Chemical composition of liquid smoke from coconut shell waste produced by SME in Rongkop Gunungkidul

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Abstract. The availability of coconut shell waste in Rongkop, Gunungkidul has the opportunity to be processed into several products, including liquid smoke products, in one month production requires ± 1000 coconuts to be made. Liquid smoke is obtained from smoke condensation in the pyrolysis process. The liquid smoke contains phenol group compounds, acid groups, and carbonyl groups such as those found in natural smoke. All three can simultaneously act as antioxidants and antimicrobials as well as providing a distinctive color and flavor effect of smoke on food products. In this study, the pyrolysis process was implemented with variations in the heating temperature at 200°C; 250°C; 300°C with 8 hours of cooking time, and 1-5 cm of coconut shell size, 5.87% moisture content with 5 kg process capacity. This pyrolysis process produces a dark brown liquid with an average pH value of 3. Each of the pyrolysis liquid fumes is analyzed using Gas Chromatography Mass Spectrometry to determine the chemical components inside. From the results showed, there were 16 chemical components identified at 200°C, the largest component was Acetic acid at 51.6%, 30 chemical components were identified at 250°C, the largest component was Acetic acid at 50.88%, 48 chemical components were identified at 300°C, and the largest component Acetic acid at 39.98%.

1. Introduction
One of UKM (Usaha Kecil Menengah) or SME (Small and Medium Enterprises) in Rongkop area conducted the process of making food preparations with the need for 1000 coconuts per month. The use of the remnants of a coconut shell will be worth more if it is used as a raw material for making liquid smoke.

Coconut shell is categorized as hard wood, but has higher lignin content and lower cellulose content [1]. Coconut shell is one of the raw materials that is very potential to be used as liquid smoke; coconut shell contains 27.7% pentose, cellulose 26.6%, lignin 29.4%, water 8%, extraction solvent 4.2%, uronate anhydrous 3.5%, and ash 0.6%. Coconut shell in general is often used as handicrafts, fuels, and raw materials for activated charcoal. In the process of making charcoal from wood biomass waste produces smoke as a burning effect, this smoke is used as liquid smoke by changing it from the gas phase to the liquid phase by the condensation process [2].
Unlike combustion, pyrolysis does not require oxygen, except for partial combustion that needs it to supply the thermal energy needed in the process. Pyrolysis is a thermal decomposition of woody biomass into three solid, liquid and gas phases. It has three variations: Mild pyrolysis, Slow pyrolysis and Fast pyrolysis. In the pyrolysis process of woody biomass, large hydrocarbon molecules are broken down into smaller hydrocarbon molecules. The chemical structure of woody biomass is altered, which produces water, acetic acid, carbon dioxide, methanol and carbon monoxide [3].

Pyrolysis compounds that have been condensed in the form of liquid smoke include phenol groups, carbonyl groups, and acid groups; all three have simultaneous antioxidant, antimicrobial activity, and have a role in providing specific flavors. Each type of wood contains cellulose and lignin and other compounds which in the pyrolysis process will produce liquid smoke with varying specifications as well [4]. Flavored food made from liquid smoke made from pyrolysis wood is reported to offer many advantages compared to fumigation in the traditional way directly from the furnace that is ease of application, speed, and uniformity of the product [5].

Pyrolysis occurs in four stages starting with water evaporation, followed by hemicellulose decomposition, cellulose decomposition, and lignin decomposition. Hemicellulose and cellulose pyrolysis occurs between 180°C and 350°C and produce carboxylic acids and carbonyl compounds, while lignin is between 300°C and 500°C and produce phenols. In addition to carbonyl, acids, and phenols, wood pyrolysis often produces compounds that are not beneficial such as polycyclic aromatic hydrocarbon (PAH), some work naturally; others are the result of incomplete combustion and usually form at pyrolysis temperatures between 500°C and 900°C [6]. Through the purification process, unwanted PAH can be removed, and the intensity of taste, color in the liquid smoke can be adjusted [7]. Liquid smoke, in addition to maintaining food quality with antioxidant and antimicrobial properties, also gives the desired color, taste, and aroma to food. The application of liquid smoke takes less time than traditional fumigation, is more environmentally friendly, and removes potentially toxic compounds while still providing the desired taste and aroma of traditional fumigation.

The quality of liquid smoke is determined from the composition of phenols, acids, and the magnitude of these components is influenced by the operating conditions of the pyrolysis process in the form of temperature, time, and distillation process [8]. Applications of liquid smoke use can be utilized for natural preservatives of mackerel fish [9], flavorings and food preservatives Sponge cake [10], smoked beef flavorings [11], tuna preservatives [12], natural preservatives tofu [13], antioxidants in processing smoked tuna [14], smoked milkfish [15], beef preservation [2], as raw material for organic pesticides on the mortality of Grayak caterpillars (Spodoptera litura F.) [1], and preservatives of parrot fish [16]. This study aims to determine the chemical compounds contained in coconut shell liquid smoke of processed food production waste in Gunungkidul regency in the pyrolysis process at 200°C, 250°C and 300°C by analyzing the results of liquid smoke using GCMS.

2. Materials and methods

2.1. Materials
The materials used for this study include coconut shell, H$_2$SO$_4$ (Merck, Germany) and aquadest. While the tools used in this study are scales, Universal pH (Merck, Germany), Moisture analyzer (AND MX 50, USA), grinder machine, 5kg capacity pyrolysis reactor, and GCMS-QP2010S Shimadzu, Japan.

2.2. Methods

2.2.1 Pyrolysis
Coconut shell waste was cleaned and separated from coconut fibers, dried in the sun for 1 day, the results of drying were taken samples for testing the moisture content with a moisture analyzer balance, and testing the lignocellulose component of the coconut shell used the Chesson [22]. Dry coconut was reduced in size to ± 1-5 cm using a grinder, and packaged with a weight adjusted to the capacity of the pyrolysis tool, which was 5kg. Next was the pyrolysis process of the pyrolysis reactor by setting at a working temperature of 200°C, 250°C, and 300°C, each process carried out for 8 hours. Liquid smoke
Condensation products from pyrolysis are collected in a container and allowed to stand for 1 day to precipitate tar. The working diagram of the pyrolysis was shown in Figure 1.

![Pyrolysis process diagram](image)

**Figure 1.** Pyrolysis process diagram

The results of liquid smoke that has been allowed to stand for 24 hours were sampled for pH testing using a universal indicator. By taking a sample of liquid smoke as much as 1 mL, then the pH was measured by dipping the universal indicator. Liquid pyrolysis results were then taken on a sample bottle and then analyzed using GCMS.

2.2.2 Analysis of coconut shell chemical composition

The chesson method to analyze the composition of lignocellulose [22]. One g (a) dry sample is added with H$_2$O in the amount of 150 ml and then refluxed at 100 °C in a water bath within 1 hour. The results are then filtered, and the residue is washed with 300 ml of hot water. Then the residue is dried to a constant in an oven then weighed (b). The residue was added as much as 150 ml H$_2$SO$_4$ with a concentration of 1 N then refluxed at a temperature of a water bath 100 °C within 1 hour. The product is filtered to neutral (300 mL) and dried (c). Dry residue was added with H$_2$SO$_4$ 72% in the amount of 10 ml and soaked at room temperature within 4 hours. The residue is then added with 150 ml H$_2$SO$_4$ of 1 N and refluxed to bath water within 1 hour. The residue is filtered and washed with H$_2$O to neutral (300 mL) and then dried (d). The residue is weighed and crushed in the furnace (e), the residue weighed and ashed in the furnace (e) Cellulose content = [(c-d)/a] x 100%; Hemicellulose content = [(b-c)/a] x 100%, Lignin content = [(d-e)/a]x 100%

2.2.3 Determination of coconut shell moisture content

To find out the moisture content of the coconut shell, with a moisture analyzer balance testing, with a sample of coconut shell as much as 1 gram, enter the sample into the moisture analyzer balance tool. Start the analysis and the results can be known from the tool displayed in the form of temperature data, analysis time and moisture content values.

2.2.4 Liquid smoke pH test

Testing for liquid smoke using ph test universal [23]. It was conducted by dipping the universal indicator in liquid smoke, observed in the color of the universal indicator.

2.2.5 Identification of chemical compound components using GCMS

Identification of the chemical components of liquid smoke used GCMS which was optimized at a column temperature of 60°C for 5 minutes, then it was increased to reach 200°C and maintained for 30 minutes, the injector temperature was set at 250°C. The carrier gas uses helium gas with a pressure of 50 kPa. MS data were arranged on the molecular weight of components between 28.00 to 600.00 within 1.80 to 70.00 minutes [17].
3. Results and discussions

3.1 Coconut shell chemical composition.
Coconut shell is a part of coconut fruit whose biological function is the protective core of the fruit and is located on the inside of the fiber with a thickness ranging from 2-6 mm. Coconut shell is widely used as raw material for liquid smoke making, because coconut shell has a high lignin content (calculated based on dry weight) and mainly composed of cellulose, hemicellulose and lignin [24]. Result of lignocellulose content analysis in coconut shell presented in table 1.

| Material                      | Lignin (%) | Cellulose (%) | Hemicellulose (%) | Water solub content | Reference |
|-------------------------------|------------|---------------|-------------------|---------------------|-----------|
| Coconut shell                 | 32.33      | 36.13         | 20.36             | 11.17               | Present work |
| Cajuput twigs                 | 45.25      | 24.25         | 15.38             | -                   | [14]      |
| Sugarcane bagasse             | 17.52      | 44.43         | 22.90             | -                   | [27]      |
| Rice straw                    | 9.99       | 29.55         | 25.35             | 24                  | [26]      |
| Oil palm empty fruit bunch    | 15.36      | 42.56         | 20.27             | 21.10               | [26]      |

Chesson analysis results showed that the content of percent Lignin 32.33 %, lower than cajuput twigs 45.25 %. The cellulose component is 36.13 %, lower than sugarcane bagasse 44.43 % and oil palm empty fruit bunch 42.56 %, while hemicellulose in coconut shell is 20.36% lower than rice straw 25.35 % and sugarcane bagasse 22.90 %. The amount of cellulose content of a substance can determine the rate of acid, furan and water in the liquid it is produced. The difference in cellulose content in this study is caused by differences in the material and place of plant growth, which can affect the content of cellulose and other chemical content of a substance [14]. Each biomass has a different composition and the amount of value depends on the species and environmental conditions [8], while the content of lignin in an ingredient will determine the flavor of the liquid smoked product, because in the process of pyrolysis lignin will produce phenolic compounds and phenolic esters such as guaiakol and siringol that affect the smoke flavor [14].

3.2 Coconut shell moisture content
Water content is one of the factors that influence the quality of the resulting pyrolysis results. Water content affects the yield and quality of the liquid smoke produced. Water content that is too high will reduce the quality of liquid smoke because it will reduce the level of the product, such as acid and phenol levels. The higher the moisture content of the raw materials used, the quality will decrease [28]. The test results using a moisture analyzer balance shows the moisture content of the coconut shell drying results of 5.88%. Percent of this water content will affect the rate of heat increase in the pyrolysis process, the higher of water content will make the process of heating slow, because the heat source is used to evaporate the water content of raw materials.

3.3 Test results of liquid smoke chemical compound components
Liquid smoke results from the pyrolysis process on the 3 temperature variables are dark brown as in Figure 2. the blackish brown color of the coconut shell liquid smoke was influenced by the content of
the carbonyl compound, that is the higher the carbonyl content, the higher the browning potential [19]. The purpose of this measurement is to determine the level of decomposition of raw materials in the pyrolysis process. A low pH value means that the smoke produced is high quality especially for use as a food preservative and good storability in food products [20].

![Image](image.png)

**Figure 2. Liquid Smoke**

Tar has carcinogenic properties so that liquid smoke cannot be used directly for the preservation of food. After each liquid smoke is allowed to stand for 24 hours to precipitate tar, to get a safer result from carcinogenic substances, liquid smoke is distilled to separate from harmful compounds that are still contained in liquid smoke [2]. The pH of the coconut shell liquid smoke is tested using a universal indicator, which results in liquid smoke have a pH value of 3. It shows that the liquid smoke produced is acidic. The source of this acidity comes from acid compounds, especially acetic acid compounds and other carboxylic acids [19]. This pH value meets the standard quality of liquid smoke from commercial product specifications with a pH range of 1.5 - 3.70 [20]. The pH value will decrease with increasing temperature and length of combustion, because more and more elements in the coconut shell break down to form chemical compounds that are acidic [1]. Liquid smoke is then analyzed by GCMS to determine the chemical composition contained in liquid smoke. The results of testing using GCMS are presented in table 2.

| No  | Component liquid smoke                      | Peak Area % | Peak Area % | Peak Area % |
|-----|---------------------------------------------|-------------|-------------|-------------|
|     |                                             | 200 °C      | 250 °C      | 300 °C      |
| 1   | Methyl Alcohol                              | 10.40       | -           | -           |
| 2   | Acetone                                     | 2.44        | 2.40        | 2.06        |
| 3   | Acetic acid, methyl ester                   | 2.73        | 3.41        | 2.58        |
| 4   | 2,3-Butanedione                             | 1.08        | 0.77        | 0.55        |
| 5   | 2-Butanone (CAS) Methyl ethyl ketone        | 0.51        | 0.42        | 0.42        |
| 6   | Formic acid (CAS) Bilorin                   | 0.59        | 0.97        | 0.87        |
| 7   | Acetic acid                                 | 51.6        | 50.88       | 39.98       |
| 8   | 2-Propanone, 1-hydroxy-                     | 1.02        | 1.46        | 2.65        |
| 9   | Propanoic acid (CAS) Propionic acid         | 2.09        | -           | -           |
| 10  | 1-Hydroxy-2-butane                          | 1.98        | 1.86        | 1.95        |
| 11  | 2-Furancarboxaldehyde (CAS) Furfural        | 12.67       | 7.63        | 3.53        |
| 12  | 2-Propanone, 1-(acetyloxy)- (CAS) Acetol    | 0.47        | 0.59        | 1           |
| 13  | 2-Furancarboxaldehyde, 5-methyl- (CAS)      | 0.60        | -           | -           |
| 14  | Benzenesulfonic acid, 4-hydroxy-            | 10.37       | -           | 13.82       |
From the results of GCMS testing, the largest chemical component of search smoke was dominated by acetic acid by 51.6% at 200°C, 50.88% at 250°C, 39.98% at 300°C, with increasing temperature in the pyrolysis process, the number of component compounds chemistry will increase, the number of components of liquid smoke compounds at a pyrolysis temperature of 200 - 300°C which was 57 compounds. The compound is a class of carboxylic acids, phenols, carbonyls, furans, hydrocarbons, alcohol, and others [19]. Acid compounds are the main constituents in liquid smoke, have a role as antimicrobials and taste-forming in food products that are preserved with liquid smoke. Acid component can inhibit the formation of spores, bacterial growth, fungi, and viral activity in food products. Meanwhile, phenol has a role as an antioxidant that can extend the storability of a food product [2]. Acetic acid produced by cellulose pyrolysis, the solution occurs in two stages, which are the reaction of cellulose hydrolysis into glucose and then pyrolysis into acids, water, furans, and phenols, from materials with high cellulosic content will also produce high total acids [1]. The results of the analysis of liquid smoke, at a temperature of 200°C, showed the largest percentage of acetic acid at 51.6%, while at temperatures above, the acetic acid percent tends to fall. Therefore, if liquid smoke will be applied to food products with a greater composition of acetic acid, it is enough to conduct pyrolysis at 200°C. To produce liquid smoke with good quality, it must use biomass raw materials from hard wood, so that high quality liquid smoke products will be obtained [21].

4. Conclusion
Most liquid component of liquid smoke from coconut shell waste is acetic acid and at a temperature of 200°C obtained 51.6%, the more the temperature is increased in the pyrolysis process, the number of liquid smoke compounds will increase. This study shows the number of 57 compounds produced by the temperature difference in the pyrolysis process. The pH value of coconut shell liquid smoke is 3 meaning that it meets the liquid smoke quality standards of commercial and acidic products. To improve the quality of liquid smoke and to make it safer from carcinogenic substances, liquid smoke purification can be conducted through the distillation process.

|   | Compound                                              | 0.45 | 0.26 | -  |
|---|-------------------------------------------------------|------|------|----|
| 15| Acetic acid, phenyl ester                            |      |      |    |
| 16| Phenol, 2-methoxy-                                   | 1.01 | 1.40 | 2.63|
| 17| 1,2-Ethanedio                                        | -    | 8.94 | -  |
| 18| Propanoic acid, methyl ester (CAS) Methyl             | -    | 0.38 | 0.85|
| 19| 2-Butanone, 3-hydroxy- (CAS) Acetoin                  | -    | 0.18 | -  |
| 20| Propionic acid                                       | -    | 2.31 | 2.27|
| 21| Furfuryl alcohol                                     | -    | 0.29 | 0.97|
| 22| 2(3H)-Furanone, dihydro- (CAS) Butyrolacton          | -    | 0.19 | 0.67|
| 23| Sulfone, butyl propyl                                 | -    | 0.53 | 0.56|
| 24| 2-Furanmethanol, tetrahydro- (CAS) Tetrahyd          | -    | 0.29 | 0.98|
| 25| 1,2-Cyclopentanedione, 3-methyl-                      | -    | 0.27 | -  |
| 26| Phenol (CAS) Izal                                     | -    | 11.41| -  |
| 27| Phenol, 2-methyl-                                    | -    | 0.33 | 0.49|
| 28| 2-Furanmethanol, tetrahydro-                          | -    | 0.25 | 0.34|
| 29| Phenol, 3-methyl- (CAS) m-Cresol                      | -    | 0.62 |    |
| 30| Cyclopropyl carbinol                                 | -    | 0.24 |    |
| 31| Phenol, 2-methoxy-4-methyl-                           | -    | 0.35 | 0.94|
| 32| Phenol, 4-ethyl-2-methoxy-                            | -    | 0.23 | 0.62|
| 33| Phenol, 2,6-dimethoxy- (CAS) 2,6-Dimethoxy           | -    | 0.82 | -  |
| 34| 1,2,4-Trimethoxybenzene                               | -    | 0.32 | 1.01|

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