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QUALITY AND SAFETY OF SMOKED CATFISH (*Aries talassinus*) USING PADDY CHAFF AND COCONUT SHELL LIQUID SMOKE

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ABSTRACT

The purpose of this research was to determine quality of smoked catfish (Arius thalassinus) using paddy chaff and coconut shell liquid smoke. The fish were divided into two groups; then processed using paddy chaff and coconut shell liquid smoke. All of the smoked catfish samples were subjected to chemical, microbiological and organoleptic analyses. The result indicated that moisture content of the paddy chaff smoked cat fish was 48.72%; a little bit lower than coconut shell smoked cat fish that was 51.27%. TPC on paddy chaff treatment was 53.33 CFU/gr; higher than coconut shell treatment that was 46.67 CFU/gr. Organoleptic value of smoked cat fish treated by paddy chaff liquid smoke was 8.26 and coconut shell was 8.22. It was found that benzo(α)pyrene content in the paddy chaff liquid smoke was not detected and in the coconut shell liquid smoke was 11.351 ppm. Examination of t-test Independent sample to the TPC and moisture content showed P>0.05.

Keywords: Smoked Catfish; Paddy chaff and coconut shell liquid smoke: TPC, organoleptic, benzo(α)pyrene.

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INTRODUCTION

Smoking method mostly imparts a desirable flavour and inhibit the growth of microbe. (Swastawati, *et al.,* 2000). The smoking process such as the use of liquid smoke offers some advantages. They are easily to applied, the concentration of liquid smoke can be controlled, results in uniformity of products, less taxing on the environment and many of smoke flavourings are also free of harmfull compounds such as polycyclic aromatic hydrocarbons (Martinez *et al.,* 2007; Swastawati, 2007) .

The most suitable smoke condensate for elaboration of particular fish could be used to evaluate sensory value, as well as microbiological, chemical and safety point of view. In related to consumer preferences, it is indicated that consumers do not like the same kind of products. For example some people require a strong smoke odour and flavour, others want a specific "wood or smoke material (Sunen, 1998; Cardinal *et al.*, 2006). The possible material used in the production of liquid smoke in Indonesia are paddy chaff and coconut shell, due to their characteristics in chemical compound. Finally, Catfsih is one of the most acceptable and popular fish species to be

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smoked in Indonesia (Swastawati, *et al*., 2006). The purpose of this research was to determine the effects of two liquid smoke flavourings on the quality of smoked catfish. The final goal was also to examine whether these flavouring agents might be able to replace traditional smoking methods. Any fish can be smoked, but species with high in fat content such as catfish is recommended because they absorb smoke faster and have better texture than lean fish, which tend to be dry and tough after smoking.

MATERIALS AND METHODS

Production of Liquid smoke flavouring

The paddy chaff and coconut shell were collected around Semarang City. They were air dried for several hours prior to process. The pyrolysis process was started with smoke generator controlled heating. The temperature was measured with a thermostat positioned in the centre of the reactor; the maximum temperature reached was 450ºC. The production was stopped when the smoke materials was totally pyrolysed.

The liquid smoke resulting from the process was filtered trough a paper filter and collected in some bottles.

Smoked cured catfish processing

The experiment on smoked catfish were prepared in the Fish Processing Product Technology Laboratory following the procedure of Indonesian National Standard/SNI (1994). A total of 10 kg of catfish were used in this experiment, and the fish were collected from Hygienic Fish Market in Semarang.

In the processing, the fish were eviscerated, cut, and washed thoroughly, and divided into two groups. One group was subjected to paddy chaff liquid smoke while the other was treated by coconut shell liquid smoke. The fish then dipped into 3% salt and 5% liquid smoke solution for 15 minutes. Then the cured fish were placed into an oven and cooked at 80ºC for 3 hours.

Chemical properties

Chemical properties of the liquid smoke were determined by AOAC (1990) and Indonesian National Standard (1994) methods.

Hydrocarbons components of liquid smoke (BBRKP, 2005)

About 5% of samples in hexane was Rippeted into 12 mL of KOH methanol solutions, then centrifused on 3000 rpm for 5 minutes. Supernatant contained acids were directly analysed using Gas Liquid Cromathography. The peaks resulted were then identified by comparison of each retention times in the standard curve.

Phenol analysis Health (Department of Indonesia, 1995)

Samples were homogenized with aquadest, then placed into iodide tube and added by 0,1 N brom solutions and 5 ml of concentrated HCl, kept it for 30 menit. After that, the samples were added by 5 mL of 20% KI solutions and 3 mL of 5 % Amylum indicator, and then titrated by Na-Tiosulfat 0,1 N solutions until the blue colour was disappeared.

Determination of pH and Moisture Content

20 mL of liquid smoke samples were put into beaker glass. Then the pH meter sensor was put into the beaker glass containing liquid smoke. The pH value was detected when the sensor was already constant.
Moisture analysis (SNI No. 01-2356-1991) Fish samples were dried by using an oven

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for ±24 hours at $100^0 \pm 5^0$C until the weight of samples were constant. The percentage of moisture content was calculated based on dry weight /wet weight and multiplied by 100%.

Organoleptic Test

Organoleptic test of the fish were evaluated using a 9-point hedonic scale for: general appearance, colour, flavour/aroma and texture. For this purposes, seven panelists were used to evaluate the fish as described by Indonesian National Standard (2006).

Benzo(α)pyrene analysis (P2O LIPI, 2005)

5 gr of samples were destructed by sodium sulfat and chloroform until homogen. The samples were then extracted by propylene carbonat and saponificated with NaOH solutions. The extract was then filtrated with calcium cloride, celite and florisil. The filtrate was then vaporized until 1 ml using water bath at 45°C. After all, the filtrate was put into the glass column (clean up) containing 10% of alumina oxid in the lower part and 10 gr of Na_2S0_4 in the upper part until the component was drop. Samples were then fractinated in the column in silica 60 reins column , 70-230 mesh and added by 10% diethyl ether and evaporated. Finally, samples were injected into Gas Chromatography to measure benzo (α) pyrene content

Microbial analysis (SNI No. 01-2354-1991)

Fish samples were diluted into concentration of 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5}. Petri disc containing samples and then incubated with the opposite position at 35° C for 48 hours. The number of colony were then calculated by hand tally counter for the amount of 25-250.

Statistical analysis

The collected data from two replications ware subjected to a *t* –test to determine the differences between LS 1 (paddy chaff liquid smoke) and LS 2 (coconut shell liquid smoke) (independent variable) for each parameter using the SPSS statistical package. Significantly different treatment means were further separated using the LSD method and significance was reported at $p < 0.05$ with means ± SE (Santoso, 2005).

RESULTS AND DISCUSSION

The data obtained on the production of liqid smoke are presented in Table 1. The material of smoke sources in Indonesia were selected based on their availability in the area. Paddy chaff and coconut shell can be found easily almost in all of provinces.

Table 1. Production of liquid smoke.

Parameter	Liquid smoke material	
	Paddy chaff	Coconut shell
Material weight (kg)	2,5	2,5
Volume of liquid smoke (L)	1,375	1,15
Persentage of liquid smoke (%)	55	46
Charcoal & evaporated component (%)	45	54

The temperature in the smoke generator reached was 450ºC. At the temperature of 488ºC the pyrolysis process was fairly complete (Guillén and Manzanos (1999). The completion of pyrolysis is depending on the smoke sources. From the pyrolytic process, paddy chaff obtained higher percentage than coconut shell, due to their biological characteristics. These liquid smokes are dark brown in colour, and their odour have been described as very aromatic

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and pleasant smoky with significant floral notes. Study by Guillén and Manzanos (1999) showed that 100 g of thyme (*Thymus vulgariis*) L powder plants resulted in 173 ml of liquid smoke. Thyme is a popular aromatic plant widely used as a spice in food processing, perfumes and popular medicine. It is an endemic plants in some regions of Spain that can grow to a height of 40 cm. While Tranggono *et al.* (1996) found that coconut shell pyrolysis produces 52,85% liquid smoke, 31,75% charcoal and ash and 15,40% of volatile gasses such as: CO_2, CO, CH_4 and hydrocarbons.

Table. 2 presented 20 major carbonyl derivatives from cellulose and hemicellulose thermal degradation detected in the volatile fraction of liquid smoke. Study by Debrah *et al.* (2007) found that liquid smoke compounds were dominated by: toluene, 2-prophenol, methoxybenzena, 1,2-Dichlorobenzene; 1,1-Bicyclohexyl; 2,4-Bis (1,1-dimethylethyl) phenol, 1,2-Benzenedicarboxylic acid diisooctyl ester, 4-Nonylphenol dan Isoxazole. The chemical compound of liquid are vary based on their specific characteristics, although the major component are usully groups of phenols, acids, aldehydes, ketones, furanes, etc.

Table 2. Percentage of major carbonyl derivatives in paddy chaff and coconut shell liquid smoke.

No	Carbonyl derivatives	Paddy chaff	Coconut shell
1	1,2-Benzenediol	6.45	6.76
2	1,2-Benzenediol,3-methoxi	1.22	4.81
3	2-Cyclopenten-1-one,2-hidroxy-3-methyl	5.14	3.93
4	2-Cyclopenten-1-one,3-ethyl-2-hydroxi	1.48	-
5	2-Furanmethanol	6.98	3.84
6	2-Furanmethanol,tetrahidro	1.83	-
7	Phenol,2-Methoxi-4-methyl-	1.68	3.45
8	Phenol	7.43	-
9	Phenol,2,6-dimethoxi	2.79	8.99
10	Phenol,2-methoxi	6.29	12.69
11	Phenol,3-methyl	-	3.96
12	Phenol,4-ethyl-2-methoxi	2.88	7.17
13	Phenol,2-methyl	1.97	2.71
14	Phenol,4-methyl	3.16	-
15	Phenol,2-Methoxi-3-methyl-	-	-
16	Phenol,4-ethyl	2.02	-
17	2-Propanone,1-(4-hidroxi-3-methoxiphenyl	1.16	-
18	Pyrazole,1,4-dimethil	-	8.05
19	1,2-Benzenedicarboxylic acid, diethyl ester	-	1.15
20	1,2-Benzenediol,3-methyl-	1.4	4.78

Major component found in paddy chaff liquid smoke were dominated by phenol; 2-furanmethanol; 1,2-benzenediol; phenol 2-methoxi; and 2-cyclopenten-1-one,2-hidroxy-3-methyl. Meanwhile, coconut shell liquid smoke were dominated by phenol,2-methoxi; phenol,2,6,-dimethoxi; pyrazole,1,4-dimethil; phenol,4-ethyl-2-methoxi; and 1,2-benzenediol, 3-methyl. Guillén and Manzanos (1999) reported that

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thyme liquid smoke was contained the main components of 2-furancarboxaldehyde; 2-furanmethanol; 3-methyl-1,2-cyclopentanedione; 1-acetoxy-propan-2-one and 3-methyl-2butanone. Other compounds in smaller concentrations contribute with similar flavour notes, such as: cyclopentanone; 2-methyl-2-cyclopenten-1-one; 3-methyl-2cyclopenten-1-one and 3-hydroxy-2-methyl-4*H*-pyan-4-one.

Phenolic compound of liquid smoke

Total phenol derivatives formed from the thermal degradation of lignin are also present and in general contribute with typical smoky notes. These fraction are important for their attributed antioxidant activity. The global phenolic derivatives found in paddy chaff liquid smoke were 25,06%, lower than that of coconut shell liquid smoke (26,28%). Study by Guillén and Manzanos (1999) found that thyme liquid smoke contained 36,0% of global phenolic derivatives.

pH value of liquid smoke

Some variations were obtained in the pH values of the liquid smoke. The pH value of paddy chaff liquid smoke obtained was 3,2; slightly higher than the coconut shell liquid smoke of 2,5. According to Hollenbeck and Marenelli (1963) *in* Tano-Debrah *et al.* (2007), the vapour phase of smoke can be separated into acids and phenols which are strongly acidic in water. Some commercial liquid smoke have the pH value between 3-4 (Giulini chemie, 1993). pH value ≤ 4 can inhibit the growth of bacteria and moulds (Darmadji, 2006).

Organoleptic value of fresh catfish

An analysis of raw material of fish was carried out with the effects of scores of samples given by 7 panellists. The results are presented in Table 3.

Table 3. Organoleptic value of fresh catfish.

Specification	Value±SD
Eye	8.08 ± 0.11
Gill	8.16 ± 0.47
Flesh and belly	8.06 ± 0.33
Texture	7.91 ± 0.35
Odour	7.75 ± 0.35
Slime	9.00 ± 0.00
Average	8.16 ± 0.43

The average of organoleptic value of raw fish were 8.16 with the characteristic of eyes perfectly fresh, convex black pupil, translucent cornea, bright red gills, no bacterial slime, outer slime water white or transparent, bright opalescent sheen, no bleacing. The values were accepted by SNI standard with the minimum organoleptic value of 7,0.

Organoleptic value of smoked catfish

In general, smoked catfish treated by paddy chaff liquid smoke showed slightly higher organoleptic scores than coconut shell liquid smoked treatment (see Table 4).

Tabel 4. Effects of liquid smoke on organoleptic value of catfish

Specification	Organoleptic value±SD	
	PLS	CLS
Appearance	7.93±1.33	7.89±1.23
Odour	8.52±1.12	8.02±0.89
Flavour	7.75±1.51	7.71±1.64
Texure	7.97±1.47	7.75±1.51
Moulds	9 ± 0.00	9 ± 0.00
Slime	9 ± 0.00	9 ± 0.00
Average	8.26±0.55	8.22±0.60

Note:
PLS =Paddy chaff liquid smoke treatment
CLS =Coconut shell liquid smoke treatment

PLS smoked catfish samples showed higher scores in appearance, odour and

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texture, while CLS showed higher score in flavour. The differences were not significant (P>0.05). This indicates that both treatments were acceptable by the panelists in term of their organoleptic point of view. Although the PLS samples gave slightly better result than the CLS samples, both samples were accepted by panelists until 4th days of storage.

Smoking has been reported to affect the colour of food (Espe *et al.,* 2004) *in* Martinez *et al.,*2007). The formation of the smoke colour is believed to originate from an uptake of coloured smoke constituents, oxidation and polymerization of smoke compounds, and reaction of smoke compounds with proteins; therefore, condensation reactions take place between carbonyls and amines, leading to the appearance of the typical smoke colour (Toth and Potthast, 1984).

It should be noted that CLS showed lower odour intensity than the PLS. The CLS showed less brightness. This indicates that there mush be a relationship between liquid smoke composition and the different type of smoke sources used to produce it. Cardinal *et al.* (2004) indicated that colour development depended mainly on carbonyls, while the flavour affordedwas largely due to the type and amounts of phenolic compounds present. These compounds also influence the antioxidant effect of the liquid smoke.

The effect of liquid smoke on the textural attributes of catfish showed that CLS was firmless compared to PLS. Although PLS was more rich in carbonyls than that of CLS. This is mainly caused by the reaction between carbonyls and proteins (Toth and Potthast, 1984).

Taking only organoleptic qualities into account, the samples were rejected by the panellist when they showed signs of softening, low elasticity, firmness, discoloration and low brightness. All samples were rejected at 4 days of storage. These results were a little bit different with Swastawati *et al.* (2008) and Chamidah *et al.* (2006) who reported the shelf life of smoked sardine (*Sardinella fimbriata*) and smoked milkfish (*Chanos chanos*) at room temperature reached until 6 days of storage.

Check sizes Microbiological Analysis of Smoked Catfish

Microbiological analyses showed that the total number of colony of fresh fish was: 2 x 10^4 cfu/g. The microorganisms counted on all samples decreased with the application of smoking process. The aveage of TPC of smoked catfish were: 46,67 cfu/g (PLS) and 53,33 cfu/g (CLS). In the Indonesian National Standard, the upper limited for TPC either for fresh and smoked fish are: 5 x 10^5 cfu/g. Statistically not significant (P>0.05) differences were detected between PLS and CLS samples. Therefore, from the microbiological point of view the use of paddy chaff and coconut shell liquid smoke were possible to use as an alternative of traditional smoking method .

The results proved that liquid smoke affect the microbiological properties of the final product. According to Catte *et al.* (1999) liquid smoke has gaven an effects on the growth of the *Lactobacillus. plantarum*. Study by Gonulalan *et al.* (2003) showed that at the beginning (0 day) liquid and traditionally smoked beef tongues samples had 1.08-1.10, 1.55-1.70, 1.00-1.05, 1.09-1.05 and 2.14-2.20 log cfu/g for total staphylococci/micrococci, APC (Total aerobic bacteria), phsycocrotrophs, halophiles and lactic acid bacteria, respectively. According to Pscizola (1995) two components that responsible for bactericidal effect are phenolic and organic acids. The combination of both had effectively to control the growth of microorganisms.

Moisture analysis of smoked catfish

No major differences were observed in chemical properties in the samples produced by both paddy chaff and coconut shell liquid

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smoke. For example, moisture contents of PLC and CLS smoked catfish were not different (P>0.05). The moisture content of fresh catfish was 78,94% and immediately reduced caused by smoking process.

The moisture content of both PLC and CLS samples were (48,72±1,11) and (51,27±1,56) respectively which were in the range of standard Indonesian smoked fish, (60% maximum). Moisture content in this study had been decreased for about 35.05 – 38.28 % during smoking process. The reduction of moisture content was also influences by the presence of salt prior smoking and its concentration.

Analyses of Benzo(α)pyrene

Several authors have studied the carcinogenic activity of liquid smoke. Although many smoke flavourings are free of harmfull compounds such as polycyclyc aromatic hydrocarbons (PAH_s), but the presence of benzo(α) pyrene (BP) in smoked fish has becoming a great of consideration nowadays. PAH_s constitute a large class of organic substances containing two or more fused aromatic rings made up of carbons and hydrogen atoms (Simon *et al*., 2006).

BP was the first PAH_s to be identified as carcinogen, as consequence, has to be studied more. It was found that benzo(α)pyrene content in the paddy chaff's liquid smoke was not detected and in the coconut shell's liquid smoke was 11.351 ppm. While PLC smoked catfish was containing BP : 0.541 ppm and CLS smoked catfish containing BP: 48.254 ppm. According to Harris and Karmas (1989), the range of BP found in smoked fish is about 1.7 - 53 ppm. Therefore, efforts are needed to decrease the presence of BP in smoked fish. This can be done by the experiment of using various free BP smoke sources plant and also by reducing the temperature of pyrolysis < 400°C (Darmadji 2006).

CONCLUSION

In conclusion, the two liquid smoke flavourings studied led to changes in the characteristic and safety of catfish flesh. These changes were similar in both paddy chaff and coconut shell liquid smoke treatment. Although each liquid smoke has specific chemical compounds but they could be used to smoked catfish.

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