Characteristics of Physical and Chemical of Cocoa Skin Liquid Smoke (Treoboma Cacao L.) on different Moisture Content

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Characteristics of Physical and Chemical of Cocoa Skin Liquid Smoke (*Treoboma Cacao L.*) on different Moisture Content

ABSTRACT

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This study aims to determine the physical and chemical characteristics of the liquid smoke of cocoa peels at different moisture content. This study used a completely randomized design (CRD) of four levels of three replications. Observation data were analyzed by ANOVA followed by Duncan's New Multiple Range Test (DNMRT) at the level of one percent and five percent. The results showed that the moisture content of cocoa skin had a very significant effect on yield, pH and phenol from the liquid smoke of cocoa skin. The higher the cocoa skin content, the higher the yield and pH, while for total phenol, the higher the moisture content of the cocoa skin, the lower the total phenol. Furthermore, the moisture content of the cocoa skin has no effect on the specific gravity, the higher the moisture content of the cocoa skin, the lower specific gravity, the results of the study of the liquid smoke color of cocoa skin visually the color produced increases from brownish yellow to light brown. Analysis of the components of chemical compounds using GC-MS produced fifty components of chemical compounds that exist in 10 percent cocoa peel moisture content. Analysis of wavelengths of liquid smoke carbonyl groups with different moisture content using forrie transform infra red (FT-IR). The treatment of liquid smoke of cocoa bags with ten percent moisture content produced meets the quality requirements set by Japanese standard wood vinegar.

Keywords: characteristics, cocoa skin, liquid smoke

1. Introduction

Cocoa (Theobroma cacao L.) is one of the plantation commodities in Indonesia which is the biggest contributor to foreign exchange after oil palm, rubber and coffee. However, in its processing, the economic value of cocoa fruit is only located in the seeds, while the cocoa peel is a waste whose utilization is limited as fertilizer and animal feed. Even though 75% of the cocoa fruit is the skin and 25% the seeds. For the Province of West Sumatra in 2017 producing cocoa of 157,106 tons / ha kept up the third place in Indonesia.

Liquid smoke is a result of distillation or condensation from the vapors resulting from combustion indirectly or directly from materials that contain a lot of carbon and other compounds, the raw materials that are widely used are wood, oil palm humps, pulp from sawmills and others (Amritama, 2007).

Liquid smoke contains various compounds that can be grouped into groups of phenol compounds, acids and groups of carbonyl compounds. Groups of these compounds act as antimicrobials, antioxidants, flavoring and coloring. Because liquid smoke can act as an antimicrobial and antioxidant, liquid smoke can be used as a preservative (Yuwanti, 2003).

2. Materials and Research Methods

2.1.Time and place

Research has been carried out at the Agricultural Technology Laboratory of Ekasakti University, Agricultural Product Technologies of Andalas University, and Kopertis Region X Padang Laboratory.

2.2. Materials and tools

The main raw material used to determine the physical and chemical properties of liquid smoke from cocoa peels at different moisture content is the dried cocoa peel. The chemicals used in this study were: Aquades, ethanol, alcohol, Na2S2O3, H2O, NaOH 0.1 N (merck), Na2CO3 5%. Materials for testing the physical properties of liquid smoke are: Picnometer, Digital scales, Better glasses, Tissue, pH meters, 250 mL volumetric flasks, Drop pipettes, 300 ml Erlenmeyer, ovens, desiccators

The tools used to make liquid smoke are pyrolyzators. The tools used for chemical analysis are a set of Shimazu QP2010 Ultra-Chromatography-Mass Spectroscopy (GC-MS) type instruments, analytical scales and IRPretige 21 type forrie transform infra red (FT-IR)

2.3.Observation variable

In this study, observations were made on the liquid smoke of cocoa peel with different moisture content, namely physical properties: yield, pH, specific gravity and color. For analysis of chemical properties, namely: phenols, chemical compounds, liquid smoke from cacao and carbonyl shells.

3. Results and Discussion

3.1. (%) Yield

The results of variance analysis showed that the level of cocoa skin moisture content had a very significant effect (P <0.01) on the yield of the liquid smoke of the cocoa skin produced. Based on the DNMRT follow-up at the level of α = 1%, the average yield of liquid cocoa skin smoke as presented in Table 1.

Table 1. Average yield of cacao skin liquid smoke

Treatment of cocoa skin moisture content (%)	(%) yield %	
A = 10	7,62	a
B = 15	8,50	b
C = 20	14,21	c
D = 25	14,37	c
KK	5,00%	

Note: The numbers followed by the same letters have an effect that is not significantly different from the level of 1% according to the DNMRT further test.

The results of the yield analysis showed that the level of cocoa skin moisture content had a very significant effect on the yield of the liquid smoke produced by the cocoa peel. Where the yield ranges from 7.62-14.37%. This causes because the water content of the cocoa peel can affect the yield of the liquid smoke of the cocoa peel. The higher the water content of the cacao bean, the higher the yield of the yield. The yield is high because cocoa skin has a high moisture content so that more liquid smoke is produced. From this it shows that the water content of cocoa peel high in smoke quality decreases, but on the contrary the water content of cocoa skin is low, the quality of the liquid smoke produced by the cocoa skin is better.

Pamori, Efendi, and Restuhadi (2015), explained that the yield of liquid smoke produced greatly depends on the condition of the process and the type of raw material used. The difference in the content of the lignin component in the old coconut fiber and coconut shell is greater than that of the young coconut fiber, the old coconut fiber lignin is around 29.23-45.84%, the coconut shell is around 33.30%. Young coconut coir

contains lignin around 20.1%. This is what affects the amount of liquid smoke condensate produced.

pH

The results of analysis of variance showed that the level of cocoa skin moisture content had a very significant effect (P <0.01) on the pH of the liquid cocoa smoke produced. Based on the DNMRT further test at the level of α = 1%. The average pH of liquid cocoa smoke can be seen in Table 2.

Table 2. Average pH of liquid cocoa smoke

Treatment of cocoa skin moisture content (%)	pH
A = 10	2.92 a
B = 15	3.73 b
C = 20	4.24 b
D = 25	4.83 b
KK	9.84

Note: The numbers followed by the same letters have an effect that is not significantly different from the level of 1% according to the DNMRT further test.

The results of pH analysis showed that the level of cocoa skin moisture content had a very significant effect on the pH of the liquid smoke produced. The average pH of liquid smoke of cocoa skin ranged from 2.92 to 4.83. This shows that the water content of the cocoa skin is getting higher (the solution is alkaline), the higher the pH produced. The use of cocoa peel with different water content in the pyrolysis process in making liquid smoke of cocoa skin affects pH. The high moisture content of cocoa peels in the raw material will reduce the quality of the liquid cocoa smoke produced. Because the amount of water that is high in the material will evaporate during pyrolysis, so the liquid smoke produced will contain a lot of water. So that the quality of liquid smoke will affect the level of acidity in the liquid smoke of the cocoa skin so that the pH value increases. This acidity level tastes from the compounds contained in cocoa skin fumes, especially other acetic acid and carboxylic. The pH produced meets the requirements of liquid smoke quality according to the Japanese wood vinegar standard, which is 1.5-3.7.

Pamori, Efendi, and Restuhadi (2015), explain the pH value of liquid smoke is also related to the high and low total titrated acid. The high total titrated acid then the pH of liquid smoke becomes low as well as vice versa the lower the total acid is titrated, the pH of liquid smoke becomes high. This is because coconut fiber has components such as hemicellulose and cellulose which when decomposed will produce organic acid compounds such as acetic acid. Acetic acid is an easily dissolved solvent with water.

Specific gravity

The results of variance analysis showed that the level of cocoa peel moisture content had no significant effect (P <0.05) on the specific gravity of liquid cocoa skin smoke produced so that the DNMRT follow-up tests were not carried out. in Table 3.

Table 3. Average density of liquid cocoa skin smoke

Treatment of cocoa skin moisture content (%)	Specific gravity
A = 10	1.039
B = 15	1.021
C = 20	0.965
D = 25	0.933
KK	27.78%

Note: The numbers followed by the same letters have an effect that is not significantly different from the 5% level according to the DMRT test.

The results of specific gravity analysis showed that the level of cocoa peel moisture content had no significant effect on the specific gravity of the liquid smoke of the cocoa skin produced. The average density of the liquid smoke of cocoa skin produced ranges from 0.933-1.039. The higher water content of cocoa peel in the manufacture of cacao skin liquid smoke affects the specific gravity produced which causes the lower the specific gravity of the liquid smoke of cocoa skin. The use of cocoa skin with different moisture content in the pyrolysis process in making liquid smoke affects the specific gravity produced. Due to the lower water content of cocoa skin liquid smoke produced less while the resulting tar is more so that it affects the specific gravity of the liquid asp of cocoa skin but on observing the specific gravity of liquid smoke the cocoa skin is allowed to stand for a week so that the specific gravity is not too influence on the specific gravity of liquid cocoa skin smoke. So the results of observations on the specific gravity of cacao skin liquid smoke from pyrolysis showed that the types of samples with different water content affect the value of density not much different from the water content of cocoa skin 10%, 15%, 20% and 25%. Specific gravity meets the quality requirements of liquid smoke according to the standard Japanese wood vinegar maximum> 1.005.

Specific weight is the ratio between the weight of an example and its volume. In the physical properties of liquid smoke, specific gravity is not directly related to the high and low quality of liquid smoke produced. But specific gravity can show the number of components present in liquid smoke. Determination of liquid smoke specific gravity was carried out using the piknometer tool (Sutin, 2008).

Color

From the results of observing the colors in plain view (visual) shows the skin moisture content of cocoa smoke from cocoa skin affects the color produced. For the water content of 10 cacao peels and 15% liquid smoke the cocoa skin produced is brownish yellow and for treatment 20 and 25% of the liquid smoke of the cocoa skin produced is light brown. Because the skin moisture content of cocoa is very influential on the color of liquid smoke produced the darker the color of the liquid smoke of the cocoa cocoa skin produced so that the content of the ingredients used is lower.

Table 4. Visible color of cacao skin liquid smoke

Treatment of cocoa skin moisture content (%)	Color
A = 10	Kuning kecoklatan
B = 15	Kuning kecoklatan
C = 20	Coklat terang
D = 25	Coklat terang

Total Phenol

The results of variance analysis showed that the level of cocoa skin moisture content had a very significant effect (P <0.01) on the total liquid phenol from the cacao produced. Based on the DNMRT further test at the level of α = 1%. The average total phenol of cocoa skin liquid smoke as presented in Table 8.

Table 8. Average total phenol (%) of cacao skin liquid smoke

Treatment of cocoa skin moisture content (%)	Total fenol (%)
A = 10	2.638 a
B = 15	1.616 b
C = 20	1.553 b
D = 25	1.475 b
KK	15.51%

Note: The numbers followed by the same letters have an effect that is not significantly different from the level of 1% according to the DNMRT further test.

The results of the total phenol analysis showed that the level of cocoa peel moisture had a very significant effect on the total phenol of the cacao skin liquid smoke produced. The average total phenol of liquid smoke of cocoa peel ranges from 2.638 to 1.475%. The higher water content of cocoa peel in the manufacture of cacao skin liquid smoke affects the total phenol produced. This shows that the higher the water content of cocoa skin the lower the total phenol value produced. The use of cocoa skin with different water content and pyrolysis temperature in the manufacture of cacao skin liquid smoke affects the total phenol produced. The difference in the total value of phenol in each treatment of the liquid smoke of the cocoa skin was influenced by the water content of the raw material of the cocoa skin. The water content in the skin of the cocoa will evaporate at a temperature of 100oC and experience condensation of water vapor through the condenser. The liquid smoke condensate produced from the cacao pyrolysis process contains a lot of water, as a result the resulting phenol compounds are mixed with water so that the quality of liquid smoke decreases.

(Anon, 2005) states that water content that is too high will reduce the quality of liquid smoke produced because of the mixed results of water vapor condensation and reduce phenol levels. Phenol levels when associated with pH and total acid titrated in liquid smoke in each treatment obtained a relationship, namely the higher the phenol content in liquid smoke, the lower the pH value produced, mean the total acid titrated liquid smoke will be higher, and vice versa if the phenol level is low, the pH becomes high and the total titrated acid becomes low.

Analysis of Cocoa Skin Liquid Chemical Compound Components

The results of the analysis of the chemical compounds components of cacao liquid smoke by Gas Chromatography-Mass Spectroscopy (GC-MS) analyzed were treatment A (10% cocoa peel moisture content). because good quality smoke is found in liquid smoke with treatment A (10% cocoa peel moisture). The best quality is seen from the yield, pH, density and color with Japanese wood videgar (Yatagai, 2002). In liquid smoke with a treatment of 10% water content identified 50 chemical components can be chosen in Figure 2.

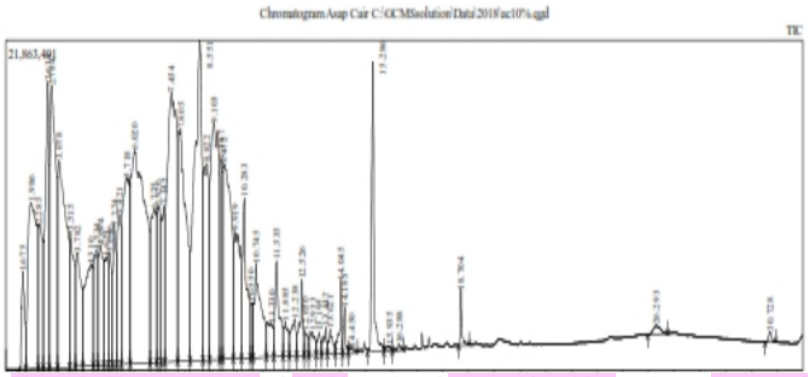

Figure 2. Chromagtogram of liquid smoke of cocoa skin with a moisture content of 10%

The results of the analysis of the Chemical Liquid Smoke Compound of Cocoa by Gas Chromatography - Mass Spectroscopy (GC-MS) produced 50 chemical components with 6 groups of chemical groups namely phenol, sirigol acid and carbonyl, alkyl esters, ketones, and acetic acid. the first group of phenol compounds with a peak area of 14.13%. The highest kotomogram peak phenol is Phenol, 2,6-dimethoxy- with a concentration of 1.24%. the two syringols with a peak area of 3.19%. The highest cyanomogram peak is at 2-Propanone, 1- (4-hydroxy-3 methoxyphenyl) - with a concentration of 2.59%. The third group is acid and carbonyl with a peak area of 25.01%. The highest peak area for acid and carbonyl is compound 9,12-Octadecadienoic acid (Z, Z) - with a concentration of 4,72%. The fourth group of alkyl esters with a peak area of 11.56%. The highest peak area on alkyl ester is 1,2-Benzenediol with a concentration of 4,41%. The fifth group of ketones with peak area was 19.7%. The highest peak area is 2.53%, namely -Penten-2-ynylamine, N, N, 4-trimethyl-. The sixth acetic acid with a peak area of 26.13%. The highest peak in acetic acid was 3.83% concentration, 11-Oxadispiro [4.0.4.1] undecan-1-one. This shows that cocoa skin has flavonide compounds so that the liquid smoke produced contains antioxidants so that the chemical compounds of liquid cocoa smoke are detected by GC-MS with the highest kotomogram, phenol.

This shows that the liquid skin of cocoa produces 50 chemical components with 6 groups of chemical groups, namely phenol, sirigol acid and carbonyl, alkyl esters, ketones, and acetic acid. This is because the most curing component of cacao skin is lignin. Because lignin compounds are an important role in liquid smoke. The results of the analysis also showed that Policyclyc Aromatic Hydrocarbon (PAH) compounds including benzo [a] pyrene were not found in the liquid smoke of this cocoa skin.

The results of the analysis of chemical compound components by GC-MS, the component with the highest percentage of phenol yairu with a concentration of 5.24% and for the largest chemical component found in the class of acetic acid compounds, namely 14 # speaker area. The results showed that the temperature of pyrolysis affected the chemical components of liquid smoke (Sihah, Wu, Huang, and Lin, 2006).

Chemical components of rubber seed shell liquid smoke using GC-MS (Gas Cotomography-Mass Spectrocopy) was detected consisting of 20 kinds of chemical compounds. The most dominant compounds were acetic acid, phenol, 2-methoxy 4-methyl, and 2-furancarboxaldehyde with the respective percentages of 45.382%, 14.382%, 11.224%, and 7.972% (Luthfiyah, 2017).

Carbon

The results of analysis with IRPretige 21 type forrie transform infra red (FT-IR) of cocoa skin liquid smoke determine the wavelength of the liquid smoke cacao carbonyl group with different moisture content. To see the wavelength of the liquid smoke carbonyl of cocoa skin with a moisture content of 10%, 15%, 20% and 25% can be seen in the Figure below.

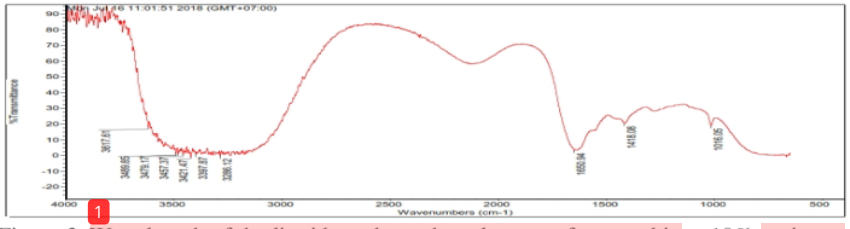

Figure 3. Wavelength of the liquid smoke carbonyl group of cacao skin at 10% moisture content

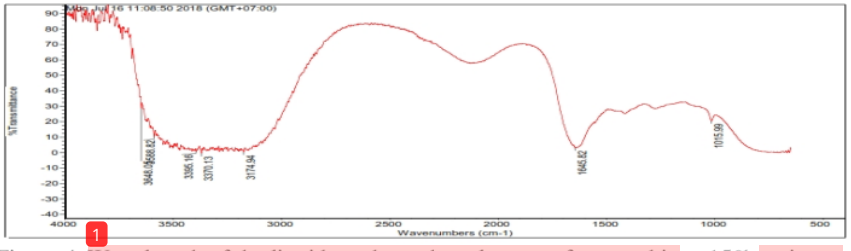

Figure 4. Wavelength of the liquid smoke carbonyl group of cacao skin at 15% moisture content

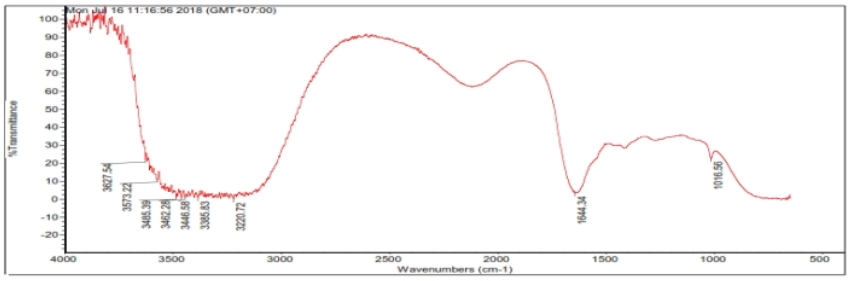

Figure 5. Wavelength of the liquid smoke carbonyl group of cacao skin at 20% moisture content

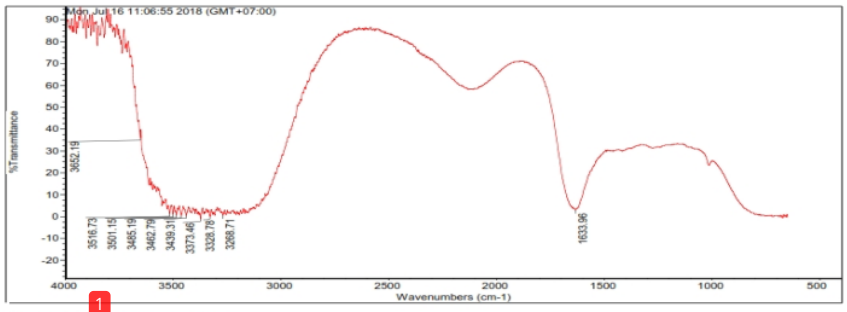

Figure 6. Wavelength of the liquid smoke carbonyl group of cacao skin at 25% moisture content

The results of analysis with the forrie transform infra red (FT-IR) cocoa skin liquid smoke determine the wavelength of the liquid smoke carbonyl group of cacao skin with different moisture content. the wavelength of the cacao skin liquid smoke carbonyl group at a moisture content of 10% uptake of 3498.85-3617.61 cm-1 the presence of OH (alcohol, phenol) compounds and uptake of 1418.16-1650.94 cm-1 presence of C = C (aromatic). the wavelength of the cacao skin liquid smoke carbonyl group at 15% moisture content uptake of 3174-3648.05 cm-1 is the presence of O-H compound (carboxylic acid). the wavelength of the cacao skin liquid smoke carbonyl group at a moisture content of 20% uptake of 3220,72-3627,54 for the presence of O-H compounds (corboxylic acids). And the wavelength of the liquid smoke carbonyl group of cacao skin at 25% moisture content at wave 1633.96 C = C (aromatic) and on absorption waves 3268.71-3516.73 N-H (amine). The presence of aromatic, amine alcohol, phenol and carboxylic acids due to FT-IR analysis of cacao skin liquid smoke shows that polymerisation of hemicellulose cellulose and hemicellulose occurs in the wavelength of the carbonyl group.

From the results of physical and chemical research conducted on liquid smoke samples from the skin pyrolysis of cacao (treobroma cacao L.) with different moisture content, namely 10%, 15%, 20%, and 25%. The fact that the liquid smoke properties that enter the Japanese standard is pH with 10% skin moisture content which is 2.93, specific gravity with 10% moisture content which is 1.039 and specific gravity with 20% cocoa peel moisture content which is 1.021. Then the brownish yellow color is obtained at the water content of 10 cocoa skin and 15% brownish yellow. Whereas for phenol, carbonyl and yield, it has not met Japanese standards because the liquid smoke produced is still grade 3.

Table 5. Results of physical and chemical properties of liquid smoke of cocoa peels with different moisture content

Parameter	10%	15%	20%	25%	Standard Jepang
Total Fenol	2,638%	1,616%	1,553%	1,475%	-
Karbonil	-	-	-	-	-
Rendemen %	7,62%	8,50%	14,21%	14,37%	-
pH	2,93	3,73	4,24	4,83	1,5-3,7
Berat jenis	1.039	1,021	0,965	0,933	>1,005
Color	Yellow Brownis	Yello Brownis	Light brown	Light brown	Yellow brownis

Source : yatagai, (2002)

4.Conclution

The results of the physical properties of the liquid smoke of cocoa peels with different moisture content of cocoa peels gave a very significant different effect on yield and pH, but it was not significantly different from the specific gravity of the liquid smoke of cocoa skin. The resulting color increases from yellow to tan to light brown. The best liquid smoke from cocoa peel with Japanese standard quality was obtained from the treatment of 10% cocoa skin liquid smoke with pH 2.93, specific gravity 1.039 and in brownish yellow color.

The results of analysis of cocoa skin liquid smoke climax on total phenol gave a very significant different effect, for analysis by GC-MS analyzed 50 chemical components and six groups of chemical groups namely phenol, syringol, acid carbonyl, alkyl esters, ketones, and acetic acid and spectrophotometer analysis IR obtains the wavelength of the cacao skin liquid smoke carbonyl group with different cocoa skin moisture content.

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