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Potential of Liquid Smoke Product of Pyrolysis of Nutmeg Shell as Smoking Raw Material

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Abstract : Nutmeg shell as agricultural waste from peeling the nutmeg fruit are abundantly available in North Sulawesi regions and unfortunately not yet optimized used. Therefore this study was designed to investigate the potential of nutmeg shell as raw material for producing liquid smoke which could be used in especially fish smoking process. The results of laboratory analysis observed that chemical composition of nutmeg shell namely hemicellulose (46.82%) , cellulose (21.34%), lignin (12.93%), crude fiber (53.67%), ash (6.16%), phenol (0.11%), carbonyl (0.38%) and total acid (0.46%) support the utilization of nutmeg shell as raw material to produce nutmeg liquid smoke. The GC-MS analysis of nutmeg liquid smoke identified 20 components where 2-Propanone, 1-hydroxy (53.63%) and phenol and its derivates (14.84%), hence smoke liquid are also potential as smoke resource for food preservative.
Keywords : Liquid Smoke, Pyrolisis, Nutmeg Shell.

Introduction

A number of smoke components play an important role in smoking process as a result of burning wood and other waste products. According to [1]wood contain a lot of chemical substances which are easily burned and some are not burned. Substances which are easily burned are anorganic compounds such as cellulose, lignin, pentose, formic acid, protein resin and turpentine, while the one that are not burned are ash compounds and water.[2] reported that hydrolisation of cellulose during pyrolisis produced glucose and further reaction produced acetic acid, water and a small portion of phenol. Lignin during pyrolisis produced phenol compounds and its derivates, and if pyrolisis process occurred at high temperature, tar could be produced. While hemicelluloses during pyrolisis process will produce furfural, furan together with carboxylate. It is interesting to note that the compounds produced during pyrolisis process such as phenolic, carbonyl and acid simultaneously have activities as antioxidant and antimicrobe and play a role in giving specific taste.

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Basically liquid smoke are suspense of solid and liquid particles in gas medium which are obtained by smoke condensation of burned wood [3]. Indonesia has an abundance of natural wood resources and agriculture waste such as teak wood, leucaena(white leadtree), coconut trunk, coconut shell and coconut fiber, paddy straw and corn cob which are potential as raw material in smoking process [4]. Besides those wood varieties and other agricultural waste which are spreaded in all regions in Indonesia, in North Sulawesi there are abundant nutmeg and candle nut shells which are not yet utilized. Indonesia is also known has a high potential of fisheries resources shown by a wide varieties of fresh fish catched. Therefore if these two potentials are put into synergy certainly it will produce products with functional and economical valuable such as smoked fish products.

Nutmeg shell which grouped as waste because it is produced from peeling off the mature or dried nutmeg has the potential to be used as smoke resource to produce a specific smoked fish product as this waste product could be found abundantly and not yet optimiselyused . Nutmeg shells are also possibly could be used to produce charcoal as well as active charcoal, because its hard texture which assumed containing very high amount of lignin, cellulose and hemicelluloses [5]. According to [6]the difference of wood variety as smoke resource will also produce different complex chemical components which are mixture of a variety of volatile and non – volatile with a wide variation of sensory properties such as phenol, sirigol and guaiacol and its derivates.

A research result showed that pyrolisis temperature of 400^{o}C was the best to produce liquid smoke with highest phenols and total acids content without the presence of benzo(a)pyrene. Smoked liquid grade 3 produced from pyrolisis process still contained tar and benzo(a)pyrene, therefore not safe to be used in smoking and preserving food [7]. Hence the pyrolisis process was continued to improve liquid smoked from grade 3 to grade 2 and 1 which are safe to apply it in food processing. The purification were carried out by redestillation once to produce grade 2 smoked liquid and another distillation will produce grade 1 smoked liquid. Destillation is a process to separate components in a mixture based on different boiling temperature or separation liquid mixture on its components by evaporation process and condensation to obtain destilate with almost pure components [8]. This purification process are aiming to get liquid smoked without danger substances and safe to be used as food preservation.

Smoked liquid are condensate of wooden smoke which soluble in water and bright yellow in colour with a very low PAH content[9]. This product is commonly could be applied in quite variety of food and giving a specific flavor, and from the commercial point of view the flavor, it could be used in food industries to produce a better organoleptic performance [10]. Some benefit in using this type of smoke are such as reducing air pollution, more consistent of smoke composition, can be used many times, more uniform smoke products quality and can be applied with concentration as expected [11.]

In Indonesia smoking process are traditionally carried out using a simple equipment with less attention to sanitation and hygienic aspects which might affected consumer's health and its surrounding environment. The weakness of traditional smoking process are such as appearness of products are less attractive and to solve this problem in developed countries are already using condensation technology to produce liquid smoke[12]. The benefit of liquid smoke are easily to apply, smoke liquid concentration used can be adjusted as consumer's likeness, uniformity in products appearance and environment friendly. The most important issue are not only its role in forming sensory characteristics but also could give food safety assurance [13].

The development of smoke liquid technology is aiming to give an affect on specific aroma, taste and color. If using agriculture waste as raw material such as nutmeg shell it has the potency of containing phenol compound as antioxidant and antibacteria, hence could preserve and give a specific umami taste of the end products [1415]. Informations on composition of smoked liquid originated from nutmeg shell are scarces and therefore this study was conducted to investigate the components of smoked liquid obtained from nutmeg shell from North Sulawesi area.

Materials and Method

Sample Preparation.

The nutmeg shell were determined its hemicelluloses, cellulose, lignin, crude fiber and ash contents before burned to produce liquid smoke as raw material for smoke liquid composition analysis using GC-MS apparatus. Smoked of burned nutmeg shell were run through an iron pipe and collected in condensation flask which turned it into liquid smoked and the first liquid smoked obtained are grade 3 with chocolate colour and very strong smoked aroma. Beside liquid smoke the pyrolisis also producing charcoal as burning result and the collected crude liquid smoke were then redestilated to obtain more pure liquid smoke. This product were brought to laboratory for determination of phenol, carbonyl and total acid contents using Gas Chromatography (GC 210A Shimadzu)[16].

Hemicellulose, Cellulose and Lignin Analysis Procedure.

2 g of nutmeg shell sample were put into 250 ml Erlenmeyer flask and 200 ml aqaudest added before heating for 2 hours, steered and strained using filter paper. After heating put this flask in oven at 105^{o}C until constant weight were reached. The residue were then removed into 250 ml Erlenmeyer flask and add 200 ml H_2SO_4 0.5 M before straining through an already known weight filter paper. Followed by adding 150 ml aquadest before heating in waterbath at 100^{o}C for 2 hours, and after heating add 300 ml before straining using constant weight filter paper, weight crus constantly before ashing in a muffle furnace at 500^{o}C then finally weight [17].

Phenol Content Analysis Procedure.

5 g of finely ground sample were put into 100ml Erlenmeyer flask and aquadest added until reaching 100ml using measurement flask, then the solution was strained until clear solution were obtained. A 1 ml clear solution were put in reaction tube and 0.5 ml follindenis (follin1 : 1) then 1 ml saturated Na_2CO_3 solution were added and kept it settling down for 10 minutes. Followed by adding aquadest until volume reached 10 ml then homogenized using vortex. Read the absorption sample using spectrophotometer at 730 nm wavelength. [17].

Carbonyl Content Analysis Procedure.

5 g of sample were put into 100ml Erlenmeyer flask and aquadest added using 100 ml measuring flask until reaching 100ml volume. 1 ml sample were taken and put into reaction tube and 1 ml 2.4 DinitrophenylHidrazyl 1% in methanol was added and then 3 drops of concentrated HCl were added before heating in waterbath at 50^{o}C for 30 minutes, cooled down before adding 1N KOH until its volume reahing 10 ml. The solution were stirred using vortex before reading the absorbance using spectrophotometer at 480 nm wavelength[17].

Acid Analysis Procedure.

10 g of sample were put in 250 ml Erlenmeyer flask diluted with measuring flask until reaching 250 ml volume, then 25 ml solution were taken in 100 ml Erlenmeyer flask, add 3 – 5 drops Phenolptalein (PP) indicator before titrated with NaOH 0.1N standard solution until the color changed into pink/light red[17].

Statistical Analysis.

The data obtained were statistically analysed using parametric test One-Way (ANOVA) and this test were used for phenol, carbonyl and total acid contents and chemicals compound of nutmeg shell (hemicelluloses, cellulose and lignin). The values were stated as means ± standard deviation (SD) and significant level ($P<0.05$) were determined using Software SPSS versi 20 (Chicago,IL,USA).

Results and Discussion

The means of parameters of liquid smoke samples measured are presented in Table 1 as follow:

Table 1.Chemical composition of nutmeg shell.

Sample	Components	%
Nutmeg shell	Hemicellulose	46.82 ± 1.17
	cellulose	21.34 ± 4.10
	Lignin	12.93± 1.21
	Crude fiber	53.67 ± 1.11
	Ash	6.16 ± 0.66
	Phenol	0.11 ± 0.01
	Carbonyl	0.38 ± 0.01
	Total acid	0.46 ± 0.01

Chemical composition of nutmeg liquid smoke.

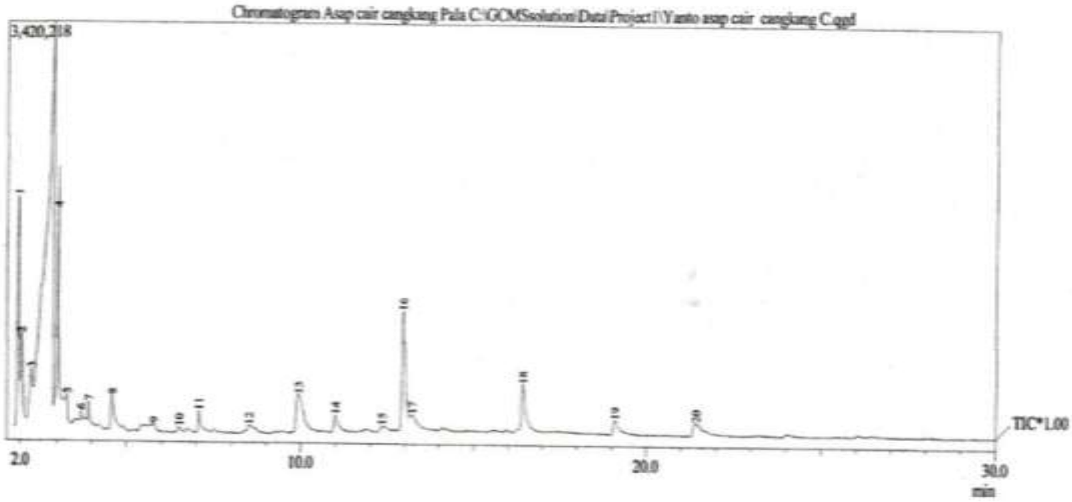
The major components of nutmeg shell in this study were hemicellulose (46.82%) , cellulose (21.34%), lignin (12.93%), crude fiber (53.67%), ash (6.16%), phenol (0.11%), carbonyl (0.38%) and total acid (0.46%). Nutmeg shells are categorized as hard wood because of high content of hemicelluloses and lignin. If this shell burned at high temperature in a room which do not have air flow a series of dissociation process of components build the nutmeg shell producing charcoal, distillate, tar and gas. Destillate is a component known as liquid smoke and the composition of nutmeg shell destillate which undergoes pyrolisis process at 400^{o}C determined using GC-MS are presented in Table 2. And the chromatogram of GC – MS analysis is presented in Figure 1.

Table 2. Composition of distillate of nutmeg shell obtained from pyrolisis process at 400^{o}C detected using GC - MS .

Composition	**Concentration (%)**
Tricyclo 4.3.1.13.8 Undecan-1-amino	7.97
Aceton	3.55
Acetic acid	3.37
2-Propanone, 1-hydroxy	53.63
Propionic acid	1.71
Pyridine	1.44
Sulfurous acid, dibutyl ester	1.93
2-furancarboxaldehyde	2.25
5- Hexen-2-0ne	1.51
2-Cyclopenten-1-0ne,2 methyl	0.26
Butyrolactone	1.41
Formaldehyde, methyl (2-propynyl) hydrazone	0.71
Phenol	4.31
1,2-Cyclopentanedione, 3- methyl	1.34
Phenol, 2- methyl	0.59
Phenol, 2-methoxy	6.83
Phenol, 4- methyl	1.47
Phenol, 2- methoxy-4-methyl	3.72
Phenol, 4-ethyl-2-methoxy	1.08
Phenol,2,6-dimethoxy	1.15

Sample Information

Sample Name	: Asap cair cangkang Pala
Sample ID	:
Data File	: C:\GCMSsolution\Data\Project1\Yanto asap cair cangkang C.qgd
Method File	: C:\GCMSsolution\Data\Project1\Asap cair.qgm



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Name
1	1.927	1.825	1.983	7762621	7.97	1877757	
2	2.027	1.983	2.175	3456126	3.55	759443	
3	2.313	2.175	2.358	3282996	3.37	472529	
4	3.004	2.358	3.183	52229798	53.63	1878881	
5	3.257	3.183	3.383	1665803	1.71	263628	
6	3.659	3.383	3.717	1401074	1.44	129343	
7	3.892	3.717	4.150	1875336	1.93	206718	
8	4.582	4.450	4.883	2188361	2.25	283347	
9	5.781	5.300	6.017	1471764	1.51	68918	
10	6.508	6.383	6.667	251896	0.26	40002	
11	7.073	7.000	7.433	1081618	1.11	170582	
12	8.496	8.367	8.867	686954	0.71	50418	
13	9.914	9.733	10.383	4193441	4.31	304702	
14	10.992	10.883	11.400	1302117	1.34	133597	
15	12.333	12.183	12.833	667721	0.69	43458	
16	12.947	12.833	13.117	6652248	6.83	968648	
17	13.200	13.117	13.550	1427809	1.47	114501	
18	16.400	16.117	16.933	3625674	3.72	388942	
19	19.089	18.967	19.383	1048139	1.08	109299	
20	21.408	21.267	21.650	1115192	1.15	90148	

Figure1 The chromatogram of GC – MS analysis of nutmeg smoked liquid.

Nutmeg shell are one of the waste product of nutmeg oil processing which have a big potential as raw material for producing active charcoal as well as smoke resource. The nutmeg shell are abundantly available and not yet optimize utilized. The possibility of using nutmeg shell as raw material for producing active charcoal is due to its hard texture which contained lignin 12.93%, cellulose 21.34%, hemicellulose 46.82% and crude fiber 53.67% and no tar found as in hard wood.

Chemical compounds in this smoke play an important role in forming the quality of smoked product because it plays an important role in forming the texture and specific color of smoked products. Based on hemicelluloses, cellulose, lignin and crude fiber contents of nutmeg shell hence this product could be used as best and high quality of smoke resource.

The phenol, carbonyl and total acid of liquid smoke produced from nutmeg shell liquid smoke are presented in Table 3 as follow:

Table 3. The Phenol, carbonyl and total acid contents of nutmeg shell liquid smoke.

Sample	Component	%
Nutmeg shell liquid smoke	Phenol	1.91 ± 0.03
	Carbonyl	2.96 ± 0.80
	Total acid	12.49± 1.40

The chemical analysis results of nutmeg shell liquid smoke as shown in Table 3 indicated that the sample contained phenol 1.91%, carbonyl 2.96% and total acid 12.49%. While from the GC – MS analysis 20 compounds were identified (Table 2 and Figure 1)with the highest concentration was 2-Propanone, 1-hydroxy(53.63%) and phenol and its derivates were 14.84%. These compounds have the capability to act as preservative and give contribution in color and taste of smoked fish product. In smoking process the components which play a role of preservative are acids, phenol derivates and carbonyl , these components are also giving aroma, forming color, functioning as antibacterial and antioxidant [18]. The research results of [19]showed that the major component of liquid smoke were 1.2. benzenedicarboxylate and dietilesther. While [20]had noted that the Compounds presence in smoke have the function of bacteriostatic and bacteriocide, compound which function as antimicrobes was phenol compounds and acetic acid.

[21]reported that in general liquid smoke composed of water 81 – 92%, phenol 0.22 – 2.9%, acid 2.8 – 4.5%, carbonyl 2.6 – 4.6%. Furthermore, phenol as one of the components in liquid smoke assumed will act as antioxidant which prevent the oxidation of protein and fat compounds hence could increase the smoked product's shelf life. The major components of phenol compound in smoked liquid were guaiacol and siringol and these components play a role in taste and color forming of smoked products.While carbonyl compounds consist of vanillin and siringaldehide and these coumpounds together with phenol compounds synergistically act as antimicrobe. The total acid contained mainly carboxylate derivates such as furfural, furan and glacial acetic acid.

Conclusion

It can be concluded that nutmeg shell which abundantly available in North Sulawesi region based on its chemical composition (Hemicelulose 46.82 %, cellulose 21.34 %, lignin 12.93 %, crude fiber 53.67 % and ash 6.16 %) have the potential as liquid smoke raw material. While the liquid smoke obtained which contained phenol 1.91%, carbonyl 2.96% and total acid 12.49% also have the potential as smoke resource in smoking process of fish in this region.

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