Characterization of Coconut Shell Liquid Volatile Matter (CS-LVM) by Using Gas Chromatography

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Abstract. Generally, the coconut shell is only used for the fuel of furnace or is just burnt in which this will just create pollution. One way of solving this problem is by re-processing the coconut shell as raw materials for making liquid volatile matter (LVM) by pyrolysis method. Coconut shell is part of the coconut fruit at which having biological function to protect fruit core and is located on the inner side of the fiber with a thickness ranging from 3-6 mm. Coconut shell is classified as hardwood, mainly composed of lignin, cellulose, and hemicellulose, with water content of approximately 6-9 %. Coconut shell is more suitable for pyrolysis process, since they contain less amount of ash, more amount of volatile matter and available with lower cost in rural areas during all the sessions of the year. This research was aimed at determining the influence of pyrolysis temperature towards the LVM volume of coconut shell. LVM was made of condensing the smoke of pyrolysis result from the coconut shell while the analysis of compound composition of LVM coconut shell used Gas Chromatography. Based on the result of the research, it was known that the pyrolysis, at the temperatures of 400°C, 500°C, 600°C and 700°C can create LVM volume as many as 204.167 mL kg⁻¹, 208.33 mL kg⁻¹ and 216.67 mL kg⁻¹. The LVM created from the pyrolysis at 400°C was made of ammonia (12.41%), acetic acid (37.27%), phenol (31.66%), furfural (4.16%), and alcohol (5.01%). The LVM created from the pyrolysis at 500°C was made of ammonia (12.22%), hydrazine (5.61%), acetic acid (40.96%), phenol (32.82%), and alcohol (3.10%), furfural (5.30%). The LVM created from the pyrolysis at 600°C was made of ammonia (15.49%), acetic acid (36.01%), phenol (32.85%), alcohol (6.75%), and furfural (4.62%). The LVM created from the pyrolysis at 700°C was made of ammonia (15.07%), acetic acid (35.20%), phenol (22.60%), alcohol (5.07%), and furfural (4.90%). From this result, it can be seen that LVM has big advantages for food flavor and other specific flavor as well as for preservative because of its antimicrobe and anti-oxidant characteristics.

1. Introduction

Biomass, defined as any hydrocarbon material mainly consisting of carbon, hydrogen, oxygen, nitrogen and some other components in small proportions [1], includes wood and its derived wastes, different organic wastes (including biodegradable MSW), agricultural and crop wastes, animal wastes, energy plantations, among others. Cashew nut (CNS) and coconut shells (CcNS) are part of this family [2]. Coconut shell is part of the coconut fruit at which having biological function to protect fruit core and is located on the inner side of the fiber with a thickness ranging from 3-6 mm [3]. Coconut shell is classified as hardwood, mainly composed of lignin, cellulose, and hemicellulose, with water content of approximately 6-9 % [3].

Coconut shell is more suitable for pyrolysis process, since they contain less amount of ash, more amount of volatile matter and available with lower cost in rural areas during all sessions of the year [4].
Pyrolysis is a thermo-chemical process in which organic material is converted into a carbon rich solid (char) and volatile matter (liquids and gases) by heating in the absence of oxygen [5]. Lignocellulosic biomass components are hemicellulose, cellulose and lignin. Researchers have already confirmed that lignin starts decomposing at low temperatures (160–170°C) and continues to decompose at low rate until approx. 900 °C. Hemicellulose is the second component to start 524 A.

Chromatography is a powerful and versatile tool for separating closely related chemical species. In addition, it can be used for the qualitative identification and quantitative determination of separated species. [24]. Some detectors are universal; that is they are sensitive to practically every compound that elutes from the column. On the other hand, there are discriminating (selective) detectors that are sensitive only to specific compounds, yielding a very uncomplicated chromatogram. The ideal situation to quantify an analytic, would be to have a detector which sees only this analytic. They can be also categorized as destructive or non-destructive of the analytic. Detectors are classified into two groups depending on retention time, structural information of the analytic concerned. For this reason, some gas chromatographs are equipped with two or three detectors linked in series. Nonetheless, the response of all detectors is dependent on the molar concentration or on the mass of analytic in the carrier gas [25].

2. Material and Method
2.1 Materials and Tools

Materials used for the manufacture of liquid smoke is a coconut shell waste. The main equipment used to obtain the coconut shell liquid smoke is pyrolysis, and liquid smoke produced in identification using Gas Chromatography Agilent brands.

2.2 Sample Preparation

Preparation of the material in this study is the material taken from the wild form of coconut shell cleaned from coir and cut into small pieces (size 2 - 3 cm) and then dried in the sun for 7-10 days.

2.3 Pyrolysis process

Pyrolysis process is done by using a pyrolysis reactor equipment with the following procedures: 1). Coconut shell sample is weighed as much as 1200 grams, 2). The sample is introduced into a pyrolysis reactor tube, 3). Pyrolysis appliance connected to the electric current, 4). The process temperature is set by means Termocouple until it reaches a temperature variations 400°C, 500°C, and 600°C. for 1 hour, 5).
Smoke coming out has been condensed and collected in a bottle, 6). After selesasi process, the reactor is cooled, 7). The resulting liquid volatile matter volume was analyzed using GC.

2.4 Identification of Chemical Components by GC

LVM constituent chemical components obtained from the results of pyrolysis GC identified in the laboratory of Forensic Makassar. The equipment uses 2 column, (1). J & W 122-5731 : 1721.65322 with column temperature of 400°C with a diameter of 30 m x 250 μm x 0.1 μm, (2). Frontier Alloy 5Ultra UA - 5 with a temperature of 450°C with a diameter of 30m x 0.25 μm 250μmx operating conditions at an oven temperature of 160°C/min, injection 250°C, helium carrier gas flow rate of 150 ml/min.

3. Results and Discussion

3.1 Pyrolysis results

Results coconut shell waste pyrolysis produces liquid distillate in the form of smoke and charcoal residue. It also obtained the gases which can not be condensed by cooling, so it could not be accommodated in the liquid reservoir. Most of these gases are trapped in the container while others apart from the reservoir through the conduit of smoke and escape into the atmosphere.

The volume of liquid smoke produced is an important parameter to determine the outcome of a process. Liquid smoke in this study were generated through a process of condensing the smoke released pyrolysis reactor. During the pyrolysis process of evaporation of various kinds of compounds. Volume smoke liquid smoke produced from each temperature are presented in Table 1.

Table 1. Volume of liquid smoke cocoa shell waste pyrolysis results with electric reactor at a temperature of 400°C, 500°C and 600°C

| Temperature (°C) | Material Weights (kg) | Charcoal weights (kg) | LVM (ml) |
|------------------|----------------------|-----------------------|-----------|
| 400              | 1.2                  | 0.3                   | 245       |
| 500              | 1.2                  | 0.35                  | 250       |
| 600              | 1.2                  | 0.33                  | 260       |

Based on Table 1 the average volume of liquid smoke produced from each successive temperature are 204.167 ml.kg⁻¹, 208.33 ml.kg⁻¹ and 216.67 ml.kg⁻¹. In this case the amount of liquid smoke generated in the pyrolysis process is very dependent on temperature pyrolysis and condensation systems used. That is appropriate condition for the formation of liquid smoke used water as the cooling medium so that the heat exchange process can occur relatively quickly. Pyrolysis at temperatures high and too long will lead to the formation of liquid smoke is reduced as the temperature of the cooling water is increasing so that the smoke generated is not completely condensed.

The quality of liquid smoke is very dependent on the composition of the chemical compounds they contain. Criteria for a good quality liquid smoke flavor and aroma as a characteristic possessed the smoke is determined by the class of chemical compounds it contains. Chemical compounds contained in liquid smoke is very dependent on the pyrolysis conditions and raw materials used. In addition, the process of pyrolysis of a material that does not last perfect can cause chemical components generated in the liquid smoke less complete. Chemicals component that have been identified in the liquid smoke include compounds phenol, carbonyl, carboxylic acid, furan, hydrocarbon, alcohol and lactone.

3.2 Chemical components of LVM

LVM generated in the pyrolysis process of waste coconut shall beforehand dissolved in methanol for chemical content are further identified. Determination of the compounds contained in liquid smoke is done by using GC equipment. Depictions of the chromatogram pattern shaped curve as a function of time. Chromatograms in Figures 1 to 3 show that the liquid smoke is generated in the pyrolysis process of waste coconut shell shows the separation of the chemical components through chromatogram peaks appearing in gas chromatography. Results chromatogram liquid smoke at a temperature of 400°C peak chromatogram start appearing at a retention time from 1.86 to 19.27 minutes (Figure 1) and identified as many as 20 compounds. Results chromatogram liquid smoke at a temperature of 500°C chromatogram peaks begin to appear on the retention time from 1.82 to 19.27 minutes (Figure 2) and identified as many as 14 compounds. While the results of the chromatogram liquid smoke at a temperature of 600°C peak cromtogram began to appear on the retention time of 1.85 to 19.27 minutes (Figure 3) and identified as many as 14 compounds.
Figure 1. Results chromatogram liquid smoke coconut shell pyrolysis temperature of 400°C

Figure 2. Results chromatogram liquid smoke coconut shell pyrolysis temperature of 500°C
Figure 3. Results chromatogram liquid smoke coconut shell pyrolysis temperature of 600°C

The compounds are believed to have the name and structure as listed in Table 2.

### Table 2. Chemical Ingredients liquid smoke coconut shall

| No. peak | Temperature (°C) | Retention time (min) | Name of compound | Concentration (%) |
|----------|------------------|----------------------|------------------|-------------------|
| 1        | 400              | 1.86                 | Amonia           | 12.41             |
| 2        | 1.9              | 2.28                 | Acetid acid      | 3.87              |
| 3        | 2.51             | 1.75                 | Hydrazine        | 0.75              |
| 4        | 2.63             | 0.95                 | Formic acid, Metil Ester | 3.33             |
| 5        | 2.71             | 3.05                 | Acetid acid      | 0.64              |
| 6        | 3.49             | 8.92                 | Acetid acid      | 0.41              |
| 7        | 3.92             | 13.12                | 2-Propanone      | 4.16              |
| 8        | 4.04             | 14.04                | Furfural, 1.3 Cyclopentanedione | 0.64             |
| 9        | 11.7             | 15.12                | Phenol           | 5.41              |
| 10       | 13.12            | 14.58                | 2-Cyclopenten    | 1.39              |
| 11       | 14.96            | 14.96                | Phenol           | 1.04              |
| 12       | 15.24            | 15.24                | Phenol           | 1.06              |
| 13       | 15.31            | 15.31                | Phenol           | 4.59              |
| 14       | 16.97            | 16.97                | 1-Propanol       | 0.86              |
| 15       | 18.03            | 18.03                | 1.2-Benzenediol  | 1.97              |
| 16       | 18.27            | 18.27                | Benzenethanol    | 1.97              |
| 17       | 19.27            | Phenol               | 5.46              |
Table 2. (Continued)

| No. peak | Temperature (°C) | Retention time (min) | Name of compound     | Concentration (%) |
|----------|------------------|----------------------|----------------------|-------------------|
| 1        | 500              | 1.82                 | Amonia               | 12.22             |
| 2        | 100              | 1.86                 | Hydrazine            | 5.61              |
| 3        | 224              | 2.24                 | Acetic acid          | 1.97              |
| 4        | 267              | 2.67                 | Acetic acid          | 2.15              |
| 5        | 271              | 2.71                 | Acetic acid          | 1.33              |
| 6        | 292              | 2.92                 | Acetic acid          | 15.39             |
| 7        | 304              | 3.04                 | Acetic acid          | 20.12             |
| 8        | 345              | 3.45                 | 2-Propanone          | 3.1               |
| 9        | 891              | 8.91                 | 2-Furancarboxaldehyde| 5.3               |
| 10       | 13.12            | Phenol               | 18.49               |
| 11       | 15.24            | Phenol               | 4.4                 |
| 12       | 16.97            | Phenol               | 3.3                 |
| 13       | 18.27            | Guaiacol, 4-Ethyl Phenol | 1.98               |
| 14       | 19.27            | Phenol               | 4.65                |

From the results of the above identification is found phenol. Where the phenolic compounds can be applied as a food preservative.

4. Conclusion

Results pyrolysis cocoa shell with temperature variations 400°C, 500°C and 600°C gained an average volume of liquid smoke respectively 204.167 ml kg⁻¹, 208.33 ml kg⁻¹, and 216.67 ml kg⁻¹. Results of the Gas Chromatography identification of unknown chemical components of liquid smoke cocoa shell has ammonia, acetic acid, propanone, furfural, and phenol. Phenol compounds can be used as a preservative applications

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References

1. S. Yaman, Energy Conversion and Management 45 (2004) 651–671.
2. P. Das, A. Ganesh, Biomass and Energy 25 (2003) 113–117.
3. Tilman D. 1981. Wood Combustion: Principles, Processes and Economics. Academics Press Inc., New York, USA.
4. Ganapathy E. Sundaram and E. Nataraja. 2009 Pyrolysis of Coconut Shell: An Experimental Investigation The Journal of Engineering Research Vol. 6, No. 2 (2009) 33-39
5. Demirbas, A., Arin, G. (2002). An Overview of Biomass Pyrolysis. Energy Sources. 24, 471-482.
6. T. Fisher, M. Hajaligol, B. Waymack, D. Kellog, Journal of Analytical and Applied Pyrolysis 62 (2002) 331–349.
7. Wu, Y., Zhang, C., Liu, Y., Fu.Z., Dai, B. dan Yin, D. 2012. Biomass Char Sulfonic Acids (BC-SO3H)-Catalyzed Hydrolysis of Bamboo under Microwave Irradiation. Bioresources. 7(4), 5950-5959.
8. H. Aripin, S. Mitsudo, I. N. Sudiana, N. Jumsiah, I. Rahmatia, B. Sunendar, L.Nurdiiwijayanto, S. Mitsudo, S.Sabchevski, Preparation of Porous Ceramic with Controllable Additive and Firing Temperature, Advanced Materials Research. Vol. 277 (2011) pp. 151-158
9. Stuerga, D. 2006. Microwaves in Organic Synthesis, Second Edition. Wiley-VCH.
10. Dehani, F. R., Argo, B. D. dan Yuliningsih, R. 2013. Utilization of Microwave Irradiation to Maximize Pretreatment Process Degradation of Lignin Jeremi Paddy. Jurnal Biopress Komoditas Tropis Vol.1 No. 1, 175-182 [In Indonesia].
11. I.N. Sudiana, Ryo Ito, S. Inagaki, K. Kuwayama, K. Sako, S. Mitsudo, Densification of Alumina Ceramics Sintered by Using Sub-millimeter Wave Gyrotron, J. Infrared, Millimeter, and Terahertz Waves. 34 (2013), 627-638.
12. Thostenson, E.T. dan Chou, T.W. 1999. Microwave processing : Fundamental and Applications, Elsevier Composites Applied Science and Manufacturing: Part A 30, 1055-1071.
13. S. Mitsudo, S. Inagaki, I.N. Sudiana, K. Kuwayama, Grain Growth in Millimeter Wave Sintered Alumina Ceramics, Advanced Materials Research, Vol.789 (2013), pp. 279-282.
14. H.M.S. Kingston, H.J. Haswell, 1997. Microwave-Enhanced Chemistry: Fundamental, Sample Preparation, and Applications, American Chemical Society.
15. M. Z. Firihu., I. N. Sudiana, S. Mitsudo, Microwaves Enhanced Sintering Mechanisms in Alumina Ceramic Sintering Experiments, Contemporary Engineering Sciences, Vol. 9, 2016, 5, 237 – 247
16. I.N. Sudiana, S. Mitsudo, K. Sako, S. Inagaki, L. O. Ngkoimani, I. Usman, H. Aripin, The microwave effects on the properties of alumina at high frequencies of microwave sintering, American Institute of Physics (AIP) Conference Proceeding, 1719, 030014 (2016); doi: 10.1063/1.4943709
17. I. N. Sudiana, S. Mitsudo, T. Nishiwaki, P. E. Susilowati, L. Lestari, M. Z. Firihu, H. Aripin, Synthesis and Characterization of Microwave on Sintered Silica Xerogel Produced from Rice Husk Ash, Journal of Physics: Conference Series, Vol. 739 No. 1, (2016) 012059
18. I. N. Sudiana, S. Mitsudo, M. Z. Firihu, Effect of Initial Green Samples on Mechanical Properties of Alumina Ceramic, Contemporary Engineering Sciences, Vol. 9, 2016, no. 12, 595-602
19. I. N. Sudiana, S. Mitsudo, M. Z. Firihu, H. Aripin, Effect of High-Frequency Microwave on Micro Hardness of Alumina Ceramic, Material Science Forum, Vo. 872, 2016, pp.114-117.
20. Girard J P. 1992. Technology of Meat and Meat Products. Ellis Horwood, New York, USA.
21. Yuilstian. 1997. The inhibition ability of liquid smoke against growth of bacterial pathogens and blight on cow tongue. Master Thesis. Study Program of Food Science and Technology. University of Gadjah Mada.
22. Lawrie R.A. 1983. Meat Science. Pargamon Press, London.
23. Astutti. 2000. Utilization of fiber and shell of coconut and oil palm shell for producing liquid smoke as natural food preservatives.http://alcoconut.multiply.com/journal/item/6.
24. Douglas A. Skoog, Donald M. west, F. James Holler, Stanley r. Crouch. 2004. Fundamentals of analytical chemistry ninth edition. Mary finch. USA
25. Francis Rouessac and Annick Rouessac. 2007. Chemical Analysis. University of Le Mans. France.