

Assessment of the Effect of Liquid Smokes on the Chemical Composition and Quality Attributes of Fish Balls During Chilled Storage
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Abstract:

This investigation was carried out to study the effect of liquid smokes produced from some agriculture wastes as beech sawdust, rice husk, sugarcane bagasse and corncob on the changes of chemical composition (moisture, crude protein, crud fat and ash content) and quality attributes namely: thiobarbituric acid (TBA) value, total volatile basis nitrogen (TVB-N), trimethyl amine nitrogen (TMAN) of fish ball during chilled storage. The results revealed that the control sample was spoiled at tenth day, whereas the fish ball samples treated with different liquid smoke remained without spoil until 15 day. The results showed that no changes in moisture, protein, fat and ash content of all samples treated with different liquid smokes compared to control sample. TBA, TVB-N, and TMAN in all treated samples with different liquid smokes didn't reach to deterioration levels. All treated samples had lower TBA value, TVB-N, and TMAN contents than that of control sample during storage period. Furthermore, the lowest TBA value, TVB-N, and TMAN contents were noticed in samples treated with rice husk after and during storage periods for 15 days, followed by samples treated with beech sawdust, sugarcane bagasse and corncob liquid smoke. Generally, all treatments of fish balls were acceptable by the end of storage period.

Keywords: *fish ball, quality attributes, chemical composition, liquid smoke.*

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Introduction:

Food smoking has a long history in preservation. The use of traditional smoking methods, or recently liquid smoking, had proven that this means of preservation still being vastly practiced in community as well as in food industry. Liquid smoking in preserving protein based foods, namely meat, fish, and cheese, had been increasingly utilized, owing to pleasant flavor and inhibitory effects on pathogens (Soldera *et al.*, 2008). Preservative effect in food smoking is achieved due to the presence of antimicrobial and antioxidant compounds, such as aldehyde, carboxylic acids and phenols (Leroi and Joffraud, 2000 and Rorvik, 2000).

Liquid smoke is usually obtained from the condensation of wood smoke produced by smoldering wood chips or sawdust under limited oxygen. Commercial liquid smoke is commonly fractionated, purified and concentrated to yield aqueous, oil or dry powder products. Through there fining process, undesirable polycyclic aromatic hydrocarbons (PAH) are removed, and the intensity of flavor and color in the refined liquid smoke is easily adjusted (Varlet *et al.*, 2010).

Liquid smoke contains the same functional components such as phenols, carbonyls and acids that are found in vaporous smoke. Liquid smoke is free of harmful compounds such as polycyclic aromatic hydrocarbons (PAHs) which are ubiquitous environmental contaminants; these are commonly found in convectional smoke, also considered carcinogenic and mutagenic molecules (Alcicek, 2013). Additional advantages of liquid smoke are environmental friend-

liness, lower cost and easy application such as direct addition, drenching or dipping, impregnated (smoked) casings and atomization (Varlet *et al.*, 2007). The smoking process is often coupled with other treatments, such as salting, addition of spices, packaging techniques and chilled storage, to produce synergistic effects on spoilage microorganisms and to increase shelf life (Visciano *et al.*, 2008).

Beech wood liquid smoke had been reported to contain acetic acid, 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, levoglucosan, formic acid, methanol, syringol, methoxy eugenol, 3-methyl-1,2-cyclopentanedione, allyl dimethoxyphenol (isomer II), 2-(5-hydroxy) furanone, methyl syringol, pentanal, propanoic acid, pyrocatechol, 1-acetyloxy-2-propanone, 1,2 cyclopentanedione, 3-hydroxy-3-methylbutanoic acid (European Food Safety Authority, 2010). maltol is one of the main furans detected in beech wood liquid smoke (Guillen and Ibargoitia, 1999).

The main volatile compounds found in rice husk liquid smoke were Phenolic compounds 4-methoxyphenol, 2-ethylphenol, 2-methoxy-4-methylphenol (4-methylguaiacol), 4-ethyl-2-methoxyphenol (4-ethylguaiacol), 2-methoxy-4-vinylphenol, and 2-methoxy-4-(1-propenylphenol) (trans-isoeugenol) and furan compounds (5-methyl-2-furancarboxaldehyde (5-methylfurfural) and 2,3 dihydrobenzofuran (Sung *et al.*, 2007) .

The major components found in bagasse were phenol, guaiacol, syringol, thymol, cavacrol, eugenol, vanil-

lin, maltol and carbonyl compounds (Siwawej and Attaviroj, 2003).

Major component of carbonyls found in corncob liquid smoke were phenol; 2 methoxy phenol; anhydride formic acid and 2,6, dimethoxy phenol (Swastawati *et al.*, 2014)

Production of fish balls follow simple preparation of fine flesh fish with starch, addition of salt and specific herbs to meet local tastes and finally formation of balls shape. Most fish ball is stored at low temperature. In addition, vacuum packaging is used in order to extend shelf life of fish balls (Holley and Patel, 2005).

The aim of this study was to examine the effect of beech sawdust, rice hush, sugarcane bagasse and corn cob liquid smokes as flavor agent on the chemical composition and quality attributes of fish balls preservation during chilled storage at $4 \pm 1^\circ\text{C}$ for 15 days.

Materials and Methods:

Materials:

Fish samples:

Forty kilograms (40 kg) of fresh keshr bayad (*lates niloticus*) were purchased from the main fish market in Assuit city, Egypt during February 2014. The edible portions were obtained by removing heads, gills, fins, scales and guts. Muscle samples were minced and homogenized

Selection of agriculture wastes:

Selected agriculture wastes were used in liquid smokes preparation namely: beech sawdust was obtained from a local furniture manufacturing, rice husk and corn cob were obtained from Elmasria Company for feed industry, Bani ghaleb, Assuit and sugarcane bagasse was obtained from

Egyptian company for sugar and integrated industries, Abokerkase factory, Elminya.

Methods:

Preparation of liquid smoke:

All types of various agriculture wastes were moisted to contain about 20% moisture content. Smoke was obtained by small laboratory smoke generator, the destructive distillation was condensed through a small condenser. The concomitant substance were removed from the obtained smoke condensates by settling about 7 days at 4°C , followed by centrifugation at 2500 rpm for 10 min., filtration by Watman No.1 papers, and titration by carbonate solution to pH 4 - 5.5. Finally it diluted with distilled water in a ratio 1:4 (condensate: distilled water) to obtain liquid smoke (Moghazy, 1994). Some modification in this method was carried out by passing the filtered liquid smoke through active charcoal filtration to obtain liquid smoke completely free from harmful substances such as benzo (a) pyrene.

Application of beech sawdust, rice husk, sugarcane bagasse and corn-cob liquid smoke on fish ball:

Fish ball was manufactured according to a formula: 1 kg of minced fish, 120 g of wheat flour and 10 g of spices. All ingredients were mixed, battered and shaped into balls (2.5-2.8 cm of diameter) followed by cooking in boiling water ($90-95^\circ\text{C}$) for about 15 minutes. During the cooking step, 8% (on the based cooked water volume before boiling) of each liquid smoke were added. Fish ball samples were packed in sterile (Polyethylene polyamide) PE/PA and stored at $4\pm 1^\circ\text{C}$. Un-

treated (0% of liquid smoke) fish ball was used as negative control (Zuraida *et al.*, 2011).

Moisture content:

Moisture content was determined by drying 5 gm of fish sample in an oven at 105°C until a constant weight according to A.O.A.C. method (2005).

The crude protein content:

Total nitrogen content was measured by the macro kjeldahl method as outlined in the A.O.A.C. (2005). The protein content was calculated by multiplying the nitrogen content by the factor 6.25 and the results expressed as % protein.

The crude fat:

Total crude fat content of dried processed fish was determined as a weight loss after 16 hrs of extraction with petroleum ether (40-60°C) using Soxhlet apparatus as described by A.O.A.C. method (2005).

The ash content:

The ash content was determined using a muffle- oven at 550°C for 24 hrs as described in A.O.A.C. method (2005).

Thiobarbituric acid value (T.B.A):

Thiobarbituric acid value was determined according to the method described by Kirk and Sawyer (1991) as follows: Ten grams of the sample were distilled with (47.5 ml of distilled water and 2.5 ml of 4 N HCl) for 10 minutes, 5 ml of the distillate were added to 5 ml of TBA solution (0.2883 gm TBA reagent / 100 ml of 90% glacial acetic acid) into stoppered tube, and then heated in a boiling water-bath for 35 minutes. After cooling, absorbance was measured at 538 nm by sequoia- Turner Moder 340 spectrophotometer. As blank, 5

ml of distilled water was used instead of distillate and the test was carried out as before mentioned. The absorbance of blank sample was checked at zero value and then the absorbance of true sample of distillate was measured. The T.B.A value was calculated by multiplying the absorbance value by the factor 7.8. The results expressed as mg of malonaldehyde / Kg sample.

Total volatile nitrogenous compounds:

Distillation of total volatile base nitrogen (TVBN) and trimethylamine nitrogen (TMAN):

Total volatile nitrogenous compounds were isolated from fish sample by steam distillation as the method described by Malle and Tao (1987). One hundred grams of processed fish were homogenized in 200 ml of 7.5% aqueous trichloro acetic acid solution. The homogenate was centrifuged at 4000 xg for 5 min and the supernatant liquid was filtered through a Buchner funnel using a Whatman filter paper No.3. The obtained filtrate was then used for determining the TVB-N and TMAN.

Total volatile bases nitrogen (TVBN):

Determination:

Twenty-five milliliters of the filtrate described above were loaded into the distillation tube apparatus followed by addition of 5 ml of 10% NaOH and 100 ml distilled water. A beaker containing 10 ml of 4% aqueous boric acid solution and 0.04 ml of methyl red and bromocresol green indicator (for titration of ammonia) was placed at the end of the condenser. Distillation was continued until a final volume of 50 ml was ob-

tained. The boric acid solution turned green when alkalized by the distilled TVBN. This solution was titrated using a 0.01 ml graduated microburette containing an aqueous 0.1N sulfuric acid solution. Complete neutralization was obtained when the color turned pink. The quantity of TVBN was determined from the consumable volume (V) as ml of sulfuric acid according the equation described by Malle and Tao (1987) and calculated as mg nitrogen/ 100g sample.

$$\text{TVBN} = V \times 16.8$$

**Trimethylamine nitrogen (TMAN):
 Determination:**

To measure TMAN alone, formaldehyde may be used to block the primary and secondary amines. Twenty milliliters of formaldehyde (16%) were added to 24 ml of filtrate, steam distillation and titration of distillate with 0.1 N sulfuric acid was then performed as TVBN determination. The TMAN content was determined from the consumable volume (V) as ml of sulfuric used for titration according the equation described by Malle and Tao (1987) and calculated as mg nitrogen/ 100g sample.

$$\text{TMAN} = V \times 16.8$$

Statistical analysis:

The data obtained from three replicates were analyzed by ANOVA using the SPSS 20.0 software statistical package program, and differences among the means were compared using the Duncan's Multiple Range test (SPSS, 2011). A significance level of 0.05 was chosen and continuous variables described by mean and standard deviation (Mean, SD).

Results and Discussion:

Changes in moisture content:

According to results given in Table (1) it could be noticed that liquid smoke treatments reduced initial moisture content of fish balls with no significant difference $P > 0.05$ from 74.74% for control sample to 74.38%, 74.44%, 74.32 and 74.48% at fish balls samples treated with beech sawdust, sugarcane bagasse, rice husk and corncob liquid smoke; respectively. This corresponds to the fact that liquid smoke can induce dehydration on food products (Leroi and Joffraud, 2000 and Rorvik, 2000). In coherence, Gomez-Guillen *et al.* (2000) showed that smoking led to connective tissue insolubility and moisture loss, resulting texture hardening.

Table (1): Changes in moisture content of fish balls treated with different liquid smokes during chilled storage at $4^{\circ}\text{C} \pm 1$ for 15 days.

Time of storage (days)	Control	Liquid smoke treatments			
		Beech sawdust	Sugarcane bagasse	Rice husk	Corn cob
0	74.74±0.08 ^{Aa}	74.38±0.22 ^{Ab}	74.44±0.06 ^{Ac}	74.32±0.05 ^{Ad}	74.48±0.07 ^A
5	74.61±0.07 ^a	74.26±0.06 ^{ABb}	74.32±0.06 ^{ABc}	74.21±0.04 ^{ABd}	74.38±0.06 ^{AB}
10	Spoiled	74.12±0.04 ^{ABCb}	74.16±0.04 ^{ABCc}	74.09±0.09 ^{ABCd}	74.16±0.03 ^{ABC}
15	Spoiled	74.04±0.04 ^{ABCb}	74.06±0.04 ^{ABCc}	73.92±0.04 ^{ABCd}	74.05±0.05 ^{ABC}

^{A-C} The same upper letters indicated significant difference between means and time of storage ($P < 0.05$). ^a
 The same lower letters indicated significant difference between control and treatments ($P < 0.05$). ^{b-d}
 The same lower letters indicated significant difference between treatments ($P < 0.05$). Data are expressed as means ± standard deviation (n = 3).

The results indicated that the control sample was spoiled at 10th than that of all fish ball samples treated with different liquid smoke continued to preservation until 15 day. This probably was due to the absence of liquid smoke which have antioxidant and antimicrobial compounds due to its preservation agents. Prolong storage, for 15 days reduce of moisture content with a significant difference $P < 0.05$ of all fish ball samples except control sample. The decrease of moisture content was presumably indicated protein deterioration (Siskos *et al.*, 2007).

Changes in protein content:

Data given in Table (2) outlined the protein content in different fish ball samples during storage at $4^{\circ}\text{C} \pm 1$ for 15 days. The data indicated that liquid smoke treatments reduced initial protein content with significant differences $P < 0.05$ of fish balls from 70.26% for control sample to

68.82%, 68.98%, 68.65% and 69.08% for fish ball samples treated with beech sawdust, sugarcane bagasse, rice husk and corncob liquid smoke; respectively.

From the results presented in Table (2) it could be observed that the control sample was spoiled at 10th than that of all fish ball samples treated with different liquid smokes which continued preservation until 15 day. This might be explained the liquid smoke antimicrobial agent. Since, the changes in food quality caused by microbiological activity made it useless for human consumption. It is important to work out such technological procedures that eliminate or limit the rate of microorganisms propagation in food products and extend their storage life (Kowalski and Prycz, 2003). Because refrigeration temperatures alone would inhibit the growth of proteolytic strains.

Table (2): Changes in protein content of fish balls treated with different liquid smokes during chilled storage at $4^{\circ}\text{C} \pm 1$ for 15 days. (% on dry weight basis)

Time of storage (days)	Control	Liquid smoke treatments			
		Beech sawdust	Sugarcane bagasse	Rice husk	Corncob
0	70.26 \pm 0.21 ^{Aa}	68.82 \pm 0.2 ^{Aab}	68.98 \pm 0.17 ^{Aac}	68.65 \pm 0.12 ^{Aad}	69.08 \pm 0.18 ^{Aa}
5	69.44 \pm 0.2 ^{Aa}	67.98 \pm 0.16 ^{ABab}	68.14 \pm 0.16 ^{ABac}	67.86 \pm 0.09 ^{ABad}	68.31 \pm 0.15 ^{ABa}
10	Spoiled	67.15 \pm 0.11 ^{ABCb}	67.27 \pm 0.09 ^{ABCc}	67.08 \pm 0.22 ^{ABCD}	67.35 \pm 0.07 ^{ABCb}
15	Spoiled	66.27 \pm 0.09 ^{ABCb}	66.37 \pm 0.09 ^{ABCc}	66.14 \pm 0.1 ^{ABCD}	66.48 \pm 0.13 ^{ABCD}

^{A-C} The same upper letters indicated significant difference between means and time of storage ($P < 0.05$). ^a The same lower letters indicated significant difference between control and treatments ($P < 0.05$). ^{b-d} The same lower letters indicated significant difference between treatments ($P < 0.05$). Data are expressed as means \pm standard deviation (n = 3).

Data revealed that crude protein ratios did not change in all samples treated with different liquid smokes with non significant differences $P > 0.05$ after and through storage period. However, the apparent decrease

in protein content with significant difference $P < 0.05$ during storage period at $4^{\circ}\text{C} \pm 1$ might be attributed to the continuous hydrolysis of protein as affected by enzymatic proteolysis

which led to formation of simple nitrogenous compound (Arafa, 2005).

Changes in fat content:

Total fat content of untreated sample (control) and fish ball samples treated with different liquid smoke during storage at 4°C±1 for 15 days was assessed and the obtained results are presented in Table (3). Data showed that fat content was increased initial fat content with significant difference P<0.05 of fish ball from 6.19% for control sample to 7.24%, 7.26%, 7.22% and 7.25% at fish ball

samples which treated with beech sawdust, sugarcane bagasse, rice husk and corncob liquid smoke, respectively. This might be due to that liquid smoke when condensed separated into three phase: an aqueous phase, an oily phase and water insoluble high density tar phase (Brimer, 2011). Likewise, it was observed that crude fat did not change in all samples treated with different liquid smoke with non significant differences P>0.05 after and through storage period.

Table (3): Changes in fat content of fish balls treated with different liquid smokes during chilled storage at 4°C±1 for 15 days. (% on dry weight basis)

Time of storage (days)	Control	Liquid smoke treatments			
		Beech sawdust	Sugarcane bagasse	Rice husk	Corn cob
0	6.19±0.08 ^{Aa}	7.24±0.03 ^{Aab}	7.26±0.04 ^{Aac}	7.22±0.03 ^{Aad}	7.25±0.02 ^{Aa}
5	5.68±0.04 ^{Aa}	6.85±0.03 ^{ABab}	6.86±0.07 ^{ABac}	6.83±0.03 ^{ABad}	6.89±0.02 ^{ABa}
10	Spoiled	6.46±0.05 ^{ABCb}	6.51±0.02 ^{ABCc}	6.46±0.03 ^{ABCd}	6.53±0.09 ^{ABC}
15	Spoiled	6.07±0.04 ^{ABCb}	6.14±0.07 ^{ABCc}	6.05±0.02 ^{ABCd}	6.09±0.05 ^{ABC}

^{A-C} The same upper letters indicated significant difference between means and time of storage (P<0.05). ^a The same lower letters indicated significant difference between control and treatments (P<0.05). ^{b-d} The same lower letters indicated significant difference between treatments (P<0.05). Data are expressed as means ± standard deviation (n = 3).

The increment of fat content was explained due to reducing the fish balls total solids Davidson *et al.* (2005). Results indicated that the control sample was spoiled at 10th than that of all fish ball samples treated with different liquid smokes continued preservation until 15 day. This probably was due to the absence of liquid smokes which had antioxidant and antimicrobial compounds due to its preservation agents.

From Table (3) it could be observed that a slight decrease in fat content in all samples with significant differences P<0.05 during storage period. This slight decrease might be

due to oxidation and hydrolysis of lipids to volatile compounds of aldehydes and ketones (El-Akel, 1988).

Changes in ash content:

Results presented in Table (4) showed the ash content in different fish ball treatments during storage at 4°C±1 for 15 days. Data showed that ash content was increased with significant difference P<0.05 of fish ball from 11.51% for control sample to 11.76%, 11.78%, 11.72% and 11.80% at fish ball samples which treated with beech sawdust, sugarcane bagasse, rice husk and corncob liquid smoke, respectively. The ash content determination of all fish ball

samples showed that there were no differences at samples treated with different liquid smokes with non sig-

nificant difference $P > 0.05$ after and through storage period.

Table (4): Changes in ash content of fish balls treated with different liquid smokes during chilled storage at $4^{\circ}\text{C} \pm 1$ for 15 days. (% on dry weight basis)

Time of storage (days)	Control	Liquid smoke treatments			
		Beech sawdust	Sugarcane bagasse	Rice husk	Corn cob
0	11.51±0.03 ^{Aa}	11.76±0.03 ^{Ab}	11.78±0.06 ^{Ac}	11.72±0.06 ^{Ad}	11.80±0.06 ^A
5	11.73±0.05 ^{Aa}	11.95±0.04 ^{ABb}	11.98±0.05 ^{ABc}	11.93±0.01 ^{ABd}	12.00±0.01 ^{AB}
10	Spoiled	12.04±0.04 ^{ABCb}	12.07±0.06 ^{ABCc}	12.01±0.04 ^{ABCd}	12.10±0.02 ^{ABC}
15	Spoiled	12.17±0.09 ^{ABCb}	12.25±0.09 ^{ABCc}	12.28±0.16 ^{ABCd}	12.22±0.12 ^{ABC}

^{A-C} The same upper letters indicated significant difference between means and time of storage ($P < 0.05$). ^a The same lower letters indicated significant difference between control and treatments ($P < 0.05$). ^{b-d} The same lower letters indicated significant difference between treatments ($P < 0.05$). Data are expressed as means ± standard deviation (n = 3).

According to Andrew (2001), the ash content of smoked fish indicated that this product was a good source of minerals, such as calcium, calcium, zinc, iron and magnesium. By extending of storage period, the ash content increased with significant difference $P < 0.05$ for all treatment moisture loss during storage.

Changes in thiobarbituric acid (TBA) content:

Fish meat is particularly susceptible to oxidative changes because of

the processing conditions, exposure of unsaturated fats and proteins to molecular oxygen. 2-Thiobarbituric acid (TBA) is widely used as an indicator of degree of lipid oxidation, and the presence of TBA reactive substances is due to the second stage of auto-oxidation (Rezaei and Hosseini, 2008) during which peroxides are oxidized to aldehydes and ketones (Lindsay, 1991).

Table (5): Changes in TBA value (mg malonaldehyde/ kg sample)* of fish balls treated with different liquid smoke during chilled storage at $4^{\circ}\text{C} \pm 1$ for 15 days.

Time of storage (days)	Control	Liquid smoke treatments			
		Beech sawdust	Sugarcane bagasse	Rice husk	Corn cob
0	0.38±0.03 ^{Aa}	0.28±0.01 ^{Aba}	0.27±0 ^{Aac}	0.27±0.01 ^{Aad}	0.26±0.01 ^{Aa}
5	3.12±0.03 ^{Aa}	0.67±0.01 ^{ABab}	0.70±0.01 ^{ABac}	0.61±0.01 ^{ABabcd}	0.77±0.01 ^{ABabcd}
10	Spoiled	0.91±0.01 ^{ABCb}	1.02±0.01 ^{ABCbc}	0.83±0.01 ^{ABCbcd}	1.13±0.01 ^{ABCbcd}
15	Spoiled	1.22±0.03 ^{ABCb}	1.29±0.01 ^{ABCbc}	1.12±0.02 ^{ABCbcd}	1.37±0.03 ^{ABCbcd}

^{A-C} The same upper letters indicated significant difference between means and time of storage ($P < 0.05$). ^a The same lower letters indicated significant difference between control and treatments ($P < 0.05$). ^{b-d} The same lower letters indicated significant difference between treatments ($P < 0.05$). Data are expressed as means ± standard deviation (n = 3).

* Egyptian Organization for Standardization (2005) reported that TBA should be less than rejection limit (4.5 mg malonaldehyde/ 1kg fish flesh).

The changes of thiobarbituric acid values of prepared fish ball samples were followed up during chilled storage for 15 day at $4^{\circ}\text{C}\pm 1$ and results were tabulated in Table (5). At the beginning of chilled storage there were no significant differences between fish ball samples prepared with adding different liquid smokes compared with control sample which had high TBA value 0.38 mg malonaldehyde/kg sample.

Table (5) indicated that there were increments of thiobarbituric acid value production with significant differences $P < 0.5$ throughout chilled storage periods at $4^{\circ}\text{C}\pm 1$ of all treatments. The lowest of (TBA) values during storage periods (15 days) with significant differences $P < 0.5$ were noticed in samples treated with rice husk, followed by samples with treated beech sawdust, sugarcane bagasse and then corncob liquid smoke. Meanwhile, the increment of (TBA) was higher in control sample which reached to 3.12 mg malonaldehyde/kg sample at 5th day and then spoiled. Davidson *et al.* (2005) investigated that liquid smoked products are more resistant to the rancid process. Antioxidizing properties of the smoke are attributed more to the components dispersed than to the dispersing phase. Phenols, less carboxylic acids, are characterized as strong antioxidants. Among the phenol group, the strongest antioxidants are 3 methylpyrocatechol and pyrogallol, then, in decreasing rate: Hydroquinone and its homologous, guaiacol resins and their homologous, monohydroxyl phenols. Antioxidizing properties displayed also formic acid, benzoate acid, salicylic acid, vanilla.

The anti-oxidizing properties of smoke retarded autooxidation of fats.

On the other hand, increasing of TBA value during chilled storage in all samples treated with different liquid smokes were observed with a significant differences $P < 0.05$ but all the investigated samples agree with Egyptian Organization Standard (2005) which reported that the thiobarbituric acid value should be less than rejection limit (4.5 mg malonaldehyde/ 1kg fish flesh).

Changes in total volatile basis (TVBN) content:

The TVBN of fish is an indicator of the freshness of the raw material (Zhou *et al.*, 2011). Changes in TVBN of different samples during the entire storage period are shown in Table (6). TVBN values of control samples showed differences from other samples on storage with highly significant differences $P < 0.5$ as storage increased also TVB-N content was higher and spoiled at 10th day than that of other samples which increased more slowly than control samples after and through storage period.

Table (6) showed that there were increments of total volatile basis nitrogen production throughout chilled storage periods at $4^{\circ}\text{C}\pm 1$ of all treatments. The lowest of (TVBN) contents during storage periods (15 days) with significant differences $P < 0.05$ were noticed in samples treated with rice husk, followed by samples treated beech sawdust, sugarcane bagasse and then corncob liquid smoke. Meanwhile, the highest value of (TVBN) was recorded for control sample which reached to 30.24 mg N/ 100g sample at 5th day and then spoiled.

Table (6): Changes in TVBN content (mg N/ 100g)* of fish balls treated with different liquid smokes during chilled storage at 4°C±1 for 15 days.

Time of storage (days)	Control	Liquid smoke treatments			
		Beech saw-dust	Sugarcane bagasse	Rice husk	Corn cob
0	9.41±0.47 ^{Aa}	8.74±0.44 ^{Aab}	8.90±0.44 ^{Aac}	8.40±0.44 ^{Aad}	9.24±0.44 ^{Abcd}
5	30.24±0.44 ^{Aa}	14.28±0.44 ^{ABab}	14.45±0.44 ^{ABabc}	13.44±0.44 ^{ABabcd}	14.78±0.44 ^{ABabcd}
10	Spoiled	22.68±0.44 ^{ABCb}	23.02±0.44 ^{ABCbc}	21.84±0.44 ^{ABCbcd}	23.52±0.44 ^{ABCbcd}
15	Spoiled	28.73±0.44 ^{ABCb}	28.90±0.44 ^{ABCbc}	28.56±0.44 ^{ABCbcd}	29.23±0.44 ^{ABCbcd}

^{A-C} The same upper letters indicated significant difference between means and time of storage ($P < 0.05$). ^a The same lower letters indicated significant difference between control and treatments ($P < 0.05$). ^{b-d} The same lower letters indicated significant difference between treatments ($P < 0.05$). Data are expressed as means ± standard deviation ($n = 3$).

* (EEC, 1995) and Connell (1990) stated that acceptability for TVBN values of fish (35 mg N/100 g fish flesh).

TVBN contents of all samples increased during storage period with highly significant differences $P < 0.05$ and were not exceeding the upper acceptability limit set by the EU (EEC, 1995) and Connell (1990) for TVBN values of fish (35 mg N/100 g fish flesh). Assumably, this is because of the impact of the various treatments of TVBN, which primarily included nitrogen from ammonia, TMA, and dimethylamine which reflected the extent of degradation of proteins and non protein nitrogenous compounds which can be explained by proteolysis, due to enzymatic and microbial activities in the samples on storage (Erkan and Özden, 2008).

Changes in trimethyl amine nitrogen (TMAN) content:

TMAN is produced from Trimethylamine Oxide (TMAO) possible partly by action of intrinsic en-

zymes but certainly through bacterial action, is the main component responsible for a pleasant "fishy" odor (Rodriguez *et al.*, 1999 and Shakila *et al.*, 2003).

Data obtained in Table (7) illustrated the changes in TMAN of different samples during the entire storage period for 15 day at 4°C±1. Meanwhile, TMAN content of control samples showed higher value with highly significant differences $P < 0.05$ from other samples on storage; as storage increased also its TMAN content which was higher and spoiled at 10th day than those other samples which increased more slowly than control samples after and through storage period. The increase of TMAN generated by proteolytic bacterial activity will be accompanied by the increase of pH (Rodriguez *et al.*, 2004).

Table (7): Changes in TMAN content (mg N/ 100g)* of fish balls treated with different liquid smokes during chilled storage at 4°C±1 for 15 days.

Time of storage (days)	Control	Liquid smoke treatments			
		Beech saw-dust	Sugarcane bagasse	Rice husk	Corn cob
0	1.85±0.09 ^{Aa}	1.34±0.09 ^{Aab}	1.51±0.09 ^{Aabc}	1.18±0.09 ^{Aabcd}	1.68±0.09 ^{Aabcd}
5	9.24±0.44 ^{Aa}	3.36±0.44 ^{ABab}	3.86±0.44 ^{ABabc}	2.18±0.44 ^{ABabcd}	4.20±0.44 ^{ABabcd}
10	Spoiled	5.38±0.44 ^{ABCb}	6.55±0.44 ^{ABCbc}	4.54±0.44 ^{ABCbcd}	7.06±0.44 ^{ABCbcd}
15	Spoiled	7.22±0.44 ^{ABCb}	7.56±0.44 ^{ABCbc}	6.55±0.44 ^{ABCbcd}	8.57±0.44 ^{ABCbcd}

^{A-C} The same upper letters indicated significant difference between means and time of storage (P<0.05). ^a
 The same lower letters indicated significant difference between control and treatments (P<0.05). ^{b-d}
 The same lower letters indicated significant difference between treatments (P<0.05). Data are expressed as means ± standard deviation (n = 3).

*Egyptian organization for Standardization (2005) for TMAN content of fish (10 mg N/100 g).

Table (7) showed that there were increments of trimethylamine nitrogen production throughout chilled storage periods at 4°C±1 of all treatments. The lowest of (TMAN) content during storage periods (15 days) with significant differences P<0.5 were noticed in samples treated with rice husk, followed by samples treated beech sawdust, sugarcane bagasse and then corncob liquid smoke. Meanwhile, the increment of (TMAN) was higher in control sample which reached to 9.24 mg N/100g sample at 5th day and then spoiled.

TMAN of treatments prepared with different liquid smoke increased with a significant differences P<0.05 during storage period and but were not exceeding the upper acceptability limit set by Egyptian Organization Standards (2005) for TMAN content of fish (10 mg N/100 g).

Conclusion:

Fish balls could be prepared using beech sawdust, rice husk, sugarcane bagasse and corncob liquid smokes. Smoked fish balls stored at 4°C±1 showed biochemical as well as quality attributes analysis values to be

within acceptable limits up to 15 days.

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تقدير تأثير سوانل التدخين على التركيب الكيمياءى ومحددات الجوده لكرات السمك اثناء
التخزين بالتبريد

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المخلص:

الغرض من هذا البحث معرفة تأثير سوانل التدخين المنتجه من بعض المخلفات الزراعيه وهى نشارة الخشب الزان، قشر الأرز، مصاص قصب السكر، وقوالح الذره على التركيب الكيمياءى (الرطوبة، البروتين الخام، الدهن الخام، والرماد) ، وقيمة حمض الثيوباربتيورك ، القواعد النيتروجنيه الطياره والترأى ميثيل امين نيتروجين على كرات الاسماك اثناء التخزين . وأشارت النتائج إلى فساد العينه الكنترول فى اليوم العاشر من التخزين مقارنة بكرات الاسماك المعامله بسوانل التدخين والتي استمرت فى الحفظ حتى ١٥ يوما. اكدت النتائج أنه لم تحدث أي تغييرات فى الرطوبة والبروتين والدهون والرماد لجميع العينات المعامله بسوانل التدخين المختلفه مقارنة بالعينه الكنترول. قيمة حمض الثيوباربتيورك، والقواعد النيتروجنيه الطياره، والترأى ميثيل امين فى جميع العينات المعامله بسوانل التدخين المختلفه لم تصل الى مستويات التدهور . وبالمثل، أدنى قيم من حمض الثيوباربتيورك، القواعد النيتروجنيه الطياره والترأى ميثيل امين قبل و أثناء فترة التخزين لمدة ١٥ يوما لوحظت فى العينات المعامله بدخان قشر الأرز، تليها نشارة الخشب الزان ، مصاص قصب السكر السائل. عموما، كانت جميع العينات من كرات الاسماك مقبولة قبل نهاية فترة التخزين.