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Characteristics of the liquid chemical properties of cocoa skin [*Theobroma cacao L.*] in different water levels

Characteristics of the liquid chemical properties of cocoa skin [*Theobroma cacao L.*] in different water levels

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Abstract. Cocoa is one of Indonesia's mainstay plantation commodities that have a large amount of production. The amount of cocoa production produces cocoa skin waste products that have not been used optimally. Cocoa skin is known to contain cellulose, hemicellulose and lignin compounds which can be processed into liquid smoke. This study aims to determine the characteristics of the chemical properties of liquid cocoa smoke in different moisture content. This study used a completely randomized design [CRD] of four levels of moisture content 10%, 15%, 20% and 25% with 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 skin moisture content of cocoa had a very significant effect on pH and phenol from the liquid smoke of cocoa skin. The higher the level of cocoa skin, the pH also increases, while for total phenol, the higher the water content of cocoa skin the lower the total phenol. Furthermore, the water content of cocoa skin does not affect the specific gravity. Analysis of chemical compound components using GC-MS was carried out on the liquid smoke of the best cocoa skin [10%] to produce fifty components of chemical compounds present in the moisture content of cocoa skin. Analysis of the wavelength of the liquid smoke carbonyl group of cacao skin with different moisture content using furrier transform infra-red [FT-IR]. The liquid smoke of cocoa skin with the treatment of ten percent cocoa peel moisture content from the pH observations fulfills the quality requirements set by Japanese standard wood vinegar.

1. Introduction

Cocoa [*Theobroma cacao* L.] is one of the plantation commodities in Indonesia, which is the largest foreign exchange contributor after oil palm, rubber, and coffee. But in the processing, the economical value of cocoa fruit only lies in the part of the seed while the cocoa skin is a waste whose utilization is limited as fertilizer and animal feed. Whereas 75% of cocoa pieces are skin and 25% seeds. West Sumatera province in 2017 is in the third-highest cocoa production in Indonesia, where is produce 157,106 tons/ha cocoa [1].

The handling of plantation waste and plantations to date is still an obstacle in the waste handling program at the farmer level. This problem is caused by several factors such as limitation of time, labor, and limitation of the disposal area. Agricultural waste and plantation especially cocoa plants have not been utilized even in some conditions have the potential to feed livestock and raw materials for the manufacture of compost, so it is necessary to do observations in supporting the program Utilization of potential waste, especially the potential waste produced by cocoa plants that are waste cocoa skin.

The skin of cocoa fruit is a lignocellulose waste that has the main components of lignin, cellulose, and hemicellulose. The cocoa peel contains cellulose 36.23%, hemicellulose 1.14% and lignin 20-27.95% [2]. Cellulose and hemicelhulose polymerized from Monosaccharides can be converted into sugars under certain conditions. Lignin is an aromatic polymer that can be converted into phenolic compounds [3]. The decomposition of lignin on cocoa skin can use the method of pyrolysis [4] into liquid smoke.

Liquid smoke is a result of distillation or condensation from the vapor combustion results indirectly or directly from materials that contain a lot of carbon and other compounds, raw materials are widely used are wood, oil palm excrescence, Sawmills and others [5].

Liquid smoke contains some compounds that can be grouped into groups of phenol compounds, acids, and groups of carbonyl compounds. The groups of compounds act as antimicrobial, antioxidant, flavoring, and color-to-color [coloring]. Because liquid smoke can act as antimicrobial and antioxidant, liquid smoke can be used as a material for wet [6].

There have been no observations of the chemical properties of the liquid smoke of cocoa bark based on different water content. The moisture content of cocoa skin as raw material for making liquid smoke determines the quality of liquid smoke produced. Based on the explanation above, the purpose of this research is to know the chemical properties of liquid smoke cocoa skin at different water levels, as well as determine the best moisture content of cocoa skin for the raw material of liquid smoke making.

2. Material and Methods

The main raw material used to determine the physical properties of liquid smoke cocoa skin at different water content is cocoa skin obtained from cocoa farmers in Padang Pariaman District [Figure 1]. Physical properties of liquid smoke testing equipment are Pycnometer, digital scales, Better glasses, Tissue, pH meter, flask 250 mL, pipette drops, Erlenmeyer 300 ml, oven, desiccator [a tool used to make liquid smoke is a pyrolysis tool [7]].

Figure 1. Cocoa Skin

This research includes making liquid smoke from cocoa skin with different water content. Determination of cocoa skin moisture content is determined by drying using the temperature of the sun at a drying temperature ranges from 30°C – 35°C. Moisture treatment includes 10%, 15%, 20%, 25% water content. The design that was used in this study was a simple complete random design [RAL] treatment with 4 treatment levels and 3 replications. Data resulted from the experiment were analyzed the variance using F-test and then continued using DNMRT at a 5% level of significance if F-test was significantly different [8].

2.1. Preparation of raw materials

For the preparation of raw materials of liquid smoke, cocoa skin is taken around the Padang Pariaman area. Cocoa skin is put aside from dirt or soil attached to the skin of cocoa. Reduction of the size of 5-9 cm using machete so that the drying process is faster. Then, cocoa skin is measure using a team of each weight that is obtained by cocoa skin samples that are 27 kg. To determine the initial moisture content of cocoa skin is done measuring material water content using Spectrometer with an initial water content obtained 80%. 6. The drying of the bark is done under the sunlight, for each of the

treatments is done differently. In the treatment A [10% cocoa skin moisture content] Seven days of drying, B treatment [cocoa water content of 15%] Six days of drying, C treatment [cocoa water content of 20%] Done drying for 4 days, and treatment D [cocoa water content of 25%] A drying period of 3 days. Then measured dry weight of the material each treatment with a spectrometer [material water content of 10, 15, 20, and 25%].

2.2. Process of pyrolysis [manufacture] liquid smoke cocoa skin

The process of making liquid smoked cocoa skin using a temperature pyrolysis 200°C [8] [9] [10]. In preparation for raw materials of cocoa skin liquid smoke, dry cocoa skin was obtained with a different water content of 10, 15, 20, and 25%. The dried cocoa skin inserted into pyrolisator for 4 hours with a capacity of 4 kg with a temperature of 400°C, for treatment A [Cocoa water content 10%], treatment B [Cocoa skin water content 15%], treatment C [Cocoa water content 20%] and in the treatment of D [cocoa water content of 25%]. Then, the burning smoke was condensated. The observation tool is done to check the condition of the appliance such as gas check, stove and pyrolisator temperature. The active charcoal bark is produced from the pyrolysis process at 200°C to produce activated charcoal and liquid smoke. Liquid smoke Grade 3 cocoa skin obtained in the process of liquid smoke pyrolysis. The liquid smoke of the cocoa skin is allowed for 1 week so that the liquid fumes with a separate cocoa skin is further filtered using a filter paper [11]. Observation of chemical properties namely pH, Total phenol [7], components of chemical compounds [GC MS], and carbonyl compounds.

3. Results and Discussion

3.1. pH

The results of the fingerprint analysis showed that the level of the cocoa water content has a distinct effect [P. < 0.05] of the resulting Cocoa smoke pH [Appendix 12]. Based on the DNMRT's advanced test of α = 5%, not all treatments show differences in cocoa smoke pH. The average cocoa smoke pH liquid can be seen in Table 1.

Table 1. The average cocoa smoke pH liquid

Cocoa Skin moisture treatment [%] pH	pH
A = 10	2.92 a
B = 15	3.73 b
C = 20	4.24 b
D = 25	4.83 b
CV	9.84

Description: Figures followed by the same letter have a distinct effect of 5% according to the DNMRT test.

Table 1 shows that the cocoa smoke pH is produced ranging from 2.92 to 4.83. DNMRT's advanced test results at the rate of 1% indicate treatment A [10% cocoa skin moisture content] Distinct with the B [15% cocoa moisture content], B treatment [15% cocoa moisture content] Does not differ real with the treatment of C [Cocoa water content 20%], the treatment of C [cocoa skin water content 20%] is no different from the real treatment D [cocoa skin water content of 25%]. The higher the water content of cocoa skin in the making of cocoa liquid smoke, the higher the pH is produced.

Based on the results of pH analysis on a sample of the highest cocoa liquid smoke skin in the treatment D [cocoa skin water content of 25%] Namely 4.83 this is due to the higher moisture content of cocoa [the solution is alkaline] then the resulting pH is higher. While the lowest value of cocoa skin liquid smoke is obtained at the treatment of A [10% cocoa skin moisture content] i.e. 2.92. The

resulting pH meets the liquid smoke quality requirements according to the Japanese wood vinegar standard of 1.5-3.7.

The use of cocoa skin with different levels in the pyrolysis process on the making of cocoa liquid fumes affects pH. The high moisture content of cocoa in raw materials will reduce the quality of liquid smoked cocoa skin. Due to the high amount of water in the material will evaporate during pyrolysis. Liquid smoke produced will contain a lot of water, so that the quality of liquid cocoa skin decreases. The decrease in the quality of cocoa liquid smoke will affect the acidity level in the liquid smoke of the cocoa skin so that the pH value rises. This acidity is derived from compounds contained in the liquid smoke of cocoa skin, especially acetic acid and other carboxylic acids.

Pamori *et al*., [12], explained the value of liquid smoke pH is also related to the high low total titration acid. The total height of the acid is titration so that the pH of liquid smoke becomes low as well as the opposite lower total acid and the liquid smoke pH becomes high. This is because coconut fiber has a component such as a hemicellulose and cellulose which when decomposition will produce organic acid compounds such as acetic acid. Acetic acid is a solvent that is easily dissolved with water. Liquid smoke produced with raw materials that have a high water content when the pyrolysis at 100°C temperature will undergo condensation when moisture through the condenser so that water will be mixed with liquid smoke. As a result, the pH value rises and the total acid levels are titration down so that the quality of liquid smoke becomes low.

3.2. Total Phenol

The results of the print analysis showed that the level of the cocoa water content has a distinct influence that is very noticeable [$P < 0.05$] to the total liquid fume phenol produced by cocoa skin. Based on the DNMRT's advanced test of $\alpha = 5\%$ It is not all the treatment shows the difference to total liquid smoked phenol of cocoa skin. The average total liquid smoked phenol of cocoa skin as presented in Table 2.

Table 2. Average total liquid smoked phenol cocoa skin

Cocoa Skin moisture treatment [%]	Total phenol [%]
A = 10	2.638 a
B = 15	1.616 b
C = 20	1.553 b
D = 25	1.475 b
CV	15.51

Description: Numbers that are followed by the same letter give a real no different influence at 5% according to DNMRT test

Table 2 shows that the total liquid smoked phenol of cocoa bark ranges from 2.638 to 1.475%. DNMRT's advanced test results at 5% indicate treatment A [liquid smoke water content 10%] Distinct from the treatment of B [liquid smoke water content 15%], treatment B [Liquid smoke moisture content 15%] Does not differ real with the treatment of C [liquid smoke moisture content 20%], Certificate C [Liquid smoke moisture content 20%] is no different from the real treatment D [liquid smoke moisture content of 25%]. The higher the moisture content of cocoa skin in the manufacture of cocoa liquid fumes affects the total phenol produced. Based on the total of the highest liquid smoked phenol cocoa skin obtained at treatment A [liquid smoke moisture content of 10%] That is 2.638% while the lowest total phenol is obtained in D treatment [liquid smoke moisture content of 25%] of 1.475%. This shows that the higher the water content of cocoa in the total value of the resulting phenol is lower.

The use of cocoa skin with different moisture content and the pyrolysis temperature in the manufacture of cocoa liquid fumes affects the total phenol resulting in decline. This decline is caused

resulting pH meets the liquid smoke quality requirements according to the Japanese wood vinegar standard of 1.5-3.7.

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The use of cocoa skin with different moisture content and the pyrolysis temperature in the manufacture of cocoa liquid fumes affects the total phenol resulting in decline. This decline is caused

by some phenolic components that have dissolved in the solvent at the previous time. The difference in the total value of phenol in each liquid fume treatment of cocoa skin is influenced by the moisture content of cocoa skin. The water content on the cocoa skin will evaporate at 100°C temperature and moisture condensation through the condenser. The liquid fume condensate produced by many cocoa pyrolysis processes a lot of water, consequently the phenol compound is mixed with water so that the quality of liquid smoke becomes decreased.

Ayudiarti and Sari [13] state that water content that is too high will reduce the quality of liquid smoke produced due to the mixing of moisture condensation results and lower phenol levels. These phenol levels when associated with pH and total acid is titration in liquid smoke in each treatment obtained the relationship is the higher levels of phenol in liquid smoke then the resulting pH value is lower, meaning the total acid titration of smoke Liquid will be higher, as well as the reverse when the phenol levels are low, the pH becomes high and the total acid titration becomes low.

Luditama [14] gets levels of phenol liquid smoke using the old coconut fiber material is about 0.89% and in the coconut shell about 1.40%. The difference in phenol levels resulting from this study is caused by the content of lignin from the smoke. Lignin is a wooden component and when decomposed will produce a phenol compound. According to Djatmiko *et al.*[15], that content lignin on coconut fruit that has been ripe about 29.2%, in crude coconut 20.1%, that coconut shell contains lignin of 33.30%. The difference in the content of lignin from the smoky material, affecting the phenol levels in the resulting liquid smoke.

3.3. Component of cocoa liquid smoke chemical compound [GC-MS]

The result of analyzing components of cocoa liquid smoke chemical compounds with Gas Chromatography-Mass Spectroscopy [GC-MS] analyzed is the treatment of A [best cocoa water content of 10%]. Because smoke with good quality is found in liquid smoke with A [10% cocoa skin moisture content] As seen on [appendix 15]. The best quality is seen from the pH parameter, with Japanese wood Videgar [16]. In liquid smoke with 10%, water content treatment identified 50 chemical components can be Views in Figure 2.

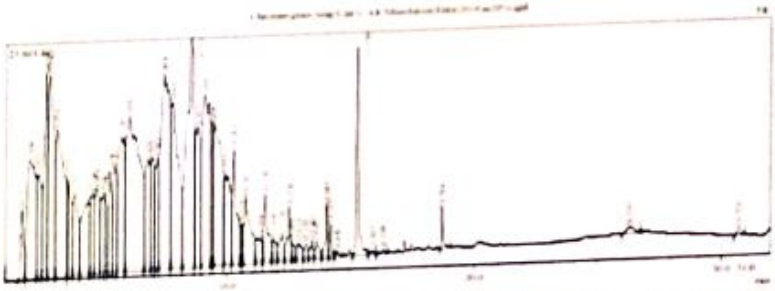

Figure 2. Chromatogram liquid smoked cocoa skin with a water content of 10%.

Luditama [14] identifies the liquid smoke component of shell and coconut fiber with temperature pyrolysis of 300 °c with GC-MS. On liquid coconut shells obtained 26 compounds with the dominant compounds of phenols [34.45%], 2.6-dimethoxy phenol [12.58%] and 2-methoxy phenol [9.81%]. While in liquid smoke coconut fiber obtained 31 compounds with the dominant compounds phenol [44.10%], 2-methoxy phenol [14.84%] and 1, 2benzenediol [7.22%].

Gani *et al.* [17] identify liquid smoke components from organic waste with a gradual extraction in its mefaction. From GC-MS obtained 61 compounds with two dominant compounds of 1.1-dimethylhydrazine [8.98%] and 2.6-methoxy phenol [8.68%]. Among the 61 compounds identified are 17 compounds and others on average 1 compound [1.6%].

From Figure 2 above, it shows that the liquid smoke of cocoa skin has 50 chemical components with 6 chemical groups that are phenol, siringol acid and carbonyl, alkyl ester, ketone, and acetic acid. Grade 3 cocoa liquid smoked chemical in the treatment of 10% water content is presented in Table 3.

Table 3. Cocoa liquid smoke Grade 3 chemical components at 10% moisture treatment

Peak#	Rtime	Peak area [%]	Component
Phenol		14.13%	
1	3.515	2.22	*Phenol*
2	4.694	1.95	*Phenol, 2-methyl-*
3	8.551	5.24	*Phenol, 2,6-dimethoxy-*
4	5.046	1.85	*Phenol, 3-methyl-*
5	5.224	2.3	*Phenol, 2-methoxy-*
6	11.885	0.57	*Phenol, 2,6-dimethoxy-4-[2-propenyl]-* .
Siringol		3.19%	
7	10.283	2.59	*2-Propanone, 1-[4-hydroxy-3methoxyphenyl]-*
8	12.238	0.6	*Ethanone, 1-[4-hydroxy-3,5dimethoxyphenyl]*
Acid and carbonil		25.01%	
9	2.285	2.35	*4-Pentenoic acid, methyl ester*
10	2.638	4.65	*Acetic acid*
11	3.078	3.4	*Butanoic acid, 4-hydroxy-*
12	4.534	1.89	*Phosphonic acid, [p-hydroxyphenyl]-*
13	5.718	3.05	*Carbamic acid, N-[2-carbamoyloxyethyl]-, 4-m*
14	11.33	0.54	*2,2-Difluoroheptacosanoic acid*
15	12.65	0.4	*3-Pyrrolidin-2-yl-propionic acid*
16	11.535	1.56	*Benzeneacetic acid, 4-hydroxy-3-methoxy-*
17	12.933	0.38	*1H-Isoindole-5-carboxylic acid, 2,3-dihydro-1,*
18	15.286	4.72	*9,12-Octadecadienoic acid [Z,Z]-*
19	18.704	0.88	*9,12-Octadecadienoic acid [Z,Z]-, 2,3-dihydrox*
20	14.045	1.19	*l-[+]-Ascorbic acid 2,6-dihexadecanoate*
Alkyl and ester		11.86%	
21	7.454	4.41	*1,2-Benzenediol*
22	9.387	3.27	*1,2,3-Trimethoxybenzene*
23	10.55	0.89	*3-Amino-4-methoxybenzamide*
24	14.183	0.73	*5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrr*

25	13.621	0.4	*2,4-Dimethoxybenzyl alcohol*
26	15.935	0.08	*Ethanol, 2-[9,12-octadecadienyloxy]-, [Z,Z]-*
27	9.919	2.08	*Xylitol, 1,5-anhydro-, triacetate*
Ketone		19.7%	
28	1.675	1.56	*2-Pentanone, 3-methyl-*
29	3.782	1.87	*2-Pentenenitrile, 4,4-dimethyl-*
30	4.31	1.64	*5,9-Dimethyl-3-decanol*
31	5.421	2.44	*2-Propanone, methyl-2-propynylhydrazone*
32	6.775	2.51	*4-Penten-2-ylamine, N,N,4-trimethyl-*
33	6.926	2.53	*Cyclopropane, 1,1,2-trimethyl-3-[2-methyl-1-p*
34	9.103	3.88	*3,6-Dimethyl-5-hepten-1-ol acetate*
35	9.472	3.18	*Pyrazole-4-carboxaldehyde, 1-ethyl-3-methyl-*
36	14.45	0.09	*9H-Pyrido[3,4-b]indole, 1-methyl-*
Acetic Acid		26.13%	
37	1.986	2.72	*Ammonium acetate*
38	2.784	4.63	*2-Tridecyne*
39	4.925	1.76	*exo-Norbornyl propionate*
40	6.02	3.49	*1,2,3-Propanetriol, monoacetate*
41	7.145	2.55	*3-Pyridinol*
42	7.805	3.82	*11-Oxadispiro[4.0.4.1]undecan-1-one*
43	8.822	3.23	*Homosalate*
44	10.745	1.54	*Diethyl Phthalate*
45	12.526	1.21	*Desaspidinol*
46	13.195	0.35	*Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3*
47	13.447	0.43	*Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3*
48	16.288	0.09	*Stigmasterol*
49	26.293	0.14	*Tricyclo[20.8.0.0[7,16]]triacontane, 1[22],7[16*
50	30.728	0.17	*E,E,Z-1,3,12-Nonadecatriene-5,14-diol*

Table 3 shows the components of the liquid smoke compound of cocoa skin, which has 50 chemical compounds. Results of GC-MS analysis on the liquid smoke treatment moisture content of 10% in the first group of phenol compounds with a peak area of 14.13%. The resulting compounds Phenol, Phenol, 2-methyl-, Phenol, 2.6-dimethoxy-, Phenol, 3-methyl-, Phenol, 2-methoxy-, Phenol, 2.6-dimethoxy-4-[2-propenyl]-. Phenol is the highest Kotomo-gram peak of Phenol, 2.6-dimethoxy- with centration of 5.24%. The highest Chromagtogram peak of Phenol as presented in Figure 3 below.

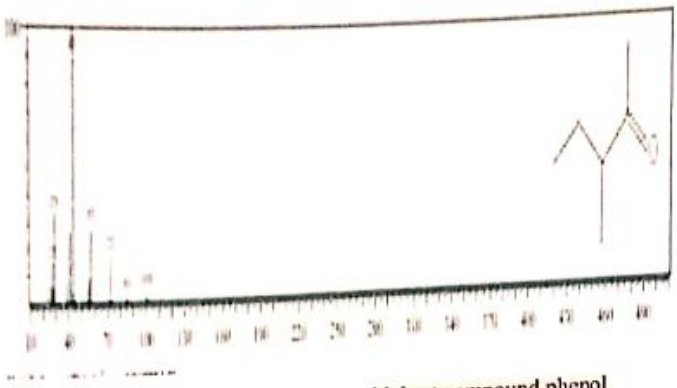

Figure. 3. Top Chromatogram highest compound phenol

The second group of Siringol with peak area 3.19% of the resulting compounds are 2-Propanone, 1-[4-hydroxy-3 methoxyphenyl]-, Etha-None, 1-[4-hydroxy-3.5 dimethoxy-phenyl]. Peak Siringol Kotomogram is the highest in 2-Propanone, 1-[4-hydroxy-3 methoxyphenyl]-with a concentration of 2.59%. The highest Chromagtogram peak of Siringol as presented Figure 4 below

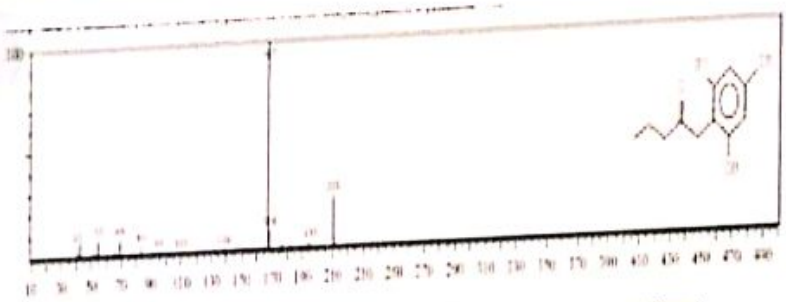

Figure. 4. Peak Chromagtogram of the highest compound siringol

The third group of acid and carbonyl with the peak area of 25.01% of the resulting compound is 4-Pentenoic acid, methyl ester, Acetic acid, Butanoic acid, 4-hydroxy-, Phosphonic acid, [P-hydroxyphenyl]-, Carbamic acid, N-[2-Carbamoylo-Xyethyl]-, 4-m, 2.2- Difluorohepta-Cosanoic acid, 3-Pyrrolidin-2-yl-propionic acid, Benzeneacetic acid, 4-hydroxy-3-methoxy-, 1H-Isoindole-5-carboxylic acid, 2.3-dihydro-1, 9.12-Octa-Decadienoic acid [Z, Z]-, 9.12-Octadecadienoic acid [Z, Z]-, 2.3-dihydro, and L-[+] -Ascorbic acid 2.6-dihexadecanoate. The highest area of the acid and carbonyl compound is 9.12-Octadecadienoic acid [Z, Z]-with a concentration of 4.72%. The highest Chromagtogram peak acid and carbonyl as presented in Figure 5 below.

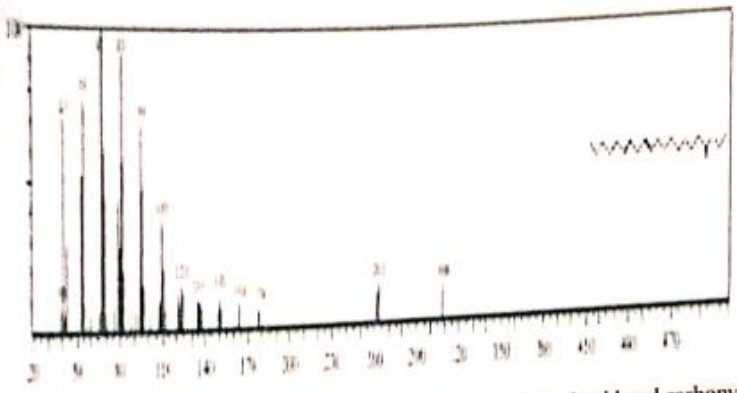

Figure. 5. Peak Chromagtogram of the highest compound acid and carbonyl

The fourth group of alkyl esters with a peak area of 11.56%. The resulting compounds are 1.2-Benzenediol, 1. 2, 3-Trimethoxybenzene, 3-Amino-4-methoxybenzamide, 5.10-Diethoxy-2. 3, 7, 8-Tetrahydro-1H, 6H-DIPYRR. 2.4 Dimethoxybenzyl alcohol, Ethanol, 2-[9.12-Octadecadienyloxy]-, [Z, Z]-, Xylitol, 1.5- Anhydro-, Triacetate. The highest area peak on the alkyl ester is 1.2-Benzenediol with a concentration of 4.41%. Peak Kromagtogram highest alkyl ester as presented in Figure 6 below.

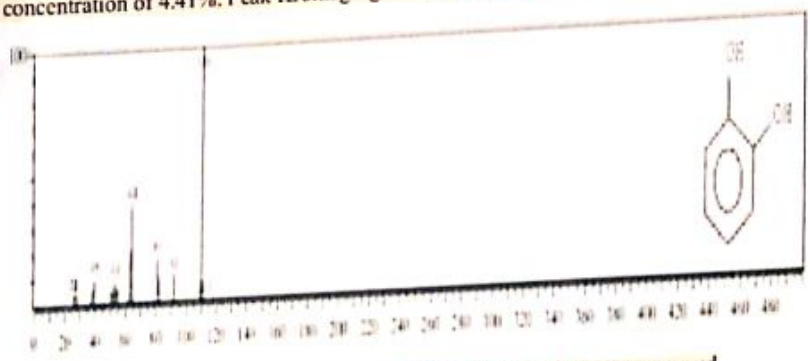

Figure 6. Top Chromagtogram of the highest alkyl ester compound

The fifth group ketone with a peak area of 19.7%. The resulting compound is 2-Pentanone, 3-methyl-, 2-Pentenenitrile, 4.4-dimethyl-, 5.9-Dimethyl-3-Decanol, 2-Propanone, methyl-2-propynylhydrazone, 4-Penten-2-Ynylamine, N, N, 4-trimethyl-, Cyclopropane, 1, 1, 2-trimethyl-3-[2-methyl-1-p, 3.6-Dimethyl-5-heptane-1-ol acetate, Pyrazole-4-carboxaldehyde, 1-ethyl-3-methyl-, 9H-Pyrido [3, 4-b] indole, 1-methyl-. The peak of the area is the highest in the 3.88% centralized concentration of 3.6-Dimethyl-5-heptane-1-ol acetate. The highest Kromagtogram peak ketones as presented in Figure 7 below.

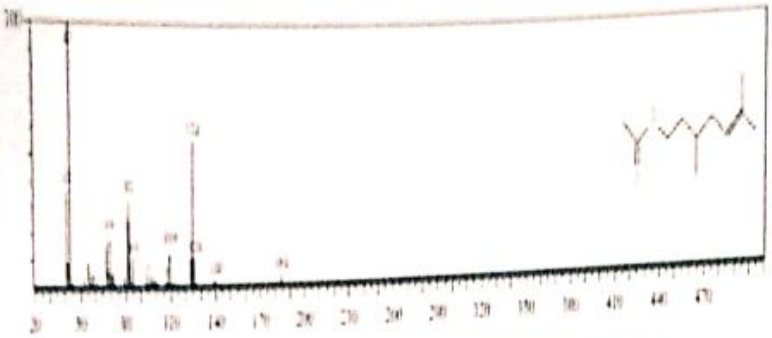

Figure 7. Peak Chromagtogram Highest ketone compounds

The sixth group of acetic acid with a peak area of 26.13%. The resulting compound is Ammonium acetate, 2-Tridecyne, Exo-Norbornyl propionate, 1, 2, 3-Propanetriol, Monoacetate, 3-Pyridinol, 11-Oxadispiro [4.0.4.1] Undecan-1-one, Homosalate, Diethyl Phthalate, Desaspidinol, Pyrrolo [1.2-a] pyrazine-1.4- Dione, Hexahydro-3, Pyrrolo [1.2-a] pyrazine-1.4-Dione, Hexahydro-3, Stigmasterol, Tricyclo [20.8.0.0 [7.16]] Triacontane, 1 [22]. 7 [16, E, E, Z-1, 3, 12-Nonadecat riene 5.14-diol. The highest peak on acetic acid is the 3.83% concentricity i.e. 11-Oxadispiro [4.0.4.1] Undecan-1-one. The highest chromatogram of acetic acid as presented in Figure 8 below.

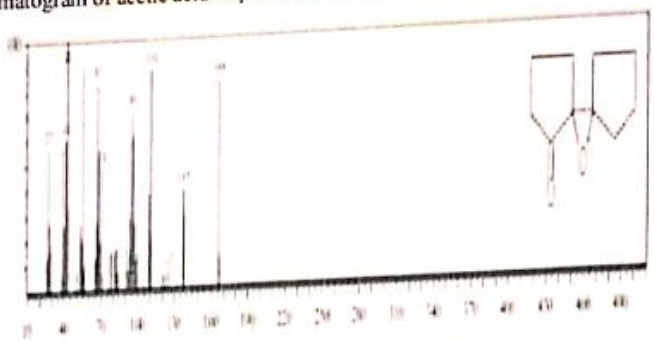

Figure 8. The highest Chromagtogram peak acetic acid compounds

This indicates that the liquid smoke of cocoa skin has been associated with 50 chemical components with 6 groups of chemicals: phenol, siringol acid and carbonyl, alkyl ester, ketone, and acetic acid. This is because most of the cocoa skin is lignin. Because lignin compounds are an important role in liquid smoke. The results of the analysis also showed that the POLICYCLYC Aromatic hydrocarbon [PAH] compounds including benzo [a] pyrene were not found in the liquid smoke of the cocoa skin.

Results of analytical components of chemical compounds with GC-MS, components with the highest percentage of phenol is 5.24% and for the most chemical components in the acetic acid, the group is 14 #peak area. The results showed that the temperature of pyrolysis affects the chemical components of liquid smoke [18].

The chemical component of rubber bean shell liquid smoke using GC-MS [Gas-spectro-Mass coffee chromatography] is detected to consist of 20 kinds of chemical compounds. The most dominant compounds are acetic acid, phenol, 2-methoxy 4-methyl, and 2-furancar-boxaldehyde with each successive percentages of 45.382%, 14.382%, 11.242%, and 7.972% [19].

3.4. Carbonyl compounds

Results of analysis with Forrier transform infrared [FT-IR] type IRPretige 21 liquid cocoa skin smoke determines the wavelength of carbonyl groups of liquid smoke cocoa skin with different water content. To see the wavelengths of the cocoa liquid smoke carbonyl with a water content of 10%, 15%, 20%, and 25% can be seen in Figures 9, 10, 11,12 below.

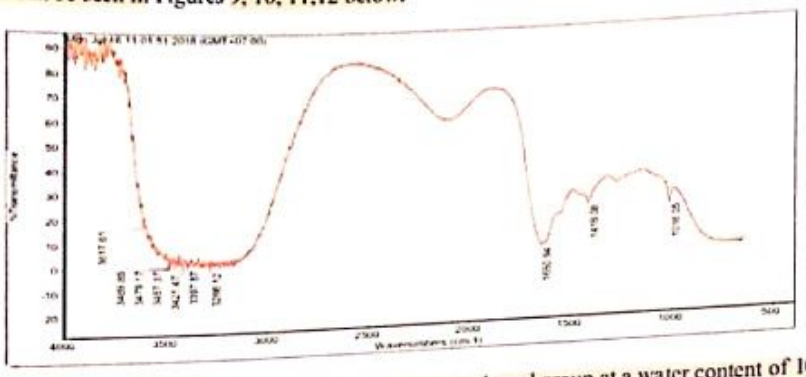

Figure 9. The wavelength of the cocoa liquid smoke carbonyl group at a water content of 10%

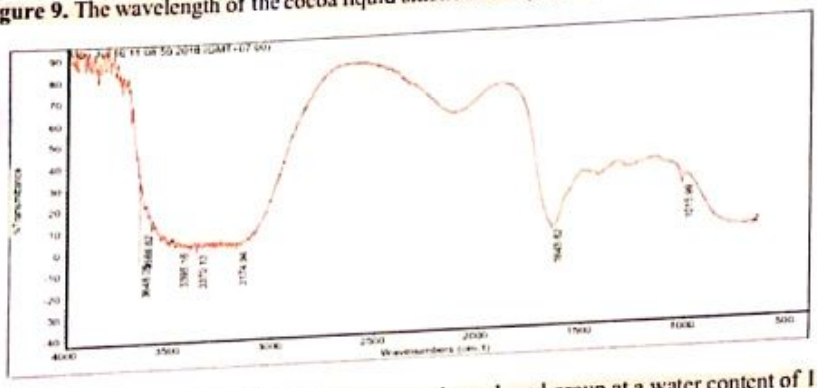

Figure 10. The wavelength of the cocoa liquid smoke carbonyl group at a water content of 15%

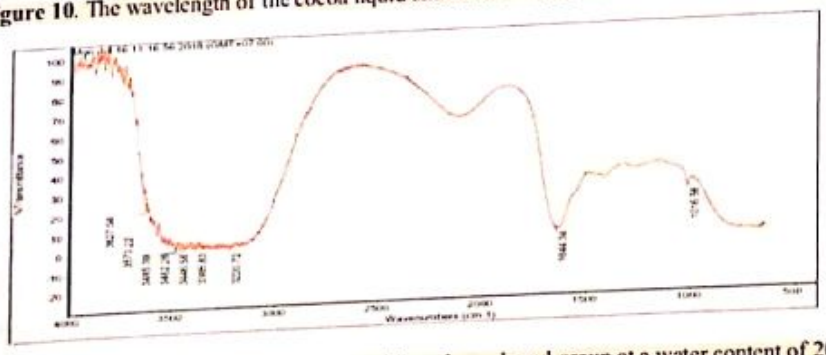

Figure 11. The wavelength of the cocoa liquid smoke carbonyl group at a water content of 20%

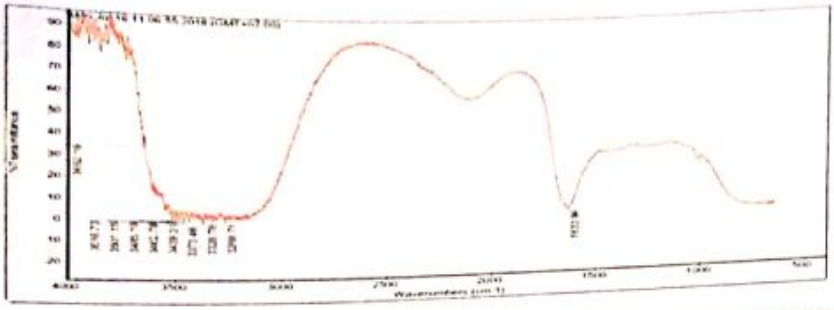

Figure 12. The wavelength of the cocoa liquid smoke carbonyl group at a water content of 25%

The result of Figure 9 shows the length of the wave group of cocoa liquid smoked carbonyl skin at a water content of 10% absorption 3498,85-3617,61 cm-1 in the presence of O-H [alcohol, phenol] and absorption 1418,16-1650,94 cm-1 of the compound C = C [aromatic]. Figure 9 shows the wavelength of the cocoa liquid smoke carbonyl group on the water content of 15% 3174-3648,05 cm-1 in the presence of O-H [carboxylic acid].

Figure 10 shows at the wavelength of the cocoa liquid smoke carbonyl group on the water content of 20% absorption 3220,72-3627,54 The presence of O-H compounds [carbolic acid]. Figure 11 shows at the wavelength of the cocoa smoke carbonyl group at a water content of 25% at a wave of 1633.96 C = C [aromatic] and on a wave of absorption 3268,71-3516,73 N-H [Amine]. The presence of aromatic compounds, alcohol amines, phenols and carboxylic acids due to the FT-IR liquid smoke cocoa analysis showed that there was the polymerization of cellulose and hemicellulose at the wavelength of carbonyl groups.

Wijaya [9] and Wiharto [10] cocoa skin showed, that there were depolymerization cellulose and hemicellulose on the number of wave 1107.14 cm-1 and the existence of C-H, lignin in the wavenumber 1730.15 cm-1. In the presence of a hydroxyl group [O-H appears on the number of waves 3441.01 cm-1 and the presence of C = C-H [Aromatic H]. In the absorption of 781,17-659,66 cm-1. Sanches et al. [20] that the FT-IR analysis for fruit waste shows 3298, 3275 and 3292 cm-1 shows the vibration of OH from alcohol and pectic acid.

From the results of physical and chemical research conducted on samples of liquid smoke pyrolysis of cocoa skin [Theobroma cacao L.] with a different water content of 10%, 15%, 20%, and 25%. The nature of liquid smoke that enters the Japanese standard is the pH with a skin moisture content of 10% namely 2.93, the weight of the type with water content 10% is 1.039 and the weight of the type with the moisture content of 20% cocoa skin 1.021. Then the brownish-yellow is obtained at 10% cocoa skin and 15% brownish-yellow. As for phenol, carbonyl and yield have not fulfilled Japanese standards because liquid smoke produced is still graded 3. The result of the physical and chemical properties of liquid smoke cocoa skin with different water content is deduced according to Table 4.

Table 4. Results of physical properties with different water content

Parameters	10%	15%	20%	25%	Japan Standard
Yield %	7.62%	8.50%	14.21%	14.37%	-
Type weight	1.039	1.021	0.965	0.933	>1.005
Colour	Brownish-yellow	Brownish-yellow	Light brown	Light brown	Yellow Brown

Source: Yatagai et al. [15]

4. Conclusion

Result of chemical analysis of cocoa liquid smoke at pH, total phenol has given a different effect very real. The results of the analysis with GC-MS analyzed 50 chemical components and six groups of chemical groups namely phenol, siringol, carbonyl acid, alkyl ester, ketone, and acetic acid. In the analysis of spectrophotometers, IR is a wavelength of carbonyl groups of cocoa fumes with different cocoa water content.

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