Coconut shell-liquid smoke production based on the redistillation-filtration technology and its characterisation

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Abstract. The utilization of coconut shell waste into liquid smoke has been carried out in recent years. However, the conventional technology that has been applied before only able to produce coconut shell-liquid smoke (CS-LS) in grade C. Whereas the further processing is needed to produce a higher quality of CS-LS into grade A. Hence, the aim of this study is to produce CS-LS based on the redistillation-filtration technology and analysed on its physical and chemical characterisation. The characteristic of CS-LS was analysed not only in physical parameters like yields, pH and density, but also identified of chemical compounds by using GC-MS method. The result showed that the redistillation and filtration technology produce CS-LS grade A and grade C was 2.17% and 0.83% respectively. The CS-LS grade A has pH and density value better than CS-LS grade C and inline with the SmokEz Enviro-23 standard. The CS-LS grade A was composed of 4 main chemical components such as phenolic, alkoxy, cycloacene, and furan compounds. While the CS-LS grade C was composed of 6 main chemical component such as phenolic, carbonyl, acid, alkoxy, ester and cycloalkene compounds. Although CS-LS grade C has more chemical compounds, CS-LS grade A has the highest phenolic compounds which is suitable to be produced commercially as a natural food preservative. Therefore, the application of redistillation-filtration technology in CS-LS production, potentially applied to SMEs or CS-LS industries in Indonesia.

1. Introduction
Charcoaling process of coconut shell through conventional pyrolysis method is still produce air pollution which indirectly cause problems for the around environment. Therefore, several researchers attempted to process smoke from the pyrolysis process of coconut shell that became liquid smoke or called coconut shell-liquid smoke (CS-LS) [1-3]. The CS-LS contain variety of compounds that act as antimicrobials such as phenol and acid acetate compounds [4], hence the liquid smoke classification divided into 3 grades, grade A, B and C. The CS-LS grade C can be used as timber preservative, grade B is used as anti-microbial and grade A is used as natural food preservative [3, 5].

The enhancement quality of liquid smoke into grade A is needed considering the liquid smoke produced from the biomass pyrolysis process still contain carcinogenic, mutagenic and cytigenic polycyclic aromatic hydrocarbon (PAH) compounds [6]. In addition, CS-LS grade A also has more dominant phenol compound when compared with CS-LS grade B and C, so it can also add antioxidant
compounds to food products. Therefore, the demand for liquid smoke grade A is quite high because of its function can replace synthetic food preservatives.

Generally, the CS-LS production starts from the smoke condensation process from the pyrolysis tank which will become grade C. The CS-LS grade C then proceed with the redistillation and followed by condensation into grade B. Furthermore, CS-LS grade B purified to produce CS-LS grade A. Therefore, the purification process by using redistillation-filtration process in this case plays important role in CS-LS production, which has high quality (grade A). On the other hand, the physical and chemical characteristics of CS-LS for grades C and A have limited information. Therefore, this research aims to produce CS-LS using redistillation-filtration technology and to analyse on its physical and chemical characterisation.

2. Materials and Method

2.1. Materials
Materials used were dried coconut shell, zeolites active, activated carbon, and distilled water. The apparatus used in this study was custom designed liquid smoke machine.

2.2. CS-LS production process
The CS-LS grade A and C production process as illustrated in Figure 1. The detailed equipment design for CS-LS production machines was refer to Fathussalam et al. study [7]. Pyrolysis process carried out in the pyrolysis chamber with capacity of 3000 kg dried coconut shell. Then smoke from pyrolysis chamber condensed through first condenser tube to produce CS-LS grade C and proceed to the distillation column. The redistillation process carried out at a temperature of 95°C with column capacity of 100L. The vapour from redistillation process then forwarded to the second condenser tube to be CS-LS grade B. Next, CS-LS grade B passed into a filtration column consisting of zeolites and activated carbon in a ratio of 1: 1 (w/w). Filtration with zeolites and activated carbon aims to absorb the benzo(a)pyrene and reduce pungent odor.

![Figure 1. Illustration of mechanism process of liquid smoke production](image)

2.3. Characterization and analysis method
In this study, the physical characteristics analysis of CS-LS grade C and A includes pH, density, yield and color. The color measurement performed using Hunter method and density using the pycnometer method. While the characterisation of chemical compounds based on the results of GC-MS. In addition, the CS-LS grade A also compared with liquid smoke standard SmokEz Enviro-23 which is standard of liquid smoke for food products in Denmark.
3. Results and Discussion

3.1. Physical characterisation of CS-LS

The quality standards of CS-LS contained in the market depend on physical characterisation of CS-LS. Therefore, the physical characteristics such as pH, density, yield and color not only determine the quality of CS-LS but also prescribe the price of CS-LS. The physical characteristics of CS-LS grade C and A are shown in Table 1.

| Physical parameters | Units | CS-LS Grade C | CS-LS Grade A | SmokEz Enviro-23 Standard |
|---------------------|-------|---------------|---------------|---------------------------|
| pH                  |       | 4.4           | 3.1           | 2.8 – 3.2                 |
| Density             | kg/L  | 1.021         | 1.002         | 1.09                      |
| Yields              | %     | 0.83          | 2.17          | -                         |
| Color               |       |               |               |                           |
| L*                  |       | 14.49 ± 0.02  | 17.94 ± 0.20  |                           |
| a*                  |       | 2.86 ± 0.06   | 2.70 ± 0.13   | -                         |
| b*                  |       | -0.21 ± 0.04  | 4.24 ± 0.63   |                           |
| c*                  |       | 2.87 ± 0.06   | 5.03 ± 0.54   |                           |
| h*                  |       | 355.84 ± 0.89 | 57.21 ± 4.29  |                           |

Based on Table 1, the acidity level of CS-LS grade C and A has difference value. The acid content of CS-LS shows the amount of acid compounds produced from the cellulose pyrolysis process. The process of purification (redistillation-filtration) generate in the loss of acid compounds. The filtration process causes some of the substance to be absorbed so that the contents in it are reduced [8]. Therefore, the CS-LS grade A has lower pH than CS-LS grade C, that indicate the CS-LS grades A more acid than CS-LS grade C. A lower pH value has benefit to maintain the phenolic content in liquid smoke. The lower pH values also can affect the shelf life and the organoleptic characteristic of liquid smoke, since the microbial or bacterial unable to survive and grow [9].

In addition, the density of CS-LS grades A and C do not show significant differences. The density value of both CS-LS grade A and C is also under the density value of SmokEz Enviro-23 standard. The density value depends on pyrolysis temperature used in pyrolysis tank. The density value will increase with increasing pyrolysis temperature. In this study, the pyrolysis process for producing CS-LS grade C and A has the same temperature, thus it does not have a significant effect on the density of CS-LS. Liquid smoke density value is influenced by pyrolysis temperature and the raw material to produce liquid smoke. The CS-LS yield of grade A and C also shows the significant differences (Table 1). By using the same amount of raw material (3000 kg dried coconut shell), CS-LS grade A produce higher in yield than CS-LS grade C. Hence, the redistillation and filtration technology application in this study, it promises to produce greater quantities of CS-LS grade A.

The color parameters can be compared quantitatively. The CS-LS grade A has high brightness or high L (lightness) value (17.94±0.20), b value of 4.24 ± 0.63 which is more likely to be yellow. In addition, the contrast value 5.03±0.54 which is greater than CS-LS grade C shows that CS-LS grade A is clearer and h value is 57.21±4.29, which indicates yellowish color. While the CS-LS grade C has colors tend to be darker indicated by b value tends to blue (-0.21±0.04), the c value or contrast 2.87±0.06 and h value which tends to magenta (355.84 ± 0.89). Based on colorimeter value in Table 1, it can be inferred that the color value of CS-LS grade C has very dark color, since it contains of carcinogenic tar and several impurities compounds. Whereas CS-LS grade A has brighter color due to the filtration process with zeolite and activated carbon. Good absorption ability by zeolites due to its porous structure, allows tar and benzo(a)pyrene compounds in liquid smoke to be trapped in the pores, whereas activated carbon has a large carbon surface and porous structure due to its granules form.
Aromatic compounds with the same or smaller molecules size than its pores can be adsorbed during filtration [3]. In addition, the liquid smoke color is influenced by the temperature of pyrolysis which causes degradation of cellulose, hemicellulose, and lignin. The bright color of CS-LS grade A indicates that it has better quality compared to dark liquid smoke (CS-LS grade C), since it was acceptable as food preservatives.

3.2. Chemical characteristics of CS-LS
The chemical characteristics of CS-LS grade C and A have significant differences, especially in phenol and acid compounds. The differences value in percent area and retention time of GC-MS results in CS-LS grade C and grade A are described in Table 2.

Table 2. Chemical characteristics of CS-LS grade C and A

| Chemical Compounds                  | Grade C | Grade A |
|-------------------------------------|---------|---------|
|                                     | Retention Time (min) | Percent Area (%) | Retention Time (min) | Percent Area (%) |
| Phenolic Compounds                  |         |         |
| Phenol                              | 2.922   | 11.45   | 2.910   | 16.78 |
| Phenol, 2-methyl-                   | 3.688   | 1.25    | 3.671   | 6.10  |
| Phenol, 4-methyl                    | 3.905   | 1.72    | 3.882   | 3.57  |
| Phenol, 2-methoxy                   | 4.185   | 6.32    | 4.173   | 33.12 |
| Phenol, 2,6-dimethyl-               | 6.191   | 0.05    | 4.362   | 0.87  |
| Phenol, 2-ethyl-                    |        |         | 4.665   | 0.75  |
| Phenol, 3,5-dimethyl                |        |         | 4.814   | 2.20  |
| Phenol, 3-ethyl-                    |        |         | 5.076   | 0.69  |
| Phenol, 2,3-dimethyl-               | 4.842   | 0.40    | 5.054   | 0.66  |
| Phenol, 2,4-dimethyl-               |        |         | 5.214   | 0.31  |
| Phenol, 2-methoxy-4-methyl          | 6.660   | 0.67    | 5.482   | 16.65 |
| Phenol, 4-ethyl-2-methoxy           |        |         | 6.642   | 6.98  |
| Phenol, 2,6-dimethoxy               |        |         | 7.591   | 0.62  |
| Phenol, 2-methoxy-4-propyl          |        |         | 7.820   | 0.16  |
| Phenol, 2-methoxy-4-methyl          | 5.499   | 2.75    |        | -     |
| Phenol, 2,6-dimethoxy               | 7.608   | 12.90   |        | -     |
| Phenol, 2,6-dimethoxy-4-(2-propenyl)| 9.940   | 8.20    |        | -     |
| 2,5-Xylenol                         | 5.425   | 0.24    |        | -     |
| 1,3-Diphenyl-1,3,5,5-tetramethyl-cyclotrisiloxane | 11.335 | 1.42    |        | -     |
| Total phenolic compound             | 48.06   |         | 89.62   |       |
| Furan Compounds                     |         |         |
| Furan, 2-ethyl                      |        |         | 2.259   | 0.13  |
| 2,4-Dimethylfuran                   |        |         | 2.476   | 2.28  |
| Total furan compound                | 0       |         | 2.41    |       |
| Acid Compounds                      |         |         |
| Benzoic acid, 2,5                   | 8.283   | 0.60    |        | -     |
| Benzoic acid, 2,4                    | 8.557   | 6.47    |        | -     |
| Benzoic acid, 4-hydroxy-3-methoxy   | 9.426   | 0.51    |        | -     |
| 2,3-Dihydro-1H-inden-1-one           | 6.757   | 0.26    |        | -     |
| Total acid compound                 | 7.84    |         | 0       |       |
| Chemical Compounds                  | Grade C          | Grade A          |
|------------------------------------|------------------|------------------|
|                                    | Retention Time (min) | Percent Area (%) | Retention Time (min) | Percent Area (%) |
| **Alkoxy Compounds**               |                  |                  |
| 2-Methoxy-4-methylphenol           | -                | -                | 5.305                | 0.45             |
| 2-Methoxy-4-methylphenol           | -                | -                | 5.402                | 0.68             |
| 2,3-Dimethoxytoluene               | -                | -                | 6.037                | 0.56             |
| 3-Hydroxy-4-methoxybenzoic acid    | 8.671            | 7.25             | -                    | -                |
| 2,3,5-Trimethoxytoluene            | 9.832            | 0.52             | -                    | -                |
| 2-methoxy-3-methylpyrazine         | -                | -                | 4.739                | 0.60             |
| cis-2-chloro-2,2a-dihydro-5,6-dime | -                | -                | 8.248                | 0.44             |
| **Total alkoxy compound**          | **7.77**         | **2.73**         |
| **Cycloalkene Compounds**          |                  |                  |
| Cyclopentanone, 2-methyl-           | -                | -                | 2.425                | 0.20             |
| Cyclohexene, 1,2-dimethyl          | -                | -                | 2.687                | 0.43             |
| Cycloheptene, methyl               | -                | -                | 2.739                | 0.25             |
| 4,4-Dimethyl-2-cyclopenten-1-one   | -                | -                | 3.168                | 0.49             |
| 2,3-Dimethyl-2-cyclopenten-1-one   | 4.053            | 0.21             | 3.202                | 0.93             |
| 1,3-Dimethyl-1-cyclohexene         | -                | -                | 3.459                | 0.19             |
| 2-Cyclopenten-1-one, 2,3-dimethyl  | -                | -                | 3.636                | 1.26             |
| 3-Ethylcyclopent-2-en-1-one        | -                | -                | 4.053                | 0.28             |
| **Total cycloalkene compound**     | **0.21**         | **4.96**         |
| **Carbonyl Compounds**             |                  |                  |
| Ethanone, 1-(4-hydroxy-3-methoxyphenyl) | 8.854            | 9.35             | -                    | -                |
| 2-Ethylidiphenylmethane            | 11.209           | 0.92             | -                    | -                |
| **Total carbonyl compound**        | **10.27**        | **0**            |
| **Ester Compounds**                |                  |                  |
| Vanillin                           | 7.848            | 0.23             | -                    | -                |
| **Total ester compound**           | **0.23**         | **0**            |

The highest compounds found in CS-LS grade A were phenolic compounds (89.62%) and followed by cycloalkene compounds (4.96%), alkoxy compounds (2.73%), and furan compounds (2.41%). The phenolic compounds as the main constituent of CS-LS make its function as a natural preservative in food and provide sensory characteristics in the form of aroma, color, and taste that is unique to food products [10]. In addition, high phenolic compounds in CS-LS grade A also has an antimicrobial function which can inhibit the growth activity of *S. aureus*, *P. aeruginosa*, *E. coli* and *C. albicans* [3, 4]. Cycloalkene that is also included in the alkene group in some plants as a compound forming lycopene and β-carotene. Furan compounds formed when hemicellulose was degradation at high temperatures [2]. A high temperature given both in the pyrolysis and the distillation process makes hemicellulose degradation higher, consequently, the furan compounds can only be detected at CS-LS grade A.

On the other hand, the CS-LS grade C has a constituent compound such as phenolic compounds (48.06%), carbonyl compounds (10.27%), acid compounds (7.84%), alkoxy compounds (7.77%), ester compounds (0.23%) and cycloalkene compounds (0.21%) as shown in Table 2. The CS-LS grade C has specific compounds like acid, alkoxy, carbonyl and ester compounds since the presence of lignin which has not been decomposed in liquid smoke and makes aromatic compounds in CS-LS grade C.
Therefore, it suitable used for wood preservatives, rubber coagulant and odor absorber [3]. Based on Table 2, it also indicated that there were no polycyclic aromatic hydrocarbons (PAH) compounds like benzo(a)pyrene and benzoic acid as tar and impurities compounds CS-LS grade A, thus causing CS-LS grade A really safe to apply for preservatives in food products.

4. Conclusions
In this study, physical and chemical characteristics of CS-LS grade A and C from redistillation-filtration processes are in accordance with the functions and uses. CS-LS grade A has dominant phenolic compound and followed by alkoxy, cycloalkene and furan compounds. The pH value and acid level of CS-LS grade A also complies with the SmokEz Enviro-23 standard so it is suitable for natural food preservatives. Whereas CS-LS grade C has dominant compounds such as phenol and followed by acid, carbonyl, alkoxy ester and cycloalkene. In addition, CS-LS grade C also has specific compounds like acid, alkoxy, carbonyl and ester compounds, which is suitable for wood preservatives, rubber coagulant and odor absorber. The application of redistillation and filtration technology to produce CS-LS has the potentially developed in SMEs and the liquid smoke industries in Indonesia.

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