Study of the physical properties of liquid smoke from cocoa rind on moisture content and different pyrolysis temperature

I Ketut Budaraga¹², Dian Pramana Putra¹
¹Faculty of Agriculture, Ekasakti University
Jalan Veteran Dalam No. 26 B Padang Sumatera Barat. 25113. Indonesia
²Corresponding author, Email: budaraga1968@gmail.com

Abstract. Cocoa is one of the flagship commodity of West Sumatera from plantation sector. Cocoa skin waste is still little in utilization. One of the utilization of cocoa fruit skin is made raw material for liquid smoke making. The purpose of this research is to know the physical properties of liquid smoke of cocoa fruit skin with different levels of water content of raw materials and the temperature of pyrolysis differently. This research has been conducted in April – May 2019. The results showed that the liquid smoke of the cocoa fruit skin at different levels of water and the temperature of pyrolysis resulted in a brownish-yellow liquid smoke color and no turbidity. The liquid smoke color is calculated based on Hue degree values. Water content of 10% at 200, 300 and 400°C temperature obtained 4.3374; 4.2635 and 4.2169 °Hue. Water content of 15% at 200, 300 and 400°C temperature obtained 4.3878; 4.3561 and 4.3342 °Hue. Moisture content of 20% at temperatures 200, 300 and 400°C obtained 4.4776; 4.4537 and 4.3342°Hue. Water content of 25% at 200, 300 and 400°C temperature obtained 4.5730; 4.5134 and 4.4829°Hue. The analysis of liquid smoke type weights are generally above the water. The weight of 10% cocoa water content in the temperature of 200, 300 and 400°C obtained 1.000963; 1.000953 dan1,00148. The weight of the cocoa content type is 15% at a temperature of 200, 300 and 400°C obtained 1.001401; 1.001677 and 1.002753. The weight of the type of cocoa skin moisture content is 20% at 200, 300 and 400°C obtained 1.004195; 1.004629 and 1,004754. The weight of the type of cocoa skin moisture content is 25% at 200, 300 and 400°C obtained 1.004288; 1.004735 and 1.005341.

1. Introduction

Liquid smoke is a chemical compound from the smoke of the results of biomass pyrolysis then condensed thereby forming fluid. The role of liquid smoke in the food industry is as preservatives (food preservative) especially anti-microbial food (antimicrobial agent) and taste givers and aromas in food products (flavouring agents). In liquid smoke contains approximately 400 chemical compounds but only about 200 types that have been identified through various studies are then grouped based on the main components of the compound's constituent such as phenolic, carbonyl and acid [1].

The raw material of liquid smoke manufacturing is sourced from different materials. Some research reports that have been done in the manufacture of liquid smoke derived from coconut shell raw materials [2]; [1]; [3], cashews bark [4], coconut fibers [2]; [5], the solid waste of palm oil (Gani et al, 2014; Oramahi et al, 2010), the nyamplung shell (Wibowo, 2012), laban's timber [6], acacia wood [7] and a rubber shell [8].

Utilization of cocoa fruit peel as a result of cocoa plantation is still very small. [9], cocoa bark can be used as a concentrated green as an antibacterial. [10], utilizing the bark of cocoa as the raw material of active carbon manufacturing. [11], utilizing the bark of cocoa as a material adsorbent rhodamine B. [12],
extreme the biologically and antioxidant components of the cocoa peel as an antioxidant and antimicrobial, [13], extracting the bark of the cocoa fruit cook and the skin of the young cocoa fruit as an antioxidant.

Nowadays there are still few reports that use cocoa peel as raw material for liquid smoke making. [14] It uses cocoa bark as raw material for liquid smoke making, but has not reported the physical properties of liquid smoke produced. Likewise, [15] The results of the research utilizing cocoa peel as raw material for liquid smoke only reported the total levels of phenol and its antibactericides. Some research results report that moisture content and pyrolysis temperature affects the physical and chemical components of the liquid smoke produced.

Based on the explanation above, researchers have conducted research on making liquid smoke using cocoa leather as raw material to utilize the waste of cocoa fruit skin that has not been utilized with different levels of moisture content and pyrolysis temperature.

2. Materials and methods
Research has been conducted in the Agricultural Technology Laboratory of Agriculture University and Laboratory of Microbiology and Biotechnology of Agricultural Products from Andalas University in April – May 2019. The study uses exploratory research plans with differing levels of raw material moisture content and the temperature of liquid smoked pyrolysis. Liquid smoke in can by using pyrolysis tools.

The material used in this research is cocoa skin that obtained from Lubuk Minturun village of Padang City which has been regulated according to treatment (10, 15, 20 and 25%) and carried out the process of pyrolysis at different temperatures (200°C, 300°C and 400°C) until the liquid smoke obtained cocoa skin, pH buffers 4 and pH 7, alcohol 96%, aquades, tissues, spray bottles and GEGEP.

The equipments used are 1 (one) set of pyrolysis, oven, colori meter (Hunter Lab), desicator, erlenmeyer 250 ml, 1000 ml cup cups, mouthpiece, picnometer 25 ml, pH meter and colori meter tool.

2.1 Making liquid smoke cocoa leather [2]
Cocoa peel weighed 48 kg and then performed a size reduction using machetes. The drying is done under the sun until it reaches the moisture content according to the treatment of 10 – 25%. It is then inserted into the pyrolysis at an initial temperature of 27 oC and closed tightly until airtight. The pyrolysis process is carried out using the temperature according to the treatment of 200, 300 and 400°C for 2-4 hours until the liquid smoke stops dripping from the pyrolisator. During the pyrolysis process, make sure that the water is flowing and the condenser spiral pipe is perfect for condensation.

2.2 Analytical procedures
The parameters observed in this study include pH value, color and weight type.

2.2.1 pH values [16]. PH-meter electrode before use is standardized using buffer solution namely acid buffer (pH 4), neutral buffer (pH 7) and buffer base (pH 10). Then cleaned using aquades and dried, the sample of liquid smoke as much as 5 mL is inserted into the Beaker glass, the pH electrode is dipped in the sample, then left until the stable readings are obtained, the pH value can be directly on a pH meter scale.

2.2.2 Color Analysis [17]. This color test is performed using the Hunterimeter ColorFlex EZ Colon tool. This tool uses white ceramic, which before the test is first calibrated. Colors can be calculated using the formula:

\[
\text{Color} = 100 - ((100-L *) 2 + A * 2 + b * 2)^{1/2}
\]

Where the values are L *, A * and b * with a value range of 0 to ± 100. L * States the Brightness (Lightness) parameter with a value of L * value of 0 means black and 100 white. The value of L * States the reflected light that produces the white, gray and black accorded color. A * represents the red – green
mixed chromatic color with a value of $+ A^*$ (positive) from 0 to +100 for the red color and the value $- A^*$ (negative) of 0 to -80 for the green color. While $B^*$ States the chromatic color of the yellow blue mixture with a value of $+ b^*$ (positive) from 0 to +70 for the yellow color and value $- b^*$ (negative) from 0 to -70 for the blue color.

2.2.3 Type weights [16]. Prepared tools and materials then the 25 ml Piknometer is cleaned with distilled water, then rinsed with alcohol. Piknometer is dried in a 100°C temperature oven for 15 minutes and then chill at room temperature. Removed the pycnometers after drying and weighed empty weight on the analytical scales record the results. Weighing is done 3 times. Inserted in the basin containing ice/cold water, empty pycnometers, until it reaches 25°C and weighed with analytical scales and recorded. Aquades is removed from the pynometer and then rinsed with alcohol 70% laudried. Fill the empty pycnometers with a sample with the corresponding volume indicated on the pycnometers. Note the weight of the samples with analytical scales. Calculated the weight of each sample type includes Aquades, by calculating the difference from the sample of the pycnometers weighing with empty piknometers.

3. Results and discussion

3.1. Liquid smoke pH value of cocoa fruit bark

The principle in testing the degree of acidity (pH) by using the pH meter equipment is a method of measuring pH based on the measurement of hydrogen ion potentiometric/electrometry using a pH-meter. Before use, the pH-meter equipment is calibrated with solution buffers according to the equipment's instructions on each measurement. The pH value of liquid smoke cocoa fruit bark tends to be acidic with differing levels of raw material moisture content and pyrolysis temperature. The pH value is one of the resulting liquid smoke quality parameters. Measurement of pH value in liquid smoke produced aims to know the level of the process of decomposition of raw materials to produce organic acids in the form of pyrolysis the liquid smoke pH value of the cocoa fruit skin is in table 1.

| Treatment               | Temperature (°C) | pH   |
|-------------------------|------------------|------|
| Water content 10%       |                  | 5.0  |
| Water content 15%       |                  | 5.1  |
| Water content 20%       |                  | 5.3  |
| Water content 25%       |                  | 5.4  |
| Water content 10%       | 200              | 5.0  |
| Water content 15%       | 300              | 4.9  |
| Water content 20%       | 400              | 4.8  |
| Water content 25%       |                  | 4.7  |
| Water content 10%       |                  | 4.7  |
| Water content 15%       |                  | 4.8  |
| Water content 20%       |                  | 4.9  |
| Water content 25%       |                  | 5.0  |

Based on table 1 shows the pH value of liquid smoke of the cocoa peel range between 4.7 – 5.4. This value belongs to the acid category. The lower the moisture content of raw materials then the lower the liquid smoke pH value of cocoa skin produced. Similarly, the temperature of pyrolysis, the higher the temperature of liquid smoke pyrolysis, the lower the pH value of liquid smoke produced by the cocoa fruit skin. This indicates that the pyrolysis process with an increasingly high temperature of up to 400°C
lasts well. This results according to the report [2] which uses liquid smoke pyrolysis temperatures up to 400°C. If low pH value means smoke produced high quality especially in terms of its use as food preservatives [18]. The low pH value overall affects the lifetime value and the shelf life of the smoke product or its organoleptic properties. Because at low pH microbes or bacteria as disruptor in the preservation process tends not to be alive and breeding well. In accordance with the explanation [19]. Measurement of pH value in liquid smoke aims to determine the level of the process of decomposition of raw materials by pyrolysis. Low pH value means smoke produced high quality especially in terms of its use as food preservatives.

Raw material water content affects the resulting liquid smoke pH value. This is in accordance with the results of the study [5] stating that the resulting liquid smoke pH value is increasing in line with the increased moisture content of cocoa berries. High moisture content in raw materials will reduce the quality of liquid smoke produced. Due to the high amount of water in the material will evaporate during pyrolysis. The resulting liquid smoke will contain a lot of water, so the quality of liquid smoke decreases. The decrease in liquid smoke will affect the acidity in the liquid smoke, so that the value of the pH rises. This acidity is derived from compounds contained in liquid smoke, especially acetic acid and other carboxylic acids [1]. The liquid smoke pH value of the research results in the same with the results of the study conducted by [20] with liquid smoke pH values ranging from 4.3 – 4.7.

3.2. Color liquid smoke cocoa skin
In general, the color of the liquid smoke pyrolysis of the cocoa skin is yellow brown. Test the color value of liquid smoke of the cocoa fruit skin using the tool Hunter Lab. The color value of liquid smoke of the cocoa fruit skin is in table 2.

| Treatment          | b* | Temperature (°C) | Hue (°) |
|--------------------|----|------------------|---------|
| Water content 10%  | 0,37| 200              | 4,3374  |
| Water content 15%  | 0,44|                  | 4,3878  |
| Water content 20%  | 0,59|                  | 4,4537  |
| Water content 25%  | 0,62|                  | 4,5730  |
| Water content 10%  | 0,44|                  | 4,2635  |
| Water content 15%  | 0,46| 300              | 4,3561  |
| Water content 20%  | 0,48|                  | 4,4776  |
| Water content 25%  | 0,49|                  | 4,5134  |
| Water content 10%  | 0,46| 300              | 4,4829  |
| Water content 15%  | 0,48|                  | 4,4196  |
| Water content 20%  | 0,48|                  | 4,3342  |
| Water content 25%  | 0,51| 400              | 4,2169  |

From table 2 above can be seen the color value of liquid smoke produced cocoa leather range between 4.2169 – 4, 5730 °Hue. Based on the above data can be known color liquid smoke of cocoa yellow brown fruit skin. The results of the study [2] gained degrees of Hue of liquid smoke from coconut shells, coconut fibers and cinnamon between 2.58 to 5.01 °Hue. The color of the liquid smoke that results in brown and clear yellow. The value B * States the chromatic color of the yellow blue mixture with a value of + b * (positive) from 0 to + 70 for the yellow color. The temperature of the liquid smoke pyrolysis affects the color of the resulting liquid smoke, the higher the pyrolysis temperature then the resulting color will be increasingly brownish yellow. The color of liquid smoke is influenced by the temperature of pyrolysis
causing degradation (cellulose, hemiselulose and lignin). This is in accordance with the results of the research conducted by [21] that the change in the temperature caused the occurrence of discoloration in liquid smoke. The higher the pyrolysis temperature then the darker the liquid smoke is produced. It is reinforced by the results of the study [2] that the longer the pyrolysis time and the higher the pyrolysis time then the color of the liquid smoke will be more brown and concentrated as well as the resulting smell stinging and sharp.

The results of this study correspond to the results of the research [22] and [23] which gets the color of the liquid smoke brownish yellow. Based on the above data can also be seen that the water content of raw materials affects the color of liquid smoke produced, the higher the water content of raw materials then the brighter (yellow) liquid smoke produced. [2] also obtained liquid smoke from various raw materials with a liquid smoke color of yellow to yellow tanned.

3.3. Weight value of liquid smoke type

Type weight is the ratio between the weight of an example with volume. In the physical properties of liquid smoke, the weight of the type does not relate directly to the low high quality of liquid smoke produced. However, this type of weight can indicate the number of components in liquid smoke. Determination of the weight of liquid smoke type is carried out using a piknometr. The weight value of liquid smoke of the cocoa skin can be seen in table 3.

| Treatment     | Tempature (°C) | Type weights |
|---------------|----------------|--------------|
| Water content 10% | 200            | 1.0096       |
| Water content 15% | 300            | 1.0167       |
| Water content 20% | 400            | 1.0275       |
| Water content 25% | 500            | 1.0386       |

Based on table 3 above can be seen the weight of liquid smoke type of cocoa fruit skin with different levels of moisture content and pyrolysis temperature. The observed weight of the pyrolysis of liquid smoke type showed that different levels of moisture affect the weight value of the resulting liquid smoke, but the difference in the weight value of the type is not much different between the water content of 10% and 25%. The type weights of the various liquid smoke samples show a not much different value i.e. ranging from 1.0096 to 1.0534.

The result of the type of weight obtained is not much different from the results of the study [2] which obtained the weight of liquid smoke ranging from 1.0167 to 1.0467. The results of this research are also almost identical with the research report [5] with the weight value of liquid smoke produced from 1.005 to 1.009. The weight value of the liquid smoke of the cocoa leather has fulfilled the quality standard of liquid smoke is large of 1.005.
4. Conclusion
From the results of the study can be concluded that the liquid smoke of the cocoa fruit skin at a level of moisture and different pyrolysis temperature results in liquid smoke brownish yellow and there is no turbidity. The liquid smoke color is calculated based on Hue degree values. Water content of 10% at 200, 300 and 400°C temperature obtained 4.3374; 4.2635 and 4, 2169° Hue. Water content of 15% at 200, 300 and 400° C temperature obtained 4.3878; 4.3561 and 4, 3342°Hue. Moisture content of 20% at temperatures 200, 300 and 400° C obtained 4.4776; 4.4537 and 4, 3342°Hue. Water content of 25% at 200, 300 and 400° C temperature obtained 4.5730; 4.5134 and 4, 4829°Hue. The analysis of liquid smoke type weights are generally above the water. The weight of 10% cocoa water content in the temperature of 200, 300 and 400 °C obtained 1.000963; 1.000953 dan1.00148. The weight of the cocoa content type is 15% at a temperature of 200, 300 and 400 °C obtained 1.001401; 1.001677 and 1.002753. The weight of the type of cocoa skin moisture content is 20% at 200, 300 and 400° C obtained 1.004195; 1.004629 and 1,004754. The weight of the type of cocoa skin moisture content is 25% at 200, 300 and 400° C obtained 1.004288; 1.004735 and 1.005341.

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