

Utilization of Liquid Smoke from Cocoa pod husk (*Theobroma cocoa* L) for Germination of Red Seed (*Capsicum annum* L)

Sriharti^{1,*}, Ashri Indriati¹, Savitri Dyah²

¹ Research Center for Appropriate Technology – Indonesian Institute of Sciences
Jl. KS. Tubun No. 5 Subang – West Java Indonesia

² Research Center for Policy and Management of Science, Technology and Innovation-Indonesian Institute of Sciences
Add.: PPKMI-LIPI, Jl. Gatot Subroto No. 10- Jakarta Selatan 12710 - Indonesia

*Corresponding author's email: srihartitriyasa [AT] gmail.com

ABSTRACT—Research has been carried out on the use of cocoa pod husks for making liquid smoke. Liquid smoke is the result of condensation from direct or indirect combustion vapors from materials that contain lignin, cellulose, hemicellulose and other carbon compounds. This research was conducted to determine the effect of liquid smoke from cocoa pod husk on the germination of red chilli seeds (*Capsicum annum* L). The first stage of this research is the manufacture of liquid smoke from the cocoa pod husk using pyrolyzer. The resulting liquid smoke is subjected to chemical and physical quality testing, and is applied as a liquid fertilizer for red chilli seeds (*Capsicum annum* L). The test results of making liquid smoke from the cocoa pod husk showed that the yield of liquid smoke produced was 19%. The results of the analysis of the chemical quality of liquid smoke in the third grade by using GCMS detected 30 chemical components, the main component as a liquid smoke characteristic is acetic acid, phenol, carbamic acid compounds. The results of the physical quality analysis of liquid smoke show a very strong smell, reddish brown, and black sediment in the form of tar. The results of the testing of liquid smoke on the germination of red chilli seeds showed that the concentration of liquid smoke (0%, 0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4% , 4.5% and 5%) have a very significant effect on the maximum growth potential and germination of red chili seeds (*Capsicum annum* L).

Keywords— Cocoa pod husk, germination seed, liquid smoke, red chilli seeds

1. INTRODUCTION

Cocoa (*Theobroma cacao* L.) is one of the plantation crops that have economic value high enough to be developed and one of the export commodities that have the potential to produce foreign exchange. Indonesia is the third-largest producer of cocoa in the world after Ghana and Ivory Coast. Cocoa production in Indonesia in 2018 amounted to 828,247 tons, from a total plantation area of 959,000 ha [1].

Cocoa fruit consists of pod shell (epicarp, mesocarp and endocarp) pulp/mucilage, beans (bean shell and been) and placenta (Figure 1). Cocoa pod husk is the mesocarp or part of the wall of the cocoa fruit that covers the outer shell until the meat is finished before the seeds. Cocoa pod husks are the largest part of cocoa fruits. Fresh cocoa fruit consists of 75.67% fruit skin, 21.74% seeds (generally in one cocoa fruit consisting of 30-40 grains and 2.59% placenta (which is the epidermis covering cocoa beans [2]. Cocoa pod husk is the outer shell that covers the cocoa beans with a rough, thick and hard texture. Cocoa pod husks are lignocellulosic wastes which contain the main components of lignin, cellulose and hemicellulose, and a small portion consists of phenolic compounds, tannins and purine alkaloids [3], whereas according to Kusuma et al in Yumas, M. (2017) contain flavonoids, terpenoids / steroids, condensed or polymerized tannins such as catechins and anthocyanins [4]. Cocoa pod husks contain 31.25% cellulose, 48.64% hemicellulose and lignin 20.11% [5]. The existence of fruit husk has not been used optimally, sometimes it is left just like plantation waste, and some are even thrown or spread around cocoa trees.

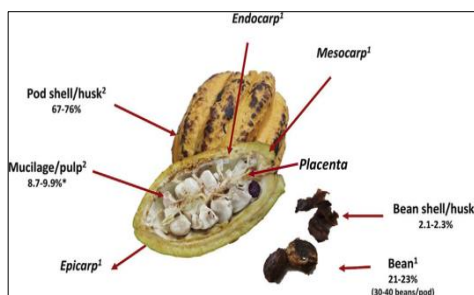


Figure 1. The Structure of Cacao Fruit (adapted from Vegaa et al and Ahmad & Sutrisno)

Rocio Campos-Vegaa, Karen H. Nieto-Figueroa, B. Dave Oomah 2018: Cocoa (*Theobroma cacao* L.) pod husk: Renewable source of bioactive compounds. *Journal Trends in Food Science & Technology*, 81 (2018) 172–184. DOI: 10.1016/j.tifs.2018.09.022

Usman Ahmad & Sutrisno, 2008, *Pengolahan Kakao*. E-learning IPB 2008.

http://web.ipb.ac.id/~usmanahmad/Pengolahankakao_ppt.htm

One of the efforts to use cacao pod husks is to make liquid smoke as fertilizer using pyrolysis method. Pyrolysis is the process of heating biomass material with limited oxygen, resulting in the decomposition of chemical compound components [6]. Pyrolysis is an interesting method to recycle waste in an effort to handle organic waste. Pyrolysis of biomass at high temperatures decomposes into carbon, tar and liquid smoke [7].

Liquid smoke is a result of condensation or condensation from direct or indirect combustion vapors from materials that contain lignin, cellulose, hemicellulose and other carbon compounds. Liquid smoke contains various chemical components including alcohol, aldehydes, ketones, organic acids such as furfural, formaldehyde which function as preservatives, phenols, quinols, and pyrogallol, which act as antioxidants, antiseptics, and anti-bacteria. Acid groups that play a role in liquid smoke are acetic acids which can stimulate plant growth. Acid compounds contained in liquid smoke are organic acids formed by the pyrolysis process of chemical components of wood such as lignin, cellulose, and hemicellulose.

Types of Liquid Smoke are distinguished from their grade. There are 3 grades of liquid smoke namely first grade liquid smoke is the result of the distillation process, is the best quality liquid smoke and does not contain harmful compounds to be applied to food products. Second grade liquid smoke is liquid smoke produced after passing through the distillation process, used for rubber clumping. Third grade liquid smoke is liquid smoke produced from the pyrolysis process which still contains tar. Third grade liquid smoke used in agriculture, is indicated to function as a hormone or enzyme, can stimulate a reaction process whose role is like hormones, the process of land improvement is faster, so that soil nutrients can be absorbed more. Liquid smoke contains nutrients needed by plants, so that it can add macro and micronutrients for plants [8]. Another possibility is that liquid smoke as an enzyme acts as a catalyst that speeds up land reactions without reacting. So that land improvement is faster and perfect.

Several studies on the use of liquid smoke in agriculture include liquid smoke from mixed wood at a concentration of 2.5% which can increase the production of Ciharang rice variety of dry land rice [9], at concentrations of 1-3% can increase the growth of sengan (*Paraserianthes falcataria*) and jaban (*Anthocephalus sp*) plants and protect against pests and diseases [10] [11], liquid smoke from coconut shell at a concentration of 0.25% can increase the yield of upland rice on the number of productive panicles and the amount of grain weight per contents of the clump [12], liquid smoke of pine wood at a concentration of 1% can accelerate the time of seed germination pine [13], liquid smoke of sengan wood waste at a concentration of 4% can increase the growth of saplings of *Gynopsis sp* [14]. Provision of liquid smoke from mindi wood (*Melia azedarach* L) waste at a concentration of 2% resulted in an average increase in the height of the sengan saplings the highest at 156.33 cm and the lowest at a liquid smoke concentration of 4% at 75.68 cm. Whereas without treatment, the highest average diameter increase was 20.08 cm and the lowest was at liquid smoke concentration of 4%, namely 7.63 cm [15].

At present few farmers in Central Sulawesi Indonesia has try to use liquid smoke from coconut shell as fertilizer in their rice field and chili plants and reporting that the result is better than if they did not spray it with liquid smoke. But sometimes it doesn't give good results due to lack of knowledge concerning the dosage of liquid smoke used. Therefore a research on the appropriate dose of liquid smoke used in order to provide optimal results on plant growth is carried out. In this study cacao pod husks was used to make liquid smoke in consideration of its availability which is abundant. The cacao pod husks becomes wastes where the farmer did not used it or did not know what to use for, and let it unused in their cacao garden. The waste in cacao garden effected the sanitation of the garden, where the wastes becoming the home of the cacao pest. For years the production of cacao in Indonesia was decreasing not only production but also quality, due to the pests that is difficult to eradicate. Therefore, the choice to used cacao pod husks in making liquid smoke is also an effort in encouraging the farmer to make their garden more clean and maintain the sanitation, and hopefully will make the cacao plant become healthier and the production and quality of the cacao is increased. The purpose of this study was to study the effect of liquid smoke from cacao pod husks as fertilizer on accelerating plant growth. Considering the experience of the farmer, this study will determines the performance of pyrolyzers, determines the chemical and physical characterization of

liquid smoke produced and tests it on seed germination and chilli growth with different dosage or different concentration of liquid smoke used to get best or optimum results.

The purpose of this study is to utilize cocoa pod husks for making liquid smoke, determine the performance of pyrolyzer, determine the chemical and physical characterization of liquid smoke and apply it to seed germination and chili growth

2. RESEARCH METHODS

2.1. Material Research

The research material used for the manufacture of liquid smoke is the cocoa pod husks originating from cocoa plantations in Cianjur district of West Java Province, Indonesia. To test the liquid smoke of cocoa pod husk on the germination, red chilli (*Capsicum annum L*) seed was use, because it has the nature of fast germination.

2.2. Research Equipment

The equipment used in this study is the pyrolyzer which can be seen in Figure 1 below.

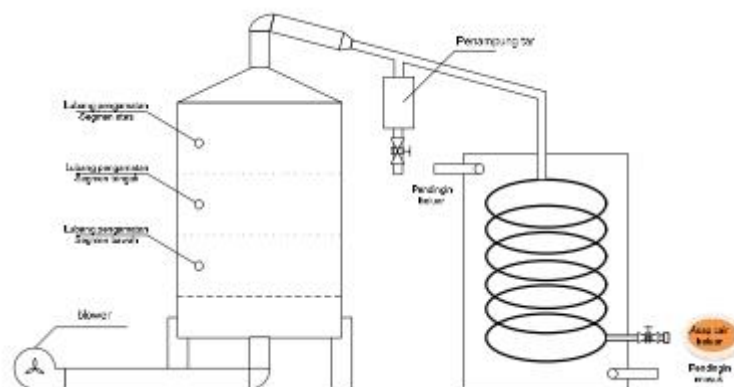


Figure 1. Pyrolyzer Scheme Equipped with a Blower

2.3. The process of making liquid smoke of cacao pod husk

Making liquid smoke of **cacao** pods using a pyrolyzer equipped with a blower and condenser. **Cacao** pods are put in a tank/drum with a capacity of 26 kg/batch, then burned for ± 4.5 hours. The carbonization process is done by closing all the drums and the limitation of the combustion air is done with the help of a blower. The resulting gas is channeled through a pipe to be cooled, so that a liquid product is produced, liquid smoke. The resulting liquid smoke is accommodated in a 20 liter plastic tub, then allowed the solid particles such as tar that are still present in the liquid smoke to settle.

Pyrolyzer performance testing

The pyrolyzer performance parameter tested is the yield. The yield is one of the important parameters to find out the results of a process. The yield can be calculated using the following formula:

$$\text{The yield (\%)} = \frac{\text{Output}}{\text{Input}} \times 100 \%$$

Note :

Output = Liquid smoke produced

Input = Raw material used

2.4. Chemical quality testing for liquid smoke.

The chemical parameters tested were pH values using a pH meter. To identify the compounds contained in liquid cacao smoke using GCMS (Gas Chromatography-Mass Spectrometry). Tests carried out at the Organic Chemistry Laboratory of the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Gadjah Mada University.

2.5. Testing the physical quality of liquid smoke

The physical properties of liquid smoke tested include density, color, odor, presence, or absence of sediments. Density is measured using the Specific Gravity meter. Color, smell, and appearance or absence of sediments are measured visually.

2.6. Chemical quality testing for liquid fertilizer

Chemical quality testing for liquid fertilizer includes pH values measured with a pH meter, total Nitrogen content analyzed by the Kjeldahl method, C-organic analyzed by a Furnace, P₂O₅, B analyzed by a spectrophotometer, K₂O analyzed by a Flame photometer, SiO₂ levels by Furnace, N-levels NH₄ and N-NO₃ by distillation, CaO, MgO, Na, Fe, Mn, Cu, Zn, Al, Pb with AAS (Atomic Absorption Spectrophotometer).

2.7. Testing of liquid smoke on the germination of red chilli seeds (*Capsicum annum L*)

Germination is a measure of the ability of seeds to grow into normal plants that produce normally under optimal conditions. The seeds used are red chilli seeds (*Capsicum annum L*), because they have fast germination properties [16].

The germination test was carried out directly by the test method on paper using straw paper. Paper Top Test method is the best method [17]. Seeds are placed on the surface of the paper consisting of three layers of paper that have been moistened with liquid smoke placed on a petri disk. Seeds are planted in a circle. Seeds that have been planted are then covered with petridisk cover and stored for 14 days. Paper straw is used in the Paper Top Test method, because paper straw has high ability to retain water, even though seven days was not given water. Physically, paper straw has high porosity, good drainage and aeration, thus allowing roots to grow, free from molds, bacteria, and toxic substances that can affect germination, and has a pH of 6.5-7 [18] [19].

2.8. Treatment of liquid smoke concentration

The liquid smoke tested was a concentration of 0% as a control, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9% and 10%. Petri disks used for each concentration are 4 pieces, each filled with 25 red chilli seeds.

2.9. Data analysis

To find out the effect of liquid smoke concentration on germination of red chilli seeds, the Variance Analysis test was done with 99% confidence level. After analysis of variance, further tests were performed with Duncan Multiple Range Test (DMRT) at 5% level.

3. RESULT AND DISCUSSION

3.1. Characteristics of cocoa pods husk

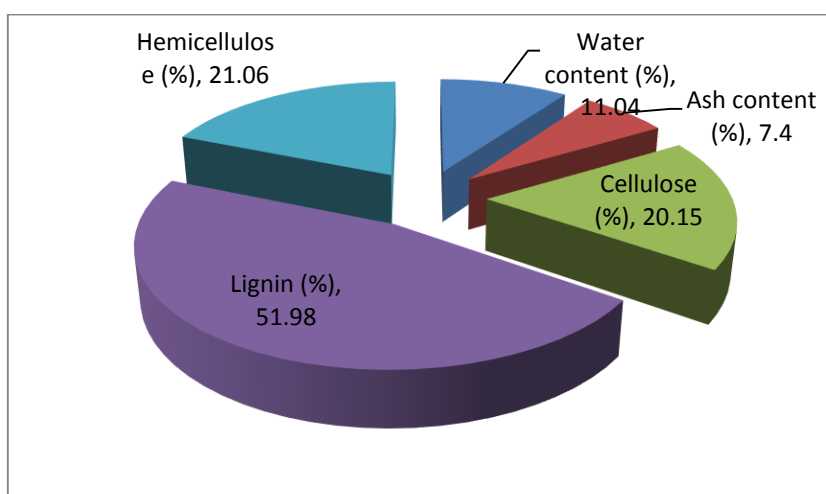


Figure 2. Chemical Composition of Cocoa Fruit Skin

The component of raw material is one of the factors that influence the compounds formed in liquid smoke. Cocoa pods contain chemical components that can be used for liquid smoke. Based on analysis results, it indicated that the cocoa fruit

skin contains 21.06% of hemicellulose, 20.15% of cellulose and 51.98% of lignin, water content 11, moisture content of 11.09% and ash content of 9.04%, as shown in figure 2.

3.3. Yield of liquid smoke

Yield is one of the important parameters to find out the results of a pyrolysis process. Liquid smoke of cocoa pods in this study was produced through a process of smoke condensation released through the pyrolysis. The yield of liquid smoke produced was 19%, the charcoal yield was 27.4%, the tar yield was 3.2%. From the results of the yield obtained it can be estimated that the substances that are wasted into gas are quite a lot which is around 50.4%, this shows that not all gases or vapors produced from the pyrolysis process can be condensed into liquid smoke. The results of the pyrolysis process are influenced by several factors including heating time, temperature and heating rate. The yield of liquid smoke produced from this study is lower than that of Asis, W.A. [20], but higher than the results of Lopies, J.E. et al [21]. Asis's research results produced a liquid smoke yield of 25%, a charcoal yield of 37%, a yield of 2.9% tar, an estimated wasted substance 35.1%. While the results of research by Lopies, J.E. et al. yield of liquid smoke produced 7.5% [21].

3.4. Chemical characteristics of liquid smoke

Table 2 shows the results of the analysis of the chemical components contained in the liquid smoke of cocoa pods. The compounds in liquid smoke different, depending on the type of material, water content and temperature used during the pyrolysis process [22]. Chemical components contained in the liquid smoke of cocoa pod husk in this study detected 30 components consisting of various compounds, where the identified compounds consisted of groups of organic acids, phenols and their derivatives, ketones, hydrocarbons, furans.

Table 1. Results of the analysis of chemical components contained in liquid smoke

No.	Retention Time (minutes)	% Area	Alleged Compound
1.	1.954	6.80	Phenol, 4- [2- (methylamino) ethyl]
2.	2.112	2.91	Boric acid
3.	2.291	6.39	Propionic acid
4.	2.536	12.36	Phenol 2-methoxy
5.	2.800	0.76	Methyl ester
6.	3.550	20.38	Acetic acid
7.	3.740	0.58	n-Butane
8.	3.850	0.26	Ethylic acid
9.	4.216	0.38	Cyclopentene
10.	7.475	3.17	2-Furanmethanol
11.	7.599	4.22	2 (3H) –Furanone
12.	7.955	5.55	2-Furancarboxaldehyde
13.	18.835	2.23	2-Furanmethanol, tetrahydro-
14.	20.549	0.45	Methyl pyrazine
15.	24.454	1.32	Cyclopentanone
16.	26.896	6.21	Phenol, 2-methoxy-4 -methyl-,
17.	27.357	0.81	3-4-diphenylisoxazolin-5-one
18.	29.387	3.81	2 methyl -2-cyclopentanone
19.	30.651	2.16	2-Cyclopentanone-1-one
20.	31.036	5.71	4-Hexen-3 one
21.	31.892	0.15	4,5 Dimethyl (CAS)
22.	31.994	0.70	Ammonium carbamate
23.	33.724	0.94	Carbamic acid, monoammonium salt (CAS)
24.	34.238	1.75	Propanal, 2-oxo (CAS) pyruvaldehyde
25.	35.117	0.19	2 Propanone, 1 (4hydroxy-3-methoxy-phenil) (CAS)
26.	35.324	6.37	Butyrolactone
27.	35.558	0.21	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- (CAS) Acetovanillone
28.	36.908	0.21	2 Phentanone
29.	37.099	0.81	5 Hydroxy 2 heptanone
30.	40.277	2.20	Furanone, dihydro-

Organic acid compounds identified in the liquid smoke of cocoa pods are acetic acid, boric acid, propionic acid, ethylic acid. This acid compound is formed due to the pyrolysis process of chemical components such as lignin, cellulose and

hemicellulose contained in cocoa pods. Acetic acid can stimulate plant growth, while propionic acid can prevent mold growth.

Phenol compounds in cocoa pod husk liquid smoke consist of phenol, 4- [2- (methylamino) ethyl] -, phenol, 2-methoxy-4-methyl-, phenol, 2-methoxy-. Phenol compounds can function as antioxidants by stabilizing free radicals. Phenol compounds have strong anti-microbial properties and one of the earliest uses is as an antiseptic and also functions as an anti-oxidant by the action of preventing oxidation of protein and fat compounds so that the process of breaking down these compounds does not occur. Phenol compounds are formed from the pyrolysis of lignin contained in the of cocoa pod husk.

The lactone compounds contained in the liquid smoke of are compound 2 (3H) -Furanone, 2-Furancarboxaldehyde, 2-Furanmethanol tetrahydro- which contains 2,23% - 5,55%. Lactone compounds or known as karrikin compounds derived from the decomposition of cellulose compounds from cocoa pod husk [23].

The hydrocarbon compounds identified in the liquid smoke of cocoa pod husk are Cyclopentene, Cyclopentanone. Curcumin analog compound. Curcumin analog compound identified in liquid smoke of cocoa pod skin is propanol-2-oxo (CAS) pyruvaldehyde, 2-propanone, 1 (4-hydroxy-3-methoxyphenyl) - (CAS) 1- (4-Hydroxy-3-MET). Curcumin compound is one of the phenol compounds that can stimulate the accumulation of ROS (Rapid reactive Oxygen Species) [24].

Acetovanillone. The acetovanillone compounds identified in the liquid smoke of cocoa pod husk are ethanone, 1- (4-hydroxy-3-methoxyphenyl) - (CAS) Acetovanillone. Acetovanillone compounds can increase ROS (Rapid reactive Oxygen Species) levels [25], thus potentially disrupting the integrity of the phospholipid membrane by breaking down phospholipids to glycerol, carboxylic acids, and phosphoric acids, this causes the function of the cytoplasmic membrane of microbial cells disrupted.

3.5. The results of physical quality analysis of liquid smoke

Table 2. Physical quality of liquid smoke of cocoa pod husks

Parameter	The quality of third grade liquid smoke	The quality of second-grade liquid smoke
Color	Reddish black brown	Yellow brown is a bit turbid
Smell of smoke	Very strong	The smoke is strong and stinging
There is / no sediment	There is black	There are no sediment
Density (gram / ml)	1,0052	1,0007

Table 2 shows the physical quality results of third and second grade liquid cocoa pod husk smoke. Liquid smoke of third grade cocoa pod husks is reddish black brown, while the second grade yellowish brown is rather turbid. The dark brown color is influenced by the content of the carbonyl compound, ie the higher the carbonyl content the higher the browning potential [26].

The color of liquid smoke is influenced by the temperature of pyrolysis which causes degradation cellulose, hemicellulose and lignin. This is confirmed by the results of research conducted by Wijaya, that temperature changes cause discoloration of liquid smoke. The color of the third grade liquid smoke is darker than the second grade, because the third grade liquid smoke still contains tar, so the color is darker. After the liquid smoke is distilled, the color tends to be brighter. It is suspected that tar greatly influences the color of liquid smoke so that when the distillation process takes place, the tar content will settle to the bottom of the redistillation equipment and not evaporate with other compounds such as phenol, carbonyl and acid so that the color of the liquid smoke from the distillate will be increasingly bright or clear. The third grade liquid smoke has a very strong smoke smell, while the second grade liquid smoke, has a strong and pungent odor. According to Serot et al. the main compound that contributes to the smell of smoke in liquid smoke is phenolic [27]. Meanwhile, according to Amirudin (2015) the influence of odor from liquid smoke is tar [28]. Liquid smoke from third grade cocoa pod husks has black sediment, while the second grade has no sediment . The black color is tar. These sediment or tar can be removed by distillation.

Density is a measurement of the mass of each unit volume of an object. The higher the type of an object, the greater the mass of each volume. The liquid smoke density of cocoa pods at the third grade was 1,0052 grams/ml and the second grade was 1,0007 grams/ml, meeting the Japanese liquid smoke standard of > 1,005 gram/ml [29]. The density of the third grade liquid smoke is higher than the second grade, because of the black tar.

3.6. Chemical quality of liquid smoke as organic fertilizer

Table 3 shows the results of chemical analysis of liquid smoke as fertilizer compared to Minister of Agriculture Regulation No. 28 / Permentan / SR.130 / 5/2009 which can be used as liquid organic fertilizer.

Table 3. Results of chemical analysis of liquid smoke of cocoa pod skin compared to the minimum requirements of organic liquid fertilizer according to Minister of Agriculture Regulation No. 28 / Permentan / SR.130 / 5/2009 [30]

Parameter	Liquid smoke third grade	Liquid smoke second grade	Indonesian National Standards (SNI)	
			Minimum	Maximum
1. Nilai pH	8,54	8,67	4	
2. C-organik (%)	2.55	1.081	≥ 4	
3. N total (%)	0.249	0.66	< 2	
4. P ₂ O ₅ (%)	0.002	0.001	< 2	
5. K ₂ O (%)	0.005	0.005	< 2	
6. Silikat (%)				
7. N-NH ₄ (%)	0.228	0.094		
8. N-NO ₃ (%)	0.018	0.004		
9. CaO (ppm)	0.002	0.001		
10. MgO (ppm)	0.004	0.002		
11. S (%)	0.010	0.09		
12. Na (%)				
13. Cl (%)				
14. Fe (ppm)	13.7	10.7	0	800
15. Mn (ppm)	1.0	0.3	0	1000
16. Cu (ppm)			0	1000
17. Zn (ppm)	0.06	0.03	0	1000
18. B (ppm)			0	500
19. Al (ppm)	5.2	5.1		
20. Pb (ppm)			≤ 12,5	

The pH value is one of the parameters of liquid smoke produced. Measurement of pH values in liquid smoke aims to determine the level of decomposition of raw materials to produce organic acids in the form of acid by pyrolysis. The pH value of liquid smoke of third grade cocoa pod husks is 8.54 and grade 2 is 8.57. This pH value does not meet the quality requirements for the quality of organic liquid fertilizers, according to Regulation of the Minister of Agriculture No. 28 / Permentan / SR.130 / 5/2009 which is at least 4 [30].

Liquid smoke of cocoa pod husks contains 4.071% C-organic content that meets the liquid fertilizer quality standards according to the Regulation of the Minister of Agriculture, which is greater or equal to 4% [30]. High or low levels of organic C in liquid smoke is thought to be influenced by high levels of lignin, cellulose, and hemicellulose in liquid smoke raw materials. The higher levels of cellulose, hemicellulose, and lignin that are decomposed will affect the high organic C in the liquid smoke it produces. Liquid smoke of cocoa pod husks contains low total Nitrogen level of 0.1081%, but meets the standards of the Minister of Agriculture's regulation, which is smaller than 2% [30]. It is suspected that the cocoa plants that are used grow on soils with N nutrient deficiency conditions, so that the absorption of N elements by plants becomes low or ineffective, consequently the cocoa plants have low N nutrient content. Thus, the liquid smoke of cocoa pods has a very high C / N ratio (> 25), which is 38. According to Bachtiar (2006), the high and low C / N ratio in liquid smoke is influenced by the high and low levels of organic C and the high and low levels of nutrient N in liquid smoke raw materials [31]. The higher the organic C content and the lower the element N content in organic matter, the higher the C / N ratio value. Because the liquid smoke of the cocoa pod husk has a very high C / N ratio, the liquid smoke is not good to be applied directly without dilution. If organic material with a very high C / N ratio is immediately applied because it can slow down the rate of decomposition of an organic material in the soil, so it is not good for plant growth. If material containing a very high C / N ratio is given directly to the planting medium, it can reduce the pH, this is supported by the opinion of Brady and Weil (2002), which states that pH is a function of H⁺ ions and H⁻ ions, the rise and fall of the pH of the planting media can be influenced by the presence of C / N ratio [32], if the presence of C / N ratio is high, the presence of base cation decreases, so the OH⁻ ion concentration decreases and the H⁺ ion increases, if the H⁺ ion increases as a result the pH decreases (the planting medium becomes sour). Budi, S. and Sasmita, S. (2015) state that a very high C / N ratio also causes symptoms of nutrient deficiency or many nutrients are immobilized, including, N and P, so that these nutrients become increasingly unavailable [33]. Conversely, if the C / N ratio is lower, then the presence of base cations such as Ca, Mg, and K increases, and increased levels of Ca, Mg, and K are positively correlated with an increase in OH⁻ ion concentration, and an increase in OH⁻ ion concentration can increase pH growing media. Dilution of organic matter which has a very high C / N ratio with water solvents is reported to reduce organic C levels and increase N levels in organic matter, so that the C / N ratio will decrease. In other words, the process of diluting organic matter can reduce the C / N

ratio of the organic material to a low-moderate level so that when applied to the planting medium it will be able to support plant growth

Liquid smoke of cacao pod husks contains macro and micro nutrients, which contain a low P₂O₅ of 0.0675%, but meets the standards of the Minister of Agriculture which is smaller than 2 [30]. According to Homer (2008), conditions during plant growth, which lack N elements are thought to affect the rate of absorption of P elements by plants. If plants grow on soil with sufficient N nutrients, this situation will cause plants to be able to absorb P in becoming more effective, conversely on soils that have N nutrient deficiency, causing plants to be unable to absorb P elements effectively, consequently the plants lack P elements The acidity conditions of the planting media also affect the high or low levels of the element P.

Liquid smoke of cocoa pod husks containing 46 ppm K₂O, 25 ppm CaO and 10 ppm MgO are quite high. Therefore, the use of liquid cocoa pod smoke is not recommended to be exposed directly into the planting medium without dilution and at high concentrations. The elements K, Ca, and Mg in liquid smoke are thought to be influenced by the high or low levels of ash in the raw material of cocoa pod husks. In addition to containing organic components such as carbohydrates composed mainly of carbon, hydrogen, and oxygen, cocoa pods also contain inorganic compounds that remain after combustion at high temperatures in conditions of abundant oxygen, , this kind of residue is known as ash. The main ash component that does not burn in wood even at very high temperatures are elements such as K, Ca, Mg, Mn, and Si [34]. Ash content of cocoa skin peel is thought to affect the levels of mineral salts dissolved in liquid smoke. Ash content of cocoa pod husk is thought to affect the levels of mineral salts dissolved in liquid smoke.

Table 4. Effect of liquid smoke concentration of cocoa pods on maximum growth potential and germination of red chili seeds (*Capsicum annum* L)

The concentration of liquid smoke	Maximum growth potential (%)	Germination (%)
Liquid Smoke 0 %	92 e	91 d
Liquid Smoke 1%	93 e	91 d
Liquid Smoke 2%	97 b	93 d
Liquid Smoke 3%	98 b	93 d
Liquid Smoke 4%	95.5 c	86 c
Liquid Smoke 5%	93 c	79.95 c
Liquid Smoke 6%	89.5 e	79 c
Liquid Smoke 7%	80 b	56.5 b
Liquid Smoke 8%	80 b	53 b
Liquid Smoke 9%	67 a	38.5 a
Liquid Smoke 10%	66.5 a	35.5 a

The results of the analysis of variance showed that the treatment of liquid smoke concentration had a very significant effect on maximum growth potential and germination power of red chilli seeds. The average percentage of germination and maximum growth potential of chilli seeds in various contracements can be seen in Table 5. The treatment of liquid smoke with an increase in concentration of 0% - 4% can increase the percentage of seed germination and maximum growth potential, then in the liquid smoke concentration of 5% - 10% a decrease in germination and a maximum growth potential occurs at a concentration of 6% - 10%. An increase in germination and maximum growth potential due to liquid smoke contains a number of nutrients that can provide a stimulating effect on plant growth depending on concentration, at high concentrations can inhibit plant growth. According to Maurya et al. liquid smoke contains karrikin which plays a role in solving the external cuticle of the seed, changing the permeability and internal cuticle of the seed which is directly related to the breakdown of seed dormancy and accelerating the process of seed development [35]. According to Dixon et al. 2009 karikkin can increase seedling growth and seed vigor in many species, namely around 1200 species of more than 80 families [36] and according to Van Staden et al. 2006 karrikin has the potential to be a stimulate of plant growth [37] . Light (2010) states that karikkin has been proven to increase the germination and seed vigor of some plant species [38] . The karrikin or lactone compounds in the liquid smoke of cacao pods identified were 2 (3H) -Furanone, 2-Furancarboxaldehyde, 2-Furanmethanol tetrahydro- whose contents were 2.23% - 5.55% as shown in table 2. The reduced percentage of germination and maximum growth potential of red chilli seeds on increasing the concentration of liquid smoke 5% - 10% affects the physiological activity of the seeds due to the presence of phenol compounds which can limit the supply of oxygen into the seed embryo, so that it can cause the germination of the germination process. Phenol compounds have a negative influence on seed quality, namely the potential as an antioxidant that causes a decrease in seed germination.

4. CONCLUSION AND RECOMMENDATION

4.1. Conclusion

- Liquid smoke yield of cocoa pods produced was 19%, charcoal yield 27.4%, tar yield 3.2%.
- Characteristics of liquid smoke of the third grade cocoa pod husks produce a reddish black brown color, while the second grade yellowish brown is rather turbid. The aroma produced by the third grade liquid smoke is very strong, while the second grade liquid smoke is strong and stinging. Liquid smoke from third grade cocoa pods has black sediment, while the second grade has no sediment. The third grade density is 1,0052 gram/ml and the second grade is 1,0007 gram/ml.
- Liquid smoke concentration significantly influences the germination capacity and maximum growth potential of red chili seeds. The best germination capacity at 2% and 3% liquid smoke concentration is equal to 93%, as well as the best maximum growth potential at 3% liquid smoke concentration that is equal to 98%.
- The higher the concentration of liquid smoke, the lower the germination capacity and maximum growth potential of red chillies. The lowest germination capacity and maximum growth potential of red chili seeds at a liquid smoke concentration of 10%, each of which amounted to 35.5% and 66.5%.
- From the analysis and experiment in laboratory scale shown that liquid smoke can be used to accelerate the growth of a plant with the use of low concentration liquid smoke (2-3%) which difference around 2% for germination and 5-6% for growth (See Table 4), but still have to be tested in the field. However the possibility is high to accelerate the growth of a plant which will benefit the farmer.
- The result from the research is supporting the presumption of the farmer on the usability of liquid smoke as fertilizer to accelerate the growth of the plant, however they don't know the precise amount or concentration of liquid smoke to give optimum results in their plants.

4.2. Recommendation

- The dosage or concentration of liquid smoke used to get the best result should be tested in the field before it is applying it in the field (cacao plantation, rice field, etc.).
- A good result, a collaboration with the farmer should be taken to test the appropriate dosage of liquid smoke to be used in order to get a good result.

5. ACKNOWLEDGEMENT

The author would like to thank the Research Center for Appropriate Technology-Indonesian Institute of Sciences as a funder of research activities through Building Cacao-Based Agroindustry in Central Sulawesi -National Priority Program 2018. Also, we would like to thank Taufik Yudi, Dadang Gandara, Edi Jaenudin, Khudaifani for their assistance during research.

6. REFERENCES

- [1] Pusat Data dan Sistem Informasi Pertanian - Kementerian Pertanian, Outlook, Kakao, Komoditas Pertanian Subsektor Perkebunan, Jakarta: Kementerian Pertanian, 2016.
- [2] Wasmun, H., Rahim, A., Hutomo, G.S.r, "Pembuatan minuman instan fungsional dari bioaktif pod husk kakao (Manufacture of functional instant beverage by processing bioactive compound of cocoa podhusk)," *e-Journal Agribisnis*, vol. 3, no. 6, December 2015.
- [3] Jusmiati, A., Rusli, R., Rijai, L., "Aktivitas antioksidan kulit buah kakao masak dan kulit buah kakao muda," *Jurnal Sains dan Kesehatan*, vol. 1, no. 2, 2015.
- [4] Yumas, M., "Pemanfaatan limbah kulit ari biji kakao (*Theobroma cacao* L) sebagai sumber antibakteri *Streptococcus mutans*," *Jurnal Industri Hasil Perkebunan*, vol. 12, no. 2, December 2017.
- [5] Listyati, "Peluang peningkatan pendapatan petani dari kulit buah kakao (Increasing revenue opportunities of skin cocoa farmers)," *Sirinov*, vol. 3, no. 3, December 2015.

- [6] Fisher, T.M., Hajaligol, Waymack, B., and Kellogg, D., “Pyrolysis behaviour and kinetics of biomass derived materials,” *Journal of Analytical and Applied Physics*, vol. 62, 2002.
- [7] Boateng, A.A., Mullen, C.A., Golberg, N.M., Hicks, K.B., McMahan, C.M., Whalen, M.C., “Energy dense liquid fuel intermediates by pyrolysis of guayule (*Parthenium argentatum*) shrub and bagasse,” *Fuel*, vol. 88, 2009.
- [8] C. d. F. Astanti, *Memproduksi cuka (asap cair) untuk kesehatan tanaman*, Second ed. penyunt., Cepu: Puslitbang Perum Perhutani, 2015.
- [9] Nurhayati, R.A. Pasaribu dan D. Mulyadi, “Produksi dan pemanfaatan cuka kayu cuka dari serbuk gergaji kayu campuran,” *Jurnal Penelitian Hasil Hutan*, vol. 24, no. 5, 2006.
- [10] Komarayati, S., Gusmailina dan G. Pari, “Produksi cuka kayu hasil modifikasi tungku arang terpadu,” *Jurnal Penelitian Hasil Hutan*, vol. 29, no. 3, 2011.
- [11] Komarayati, S., “Produksi, kualitas, manfaat arang dan cuka kayu yang dihasilkan dari tungku drum modifikasi,” dalam *Prosiding Seminar MAPEKI VX*, Makasar, 2012.
- [12] Yugi, A.R. Sajuri dan Darjanto, “Tumpang sari padi rumput dan aplikasi asap cair tempurung kelapa terhadap pertumbuhan, fisiologi dan hasil padi gogo,” *Pena Jurnal Ilmu Pengetahuan dan Teknologi*, vol. 31, no. 2, 2017.
- [13] Sumantoro, P. Dan Astanti, F., “Pengendalian penyakit lodoh dan bercak daun pada persemaian pinus (*Pinus merkusii*) dengan cuka kayu,” dalam *Prosiding Seminar Nasional Kesehatan Hutan dan Kesehatan Pengusahaan Hutan untuk Produktifitas Hutan*, Bogor, 2012.
- [14] Gusmailina, S. Komarayati, H. S. Wibisono, “Pengaruh arang dan asap cair terhadap pertumbuhan anakan *Gynopsis sp* (The effect of charcoal and liquid smoke on *Gynopsis sp* seedlings growth),” *Jurnal Penelitian Hasil Hutan*, vol. 36, no. 1, March 2018.
- [15] Komarayati, S., Gusmailina, Pari, G., “Pengaruh arang dan cuka kayu terhadap peningkatan pertumbuhan dan simpanan karbon (The Effects of Charcoal and Wood Vinegar to Growth Increase and Carbon Store),” *Jurnal Penelitian Hasil Hutan*, vol. 32, no. 4, December 2014.
- [16] Copeland L O and McDonald, Principles of Seed Science and Technology, 4th edn ed., Norwell, Massachusetts : Kluwer Academic Publishers, 2001.
- [17] Yuniarti, N., Megawati, Leksono, B., “Pretreatment Technique and Germination Method to Maintain (in Indonesian),” *Jurnal Penelitian Kehutanan Wallacea*, 2013.
- [18] Yuniarti, N., Megawati, Leksono, B., “Pengaruh Metode Perkecambahan dan Substrat Kertas terhadap Viabilitas Benih *Eucalyptus pelita* F. Mull (The effect of Method and Germination Paper Substrate on Viability *Eucalyptus pelita* F. Mull),” *Jurnal Penelitian Kehutanan Wallacea*, vol. 6, no. 1, 2017.
- [19] Hardiwinoto, S., Nurjanto, H.H., Nugroho, A.W., & Widiyatno, “Pengaruh komposisi dan bahan media terhadap pertumbuhan semai pinus (*Pinus merkusii*),” *Jurnal Penelitian Hutan Tanaman*, vol. 8, no. 1, 2011.
- [20] Asis, W.A., “Penentuan kandungan fenolik total asap cair limbah kulit kakao hasil pirolisis dan uji aktifitasnya dalam menghambat pertumbuhan jamur *Fusarium oxysporum*,” Kendari, 2018.
- [21] Lopies, J.E., Puspita, D.F. dan Wahyudi, R., “Quality of Cocoa Pod Husk Liquid Smoke on Various Pyrolysis Condition,” Makasar, 2015.
- [22] Montazeri, N., A.C.M. Olivera, B.H. Himelbloom, M.B. Leigh and C.A. Crapo, “Chemical characterization of commercial liquid smoke products,” *Food Science and Nutrition*, vol. 1, 2013.
- [23] Flematti RG, Merritt JD, Piggott JM, Trengove DR, Smith MS, Dixon WK, Ghisalberti LE., “Burning vegetation produces cyanohydrins that liberate cyanide and promote seed germination.,” *Nature Communication*, vol. 2, no. 360, 2011.
- [24] Thayyullathil F, Chathoth S, Hago A, Patel M, Galadari S., “Rapid reactive oxygen species (ROS) generation induced by curcumin leads to caspase dependent,” *Free Radical Biology and Medicine*, vol. 45, no. 10, 2008.
- [25] Riganti C, Costamagna C, Bosia A, Ghigo D., “The NADPH oxidase inhibitor apocynin (acetovanillone) induces oxidative stress,” *Toxicology and Applied Pharmacology*, vol. 212, no. 3, 2005.
- [26] Vivas, N., C. Absalon, p. Soulie and E. Fonquet, “Pyrolysis gas chromatography mass spectrophotometry *Quecas sp* wood,” *Journal of Analytical and Applied Pyrolysis*, vol. 75, 2006.
- [27] Sérot, T., Baron, R., Knockaert C., Vallet J.L., “Effect of Smoking Processes on The Contents of 10 Major Phenolic Compounds in Smoke Fillets of Herring (*Cuplea harengus*),” *Food Chemistry*, vol. 85, 2004.
- [28] Amiruddin, “Bbeberapa Sifat Fisika dan Rendemen Asap Cair Grade III, II dan I dari Limbah Buah Kelapa Muda (*Cocos nucifera*L.),” Samarinda, 2015.
- [29] M. Yatagai, “Utilization of Charcoal and Wood Vinegar in Japan,” Bogor, 2002.
- [30] Departemen Pertanian, “Pupuk Organik, Pupuk Hayati dan Pembenahan Tana,” Jakarta, 2009.

- [31] Bachtiar, E., Ilmu Tanah, Medan: Universitas Sumatera Utara, 2006.
- [32] Brady CN, Weil RR., The nature and properties of soils, 13th Edition. ed., New Jersey- USA: Prentice- Hall Inc., 2002.
- [33] Budi S. dan Sasmita, S., Ilmu dan Implementasi Tanah, Malang: Universitas Muhammadiyah, 2015.
- [34] Sjostrom E., Kimia Kayu: Dasar-dasar dan Penggunaan., Second ed. penyunt., Jogjakarta: Universitas Gajah Mada Press, 1995.
- [35] Maurya S K, Srivastava A and Garg S.K., “Karrikin : A seess stimulant,” *Life Sciences Leaflets* , vol. 57, pp. 86-94, 2014.
- [36] Dixon K W, Merritt D J, Flematti G R, Ghisalberti E L., “Karrikinolide a phytoactive compound derived from smoke with application in horticulture, ecological restoration and agriculture,” *Acta Horticulturae*, vol. 813, 2009.
- [37] Van Staden J, Sparg GS, Kulkarni GM, Light EM., “Post germination effects of the smoke-derived compound 3-methyl-2Hfuro[2,3-c]pyran-2-one, and its potential as a preconditioning agent,” *Field Crops Res*, vol. 98, 2006.
- [38] Light M.E., Burger B.V., Staerk, D., Kohout, L., Van Staden, J., “Butenolides from plant derived smoke, natural plant growth regulator with antagonistic actions on seed germination,” *Journal of Natural Products*, vol. 73, 2010.