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Utilization of Various Types of Agricultural Waste Became Liquid Smoke using Pyrolysis Process

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Abstract
High quality wood is getting harder to come by, this situation tends to increase the use of low-quality wood that is easy fragile that it can not be used in its natural form. For wood materials which could potentially be of good quality preservation needs to be done. To find solutions to these weaknesses, in order to be a good quality wood hence the need for the provision of technology on the timber of liquid smoke. The purpose of this study was to determine the quantity and quality of each type of agricultural waste ie rice husks, corn cobs, coconut fibers and coconut shell for the manufacture of liquid smoke. This study begins with the pyrolysis process with materials such as husks, corncob, coconut shell, and coconut fibers. At first 3 kg of raw materials that have been cleaned and has been reduced in size inserted into the pyrolysis reactor, heated to a temperature of 400^0C for 5 hours, and smoke streamed out into the condensation pipe to obtain a liquid smoke while methane gas remains a not noncondensed. The results of this study indicate that the liquid smoke content for phenol of fibers, coconut shells, husks, and corn cobs are 2.97%; 3.04%; 1.30%; 1.38%. Liquid smoke content for the acidity of fibers, coconut shells, husks, and corn cobs are 6.8%; 7.3%; 1.6%; 1.3%. Liquid smoke pH value of the acidity of coconut shells, corn cobs, husks and fibers are 1.41; 2.47; 2.62; 3.36. Total yield of liquid smoke from acidity of fibers, coconut shells, husks, and corn cobs are 28.01%; 26.35%; 25.38%; 27.58%. Agricultural waste which has the best quality as a natural preservative for wood is coconut shell .
Keywords: liquid smoke, agricultural waste, antioxidant, antibacterial

1. Introduction

High quality wood is getting harder to come by, this situation tends to increase the use of low-quality wood. Low-quality wood has its drawbacks, including low dimensional stability, which is easily inflated and the wood shrinks when it is in a great environment humidity changes.

Low quality wood to be processed before it is used both for building and other purposes. The structure of low-quality wood fibers does not have to function mechanically so very fragile and unstable. Content component of wood is cellulose, hemicellulose, lignin, fibers, parenchyma, water, ash, and starch. High levels of water causes a low dimensional stability of wood. Parenchyma containing starch the top of the tree up to 40%, this causes the physical and mechanical characters of low timber (easily broken / cracked) and easily attacked by termites.

Low quality timber has three drawbacks, namely: poor dimensional stability, low power, and low durability so it can not be used in its natural form. For wood materials which could potentially be of good quality is necessary to preserve.

Other major issues that also occur in the processing of rubber material (bokar) is a low quality bokar and foul odors since from the garden. Low quality Bokar is due to farmers using not recommended latex (rubber) materials freezer and soak bokar in the pond / river for 7-14 days. This will spur the growth of bacteria which destroy the natural antioxidants in the bokar. The stench stung happen also due to the growth of spoilage bacteria that perform protein in the biodegradation bokar into ammonia and sulfides. Both of these things happen because the latex freezer materials used today can not prevent the growth of bacteria.

To find solutions to these weaknesses, in order to be a good quality wood hence the need for the provision of technology on the timber is adding liquid smoke. The liquid smoke has the ability to preserve the wood against fungal decay mainly white like Ganoderma sp and Paliporus alcularis fungus and spraying liquid smoke on rubber processing can remove / neutralize the stench and liquid smoke can freeze latex (rubber) perfectly with high plasticity values, and physical character of vulcanization equal or even better than the rubber that produced with formic acid (ant) freezing. Liquid smoke can overcome the stench of rubber that has not been able to overcome, because it contains 67 kinds of compounds that can prevent and off bacterial growth (which play a role in the onset of the stench) and compounds that easily evaporate and the specific smells of smoke.

Author (Yuniningsih S. et al, 2013) have presented a study of liquid smoke from coconut shell has been done with the optimal temperature 400^oC but if compared with various types of agricultural waste materials is not known with optimal quality and quantity of agricultural waste which is best for the manufacture of liquid smoke product grade 3. potential utilization of agricultural waste help the problems faced by rubber farmers and wood industrial in order to get a more durable wood quality if without added liquid smoke.

Liquid smoke obtained from smoke condensation by the pyrolysis process of wood constituents such as cellulose, hemi-cellulose and lignin. The most important group of chemical compounds that produced in the fumigation are phenols, carbonyls, acids, furans, alcohols, esters, lactones and polycyclic aromatic hydrocarbons. Two dominant compounds that act as bacteriostatic is phenol and organic acids are able to control bacterial growth. Phenol is obtained from the pyrolysis of lignin, whereas the organic acids from the pyrolysis of cellulose and hemicellulose. The higher lignin content, the greater the expected phenol obtained.

Liquid smoke contains a variety of compounds that can be grouped into groups of phenolic compounds, acids and carbonyl compounds group. Groups of these compounds play a role as antimicrobial, antioxidant, giving flavor and color formers (Girrad, 1992; Pszczola, 1995; Tranggono et al., 1996; Darmadji, 2006). Because of the liquid smoke may play a role as an antimicrobial and antioxidant, then liquid smoke can be used as a preservative (Yuwanti, 2003), wood anti-fungal and anti-termite and can be used for clotting rubber and natural pesticides (Darmadji, 2006).

Groups of compounds in liquid smoke that supports antimicrobial characters are phenol and acid. Phenolic compounds can extend microbial lag phase in the body or in the products, whereas the growth rate in the exponential phase does not change, unless extremely high concentrations of phenol. Beside as the antimicrobial, phenolic compounds also inhibit the oxidation of fat by preventing the formation of free radicals that have an impact on the prevention of the formation of oxidative off flavors (Pszczola, 1995). Group of carbonyl compounds play a role as a giver aroma (flavor) for food products and insect repellent.

The content of the liquid smoke compounds framer will determine the organoleptic characters of liquid smoke and determine the quality of the product curing. Composition and organoleptic characters of liquid smoke is highly dependent on the characters of wood, pyrolysis temperature, amount of oxygen, wood moisture, wood particle size and tool to produce liquid smoke (Girard, 1992).

The purpose of this study was to determine the quantity and quality of each type of agricultural waste ie rice husks, corn cobs, coconut fibers and coconut shell for the manufacture of liquid smoke.

2. Methods

2.1 Materials and tools

Raw materials used in this study are coconut shell, coconut fibers, rice husks and corn cobs. The fuel used in the pyrolysis process is LPG. Chemicals that are used to smoke qualities are NaOH solution, KI, $Na_2S_20_3$, starch, concentrated HCl, methanol and distilled water.

Equipment used include pyrolysis reactor made of stainless steel pipe, equipped with tar catcher and a set of condensation tools. The reactor serves to burn raw materials to be used. In the pyrolysis process produces a substance in three forms namely solid, liquid and gas. The results from the condensation is grade 3 liquid smoke. Equipment used for analysis testing of liquid smoke are Waterproof pH meter, Erlenmeyer lid, thermometer, split bottle, the titration, and glassware are common in chemical laboratory, while the main equipment used is Gas Chromatography and Mass Spectrometry (GCMS) of Hewlett Packard 6890 MSD 5973 GC equipped with Chemstation data base system and a Shimadzu GC with HP5 30 meters column length.

2.2 Implementation Research

This study begins with the pyrolysis process with varying material such as rice husks, corncob, coconut shell, and coconut fibers. At first 3 kgs of shell material that has been cleaned and has been reduced in size inserted into the pyrolysis reactor, heated to a temperature of 400^0C for 5 hours, will obtain 3 fractions: 1. Fraction of solid in the form of charcoal, 2. Fraction of heavy tar, 3. light fraction as methane gas and smoke. From the light fraction will be channeled into the pipe so that the condensation of liquid smoke obtained while methane gas remains a non noncondensed (can be used as fuel). The quality parameters of liquid smoke is covering the determination of pH, total phenols, and acid levels. The quantity parameters of liquid smoke is through the determination of yield.

3. Results And Discussion

Liquid smoke production of various types of raw materials that have been carried out using pyrolysis reactor. Materials were chopped and sun dried then put the material into the pyrolysis reactor on the stove, and then heated with a heater and the smoke accommodated by passing through the condenser so that it flows in the form of liquid smoke. From the results of liquid smoke coming out then conducted content analysis of liquid smoke test to determine the quality of liquid smoke by using a Gas Chromatography Mass Spectrometri (GC / MS).

This study uses raw materials derived from agricultural waste, such as: coconut shell, rice husks, corn cobs and coconut fibers that are generally not utilized optimally.

Composition and water content of the raw materials will greatly affect the characters of liquid smoke and the resulting compounds. The expected compound are phenol and acetic acid and its yield and pH value. The increase in the water content of the raw materials will reduce the content of phenol, acids and formaldehyde in

the smoke, also it can increase the levels of phenolic compounds and its products flavor more acidic.

To reduce the water content of the material it is made using sun drying until completely dry. Large size of raw materials such as coconut shell, coconut fibers, corn cobs and husks reduced in size so that makes it easier combustion process in the pyrolysis reactor.

3.1 The yield

The yield is one of the most important parameters to determine the outcome of a process. Liquid smoke in this study produced by the condensation of smoke released by pyrolysis reactor. During the pyrolysis process of evaporation of various kinds of chemical compounds. Liquid smoke data produced in the pyrolysis process is presented in Table 1.

The results of measurements of the yield of liquid smoke on various types of agricultural waste materials (Table 1) shows the liquid smoke yields are at the highest 32.35% from coconut fibers compared with the yield of liquid smoke from rice husks (29.53%), coconut shell (30 , 50%), and corn cobs (31.65%).

Table 1. Ingredients Liquid Smoke from some type Agricultural Waste

Agricultural Waste Type	Liquid Smoke Content		
	Liquid Smoke Quality		Liquid Smoke Quantity
	phenol	acidity	The yield of (%)
Fibers	2,97 %	6,8 %	32,35 %
Coconut shells	3,04 %	7,3 %	30,50 %
Rice Husks	1,30%	1,6 %	29,53 %
Corn Cobs	1,38 %	1,3 %	31,65 %

Total yield of liquid smoke produced in the pyrolysis process is very dependent on the type of raw materials used. The yield of liquid smoke coconut fibers as much as 32.35% and smallest liquid smoke of rice husks was 29.53%. This is because the type of raw materials used affects the amount of yield, the type of coconut fibers has a water content of 26.0% and rice husks 31.4%. The yield differences of liquid smoke is caused by a type of wood that had levels of lignin, varied cellulose (Tranggono, 1997 in Fatima, 2009) .

Almost all the water in the liquid smoke evaporates and increase the yield obtained. In Figure 1 will appear a different color based on the type of materials from agricultural waste.

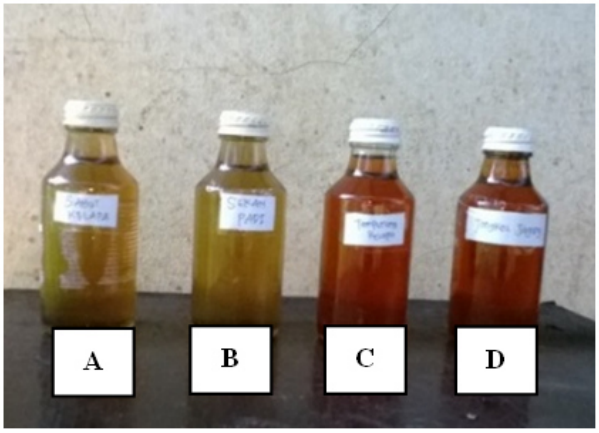

Figure 1. Liquid smoke colors from varied agricultural waste
A.Coconut fibers; B. Rice husks ; C. Coconut shell; D. Corn cobs

Based on Figure 1. differences in color is visible, it depends on the type of raw material i.e. is the type of raw materials including hardwood species (shells and corn cobs) will be darker in color (brownish red) when compared with the type of soft wood (fibers and husks) lighter color (yellow brownish).

In the liquid smoke there are compounds that can affect the color of liquid smoke. Compounds in liquid smoke most domonant in the formation of brown color is carbonyl. Described in Ruiter (1979) components of the carbonyl that can increase its browning occurs is glikoaldehid and metilglioksal which is the active ingredient browner with amino groups. The mechanism of formation of this color is the same reaction with non-enzymatic Maillard browning reactions. Maillard reactions are reactions between carbohydrates, especially reducing sugars with primary amine groups. Among the carbonyl component, there are four components that influence, namely glikoaldehid, metilglioksal, formaldehyde, and asetol. Glikoaldehid and metalglioksal are browner active ingredient with amino groups, but asetol has the lower potential browner.

3.2 Liquid Smoke Quality

The quality of liquid smoke is very dependent on the composition of chemical compounds contained in liquid smoke. The compounds contained in liquid smoke heavily influenced by pyrolysis conditions and type of raw material (Nakai, 2006, in Gani, 2007). Carboxylic acid group of compounds is the most abundant compound in the liquid smoke. This is due to the amount of cellulose and hemicellulose content of each ingredient. Cellulose pyrolysis takes place in two stages: the first stage is an acid hydrolysis reaction followed by dehydration to produce glucose, while the second stage is the formation of acetic acid and its homologs together with water and a small amount of furan and phenol (Girard, 1992).

The composition of smoke produced is influenced by several factors such as basic material, water content and combustion temperature are used instead. Material from the hard wood contains cellulose and hemicellulose were higher than softwood, with a higher content of compounds that are used hardwood better than softwood because it can produce better aroma and richer content of aromatic compounds and acidic compounds.

The analysis results show 13 identified components in the liquid smoke from the pyrolysis raw materials. These compounds are derived from the overall thermal degradation of wood carbohydrates such as carbonyls, acids, furan and pyran derivatives. It also comes from the thermal degradation of lignin, such as phenol, guaiacol and syringol (Budijanto, 2008).

The quality of liquid smoke produced in this study is determined by the phenol and acid levels because that two compounds have the greatest role as an antimicrobial agent. The higher levels of phenol and acid levels of liquid smoke, then the ability to suppress the growth of microorganisms of the liquid smoke is higher. This is consistent with Pszczola (1995) that the two main compounds in liquid smoke is known to have bactericidal effects / bacteriostatic are phenols and organic acids, a combination of both can work effectively to control the growth of microbes, besides phenols also have antioxidant activity is quite large.

Grade 3 is a liquid smoke coming from the distillation at a temperature of 100 ° C to 125 ° C. Grade 3 liquid smoke has quality below grade 1 liquid smoke quality because it has a lower phenol content and acid levels. This is because liquid smoke grade 3 has a water component in large amounts, so that the water can decrease the density and quality of liquid smoke. The acidity of the liquid smoke is also influenced by the levels of phenol in the liquid smoke. The higher levels of phenol, then liquid smoke will become more acidic, it can be demonstrated in Table 1. According Darmadji (1995), phenols and organic acids function as antimicrobial agents in liquid smoke, and its role will increase if there are two compounds with together.

3.3 Phenol levels

Phenol is an active substance which can provide antibacterial and antimicrobial effects on liquid smoke. Phenol levels in liquid smoke produced from coconut shell showed the highest levels of 3.04% compared to the fibers (2.97%), ash (1.30%), and corn cobs (1.38%). The results of lignin pyrolysis will produce phenolic compounds. These compounds play a role as flavor giver and as an antioxidant. High levels of phenol in coconut shell liquid smoke gives a very good indication of liquid smoke is used as a preservative and inhibiting the damage caused by the oxidation of fat.

3.4 Acidity levels (Acetic Acid)

Acid levels is one of the chemical characters that determine the quality of liquid smoke produced. Organic acids have a high role in the liquid smoke is acetic acid. Acetic acid is formed in part from the lignin. This occurs because the process takes place in an optimal pyrolysis raw materials burned up completely until no more droplets of liquid smoke coming out making it possible for the components of the wood to decompose completely into liquid smoke compounds constituent, including organic acids.

Levels of acetic acid liquid smoke produced from coconut shell 7.3% greater when compared with fibers (6.8%), husks (1.6%), and corn cobs (1.3%). Acetic acid is classified as acidic compounds which affect pH and liquid smoke flavor and life shelf of smoked products as well have a role as an anti-bacteria (Girard, 1992). These acidic compounds were generated pyrolysis of cellulose (Vivas, 2006).

3.5 Measurement Results of Liquid Smoke pH Value

PH measurements carried out on the liquid smoke that has been separated from the tar by using a pH meter. The results of the measurement of acidity (pH) of liquid smoke produced from coconut shell is smaller 1.41 than the corn cob (2.47), fibers (2.62), and rice husks (3.36). This shows that the liquid smoke produced is acidic. This acidic derived from acid compounds contained in liquid smoke mainly acetic acid and other acids.

Besides it, phenol levels also affect the pH of the liquid smoke because of the acidic character of phenol has an influence on the aromatic ring. Results from comparing the levels of acetic acid and pH value of the three liquid smoke can be seen in Table 2, when the liquid smoke has a low pH value, the quality of the resulting liquid smoke is high because the overall effect on long-lasting value and life shelf of the smoke product and its

organoleptik character. According Yatagai (2004) in Pujilestari (2010), that a good liquid smoke pH ranged from 1.5 to 3.7 due to the low pH conditions sporulating microbes that can not live and breed so that it can inhibit the growth of spoilage microbes.

In Table 2 it can be seen that the liquid smoke of coconut shell has a pH of smallest compared with liquid smoke of husks, corn cobs and coconut fibers because acetate acid content is high at 7.3%. From these results it can be seen that liquid smoke from coconut shell has antibacterial characters better than liquid smoke of coconut fibers, husks and corn cobs.

This is because of coconut shell to have the hemicellulose component more than coconut fibers, rice husks, and corn cobs so that the amount of acid produced greater. Hemicellulose is decomposed wood components that will result if the compounds of organic acids such as acetic acid. In addition, differences in the pH value of fibers, coconut shells, husks, and corn cobs are also influenced by the phenol levels of some of these agricultural waste material. The higher phenol content of liquid smoke, then the lower the pH value of liquid smoke (more acidic). This can be seen in Table 2, where the coconut shell has a higher phenol content than other types of agricultural waste material so that coconut shell has a lower pH than other types of agricultural waste materials (fibers, corn cobs and husks).

Table 2. Comparison with Phenol pH value and acidity (Acetic Acid)
Liquid Smoke from various type Agricultural Waste

No	Agricultural Waste type	Phenol	Acidity (Acetic Acid)	pH Value
1	Fibers	2,97 %	6,8 %	2,62
2	Coconut shell	3,04 %	7,3 %	1,41
3	Husks	1,30%	1,6 %	3,36
4	Corn cobs	1,38 %	1,3 %	2,47

To get a good smoke should use hardwoods such as mangrove wood, Rasamala wood, powders and sawn teak wood and coconut shell in order to obtain a good smoked products (Astuti, 2000). From the compound content of the three material used as raw material maker of liquid smoke can be seen that the antibacterial characters of coconut shell liquid smoke is better than liquid smoke of coconut fibers, rice husks and corn cobs.

3.6 Preservatives in Wood Structures

Groups of compounds in liquid smoke that supports antimicrobial characters are phenol and acid. Phenolic compounds can extend the lag phase of microbes in the body or in the products, while the growth rate in the exponential phase does not change, except for very high concentrations of phenol. In addition to the antimicrobial role of phenolic compounds also inhibit the oxidation of fat by preventing the formation of free radicals that have an impact on the prevention of the formation of oxidative off flavors (Pszczola, 1995).

The structure of low-quality wood fibers does not have mechanically function so very fragile and unstable. Content component of wood is cellulose, hemicellulose, lignin, fibers, parenchyma, water, ash, and starch. High levels of water causes a low dimensional stability of wood. Parenchyma of the top of the tree containing starch up to 40%, this causes the physical and mechanical characters of low timber (easily broken / cracked) and easily attacked by termites. The liquid smoke has the ability to preserve the wood against fungal decay mainly white like Ganoderma sp and Paliporus alcularis fungus and spraying liquid smoke on rubber processing can remove/neutralize stench and liquid smoke can freeze latex (rubber) perfectly with the high value of plasticity, and even better in comparison with rubber produced by freezer formic acid (ant). Liquid smoke can overcome the stench of rubber that has not been able to overcome, because it contains 67 kinds of compounds that can function to prevent and off bacterial growth (which play a role in the onset of the stench) and compounds that easily evaporate and the specific smells of smoke.

Two dominant compounds as bacteriostatic role are phenol and organic acids are able to control the growth of bacteria. Phenol is obtained from the pyrolysis of lignin, whereas the organic acids from the pyrolysis of cellulose and hemicellulose. The higher lignin levels, the greater the acidity (acid acetate) were obtained. The biggest lignin levels is in coconut shell liquid smoke 29.4% compared with liquid smoke coir (29.23%); rice husks (9.50%); corn cobs (6%). This will be shown in Figure 2. i.e. comparative wood structure that is smeared with liquid smoke and wood that not smeared with liquid smoke.

Figure 2. Comparative wood structure
A. Wood smeared with liquid smoke; B. Wood not smeared with liquid smoke

4. Conclusions And Suggestions

4.1 Conclusions

1. Liquid smoke content for phenol of fibers, coconut shells, husks, and corn cobs are 2.97%; 3.04%; 1.30%; 1.38%.
2. Liquid smoke content for the acidity of fibers, coconut shells, husks, and corn cobs are 6.8%; 7.3%; 1.6%; 1.3%.
3. Liquid smoke pH value of the acidity of coconut shells, corn cobs, husks and fibers are 1.41; 2.47; 2.62; 3.36.
4. Total yield of liquid smoke from acidity of fibers, coconut shells, husks, and corn cobs are 28.01%; 26.35%; 25.38%; 27.58%.
5. Agricultural waste which has the best quality as a natural preservative for wood is coconut shell.

4.2 Suggestions

In further research needs to be done results optimization one of the best agricultural wastes is using purification process for the manufacture of liquid smoke as a natural preservative that will be utilized primarily for the community.

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