Utilization of liquid smoke corn cobs for germination tomato (Solanum lycopersicum) seeds

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Abstract. Corn cobs are agricultural wastes that are often found in Indonesia, which so far are still not widely used as products that have added value. Corn cob contains 41% cellulose, 36% hemicellulose, and 6% lignin, so it can be used for making liquid smoke. Liquid smoke is one of the results of condensation or condensation from the steam produced by combustion directly or indirectly from materials that contain a lot of lignin, cellulose, hemicellulose, and other carbon compounds. The method used for making liquid smoke is the pyrolysis method that is using pyrolizer, by burning and heating above the furnace, which will produce smoke and will then be condensed into liquid smoke. In this study, the performance of liquid smoke equipment testing. The liquid smoke produced was carried out chemical and physical characterization and tested for seed germination and tomato growth (Solanum lycopersicum). The results of the research on making liquid smoke from corn cobs showed that the yield of liquid smoke was 28.37%, pH value 3.506. The results of the analysis of the chemical characterization of third-grade liquid smoke using GCMS detected approximately 32 chemical components. The results of the physical characterization analysis of liquid smoke showed a very strong odor, brownish red, and there were black sediments in the form of tar. The test results showed that the concentration of liquid smoke (0%, 0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4%, 4.5% and 5%) significant effect on seed germination and tomato growth (Solanum lycopersicum).

1. Introduction
Indonesia is among the ten largest corn-producing countries in the world at number 8 after Argentina, Ukraine, India, and Mexico, with an average production rate of 2012 - 2016 of 18.57 million tons per year or contributing 1.99% to corn production world [1]. The part of the corn plant that is widely used is the seeds which using as food ingredients, and other parts are often not used and become waste. Corn cob waste is usually in the form of straw, cob, and corn husk, which is quite large, amounting to 40 - 50%. According to Koswara, the weight of corn cobs is around 30% of the total weight, which is influenced by the corn varieties. If converted to corn production, then the availability of corn cobs is 5.571 million tons [2]. So far, corn cobs have not used optimally, and it still limited as raw material for animal feed, fuel, or wasted, which has the potential to pollute the environment. Therefore, it needs to be studied more deeply about the potential of corn cobs waste to be developed in terms of tackling agricultural waste, product development innovation, and economic value.

Some research that was carried out in the utilization of corn cobs is as raw material for making particle boards [3], bioethanol making [4], activated charcoal materials [5] xylan corn cobs are...
converted to xylitol [6], as a textile wastewater adsorbent [7]. In this study, corn cobs using as raw materials for making liquid smoke. Corn cobs are one of the lignocellulosics wastes containing cellulose, hemicellulose, and lignin because according to Lorenz and Kulp in Martina et al. corn cobs contain 41% cellulose, hemicellulose 36%, 6% lignin, 3% pectin, 0.014% starch, 1.5 ash %, and water 9.6% [8].

Liquid smoke is a by-product of carbonization or combustion of lignocellulosic material with limited air (pyrolysis), which involves decomposition reactions due to the influence of heat, polymerization, and condensation/smoke condensation into a liquid form [9]. Liquid smoke has radiational qualities, which provide a stimulating effect on growth but depend on the concentration of the mixture, so liquid smoke contains a small amount of nutrients that can be directly absorbed by plants. Liquid smoke increases rooting, helps in regulating nutritional conditions from the soil, and balances microbiological populations. Changes in the microbial population not only significantly reduce the tendency of bound soil diseases but also increase root vitality and therefore allow better absorption of nutrients. The aim of this study was to determine the performance of liquid smoke devices by utilizing corn cobs, physical and chemical characterization, and their application to seed germination and tomato growth (Solanum lycopersicum).

2. Materials and methods

2.1 Materials
The research material used for making liquid smoke is a hybrid variety PP 21 corn cobs originating from Ciburuluy hamlet, Sukatani village, Tanjungmekar sub-district, Sumedang district. For testing liquid smoke on germination and growth, tomato seeds were used (Solanum lycopersicum).

2.2 Research equipment
The equipment used in this study is a Pyrolizer which can be seen in Figure 1 below.

![Figure 1. Pyrolizer scheme equipped with blowers and condensers.](image)

2.3 Characterization of raw materials for corn cobs
The characterization of the raw material for corn cobs tested was water content. Water content was analyzed by gravimetric method by drying using an oven at 105°C, ash content using furnaces at a temperature of 600°C [10]. Levels of lignin, cellulose and hemicellulose were analyzed by the Chesson method [11].

2.4 The process of making corn cob liquid smoke
Manufacturer of corn cob liquid smoke using pyrolizer equipped with blowers and condensers. Corn cob putting in the drum with a capacity of 21.5 kg per batch, then burned for ± 6 hours. The carbonization process is carried out by closing all drums and limiting the combustion air with the help of a blower. The resulting gas is flowed through a pipe to be cooled so that a liquid product producing, namely liquid smoke. The liquid smoke produced is accommodated in a 20-liter capacity.
2.5. Testing the chemical quality and physical of liquid smoke
The chemical parameters tested were pH values using a pH meter. To identify the compounds contained in corn cob liquid 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. 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, odor, and appearance or absence of sediments are measured visually.

2.6. Testing the germination of tomato seeds (Solanum lycopersicum) in liquid smoke
Germination, according to seed physiologists, is the appearance of radicles through seed skin [12]. Germination is the ability of the seeds to grow normally in an optimum state. Observation of germination carried out by calculating sprouts that meet the criteria for normal germs and divided by the number of germinated seeds multiplied by 100%. The germination test is carried out directly with the test method on paper using a paper straw. The planting media used were three sheets of paper which had been moistened with liquid smoke of corn cobs formed according to the planting place, namely the petri dish. Tests were carried out by adding four replicates of tomato seeds. One repetition of the seeds germinated as many as 25 grains in each petri dish. Paper straw is used in the Paper Top Test method because the paper has high water retention, even though it is not given water for seven days [13]. In this study, an observation of the length of the germs was carried out on the 14th day. Measuring the length of the sprouts using a ruler, measured from the roots to the tips of the leaves.

2.7. Treatment of liquid smoke concentration
The liquid smoke of corn cobs tested is concentration. The concentration of liquid smoke carried out is 0% as a control, 0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4%, 4.5% and 5%, each carried out 4 replications. Each petri disk is filled with 25 tomato seeds.

3. Results and discussions

3.1 Characteristics of raw materials
The characteristics of corn cobs raw material used in this study were cob from hybrid variety PP 21 with a harvest age of 90 days and having a moisture content of 9.4%.. Water content is one of the factors that affect the quality of pyrolysis products produced. The moisture content of the raw materials used can affect the yield and quality of liquid smoke produced [14],[15]. Water content that is too high will reduce the quality of liquid smoke because it will reduce the level of the product produced, such as acid levels and phenol [14]. The higher the water content of the raw material used, the lower the quality of the liquid smoke produced.

The components of cellulose, hemicellulose, and lignin are the three chemical components in wood which influence the quality of liquid smoke produced. The higher the level of the three compounds in the raw material, the more quality the liquid smoke will producing. The lignin content of corn cobs used as raw material for liquid smoke will determine the odor of the liquid smoke product [16]. Girard suggested that lignin pyrolysis will produce phenolic life, such as guaiacol and syringol, which affect the odor of liquid smoke. The results of cellulose pyrolysis will determine the levels of acids, furans, phenols and water in liquid smoke produced, while hemicellulose will affect furfural, furan, carboxylic and acetic acid levels [16].

3.2. The yield of liquid smoke
Yield is one of the important parameters for knowing the results of a process. The liquid smoke in this study producing by the process of smoke condensation released by the pyrolysis reactor, which was 21.5 kg from the raw material of corn cobs with the yield of liquid smoke was 28.37% with corn cob water content of 9.14%. The results of this amount obtain from the condensation of the combustion process of corn cobs after 6 hours, where after 6 hours there are no more liquid smoke droplets coming
out. So that the maximum time for the liquid smoke pyrolysis process in 6 hours is to get third-grade liquid smoke.

The yield of liquid smoke was lower than the results of the study by Nurhaliza et al., which yielded 30.4% dry corn cob [17]. The percentage of yield obtained depends on the moisture content of the corn cobs and the condensation system used. This condition is following what was stated by Tranggono et al. (1997), that for the formation of liquid smoke water is used as a cooling medium so that the heat exchange process can occur quickly [18]. Percent of yield produced varies due to the levels contained in each varying ingredient. The high and low yield of liquid smoke in the pyrolysis process is influenced by several factors, including the type of plant, raw material, and the method of combustion carried out.

Pyrolysis produces charcoal as a residual reaction, which is 41.86%. The charcoal produced does not meet the Indonesian National Standards, where the charcoal produced is not perfect, the color is not evenly distributed. The overall calculation, the total yield is 70.23%. Thus the lost mass from the conversion of corn cobs is 29.77%. According to Tranggono et al. (1997), the component consists of volatile compounds and cannot be condensing with water as a cooling medium. The component includes gas CO₂, CO, H₂, CH₄, and some hydrocarbons [18].

3.3. Physical characteristics of liquid smoke

The odor is one of the supporters of taste that determines the quality of a product. The arising of the odor because the odor is volatile is slightly soluble in water and fat. Test results of the odor of liquid smoke from pyrolysis results in a strong odor. The odor of smoke formed is mostly influenced by the presence of phenol, and carbonyl compounds and a small part is also affected by acids. Phenol compounds that act as one of the contributors to smoke odor consist of high boiling phenols and low boiling phenols [9].

The results of the color test for liquid smoke showed that the liquid smoke of the corn cobs of pyrolysis results was brownish-red. Liquid smoke which is initially brownish red can turn brown if it is not immediately distilled. This can be caused by the oxidation process of phenolic compounds in liquid smoke. The color of liquid smoke is influenced by the presence of carbonyl compounds which decompose and have a role in staining and are influenced by the content of phenol and acidity in liquid smoke. Overall, the liquid smoke obtained is meet with the standard color of the Japanese wood vinegar, which is brownish [19].

In the physical properties of liquid smoke, the density is not directly related to the high and low quality of liquid smoke produced. But the density can show many components in liquid smoke. Determination of liquid smoke density was carried out using a Specific Gravity meter.

In the third-grade liquid smoke, corn cobs contain black sediments, namely tar. Tar is the result of thermal decomposition of corn cobs in the pyrolysis process, which was mostly formed in the lignin pyrolysis process. Tar is a thick liquid because there is a lot of solid, solid black, a pungent odor, and has a high boiling point. According to Halim, et al., tar content is influenced by the lignin content of the hydrolyzed material, the more lignin content of the material, the more tar is produced. Tar constituents include acid compounds, phenols, and carbonyl. These compounds have a contribution in providing characteristic properties of odor, color, flavor and antioxidants, and antimicrobials.

3.4. Chemical characterization of liquid smoke

3.4.1. Characteristics of acidity (pH).

The pH value is one of the quality parameters of liquid smoke produced. This pH value indicates the level of the decomposition process of corn cob components that occurs to produce organic acids in liquid smoke. The overall pH value affects the preservative value and the shelf life of the smoke product or its organoleptic properties. The pH value of the corn cob liquid smoke equal to 3.506. The pH value of liquid smoke produced by liquid corn cob fumes fulfills the requirements of the Japan Association liquid smoke quality required for the production of liquid smoke, which is between 1.5-3.7. [19]. The low acidity value is of good quality, especially as an anti-bacterial because it has a high extractive content. Extractive substances produce compounds such as fat, wax, fatty acids, and alcohol.
The higher the total phenol level in liquid smoke, the lower the pH value [21], furthermore that liquid smoke contains phenols and carbonyl which act as preservatives, anti-bacteria, and antioxidants [9].

### 3.4.2. Identification of compound components in liquid smoke

The chemical compounds in liquid smoke are very dependent on the type of material used, it was strongly influenced by the ratio of the content of cellulose, hemicellulose, and lignin [22], and differences in the water content of samples at pyrolysis can affect the amount of volatile compounds obtained. According to Zaitsev et al. (1969) in Aisyah (2018), liquid smoke contains several antimicrobial substances, including acids and derivatives (formic, acetate, butyrate, propionate, and methyl esters), alcohol (methyl, ethyl, propyl, acyl, and isobutyl alcohol), aldehydes (formaldehyde, acetaldehyde, furfural, and methyl furfural), hydrocarbons (silene, cumene, and simene), ketones (acetone, methyl ethyl ketone, methyl propyl ketone, and ethyl propyl ketone), phenol, pyridine, and methyl pyridine [23].

The results of the analysis of compound components of corn cob liquid smoke using GC-MS can be seen in Table 1. The GC-MS analysis (table 1) identified 32 compounds consisting of various compounds, where the identified compounds consisted of groups of organic acids (acetic acid, propanoic acid), phenols and their derivatives, ketones, aldehydes, furans. Based on the area, the main component of corn cob liquid smoke is acetate acid compound, which dominates at 44.52%, as shown in table 1. Acetic acid was formed from lignin and carbohydrate component of cellulose [24]. Acetic acid is an organic acid which has a great role in the utilization of liquid smoke. This acetic acid is classified as an acid compound that affects the pH value of liquid smoke, which has an antibacterial role [16].

The results of Anggraini's study showed that the liquid smoke of corn cobs contained higher acetic acid at 84.45% with a retention time of 2,240 minutes [25]. The results of Handayani study showed that the content of acetic acid in corn cob liquid smoke was 75.6%, with a retention time of 3.197 minutes [26] and the results of Solichah (2013) acetic acid content of 56.58%, with a retention time of 12,264 minutes [27].

Phenol compounds in corn cob liquid smoke consist of Phenol, 4-[2- (methylamino) ethyl] -, Phenol (CAS) Izal, Phenol, 2-methoxy-, Phenol, 4-methyl-, Phenol, 2-methoxy-4 -methyl-, Phenol, 4-ethyl-, Phenol, 4-ethyl-2-methoxy-, Phenol, 2,6-dimethoxy- which have a small content of 0.32-4.4%, this is due to the low pyrolysis temperature of 145.5 °C, so that the lignin contained in corn cobs has not decomposing due to the lack of heat generated from pyrolysis, lignin degradation is more complicated than cellulose degradation. High phenol content at 300 °C and 350°C, this is because lignin, which is a phenol-forming compound in liquid smoke has decomposed more optimally [28]. Cardinal et al. (2006) [29] and Girard (1992) [16] suggest that lignin pyrolysis will produce phenolic compounds and phenolic ether, which affect the odor of smoke and the sensory properties of the product. Phenol and organic acids are the main compounds in liquid smoke, which affect bacteria. In combination, the two compounds work effectively to control microbial growth [29][16].

The lactone compounds contained in the liquid smoke of corn cobs are compound 2 (5H) - Furanone, 2 (3H) - Furanone, dihydro-, 2-Furancarboxaldehyde, 2-Furanmethanol, 2-Furanmethanol, tetrahydro-which contains 0.57% - 3.80%. Lactone compounds or known as karrkin compounds derived from the decomposition of cellulose compounds from corn cobs [30]. The analogous curcumin compound was identified in the liquid smoke of corn cobs 2-propanone, 2-propanone1-hydroxy whose content was 2.01 - 4.98%. Curcumin compounds are one of the phenol compounds that can stimulate the accumulation of Rapid reactive Oxygen Species (ROS). ROS compounds can regulate plant defenses against biotic and abiotic stress [31].
Table 1. Analysis of components of corncob liquid smoke constituents

| Retention Time (minutes) | % Area | Alleged Compound                                      |
|--------------------------|--------|------------------------------------------------------|
| 2.100                    | 0.18   | Acetaldehyde                                         |
| 2.425                    | 2.53   | Phenol, 4-[2-(methylamino)ethyl]-                     |
| 2.525                    | 9.22   | Methylamine-D2                                        |
| 2.917                    | 0.14   | Methanamine                                          |
| 3.542                    | 2.01   | 2-Propanone                                          |
| 3.867                    | 0.28   | Methyl Acetate                                       |
| 6.158                    | 0.94   | Ethene, fluoro-                                      |
| 7.725                    | 44.52  | Acetic acid                                           |
| 9.500                    | 4.98   | 2-Propanone, 1-hydroxy-                              |
| 10.525                   | 0.34   | Methyl Glycollate                                    |
| 11.825                   | 4.69   | Propanoic acid                                       |
| 14.208                   | 3.90   | 1-Hydroxy-2-butanone                                 |
| 15.925                   | 0.47   | Butanoic acid                                        |
| 16.583                   | 0.57   | 2-Furanmethanol, tetrahydro-                         |
| 17.250                   | 3.80   | 2-Furancarboxaldehyde                                |
| 18.808                   | 2.96   | 2-Furanmethanol                                      |
| 19.183                   | 1.71   | 2-Propanone, 1-(acetyloxy)-                           |
| 20.933                   | 0.27   | Ethanone, 1-(2-furanyl)-                              |
| 23.358                   | 2.04   | 2(3H)-Furanone, dihydro-                             |
| 23.508                   | 0.73   | 2(5H)-Furanone                                       |
| 23.642                   | 0.30   | 2-Butanone, 1-(acetyloxy)-                            |
| 24.425                   | 0.48   | 3-Methyl-2-Cyclopenten-1-One                         |
| 25.133                   | 0.68   | 2-Furanmethanol, tetrahydro-                         |
| 26.858                   | 4.20   | Phenol (CAS) Izal                                    |
| 29.358                   | 2.76   | Phenol, 2-methoxy-                                   |
| 30.600                   | 0.69   | Phenol, 4-methyl-                                    |
| 31.975                   | 1.81   | Pentanal                                             |
| 33.683                   | 0.41   | Phenol, 2-methoxy-4-methyl-                          |
| 34.250                   | 0.73   | Phenol, 4-ethyl-                                     |
| 35.300                   | 0.39   | Geraniol                                             |
| 37.067                   | 0.32   | Phenol, 4-ethyl-2-methoxy-                           |
| 40.258                   | 1.08   | Phenol, 2,6-dimethoxy-                               |

3.5. Results of tested liquid smoke on the germination and maximum growth potential of tomato seeds (Solanum lycopersicum).

Seed germination is a benchmark for the ability of seeds to grow normally. The germination power test is carried out to determine the potential of seeds that can germinate from a group or unit of seed weight. The testing of seed germination is useful for determining the seeds of land area unity and checking seed quality. The results of the analysis of variance showed that the concentration of liquid smoke had a significant effect on germination and the maximum growth potential of tomato seeds. The highest germination and maximum growth potential of tomato seeds seen in the concentration of 1% liquid smoke, each of which was 96% and 99% (table 2). Rahayu et al. (2014) state that the maximum growth potential of seeds is influenced by the number of seeds germinating. The more seeds germinate, the higher the potential for seed growth, and vice versa [32]. Germination and maximal growth potential at the concentration of liquid smoke 0% were not significantly different from 0.5%, 1%, 1.5% and 2%, significantly different from the concentrations of 2.5%, 3%, 3.5%, 4, 5% and 5%, as shown in table 2. The concentration of liquid smoke 2.5% was not significantly different from 3%, but it was significantly different with concentrations of 4%, 4.5%, and 5%. The concentration of 4% is not significantly different from 4.5% and 5%. The lowest germination and maximum growth potential are seen in the concentration of 5% of corn cob liquid smoke, which was 9% and 15% respectively.
The lower the concentration of liquid smoke, the lower the sprout power and maximum growth potential.

**Table 2. Effect of concentrations of coconut shell liquid smoke on the potential for maximum growth and germination of tomato seeds**

| The concentration of liquid smoke | Germination (%) | Maximum growth potential (%) |
|----------------------------------|----------------|-----------------------------|
| Liquid Smoke 0 %                 | 94 a           | 94 a                        |
| Liquid Smoke 0.5%                | 92 a           | 95 a                        |
| Liquid Smoke 1%                  | 96 a           | 96 a                        |
| Liquid Smoke 1.5%                | 88 a           | 94 a                        |
| Liquid Smoke 2%                  | 91 a           | 93 a                        |
| Liquid Smoke 2.5%                | 75 ab          | 82 ab                       |
| Liquid Smoke 3%                  | 85 ab          | 89 ab                       |
| Liquid Smoke 3.5%                | 61 bc          | 68 bc                       |
| Liquid Smoke 4%                  | 22 c           | 39 c                        |
| Liquid Smoke 4.5%                | 10 c           | 29 c                        |
| Liquid Smoke 5%                  | 9 a            | 15                          |

The results of the analysis of variance showed that the concentration of liquid smoke had a very significant effect on the maximum growth potential and germination of tomato seeds, as seen from $F_{	ext{count}}$ of 26.35 and 9.56 greater than $F_{	ext{table}}$ 3.2 and 3.26 with 99% significance level. The Duncan test results showed that the maximum growth potential and germination power at 0.5% liquid smoke concentration differed from 1% concentration. 1.5%, 2%, 2.5%, 3% as shown in table 2. The occurrence of this difference is due to liquid smoke containing several nutrients that can provide the effect of stimulating plant growth depending on its concentration, at high concentrations, it can inhibit plant growth. According to Maurya et al., liquid smoke contains carbohydrate are effective in breaking the seeds and also controls the seedling growth of the plant [33]. The karrikin or lactone compounds in the liquid corn cobs identified are 2 (5H) -Furanone, 2 (3H) -Furanone, dihydro-, 2-Furancarboxaldehyde, 2-Furanmethanol, 2-Furanmethanol, tetrahydro-which contain 0.57% - 3.80% as shown in table 1. Karrikin is reported to increase seedling growth and seed vigor in many species, which is about 1200 species of more than 80 families [34]. The value of maximum growth potential and germination is closely related to the concentration of liquid smoke, the lower the concentration will cause the potential value of growth and germination to increase. The best concentration of liquid smoke is 0.5%, which results in the highest germination and maximum growth potential, each at 96% and 99%.

The results of the analysis of variance showed that the concentration of liquid corn cob smoke has a significant effect on the length of tomato sprouts. The Duncan test results showed that the length of tomato sprouts in liquid smoke concentrations of 0% and 0.5% were not significantly different, but significantly different with concentrations of 1%, 1.5%, 2%, 2.5%, 3%, 3.5 %, 4%, 4.5% and 5%, as shown in table 3. The concentration of liquid smoke 1% was not significantly different from the concentrations of 1.5%, 2%, 2.5%, 3% and 3.5%, but significantly different with concentrations of 4%, 4.5% and 5%. The best concentration that produces tomato sprout length is the concentration of liquid smoke is 0% and 0.5%, which produces an average length of 11.81 cm for concentrations of 0% and 10.80 cm for 0.5%. The lowest concentration that produces the lowest sprout length is 4%, 4.5%, and 5%. The higher the concentration of liquid corn cob, the lower the length of the sprouts.

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4. Conclusion
The chemical smoke characteristics of the third grade from the results of pyrolysis of corn cobs produced a yield of 28.37%, a pH value of 3.506 that met Japanese quality specification standards. The results of GCMS analysis of liquid smoke were found in 32 chemical components, most of which were acetic acid, which was 44.41%. The third-grade liquid corn cob smoke can accelerate the process of seed development, and the best concentration is 1% which results in the maximum growth potential and the highest germination of tomato seeds (Solanum lycopersicum) which is 96%.

The highest length of tomato sprouts at the concentration of liquid smoke is 0%, which is 11.81 cm, which is not significantly different from the concentration of 0.5%, which is 10.80 cm. The lower the concentration of liquid smoke, the better the sprout power, the maximum growth potential, and the length of tomato sprouts.

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