Production of Liquid Smoke From the Process of Carbonization of Durian Skin Biomass, Coconut Shell and Palm Shell for Preservation of Tilapia Fish

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Abstract. The Liquid smoke can be use for food preservation, be obtained from pyrolysis of materials containing cellulose, hemicellulose, and lignin. The form of liquid smoke that has the ability to preserve, for their phenolic compounds, acids and carbonyl. The purpose of this research is to know the quality of liquid smoke from process of charcoal the biomass obtained from rotary pyrolysis carbonisator as fish preservative, the effect of liquid smoke on the chemical and organoleptic properties of fish, and the resilience of fish after being given smoke liquid. The method of experiments with skin biomass of durian, coconut shell, and palm shell. Biomass is dried, then is burned in rotary carbonisator pyrolysis. The results of the process are namely liquid, tar and charcoal smoke. Next, Liquid smoke is precipitated and then it is distilled twice, namely ordinary distillation and vacuum distillation. Results combustion produces liquid smoke with a yield of 19% on the skin of durian, 23.6% on coconut shell, and 20.8% on palm shells. Organoleptic test results on the fish with the addition of liquid smoke from the skin of durian with a concentration of 5% is most preferred by the panellists in terms of color, aroma, flavor, and texture.

1. Introduction
Preservatives of food and beverage products have become inseparable in food industry. The food industry provides solutions by adding hazardous ingredients in food processing, such as the use of dyes, flavors, and preservatives. These ingredients can cause some dangerous diseases, if consumed in a long period of time. One solution that can be utilized is using natural preservatives that can be obtained from organic materials. One of them is by utilizing liquid smoke in the process of carbonization pyrolysis biomass as biobriquette raw material [12]. Pyrolysis of this waste results in the formation of three final products: gas, oil and charcoal, all of which have potential for use in various applications [8]. Oil here can be liquid or tar, and this depends on the raw material that is pyrolysis. The smoke produced from burning of biomass is condensed and generate liquid smoke. Smoke can also be obtained from biobriquet carbonization process where all this time it has been removed without re-use it. Therefore, research needs to be done by using smoke as preservative. Liquid smoke as pyrolysis results depend on basic materials and pyrolysis temperature [3]. Liquid smoke can be used as fish preservative. In the community, fish preservation is generally performed traditionally with curing method, by contacting the smoke directly into fish. The resulting fish smells of stinging smoke and has
blackish brown color. Therefore, we use organic liquid smoke from biomass smoke as preservative that is not too smelly. From the case, that it is necessary to diversify smoker materials, thus affecting the increase of production and the quality of liquid smoke. The quality and quantity of liquid smoke is also influenced by the condition of production process, including the ignition, pressure, temperature, and combustion duration. In liquid smoke, there are still tar compounds containing Polycyclic Aromatic Hydrocarbon (PAH) compound. This compound is an aromatic chain that causes cancer. To reduce the amount of PAH contained in the liquid smoke, it can be purified like purification of liquid smoke by distillation [6] and purification by using active charcoal [11]. As a preliminary study to obtain the curing temperature using pyrolysis spinning carbonisator [12], biomass used durian skin biomass, coconut shell, and palm shell at temperature of 200°C, 300°C, and 400°C [1]. We founded that optimum temperature in durian peel biomass pyrolysis is 140°C to 175°C. The smoke obtained can be used as liquid smoke. If optimum temperature is exceeded, pyrolysis will produce black tar. This can be shown from the results of the study pyrolysis in brown algae Saccharina japonica can be produced bio-oil and bio-char at a temperature of 450°C [2]. The purpose of this research is to find out whether liquid smoke can be used as a preservative of fish, then to know the composition that exist in liquid smoke and the quality of liquid smoke as a preservative of fish from biomass durian skin, coconut shell, and palm shells and to know the resilience of fish preserved by using liquid smoke from biomass.

2. Experimental section

2.1. Material
Tools used are series of spinning pyrolysis carbonization reactor, series of distillation tools, GC-MS Tool. Material: Durian skin biomass, palm shell, coconut shell from Padang

2.2. Research Parameters
Research fixed parameters i.e pyrolysis carbonization temperature: 140 to 175 °C, carbonization time of 120 minutes; parameter variables: biomass type: durian skin, coconut shell and palm shell; Liquid Smoke Concentration 1%; 2.5%; 5%. Test parameters: Tilapia fish, Output Parameters: yield, pH, Density, Composition of liquid smoke compound, Color and flavor of liquid smoke, Durability of fish preservation, fish organoleptic (color, scent, texture, flavor).

2.3. Working Procedure
Capture of Liquid Smoke; Biomass (durian shell, palm shell, coconut shell) is reduced in size and dried about 4-5 days under sunlight, then biomass is incorporated in pyrolysis carbonisator and fire heated if for 120 minutes at 175 °C temperature, the liquid smoke coming out is accommodated in a trophy cup, the result of pyrolysis process are three products i.e. liquid smoke, tar, and charcoal. Liquid smoke is obtained from smoke condensation at pyrolysis process and precipitated for a week. Liquid Smoke Distillation Stage; Liquid smoke after precipitation (liquid smoke Grade III) is distilled by vacuum distillation until liquid smoke comes out from the condenser end. Temperature along the process is recorded. The distillation produce Grade II liquid smoke, then distilled again to obtain Grade I liquid smoke that can be applied as food preservative.
Analysis stages; Analysis stage performed on liquid water are rendemen, GC-MS, pH and density. Testing Stage of Fish Preservation Durability; Tilapia is weeded by throwing the scales, split the fish into a butterfly shape, then discarded gills, stomach contents, dirt and black abdominal wall layers. Then liquid smoke solution is prepared, made with concentrations of 1%, 2.5%, and 5%. To make liquid smoke with concentration of 1% is by taking 5 ml of liquid smoke, then added clean water of 500 ml. The fish is soaked in liquid smoke with a determined concentration for 30 minutes, then it drained until the surface dries. It was then dried at 40 °C for 30 minutes, 60 °C for 30 minutes, and 80 °C for 8 hours in oven. Then the fish is left cold in open air and then packed. Smoked Tilapia is packed with plastic and stored in storage room for 15 days.
Organoleptic Testing Stage: Each sample is placed on a white container or plate to be able to see the color difference clearly. The panelist tastes the test sample, before and after it, he should drink to wash the mouth. The panelist is required to state his / her level of satisfaction to the sample presented, by assigning a number of 1, 2, 3, 4, and 5 in each sample column considered to be in accordance with the panelist's preference level.

3. Results and Discussion

3.1. Pyrolysis Carbonization Process

Liquid smoke as a result of biomass pyrolysis, conducted using spinning carbonisator pyrolysis reactor, has black colored result. This type of liquid smoke is called liquid smoke Grade III. This liquid can not be used for food because it contains tar, but only used for wood preservation. In order for the liquid smoke pyrolysis product to be used for the preservation of fish, the liquid must be purified. The yield is shown in Table 1.

| Type of Biomass | Product form at Temperature (°C) | Liquid Smoke Yield Grade III (%) |
|----------------|---------------------------------|---------------------------------|
|                | T = ±140                        | T = ±170                        | T = ±175                        |
| Durian Shell   | Liquid Smoke                    | Tar                             | 19,0                            |
| Coconut Shell  | Smoke                           | Liquid Smoke                    | 23,6                            |
| Palm shell     | Smoke                           | Smoke                           | Liquid Smoke                    | 20,8                            |

3.2. Liquid Smoke Purification

The next step to obtain liquid smoke for fish preservation is purification by using distillation 2 times. The first distillation with pyrolysis liquid smoke (liquid smoke Grade III) will produce second Grade liquid smoke. Class II liquid smoke is for fast food preservation, such as meatballs and instant noodles[14]. Liquid smoke Class II has brownish yellow color. To get liquid smoke for fish preservation, the Grade II liquid smoke is distilled again to obtain Grade I liquid smoke. The Grade I liquid smoke is clear yellow. The result and optimum temperature for each Grade of liquid smoke at the purification stage can be seen in Table 2.

| Type of Biomass | Grade | Temperature (°C) | Time (hour) | Yield (%) |
|----------------|-------|-----------------|------------|-----------|
| Durian Shell   | Grade II | 84              | 1,35       | 18        |
|                | Grade I  | 94              | 1,15       | 14,8      |
| Coconut Shell  | Grade II | 83              | 1,00       | 22,6      |
|                | Grade I  | 81              | 1,07       | 18,8      |
| Palm Shell     | Grade II | 84              | 1,20       | 19,5      |
|                | Grade I  | 88              | 1,25       | 16,3      |

From Table 2, it can be seen that temperature of Grade I and II is optimum temperature. This is because at the time of purification, the constant temperature is at that specific degree and it does not increase, because the purification is conducted by vacuum distillation. The temperature will increase when liquid smoke in boiling flask is exhausted and only tar is left in biomass liquid smoke. The yield of liquid smoke on pyrolysis carbonization process of each sample was 19% of durian shell biomass, coconut shell biomass 23.6%, and 20.8% shellfish biomass (Table 1). The yield in Grade II and Grade I decreased because the tar contained has begun to decrease, the yield is still very small, and can be caused by several factors are heating temperature, moisture content and the particle size of biomass used. To obtain liquid smoke with high yield, the heating should be carried out to 400°C while in this
study the maximum temperature is only 175°C, resulting in very small yield. Form of Grade III liquid smoke as pyrolysis results and Grade I and II as results of vacuum distillation can be seen in Figure 1 and Figure 2.

Figure 1. Liquid smoke as Pyrolysis Grade III, II, I

Figure 2. Liquid smoke as Pyrolysis Grade I

Liquid smoke biomass from durian skin, coconut shell and palm shell have clear color difference. In Figure 1 b. it can be seen that distillation of liquid smoke of Grade I palm shell has a slightly darker brown color than liquid smoke durian skin, while coconut shell smoke has the clearest result. This is because the content in the biomass varies, and when purified by distillation there is compound content that lost from the liquid smoke.

3.3. Liquid Smoke Test

3.3.1. GC-MS Test for Determining Liquid Smoke Chemical Composition

The quality of liquid smoke depends on the composition of the chemical compounds contained in the liquid smoke. The compounds contained in the liquid smoke are affected by the pyrolysis conditions and the raw materials used. Below is the result of GC-MS liquid smoke analysis from purification result with redistillation process can be seen in Table 3. The components identified in liquid smoke, primarily derived from thermal degradation of wood carbohydrates [4], such as ketones, carbonyls, acids, furans and pyran derivatives. In this study, the most common components found in durian leather and coconut shell smoke are alcohols 16.74 and 35.57%, whereas in the palm oil liquid shell the most abundant component is carbonyl 12.24%. The difference of chemical composition in liquid smoke is due to the difference of raw materials used and also influenced by pyrolysis temperature used to produce liquid smoke. In this study the pyrolysis temperature used on durian skin is 140°C, coconut shell 170°C, and palm shell 175°C. This is because at the time of research with temperatures exceeding the temperature range, liquid smoke has produced tar, an undesirable component in the resulting liquid smoke. The most influential components in liquid smoke are carbonyl, acids and phenols.

Table 3. Major Compound Content on Liquid Smoke Distillation Result of Durian Skin, Coconut and Palm shell

| No | Compound name                        | Durian skin | Coconut shell | Palm shell |
|----|--------------------------------------|-------------|---------------|------------|
| 1  | Carbonil = (Aldehyde dan Keton)      | 12.31       | 0.62          | 12.24      |
| 2  | Acid and Derivatives                 | 11.43       | 0.07          | 5.13       |
| 3  | Furan and Pyran Derivatives          | 14.79       | 0.11          | 4.1        |
| 4  | Phenol                               | 8.68        | 2.71          | 3.06       |
| 5  | Alcohol                              | 16.74       | 35.57         | 5.11       |
| 6  | Metil, etil, eter                    | 13.22       | 18.32         | 8.39       |

According to Hamm and Potthast in Girard [5], maximum levels of phenol, carbonyl and acid compounds are 600°C. Each component has different effects. Carbonyl has a major influence on color, whereas its effect on the taste of asphalt product is less prominent due to interaction between carbonyl and amino groups. Acids derived from liquid smoke may affect flavor, pH, and shelf life [7]. While...
phenol contributes in dye smoke product. Liquid smoke containing phenol, carbonyl, and acid compounds can simultaneously act as antioxidants and antimicrobials and influence the color and distinctive flavors of food products[8]. The analysis results shows that Polycyclic Aromatic Hydrocarbon (PAH) compounds including benzopyren are not found in this liquid smoke. The most influential factor in the formation of PAH compounds is pyrolysis temperature.

3.3.2. Physical property Test of Liquid smoke (pH and Density)

The physical test of Grade I liquid smoke is shown in Table 4 and Japanese vinegar standard is used as standard comparator [14].

| Parameter          | Physical properties of liquid smoke Grade I | Standard Wood Vinegar Japan | [14]       |
|--------------------|---------------------------------------------|-----------------------------|------------|
|                    | Durian skin                                 | Coconut Shell               | Palm Shell |
| Density            | 1.002                                       | 1.0107                      | 1.0015     | >1.005     |
| pH                 | 3.83                                        | 2.4                         | 2.32       | 1.5-3.7    |
| Color              | clear yellow                                | clear yellow                | clear yellow | Yellow Brown |
| Transparency       | Transparent                                 | Transparent                 | Transparent (impureless) |           |

From Table 4, it can be seen that the density of liquid smoke from variety of biomass ranges from 1.002 to 1.015 and this is in accordance with Japanese standards. pH of liquid smoke from various purification processes is strongly influenced by acetic acid or phenol contained in liquid smoke. Acetic acid compounds may affect pH of liquid smoke, the taste and shelf life of smoke product. In addition, phenol levels also affect pH of liquid smoke because phenol has acid properties that are the effect of aromatic rings [13]. The test results showed that pH value of each liquid smoke is low. This means that the resulting liquid smoke has a good quality, especially as an anti-bacterial. Based on the pH above, liquid smoke that has a good quality is liquid smoke derived from palm shell biomass. This is because at low pH, microbes or bacteria tend not to live and breed well [9].

3.3.3. Organoleptic Test Results

The organoleptic test used in this study was sensory test. Sensory test is one assessment of a food product performed by humans as a measure using its five senses. The senses that act in this sensory test are vision (color), smell, touch (texture), and taste (flavor). The sensory properties proposed to 5 fixed panelists were color, smell, texture, and taste, treatment with 1%, 2.5%, and 5%. Panelist assessment was determined by choosing a range of 1-5 scores with a score of 1 being the least preferred and score 5 was the most favored. The results of panelist assessment can be seen in Table 5.

| Sample                      | Kode sample | ConcentrationLiquid Smoke (%) | Average analysis (score) |
|-----------------------------|-------------|--------------------------------|--------------------------|
|                             |             | flavor      | Taste | Color | Texture |
| Fish + liquid smoke Durian  | A           | 1           | 4.4   | 4.2   | 4.1     | 4.2     |
| Skin                        |             | 2.5         | 4.8   | 3.6   | 4.4     | 4.5     |
|                             |             | 5           | 3.8   | 5     | 5       | 5       |
| Fish + liquid smoke Coconut | B           | 1           | 4.4   | 4.2   | 4.6     | 4.2     |
| Shell                       |             | 2.5         | 4.2   | 4.6   | 5       | 4.6     |
|                             |             | 5           | 4     | 4     | 4.2     | 4       |
| Fish + liquid smoke Palm    | C           | 1           | 4     | 4.6   | 5       | 4.6     |
| Shell                       |             | 2.5         | 3     | 4.6   | 4.7     | 4.6     |
|                             |             | 5           | 4.6   | 3.8   | 4.5     | 4.4     |
| Non-Smoked Fish             | D           | 1.6         | 3.4   | 2.4   | 3.4     |
| Traditional Smoked Fish     | E           | 3           | 3.3   | 2     | 3       |
Explanation: 1=Very Dislike, 2=Dislike, 3=Average, 4=Like, 5= Really like

From Table 5, it can be seen that the result of statistical analysis with Kruskal-Wallis Test indicates that panelists prefer fish color at sample A,B,C compared to sample D and E. This is because fish with liquid smoke biomass have a lighter color than others. While fish without liquid smoke has a slightly darker color compared to fish with liquid smoke biomass and traditional smoked fish is very dark and less attractive to panellists. Sample A at concentration of 5% preferably with a score of 5. In terms of flavor, sample A with a concentration of 2.5% with score is 4.8. This is shows that flavor of product is very preferred, does not cause the smell too stingy, and does not cause fishy smells. While the least favorable scent is the smokeless fish. is score only 1.6. This is because the scent on the product still smells fishy. Texture is a sensation that can be used by mouth or by touching the fingers. Texture analysis from the panelist showed that the most preferred texture are sample A with 5% concentration and score 5. While the most unlikable texture is traditional smoked fish obtained score 3 because it is still has soft texture and not tasteful. Flavor can also be used as indicator of damage on the product. The results of panelists’ assessment on the most favoured flavor are sample A with concentration of 5% and score is 5, which indicates the taste in the product is well liked, and has a distinctive flavor. While the least favored taste is the sample E, with score is 3.3. This is because the panelists feel that the fish taste of smoke is too strong, that make its original taste reduced.

3.3.4. Fish Endurance Test

According to Wibowo [9], fish curing can be done by cold or hot curing. Cold curing is a method of curing carried out at low temperatures, ie at room temperature and not higher than 33°C or about 15-33°C. The use of low temperatures is intended to make fish meat is not cooked or proteins inside are not coagulated. As a result, the resulting smoked fish is still considered to be half cooked. While hot curing is conducted at high temperatures that is 80°C-90°C. Hot curing basically consists of three stages. The first stage is initial drying stage above room temperature at 30-40°C for 30-60 minutes. The second stage, is the first maturation stage where the temperature is slowly raised to 50-60°C for 30-45 minutes. The third stage is final maturation stage, where the temperature is raised to about 80°C for 3-8 hours. In this study, the fish resilience test was conducted by comparing the dipped tilapia fish and then baked, with the tilapia dipped in liquid smoke and left at room temperature. Analysis results can be seen in Table 6.

Table 6. Results of Panelists’ Assessment on Fish Organoleptic Test

| Sample                      | Flavor          | Color             | Texture | Durability (day) |
|-----------------------------|-----------------|-------------------|---------|------------------|
| Fish + Liquid Smoke baked   | smelled of smoke | not fishy        | Hard    | 30               |
| Fish + Liquid Smoke Room    | Rotten Smell    | pale white        | Soft    | 1                |
| Temperature                 | Stingy          | Reddish           |         |                  |

From Table 6, Judging from the results of fish endurance test, fish with liquid smoke and left at room temperature is not feasible to be consumed because after a day stand, because the smell will sting and blood out. While fish with liquid smoke is roasted (hot curing), fish is worth consuming despite even though having passed 30 days because of its hard texture and not fishy. So it can be concluded that liquid smoke from biomass is not suitable for cold curing and is only suitable for hot curing (heating at temperatures of >80 °C). The results of tilapia fish were given liquid smoke, then dried with an oven can be seen Figure 3.
Figure 3. The results of tilapia fish were given liquid smoke and then dried with an oven.

4. Conclusion
Waste of Durian skin, coconut shell, and palm shell biomass can be utilized as an alternative of curing material to produce liquid smoke and charcoal. From the analysis using GC-MS, durian skin has carbonyl area of 12.31%, acid and derivative 11.43%, and phenol 8.68%. Coconut shell has carbonyl area of 0.62%, acid and its derivative 0.07%, and phenol 2.71%. And palm shell has carbonyl area of 12.24%, acid and its derivative 5.13%, and phenol 3.06%. Yield of liquid smoke of durian skin, coconut shell and palm shell from pyrolysis process at temperature of 140-175°Cis 19%; 23.6% and 20.8% respectively. Variations in the concentration of liquid smoke are very influential on organoleptics (color, texture, flavor, and taste) of fish. From the result of the whole organoleptic test, the most preferred by panelists are fish + liquid smoke of durian skin with a concentration of 5%.

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