Characterization of Liquid Volatile Matter Rice Husk Using Gas Chromatography

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Abstract. Rice husk is one type of organic waste that has not been used optimally. Rice husks contain cellulose, hemicellulose and lignin, so they are potentially processed as liquids volatile matter (LVM). The purpose of this study was to determine the effect of pyrolysis temperature on the density and chemical composition of rice husk LVM. This study began with the collection of rice husks. Rice husk is dried and then heated with high temperature 400°C, 500°C, and 600°C. The heating temperature is maintained for 15 minutes, respectively. The process of pyrolysis of rice husk produces charcoal, tar, and smoke. Condensed smoke is called rice husk LVM. The density of rice husk LVM at each pyrolysis temperature is different, namely 0.416 g/cm³, 0.714 g/cm³, and 1.139 g/cm³. The rice husk LVM is characterized using gas chromatography. Characterization results showed that the chemical composition of rice husk LVM consisted of ammonia, propanone, acetic acid, hexane, furfural, phenol, etc.

1. Introduction

Rice is the main food crop that can grow in all parts of Indonesia. Indonesian rice production from 1993 to 2015 has always increased and reached more than 75 million tons in 2015 [1]. Rice grains are ground to separate rice granules and husk. The weight of rice husks is 20-30% of the weight of rice seeds. If rice production is high, rice husk production will also be high. Meanwhile, only a small portion of rice husks were used, among others, to burn red bricks, pedestal chicken hens, and others [2].

Rice husk contains 42.2% cellulose, 18.47% hemicellulose, 19.4% lignin, 17.33% ash, and 2.6% water [3]. The lignocellulosic material is potentially processed into more useful materials such as char [2], briquettes [4,5], liquid smoke [6,7], and tar [8]. Biomass processing is carried out by heating at high temperatures above 300°C [4,6,7]. Biomass heating methods include carbonation method [4], pyrolysis [6,7], and microwave [9].

The advantages of pyrolysis method compared to other methods, pyrolysis can produce three products at once, namely charcoal, tar, and smoke. During the pyrolysis process, biomass compounds are gradually degraded. Hemicellulose is degraded at 220°C-315°C, cellulose is degraded at 315°C-400°C, and lignin is degraded in a wider temperature range than 160°C-900°C[10]. Hemicellulose is degraded into acetic acid, furfural, furan, furanone, methanol, formaldehyde, acetone, acetone, lactone, etc. Cellulose is degraded to levoglucon, hydroxyl acetaldehyde, furfural, hydroxyl methylfururfuraluran, methanol, etc. Lignin is degraded to 2-methoxyphenol, 2,6-in methoxyphenol,
cathecols, phenol, alkyl phenol, methanol, furfural, acetic acid, formaldehyde, acetone, acetal, lactone, etc. [11].

Pyrolysis is a thermo-chemical process in which organic matter is converted into solid carbon and volatile substances by heating without oxygen [12]. Pyrolysis products include charcoal, tar, condensed smoke, and uncondensed smoke [13]. Smoke is a suspension of solid and liquid particles in the gas medium. Smoke is produced by incomplete combustion of the decomposition of constituent polymers into low molecular weight organic compounds due to heat effects including oxidation, decomposition, polymerization, and condensation [14]. Condensed smoke is referred to as liquidvolatile matter (LVM). LVM compounds were identified using gas chromatography (GC) [6,7,11,15,16].

LVM rice husks have been tested as organic insecticides in cocoa plants. LVM phenol content of rice husk gives a distinctive aroma that causes the death of insects in cocoa plants [17]. LVM is also potential for a variety of applications, including preservative fishery products [18, 19], control of cabbage pests [20], as fertilizer [21], and others.

2. Materials and Method
2.1 Materials and Tools

The raw material used to make LVM is rice husk. The main tool used to produce LVM rice husks is a pyrolysis device. Rice husk mass and LVM mass were measured using digital scales, LVM rice husk volume was measured using a measuring cup. Rice husk LVM compounds were identified using the Gilent GC brand, MSD Chemstation type 1431 Ms. 5975.

2.2 Sample Preparation

Rice husks were taken in Lambusa Village, Konda District, South Konawe Regency, Southeast Sulawesi Province. Rice husk is dried in the sun for 3 days to reduce water content.

2.3 Pyrolysis process

The pyrolysis process is carried out by the following procedure: 1). Rice husk is measured as 400 gram, 2). It is inserted into the pyrolysis reactor tube, 3). Pyrolysis devices are connected to an electric current source, 4). Thermocouples on pyrolysis devices are set from room temperature to reach the desired pyrolysis temperature of 400°C, 500°C, and 600°C. Each process lasts for 15 minutes. The pyrolysis device used in this study is integrated with the condenser. Smoke that has been condensed into condensate called LVM rice husk. LVM rice husks are stored in bottles, 5). Pyrolysis reactor cooled.

2.4 Measuring Volume and Mass of LVM Rise Husk

The volume and mass of LVM rice husks are measured using measuring cup and digital balance respectively.

2.5 Identification of Chemical Components by GC

Chemical components of LVM rice husk constituents were identified using GC in the Makassar Forensic laboratory. The equipment uses 2 columns, (1). J & W 122-5731: 1721.65322 with a column temperature of 400°C with a diameter of 30 mx 250 µm x 0.1 µm, (2). Frontier Alloy 5Ultra UA - 5 with a temperature of 450°C with a diameter of 30m x 0.25µm x 250µm operating conditions at oven temperature 160°C /min, injection 250°C, helium carrier gas flow rate of 150 µl /min.

3. Result and Discussion

The pyrolysis process of rice husk in the pyrolysis reactor at a temperature of 400°C, 500°C, and 600°C each produces charcoal, tar, LVM, and the non-condensed smoke. Charcoal is formed as a
residue of rice husk pyrolysis in the reactor. Smoke coming out of the reactor towards the condenser was condensed and changed from gas to liquid. Non-condensed smoke is released into the atmosphere.

Parameters of pyrolysis products include mass, \( m \), volume, \( V \), and density, \( \rho \), at each pyrolysis temperature, \( T \), presented in Table 1. LVM volume is an important parameter for determining rice husk LVM density. The density of rice husk LVM at each pyrolysis temperature is shown in the seventh column in Table 1.

| \( T(\degree C) \) | \( m_{\text{char}} \) (g) | \( m_{\text{tar}} \) (g) | \( m_{\text{uncondensed smoke}} \) (g) | \( m_{\text{LVM}} \) (g) | \( V_{\text{LVM}} \) (ml) | \( \rho_{\text{LVM}} \) (g/cm\(^3\)) |
|-------------------|------------------|------------------|----------------------|----------------|------------------|------------------|
| 400               | 200              | 50               | 130                   | 20             | 48               | 0.416            |
| 500               | 100              | 30               | 220                   | 50             | 70               | 0.714            |
| 600               | 90               | 20               | 200                   | 90             | 79               | 1.139            |

Rice husk LVM density increases at higher pyrolysis temperatures. Pyrolysis of rice husk at 600\( \degree \)C produces the largest density of LVM rice husk 1.139 g/cm\(^3\). The mass and volume of rice husk LVM depend on the pyrolysis temperature and the condensation system used, so the density of LVM also depends on both. The approach taken to form LVM is to use water as a coolant so that the heat exchange process takes place relatively quickly. Pyrolysis at high temperature and very long time will cause LVM formation to decrease as the temperature of cooling water increases so that the smoke is not entirely condensed [6,7].

Uncondensed smoke is not measurable, but can be estimated from other parameters. The estimated mass of uncondensed smoke is shown in Table 1 fourth column. Estimated mass of smoke is obtained from the calculation of the rice husk mass raw material of 400 grams minus charcoal mass, tar mass, and LVM mass at each pyrolysis temperature. The pyrolysis temperature also determines the composition of the resulting LVM chemical compound.

Chemical compound LVM rice husk is identified using GC. The characterization results using GC is a chromatogram showing the relationship of retention time and abundance of the compound. Chemical retention times vary depending on the molecular weight. The smallest molecular weight compound will have a small retention time as well. Chromatogram of LVM rice husk produced at 500\( \degree \)C pyrolysis temperatures are shown in Figures 1.

![Figure 1](image-url)
The chromatogram data were supplemented by interpretation of retention time, compounds, and concentration of rice husk LVM compounds. Concentrations of rice husks LVM compounds at pyrolysis temperature 400°C, 500°C, and 600°C were shown in Table 2, Table 3, and Table 4, respectively.

Table 2. LVM compounds of rice husks produced at 400 °C

| Retention (minute) | Compounds     | Concentration (%) |
|-------------------|---------------|-------------------|
| 1.87              | Ammonia       | 20.18             |
| 1.90              | Methanol      | 11.02             |
| 2.64              | butanedione    | 0.93              |
| 2.68              | acetid aced   | 0.71              |
| 2.71              | hexane        | 19.44             |
| 2.75              | hexane        | 12.13             |
| 2.97              | acetid acid   | 14.17             |
| 3.50              | propanone     | 6.66              |
| 8.95              | furfural      | 5.65              |
| 9.79              | furanmethanol | 2.41              |
| 13.64             | furanmethamine| 1.06              |
| 15.25             | phenol        | 3.08              |
| 16.22             | phenol        | 1.32              |
| 16.98             | benzene       | 1.42              |
| 18.27             | guaiacol      | 1.12              |
| 18.36             | benzenediol   | 1.16              |

Table 3. LVM compounds of rice husks produced at 500 °C

| Retention (minute) | Compounds              | Concentration (%) |
|-------------------|------------------------|-------------------|
| 1.90              | Ammonia                | 2.16              |
| 2.15              | Propanone              | 1.07              |
| 2.65              | pentanone              | 1.29              |
| 2.74              | hexane                 | 4.94              |
| 2.82              | acetid acid            | 2.2               |
| 3.00              | acetid acid            | 12.85             |
| 3.52              | propanone              | 4.68              |
| 8.94              | furfural               | 5.7               |
| 9.78              | furanmethanol          | 1.96              |
| 12.69             | furancarboxaldehyde    | 1.57              |
| 13.12             | phenol                 | 2.94              |
| 14.05             | cyclopenten            | 2.61              |
| 14.59             | phenol                 | 1.47              |
| 14.96             | benzenemethanol        | 3.25              |
| 15.25             | phenol                 | 9.06              |
| 16.51             | phenol                 | 5.11              |
| 16.98             | phenol                 | 8.41              |
| 18.77             | methoxy                | 0.99              |
| 19.27             | phenol                 | 2.27              |
Table 4. LVM compounds of rice husks produced at 600 °C

| Retention (minute) | Compounds               | Concentration (%) |
|-------------------|-------------------------|-------------------|
| 1.90              | Ammonia                 | 16.67             |
| 2.73              | hexane                  | 8.34              |
| 3.01              | acetid acid             | 10.09             |
| 3.52              | propanone               | 4.16              |
| 8.94              | furfural                | 5.53              |
| 12.69             | furancarboxaldehyde     | 1.83              |
| 13.12             | phenol                  | 5.15              |
| 14.05             | cyclopenten             | 2.52              |
| 14.59             | phenol                  | 2.51              |
| 14.96             | benzenemethanol         | 5.61              |
| 15.25             | phenol                  | 10.06             |
| 16.51             | phenol                  | 7.44              |
| 16.98             | phenol                  | 10.49             |
| 18.27             | guaiacol                | 7.12              |
| 19.27             | phenol                  | 2.48              |

At pyrolysis temperature 400°C, 500°C, and 600°C there are 13, 12, and 10 compounds respectively. The type of compound varies at each pyrolysis temperature. Compounds where always present at every temperature of pyrolysis are ammonia, propanone, acetid acid, hexane, furfural, and phenol. Propanone highest abundance 6.66% at 400°C, acetid acid 15.05% at 500°C, 31.75% hexane at 400°C, and phenol 38.13% at 600°C. Unfortunately the abundance of its compounds does not show any particular tendency at any pyrolysis temperature. This is thought to be related to the temperature of the pyrolysis and the condensation system used to cause completely non-condensed smoke. The compounds appearing in LVM produced at 400°C partially reappear, partially disappearing, and there is two compounds that only appears at 500°C. Methanol, furanmethamine, and benzene only appear at 400°C. Pentanone and methoxy only appears at 500°C. Compounds at 600°C always appear at 400°C and 500°C. Hexane most abundance at temperature 400°C, meanwhile phenols are most abundant at temperatures of 500°C and 600°C. LVM of rice husk does not contain benzoapiren so that potentially is applied to foodstuffs either as food preservatives [22], fertilizers, and others.

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