Comparison of activated zeolite and activated carbon as adsorbent on liquid smoke purification

Seri Maulina1,2, Ekanzha Rizqandy Kamny*1, and Rizki Amalia1

1Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara
2Sustainable Energy and Biomaterial Center of Excellence, Faculty of Engineering, Universitas Sumatera

*Email: ekanzhakamny@gmail.com, maulina_harahap@yahoo.com

Abstract. This study aims to compare the using of activated zeolite with activated carbon as an adsorbent in the process of adsorption of liquid smoke. Liquid smoke was obtained from condensation of vapour produced by the pyrolysis of oil palm fronds. Adsorption of liquid smoke was carried out at temperature of 60 °C for 60 minutes with a ratio of adsorbent to liquid smoke 1:10. The parameters observed in this study were acetic acid, phenol compounds and carbonyl compounds which were analyzed using GC-MS. The results showed that the most dominant compounds which reduced after the adsorption process were carbonyl. Carbonyl compounds played a role in producing smoke scents. Adsorption process reduced the stinging scent of liquid smoke. The adsorption using activated zeolite showed an increase in acetic acid levels in liquid smoke with an average percentage increase of 11.29%, while the levels of phenol and carbonyl compounds decreased with an average percentage reduction of 14.35% for phenol compounds and 81.19% for carbonyl compounds. While on the adsorption by using activated carbon, acetic acid levels also increased with an average percentage increase of 0.58%, while phenol and carbonyl compounds decreased with an average reduction percentage of 31.19% and 83.35%.

1. Introduction

Liquid smoke is a result of vapors condensation from direct or indirect combustion from materials that contain lignin, cellulose, hemicellulose and other carbon compounds. Pyrolysis is one method that can be used to convert biomass into products of high economic value products. The pyrolysis process is carried out at high temperatures in order to break the chemical compounds of cellulose, hemicellulose and lignin to produce oxygen-rich molecular fragments [1].

The process of pyrolysis involves various reactions that are decomposition, oxidation, polymerization, and condensation [2]. Liquid smoke contains several components that support its functional properties and useful for food preservation, among others phenol, carbonyl, and acid compounds. These compounds act as antioxidants, brown formation, and as an antibacterial or antifungal [3]. Phenolic and carbonyl compounds are useful in giving flavor (smell) and taste of smoke on smoked products [4, 5].

The resulting aroma is too sharp so it needs to be done further process to produce a lighter liquid smoke flavor. One method that can be done is by the process of adsorption using activated zeolite and activated carbon.
2. Theory
Liquid smoke resulting from pyrolysis needs purification process. The liquid smoke purification process in this study includes the adsorption process using activated zeolite and activated carbon.

2.1 Activated Zeolite
Indonesia has a large deposit of zeolite and located on volcanic mountain such as Sumatra, Java and Nusa Tenggara Timur [6]. Zeolite is a mineral with silica alumina group which is crosslinked by binding of oxygen atoms with tetrahedral structures (Al,Si)O$_4$ are hydrated by alkali metals and alkali lands [7]. The typical structure of a zeolite is that most are canals and pores. The zeolite surface area can be enlarged by activating [8].

Activation of natural zeolites can be done both physically and chemically. Physical activation is carried out through size reduction, sifting, and heating at high temperatures, the aim being to remove organic impurities, enlarge pores, and expand surfaces. While chemical activation is done through acidification to remove inorganic impurities [9]. In research conducted by Gressangga [10], zeolite is able to adsorb phenol content of 0.52% and 2-methoxyphenol by 28.4%.

2.2 Activated Carbon
Activated carbon is a porous carbon material that has been reacted with gases or with the addition of chemicals before, during or after carbonization to improve its adsorption. In the industrial world activated carbon is generally used to remove odors, tastes, colors, and other organic contaminants [11]. Activated carbon can be produced from biomass such as bamboo [12], tobacco [13], cherry seeds [14] and coconut shells [15]. Activated carbon produced from plant biomass generally has lower quality compared to anthracite, coal and peat because there are volatile materials [16]. It needs efforts to improve the quality of the activation process and will improve the quality of activated carbon produced [17, 18].

3. Method
Liquid smoke from pyrolysis of oil palm fronds with temperature variations of 400 °C, 500 °C, 600°C with times 60 minutes, 90 minutes, 120 minutes adsorbed with zeolite which has been activated by using H$_2$SO$_4$ and activated carbon activated by using Na$_2$CO$_3$. Adsorption was carried out at 60 °C for 60 minutes. The adsorbed liquid smoke was analyzed using GC-MS Shimadzu QP 2100 brans.

4. Results and Discussions
The results of this study include the effect of adsorption using activated zeolite and activated carbon on acetic acid, phenol and carbonyl compounds.
In Figure 1, it can be seen that the ability of purification carried out by the adsorption process using activated zeolite and activated carbon will reduce the amount of acetic acid compounds present in liquid smoke. The percentage changes in the levels of acetic acid compounds after adsorbed with activated zeolite and activated carbon as shown in Table 1.

Table 1. Percentage change in acetic acid after adsorption

| Run | Temperatures (°C) | Time (minutes) | Area (%)   | Change in adsorbed with activated zeolite (%) | Change in adsorbed with activated carbon (%) |
|-----|-------------------|----------------|------------|-----------------------------------------------|---------------------------------------------|
|     |                   |                | Pyrolysis   | Adsorbed with activated zeolite | Adsorbed with activated carbon |                  |                  |
| I   | 400               | 60             | 59.44       | 52.73                                         | 83.52                                      | 11.29 (-)       | 40.51 (+)       |
| II  | 400               | 90             | 77.53       | 84.11                                         | 92.01                                      | 8.49 (+)        | 18.68 (+)       |
| III | 400               | 120            | 81.67       | 82.60                                         | 90.63                                      | 1.14 (+)        | 10.97 (+)       |
| IV  | 500               | 60             | 75.92       | 94.80                                         | 93.69                                      | 24.87 (+)       | 23.41 (+)       |
| V   | 500               | 90             | 76.68       | 95.35                                         | 90.93                                      | 24.35 (+)       | 18.58 (+)       |
| VI  | 500               | 120            | 83.54       | 94.73                                         | 92.53                                      | 13.39 (+)       | 10.76 (+)       |
| VII | 600               | 60             | 76.94       | 95.96                                         | 91.43                                      | 24.72 (+)       | 18.83 (+)       |
| VIII| 600               | 90             | 88.53       | 91.99                                         | 89.31                                      | 3.91 (+)        | 0.88 (+)        |
| IX  | 600               | 120            | 89.29       | 93.20                                         | 88.77                                      | 4.38 (+)        | 0.58 (-)        |

From Table 1, showed that the levels of acetic acid compounds in liquid smoke increased after adsorption by using activated zeolite and activated carbon generally. At pyrolysis temperatures of 400 °C for 60 minutes and at the pyrolysis temperature of 600 °C 120 minutes, by using activated zeolite and activated carbon decreased. Activated carbon itself has a basic surface so it will be more effective in binding acids [19], so that acetic acid levels should decrease after adsorbed with activated carbon. According to Oktafany [20], zeolites have pores that are able to adsorb acetic acid that is in liquid smoke. So that after the adsorption process, acetic acid will decrease. In addition, elements with greater molecular weight will be more easily adsorbed [21]. The molecular weight of acetic acid is smaller than that of phenol and carbonyl compounds, so that the pores of the adsorbent are first filled with phenol and carbonyl compounds until they are full.
Research conducted by Fadhil [22], in the pyrolysis of oil palm fronds was also obtained that acetic acid content increase after adsorption. Percentage of change in acetic acid after the adsorption treatment using activated zeolite was 11.29%, while the adsorption using activated carbon was 0.58%.

![Levels of Phenolic Compounds in Liquid Smoke](image)

**Figure 2.** Levels of phenolic compounds in liquid smoke

The ability of purification by adsorption process using activated zeolite and activated carbon will reduce the amount of phenol compounds present in liquid smoke as shown in Fig 1. The percentage changes in the levels of phenol compounds after adsorbed with activated zeolite and activated carbon can be seen in Table 2.

| Run | Temperatures (°C) | Time (minutes) | Pyrolysis Area (%) | Adsorbed with Activated Zeolite | Adsorbed with Activated Carbon | Change in Adsorbed with Activated Zeolite (%) | Change in Adsorbed with Activated Carbon (%) |
|-----|-------------------|----------------|--------------------|---------------------------------|---------------------------------|-----------------------------------------------|-----------------------------------------------|
| I   | 400               | 60             | 4.54               | 6.81                            | 2.45                            | 50.00 (+)                                     | 46.04 (-)                                    |
| II  | 90                | 4.78           | 3.31               | 2.19                            | 30.75 (-)                       | 54.18 (-)                                    |
| III | 120               | 5.42           | 6.06               | 4.87                            | 11.81 (+)                       | 10.15 (-)                                    |
| IV  | 60                | 6.28           | 5.20               | 2.64                            | 17.20 (-)                       | 57.96 (-)                                    |
| V   | 500               | 90             | 5.76               | 4.65                            | 19.27 (-)                       | 19.79 (-)                                    |
| VI  | 120               | 5.66           | 5.27               | 4.03                            | 6.89 (-)                        | 28.80 (-)                                    |
| VII | 60                | 6.52           | 6.80               | 5.16                            | 4.29 (+)                        | 20.86 (-)                                    |
| VIII| 600               | 90             | 6.4                | 6.09                            | 4.84 (-)                        | 23.91 (-)                                    |
| IX  | 120               | 7.32           | 6.80               | 5.93                            | 7.10 (-)                        | 18.99 (-)                                    |

Table 2. Percentage change in phenolic compounds after adsorption

Adsorption process by using activated zeolite has the ability to reduce compounds that contribute to the dark color (carbonyl) and the strong odor of smoke (phenols and their derivatives) from liquid smoke [22]. According to Emelda [23], decrease in adsorption rate caused of the active side of the adsorbent being filled and saturated and unable to adsorb. Based on the results obtained, the adsorption process has the ability to eliminate phenol compounds in liquid smoke, but with insignificant amounts.
Adsorption using activated carbon results in a decrease in phenol levels. Activated carbon are able to reduce phenol compound in liquid smoke [24, 25]. Reducing of phenol compound in liquid smoke because of the reaction of phenol hydroxyl group to form bonds with carboxyl groups on the surface of activated carbon [19]. The percentage of phenol change after the adsorption treatment using activated zeolite was 14.34% while the adsorption using activated carbon was 31.19%.

![Figure 3. Levels of carbonyl compounds in liquid smoke](image)

In Figure 3, it can be seen that the ability of purification carried out by the adsorption process using activated zeolite and activated carbon will reduce the amount of carbonyl compounds present in liquid smoke. The percentage changes in the levels of carbonyl compounds after adsorbed with activated zeolite and activated carbon can be seen in Table 3.

The results showed that the levels of carbonyl compounds in liquid smoke decreased after adsorption using activated zeolite and activated carbon, but while at pyrolysis temperatures of 400 °C 60 minutes, the levels of carbonyl adsorbed using activated zeolite increased and at pyrolysis temperatures of 600 °C 120 minutes, the levels of carbonyl adsorbed using activated carbon increased.

| Run | Temperatures (°C) | Time (minutes) | Pyrolysis | Adsorbed with activated zeolite | Adsorbed with activated carbon | Change in adsorbed with activated zeolite (%) | Change in adsorbed with activated carbon (%) |
|-----|-------------------|----------------|-----------|---------------------------------|-------------------------------|---------------------------------------------|---------------------------------------------|
| I   |                   | 60             | 32.56     | 36.47                           | 5.84                          | 12.01 (+)                                   | 82.06 (-)                                   |
| II  | 400               | 90             | 15.85     | 12.58                           | -                             | 20.63 (-)                                   | 100 (-)                                     |
| III | 500               | 120            | 12.91     | 9.18                            | 1.32                          | 28.89 (-)                                   | 89.78 (-)                                   |
| IV  | 60                | 15.20          | -         | 1.19                            | 100 (-)                       | 92.17 (-)                                   | 91.67 (-)                                   |
| V   | 500               | 90             | 15.00     | -                               | 1.25                          | 100 (-)                                     | 91.01 (-)                                   |
| VI  | 120               | 10.79          | -         | 0.97                            | 100 (-)                       | 95.24 (-)                                   | 91.01 (-)                                   |
| VII | 60                | 14.91          | -         | 0.71                            | 100 (-)                       | 24.85 (-)                                   | 230 (+)                                     |
| VIII| 600               | 90             | 5.07      | -                               | 3.81                          | 100 (-)                                     | 24.85 (-)                                   |
| IX  | 120               | 1.07           | -         | 3.53                            | 100 (-)                       | 230 (+)                                     |

Table 3. Percentage change in carbonyl compounds after adsorption

The adsorption process has the ability to reduce compounds that contribute to the dark color (carbonyl) and strong smoke odors (phenols and their derivatives and carbonyl) from liquid smoke [22]. Based on the results obtained, the adsorption process has the ability to eliminate carbonyl
compounds in liquid smoke. An increase in the carbonyl compound after the adsorption may occur because the number of carbonyl particles to be adsorbed in the solution is not proportional to the number of adsorbent particles. The adsorbent will reach the saturation point and the adsorption becomes even lower because the adsorbent pores were fully filled with liquid smoke particles [26]. The percentage of carbonyl change after adsorption treatment using activated zeolite was 81.19% while the adsorption using activated carbon was 83.35%.

5. Conclusion
It is obtained that activated zeolite and activated carbon were able to adsorb phenolic and carbonyl compounds which contribute to the dark color (carbonyl) and strong smoke odors (phenols and their derivatives and carbonyl) in liquid smoke. The changes in the percentage of acetic acid, phenol and carbonyl after the adsorption treatment using activated zeolite was 11.29%, 14.34%, and 81.19%. While the change in the percentage of acetic acid, phenol and carbonyl after adsorption treatment using activated carbon were 0.58%, 31.19%, and 83.35%.

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