Asian Journal of Chemistry; Vol. 32, No. 7 (2020), 1728-1732

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.21657

Analysis of Liquid Volatile Matters from Coconut Shell Pyrolysis by GC-MS and Its Potential as Antifungal Agent

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Received: 18 December 2019; *Accepted*: 12 April 2020; *Published online*: 27 June 2020; AJC-19939

Indonesia is one of the highest producers of coconut in the world and at the same time coconut shell waste is also high. This study used gas chromatography-mass spectrometric (GC-MS) analysis for the liquid volatile matter (LVM) generated from coconut shell pyrolysis and to examine its potential as an antifungal agent. Pyrolysis was performed at 600 ºC. The LVM was 29% (v/w) and had pH 3 and 1.087 g mL^{-1} density. To determine chemical constituents using GC-MS, the standard NIST MS software was used. The spectrogram analysis of LVM revealed five main compounds, namely phenol (21.92%); (*Z*)-4-methyl-5-(2-oxopropylidene)-5*H*-furan-2-one (13.06%); 2,6-dimethoxyphenol (11.54%); 2-methoxyphenol (9.07%) and 2-hydroxy-3-methyl-2-cyclopenten-1-one (7.66%). The LVM showed a excellent fungicidal activity against *Phytophthora palmivora* at a concentration of 0.125% (v/v).

Keywords: Liquid volatile matter (LVM), Coconut shell, Pyrolysis, GC-MS, Antifungal activity.

INTRODUCTION

Indonesia, with its high production of coconuts, simultaneously produces increasing coconut waste. The coconut shell, in particular, has not been well utilized. The coconut shell belongs to the hard wood group, which contains lignocellulose. Lignocellulose consists of three main components: cellulose, hemicelluloses and lignin. Coconut shell can be converted into useful materials by using certain methods, such as pyrolysis. Using pyrolysis, lignocellulose in coconut shell can be converted into liquid volatile matter (LVM), which is produced through the smoke vapour dispersion of oxygen-free combustion products in a pyrolysis reactor [1,2].

During pyrolysis, lignocelluloses is broken down by using heat with limited oxygen in an inert atmosphere, leading to the formation of various products, such as liquid fuel, solid residue, and gas, based on the materials, methods, and conditions used for pyrolysis [3-4]. Gasification and liquefaction of biomass with pyrolysis is as key thermodynamic processes for converting biomass to LVM. The LVM produced through pyrolysis is considered a relatively new low cost, clean and green bioenergy, making it an attractive alternative to conventional fuel because of its eco-friendly nature [6,7]. The liquid smoke composition depends on raw materials used, burning duration, and burning temperature. Liquid smoke can be used to improve aroma, texture and taste of food products, such as meat and fish. Furthermore, it can be used to provide pure chemicals [8,9]. Nonetheless, the advantage with thermochemical conversion of biomass is its ability to produce liquid fuel from any organic matter, particularly lignocellulosic biomass [10].

In general, hemicellulose pyrolysis produces furfural, furan and acetic acid and its derivatives. Cellulose produces carboxylic acids, carbonyls and lignin, which further break down into phenol and phenolic ether and its derivatives [11-13]. Lignin begins decomposition at low temperatures (160-170 ºC) and continues to decompose at low rate until approximately 900 ºC. The second component to decompose is hemicellulose followed by cellulose from approximately 200 ºC to 400 ºC. During this interval, main decomposition occurs, accounting for the highest decomposition of biomass through degradation reactions. At more than 400 ºC, aromatization occurs at a low mass loss rate [14,15].

The chemical compounds in LVM obtained from coconut shell were analyzed by using GC-MS. The results thus obtained can help optimize LVM as antifungicides. One of the most common causes of fruit rot fungus is *Phytophthora palmivora*. This study used GC-MS to analyze the chemical structures of the main components of LVM obtained from coconut shell pyrolysis. Identifying the composition of LVM compounds would reveal the potential benefits of LVM, including as an antifungal agent for *Phytophthora palmivora*.

EXPERIMENTAL

Cocunut shells were procured from the local nearby field. The apparatus used in this research were a series of pyrolysis tools, gas chromatography-mass spectrometry (GC-MS) Thermo scientific Trace 1300 GC/ISQ, analytic balance scales, heater, filter paper (Whatmann), petri dish, micropipet, pycnometer, pH meter, autoklav, vortex, laminar air flow.

Pyrolysis of coconut shell: Liquid volatile matter (LVM) was produced by using a pyrolysis reactor at 600 ºC for 1 h. Coconut shells were dried under the sun for 3-4 days and then cut pieces of 2-3 cm before using them for pyrolysis. LVM obtained was filtered using Whatman filter paper. The filtrate produced was then centrifuged at 4500 rpm for 20 min. Furthermore, the liquid phase of the centrifugation was diluted with ethanol p.a. to 7:3 (% v/v).

GC-MS analysis: The main chemical compound of LVM was analysed using GC-MS Thermo scientific Trace 1300 GC/ISQ. LVM extract of 1 µL was injected into GC-MS with the ionization type Electron Impact 70 eV. The injector temperature was maintained at 290 ºC, detector temperature at 290 ºC, column temperature at 70-280 ºC, column length at 30 m and column diameter at 25 mm. Temperature rise was maintained at 5 ºC/min. Helium was used as a carrier gas with a flow rate of 60 mL/min.

Antifungal activity against *Phytophthora palmivora*: The antifungal activity of LVM against *P. palmivora* was tested by using the dilution method. *P. palmivora* from was grown on solid PDA media mixed with coconut shell LVM in various concentrations. The petri dishes were incubated at 37 ± 0.1 ºC for 8 days. The inhibition of *P. palmivora* fungus growth commenced on the first day (soon after incubation). However, the control petri dish was filled with fungi. At the end of the observation period, the inhibition zones were measured. The growth was indicated by colour changes (from colourless to beige white). The positive antifungal activity was suggested based on the growth inhibition zone. The analysis of LVM inhibition power on the growth of *P. palmivora* fungus was determined [16] using the following eqn.:

$$P\,(\%) = \frac{(a-b)}{a} \times 100$$

where % P = inhibition percent; a = the diameter of fungal colonies on control; b = the diameter of fungal colonies on sample. The LVM concentration used was 0.025; 0.050; 0.075; 0.10; 0.125 (% v/v) and ethanol:aquades (7:3) as control. The total volume of solid PDA in the petri dish was 20 mL. The ratio of LVM:PDA solid used in PDA media is presented in Table-1.

TABLE-1
LVM CONCENTRATION COMPOSITION IN PDA MEDIA

LVM (% v/v)	LVM (mL)	PDA (mL)
0	0	20.000
0.025	0.005	19.995
0.050	0.010	19.990
0.075	0.015	19.985
0.100	0.020	19.980
0.125	0.025	19.975

RESULTS AND DISCUSSION

Characterization of liquid volatile matter from coconut shell pyrolysis: In this study, LVM was produced through smoke condensation in a pyrolysis reactor at 600 ºC with a heat flow rate of 9 ºC/min ± 1. The LVM obtained from pyrolysis at each of the working temperatures was 29% (v/w). These substances had a pH of 3 and density of 1.087 g/mL at 25 ºC. Pyrolysis at high temperatures results in the condensation reaction of newly formed compounds and aromatization of aromatic polycyclic hydrocarbons [17]. This may be attributed to primary or secondary decomposition of coconut shells with an increase in temperature. One of the factors affecting pyrolysis results is the heater flow rate. LVM has acidic properties because of the presence of organic acids, such as carboxylic acids and phenolic acids. These acids are almost always naturally present in plant products including coconut shells, but their content vary. The mass-volume relationship of the LVM must be established to determine LVM density [18].

The volatility properties and fixed carbon contents of pyrolytic products indicate the presence of three main components, namely lignin, cellulose and hemicellulose, at significantly different proportions. As cellulose contains a higher amount of volatile components than lignin and hemicellulose, it is expected to produce the highest proportion of volatile products followed by hemicellulose. The highest fixed carbon content of lignin leads to the highest production of bio-char [19].

Analysis of liquid volatile matter: The LVM obtained from pyrolysis is a highly complex mixture of valued chemicals. This LVM was investigated because it is not unequivocally known what constitutents are exactly present in a given material, thus GC-MS was applied to identify the pyrolytic liquid products [20]. In this research, analysis of the major constitutents present in the LVM was carried out with GC-MS and their structures were identified by using NIST MS database (Table-2).

The GC-MS spectrum of LVM analyzed from cocunut shell at the pyrolysis temperature of 600 ºC is shown in Fig. 1. The spectrogram analysis showed that chemical compounds of LVM were phenol (at a retention time [RT] of 2.88 min and a molecular weight [*m/z*] of 94 g/mol; Fig. 2); 2-hydroxy-3-methyl-2-cyclopenten-1-one (RT 3.28 min and *m/z* 112 g/mol; Fig. 3); 2-methoxyphenol (RT 3.45 min and *m/z* 124 g/mol; Fig. 4); (*Z*)-4-methyl-5-(2-oxopropylidene)-5H-furan-2-one (RT 4.93 min and *m/z* 152 g/mol; Fig. 5); and 2,6-dimethoxyphenol (RT 5.69 min and *m/z* 154 g/mol; Fig. 6). At all working temperatures of pyrolysis, phenolic compounds were dominant components of LVM. This is because thermal decomposition

TABLE-2
ANALYSIS OF CHEMICAL COMPOUNDS OF LVM BY GC-MS AT PYROLISIS TEMPERATURE 600 °C

Retention time (min)	Chemical formula	Area (%)	m.f.	m.w.
2.88	Phenol	21.92	C_6H_6O	94
3.28	2-Hydroxy-3-methyl-2-cyclopenten-1-one	7.66	$C_6H_8O_2$	112
3.45	2-Methoxy phenol	9.07	$C_7H_8O_2$	124
4.93	(Z)-4-Methyl-5-(2-oxopropylidene)-5*H*-furan-2-one	13.06	$C_8H_8O_3$	152
5.69	2,6-Dimethoxy phenol	11.54	$C_8H_{10}O_3$	154

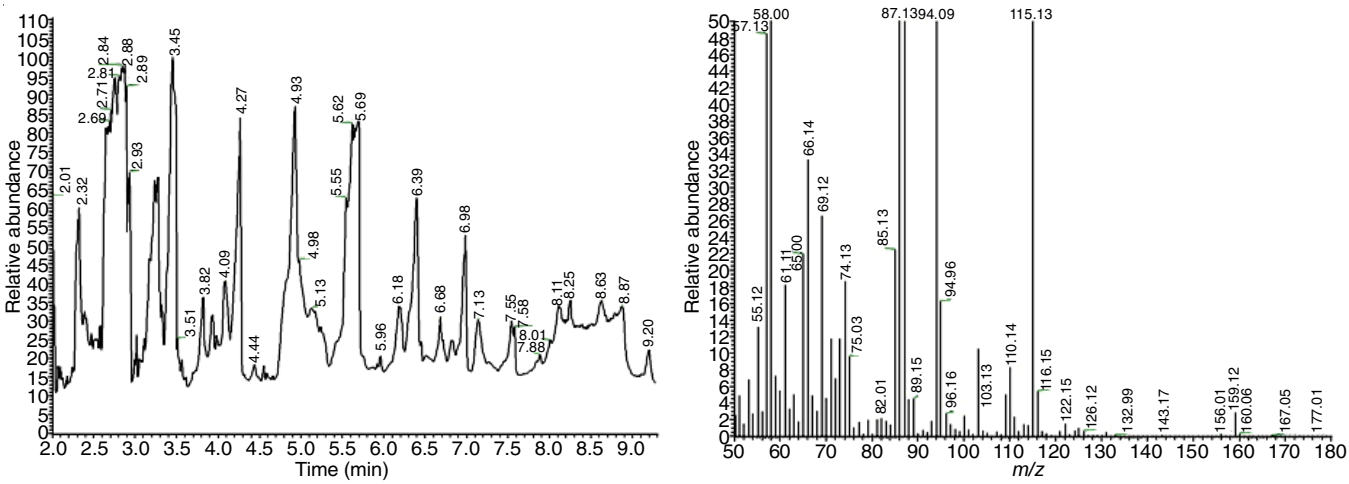

Fig. 1. Spectrogram of coconut shell LVM at pyrolisis temperature 600 ºC

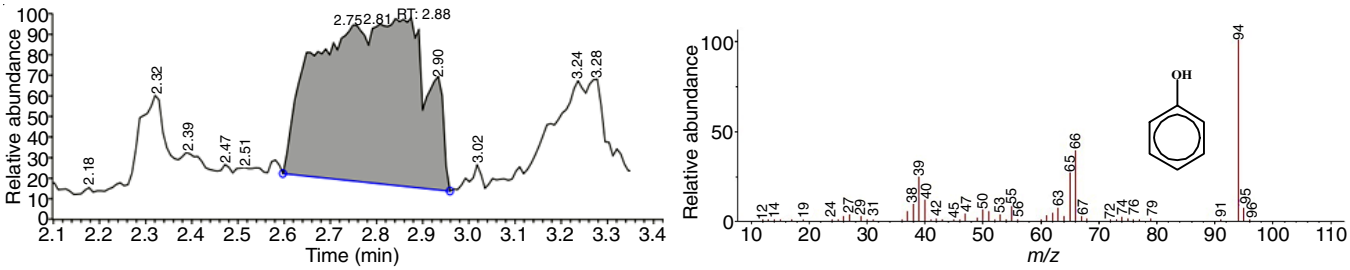

Fig. 2. Spectrogram phenol compound of coconut shell LVM at pyrolisis temperature 600 ºC

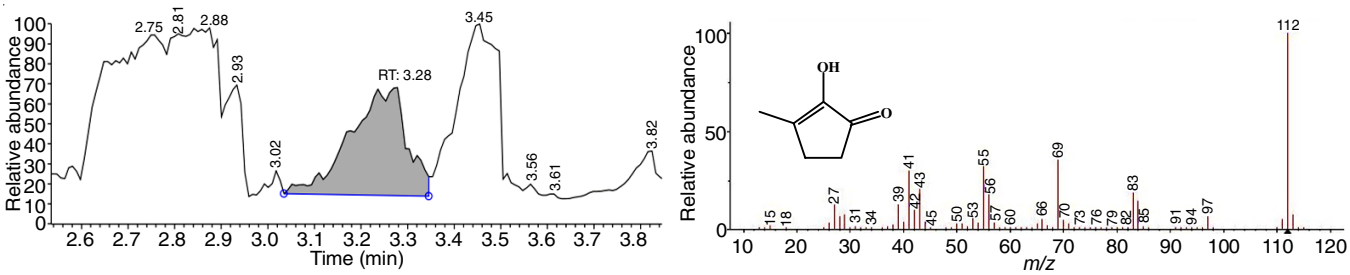

Fig. 3. Spectrogram 2-hydroxy-3-methyl 2-cyclopenten-1-one compound of coconut shell LVM at pyrolisis temperature 600 ºC

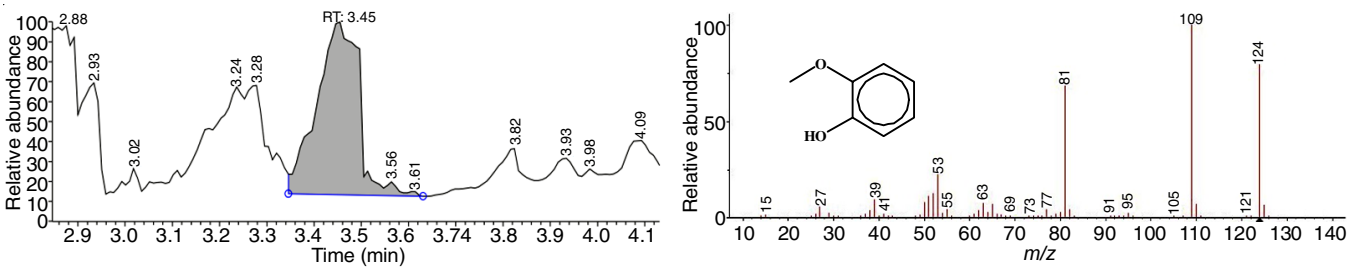

Fig. 4. Spectrogram 2,6-dimethoxy phenol compound of coconut shell LVM at pyrolisis temperature 600 ºC

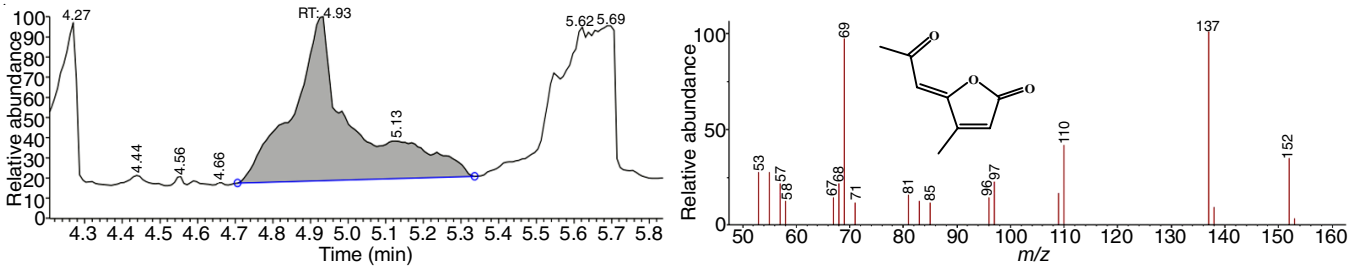

Fig. 5. Spectrogram (*Z*)-4-methyl-5-(2-oxopropylidene)-5*H*-furan-2-one compound of coconut shell LVM at pyrolisis temperature 600 ºC

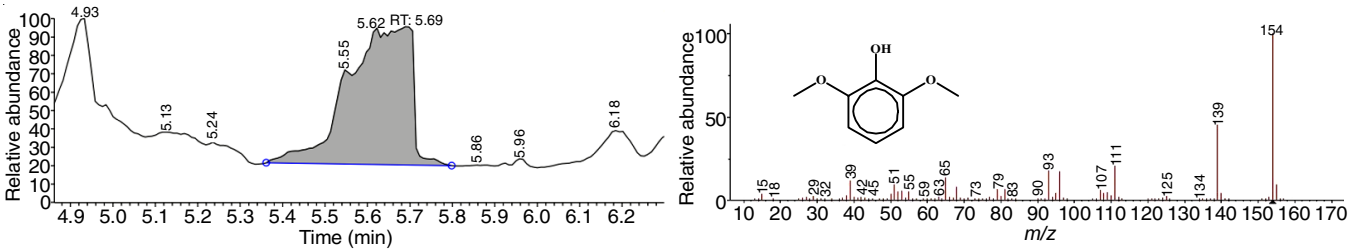

Fig. 6. Spectrogram 2,6-dimethoxy phenol compound of coconut shell LVM at pyrolisis temperature 600 ºC

of lignin occured at > 300 ºC generating aromatic compounds such as phenol and its derivatives [21,22].

Antifungal activity of liquid volatile matter against *Phytophthora palmivora*: A dilution method was used to test the antifungal activity of LVM against *P. palmivora*. *P. palmivora* growth was observed from the first day of incubation until *P. palmivora* fungal colony filled in the control petri dish, which was until the eighth day.

The LVM obtained from coconut shells could suppress *P. palmivora* mycelial growth (Table-3). The phenolic components of plant extracts provide it antifungal properties [23]. The coconut shell LVM exhibited 60% antifungal activity against *P. palmivora* at a 0.1% v/v concentration, whereas at 0.125% v/v, LVM exhibited 100% activity. The coconut shell LVM can inhibit *P. palmivora* growth as it contains a high amount of phenolic compounds and phenolic compounds are one of the main inhibitors of fungal growth [24,25].

TABLE-3
INHIBITORY EFFECTIVENESS OF THE LVM AGAINST *Phytophthora palmivora*

LVM concentration (%)	Inhibition (%)
0	0
0.025	10
0.050	20
0.075	35
0.100	60
0.125	100

Conclusion

Liquid volatile matter (LVM) generated from coconut shell pyrolysis was analyzed by GC-MS technique. Using NIST MS database, the main chemical compounds of LVM from coconut shell pyrolysis were phenol, (*Z*)-4-methyl-5-(2-oxopropylidene)-5*H*-furan-2-one (13.06%); 2,6-dimethoxyphenol (11.54%); 2-methoxyphenol (9.07%) and 2-hydroxy-3-methyl-2-cyclopenten-1-one (7.66%). At 0.0125% LVM concentration exhibited 100% fungicidal activity against *P. palmivora*. The results suggested that LVM generated from coconut shell pyrolysis is highly potential as antifungal agent.

ACKNOWLEDGEMENTS

The authors are grateful to Directorate of Research and Community Service, Ministry of Research Technology and Higher Degree, the Republic of Indonesia and Halu Oleo University, Kendari, Indonesia for the financial support.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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