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# Assessment of Efficiency of an Indigenous Liquid Smoke for *masmin* Production

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## Abstract

The aim of this study was to develop a methodology for the production of liquid smoke from coconut husk and to evaluate efficiency of the same in *masmin* production. The developed method can produce 1.5 l of liquid smoke per hour. It had total phenolic content of 1348 ppm and carbonyl content of 38.03 mg $ml^{-1}$. Titratable acidity and pH were found to be 1.88% by weight of acetic acid and 4.34, respectively. Total PAH content in the liquid smoke was found to be 0.79 ppb of which phenanthrene was found in highest level (0.54 ppb). Benzo[a]pyrene was not detected. The developed liquid smoke was found to be compliant with current regulatory limits in terms of PAH. It was observed that soaking of cooked skipjack tuna loins in liquid smoke added with 5% salt, for a duration of 30 min produced *masmin* with similar flavour of traditional *masmin*.

**Keywords:** Coconut husk liquid smoke, composition, liquid smoked *masmin*

## Introduction

Smoking is one of the oldest methods of food preservation and is still widely used in most of the countries. It gives a characteristic flavour and colour to the product and increases shelf-life as a consequence of the combined effects of preliminary salting and antimicrobial activity of some smoke components (formaldehyde, carboxylic acids and phenols). Traditional smoking involved hanging meat on the ceiling of dwelling and permitting smoke resulting from fire to pass around and through the product. Smoked foods are still widely in demand due to their characteristic flavour. In Europe, about 15% of fish for human consumption is offered in the form of cold or hot-smoked products (Stolyhwo & Sikorski, 2005). Production of smoked and salted fish is an important industry in France and represents 17% of the market share for aquatic products (Girard & Paquotte, 2003). Smoke-cured bacon is a traditional Chinese delicacy used as the main meat food in Hubei, Sichuan, Hunan, Guizhou, Yunnan of China. It is made by salting, smoking and dry-curing of pork (Yu & Sun, 2005). *Katsuobushi* is a traditional and popular smoked, dried, fermented product in Taiwan and Japan (Collette & Nauen, 1983).

*Masmin* or *mas* is a traditional smoked and dried product prepared from skipjack tuna (*Katsuwonus pelamis*) produced in Lakshadweep, India. *Masmin* production contributes a major share to the economy of islands through domestic trade and export to countries like Sri Lanka, Singapore and Malaysia. Skipjack tuna loins are cooked in sea water and allowed to cool in the same water for about 6h. After cooling, the loins are smoked for 4 to 5 h using coconut husk followed by sun drying for about 10 days. This smoking and drying cycle is repeated several times. *Masmin* is very hard and resembles a dark piece of wood and can be stored for a period of 1-2 years with proper packaging. Due to the heavy smoking practiced during its production, *masmin* contains high levels of carcinogenic PAHs in it. PAHs are ubiquitous environmental contaminants formed during incomplete combustion of organic materials. Most of them have low solubility in water and generally are very lipophilic (Danyi et al., 2009). PAHs originate from environmental sources (natural and anthropogenic), industrial food processing (e.g., heating, drying and smoking processes), packaging materials and certain cooking practices (e.g., grilling, roasting and frying

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processes) (EFSA, 2008). Human exposure to PAHs occurs in three ways, inhalation, dermal contact and consumption of contaminated foods. Diet is the major source of human exposure to PAHs as it accounts for 88 to 98% of such contamination (Farhadian et al., 2011). The most important factor affecting the formation of PAHs during traditional smoking is the temperature of smoke generation. By lowering the temperature of the smouldering to 300–400°C, the PAH content in the smoke can be minimised (Stolyhwo & Sikorski, 2005). PAH contamination can also be reduced by replacing direct smoking with indirect smoking or by the use of smoke flavourings (Visciano et al., 2008). On a commercial scale liquid smoke is produced by drying the sawdust from 40% moisture to 5-6% moisture and subjecting to pyrolysis using a calciner incinerator or rapid thermal processing techniques. Pyrolysis of wood is done in an oxygen starved atmosphere by heating up to 400 to 650°C and reducing the temperature to 350°C thereby obtaining a liquid product.

The aim of this study was development of a simple method for the production of liquid smoke from coconut husk. The composition (total phenolic content, total carbonyls, titratable acidity, pH and PAH content) of the developed liquid smoke was analysed. A preliminary study on production of *masmin* using liquid smoke was also attempted.

## Materials and Methods

The liquid smoke production unit consisted of an incineration chamber, a Davies double surface vertical condenser, a stop cock, a submersible pump and a steam generator. A schematic diagram of the setup is shown as Fig. 1. Coconut husk is burned inside the metallic incineration chamber and the generated smoke is directed to the condenser through a bent provided at the top of incineration chamber. The condenser was maintained at 3±2°C by continuous circulation of chilled water using a submersible pump. Steam produced from the steam generator was introduced into the incineration chamber through an inlet port situated near the bend. The steam inlet was so adjusted that it directs the entire steam in to the condenser without being trapped inside the incineration chamber. The co-movement of smoke and steam inside the setup allows proper mixing of smoke components. Upon reaching the condenser, this steam-smoke mixture gets condensed and the liquefied smoke is collected through the stop cock. Collected liquid was allowed to cool and double filtered through Whatman No: 1 filter paper and stored in amber coloured bottles. This method is having a capacity of generating 1.5 litres of liquid smoke per hour.

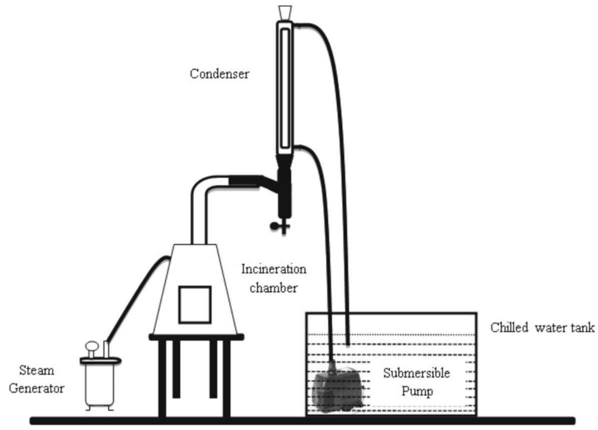


Fig. 1 Liquid smoke production unit

All the chemicals used in this study were of analytical grade and acetonitrile was of HPLC grade, all obtained from Merck (Billerica, MA, USA). Water PAH standard EPA 610 Polynuclear Aromatic Hydrocarbons Mixture was obtained from Supelco (Bellefonte, PA, USA).

Total phenolic content (TPC) of liquid smoke was measured using Folin- Ciocalteu method as described by Amin et al. (2004) with slight modifications and expressed as gallic acid equivalent. Estimation of total carbonyl content was done according to JECFA (2001) with slight modifications. For determining titratable acidity, 1 ml liquid smoke was pipetted into a 250 ml beaker, diluted with 100 ml distilled water and titrated with 0.1 N sodium hydroxide solution to an equivalence point of pH 8.15, as determined using a pH meter (CyberScan PC 510 model, Eutech instruments, Singapore) equipped with a probe (EC-FC72522-01B). The titratable acidity (Y) as percent by weight of acetic acid was calculated using the following equation (1 ml of 0.1 N sodium hydroxide is equivalent to 60.05 mg acetic acid).

$$Y = \frac{\text{Amount of titer (ml) X Normality of NaoH X 60.05}}{\text{Sample volume (ml) x 100}} \text{ x 100}$$

For determination of pH, an aliquot of 20 ml liquid smoke was taken in a beaker and pH at 25°C was recorded using the pH meter.

Extraction of Polycyclic aromatic hydrocarbons (PAHs) from liquid smoke was done according to the method described by APHA (2005). Used extract was subsequently analysed in a HPLC (Hitachi High-Technologies Corporation, Tokyo, Japan).

Fresh Skipjack tuna were purchased from nearby market and transported to the lab in iced condition with a fish to ice ratio of 1:1 (w/w). The fish were beheaded, gutted, washed in potable water and cooked in 5% brine and allowed to cool in the same water. From cooked fish, loins were separated manually and soaked in liquid smoke for different time durations (15, 30, 60, 90 and 120 min) and then dried at 60°C in an electrical oven to moisture content below 10%.

Difference-from-control test as described by Meilgaard et al. (1999) was adopted for the sensory analysis of the samples. Commercially available *masmin* was used as control. Ten member trained panel evaluated the samples using a 7-point hedonic scale. A score of 7 denoted no difference from control and 1 denoted very large difference from control. A score of 3.5 was considered as the margin of acceptance. The samples were scraped into thin flakes using a knife and presented in coded plates. Panellists were asked to score for resemblance of each sample including the blind control with the known control. The mean difference from control, to the test samples and blind control was determined. One way ANOVA at 5% level of significance was performed to compare the treatment means. Tukey's multiple comparison tests was used for post-hoc analysis. All the statistical analysis were performed in IBM SPSS Statistics version 20 and data reported as mean ± standard deviation.

## Results and Discussion

Composition of the developed liquid smoke is given in Table 1. Total phenolic content was found to be in the range of 1348 ± 170 ppm. Phenols and phenolic esters are produced during the pyrolysis of lignin. They include guaiacol (2-methoxyphenol) and syringol (2, 6-dimethoxyphenol), along with their homologous derivatives, a variety of associated compounds with methyl, ethyl, propyl, vinyl, allyl and propenyl side chains are also generated (Maga, 1988). Phenols have been unanimously accepted as the principal compounds responsible for the characteristic flavour of smoked foods (Bratzler et al., 1969; Kjallstrand & Petersson, 2001). Some of them have also been reported to influence the colour of the smoked products (Darmadji, 2002). Fronthea et al. (2007) have reported phenolic content of 335 and 4812 ppm in liquid smoke produced from corn cob and lamtoro wood, respectively.

Table 1. Composition of liquid smoke developed from coconut husk

| Parameters | Results |
|---|---|
| Total phenolic content | 1348±170 ppm |
| Total carbonyl content | 38.03±7.33 mg $ml^{-1}$ |
| Titratable acidity | 1.88±0.07% acetic acid |
| pH | 4.34 ± 0.71 |

The developed liquid smoke had a total carbonyl content of 38.03±7.33 mg $ml^{-1}$. Carbonyl class represents the largest number of compounds identified till date from wood smoke. Most carbonyls originate through the thermal decomposition and rearrangement of cellulose and hemicellulose via classical carbohydrate degradation schemes (Kim et al., 1974). Development of the characteristic colour of smoked foods is a result of Maillard reaction, in which the carbonyl groups present in the smoke react with the amino groups present on the food surface to produce a brown colouration (Maga, 1988). 1-hydroxy-2-butanone, has been unanimously agreed to be the most abundant carbonyl compound in liquid smoke by several authors (Fiddler et al., 1970; Wei et al., 2010; Montazeri et al., 2013).

Titratable acidity in the developed liquid smoke was 1.88 ± 0.07%. Motazeri et al. (2013) have reported a total acidity of 0.7-2.3% in commercial refined liquid smokes. Acidity of liquid smokes obtained from coconut shell was reported to be 1.86% (Lombok et al., 2014). Acidity of liquid smoke is primarily depended on the wood source, processing steps and refining parameters (Guillen & Ibargoitia, 1999; Rozum, 2007; Sung et al., 2007; Toledo, 2007).

The pH of liquid smoke is related to the level of decomposition of chemical component of the source material resulting in organic acids. pH of liquid smoke developed in this study was 4.34 ± 0.71 (Table 1). Liquid smoke with lower pH values gives better preservation to the food (Wijaya et al., 2008). Generally pH values of liquid smoke range from 1.5 - 5.5 (Toth & Potthast, 1984). However liquid smoke prepared from black tea leaves was having an alkaline pH of 7.7 (Sung et al., 2007).

Content of polycyclic aromatic hydrocarbons in the liquid smoke is given in Table 2. Total polycyclic aromatic hydrocarbon content was 0.79±0.05 ppb. PHE was the individual PAH found in highest level followed by FLR. BaP content was found to be below detection limit. Fronthea et al. (2007) while investigating the PAH content in liquid smoke produced from lamtoro wood and corn cob, also found a BaP content below detection limit. European Union regulation No. 2065/2003 describes a formal production process for smoke flavourings and also recommends that the level of BaP and BaA in a primary smoke condensate should not exceed 10 and 20 ppb, respectively (EC, 2003). None of these compounds were detected in the developed liquid smoke. Further, European Union (2011) has set a maximum level of 5 ppb for benzo[a]pyrene and 30 ppb for "PAH4" (sum content of Benzo [a] pyrene, benzo [a] anthracene, benzo [b] fluoranthene and chrysene) in smoked fish and fishery products. Liquid smoke developed in this method can be used for developing fish products in compliance with these regulations.

Table 2. Polycyclic aromatic hydrocarbon content in liquid smoke from coconut husk

| PAH's | Quantity (ppb) |
|---|---|
| Naphthalene | ND |
| Acenaphthylene | ND |
| Fluorene (FLR) | 0.141 ± 0.021 |
| Phenanthrene (PHE) | 0.54 ± 0.11 |
| Anthracene | 0.0671 ± 0.0071 |
| Fluoranthene | 0.0442 ± 0.0142 |
| Pyrene | ND |
| Benzo(a)anthracene (BaA) | ND |
| Chrysene | ND |
| Benzo(b)fluoranthene | ND |
| Benzo(k)fluoranthene | ND |
| Benzo(a)pyrene (BaP) | ND |

*ND- Not detected

Result of the sensory evaluation (Table 3) indicated that soaking of cooked skipjack tuna loins in liquid smoke, for a duration of 30 min can produce masmin with similar flavour profile of traditional masmin ($p>0.05$) as the mean difference is less in this case. A bitter flavour was associated with *masmin* produced at higher soaking durations. Slight burning sensation, especially in the exterior layer was observed in samples soaked for over 90 min. Liquid smoked *masmin* produced by soaking for 15 min showed less smoke aroma.

Table 3. Result of the sensory evaluation

| Treatments | Mean difference from control |
|---|---|
| 15 min | $2.03 \pm 0.57^b$ |
| 30 min | $0.80 \pm 0.20^a$ |
| 60 min | $1.87 \pm 0.15^b$ |
| 90 min | $2.97 \pm 0.15^c$ |
| 120 min | $4.00 \pm 0.20^d$ |
| Blind control | $0.20 \pm 0.26^a$ |

It is evident from the present study that liquid smoking can be used as an efficient alternative to traditional smoking for the production of traditional *masmin*. The developed liquid smoke was found to be safe in terms of its PAH content and masmin prepared using liquid smoke had similar sensory characteristics similar to traditionally produced masmin which can be adopted commercially.

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