained cellulose (46.09-48.25%), hemicellulose (11.27-20.63%), lignin (22.68-31.18%), and extractive (15.03%) [14]. High holocelluloses and lignin content make the produced wood vinegar will have high acetic acid and phenol content.

The activity of the wood vinegar constituent has been widely studied. Yatagai et al. [4] report that the acid contained in wood vinegar is the main contribution to the termiticide activity and this activity is largely influenced by acetic acid due to its high content in wood vinegar. The second-largest component in wood vinegar was phenolic compounds, including phenol (3.27%), p-cresol (2.53%), cresol (2.09%), catechol (5.23%), 2,6-dimethoxyphenol (5.52%), 2-methoxyphenol (guaiacol 6.14%), 1,2-benzenediol, 3-methoxy- (1.22%), phenol, 4-ethyl-2-methoxy- (1.35%), 1,2-benzenediol, 4-methyl- (1.46%), 1,2,3-trimethoxybenzene (1.99%), and benzene, 1,2,3-trimethoxy-5-methyl- (1.32%). According to Prianto et al. [15], phenol was a component that could synergize with
azadirachtin (Azadirachta indica), as an antifeedant against S. litura. Yang et al. [16] also reported that syringol (29.54\%) and guaiacol (12.36\%) were the main components of wood vinegar from Litchi chinensis wood. The high content of guaiacol, phenol, p-cresol, cresol, and furfural showed antibacterial/antifungal activity. Furfural, cresol, and 3-methyl-1,2-cyclopentanedione also can be used as a flavoring agent [17]. Allyl mercaptan is the main compound with a distinctive odor in garlic. [18]. Allyl Mercaptan is the most powerful organosulfur compound that inhibits histone deacetylase (HDAC) [19]. Nurhayati et al. [1] stated that the content of methanol and furfural could act as an acceleration of plant growth. In contrast, phenols and cresols function could act as inhibitors of plant growth. Various characteristics caused by certain chemical compounds in wood vinegar can have beneficial effects on plant growth.

**Table 3. Identification of chemical compounds in the wood vinegar from acacia barks using GC-MS.**

| No. | Peak | Ret. Time (min) | Compound | Similarity (%) | Molecular formula | Concentration (%) |
|-----|------|-----------------|----------|----------------|------------------|-------------------|
| 1   | 1.605| Acetone         | 97       | C₂H₆O           | 2.26             |
| 2   | 1.732| Acetic acid     | 98       | C₂H₆O₂          | 47.36            |
| 3   | 1.890| Allylmercaptan  | 90       | C₃H₆S           | 2.04             |
| 4   | 1.964| Propanoic acid  | 97       | C₃H₆O₂          | 4.30             |
| 5   | 2.879| Furfural        | 92       | C₃H₄O₂          | 5.05             |
| 6   | 5.077| 2-Furancarboxaldehyde, 5-methyl- | 90 | C₃H₆O₂ | 1.42 |
| 7   | 5.757| Phenol          | 97       | C₄H₈O           | 3.27             |
| 8   | 6.705| 1,2-Cyclopentanedione, 3-methyl- | 96 | C₅H₉O₂ | 1.32 |
| 9   | 8.195| p-Cresol        | 98       | C₃H₆O           | 2.53             |
| 10  | 8.433| Phenol, 2-methoxy- | 98 | C₃H₈O₂ | 6.14 |
| 11  | 8.808| 3-Pyridinecarboxylic acid, 4-hydroxy- | 88 | C₆H₆NO₃ | 2.79 |
| 12  | 10.898| Creosol         | 96       | C₅H₁₀O₂         | 2.09             |
| 13  | 11.038| Catechol        | 98       | C₅H₈O₂         | 5.23             |
| 14  | 11.167| Pyridine, 2-pentyl- | 93 | C₆H₁₄N | 1.34 |
| 15  | 12.224| 1,2-Benzenediol, 3-methoxy- | 95 | C₆H₁₀O₃ | 1.22 |
| 16  | 12.777| Phenol, 4-ethyl-2-methoxy- | 93 | C₆H₁₂O₂ | 1.35 |
| 17  | 12.990| 1,2-Benzenediol, 4-methyl- | 96 | C₆H₁₀O₃ | 1.46 |
| 18  | 14.287| Phenol, 2,6-dimethoxy- | 97 | C₆H₁₀O₃ | 5.52 |
| 19  | 16.918| 1,2,3-Trimethoxybenzene | 85 | C₅H₁₂O₃ | 1.99 |
| 20  | 18.566| Benzene, 1,2,3-trimethoxy-5-methyl- | 85 | C₅H₁₄O₃ | 1.32 |

In the carbonation process, the constituent components of lignocellulose materials are decomposed to produce different parts of wood vinegar. Table 4 shows the comparison of chemical components of wood vinegar of acacia barks and acacia wood. Based on the main components compared, wood vinegar of acacia barks had higher phenol component content (32.12\%), and acetic acid (47.36\%), while wood vinegar of acacia wood had 5.40\% and 19.76\%, respectively. Phenol and acetic acid are a major component of wood vinegar and exhibit the quality of wood vinegar. Phenol and organic acids are an important compound in wood vinegar, because of their toxic, repellent, and antifeedant activity against insect pests [4,20]. Wood vinegar from acacia wood had higher furfural (7.03\%), and cresol (7.99\%) contents than wood vinegar from acacia bark, which are 5.05\% and 2.09\%, respectively. Both types of wood vinegar also contained components that were not owned by others. In acacia barks,
there were propanoic acid (4.30%), and acetone (1.42%), while methanol (4.93%) was only found in the acacia wood.

Tar is a part of wood vinegar separated by settling from wood vinegar. The content of chemical compounds in tar had been carried out by GC-MS analysis, where the main compound contained in tar acacia barks was pentanoic acid (90.29%) at a retention time of 1.755 min. The content of pentanoic acid was not found in wood vinegar from acacia wood [1]. Therefore, this component was one of the differentiators from the component of acacia wood decomposition.

Table 4. The chemical component of the acacia wood vinegar.

| No. | Compound            | Acacia barks (%) | Acacia wood [%] |
|-----|---------------------|------------------|-----------------|
| 1   | Phenol derivatives  | 32.12            | 5.40            |
| 2   | Acetic acid         | 47.36            | 19.76           |
| 3   | Furfural            | 5.05             | 7.03            |
| 4   | Propanoic acid      | 4.30             | -               |
| 5   | Creosol             | 2.09             | 7.99            |
| 6   | Acetone             | 1.42             | -               |
| 7   | Methanol            | -                | 4.93            |

4. Conclusion

The carbonation process of acacia barks has been successfully carried out with a steel pyrolysis reactor. The carbonation process produced charcoal, wood vinegar, non-condensed gas, and tar, i.e., 66.33; 21.45; 12.70 and 0.06%, respectively. The identification of wood vinegar using GC-MS obtained 20 chemical compounds and while tar obtained two chemical compounds. The major components of wood vinegar were acetic acid (47.36%) and phenolic compounds (32.12%), while tar was dominated by pentanoic acid (90.29%).

Acknowledgment

The authors would like to thank the Ministry of Research, Technology, and Higher Education, for funding this research through Saintek Kemenristekdikti scholarship.

5. References

[1] Nurhayati T, Roliadi H and Bermawie N 2005 Production of mangium (Acacia mangium) wood vinegar and its utilization J. For. Res. 2: 13–25
[2] Pimenta A S, Monteiro T V C and Lima K M G 2018 Chemical composition of pyroligneous acid obtained from Eucalyptus GG100 clone Molecules 23: 1–12
[3] Wu Q, Wu Q Z, Shouyu H, Baoxin Z, Hongjun D, Wenxiang L, Dahai T and Wenjiao 2015 Study on the preparation of wood vinegar from biomass residues by carbonization process Bioresour. Technol. 179: 98–103
[4] Yatagai M, Nishimoto M, Hor i K, Ohira T and Shibata A 2002 Termiticidal activity of wood vinegar, its components and their homologues J. Wood Sci. 48: 338–342
[5] Badan Pusat Statistik 2015 Forestry Statistics (in Indonesian) 3: 54–67
[6] Zoltan P, Ildiko R M, Galina G and Zoltan B 2016 The utilization of tree bark. Bioresour. 11: 7859-7888
[7] Senter S D, Robertson J A and Meredith F I 1989 Phenolic compounds of the mesocarp of cresthaven peaches during storage and ripening J. Food Sci. 54: 1259–1268
[8] AOAC 2005 Association of official analytical chemistry official method of analysis (Washington D.C.: AOAC)
[9] Souza J B G, Re-Poppi N and Raposo J L 2012 Characterization of pyroligneous acid used in agriculture by gas chromatography-mass spectrometry J. Braz. Chem. Soc. 23: 610–617
[10] Loo A Y 2008 Isolation and characterization of antioxidant compounds from pyrroligneous acid of *Rhizophora apiculata* [Thesis] Univ. Sains Malaysia.

[11] Oramahi H A and Yoshimura T 2013 Antifungal and antitermitic activities of wood vinegar from *Vitex pubescens* Vahl. *J. Wood Sci.* 17: 60-69

[12] Bilelah D, Li L and Kim Y H 2012 Gas Chromatography-Mass Spectrometry analysis and chemical composition of the bamboo-carbonized liquid *Food Anal. Methods* 5: 109–112

[13] Saloko S, Darmadji P, Setiaji B and Pranoto Y 2014 Antioxidative and antimicrobial activities of liquid smoke nanocapsules using chitosan and maltodextrin and its application on tuna fish preservation *Food Biosci.* 7: 71-79

[14] Amini M H M, Rasat M S M, Ahmad M I, Wahab R E, Puad W, Wan M N, Abdul RR and Nur H 2017 Chemical composition of small diameter wild leucaena leucocephala species *ARPN J. Eng. Appl. Sci.* 12: 3169–3173

[15] Prianto A H, Yulizar Y B and Simanjuntak P 2019 The synergy effect of azadirachtin and minor components of neem seed oil on antifeedant activity of *Spodoptera litura* *Bulletin of Research on Spice and Medicinal Crops* 30: 27–34

[16] Yang J-F, Yang C H, Liang M T, Gao Z J, Wu Y W and Chuang L Y 2016 Chemical composition, antioxidant, and antibacterial activity of wood vinegar from *Litchi chinensis* *Molecules* 21: 1-10

[17] Suroso A S 2013 The quality of used cooking oil in terms of peroxide numbers, acid numbers and water content (in Indonesian) *J. Kefarmasian Indonesia* 3: 77–88.

[18] Minami T, Takashi B, Takashi I, Katsuhiro M, Masanori O and Yuko O 1989 Components of human breath after the ingestion of grated raw garlic *J. Food Sci.* 54: 763–765

[19] Nian H, Delage B, Pinto J T and Dashwood R H 2008 Allyl mercaptan, a garlic-derived organosulfur compound, inhibits histone deacetylase and enhances Sp3 binding on the P21WAF1 promoter *Carcinogenesis* 29: 1816–1824

[20] Ma X, Wei Q, Zhang S, Shi L and Zhao Z 2011 Isolation and bioactivities of organic acids and phenols from walnut shell pyrroligneous acid *J. Anal. Appl. Pyrolysis* 91: 338–343