The effect of replacing oil with water and NaCl with KCl on soybean oil hydrolysis and oxidation in canned skipjack tuna fish at the end of the 18-month shelf life

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Abstract The effects of replacing oil with water (0, 3, 6, and 10% based on total net weight of the product) and replacing NaCl with KCl (0, 50, and 100%) at different replacement levels were surveyed. Hydrolysis (acidity number), peroxide value, and thiobarbituric acid (TBA) index were evaluated at the end of the 18-month shelf life in canned skipjack tuna fish. Results showed that the TBA index was not affected, whereas the peroxide value was affected by replacing oil with water and NaCl with KCl ($p>0.05$), so that by increasing in replacing oil with water and replacing NaCl with KCl, the peroxide value was significantly decreased ($p<0.05$). Hydrolysis (acidity number) was affected by replacing oil with water ($p<0.05$); however, it was not affected by replacing NaCl with KCl ($p>0.05$). It was found out the best suggestion is 10% replacing oil with water and 50% replacing NaCl with KCl.

Keywords: canned tuna fish, potassium chloride, hydrolysis, oxidation, thiobarbituric acid

Introduction

During fish preservation and preparation, fish quality can be decreased by several factors. The types and extent of reactions as well as the physical and chemical changes that occur during cooking depend on the cooking style and the fat content of the fish. Fish fat and soybean oil used in canned tuna fish are usually altered by two chemical processes (hydrolysis and oxidation), which usually change their useful properties and functions (1). The products of the breakdown by oxidation and hydrophilic reactions are hydroperoxides, aldehydes, ketones, and fatty acids, which can alter the smell, taste, texture, color, and nutritional value of the fish (2,3). Consequently, these changes may cause a decrease in consumer satisfaction toward this important meal source. The quality of soybean oil is usually affected by several aspects, such as high moisture and strong heat and light conditions (USA Agricultural Research Center). Substituting some amount of the soybean oil with water decreases the undesirable health effects associated with the oil and reduces factory costs during canning. According to a previous research, using KCl instead of sodium salt decreases hydrolysis and prevents fat oxidation and the production of dangerous peroxide forms (4). Reducing fat and sodium salt in the diet has proved to benefit patients with stomach cancer, type 1 diabetes, hypertension, and kidney insufficiency (5).

Controlling fat oxidation in canned fish is important to maintain the food's nutritional value.

In the many countries, including Iran, canned tuna fish is processed in severe heat treatments, i.e., it is processed in an autoclave at 121°C for 1 h, whereas replacing oil with water in severe heat processing is caused hydrolysis of triglyceride and produces free fatty acids that are susceptible to oxidation in the liquid phase; therefore, this study surveys the effect of replacing NaCl with KCl salt for inhibiting of soybean oil oxidation and hydrolysis caused by replacing oil with water. To reduce soybean oil oxidation, the effect of substituting oil with water and that of substituting NaCl with KCl were evaluated. Oil was replaced with water at four different levels (0, 3, 6, and 10% of the total net weight of the product, i.e., percentage of water in the liquid phase is 0, 14.14, 28.28, and 47.12%, respectively), whereas NaCl was replaced with KCl at three different levels (0, 50, and 100% KCl replacement corresponding to 0, 0.5, and 1% KCl, respectively, based on the total net weight of the product). Subsequently, the effects of these substitutions on the amount of acid hydrolysis, fatty acid oxidation through peroxide number, and malondialdehyde content at the end of the 18-month shelf life were determined. The findings of this study could be used to provide a solution for the persistent problem of oxidation in canned food products.

Materials and Methods

Production process Skipjack tuna caught from the Indian Ocean was frozen at -18°C in the Bandar Abbas factory. Prior to preparation, the fish was defrosted for 12 h, cut (head and body), and cooked. The fish was again cut and placed in containers without leaks, to which different percentages of salt, oil, and water were added. The containers were then sealed and autoclaved at 121°C for 1 h for sterilization. The product had a net weight of 180 g, including 140 g of skipjack tuna fish meat, 38.2 g of soybean oil, and 1.8 g of NaCl salt (based on the percentage of total net weight of the final product, including 77.78, 21.22, and 1%, respectively). The main goal this study was to evaluate oil hydrolysis (acidity number), peroxide value, and thiobarbituric acid (TBA) index at the end of the 18-month shelf life of the final product. For reducing the storage time, accelerated aging program was used for equalizing the shelf life. So that in this study 18 months at 22°C (ambient or warehouse temperature) was changed with 90 days at 48°C (incubator) with $Q_{10}=2$.

Determination of the acidity number of soybean oil Oil (5 g), ethanol (30 mL), and phenolphthalein (5 drops) were mixed in an Erlenmeyer flask. Addition of KOH (0.1 N) yielded a pink solution after 13 s (6):

$$\text{Acidity number (based on Oleic acid)} = \frac{0.282N \cdot V \cdot 100}{W}, \quad (\text{Eq. 1})$$

$$\text{Peroxide value} = \frac{\text{Consumed volume of sodium thiosulfate} \times \text{normality of sodium thiosulfate} \times 1000}{\text{Weight of soy bean oil (g)}} \quad (\text{Eq. 2})$$

Determination of TBA index Oil (3 g) from the canned fish was mixed with 10 mL of carbon tetrachloride. Approximately 10 mL TBA was added, and the resulting mixture was placed in a 3,000xg centrifuge. The supernatant was heated in a boiling water bath for 30 min, and the absorbance at 530 nm was determined using a Cary 50 spectrophotometer (6). E was calculated according to the following equation:

$$E = \frac{e}{d \cdot a}, \quad (\text{Eq. 3})$$

where e is the measured absorbance, d is the light-cell diameter, and a is the sample amount in grams.

Sensory evaluation A panel of 100 assessors participated in the descriptive sensory analyses. All students were pursuing their master's degree in food science and technology from Islamic Azad University (Khorasgan branch in Iran). The panel was recruited and screened according to the accepted international standards (ISO 8586-1:1993, ISO 8589:1998, and ISO/DIS 13299:1998). This experienced-trained panel had a high level of discrimination and sensitivity in measurement. All assessors were trained to conduct a descriptive analysis and were involved in developing the descriptive

Table 1. Frequency of selection of the salty, bitter, and metallic taste attributes by a panel of 100 people for the canned skipjack tuna fish in different levels of replacing NaCl by KCl at the end of the 18-month shelf life

Replaced salt (%) (based on the total weight of the product)	Frequency (%)		
	Salty	Bitter	Metallic
0 (0% KCl+1% NaCl)	90 ^a	1 ^b	3 ^b
50 (0.5% KCl+0.5% NaCl)	95 ^a	7 ^b	9 ^b
100 (1% KCl+0% NaCl)	15 ^b	77 ^a	70 ^a

Value followed by the same letter in each column is not significantly different at $p \leq 0.05$ by ANOVA.

where N is the normality of alcoholic KOH used in titration, V is the volume of alcoholic KOH used in titration, and W is the weight of the oil sample.

Peroxide value measurement Oil (5 g) from the canned fish, acetic acid (30 mL), chloroform (20 mL), and 0.5 mL of saturated solution of potassium iodide were combined and allowed to stand for 1 min in the dark. Subsequently, 30 mL of distilled water and 0.5 mL of starch solution were added. The amounts of free iodine and 1% sodium thiosulfate solution required for eliminating the blue color were determined. The measurements were then used to calculate the peroxide value according to the following equation (6):

vocabulary for the canned skipjack tuna fish. According to Table 1, the panel of assessors evaluated the frequency (%) of selecting the salty, bitter, and metallic taste attributes in canned skipjack tuna fish.

Statistical analysis A factorial test was performed according to the experimental design. Results were analyzed using the SPSS program (version 22). Mean values were compared, and significant differences at the 5% level of confidence were determined using the Duncan's test. Diagrams were constructed using the Microsoft Excel 2010 software.

Results and Discussion

Effect of replacing soybean oil with water on acidity number, peroxide value, and TBA index of soybean oil in canned tuna fish at the end of the 18-month shelf life The acidity number, peroxide value, and TBA index were evaluated for the canned tuna fish prepared in different percentages of oil replaced with water (0, 3, 6, and 10% based on the total weight of the product) (Table 2). The sample acidities of the canned fish showed a significant increase with increasing water content. Fish prepared in 10% replaced water

Table 2. Chemical analysis of soybean oil in the canned skipjack tuna fish prepared in different levels of replacing soybean oil by water at the end of the 18-month shelf life

Replaced water (%) (based on the total weight of the product)	Acidity number g free fatty acid (oleic acid)	Peroxide value meq O ₂	TBA index mg malondialdehyde
	100 g oil	kg oil	kg oil
0	2.68±0.18 ^d	0.24±0.05 ^a	0.13±0.02 ^a
3	3.91±0.15 ^c	0.04±0.01 ^b	0.12±0.02 ^a
6	4.50±0.18 ^b	0.07±0.01 ^b	0.15±0.02 ^a
10	5.24±0.14 ^a	0.05±0.01 ^b	0.17±0.02 ^a

Assays were performed in triplicate. Mean±SD value followed by the same letter in each column is not significantly different at $p \leq 0.05$ by ANOVA.

Table 3. Chemical analysis of soybean oil in the canned skipjack tuna fish prepared in different levels of replacing NaCl by KCl at the end of the 18-month shelf life

Replaced salt (%) (based on the total weight of the product)	Acidity number g free fatty acid (oleic acid)	Peroxide value meq O ₂	TBA index mg malondialdehyde
	100 g oil	kg oil	kg oil
0 (0% KCl + 1% NaCl)	4.27±0.2 ^a	0.23±0.04 ^a	0.15±0.01 ^a
50 (0.5% KCl + 0.5% NaCl)	4.14±0.16 ^a	0.03±0.01 ^b	0.14±0.02 ^a
100 (1% KCl + 0% NaCl)	3.85±0.18 ^a	0.03±0.01 ^b	0.14±0.02 ^a

Assays were performed in triplicate. Mean±SD value followed by the same letter in each column is not significantly different at $p \leq 0.05$ by ANOVA.

exhibited the highest acidity (5.24 g free fatty acid/100 g oil) among the four samples ($p < 0.05$). The peroxide value (0.24) of fish prepared in 0% replaced water significantly differed from those of the other preparations (3, 6, and 10% replaced water). The TBA test showed no significant differences among the four different preparations ($p < 0.05$).

This observation suggested that hydrolysis was facilitated by increasing water content. The increase in acidity may be particularly caused by a concomitant increase in free fatty acid formation from the reaction of water with fat. The peroxide test results showed that by increasing the water content, the peroxide amount significantly decreased ($p < 0.05$). Conversely, TBA tests showed that increasing water content did not significantly promote malondialdehyde production ($p > 0.05$). The inverse relation between the peroxide value and the TBA index also showed that the malondialdehyde content did not increase with increasing water content. The peroxide index could not be used to solely reflect fat quality due to its transitory nature. Therefore, high peroxide index is correlated with poor taste, whereas low peroxide index does not necessarily reflect good taste and smell (7-9). Furthermore, for meat products, the permissible value for peroxide value was 2 meq O₂ per kg oil. Therefore, the results in this study revealed that no risky health are given to consumers and water replacement remains beneficial for them economically and nutritionally. According to the results of this study, water replacement has led to a decrease in oil oxidation and has not induced significant increase in malondialdehyde production.

Effect of replacing NaCl with KCl on acidity number, peroxide value, and TBA index of soybean oil in canned tuna fish at the end of the 18-month shelf life The acidity number, peroxide value, and TBA

index of the canned fish prepared in different percentages of KCl as a substitute for sodium salt (0, 50, and 100% replacement) were compared (Table 3). The acidity values showed no significant difference among the three salt preparations. The maximum value for acidity was obtained from the preparation with no KCl replacement (4.27%). The peroxide values in without replacement treatment (0% KCl + 1% NaCl) showed significant difference with the other treatments ($p < 0.05$). The peroxide level for the preparation with no KCl replacement showed the highest value at 0.23. The TBA test comparison revealed no significant differences among the different salt preparations ($p > 0.05$).

The extent of hydrolysis, as reflected by acidity number, insignificantly decreased with increasing KCl replacement ($p > 0.05$). Minimum acidity was observed in the preparation with 100% KCl salt replacement. The highest peroxide value was found in the preparation with 0% KCl salt replacement, whereas the lowest peroxide value was observed in the preparation with 50 and 100% KCl replacement. So that could be caused by the possible greater oxidative effect of sodium than potassium. Similar to the results of Calligaris and Nicoli (4), the peroxide value was significantly greater in the preparation with more NaCl content, whereas more KCl replacement (i.e., 50 and 100%) resulted in a lower peroxide value. These findings also confirmed the research of Matlock *et al.* (10) and Jin *et al.* (11). They concluded that sodium promotes greater peroxide production and suggested that fat oxidation and peroxide formation can be prevented by completely replacing sodium salt with potassium salt. In this study, the TBA index (malondialdehyde amount) has not been significantly altered by replacing NaCl with KCl. Conversely, the results of previous studies suggested that replacing NaCl with KCl could decrease malondialdehyde production (8,9).

Table 4. Chemical analysis of soybean oil in the canned skipjack tuna fish prepared in different levels of replacing soy bean oil by water and NaCl by KCl at the end of the 18-month shelf life

Replaced water (%)	Replaced salt (%)	Acidity number g free fatty acid (oleic acid)	Peroxide value meq O ₂	TBA index mg malondialdehyde
(based on the total weight of the product)		100 g oil	kg oil	kg oil
0	0 (0% KCl, 1% NaCl)	2.97±0.41 ^{ef}	0.53±0.13 ^a	0.12±0.03 ^a
	50 (0.5% KCl, 0.5% NaCl)	2.87±0.21 ^{ef}	0.11±0.04 ^c	0.13±0.03 ^a
	100 (1% KCl, 0% NaCl)	2.22±0.31 ^f	0.08±0.04 ^{bc}	0.15±0.03 ^a
3	0 (0% KCl, 1% NaCl)	3.98±0.31 ^{cd}	0.08±0.04 ^{bc}	0.15±0.04 ^a
	50 (0.5% KCl, 0.5% NaCl)	4.17±0.30 ^{cd}	0.04±0.02 ^{bc}	0.13±0.03 ^a
	100 (1% KCl, 0% NaCl)	3.58±0.13 ^{de}	0.00±0.00 ^c	0.09±0.01 ^a
6	0 (0% KCl, 1% NaCl)	4.70±0.42 ^{abc}	0.19±0.08 ^b	0.15±0.03 ^a
	50 (0.5% KCl, 0.5% NaCl)	4.37±0.30 ^{bcd}	0.03±0.02 ^{bc}	0.16±0.05 ^a
	100 (1% KCl, 0% NaCl)	4.45±0.19 ^{bcd}	0.00±0.00 ^c	0.14±0.03 ^a
10	0 (0% KCl, 1% NaCl)	5.42±0.30 ^a	0.13±0.06 ^{bc}	0.17±0.04 ^a
	50 (0.5% KCl, 0.5% NaCl)	5.16±0.19 ^{ab}	0.04±0.02 ^{bc}	0.15±0.03 ^a
	100 (1% KCl, 0% NaCl)	5.15±0.25 ^{ab}	0.00±0.00 ^c	0.18±0.05 ^a

Assays were performed in triplicate. Mean±SD value followed by the same letter in each column is not significantly different at $p \leq 0.05$ by ANOVA.

Combined effects of replacing soybean oil with water and NaCl with KCl on acidity number, peroxide value, and TBA index of soybean oil in canned tuna fish at the end of the 18-month shelf life

According to Table 4, the highest acidity (5.42%) was observed in the preparation with 10% water and 0% KCl replacement. Less acidity (2.22%) was observed in the preparation with 0% water and 100% KCl replacement. For all preparations with various water contents, the preparation without replacement NaCl exhibited greater acidity than the other two salt preparations. This finding showed that KCl insignificantly decreased hydrolysis. However, the acidity in all salt preparations increased with increasing water content. This result suggested that the preparation without replacement NaCl released more fatty acid by increasing the water content in the environment, which consequently increased the acidity number (because of triglyceride hydrolysis by water). This evidence confirmed the findings obtained by Sahoo *et al.* (12). By analyzing the combined effects of oil and salt replacement in each level of replaced water i.e., 3, 6, and 10% (Table 4), we found that the peroxide value was 0 in 100% KCl replacement. A decrease in peroxide value was also found in 50 and 100% KCl replacement; however, this difference was not significant ($p > 0.05$). In this study, the preparation with no replacement with KCl exhibited the greatest peroxide value in each level of replaced water (Table 4) and the peroxide value decreased with increasing amount of KCl. Thus, the results agreed with the peroxide-promoting property of sodium, which was suggested by Wu *et al.* (13). The decrease in the peroxide value may be related to the formation of other combination products (e.g., epoxies, ketones, and hydroxyl fatty acids) at the end of the 18-month shelf life. Malondialdehyde levels were the same in all salt and water preparations ($p > 0.05$). The maximum amount of malondialdehyde was observed in the preparation with 100% KCl replacement and 10% water replacement, with a value of 0.18 mg of malondialdehyde per kg oil.

Overall, the results showed that the TBA index was not affected, whereas the peroxide value was affected by replacing oil with water and by replacing NaCl with KCl. Hydrolysis (acidity number) was affected by replacing oil with water; however, it was not affected by the replacing NaCl with KCl. Therefore, according to the three indexes and sensory evaluation in terms of salty, bitter, and metallic taste attributes (Table 1) in which there was no significant difference between preparation 0 and 50% KCl replacement ($p > 0.05$). Therefore, the best suggestion is 10% replacing oil with water and 50% replacing NaCl with KCl. This combination decreased factory production costs of the canned fish while providing greater benefits to human health using less sodium salt and oil according to standard limitations.

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