Chemical Identification of Coconut Shell Liquid Smoke

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Abstract. Coconut shell liquid smoke is produced from a chemical pyrolysis process that involved smoke bearing water vapor from burning coconut shells in very high temperature. Materials used in this study were coconut shell liquid smoke with three different grades. Visually, grade 1 liquid smoke was clear. Grade 2 liquid smoke was reddish in color and not as clear as grade 1, while grade 3 was dark brown. This difference may indicate that each grade had different chemical compositions. The aim of this study was to identify the chemical compounds of the three different grades of coconut shell liquid smoke using Gas Chromatography-Mass Spectroscopy (GC-MS). Extraction was carried out using Head Space Solid Phase Micro Extraction (HS-SPME). Result showed that the coconut shell liquid smoke contains high content of polyphenol. Polycyclic Aromatic Hydrocarbons (PAHs) including benzo(a)pyrene were also found. The findings of this study may be useful as basis in the determination of the application of the different grades of coconut shell liquid smoke.

1. Introduction
Coconut (Cocos nucifera) is one of the main commodities in Indonesia and is known as a zero-waste-tree. It yields a wide range of products, from utilization of all parts of the tree into useful goods and materials for human benefits. Copra, virgin coconut oil, personal care products, biodiesel, bottled coconut water, coconut milk, coconut powder, desiccated coconut, and coco vinegar are among the favored products of coconut. However, the utilization of coconut shell has yet optimum.

Coconut shell belongs to hard wood group that contains three main components: cellulose, hemicelluloses, and lignin. Cellulose decomposition by heat results in anhydroglucose, carbonyl compound and furan. Decomposition of hemicellulose is similar to that of cellulose, but resulting in acetate acid and carbon dioxide [1].

Coconut shell is not commonly utilized for high value products. Traditionally, it is simply burned and used for cooking. The activity of using coconut shell for cooking may result in dangerous waste and increase air pollution [1]. Pyrolysis, followed by condensation, can produce high quality liquid smoke from coconut shell. The process involves the smoldering of coconut shell chips (approximately 400°C) and condensation under limited oxygen to get liquid smoke [2, 3].

Coconut shell liquid smoke is known to be a good food preservation agent, as a substitution of formalin. It has antimicrobial and antibacterial activities, therefore has inhibitory effects on pathogens [4, 5, 6]. Antimicrobial and antioxidant compounds present in coconut shell liquid smoke are aldehyde, carboxylic acids and phenols [7, 8].
Regarding its chemical properties, coconut shell liquid smoke may contain Polycyclic Aromatic Hydrocarbon (PAH) and its derivatives, which is formed during its production process from coconut shell. Some of these components are carcinogenic. Acid compounds together with phenol and carbonyl synergistically act as antimicrobial. The largest amount of acid compounds contained in liquid smoke are derivations of carboxylate acid such as furfural, furan, acetate acid, propionate acid, butyric acid and valerate acid [9].

Commercial full-strength coconut shell liquid smoke is fractionation and purified. Purification using zeolites and activated carbon can reduce the content of PAH in coconut shell liquid smoke, but also end the active components of liquid smoke that functions as an antioxidant and antimicrobial.

There are three grading of coconut shell liquid smoke, i.e. grade 1, 2 and 3. The difference between each grade lies on the extent of filtration stages, which influence its physicochemical characteristics. The more refined is labeled Grade 1 and the less refined was Grade 3. Surely, Grade 1 has the best characteristics for consumers’ convenience and preference, while Grade 3 may have some undesirable characteristics, although these characteristics were not less beneficial. Grade 1 is very yellowish and has the highest clarity compared to the other grades (Figure 1). It is using as food preservatives for meatball, noodle, sausage, tofu, etc. Grade 2 is yellowish and usually used as antioxidant and antimicrobial agent, while Grade 3 is very dark with sharp odor, often used as wood preservatives, rubber coagulant and odor absorber.

![Figure 1. Coconut shell liquid smoke from different grades](image)

Despite the potential of coconut shell liquid smoke, it has to be utilized appropriately, considering the chemical composition and its characteristics where odor, flavor and color of the product may be affected. Certain products have to maintain their organoleptic properties to consumers’ preferences. For raw food, the odor, flavor and color may be recovered or improved by cooking and other handling process. However, other products may not have this advantage. Thus, refining process is often done to liquid smoke to reduce the undesirable odor, flavor and color [3]. Refined liquid smoke is more flexible in applications to various food or non-food products, compared to non-refined coconut shell liquid smoke [10].

The goal of this study was to identify the important chemical characteristics of a full-strength coconut shell liquid smoke (Grade 3), and refined liquid smoke products (Grade 1 and 2). The chemical volatile and semi-volatile constituents of these products were identified using Gas Chromatography-Mass Spectrometry (GC-MS) analysis. pH and benzo [a] pyrene were also determined. The findings of this study may be useful as basis in the determination of the application of the different grades of coconut shell liquid smoke.
2. Material and method
Coconut shell liquid smoke (CS-LS) with three different grades were obtained from Indonesia Liquid Smoke, Ciracas, East Jakarta. The production stages included processing coconut shell in furnace with 400-500°C for 1-2 hours and followed by condensation of the smoke. The outcome was graded as Grade 3 coconut shell liquid smoke. Grade 2 was produced from distillation and filtration of the condensed smoke using zeolite. Grade 1 was the result of further filtration of Grade 2 coconut shell liquid smoke using activated carbon.

Chemical compounds of coconut shell liquid smokes (CS-LS)
Chemical compounds of coconut shell liquid smoke were identified using Gas Chromatography-Mass Spectrometry (GC-MS) [11]. Compounds were identified by comparing their mass spectra with data from a mass spectral Data Base Library in the GC-MS data system. Extraction was carried out using Head Space Solid Phase Micro Extraction (HS-SPME). Evaporated solvent of the sample at 60°C for 30 minutes were collected. The type of GC-MS was used Agilent 7890a and MS Agilent 5975c with triple axis detector. Column used was HP-5MS (30m x 250µm x 0.25µm) with 5% phenyl methyl siloxane as filler. The injector 250°C splitless, carrier gas helium with flow rate of 0.8ml/minute. The oven was programmed at 60°C for 2 minutes, then 5°C/minute to 200°C and 10°C to 290°C for 5 minutes. Scan mass was 33-550 amu, MS source 230°C and MS quad 150°C. GC Agilent 7890a and MS Agilent 5975c with triple axis detector were included. Benzo [a] pyrene was separately identified using high performance liquid chromatography (HPLC).

3. Result and discussion

3.1. Identified chemical compounds
Several volatile compounds were detected from GC-MS analysis (Table 1.). Result of GC-MS analysis showed that coconut shell liquid smoke contained organic acid, phenols, furan, aldehyde, and ketones. Organic acid was the result of the partial pyrolysis of wood cellulose and hemicellulose. Organic acid identified from three grades of CS-LS was acetic acid. Based on the chromatogram, it appeared that acetic acid changed very significant in the purification process. Purification process resulted in a reduction in total acetic acid ion; however, a very large decline occurred in the purification of liquid smoke with zeolite (Grade 2 CS-LS) (Figure 1, 2, 3).

Refining process reduced aldehyde and ketones. The less refined CS-LS (Grade 3) contained the highest proportion of aldehydes and ketones. Results also showed that there were several compound changes after refining process. 2-Methoxy-6-methylphenol, phenol, 2,6-dimethoxy, and phenol, 2-methoxy-4-propyl were not found in the Grade 2 and 1. Phenolic compounds, such as phenol, 2-methoxyphenol (guaiacol), 3,4dimethoxyphenols, and 2-methoxy-4-methyl phenol were prominent in CS-SL and play a major contribution to antibacterial activity [12]. Others volatile compounds were also changed in the group of furan, aldehydes and ketones.

Furfural was found in all grades of CS-LS. Furfural was a furans compound, and it was a result from thermal breakdown of cellulose and hemicellulose and contribute overall smoky odor to liquid smoke that soften partially the heavy smoky aroma of phenolic compounds [10].

| Compounds | Grade 1 | Grade 2 | Grade 3 |
|-----------|---------|---------|---------|
|           | t_R     | Compounds | t_R     | Compounds | t_R     | Compounds |
| Organic acids | | | | | | |
| Phenol     | 7.92    | Phenol    | 8.00    | Phenol    | 7.93    | Phenol    |
| Compounds                        | Grade 1 | t<sub>R</sub> | Grade 2 | t<sub>R</sub> | Grade 3 | t<sub>R</sub> |
|---------------------------------|---------|--------------|---------|--------------|---------|--------------|
| Phenol, 3-methyl                | 10.38   |              | Phenol, 2-methyl | 9.03    | Phenol, 2-methyl | 9.82    |
| Phenol, 2-methoxy               | 10.77   |              | Phenol, 4-methyl | 10.48   | Phenol, 4-methyl | 10.62   |
| Phenol, 3,5-dimethyl            | 12.32   |              | Phenol, 2-methoxy | 10.87   | Phenol, 2-methoxy | 10.96   |
| Phenol, 4-ethyl                 | 12.89   |              | Phenol, 3,5-dimethyl | 12.33   | Phenol, 3,5-dimethyl | 13.33   |
| Phenol, 2-methoxy-4-methyl      | 13.64   |              | Phenol, 3-ethyl  | 13.05   | Phenol, 3-ethyl  | 13.79   |
| Phenol, 4-ethyl-2-methoxy       | 16.04   |              | Phenol, 2-methoxy-4-methyl | 13.72   | Phenol, 2-methoxy-4-methyl | 16.18   |
| Furan, 2-ethyl                  | 8.03    |              | Phenol, 4-ethyl-2-methoxy | 16.13   | Phenol, 4-ethyl-2-methoxy | 18.18   |
| Furan, 2-ethenyl                | 4.34    |              | Phenol, 2,3,6-trimethyl | 17.08   | Phenol, 2,3,6-trimethyl | 18.42   |
| Furan                           | 4.47    |              | 4.34    |              | 4.80    |              |
| Furfural                        | 4.34    |              | Furfural | 4.80        |         |              |
| 3-Furaldehyde                   | 6.27    |              | 16.86   |              | 3.26    |              |
| 1,2-Cyclopentanediene, 3-methyl | 9.24    |              | 17.29   |              | 4.31    |              |
| 2-Cyclopenten-1-one, 2,3,4-trimethyl | 11.22   |              | 19.1789 |              | 7.16    |              |
| 1,2,3-Trimethoxybenzene         | 16.81   |              | 19.44   |              | 8.23    |              |
| Benzene, 2-propenyl             | 17.06   |              | 21.42   |              | 9.65    |              |
| 1-Methyl-2-one                  | 21.41   |              | 11.30   |              | 11.50   |              |
| 1,2,3-Trimethoxybenzene         | 16.81   |              |         |              |         |              |
| Benzene, 1-ethenyl-4-methyl     | 21.41   |              |         |              |         |              |
The quality of liquid smoke was determined by phenol and acid levels due to their roles as antioxidant and antimicrobial agent. The higher levels of phenol and acid levels of liquid smoke was correlated with the higher antioxidant activity and antimicrobial activity [13]. The less refined CS-LS had the highest phenolic content and the lowest pH. Acidity of liquid smokes depends on the wood source, processing steps and refining parameters. Liquid smokes are usually acidic with a pH of 1.5–5.5 [10]. Acidity level correlates with the amount of organic acids in liquid smoke. Result of GC-MS analysis showed that CS-LS contained acetic acid. Highest acetic acid total ion count showed by Grade 3 CS-LS (Figure 3). Grade 2 had the highest value of pH, likely caused by the affect of zeolite used in the purification process. Visually, Grade 1 liquid smoke was clear. Grade 2 liquid smoke was reddish in color and not as clear as Grade 1, while Grade 3 was dark brown. This difference may indicate that each grade had different chemical composition.

| Compounds | Grade 1 | Grade 2 | Grade 3 |
|-----------|---------|---------|---------|
| tR        | Compounds | tR        | Compounds | tR        | Compounds |
| 11.94     | 2,5-Dimethylhydroquinone | 13.89     | 2-Cyclohexen-1-one, 2-(2-methyl-2-propenyl) | 14.89     | 3,4-Dimethoxytoluene |
| 16.55     | 2,5-Dimethoxytoluene | 16.77     | 2-Methyl-1-indadone | 16.87     | 1,2,3-Trimethoxybenzene | 3,4,5-Trimethoxytoluene |

**Table 2. pH of CS-LS**

| CS-LS Grade | pH       |
|------------|----------|
| 1          | 2.79±0.02 |
| 2          | 3.12±0.3  |
| 3          | 2.76±0.03 |
Figure 2. Chromatograms of grade 1 CS-LS

Figure 3. Chromatograms of grade 2 CS-LS
3.2. Benzo [a] pyrene of CS-LS
Benzo [a] pyrene (BaP) is one of polycyclic aromatic hydrocarbon (PAH) compounds that has carcinogenic risk. Results showed that Grade 3 CS-LS had the highest concentration of benzo[a]pyrene. It confirmed that purification process in the CS-LS reduced PAH compound, including BaP. Zeolite has absorber ability due to its porous structure, allowing BaP in liquid smoke to be caught in its pores. Zeolite can absorb a considerable amount of molecules with same or smaller size than zeolite’s pores [14].

| CS-LS Grade | Benzo [a] pyrenz (ppm) |
|-------------|------------------------|
| 1           | 13.316                 |
| 2           | 16.103                 |
| 3           | 25.203                 |

4. Conclusion
The major compound of three grade CS-LS were phenolic. The concentration of several compound changed after refining process. Compounds that decreased significantly after purification process were acetic acid, aldehyde, and ketones. Either Grade 1, 2, or 3 still contained benzo[a]pyrene, where the highest content was shown in grade 3.

5. References
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