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Study of chemical components of liquid smoke from cocoa rind in two variations of moisture content by using GC-MS method

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Study of chemical components of liquid smoke from cocoa rind in two variations of moisture content by using GC-MS method

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Abstract. The purpose of this study was to determine the chemical components contained in cocoa smoke liquid smoke at two different moisture contents by using gas chromatography-mass spectrometry (GC-MS) method. The sample was cocoa rind with a moisture content of 10% and 25% that were hydrolyzed at 200°C. The results showed that the dominant chemical components in liquid smoke at 10% moisture content were: hexadecanoic acid (palmitic acid), butyrolactone, 2,6-dimethoxy-phenol; 5-methyl-5-hexen-3-in-2-ol and 2-methoxyphenol. While the liquid smoke at 25% moisture content contained: hexadecanoic acid (palmitic acid), octadecanoic acid, 2,6-dimethoxy-phenol, (9z)-octadec-9-enoic acid and 2-methoxy phenol. The abundance of beneficial chemical components contained, making the liquid smoke of cocoa rind has a high economic value. However, the phenol compound contained, resulting in the liquid smoke of the cocoa rind requires a further refining process.

Keywords: Cocoa Rind, Liquid Smoke, Palmitic Acid, GC-MS

1. Introduction

Cocoa farmers generally only use cocoa beans during harvesting, while cocoa rind is usually used as animal feed ingredients and the rest is left to become waste around the plantation area. Cocoa peel waste produced in large quantities will be a problem if it is not handled properly because this solid waste production reaches more than 60% of the total fruit production, this will be a great potential to pollute the surrounding environment. Therefore, there is a need for a solution, one of which is the manufacture of liquid smoke [1].

Liquid smoke can be obtained by condensing or condensing biomass from the pyrolysis process. Liquid smoke is a mixture of solutions from wood smoke suspensions in water made by condensing or condensing the results of wood pyrolysis [2]. This pyrolysis process produces gas, solids and liquid smoke. Smoke is produced by incomplete combustion which involves decomposition reactions of polymer constituents into low molecular weight organic compounds due to the influence of heat which includes oxidation, polymerization, and condensation reactions. During combustion, components of wood including cellulose, hemicellulose, and lignin will undergo the pyrolysis process to produce various compounds including phenols and their derivatives, carbonyl (ketones and aldehydes), carboxylic acids, furans, alcohols, lactones, polycyclic aromatic hydrocarbons and so on. The most important components in contributing to the smoking reaction are three compounds, namely phenol, acid and carbonyl [4].

Several studies on the production and utilization of liquid smoke have been carried out, among others: the development of liquid smoke producing devices from rice husks to produce organic insecticides [5], making liquid smoke from rubber shells as latex coagulants [6], chemical components of pyrolysis liquid smoke solid palm oil waste [7], making liquid smoke from coconut fiber with non pyrolysis technique [8], activity test and antibacterial liquid smoke originating from cinnamon bark and peanut shell [9].

Pyrolysis involves various reaction processes, namely decomposition, oxidation, polymerization, and condensation. The process that occurs during pyrolysis according to the increase in temperature is removal of water from wood at a temperature of 120-150^oC, pyrolysis of hemicellulose at a temperature of 200-250^oC, pyrolysis of cellulose at temperatures of 280-320^oC and pyrolysis of lignin at 400^oC. Pyrolysis at a temperature of 400^oC produces compounds that have high organoleptic quality and at higher temperatures a condensation reaction for the formation of new compounds and oxidation of condensation products followed by linear increases in tar and polycyclic aromatic hydrocarbons [4].

The chemical components of wood which decompose during the pyrolysis process are hemicellulose, cellulose, and lignin. Hemicellulose is the component that undergoes the earliest pyrolysis producing furfural, furan, acetic acid, and homologs. Pyrolysis of pentosan forms furfural, furans and their derivatives along with a long series of carboxylic acids. Together with cellulose pyrolysis hexose forms acetic acid and homologs. Lignin in pyrolysis produces compounds that play a role in the smell of smoke from smoked products. These compounds are phenols and phenolic ethers such as guaiakol (2-methoxyphenol) and their homologs and derivatives. The next process is cellulose pyrolysis producing acetic acid compounds, and carbonyl compounds such as acetaldehyde, glyoxal and akreolin. Lignin pyrolysis will produce phenol compounds, guaiakol, syringol together with homologs and their derivatives.

Liquid smoke has functional properties as an antioxidant, antibacterial and forming colors and distinctive taste. These functional properties are related to the components contained in the liquid smoke. Liquid smoke has the ability to preserve food ingredients because of the presence of acidic compounds, phenol derivatives, and carbonyl [3]. To produce liquid smoke that is of high quality and optimum liquid smoke yield, a pyrolycerator is needed which can increase the quantity and quality of liquid smoke.

In some situations, GC can help in identifying a complex such as liquid smoke. In gas chromatography, the mobile phase is a carrier gas, which is usually a pure gas such as helium or non-reactive, such as nitrogen gas. A stationary phase is a microscopic stage of a liquid layer or polymer that supports pure gas, in a part of glass or metal pipe system called a column. The instrument used to carry out this analysis is called gas chromatography - mass spectroscopy (GC-MS). So far there has been no study to look at the chemical components of cocoa pod liquid smoke. In this research, the chemical components of liquid smoke from cocoa peel with different moisture content than GC-MS were examined.

2. Methodology

This research was carried out by bringing raw materials from brown rind from Padang Pariaman Regency. Furthermore, the production process of brown leather liquid smoke was carried out in the mechanical engineering production laboratory of the Faculty of Engineering, Ekasakti University, and the liquid smoke maker was produced in the welding workshop which was reached in Padang City. The chemical components using the GC-MS method were analyzed in the Center Instrumentation Laboratory of the Faculty of Agricultural Technology Andalas University in May 2019.

The tools used include: thermometer IR temperature 600^oC sellery brands, brand value vacuum pumps, San-EI brand water pumps SE 125A model with pump suction power 42 liters / minute, digital scales, tools to make pyrolysis tank (pyrolyzer) namely stainless steel pan volume of 32 liters, diameter of 30 cm, height of 30 cm and thickness of 5 mm equipped with tar size 10 x 12 cm, stainless steel pipe diameter of 0.75 inches, length of 1.5 meters connecting pyrolysis tank with condenser, for condenser pipes using stainless pipes stell 0.75-inch diameter 8 meters long, there are 12 rounds of diameter 30 cm, for operation the win gas brand 0100 gas stove is used, and 2 containers of liquid smoke from plastic and glass. The material used is cocoa fruit rind with 10% and 25% moisture content as measured by the MBI-TM-20 type multi-digital moisture content measuring device. The MS GC Shimadzu brand is equipped with a carrier gas backup (injector), a place for injecting substances, columns, detectors and recording devices displayed on the computer.

The procedure for making liquid smoke starts with preparing 2 kg of raw material for cocoa fruit skin, the water content is 10% and 25%. Each raw material is first cleaned, reduced in size from 2 to 4 cm, dried in the sun, and measured in its moisture content using the MBI-TM-20 type multi-digital moisture meter. Then, the ingredients of the cocoa peel with different moisture content are inserted into the pyrolyzer and closed tightly so that the condition is completely airtight. Pyrolysis pipe joints are checked and are really strong and do not leak, and a vacuum compressor pump can work safely. Cooling water is sure enough and the water circulation pump runs smoothly. The heating source (gas stove) is turned on, while the temperature moves on the temperature gauge according to what is desired and the time of pyrolysis is noticed until the first smoke comes out and liquid smoke comes out.

During the pyrolysis process, the flowing water is sufficient and inundates the condenser spiral pipe so that the condensation process can take place perfectly. The pyrolysis process is considered complete if there is no more liquid smoke coming out from the pyrolysis tank. After the pyrolysis stage is complete, the cooling process is carried out by waiting until the temperature drops (room temperature), after the temperature drops, the lid is opened valve and activated charcoal pyrolysis results are weighed, including the volume of liquid smoke measured, tar separated by opening tar reservoir on the pyrolysis pipe and the weight of charcoal obtained. Documentation of liquid smoke making equipment can be observed in Figure 1.

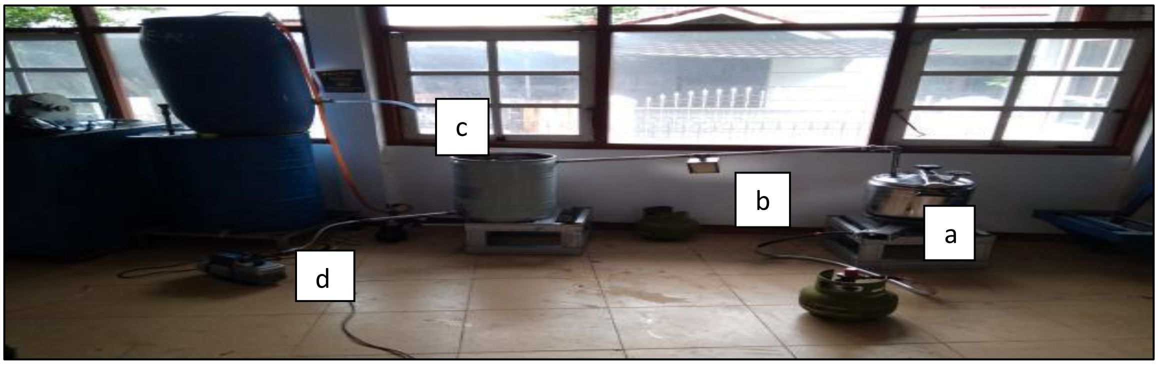

Figure 1. Construction of the liquid smoke maker: a). Pyrolysis tube b). Smoke pipe, c) Condenser, d). Liquid smoke container.

After liquid smoke with a moisture content of 10% and 20% were completed at a pyrolysis temperature of 200°C, all GC-MS equipment was prepared such as columns, detection devices, temperature, and carrier gas flow. Everything is arranged until conditions such as those printed on each monograph, a solution of a number of substances listed on each monograph are injected at the injection site using a micro-injector. Separation of components is detected and described in chromatography. The X axis in the chromatogram is expressed in retention time (time from sample injection to peak curve on the chromatogram) or retention volume (retention time x carrier gas flow rate) which is constant for each substance under a constant condition. This basis is used for identification. From the area of the curve peak or the height of the curve, the component of the substance can be determined quantitatively.

Usually GC-MS equipment before being used in the sample, there is a calibration treatment with the procedure as follows: one row of solution is made. After that, the solution is injected with the same volume into the injection site. The calibration line is drawn from the chromatogram, with the weight of the substance on the horizontal axis, and the height of the curve peak or area of the peak curve on the vertical axis. Substance solutions are made as shown on each monograph. From the chromatogram obtained with the same conditions such as how to obtain a calibration line, the area of the curve peak area or the height of the curve peak is measured. The amount of substance is calculated using a calibration line. In this way of working, everything must be done with conditions that are truly constant. The GC-MS instrument can be observed in Figure 2.

Figure 2. GC-MS instrument for analysis of chemical components of cocoa rind liquid smoke

3. Results and Discussion

Identification of liquid smoke components from cocoa peel with variations in water content was carried out using the Gas Chromatography - Mass Spectroscopy or Gas Chromatography - Mass Spectroscopy (GC-MS) method. This method can be used to identify a compound, both one component and a mixture [10]. This GC-MS method has advantages in identifying molecular structures based on fragmentation [11]. In addition to identifying, the GC-MS method also functions as a separation technique, especially for essential oils [12]. Analysis using GC-MS showed that liquid smoke from cacao rind contained 48 organic compounds for 10% moisture content and 47 organic compounds for 25% moisture content. As many as 22 compounds contained in these two variations have a percentage above 1%. Some of these components are classified as saturated fatty acids, phenolic compounds, lactone compounds, and acetic acid derivatives. In addition, from the results of GC-MS analysis, also found compounds used as food additives, namely 5-methyl-5-hexen-3-in-2-ol at 10% moisture content and 3-ethyl-2-hydroxy-2 -cyclopentene-1-on at 25%

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moisture content. Compounds contained in liquid smoke with two variations in water content, can be observed in Table 1 and Table 2.

Table 1. Chemical components with more than 1% in liquid smoke of cocoa rind with a moisture content of 10%

No	Chemical Components	Persentage (%)
1	Hexadecanoic acid ($C_{16}H_{32}O_2$)	17,70
2	Butyrolactone ($C_4H_6O_2$)	7,31
3	2,6-Dimethoxyphenol ($C_8H_{10}O_3$)	6,20
4	5-Methyl-5-hexen-3-in-2-ol ($C_7H_{10}O$)	5,43
5	2-Methoxyphenol ($C_7H_8O_2$)	4,85
6	Propylene carbonate ($C_4H_6O_3$)	4,78
7	Cyclopentanedion, 3-methyl-1,2- ($C_6H_8O_2$)	4,26
8	1,2-Benzenediol ($C_6H_6O_2$)	4,26
9	Acetamide (C_2H_5NO)	3,86
10	Acetamide, N,N-dimethyl- (C_4H_9NO)	3,51
11	Hexanoic acid, 2-methylphenyl ester ($C_{13}H_{18}O_2$)	3,43
12	2H-Pyran-2-one, tetrahydro- ($C_5H_8O_2$)	3,00
13	4-Methyl-1,2-benzenediol ($C_7H_8O_2$)	2,87
14	2,4-Hexadiene, 2,3-dimethyl- (C_8H_{14})	2,58
15	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- ($C_7H_{10}O_2$)	2,05
16	2-Methyl-2,3-divinyloxirane ($C_7H_{10}O$)	1,90
17	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- ($C_{10}H_{12}O_3$)	1,69
18	1,2-Benzenediol, 3-methyl- ($C_7H_8O_2$)	1,37
19	1,4-Benzenediol, 2-methyl- ($C_7H_8O_2$)	1,33
20	1,2-Benzenediol, 3-metoxy- ($C_7H_8O_3$)	1,18
21	2-Pentanone, 1-(2,4,6-trihydroxyphenyl)- ($C_{11}H_{14}O_4$)	1,16
22	Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	1,01

Table 2. Chemical components with more than 1% in liquid smoke of cacao rind with 25% moisture content

No	Chemical Components	Persentage (%)
1	Hexadecanoic acid ($C_{16}H_{32}O_2$)	12,30
2	Octadecanoic acid ($C_{18}H_{36}O_2$)	8,84
3	Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)	5,78
4	(9Z)-Octadec-9-enoic acid ($C_{18}H_{34}O_2$)	4,90
5	Phenol, 2-methoxy- ($C_7H_8O_2$)	4,50
6	3,5-Heptadien-2-one ($C_7H_{10}O$)	3,06
7	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- ($C_{10}H_{12}O_3$)	3,04
8	Butyrolactone ($C_4H_6O_2$)	2,87
9	3-Methyl-1,2-cyclopentanedione ($C_6H_8O_2$)	2,69
10	Benzene, 1,2,3-trimethoxy-5-methyl- ($C_{10}H_{14}O_3$)	2,25
11	1,2-Benzenediol ($C_6H_6O_2$)	2,24
12	Acetamide (C_2H_5NO)	2,23
13	Cyclopropil carbinol (C_4H_8O)	2,13
14	3-Isopropyl-5-(phenoxymethyl)-2-oxazolidinone ($C_{13}H_{17}NO_3$)	1,81
15	Phenol (C_6H_5OH)	1,69

16	1,2-Benzenediol, 3-methyl- ($C_7H_8O_2$)	1,68
17	Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)	1,63
18	2-Cyclopenten-1-one, 2,3-dimethyl- ($C_7H_{10}O$)	1,22
19	Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	1,11
20	2,5-Dimethylhydroxyquinone ($C_8H_{10}O_2$)	1,11
21	Tetradecanoic acid ($C_{14}H_{28}O_2$)	1,11
22	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy ($C_7H_{10}O_2$)	1,03

The 5 dominant compounds contained in the liquid smoke of cocoa rind with 10% moisture content were hexadecanoic acid; butyrolactone; 2,6-dimethoxyphenol; 5-methyl-5-hexen-3-in-2-ol and 2-methoxyphenol with successive retention times: 18,865 minutes; 2,829 minutes; 9,206 minutes; 2,275 minutes, and 4,551 minutes, respectively. While for liquid smoke of cocoa rind with 25% moisture content, five dominant compounds are: hexadecanoic acid; octadecanoic acid; 2,6-dimethoxyphenol; (9Z)-octadec-9-enoic acid and 2-methoxyphenol with successive retention times: 18,766 minutes; 13,791 minutes; 9,013 minutes; 13,016 minutes and 4,599 minutes. Retention time is the time needed by a compound to move through the column towards the detector. Retention time was measured based on the time at which the sample is injected until the sample shows the maximum peak height on the chromatogram of the compound. Retention time is the most important function of gas chromatography due to as a key parameter for separating, identifying and determining the number of compounds contained in a mixture [13].

The most dominant compound found in the two variations of water content was hexadecanoic acid ($C_{16}H_{32}O_2$), or often known as palmitic acid. The difference between the two variations is the percentage of the compound. For liquid smoke with a moisture content of 10%, palmitic acid has a percentage of 17.70%. While for liquid smoke with 25% moisture content, palmitic acid has a percentage of 12.30%. The percentage of palmitic acid in liquid smoke of cocoa rind with a moisture content of 10% is greater than the moisture content of 25%. This is caused by palmitic acid and water has the opposite polarity. Palmitic acid is an example of saturated fatty acids which are widely found in nature [14]. In industry, palmitic acid is widely used in the field of cosmetics and coloring. In terms of nutrition, palmitic acid is an important source of calories but has a low antioxidant power. The structural formula of palmitic acid can be observed in Figure 3. Characteristics of palmitic acid can be observed in table 3.

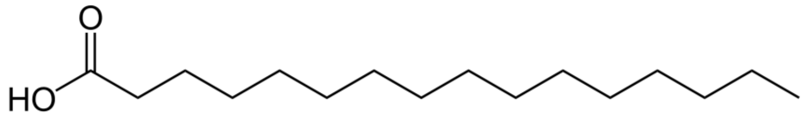

Figure 3. Formula structure of hexadecanoic acid / palmitic acid.

Table 3. Chemical and physical properties of palmitic acid.

Characteristics palmitat acid	
Chemical formula	$C_{16}H_{32}O_2$
Molar mass	256,42 g/mol
Appearance	White crystal
Density	0,853 g/mL pada 62 ^{o}C
Melting point	62,9 ^{o}C
Boiling point	351-352 ^{o}C

Another dominant compound found in liquid smoke of cocoa rind with a 10% moisture content is 2,6-dimethoxyphenol or better known as oleic acid which was a saturated fatty acid and 5-methyl-5-hexen-3-in-2-ol which often used as a food additive or food flavoring. The structure formula for 5-methyl-5-hexen-3-in-2-ol can be observed in Figure 4 and its characteristics in table 4.

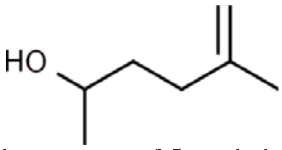

Figure 4. Formula structure of 5-methyl-5-hexen-3-in-2-ol.

Table 4. Chemical and physical properties of 5-methyl-5-hexen-3-in-2-ol.

Characteristics of 5-methyl-5-hexen-3-in-2-ol	
Chemical formula	$C_7H_{14}O$
Molar mass	110,156 g/mol
Appearance	Pale yellow liquid
Density	0,8$\pm$0,1 g/mL
Boiling point	163,2$\pm$9 ^{o}C

Whereas the other dominant compound found in liquid smoke of cocoa peel with 25% moisture content as octadecanoic acid or better known as stearic acid. This compound also includes saturated fatty acids. Stearic acid is used in making medicines. Recently, stearic acid has also been used in the development of drug delivery systems because they are considered inert, inexpensive and biocompatible, and have low toxicity [15]. In addition, stearic acid is also used as a system for carrying cyclosporine-A drugs and to cover the bitter taste of compound drugs [16][17]. The structural formula for stearic acid compounds can be observed in Figure 5 and its characteristics in table 5.

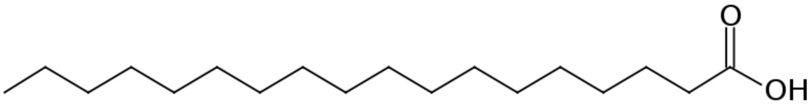

Figure 5. The structure formula of octadecanoic / stearic acid.

Table 5. Chemical and physical properties of stearic acid.

Characteristics of stearic acid	
Chemical formula	$C_{18}H_{36}O_2$
Molar mass	284,484 g/mol
Appearance	White crystal
Density	0,847 g/mL pada 70 ^{o}C
Melting point	69,3 ^{o}C
Boiling point	361 ^{o}C

Phenol compound was also contained in two variations in water content, namely: 0.84% for water content of 10% and 1.69% for water content of 25%. Phenol are corrosive compound that can cause chemical combustion in exposed skin. The percentage of phenol in liquid smoke of cocoa rind with a moisture content of 10% is smaller than 25% moisture content.

Based on the type, the compounds in the liquid smoke of cocoa rind, both with 10% and 25% moisture content, are divided into four groups, namely: aromatic compounds, carboxylic acids and esters. Classification of compounds contained in liquid smoke with variations in water content can be observed in table 6, table 7 and table 8.

Table 6 shows that the liquid smoke of cocoa rind with variations in water content contains benzene aromatic compounds and their derivatives, such as: phenols, phenolic compounds and quinones. Phenol is a compound with an OH group attached to the benzene ring. Meanwhile, phenolic compounds and quinones are phenol derivative compounds [18]. For groups of aromatic compounds, both variations in water content are dominated by phenolic compounds that can be used as medicinal ingredients.

Table 6. Aromatic compounds contained in the liquid smoke of cocoa rind with variations in water content

Cocoa rind liquid smoke	
Water content 10%	Water content 25%
2,6-Dimethoxyphenol	Phenol, 2,6-dimethoxy-
2-Methoxyphenol	Phenol, 2-methoxy-
1,2-Benzenediol	Benzene, 1,2,3-trimethoxy-5-methyl-
4-Methyl-1,2-benzenediol	1,2-Benzenediol
1,2-Benzenediol, 3-methyl-	Phenol
1,4-Benzenediol, 2-methyl-	1,2-Benzenediol, 3-methyl-
1,2-Benzenediol, 3-methoxy-	Phenol, 4-ethyl-2-methoxy-
Phenol, 2-methoxy-4-methyl-	Phenol, 2-methoxy-4-methyl-
Phenol	2,5-Dimethylhydroxyquinone

Table 7 shows compounds classified to carboxylic acids and their derivatives. Carboxylic acid compounds that dominate liquid smoke with two variations of water content were saturated fatty acids, namely: hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), (9Z)-octadec-9-enoic acid (oleic acid) and tetradecanoic acid (myristic acid). In addition, the two variations also contain acetamide which is a derivative of acetic acid. The liquid smoke of cocoa rind with 25% moisture content has more saturated fatty acids than liquid smoke from cocoa rind with a moisture content of 10%.

Table 7. Carboxylic acid compounds contained in the liquid smoke of cocoa rind with variations in water content

Cocoa rind liquid smoke	
Water content 10%	Water content 25%
Hexadecanoic acid	Hexadecanoic acid
Acetamide	Octadecanoat acid
Acetamide, N,N-dimethyl-	(9Z)-octadec-9-enoic acid
	Acetamide
	Tetradecanoic acid

The group of ester compounds contained in liquid smoke with two variations in water content can be observed in table 8. The group of ester compounds contained in the two variations were lactone compounds and fatty acid esters. Lactone compounds are cyclic esters which are condensation products of alcohol and carboxylic acids in the same compound. Lactone compounds contained in liquid smoke with two variations of water content are butyrolactone. However, liquid smoke with a water content of 25% contains other lactone compounds, namely 3-Methyl-1,2-cyclopentanedione or better known as maple lactone. Lactone compounds are commonly used in the food industry as the aroma of various foods and fruits [19]. In addition, lactone compounds are also used in other fields, for example, as precursors in the production of biodegradable polyesters such as polycaprolactone (PCL) because of their suitable properties [20].

Table 8. Esters contained in the liquid smoke of cocoa peel with variations in water content

Cocoa rind liquid smoke	
Water content 10%	Water content 25%
Butyrolactone	**Butyrolactone**
Propylene carbonat	3-Methyl-1,2-cyclopentanedione
Hexanoic acid, 2-methylphenyl ester	Hexadecanoic acid, methyl ester
Butiric acid, 2,2-dimetil-, vinyl ester	
Hexadekanoic acid, methyl ester	

The fatty acid ester compounds contained in liquid smoke with two variations of water content are hexadecanoic acid, methyl ester or better known as methyl palmitate. Methyl palmitate belongs to fatty acid methyl esters (FAME) compounds. Methyl palmitate is one of the main components of biodiesel fuel [21]. Biodiesel is a fuel consisting of monoalkyl esters of long chain fatty acids derived from vegetable oils, animal fats, or mixtures thereof. Biodiesel is produced by transesterification of triglycerides with short chain alcohols, usually methanol or ethanol, in the presence of a catalyst, which leads to the formation of a mixture of fatty acid methyl ester (FAME) or fatty acid ethyl esters (FAEE) [22][23][24]. In addition to methyl palmitate, liquid smoke with a 10% moisture content also contains other fatty acid esters, such as: hexanoic acid, 2-methylphenyl ester (methyl hexanoic) and butyric acid, 2,2-dimethyl-, vinyl ester (vinyl 2,2-dimethylbutanoic).

4. Conclusion

The biggest component in the liquid smoke of cocoa peel both with 10% and 25% moisture content is hexadecanoic acid or better known as palmitic acid which is widely used in the field of cosmetics and dying. In addition there are also components that can be used as food additives, both in liquid smoke with 10% moisture content and 25% moisture content. The phenolic compounds contained can act as scents that are typical of food and drink, as well as antioxidants. Because of many useful chemical components contained, the liquid smoke of cocoa rind has a high economic value. However, the phenol compound contained in it, result in the liquid smoke from the cocoa rind requires further refining processes.

5. References

[1] Harsini and Susilowati Pemanfaatan kulit buah kakao dari limbah perkebunan kakao sebagai bahan baku pulp dengan proses organosolv 2010 *J. Ilmu. Tek.. Lingkungan* **2**(2) 80–89
[2] Darmadji P 1996 Aktivitas antibakteri asap cair yang diproduksi dari bermacam-macam limbah pertanian Laporan Penelitian Mandiri, DPP-UGM **16** 19–22
[3] Darmadji P 2002 *Optimasi pemurnian asap cair dengan metode redistilasi* Proseding Seminar Nasional PATPI
[4] Girrard J P 1992 *Technology of meat and meat product* (New York: Ellis Hardwork)
[5] Putri, R E, Mislaini and Lisa S N Pengembangan alat penghasil asap cair dari sekam padi untuk menghasilkan insektisida organik 2015 J. Tek. Pertanian Andalas **19**(2) 30–36
[6] Prasetyowati, Hermanto M and Salman Farizy S Pembuatan asap cair dari cangkang buah karet sebagai koagulan lateks 2014 *J. Tek. Kim.* **20**(4) 14–21
[7] Haji A G Komponen kimia asap cair hasil pirolisis limbah padat kelapa sawit 2013 *J. Rekayasa Kim. dan Lingkungan* **9**(3) 109–116
[8] Feti F Komposisi dan aktivitas antibakteri asap cair sabut kelapa yang dibuat dengan teknik pembakaran non pirolisis 2011 *Agritech* **31**(4): 305–311
[9] Yefrida, Aprilina F, Leone I T, Refilda and Salim M Uji aktivitas anti bakteri asap cair yang berasal dari batang kayu manis dan kulit kacang tanah 2009 *J. Ris. Kim.* **2**(2) 190–194
[10] Sastrohamidjoyo H 1985 *Spektroskopi* (Yogyakarta: Liberty)

[11] Harbone J B 1987 *Metode Fitokimia. Penuntun Cara Modern Menganalisis Tumbuhan 2* (Bandung: ITB)
[12] Marriot P J, Shellie R and Cornwell C Review: gas chromatographic technologies for the analysis of essential oils 2001 *J. of Chromatography A* **936**(1) 1–22
[13] Etxebarria N, Zuloaga O, Olivares M, Bartolomé L J and Navarro P Review: retention-time locked methods in gas chromatography 2009 *J. of Chromatography A* **1216**(10) 1624–29
[14] Winarno F G 2004 *Kimia Pangan dan Gizi* (Jakarta: PT Gramedia Pustaka Utama)
[15] Killen B U and Corrigan O I Factors influencing drug release from stearic acid based compacts 2001 *Int. J. of Pharm.* **228**(1-2) 189–198
[16] Zhang Q, Yie G, Li Y, Yang Q and Nagai T Studies on the cyclosporine A loaded stearic acid nanoparticles 2000 *Int. J. of Pharm.* **200**(2): 153–159
[17] Robson H J, Craig D Q M and Deutsch D. An investigation into the release of cefuroxime axetil from taste-masked stearic acid microspheres. Part I: The influence of the dissolution medium on the drug release profile and the physical integrity of the microspheres 1991 *Int. J. of Pharm.* **190**(2) 183–192
[18] Fessenden R J and Fessenden J S 1992 *Kimia Organik Jilid 1 Edisi Ketiga* (Jakarta: Erlangga)
[19] Berger R G 2007 *Flavours and Fragrances Chemistry, Bioprocessing and Sustainability* (Berlin: Springer)
[20] Ravotti R, Fellmann O, Lardon N, Fischer L J, Stamatiou A and Worlitschek J Investigation of lactones as innovative bio-sourced phase change materials for latent heat storage 2019 *Molecules* **24**(7) 1300
[21] Knothe G "Designer" Biodiesel: Optimizing fatty ester composition to improve fuel properties 2008 *Energy Fuels* **22**(2) 1358–64
[22] Knothe G, Gerpen J V and Krahl J 2005 *The Biodiesel Handbook* (Champaign: AOCS Press)
[23] Pandey A 2009 *Handbook of Plant-based Biofuels* (Boca Raton: CRC Press Taylor & Francis Group)
[24] Pratas M J, Freitas S, Oliveira M B, Monteiro S C, Lima A S and Coutinho J A P Densities and Viscosities of Fatty Acid Methyl and Ethyl Esters 2010 *J. of Chem. & Engineering Data* **55**(9) 3983–90

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