Quality improvement of smoke liquid from oil palm fronds pyrolysis through adsorption - distillation process by using zeolite as adsorbent

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Abstract. Oil palm plantations produce significant amounts of oil palm fronds as a waste. The availability of oil palm fronds is very potential to be processed into liquid smoke. Liquid smoke is obtained from the condensation of vapor from smoke as a result of decomposition of organic compounds contained in oil palm fronds in the pyrolysis process. This study aims to determine the increased quality of liquid smoke through the adsorption process by using activated zeolite and distillation with used pyrolysis temperature were 400 °C, 500 °C, and 600 °C for 60 minutes, 90 minutes, and 120 minutes. Analysis of the composition of liquid smoke compounds using by GC-MS Shimadzu QP 2100 brans. Parameters observed included total carboxylic acid, phenol, and carbonyl. The results of the study obtained the highest carboxylic acid content after distillation obtained was 89.58% at pyrolysis temperature of 500 °C 120 minutes, phenol was 7.32% at pyrolysis temperature of 600 °C 120 minutes, and carbonyl was 35.58% at pyrolysis temperature of 400 °C 60 minutes.

1. Introduction
Oil palm fronds are products of oil palm plantations that can be obtained along the year with harvesting fresh fruit bunches [1]. The area of oil palm plantations Indonesia in 2017 is estimated to reach 12.30 million ha. In 1 ha oil palm plantations are estimated to produce 6400-7500 fronds/year in weights of 4.5 kg dry weight per fronds [2] [3] [4] [5]. The abundance of oil palm fronds is supported by the rapid growth of the oil palm industry in Indonesia, so research needs to be done by utilizing oil palm fronds as raw material [6] [7] [8] [9]. The components in oil palm fronds consist of cellulose, hemicellulose, lignin and will produce useful products if pyrolyzed [10].

According to Oktafany [11] pyrolysis is an irregular decomposition process of organic materials caused by heating without contact with air. The smoke produced from the high-temperature combustion process will enter the condenser and inside the condenser the smoke will condense. Condensation will change gas into a liquid known as liquid smoke.

Liquid smoke can preserve food because of the presence of acidic compounds, phenols, and carbonyl. It has been used extensively in food systemsto give flavor characteristics that are similar to smokedfood products. These may be used to preserve quality and ensure the safety of foods [12].
In this study liquid smoke produced from the pyrolysis process needs to be carried out purification process in the form of adsorption and distillation to increase the quality of liquid smoke. The process of adsorption of liquid smoke using activated zeolite as an adsorbent. Zeolite has a high selective cation exchange capacity (CEC) makes it suitable for various uses in removing impurities [11].

Liquid smoke that has gone through the purification process with adsorption is still pitch black and the smoke smell is not stinging. Distillation is a way to purify liquid smoke based on boiling point differences, carried out to remove unwanted and dangerous compounds, such as Polycyclic Aromatic Hydrocarbon (PAH) and tar [13].

2. Method
This study aims to determine the increased quality of liquid smoke through the adsorption process with activated zeolite and distillation. In this study, the process of producing liquid smoke has 3 stages: pyrolysis, liquid smoke purification by adsorption using zeolite as an adsorbent and distillation.

2.1. Pyrolysis of liquid smoke
Oil palm fronds are the main raw material for making liquid smoke. The equipment used to make liquid smoke is the pyrolysis reactor circuit. While the equipment used for analysis include analytic balance sheets, pH meters, glass funnels, filter paper, and other analytical support equipment.

Oil palm fronds are chopped into small sizes and then dried until the weight is constant. For each pyrolysis process, 1,000 grams of raw material is used. Raw materials are pyrolyzed at temperatures of 400 °C, 500 °C, and 600 °C with 60 minutes, 90 minutes and 120 minutes. Furthermore, liquid smoke was analyzed using GC-MS Shimadzu QP 2100 brans.

2.2. Purification of liquid smoke with activated zeolite
Liquid smoke will be adsorbed by using activated zeolite that has been activated by H₂SO₄. Activated zeolite was added to anerlenmeyer containing liquid smoke and stirred using a magnetic stirrer for 60 minutes.

2.3. Purification of liquid smoke by distillation
Liquid smoke has been purified with zeolite is then subsequently distilled to obtain pure liquid smoke, and was analyzed using GC-MS Shimadzu QP 2100 brans.

3. Result and discussions
The results of the oil palm fronds pyrolysis produce condensate in the form of smoke liquid mixed with tar and charcoal residues. The condensate liquid is solid black, and smells of smoke, known as liquid smoke from the oil palm fronds pyrolysis. After pyrolysis liquid smoke will pass through 2 stages of purification, which is adsorption with the treated zeolite and distillation. Figure 1 below shows liquid smoke obtained from the results of this study.
Figure 1 shows the result of pyrolysis, adsorption, and distillation of liquid smoke. It was seen that the pyrolysis process of liquid smoke produced was pitch black. After passing the adsorption process liquid smoke was still pitch black, but the heavy fractions such as tar were partially lost and the smell was reduced due to zeolite adsorbing the tar. The distillation process changed liquid smoke becomes clearer bright yellow, because of separation tar in liquid smoke. The following are Japan and FAO liquid smoke quality standards

| Parameter          | Standards of liquid smoke |
|--------------------|---------------------------|
| Organic acid (%)   | 1 – 18                    | [8] |
| pH                 | 1.5 – 3.7                 | [8] |
| Color              | Light yellow-brown/light brown | [8] |
| Phenol (%)         | 0.1 – 16                  | [9] |
| Carbonyl (%)       | 2 – 25                    | [9] |
| Acetic acid (%)    | 2 – 20                    | [9] |

The result in this study will be discussed in 3 parts, namely the parameters of testing the quality of liquid smoke total will discuss as carboxylic acid, phenol, and carbonyl.

3.1 Total carboxylic acid compounds from GCMS analysis
In this study, it can be seen that liquid smoke obtained from oil palm fronds contains acidic compounds. Figure 2 shows a graph of the GCMS analysis of the total content of acid compounds in liquid smoke after distillation.
Organic acids have a bactericidal/bacteriostatic effect means it able to inhibit the development of microbes and known as antibacterial [17]. The main source of acid formation is the degradation of cellulose and hemicellulose [18]. The content of cellulose and hemicellulose contained in oil palm fronds is 58% and 24% [12]. So if the content of cellulose and hemicellulose in the material is high, the acid level in the liquid smoke obtained will also be high. The highest carboxylic acid content after distillation obtained was 89.58% at pyrolysis temperature of 500°C and pyrolysis time of 120 minutes.

3.2 Total phenol compounds from GCMS analysis
In this study, it can be seen that liquid smoke obtained from oil palm fronds contains phenol compounds. Figure 3 shows a graph of GCMS analysis of the total content of phenol compounds in liquid smoke after distillation.

Phenol contributes significantly to smoke condensation has the potential as an antioxidant [20]. Phenol compounds in liquid smoke also play a role in the color and taste of smoke [12]. Phenol compounds in liquid smoke result from the degradation of lignin contained in raw materials [21]. The lignin content found in oil palm fronds is 20.48% [22]. The highest phenol content after distillation obtained was 7.32% at pyrolysis temperature of 600°C and pyrolysis time of 120 minutes.

3.3 Total carbonyl compounds from GCMS analysis
In this study, liquid smoke obtained from oil palm fronds contains carbonyl compounds. Figure 4 shows a graph of GCMS analysis of the total levels of carbonyl compounds in liquid smoke after distillation.
Carbonyl compounds impart sweet or sweet-burnt and tend to soften the heavy smoky aroma associated with phenolic compounds [12]. Cellulose and hemicellulose will be converted into carbonyl compounds during pyrolysis. The higher the level of cellulose and hemicellulose, the higher the carbonyl content obtained [21]. The highest carbonyl content after distillation obtained was 35.58% at pyrolysis temperature of 400 °C and pyrolysis time of 60 minutes.

4. Conclusions
Based on the objective that has been done liquid smoke can be seen as an increase in the quality of liquid smoke after going through the adsorption purification stage using activated zeolite and distillation. This was evidenced by the liquid smoke was pitch black to bright yellow due to being separated by tar compounds and the reduced smell of stinging liquid smoke.

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