Improving the quality of liquid smoke from pyrolysis of oil palm fronds with the adsorption–distillation purification process

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Abstract. Oil palm fronds have the potential to be processed into liquid smoke. The main compounds contained in liquid smoke are acids, phenols and carbonyl produced from the decomposition of cellulose, hemicellulose and lignin. The aim of this research is to purify the liquid smoke from the oil palm frond pyrolysis through the adsorption process with activated zeolite and distillation. The pyrolysis process takes place at a pyrolysis temperature of 400°C for 120 minutes, and the distillation process was carried out at the temperature of 150°C, 175°C and 200°C with 30 minutes, 45 minutes and 60 minutes. The analysis of liquid smoke conducted using the GC-MS Shimadzu QP 2100 brans instrument. The results indicated the highest acetic acid in liquid smoke was 63.09% at a distillation temperature of 150°C for 45 minutes. The highest total phenol content was 12.44% at 200°C distillation temperature for 60 minutes, and the highest total carbonyl content was 21.56% at 200°C distillation temperature for 60 minutes.

1. Introduction

Pyrolysis is a thermal conversion process where the material is treated in an inert atmosphere without oxygen [1]. The pyrolysis process takes place at high temperature of 400°C - 500°C to produce condensed steam in the form of a liquid-based product, containing organic compounds (around 70-80%) and water (20-30%) [2]. These organic compounds are acids including formic acid, acetic acid, propanoic acid, aldehydes, ketones, furans, furfural, guaiacol and compounds with high molecular weight, named tar [3].

Liquid smoke has the ability to preserve food ingredients due to the presence of acidic and phenolic compounds. These compounds have contributions in giving the characteristics of aroma, color, taste, and also as an antioxidant and antimicrobial in food ingredients such as meat, fish, and cheese [4], [5]. To obtain liquid smoke in accordance with FAO standard, the purification process required in the form of adsorption and distillation [6].

The liquid smoke adsorption process uses activated zeolite as adsorbents. Darmadji reported that the liquid smoke adsorption process using activated zeolite was able to reduce the number of micro particle compounds such as tar [4]. Furthermore, distillation is a way to purify liquid smoke by the process of separating a solution based on differences in boiling points [7]. Liquid smoke distillation carried out to eliminate unwanted and dangerous compounds.

2. Materials and Method

This study uses oil palm fronds as the main raw material in making liquid smoke from oil palm plantations around the University of North Sumatra, Medan, North Sumatra, Indonesia. Supporting materials used in this study are natural zeolite as an adsorbent, sulfuric acid (H₂SO₄) as an activator of
zeolite and *aquadest* (H$_2$O). The equipments used for analysis are analytical balance, pH meter, glass funnel and filter paper.

This research was conducted using the pyrolysis process at temperature of 400°C for 120 minutes to produce liquid smoke. Before the pyrolysis process, the oil palm fronds cut into small sizes using a chopper machine. Cut and dried oil palm fronds put in to the pyrolysis reactor. The condensate in the form of liquid smoke then stored for 2 x 24 hours and filtered using filter paper to separate the tar compounds.

Liquid smoke produced from the pyrolysis process will be purified by the process of adsorption and distillation. Liquid smoke is adsorbed with activated zeolite at the temperature of 60°C for 30 minutes. After the adsorption process, liquid smoke distilled at temperatures of 150°C, 175°C and 200°C for 30 minutes, 45 minutes and 60 minutes. Liquid smoke analysis carried out using the GC-MS Shimadzu QP 2100 brans instrument to determine the composition of liquid smoke after pyrolysis and after the purification process.

3. Results and Discussions
The results of pyrolysis of oil palm fronds produce condensate in the form of liquid smoke mixed with tar and char residue. Figure 1 displays the liquid smoke obtained from the pyrolysis.

![Figure 1](image)

**Figure 1.** (a) Pyrolysis reactor (b) Liquid smoke resulted from pyrolysis (c) Liquid smoke after precipitation and filtration

Liquid smoke produced from the pyrolysis process of oil palm fronds at a temperature of 400°C for 120 minutes contain components of carboxylic acid compounds, carbonyl, and phenol derivatives. The results obtained in this study did not differ from the previous research literature, such as the pyrolysis process using raw materials of coconut shell [8], gleam wood [9], and oil palm shells [10]. These organic compounds produced from the thermal decomposition of cellulose, hemicellulose compounds, and the decomposition of lignin contained in the raw material [11].

Liquid smoke obtained from the pyrolysis of oil palm fronds must go through a refining process before being used as a food preservative. In this research, liquid smoke purified by the adsorption and distillation process. Adsorption process intends to eliminate contaminants in liquid smoke such as polyaromatic hydrocarbons (PAH) and tar. After the adsorption process, liquid smoke distilled to separate impurities such as tar in the liquid smoke, so that the liquid smoke obtained has high preservation properties and protected from carcinogenic compounds such as PAH, HAA, and tar [13],
[14]. Figure 2 shows the results of purification of liquid smoke before and after the adsorption and distillation process.

![Figure 2](image1.png)

**Figure 2.** Liquid smoke (a) before the adsorption process (b) after the adsorption process (c) after the distillation process, and (d) distillation tar residue

The color of liquid smoke before (a) and after (b) the adsorption process is solid black. After the distillation process, the color of liquid smoke changes into brown (c). This is caused by the content of tar compounds which are basically black and high molecular weight components have been separated from the liquid smoke (d).

The functional compounds contained in the liquid smoke such as acetic acid has a bactericidal effect/bacteriostatic, it is able to inhibit the growth of microbes and is known as an antibacterial [15], [16], phenol acts as antioxidants and forming aromas contained in the liquid smoke, and carbonyl has a role in coloring and flavors in food [17], [18]. The levels of acetic acid, phenol and carbonyl compounds amend after passing the purification stages. Table 1 shows the quality standards of liquid smoke as a food preservative.

| Parameter        | Quality Standards |
|------------------|-------------------|
| Color appearance | Yellow/light brown|
| Acetic acid      | 2-20%             |
| Carbonyl         | 2-25%             |
| pH               | 1.5-3             |
| Phenol           | 0.1-16%           |
| Benzo(a)pyrene   | Max 2 μg/kg       |

The quality of liquid smoke from the appearance of color undergoes a change from jet black to clearer color after passing through adsorption and distillation process. The results of this study discuss about three important components contained in liquid smoke: acetic acid, phenol and carbonyl.

### 3.1 The Levels of Acetic Acid Compounds in Liquid Smoke After The Adsorption and Distillation Process

The effect of adsorption using activated zeolite and distillation on acetic acid compounds in liquid smoke can be seen in Figure 3.
The process of adsorption and distillation on liquid smoke can affect the levels of acetic acid in the liquid smoke. The percentage change in the levels of acetic acid in liquid smoke from the pyrolysis process and after the process of adsorption and distillation can be seen in Table 2.

### Table 2. Levels of Acetic Acid in Liquid Smoke after the Adsorption and Distillation Purification Process

| Run | Temperature (°C) | Time (minutes) | Area (%) | Pyrolysis | Adsorption | Distillation | Pyrolysis to Adsorption Change (%) | Adsorption to Distillation Change (%) |
|-----|------------------|----------------|----------|-----------|------------|--------------|-----------------------------------|--------------------------------------|
| I   | 150              | 30             | 59.56    | -         | +23.31     | +24.59       |                                   |                                      |
| II  |                  | 45             | 63.09    | +30.62    |            |              |                                   |                                      |
| III |                  | 60             | 60.18    | +24.59    | +26.25     | +22.85       |                                   |                                      |
| IV  | 175              | 30             | 60.98    | -9.46     | +19.75     |              |                                   |                                      |
| V   |                  | 45             | 57.84    | +13.14    | +11.63     |              |                                   |                                      |
| VI  |                  | 60             | 59.34    | +13.14    |            |              |                                   |                                      |
| VII | 200              | 30             | 54.65    | +13.85    |            |              |                                   |                                      |
| VIII|                  | 45             | 54.99    | +13.85    |            |              |                                   |                                      |
| IX  |                  | 60             | 53.92    | +11.63    |            |              |                                   |                                      |

+ = increased
- = decreased

The levels of acetic acid compounds in liquid smoke decrease after adsorption using activated zeolite. This is due to the fact that zeolite pores are able to absorb acetic acid which contains polar carboxyl groups in liquid smoke [20], so that the levels of acetic acid decrease after being adsorbed with activated zeolite [21].

After the adsorption process is carried out, the next process is to separate the active substance or non-refrigerant compounds such as polyaromatic hydrocarbons (PAH) and tar in the liquid smoke by distillation. Acetic acid compounds increased after the distillation process, this is due to the distillation process removes impurities such as tar and polyaromatic hydrocarbons (PAH) [22].

In general, Figure 3 shows that the levels of acetic acid decrease with the increasing of distillation temperature. The level of acetic acid at a temperature of 150°C is higher than the level of acetic acid at
a temperature of 175°C and 200°C. This is because high temperatures will form other compounds such as phenols which can reduce the levels of acetic acid in liquid smoke.

Based on the theory, through the distillation process, each component in a solution will evaporate at its boiling point [23, 24]. Acetic acid has a boiling point of 118 °C [25]. The distillation temperatures used in this study are 150°C, 175°C and 200°C, so that after the distillation process the acetic acid levels decrease with the increasing of distillation temperature. The acetic acid levels obtained in this study had met the FAO standard for each run as in Table 1. The highest levels of acetic acid obtained at a temperature of 150°C in 45 minutes which is 63.09%.

3.2 The Levels of Phenolic Compounds in Liquid Smoke After Adsorption and Distillation Process

The effect of adsorption using activated zeolite and distillation on phenolic compounds in liquid smoke can be seen in Figure 4.

![Figure 4](image)

**Figure 4.** Phenolic compounds in liquid smoke after the adsorption and distillation process

The process of purification of adsorption and distillation on liquid smoke from pyrolysis can affect the levels of phenolic compounds in the liquid smoke. The percentage change in the level of phenolic compounds in liquid smoke from the oil palm frond pyrolysis and after the process of adsorption and distillation can be seen in Table 3.

| Run | Temperature (°C) | Time (minutes) | Pyrolysis Area (%) | Adsorption to Distillation Change (%) | Adsorption to Distillation Change (%) |
|-----|------------------|----------------|--------------------|--------------------------------------|--------------------------------------|
| I   | 150              | 30             | 2.09               | - 85.35                              |                                       |
| II  | 150              | 45             | 1.92               | - 86.54                              |                                       |
| III | 175              | 60             | 2.15               | - 84.93                              |                                       |
| IV  | 175              | 30             | 1.87               | - 86.89                              |                                       |
| V   | 175              | 45             | 10.24 14.27        | +0.39                                | - 86.40                              |
| VI  | 200              | 60             | 1.53               | - 89.27                              |                                       |
| VII | 30               |                | 12.41              | - 13.03                              |                                       |
| VIII| 45               |                | 12.11              | - 15.13                              |                                       |
| IX  | 60               |                | 12.44              | - 12.82                              |                                       |

+ = increased  
- = decreased
The results showed that after the adsorption process the levels of phenolic compounds had increased. The adsorption process can remove impurities such as tar and polyaromatic hydrocarbons (PAH), therefore the percentage of phenolic compounds increase [22].

After the purification adsorption process, the next stage is distillation. The phenolic compounds decrease after the distillation process, due to the high boiling point of phenol (182°C) [26] in the other hand, the distillation temperatures used in this study are 150°C and 175°C, what makes the phenolic compounds has not been completely evaporated because it has not yet reached the boiling point and obtained a small phenol content. The distillation process uses the basis that some components will evaporate at their boiling points [27]. So in general, after the distillation process the levels of phenolic compounds will increase at 200°C. The higher the distillation temperature, the higher the phenol content obtained in the liquid smoke [8].

The levels of phenolic compounds obtained in this study have met the FAO standard for each run as in Table 1. The highest phenol content obtained at 200°C for 60 minutes in the amount of 12.44%.

3.3 The Levels of Carbonyl Compounds in Liquid Smoke After The Adsorption and Distillation Process

The effect of adsorption using activated zeolite and distillation on carbonyl compounds in liquid smoke can be seen in Figure 5.

![Figure 5. Carbonyl compounds in liquid smoke after the adsorption and distillation process](image_url)

The process of purification of adsorption and distillation on liquid smoke can affect the levels of carbonyl compounds in the liquid smoke. The percentage change in carbonyl content in liquid smoke from the oil palm frond pyrolysis after the adsorption and distillation can be seen in Table 4.

The carbonyl compounds level increase after the adsorption process. The adsorption process can remove impurities such as tar and polyaromatic hydrocarbons (PAH), therefore the percentage of carbonyl compounds increase [22].
Table 4. Carbonyl Content in Liquid Smoke after the Adsorption and Distillation Purification Process

| Run | Temperature (°C) | Time (menit) | Area (%) | Pyrolysis to Adsorption Change (%) | Pyrolysis to Distillation Change (%) | Adsorption to Distillation Change (%) |
|-----|------------------|--------------|----------|----------------------------------|--------------------------------------|--------------------------------------|
| I   | 150              | 30           | 17.33    | -25.43                           | 25.30                                | 12.86                                |
| II  | 45               | 45           | 17.36    | -21.25                           | 23.66                                | 11.91                                |
| III | 60               | 60           | 20.25    | -11.91                           | 23.66                                | 11.91                                |
| IV  | 175              | 30           | 18.30    | -21.25                           | 23.66                                | 11.91                                |
| V   | 200              | 45           | 22.75    | 17.74                            | +2.15                                | -23.66                               |
| VI  | 60               | 60           | 20.81    | -10.45                           | 23.66                                | 11.91                                |
| VII | 30               | 21.47        | 21.47    | -7.61                            | 23.66                                | 11.91                                |
| VIII| 200              | 20.81        | 20.81    | -10.45                           | 23.66                                | 11.91                                |
| IX  | 60               | 21.56        | 21.56    | -7.22                            | 23.66                                | 11.91                                |

+ = increased
- = decreased

After the adsorption process, the next process is distillation. The carbonyl compounds level decrease after the distillation process. It is caused by during the distillation process, the temperature used is high enough so that the levels of other compounds such as acetic acid increase and causes the percentage of carbonyl compounds to decrease in liquid smoke. The carbonyl compounds are volatile components because they have a low boiling point of 110°C. Distillation temperatures used in this study were 150°C, 175°C, and 200°C.

In Figure 5, the levels of carbonyl compound at distillation temperatures of 150°C are lower than carbonyl levels at distillation temperatures of 200°C and 175°C. It is caused by at the distillation temperature of 150°C, the levels of carbonyl compounds obtained are very high, resulting in levels of carbonyl compounds at a temperature of 150°C becomes lower. In addition, the content of the tar components in liquid smoke which make the appearance of liquid smoke color becomes jet black is separated in the distillation process and resulting in clearer color of liquid smoke. The carbonyl compounds obtained in this study had met the FAO standard for each run as in Table 4. The highest carbonyl content obtained at 200°C for 60 minutes in the amount of 21.56%.

4. Conclusion
Purification processes by means of adsorption with activated zeolite and distillation improves the quality of liquid smoke. The adsorption process can reduce the sharp odor of liquid smoke but the color of liquid smoke is still black because the tar compound content is still not separated from the liquid smoke. The distillation process can separate the tar compound from liquid smoke, thus the liquid smoke color turns from jet black to clearer color. After going through the adsorption and distillation process, the highest levels of acetic acid obtained was 63.09% at 150°C for 45 minutes. The highest total phenol content obtained was 12.44% at the distillation temperature of 200°C for 60 minutes, and the highest total carbonyl content obtained was 21.56% at the distillation temperature 200°C for 60 minutes.

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