Improving the quality of liquid smoke from oil palm fronds through adsorption and distillation processes

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Abstract. This research aims to obtain information regarding purification of liquid smoke from the pyrolysis of oil palm fronds to be used as a preservative product following food quality standards. This research started by performing the pyrolysis of oil palm fronds at 250 °C for 2 hours to produce liquid smoke. Subsequently, the liquid smoke from the pyrolysis was purified in two stages, namely adsorption and distillation. The adsorption which was carried out at 60 °C for 1 hour by using an activated zeolite, resulted in liquid smoke which still contains a tar contaminant compound. The analysis of the liquid smoke after adsorption showed a decrease in the composition of carbonyl and phenol compounds but in trace amounts. Meanwhile, the distillation was carried out at 125, 150, 175, and 200 °C and at 15, 30, 45, and 60 minutes, which resulted in a liquid smoke that is free of tar. The research revealed that the recommended temperature and time of distillation was at 150 °C and 45 minutes with tar residue of 2.4 %, total acid of 5.15 % and a pH of 2.3. Furthermore, GC-MS analysis indicated that the resulting liquid smoke was dominated by acetic acid compounds of 45.46 % (w/w).

1. Introduction

Production of palm oil plantation in Indonesia continuously increases every year. The agriculture census data report Indonesia’s palm oil plantation in 2010 by 21.95 million ton and increase in 2016 by 33.23 million ton [1] [2] [3] [4] [5]. The increasing in palm oil plantation production will increase the number of waste, either liquid waste or solid waste. Oil palm fronds are one of an abundantly solid waste from palm plantation. It is due when harvest time of fresh fruit bunch, 1-2 stems of oil palm frond are cut to facilitate pollination and harvest easily. The plantation will produce 22 stems of oil palm frond each tree every year, and each stem has a weight 2.2 kg, so in 1 ha palm oil plantation will generate 6.3 tonnes oil palm fronds every year [6]. Oil palm fronds consist of cellulose (34.89 %), hemicellulose (27.14 %) and lignin (19.87 %) [7]. Based on the chemical content, oil palm fronds have potential to be leveraged as an economically valued product.

Pyrolysis is one of the methods that can be used to convert biomass to become a highly valued product. Pyrolysis process was conducted at high temperature to break chemical bonding from cellulose, hemicellulose and lignin to generate molecules that rich of oxygen [8]. Pyrolysis process at a high temperature of 500 °C [9] produces vapor that will be condensed to obtain liquid smoke, which normally contains organic compounds (about 70-80 %) and water (20-30 %). The organic compounds are formic acid, acetic acid, propanoic acid, aldehyde, ketone, furan, furfural, phenol and a high molecular compound known as tar [10].

Acetic acid is the largest composition of carboxylic acid which has antimicrobial activity and for 5 % concentration has a bactericidal effect on the food. Phenol compound can give a specific taste for
the food sourcing from guaiacol, 4-methyl guaiacol, and 2,6-dimethoxyphenol (syringol), whereas carbonyl (aldehyde, ketone) will contribute as a coloring in the food texture [6]. Based on the chemical content contained in the liquid smoke, it has an opportunity that the liquid smoke can be used as a natural food preservative product to substitute a harmful substance such as formalin and borax.

Some research has been conducted regarding pyrolysis of biomass form various types of raw material such as coconut shell [11], sawdust or wood [12], oil-palm shell [13], and oil palm fronds [14]. The result revealed that the liquid smoke obtained from the pyrolysis process can’t be used directly as a natural preservative to the food, because the existence of harmful substance known as tar causing the dark color of liquid smoke. It is necessary for functional compounds (acetic acid, phenol, carbonyl) must be separated from tar contained in the liquid smoke to improve the quality of liquid smoke following the standard that shown in table 1 [15].

Table 1. Quality standards of liquid smoke [15].

| Parameter                | Description          |
|--------------------------|----------------------|
| The appearance of color  | Yellow/Light brown   |
| Acidity                  | 2 – 20 % (as acetic acid) |
| pH                       | 1.5 – 3              |

Based on the research conducted, adsorption using activated zeolite has been claimed able to contribute in the purification of liquid smoke [16]. The research was conducted by two stages of adsorption and distillation. However, there is an irregularity in its research design because the sample analysis was performed after the distillation process. It caused to a bias of information on the adsorption process, because the obtained data from sample analysis was not exactly known whether to be influenced by adsorption or distillation. Therefore, it needs to look research forward to keep the purification process clearly understood. This paper covers a description of the performance of each purification process between adsorption and distillation by performing analysis separately between adsorption and distillation. Other than that, this research also aims to obtain information regarding the effect of temperature and time of the distillation on acid content, pH, and its performance in eliminating contaminant compound (tar).

2. Materials and method

2.1. Materials

This research used oil palm fronds as a raw material to produce liquid smoke obtained from a local plantation in Sumatera Utara, Indonesia. Before the pyrolysis was carried out, oil palm fronds were cut into small size by using chopper to broaden the surface area. Besides, other materials used in this research were natural zeolite, sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), purified water, phenolphthalein indicator, and sodium hydroxide (NaOH).

2.2. Method

This research was started by performing the pyrolysis process at 250 °C for 2 hours in the pyrolysis reactor equipped with a condenser to condense smoke generated from the process. Figure 1 gives the schematic diagram of pyrolysis reactor.
Decantation was used for crude smoke liquid for 2 x 24 hours to allow solid particle settling in the bottom before further process. Adsorption of crude liquid smoke has been conducted by using zeolite which was activated using H$_2$SO$_4$ 1.2 M at 78 °C for 60 minutes. Adsorption process took for 30 minutes at 60 °C, equipped with a magnetic stirrer at 125 rpm and the ratio of zeolite: crude liquid smoke was 1 gram: 10 ml. Then, the crude liquid smoke was performed by distillation process at 125, 150, 175, and 200 °C for 15, 30, 45, and 60 minutes. The following figure is the sketch of the adsorption and distillation process.

![Figure 1](image1.png)

**Figure 1.** Design of pyrolysis reactor equipped with condenser.

Analysis parameters were performed including total acid by titration [17], composition analysis by GC-MS Shimadzu QP 2100 brans and pH value by pH meter.

### 3. Results and discussion

The result showed that the crude liquid smoke after the adsorption process indicated containing contaminant compound which can be seen in figure 3. The crude liquid smoke generated after the adsorption process was still dark color which means the contaminant compounds has not wholly eliminated.
Figure 3. The result of liquid smoke after adsorption process still containing contaminant (tar).

Table 2. Comparison of liquid smoke composition before and after adsorption.

| Substances                                    | Liquid smoke composition (%) | Before adsorption | After adsorption |
|-----------------------------------------------|------------------------------|-------------------|------------------|
| Acetic acid                                   | 47.36                        | 51.01             |
| Propanoic acid                                | 1.44                         | 2.05              |
| 2-furancarboxaldehyde                        | 4.64                         | 3.97              |
| 1-hydroxy-2-propanone                        | 9.54                         | 8.58              |
| 1-hydroxy-2-butanone                         | 1.7                          | 1.54              |
| 1-acetyloxy-2-propanone                      | 1.38                         | 1.25              |
| 2-methyl-2-cyclopentanone                    | 0.85                         | 0.68              |
| Butyrolactone                                | 1.95                         | 1.73              |
| 3-methyl-2-cyclopentanone                    | 1.06                         | 0.97              |
| 2-hydroxy-3-methyl-2-cyclopentanone          | 0.93                         | 0.76              |
| 3-hydroxy-2-butanone                         | -                            | 0.55              |
| 2,3-dimethyl-2-cyclopentanone                | -                            | 0.55              |
| 2-butan-1,4-diol                              | 0.92                         | -                 |
| Tetrahydro-2-furan methanol                  | 0.82                         | 0.69              |
| 2-furan methanol                             | 1.31                         | 1.19              |
| phenol                                       | 17.97                        | 16.97             |
| 2-methyl-phenol (o-cresol)                   | 4.15                         | 4.05              |
| 2-methoxyphenol (guaiacol)                   | 1.41                         | 1.34              |
| 2,6-dimethoxy phenol (syringol)              | 1.89                         | 1.48              |

From table 2, there is an indication that the composition of compounds in liquid smoke decrease after the adsorption process is performed. The compounds are all of the carbonyl groups such as aldehyde, furan, ketone whereas phenolic compounds also decrease, such as phenol, 2-methyl-phenol, 2-methoxy phenol, and 2,6-dimethylphenol. Based on the result obtained, the adsorption process can reduce compounds contributing to dark color (carbonyl) and strongly smoky odor (phenolic and derivatives) from liquid smoke, but in insignificant amount.

However, the distillation method can obtain a good result in eliminating contaminant compounds in liquid smoke. The dark color liquid smoke becomes bright yellow liquid smoke. The distillation process also produces a solid residue of tar, black and granular grain-like crust. The following figure gives distillate and residue (tar) obtained from this research.
The percentage of residue and acid content total obtained depends on the temperature and time of conducted distillation. The indication of different temperature and time on distillation process aims to have the best operation condition to obtain the minimum temperature and time operation performed with maximum reduced residue and acid content total following the food standard (FAO) in table 1. Graph of the effect of distillation time on the residual content at various temperatures and the effect of distillation time on acid content total at various temperatures can be seen in figure 5.

The best total acid content obtained was 5.15% and residue 2.4%, at a temperature of 150 °C at 45 minutes and considered fulfilled the smoke quality standard according to FAO standard in table 1. The temperature of 175 °C and 200 °C is also able to obtain distilled liquid smoke with more minimum residue, but acid content total not much different with a temperature of 150 °C at 45 minutes. The lower distillation temperatures were chosen because it will consume less energy in distillation process and will save the cost of production.

The quality of liquid smoke obtained after the distillation process at 150 °C and 45 minutes shows a good result. Table 3 gives the comparison between various commercial liquid smoke and liquid smoke obtained in this research.
Table 3. Comparison of various commercial liquid smoke and liquid smoke obtained in this research.

| Type/Brand of liquid smoke | Manufacturer        | Percentage of acid total | pH value | Reference |
|---------------------------|---------------------|--------------------------|----------|-----------|
| Liquid smoke form oil palm fronds | Result of this research | 5.15 % | 2.3 | - |
| Code10-poly | Masterstate Inc. | 10.3 % | 2.3 | [14] |
| AM-3 | Masterstate Inc. | 1.8-2.1 % | 4.25-4.85 | [14] |
| AM-10 | Masterstate Inc. | 2.3 % | 4.2 | [14] |
| 1291 | Masterstate Inc. | 0.7 % | 5.7 | [14] |
| FAO Standard | Masterstate Inc. | 2-20 % | 1.5-3 | [11] |

Based on the information above, it can be concluded that liquid smoke obtained from oil palm fronds is appropriate with commercial liquid smoke called code 10-poly. The result also shows characteristics which are appropriate with a standard issued by FAO. It shows that quality and prospects of the use of liquid smoke obtained from oil palm fronds have promising opportunities for enhancing economic value from oil palm fronds.

4. Conclusions
Adsorption process was not able to produce liquid smoke that free of tar. Tar as contaminant was able to be eliminated after the distillation process conducted at the recommended temperature 150 °C for 45 minutes. The liquid smoke obtained from this research is appropriate with commercial liquid smoke called code 10-poly and FAO standard with 5.15 % acid total and pH 2.3.

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