Utilization of Waste Palm Kernel Shells and Empty Palm Oil Bunches as Raw Material Production of Liquid Smoke

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Abstract. The availability of waste shells and empty palm oil bunches is very potential to be processed into liquid smoke. Liquid smoke is obtained from condensation of smoke resulting from the decomposition of organic compounds contained in shells and empty bunches of oil palm in the pyrolysis process. In this study investigated the effect of mass variations of raw materials and heating temperature on the shell pyrolysis process and empty fruit bunches of oil palm into liquid smoke. Variations in mass of raw materials are (125 grams of empty bunches and 375 grams of oil palm shells; 250 grams of empty bunches and 250 grams of oil palm shells; 375 grams of empty bunches and 125 palm oil shells) with heating temperatures at 400ºC and 500ºC. The parameters measured are density, color and aroma, yield on each sample, pH, concentration of acetic acid and phenol. From the results of the study, it is known that the sample that produces the most liquid smoke is a mixture of 125 grams of empty bunches and 375 grams of palm oil shells at a temperature of 500ºC which is 266 mL. The liquid smoke is then purified by the distillation method to a temperature of 150ºC. Liquid smoke color changes from black brown to clear to brass, liquid smoke has a sharp aroma of smoke. The mass of liquid smoke is 0.9866 g/mL with pH 2. The concentration of acetic acid is 10.793% and phenol is 56.856%.

Keywords: distillation, pyrolysis, acetic acid, phenol

1. Introduction
Palm oil is one of Indonesia’s mainstay commodities whose development is very rapid [1]. In addition to high palm oil production, by products or waste generated from palm oil processing are also high, both liquid and solid waste [2]. The solid waste is in the form of empty oil palm bunches and palm kernel shells [2]. Indonesia is the largest producer of palm oil in the world, with spread throughout Indonesia, especially South Kalimantan. The area of oil palm plantations in South Kalimantan in 2013 reached 372,720 Ha, consisting of smallholder plantations (69,449 Ha), large private plantations (298,365 Ha) and large state plantations (4,906 Ha)[3]. In its processing, to make 1 ton cubic meter of crude palm oil, the industry produces waste including 0.70 tons of palm fiber waste, 0.35 tons of cubic meters of palm kernel shell, and 1.1 tons of cubic meters of empty palm oil bunches [4]. Based on these data, a solution is needed to overcome the problem of waste palm kernel shells [2] and empty oil palm bunches [5]. One solution that can be used is the manufacture [6] of liquid smoke, the waste can be used as raw material [7] for making liquid smoke.

Empty palm oil bunches are palm oil mill waste [8, 9] which is very abundant. Every processing of 1 ton of Fresh Fruit Bunches will be produced as much as 22-23% empty palm oil bunches or 220-230 kg empty palm oil bunches. If in a factory with a processing capacity of 100 tons/hour with an operating time of 1 hour, it will produce 23 tons of empty palm oil bunches [10].
The content of the empty palm oil bunches [11] and palm kernel shells [12] can be seen in Table 1.

Table 1. Composite content of empty palm oil bunches and palm kernel shells

| Contents            | Value (%) | empty palm oil bunches | palm kernel shells [12] |
|---------------------|-----------|------------------------|-------------------------|
| Cellulose           | 33.25     | 26.6                   |
| Hemicellulose       | 23.25     | 27.7                   |
| Lignin              | 25.83     | 29.4                   |
| Water content       | 8.56      | 8                      |
| Extractive substances | 4.19      | 4.2                    |

Liquid smoke is a dispersion of steam in water. One way of making liquid smoke is by condensing smoke from combustion without oxygen from wood. During combustion, components of wood include cellulose, hemilulose and lignin [5] which will undergo pyrolysis to produce various compounds including phenol, carbonyl, acid, furans, alcohol, lacto, aromatic polycyclic hydrocarbons and others [13]. During this time hard wood materials such as mangium, tusam and sengon are widely used as materials [6, 8] for making liquid smoke [14].

Smoke is defined as a suspension of solid and liquid particles in the gas medium [13]. While liquid smoke according to [15] is a solution mixture of wood smoke dispersion in water made by condensing smoke from wood pyrolysis. Liquid smoke has antibacterial properties, is easy to apply and is safer than conventional acids and tar fractions containing aromatic hydrocarbons can be separated, so liquid smoke products are free of pollutants and carcinogens. This can occur if smoke settles on the surface or seeps into smoked food ingredients [16].

The chemical composition of liquid smoke and its percentage according to [17] is presented in the Table 2.
Compounds that play an important role as antimicrobials are phenol and acetic acid compounds, and their role is increased when both compounds are together [15]. Bacteria cannot grow because of the low pH of liquid smoke, which is 1.5-3.7 [18]. If liquid smoke has a low pH, the quality of liquid smoke produced is high in terms of its use as a food preservative because overall it affects the long-lasting value and shelf life of smoke products. This is because at a low pH, microbes or bacteria as a nuisance in the preservation process tend not to be able to live and reproduce properly [14]. Liquid smoke can also be used to eliminate odors in latex, phenol compounds contained in liquid smoke can kill spoilage bacteria that degrade proteins into amino acids, so as not to cause foul odor in latex. Phenol contained in liquid fumes has a high static bactericidal nature which causes bacteria to not multiply and are fungicidal so that fungi cannot grow [19].

Pyrolysis is Burning is the result of a large number of complicated reactions. One reaction that occurs is pyrolysis, which is the thermal breakdown of large molecules into small molecules without the presence of oxygen. Pyrolysis of large molecules in wood, for example, produces smaller gas molecules, which then react with oxygen above the surface of the wood [20]. Pyrolysis is a process of oxidation, polymerization and condensation of carbon-containing materials, both from plants, animals and mining goods to produce charcoal (carbon) and fumes that can be condensed to distillate [21].

According to [13], the reactions that occur during wood pyrolysis are:
1. Removal of water from wood at a temperature of 120-150°C;
2. Pyrolysis of hemicellulose at a temperature of 200-250°C which produces furfural, furan, acetic acid and its homolog;
3. Pyrolysis of cellulose at a temperature of 280-320°C which produces acetic acid compounds and carbonyl compounds such as acetaldehyde, glyoxal and acrolein;
4. Pyrolysis of lignin at 400°C produces phenol compounds, guaiacol, siringol together with homologues and their derivatives.

2. Methodology
This research uses pyrolysis process for 1 hour and distillation temperature to 150 °C, while the composition of empty fruit bunches, palm kernel shells and temperature can be seen in Table 3.

Table 2. Chemical composition of liquid smoke

| Chemical Composition | Value (%) |
|----------------------|-----------|
| Water                | 11 – 92   |
| Phenol               | 0.2 – 2.9 |
| Acid                 | 2.8 – 4.5 |
| Carbonyl             | 2.6 – 4.6 |
| Tar                  | 1 - 17    |

Table 3. Mass variations of palm kernel shells, empty palm oil bunches, and pyrolysis temperature

| Variable Names | Empty palm oil bunches (g) | Palm kernel shells (g) | Pyrolysis temperature (°C) |
|----------------|----------------------------|------------------------|----------------------------|
| V1-400         | 125                        | 375                    | 400                        |
| V2-400         | 250                        | 250                    | 400                        |
| V3-400         | 375                        | 125                    | 400                        |
| V1-500         | 125                        | 375                    | 500                        |
| V2-500         | 250                        | 250                    | 500                        |
| V3-500         | 375                        | 125                    | 500                        |
2.1. Materials
The materials used in this experiment are palm kernel shells, empty palm oil bunches and universal pH paper.

2.2. Methods
2.2.1. Preparation of Liquid Smoke Production
The process of making liquid smoke uses the pyrolysis method, which is by taking liquid smoke from raw materials (palm shells and empty palm oil bunches). This is done by inserting a mixture of palm kernel shells and empty palm oil bunches that have been cut into the burning boiler and igniting the fire continuously. The kettle is closed so that smoke is passed through a pipe connected to a cooling pipe to condense smoke. This melting smoke is then stored and referred to as liquid smoke.

2.2.2. Liquid Smoke Purification
Liquid smoke purification is done by distillation. Liquid smoke incorporated into the two-neck flask and heated using an electric heating to a temperature of 150°C. The distillation process is performed to remove the carcinogenic tar contained in the liquid smoke. The steam is formed and into the coolant pipe behind and distillate is collected in a flask.

2.2.3. Results Analysis
Samples were injected into GC-MS using standard acetate and phenol. The compound mixture passed by the gas chromatography will be separated into individual components. Some dominant components were further analyzed by mass spectrophotometers. With the computer can be determined the types of compounds with known standards. For pH analysis, a sample of 10 ml was measured using universal pH paper. And the last, the sample is filled into pycnometer to exceed the mark tera, then shut down and prevented from any air bubbles, then weighed. So the sample density can be known.

3. Results and Discussion
3.1 Effect of Raw Materials and Temperature on Liquid Smoke Results
Production of liquid smoke obtained in this study ranged from 32.6 to 53.2%. Liquid smoke from raw materials of 125 gram of empty palm oil bunches and 375 grams of palm kernel shells, 250 gram of empty palm oil bunches and 250 gram of palm kernel shells, and 375 gram of empty palm oil bunches and 125 gram of palm kernel shells at a temperature of 400 °C, respectively yielding 188 gram, 189 gram and 163 gram of liquid smoke. While liquid smoke from raw materials 125 gram empty palm oil bunches and 375 gram of palm kernel shells, 250 gram empty palm oil bunches and 250 gram of palm kernel shells, and 375 gram of empty palm oil bunches and 125 gram of palm kernel shells at a temperature of 500°C in a row produces 266 gram, 210 gram and 198.4 gram of liquid smoke.

| Table 4. Liquid smoke results in the amount of raw material and temperature differences |
|----------------------------------------|-----------------|----------------|----------------|----------------|
| Pyrolysis temperature (°C) | Variable Names | Empty Palm Oil bunches (g) | Palm kernel shells (g) | Yield liquid smoke (g) | Yield liquid smoke (%) |
|-----------------|-----------------|----------------|----------------|----------------|
| 400 | V1-400 | 125 | 375 | 188.0 | 37.6 |
| 400 | V2-400 | 250 | 250 | 189.0 | 37.8 |
| 400 | V3-400 | 375 | 125 | 163.0 | 32.6 |
| 500 | V1-500 | 125 | 375 | 266.0 | 53.2 |
| 500 | V2-500 | 250 | 250 | 210.0 | 42.0 |
| 500 | V3-500 | 375 | 125 | 198.4 | 39.7 |
Figure 2. Graph liquid smoke results in the amount of raw material differences and at 400 °C

Based on Figure 2, liquid smoke produced at 400°C ranges from 32.6% to 37.8%. The pyrolysis process was carried out for 1 hour in each variation of the composition of the raw material so that the most yield was known in the variation of 250 grams of empty palm oil bunches and 250 grams of palm kernel shells which was 37.8%. It can be seen that the difference in yield produced in the pyrolysis of 250 grams of empty palm oil bunches and 250 grams of palm kernel shells is only 0.2%, this is probably caused by the incomplete pyrolysis of lignin, because the new lignin decomposes at 400°C[13], so there were no significant changes in the variation of raw material composition between 125 grams of empty palm oil bunches and 375 grams of palm kernel shells with the composition of raw materials of 250 grams of empty palm oil bunches and 250 grams of oil palm kernel shells.

Figure 3. Graph liquid smoke results in the amount of raw material differences and at 500°C
Based on the Figure 3, it can be seen yield liquid smoke produced at 500°C temperature range from 42% to 53.2%. The pyrolysis process is carried out for 1 hour in each variation of the composition of raw materials so that the most yield is known to be produced in the variation of 125 grams of empty palm oil bunches and 375 grams of palm kernel shells which is 53.2%. This is. It’s because at higher temperatures there is a more perfect combustion and decomposition of cellulose, hemicellulose and lignin compounds. This is in accordance with what was [22] stated, i.e. the higher the temperature pyrolysis of the charcoal produced on the wane, this is due to the increasing decomposition or further reaction increased tar and charcoal into gas due to high temperatures.

Based on Figure 2 and Figure 3, both have research trends, that is the variation in composition of 375 grams of empty palm oil bunches and 125 grams of palm kernel shells producing the least yield while in the variation of composition of 250 grams of empty palm oil bunches and 250 grams of palm kernel shells and variations the composition of 125 grams of empty palm oil bunches and 375 grams of palm kernel shells produces higher yields. Especially at a temperature of 500°C, because the cellulose, hemicellulose and lignin pyrolysis processes are more perfect so that the liquid smoke produced is more than 53.2%. It’s also because the decomposition process of each compound became more perfect which caused more liquid smoke to be produced. In addition, in this study using palm kernel shells containing 29.4% lignin and 26.6% cellulose and oil palm empty fruit bunches containing 25.83% lignin and 33.25% cellulose so that more compounds can be decomposed into phenols and acetic acid which have an important role in liquid smoke.

3.2 Color and Flavor Liquid Smoke

Liquid smoke color looks blackish brown with a strong smoke flavor. The emergence of color and flavor is determined by the presence of phenol and carboxaldehyde compounds which are quite high in liquid smoke. Besides that burning of palm kernel shells and empty palm oil bunches also produces tar which can reduce the quality of liquid smoke and make the color of liquid smoke become black. A very significant color change occurs after purification of liquid smoke by distillation method, black brown liquid smoke changes color becomes clear yellowish after distillation because liquid smoke has been separated with tar which causes the color of blackish brown smoke. The following is a picture of liquid smoke before and after purification.

![Figure 4. (a). Liquid smoke before distillation; (b). Liquid smoke after distillation](image)

3.3 Purification of Liquid Smoke

Purification of liquid smoke is carried out on the highest yield samples, that is in samples with 125 grams of empty palm oil bunches and 375 palm kernel shells which are hydrolysed at 500°C. This sample produces liquid smoke of 266 gram or 53.2%. The purification process is carried out by distilling liquid smoke to 150°C to eliminate tar which is an impurity and carcinogenic to liquid smoke. The boiling point of acetic acid and phenol is 118.1°C and 182°C, while the boiling point of tar is an impurity in liquid smoke 496°C. The distillate obtained was 182 gram or 68.5%, so it was believed that there were as many as 84 gram of tar or 31.5% of the liquid smoke produced.
3.4 Liquid Smoke Specific Gravity

Specific weight is the ratio between the weight of a sample and its volume. Determination of the density of liquid smoke is done by using a picnometer. The result of specific gravity of liquid smoke that has been purified is 0.9866 g/mL.

3.5 Liquid Smoke pH

The pH value is one of the quality parameters of the resulting liquid smoke. The pH of liquid smoke in this research was 2.

3.6 Chemical Properties of Liquid Smoke (Acetic Acid and Phenol)

Analysis of the chemical properties of liquid smoke from palm kernel shells and empty palm oil bunches was carried out using GC-MS to determine the types of compounds found in liquid smoke. The compound mixture passed in gas chromatography will be separated into individual components as follows:

Acidic compounds that have antimicrobial properties can be analyzed using GC-MS. Liquid smoke analyzed was the result of pyrolysis of 125 grams of empty bunches and 375 grams of palm shells at 500°C which had been distilled so that it was known that the concentration of acetic acid contained in liquid smoke was 10.793%. Acetic acid is formed from the decomposition of hemicellulose, as [13] said, organic acid compounds are formed from pyrolysis of wood components such as hemilulose at 200-250°C and cellulose at 280-320°C. The material that is more dominant in this pyrolysis is the palm shell which according to [12] has a cellulose content of 26.6% and hemilulose 27.7%.

Phenol compounds produced in this study amounted to 56.856% which were analyzed using GC-MS. Phenol is produced from decomposition of lignin at 400°C [13]. This research pyrolysis was carried out at a temperature of 500°C so that perfect lignin decomposition occurred which caused phenol to be the most dominant compound in liquid smoke.

![Figure 5. Liquid smoke chromatogram palm kernel shells and oil palm empty fruit bunches](image)

4. Conclusion

The pyrolysis process at a temperature of 400°C produces the maximum yield of liquid smoke by 37.8% with a raw material of 250 grams of palm kernel shell and 250 grams of empty palm oil bunches while pyrolysis at a temperature of 500°C produces the highest yield of 53.2% with a raw material of 375 grams of palm kernel shell and 125 grams of empty palm oil bunches.
Liquid smoke with the highest yield is produced from pyrolysis of 125 grams of empty palm oil bunches and 375 grams of palm kernel shells at a temperature of 500°C which is 266 mL with pH and acetic acid content of 10.793% and phenol levels of 56.8856%. The purification process of liquid smoke can be done by distillation in a temperature of 150 °C.

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