Characterization of Liquid Volatile Matter (LVM) of Cashew Nut Shell using Pyrolysis and Gas Chromatography

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Abstract. Cashew nut are excellent products in Southeast Sulawesi. Cashew nut is one part of the cashew plant untapped waste. Cashew nut shell potential as a producer of liquid volatile matter (LVM) and charcoal because it contains lignocellulos. LVM is the smoke condensation products obtained from the pyrolysis reactor can used for adhesive of briquettes hybrid application. The aim of this research is to produce LVM of cashew nut shell by pyrolysis and analyze the content by Gas Chromatography (GC). The research procedure begin with drying the cashew nut, the sample inserting into the pyrolysis reactor then heating with three variations of temperature respectively is 400 °C, 500 °C and 600 °C. Cashew nutshell have been heating by pyrolysis process with high temperatures resulting charcoal and LVM separately. Volume LVM measured, then identify is components using GC. LVM obtained respectively 200 ml kg⁻¹, 340 ml kg⁻¹, and 340 ml kg⁻¹. Chromatogram of the GC from LVM of cashew nut shell has ammonia, hexane, acetic acid, propanone and phenol. Phenol compounds can be used as a adhesive for hybrid briquettes applications.

1. Introduction

Indonesia as an agricultural country, especially a lot of waste southeast Sulawesi plantations underutilized. Cashew nut are excellent products in Southeast Sulawesi. Cashew nut is one part of the cashew plant untapped waste. One way of handling this is to do are-processing to make cashew nut as a raw material for making liquid volatile matter (LVM) [1]. LVM from Cashew nut shell is a versatile material with many applications in the manufacture of friction dust for brake linings and clutch facing, different types of coatings, adhesives, and pesticides among many others [2]. LVM is the result of condensation or condensing steam pyrolysis results of materials containing lignocellulose and other carbon compounds [3]. In the other side, lignocellulosic biomass basic components are hemicellulose, cellulose and lignin so has the potential to be used as raw material for making LVM [4].

Pyrolysis is a process that converts biomass directly into solid, liquid, and gaseous products by thermal decomposition in the absence of oxygen [5]. Moreover, pyrolysis has been the source of many basic organic chemicals such as phenol, acetic acid, and acetone [6]. In this study, the compounds of LVM identified using Gas Chromatography (GC). GC is an instrumental chromatography configuration, meaning we have electronic detection and peaks on a computer screen [7]. Pyrolysis is commonly applied heater (electric heater or furnace) during heating. Recently, progress in electromagnetic radiation source especially in microwave frequency range. open opportunity to heat material by using this waves as an alternative energy for heating. This method was applied and reported for synthesizing organic material [8-10], ceramics processing [12-16], enhancing mechanical properties of ceramics [17-18], and chemical
reaction [19-20]. The application microwave for pyrolysis has been performing in Halu Oleo University and will be reported in separated papers.

LVM that produced from the pyrolysis process cashew nut shell can be made in raw materials for the application of adhesive for hybrid briquettes, because the compound like phenol content than can be used as an adhesive [2].

2. Material and Method

2.1 Materials and Tools

Materials used for the manufacture of LVM is a cashew nut shell waste. The main equipment used to obtain the cashew nut shell LVM is pyrolysis, and LVM produced in identification using Gas Chromatography Agilent brands. Preparation of the material in this study is the material dried in the sun for 1-2 weeks.

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 selasasi 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 cashew nut 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 cashew nut shell waste pyrolysis results with electric reactor at a temperature of 400°C, 500°C and 600°C

| Temperatures (°C) | Material Weights (kg) | Charcoal weights (kg) | LVM (ml kg⁻¹) |
|------------------|----------------------|-----------------------|--------------|
| 500              | 0.5                  | 0.16                  | 200          |
| 600              | 0.5                  | 0.14                  | 340          |
| 700              | 0.5                  | 0.11                  | 340          |

Based on Table 1 the average volume of liquid smoke produced from each successive temperature 200 ml kg⁻¹, 340 ml kg⁻¹, and 340 ml kg⁻¹. In this case the amount of LVM generated in the pyrolysis process is very dependent on temperature pyrolysis and condensation systems used. That is appropriate condition for the formation of LVM 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 LVM is increased. The quality of LVM is very dependent on the composition of the chemical compounds they contain. Criteria for a good quality LVM flavor and aroma as a characteristic possessed the smoke is determined by the class of chemical compounds it contains. Chemical compounds contained in LVM 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 LVM less complete. Chemicals component that have been identified in the LVM include compounds ammonia, hexane, phenol, acetid acid, furan and ketones.

3.2 Chemical Components of Liquid Smoke

Liquid smoke generated in the pyrolysis process of waste cashew nut shell first filtered using filter paper for 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 LVM is generated in the pyrolysis process of waste cashew nut shell shows the separation of the chemical components through chromatogram peaks appearing in GC. Results chromatogram LVM at a temperature of 400°C chromatogram peaks start appearing at a retention time from 1.88 to 18.46 minutes (Figure 1) and identified as many as 17 compounds. Results chromatogram LVM at a temperature of 500°C chromatogram peaks begin to appear on the retention time from 1.88 to 16.50 minutes (Figure 2) and identified as many as 10 compounds. Results chromatogram LVM at a temperature of 600°C chromatogram peaks begin to appear on the retention time from 1.88 to 17.17 minutes (Figure 3) and identified as many as 8 compounds.

![Figure 1. Chromatogram LVM of cashew nut shell at temperature 400°C](image1)

![Figure 2. Chromatogram LVM of cashew nut shell at temperature 500°C](image2)
Figure 3. Chromatogram LVM of cashew nutshell at temperature 600°C

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

| Peak | Temperature (°C) | Retention Time (min) | Name of compound | Concentration (%) |
|------|-----------------|----------------------|-----------------|------------------|
| 1    | 400             | 1.88                 | Ammonia         | 45.42            |
| 2    | 2.14            | 2-Propanone, Aceton (Ketone) | 0.79          |
| 3    | 2.65            | Acetic Acid          | 1.32            |
| 4    | 2.72            | Hexane               | 12.92           |
| 5    | 2.89            | Acetic Acid          | 17.5            |
| 6    | 3.5             | 2-Propanone, Hidroxy Aceton (Ketone) | 4.48          |
| 7    | 8.96            | Furfural, 2-Furan Karboxaldehyde | 1.55          |
| 8    | 13.12           | Phenol               | 1.68            |
| 9    | 14.03           | 1,2-Siklopentanedione | 0.83          |
| 10   | 14.96           | 3-Methyl Phenol      | 0.85            |
| 11   | 15.05           | 2-Piran              | 1.71            |
| 12   | 15.07           | 3,4-Metoxy benzoik Acid | 1.93          |
| 13   | 15.24           | Mequinol             | 0.93            |
| 14   | 15.31           | 2-Metil Amino        | 1.45            |
| 15   | 17.01           | 2-ethoxy Phenol      | 1.30            |
Table 2. (continued)

| Peak | Temperature (°C) | Retention Time (min) | Name of compound | Concentration (%) |
|------|------------------|----------------------|------------------|------------------|
| 16   | 17.2             | Siringol             |                  | 1.16             |
| 17   | 18.46            | Hidroquinon          |                  | 4.19             |
| 1    | 500              | 1.88                 | Ammonia          | 35.85            |
| 2    | 1.92             | Hydrazine            |                  | 10.65            |
| 3    | 2.15             | 2-Propanone, Aceton (Ketone) |             | 1.39             |
| 4    | 2.73             | Hexane               |                  | 18.64            |
| 5    | 2.79             | Acetic Acid          |                  | 4.17             |
| 6    | 2.88             | Acetic Acid          |                  | 15.47            |
| 7    | 3.5              | 2-Propanone, Hidroxy Aceton (Ketone) |   | 6.81             |
| 8    | 13.11            | Phenol               |                  | 2.64             |
| 9    | 14.96            | 3-Methyl Phenol      |                  | 4.03             |
| 10   | 16.5             | 4-Ethyl Phenol       |                  | 0.36             |
| 1    | 600              | 1.88                 | Ammonia          | 36.13            |
| 2    | 2.72             | Hexane               |                  | 36.03            |
| 3    | 2.81             | Acetic Acid          |                  | 7.35             |
| 4    | 2.86             | Acetic Acid          |                  | 7.10             |
| 5    | 3.48             | 2-Propanone, Hidroxy Aceton (Ketone) |   | 5.29             |
| 6    | 13.11            | Phenol               |                  | 1.89             |
| 7    | 14.96            | 3-Methyl Phenol      |                  | 3.21             |
| 8    | 17.17            | 2,3-Dihydro-Benzofuran |                | 3.00             |

From the results of the above identification is found phenol. Where the phenolic compounds can be applied as a adhesive hybrid briquettes.

Table 3. Chemical Phenol LVM of cashew nut shell

| Temperature (°C) | Totally of Phenol (%) |
|-----------------|------------------------|
| 400             | 10.11                  |
| 500             | 7.03                   |
| 600             | 5.1                    |

4. Conclusion

Results pyrolysis of cashew nutshell with temperature variations 400°C, 500°C and 600°C gained an average volume of LVM respectively 200 ml.kg⁻¹, 340 ml.kg⁻¹ and 340 ml.kg⁻¹. Pyrolysis process is very dependent on temperature pyrolysis and condensation systems used. That is appropriate condition for the formation of LVM 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 LVM is increases. Results of the Chromatogram of the GC from LVM of cashew nut shell has ammonia, hexane, hydrazine, acetic acid, propanone and phenol. Phenol compounds can be used as a adhesive for hybrid briquettes applications. So, based on the table 3, at temperature pyrolysis 400°C compound phenol very good for adhesive briquettes hybrid application.

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References
1. Risfaheri, dkk, 2004. Pemisahan Kardanol dari Minyak Kulit Biji Jambu Mete dengan Metode Destilasi Vakum. Jurnal Penelitian Pascapanen Pertanian, 1(1): 1-11. [In Indonesian]
2. Patrick M. Mwangi, Christopher Aule and George T. Thiong’o Energy Studies Of Some Cashew Nut By-Products In Kenya (Chemistry Department, Jomo Kenyatta University of Agriculture and Technology, P. O. Box 62000-00200, Nairobi, Kenya)
3. HarsonoSoni 2008 Pengembangan Teknologi Produksi Asap Cair (Laporan Hilink II, September 2008 Universitas Jember). [In Indonesian]
4. T. Fisher, M. Hajaligol, B.Waymack, D. Kellog, Journal of Analytical and Applied Pyrolysis 62 (2002) 331–349.
5. Pütün,2007. A.E., Comparision between the Slow and the Fast Pyrolysis of Tabacco Residue. Industrial Crops and Products, 26: p. 307-314.
6. Bhatia, V.K.,1988.Biomass as a non-fossil fuel source - an overview. Res. Ind., 33 p. 154-61.
7. John Kenkel, 2013. Analytical Chemistry for Technicians 4th Edition. CRC Press Taylor and Francis Group, London.
8. 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.
9. H. Aripin, S. Mitsudo, I. N. Sudiana, N. Jumsiah, I. Rahmatia, B. Sunendar, L. Nurdiwijayanto, S. Mitsudo, S. Sabchevski, Preparation of Porous Ceramic with Controllable Additive and Firing Temperature, Advanced Materials Research. Vol. 277 (2011) pp. 151-158
10. Stuerga, D. 2006. Microwaves in Organic Synthesis, Second Edition. Wiley-VCH.
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. W. H. Sutton, Microwave Processing of Ceramic Materials, Microwave Solutions for Ceramic Engineers, Am. Cer. Soc., Ed.by D.E. Clark, D.C. Folz, C.E. Folgar, M.M. Mahmoud , pp.35-65 (2005).
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. 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
15. Sudiana, I.N., 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
16. 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
17. 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.
18. I. N. Sudiana, S. Mitsudo, M. Z. Firihu, H. Aripin, Effect of High-Frequency Microwave on Micro Hardness of Alumina Ceramic, Material Science Forum, Vol. 872, 2016, pp.114-117
19. H.M.S. Kingston, H.J. Haswell, 1997. Microwave-Enhanced Chemistry: Fundamental, Sample Preparation, and Applications, American Chemical Society.
20. Thostenson, E.T. dan Chou, T.W. 1999. Microwave processing : Fundamental and Applications, Elsevier Composites Applied Science and Manufacturing: Part A 30, 1055-1071.