Redistillation and characterization of liquid smoke from ulin wood (*Eusideroxylon zwageri* Teijsm. & Binn.) and its ability as a chitosan solvent

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**Abstract.** The purpose of this research was to study the solubility of chitosan in the liquid smoke as a preliminary study for the application of liquid-chitosan combination as a bioimmunizer and growth booster in plants and as a preservative in fish processing. This research focused on redistillation and characterization of the liquid smoke from ulin wood (*Eusideroxylon zwageri* Teijsm. & Binn.) and its ability as a chitosan solvent. The purpose was to obtain the scientific data on the yield redistillation, characterization of the liquid smoke (pH, total acid, total phenol, and composition), and its ability as a chitosan solvent. This liquid smoke was the side product of ulin wood charcoal in South Kalimantan. The results showed that the yield of liquid smoke from redistillation was 76.14% and the characteristics were containing 2.21 pH, 3.38% g/mL of total acid, 3.05 g/L of total phenol, and other chemical compositions such as carboxylic acid (73.08%), alcohol (14.73%), carbonyl (9.43%), phenolic (1.56%), and ether (1.21%). This research also uncovered that the solubility of chitosan in the liquid smoke increased along with the higher value of the liquid smoke concentration, and the liquid smoke concentration of 5% was able to dissolve more than 50 g/L of the chitosan.

1. **Introduction**

Liquid smoke and chitosan have been widely recognized and applied in various fields of technology. Liquid smoke is widely applied in the fields of food science (preservatives, flavors, and color), health, and agriculture [1], whereas chitosan is widely applied in the fields of pharmaceuticals, agriculture, biochemistry, preservation, health, and as adsorbent. Purba et al. [2] have reviewed the utilization of liquid smoke and chitosan as a preservative in tofu and meatballs.

Liquid smoke is the result of incomplete combustion (pyrolysis) from organic matter/biomass (wood and agricultural waste) that produces smoke (steam) and is condensed to form a liquid. This liquid smoke contains three major groups of compounds, namely carboxylic acids, carbonyl, and phenol [3]. Meanwhile, chitosan is a natural cationic biopolymer abundant in nature with the structure of β-(1.4)-2-amino-2-deoxy-D-glucose. Chitosan can be obtained from the results of chitin deacetylation that is contained in shrimp, insect, fungi, Mollusca, and arthropod shells through various isolation processes of deproteination, demineralization, depigmentation, and deacetylation [4].

One of the most frequent problems in chitosan applications is its solubility. Chitosan is not water-soluble and some of the solvents (alcohol, acetone) are slightly soluble in strong acids (HCl, HNO₃, H₃PO₄), and easily soluble in weakly dilute acids (acetic acid and formic acid). Chitosan is soluble in organic acid through the protonation of free amino groups (-NH₂) to cationic amino [1].
Liquid smoke is potential as a solvent for chitosan because one of the main components contained in it is the carboxylic acid group. Based on the acid content possessed by liquid smoke and the solubility property of chitosan, it can be predicted that chitosan can be dissolved in liquid smoke easily. Thus, in some applications using a combination of chitosan and liquid smoke can be done at once without the addition of a solvent. In this research, the liquid smoke is the side product of ulin wood charcoal (pyrolysis) \[5\].

Wood pyrolysis generally produces the liquid that still contains many carcinogenic substances (PAH and tar), thus it is important to do a redistillation \[6\]. Redistillation is a process of separating the components in a mixture based on their boiling points \[7\]. This is why the redistillation process is necessary to remove the tar compound contained in the liquid smoke. The characteristics of the resulting liquid smoke depend on the pH value, total acid, total phenol, and composition so that it is essential to characterize the liquid smoke. Based on the above description, this research aims to study the redistillation and characterization of liquid smoke from ulin wood and its ability as a chitosan solvent.

2. Materials and methods

2.1. Experimental principle

The redistillation of liquid smoke resulted in residue and distillate. The residue was a blackish-brown viscous liquid (figure. 1.a) which was tar and distillate (figure. 1.b) containing a group of acidic, carbonyl, and phenol compounds. The distillate was characterized by physical and chemical properties included pH, total acid, total phenol, and composition. The total acid was analyzed by a titration method, while the total phenol was analyzed using UV-Vis Spectrophotometry, and the composition was analyzed using GC-MS. The presence of acidic compounds in liquid smoke made the chitosan soluble. The solubility of chitosan in liquid smoke was analyzed by the gravimetric method.

2.2. Reagents and instruments

Here are the list of reagents and instruments used in this study. Liquid smoke ulin wood: wood charcoal production in Takisung, Tanah Laut, South Borneo-Indonesia \[5\]; Chitosan (medium molecule weight; 200-800 cPs; deacetylation degree 80-85%): Sigma-Aldrich; NaOH pellets: Merck; Na\(_2\)CO\(_3\): Merck; indicator Phenolphthalein (PP): Merck; ethanol p.a: Merck; gallic acid p.a; Merck; reagent Follin-Ciocalteu 10%: Merck; Thermometer: Beurer; water bath: Daihan Labtech; centrifuge: Hettich; analytical balance: Shimadzu; vortex shaker: Thermo scientific; buret: Duran; oven: Memmet; a set of distillation tools: Duran; Gas Chromatography- Spectroscopy Mass (GC-MS): Shimadzu QP2010S; UV-Vis Spectrophotometer: Hitachi, Japan.

2.3. Redistillation of liquid smoke

As much as 500 mL of liquid smoke was redistilled at a temperature of 25-140°C, and the resulting distillate was put in an Erlenmeyer and the yield was calculated with the equation 1.

\[
\text{Yield (\%) = } \frac{\text{Volume of condensate (mL)}}{\text{Volume of sample (mL)}} \times 100 \% \tag{1}
\]

2.4. Characterization of the liquid smoke

2.4.1. Degree of Acidity (pH) and Total Acid. Measurement of the degree of acidity (pH) of liquid smoke was done using a pH meter. 5 ml of distilled liquid smoke was put into a 50 ml measuring flask, then the aquadest was added to the boundary marker. A total of 10 mL of solution was taken, 2-3 drops of PP indicator were added, and titrated with 0.1 N NaOH. The total acid was determined by the equation 2.

\[
\text{%Total Acid} = \frac{\text{Volume of NaOH} \times N \text{NaOH} \times MW \text{acetic acid}}{\text{Volume of liquid smoke} \times 1000} \times 100\% \tag{2}
\]
2.4.2. **Total phenol content.** 0.1 mL of liquid smoke was added with ethanol p.a in a 10 mL flask. As much 0.5 mL of solution was taken then added with 0.75 mL of 10% Follin-Ciocalteu reagent and 2 mL of Na2CO3 2%, shaken in a vortex shaker and allowed to stand for 18 minutes. The absorbance was determined with spectrophotometer UV-Vis at 700-800 nm wavelength. The standard curve making was done using the gallic acid.

2.4.3. **GC-MS analysis.** 1 μL of sample was injected into GC-MS in an oven at a temperature of 50-300°C with a temperature rise rate of 5°C/min, 13 kPa of a pressurized helium carrier gas, a total rate of 40 mL/min, and a split ratio of 66.8. The chromatogram was then compared to the data bank.

2.5. **Determination of the solubility of chitosan in liquid smoke**

As much as 0.5 grams of chitosan was dissolved in 10 mL of liquid smoke, heated in a water bath at 60°C for 30 minutes. After that, it was centrifuged at a rate of 1500 rpm for 20 minutes, then filtered and dried in an oven at 100°C for 24 hours until the weight was constant. The solubility was calculated based on the following equations 3, 4, and 5.

\[
W_{\text{dissolved chitosan}} = W_{\text{sample}} - W_{\text{insoluble chitosan}}
\]

\[
\% \text{Solubility chitosan (b/b)} = \frac{\text{weight of dissolved chitosan (g)}}{\text{weight of sample chitosan (g)}} \times 100\%
\]

\[
\text{Solubility (g/L)} = \frac{\text{amount of soluble chitosan (g)}}{\text{volume of solvent (L)}}
\]

3. **Results and discussion**

3.1. **Yield and physical characteristics of the redistilled liquid smoke**

Redistillation of the liquid smoke was carried out to separate the heavy fractions (PAH and tar) contained in the liquid fumes from the light fractions (phenol, carbonyl, and acid groups) based on their boiling points. Based on table 1, it can be seen that the obtained value for the redistillation yield of liquid smoke is 76.14%. This shows that the residue as the result from redistillation using wood smoke in this study is quite high (23.86%). The high residuals obtained indicated that the tar content in the ulin wood smoke was quite a lot. The liquid smoke before and after redistillation can be seen in figure 1.

![Figure 1. Liquid smoke before (a) and after (b) redistillation](image)

Figure 1 shows that the liquid smoke color has changed from (a) to (b) after redistillation. The change from dark brown (before redistillation) to clear yellow (after redistillation) might because the compounds of the light fraction of liquid smoke (phenolic, acid, and carbonyl) have separated from the heavy fraction compounds (PAH and tar) based on the boiling points. The boiling points of the PAH...
were above 200°C (e.g. naphthalene 218°C, anthracene 340°C, pyrene 404°C dan benzopyrene 495°C). Besides, the liquid smoke from redistillation in this study had a distinctive smell (scent). This indicated that there was a group of phenolic compounds, carbonyls, and acids that had an important role in producing the smoke scent. Muhammad et al. [8] pointed out that the presence of acid compounds mixed with carbonyl and phenol will cause a strong scent.

3.2. Characteristics of the redistilled liquid smoke

| Redistillation temperature (°C) | Yield (%) | pH | Total acid (%g/mL) | Total phenol (g/L) | Color | Scent |
|-------------------------------|-----------|----|--------------------|-------------------|-------|-------|
| 90-140                        | 76,14     | 2,21 | 3,38               | 3,05              | yellow | typical liquid smoke |

3.2.1. Degree of acidity (pH) and total acid. Based on the data in table 1, the characteristics of liquid smoke as the result from redistillation was having pH of 2.21 and total acid as much as 3.38% g/mL. In comparison, the results of research by Achmadi et al. [3] showed higher values (pH 3.2; total acid 9.2%) which indicated that in this present study the degree of acidity was high (low pH), but the total acid was low. In other words, the acid compound in the liquid smoke had a large Ka (acid equilibrium constant) value in this study.

The pH value and total acid from the redistillation results showed the decomposition of the chemical compounds which were present in the raw material when the pyrolysis produced the groups of organic acid compounds. The dominant organic acid compound present in liquid smoke is usually a carboxylic acid group. Carboxylic acids are formed from components in the liquid smoke raw materials such as cellulose and hemicellulose [9].

3.2.2. Total phenol content. Based on table 1, it can be seen that total phenol content obtained was 3.05 g/L. When compared with the results of other studies using different raw materials such as coconut shell and coconut fiber [10], bamboo [11], various wood [12], the liquid smoke had a different total phenol content. This indicated the influence of lignin content on raw materials. Indeed, the more amount of lignin decomposed into groups of phenol compounds causes higher levels of phenol in the liquid smoke. The amount of decomposed lignin depends on the amount of lignin in the feedstock and the pyrolysis temperature used [13]. Another suspected influential factor was the pyrolysis temperature. The higher the pyrolysis temperature, the more lignin broke down so that the phenol content in the liquid smoke was higher, too.

3.2.3. Composition analysis of liquid smoke using GC-MS. GC chromatogram and the components of the liquid compounds from the redistillation result based on MS data can be seen in figure 2 and table 2.

Based on the data in table 2, 12 compounds were identified in the liquid smoke of ulin wood. The identification results of compound components in the ulin wood smoke could be divided into some groups, namely acidic (acetic acid, propanoic acid, and citric acid), phenolic (o-Guaiakol), alcohols (methyl alcohol and ethyl alcohol), ketones (acetone and 3.5-Cycloheptadienone), ethers (ethylene glycol diglycidyl ether), and esters (butyrolactone, γ-valerolactone, and ethyl heptanoate) groups. The main component of the liquid wood smoke composition was acetic acid which reached 71.57%. Acetic acid is a compound that is very suitable for dissolving chitosan [4]. Liquid smoke with high acetic acid content has a great potential to be a solvent for chitosan. Similarly, the results of Rinaldi et al. [14] showed that acetic acid became the dominant component with a percentage of more than 50%. However, a different finding was found by Janairo and Amalin [15] where the main content of liquid
smoke was phenolic. Furthermore, the data in table 2 also show that in the redistilled wood smoke there is no compound of heavy fractions (PAH and tar) found, such as pyrene, perylene, benzo(a) anthracene, and benzo(a)pyrene.

![Figure 2. GC Chromatogram of ulin wood liquid smoke from the redistillation result.](image)

### Table 2. The components of ulin wood liquid smoke resulting from the redistillation result.

| Peak | Retention time (minute) | % Area | Molecular formula | Presumption of compound |
|------|-------------------------|--------|-------------------|-------------------------|
| 1    | 2.320                   | 12.19  | CH₄O              | Methyl alcohol          |
| 2    | 2.416                   | 2.54   | C₂H₂O             | Ethyl alcohol           |
| 3    | 2.510                   | 5.80   | C₃H₆O             | Acetone                 |
| 4    | 2.962                   | 4.77   | C₂H₄O₂            | Acetic acid             |
| 5    | 3.446                   | 66.80  | C₂H₄O₂            | Acetic acid             |
| 6    | 4.125                   | 0.85   | C₆H₁₀O₄           | Ethylene glycol diglicidyl ether |
| 7    | 4.294                   | 1.08   | C₃H₆O₂            | Propanoic acid          |
| 8    | 10.582                  | 3.14   | C₄H₆O₂            | Butyrolactone           |
| 9    | 10.775                  | 0.43   | C₆H₈O₇            | Citric Acid             |
| 10   | 12.132                  | 0.49   | C₆H₈O₂            | γ-Valerolactone         |
| 11   | 17.225                  | 1.21   | C₇H₁₂O₂           | 3,5-Cycloheptadienone   |
| 12   | 29.710                  | 0.35   | C₇H₁₀O₂           | Ethyl heptanoate        |
| 13   | 39.417                  | 0.36   | C₇H₁₀O₂           | Ethyl heptanoate        |
**Figure 3.** The graphic of correlation between pH value and liquid smoke concentration.

### 3.3. The solubility of chitosan in the liquid smoke

Figure 3 shows that the higher the liquid smoke concentration, the lower was the pH value of liquid smoke. However, the decrease in pH of the solution was not significant when compared with the increased concentration of liquid smoke in the solution. This indicated that the acids contained in the liquid smoke were weak. Weak acids only slightly release the [H+] at equilibrium because they have a small Ka value (Ka value of acetic acid is $1.8 \times 10^{-5}$). Therefore, in this study the measured pH did not change too much even though the acid concentration changed significantly.

**Table 3.** The degree of chitosan solubility in the liquid smoke concentration.

| Liquid smoke concentration (v/v) | pH of dilution | Chitosan solubility (g/L) | pH of solution |
|----------------------------------|----------------|--------------------------|---------------|
| 1.0%                             | 3.204          | 3.7                      | 5.141         |
| 2.0%                             | 3.183          | 4.2                      | 4.541         |
| 5.0%                             | 3.088          | >50                      | *             |
| 7.5%                             | 2.925          | >50                      | *             |
| 10.0%                            | 2.871          | >50                      | *             |
| 12.5%                            | 2.856          | >50                      | *             |
| 15.0%                            | 2.780          | >50                      | *             |

The data in table 3 shows that the liquid smoke resulting from redistillation with a concentration of 5.0% is able to dissolve more than 50 g/L of chitosan, while the smoke concentrations of 1% and 2% can only able to dissolve the maximum of 3.7 g/L and 4.2 g/L chitosan. The lowest solubility of chitosan in the liquid smoke was at the concentrations of 1.0% and 2.0%. This probably occurred due to the effect of the addition of chitosan which caused the pH of liquid smoke concentration of 1% and 2% to increase from 3.204 and 3.183 to 5.141 and 4.541. Besides, at the concentrations of 5.0%-15.0%, the addition of chitosan did not significantly affect the pH value of the solution. Meanwhile, based on the chitosan solubility data above, a smoke concentration of more than 5.0% can dissolve chitosan significantly. In conclusion, this liquid smoke has the potential to be a good solvent for chitosan.

### 4. Conclusion

In conclusion, the results of this study revealed that the redistillation yield of liquid smoke was 76.14%. Furthermore, this study defined some characteristics of the liquid smoke, namely containing 2.21 pH, 3.38% g/mL of the total acid, and 3.05 g/L of the total phenol. The GC-MS analysis results also showed that the twelve compound components could be divided into several composition groups, namely acids (73.08%), alcohols (14.73%), phenolic (12.1%), and carbonyls (5.19%). Besides, the concentration of liquid smoke has a correlation with the degree of solubility of chitosan. The liquid smoke concentration of 5% (v/v) was able to dissolve more than 50 g/L of chitosan.

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