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Shelf-Life Prediction of Indonesian Fish Cracker Fried with Mix Palm-Sesame Oil using Accelerated Shelf-Life Test (ASLT)

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Abstract: ***Cracker products, especially fish cracker was known to have short shelf-life and easily rancid due to oxidation deterioration. This research was aimed to extend fish cracker shelf-life by frying fish cracker using oil which made from mixing palm oil with sesame oil. Shelf-life was determined using Accelerated Shelf-Life Test (ASLT) with Arrhenius model based on thiobarbituric acid value (TBA). Experiment was conducted at temperature of 25° C, 35° C and 45° C until 15 days to follow oxidation level through TBA value. Results showed that ASLT method could be used to predict shelf-life of fried fish cracker with mix palm-sesame oil (90 : 10 v/v) that the main deterioration was due to oxidation reaction. The shelf-life of regular fish cracker (fried only with palm oil) was 48 days and those fried by mixed oil was 67 days. Frying fish cracker on mixed oil (palm-sesame) was able to extend shelf-life up to 19 days by reducing rancidity reaction.***

Keywords: Fish cracker, shelf-life, mixed oil, sesame oil, ASLT.

1. Introduction

Crackers are a popular food among the people of Indonesia. Crispy texture and savory taste are the elements that differentiate this food with other types of food. Characteristics of crackers are able to make the customer not easy to get bored to always consume this delicious dry food. One popular cracker among the people of Indonesia, especially on the island of Sumatra is a Palembang fish cracker. In the local language of Palembang, fish crackers are called by the name of *kemplang*. *Kemplang* is made through a series of processes in the form of material mixing, steaming, cooling, slicing, drying and frying. *Kemplang* made from the main ingredients of fish that generally comes from fresh water. The most used type of freshwater fish to make fish cracker in Indonesia is snakehead fish.

Like other crackers, *kemplang* quite susceptible to damage due to uncontrolled environmental influences (the presence of oxygen and water vapor). *Kemplang* that are not given a protective layer (packaging) can experience a decrease in crispness (increase of water contain), and rancidity (oxidation which casuse by oxygen and light) in a relatively fast [1]. Many studies have attempted to use other types of plastics to reduce the damage of fish crackers from oxidation, including the use of polyethylene, polypropylene, nylon and metallized packaging [2]. The best packaging to extend the shelf-life of *kemplang*, which has a cheaper price and is very familiar to use as a packaging material for *kemplang* is polypropylene. This type of packaging is commonly used as a *kemplang* packaging because it is easily formed, quite resistant to water vapor and has a fairly transparent appearance, but unfortunately this type of plastic is not sufficiently resistant to oxygen making it less suitable for oxygen-sensitive food products such as *kemplang*. Using the Accelerated Self Life Test (ASLT) method of polypropylene packaging can reduce oxidative damage of fish crackers for 37 days [2].

Effect of oxidation is the main cause of rancidity in fish crackers, the presence of oxygen and light causes the destruction of fatty compounds in fish crackers into the compounds that cause rancidity. The oxidized lipids compound that cause the rancid odor are derived from the oil which used to fry fish crackers. At the beginning of the storage period using polypropylene packaging, the first damage is rancidity followed by a decrease in crispness. Consuming oily food that smells rancid because the process of oxidation is danger and has been widely studied. Rancidity in foods containing fat is an indicator of oxidation. The rancid odor of fish crackers is caused by the hydrolysis of fat into free fatty acids due to the oxidation process, thereby forming free fatty acids which have low volatile molecular weight, causing the oil to become rancid.

There is no other way to protect the damage of fish crackers packed using polypropylene packaging from oxidation damage in addition to providing direct protection to the fish crackers. The possible way is to add antioxidants into fish crackers. The addition of other ingredients that preserve fish crackers from oxidation damage is using a substance / compound that has high antioxidant properties and should be comes from nature antioxidant compound. Antioxidants should not come from synthetic compound and do not have side effects that are detrimental to health. The presence of natural antioxidants has been explored, one of which is the antioxidants that exist in sesame oil. Sesame (*Sesamum indicum*, sp.) has known as a producer of vegetable oils (sesame oil) which has many benefits, both as an antioxidant and its effect on human health. Sesame oil is widely used as an antioxidant due to the presence of lignan compounds (sesamin, sesamolin and sesamol) in sesame seed [3]; [4];

[5]; [6]. In 100 g of sesame seeds from roasted sesame seeds contain 638 mg sesamin, 292 mg sesamolin, and 11.5 to 16.1 mg sesamol [7]. Sesame lignans are often the focus of research as a source of antioxidants in sesame oil is sesamol and sesamolin. Sesamol is naturally present in sesame oil from raw sesame seeds and can increase if the sesame seeds are roasted at temperatures up to 200° C [8]; [9]. Sesamol arises from the breakdown of sesamolin compounds in raw sesame seeds which are roasted to a temperature of 200° C [10]. Increasing the content of some lignans in sesame oil after heating process has been widely used as a source of natural antioxidants, either as antioxidants in food systems or natural sources of antioxidants in an effort to improve the health of the human body.

Although lignan sesame has been widely studied, it is able to protect other vegetable oils from oxidative damage and its good effects on health, especially sesamol compounds that are proven to have strong antioxidant properties, also need to know how its ability in other food systems especially in fish crackers to protect it from oxidative damage. Therefore, the aim of this research is to know the ability of bioactive compounds in sesame seeds which have high antioxidant ability to protect the fish crackers from oxidative damage and could extend the shelf-life.

2. Research Method

2.1. Tools and Materials

The materials grouped into research materials and chemicals for analysis. The main material was raw fish crackers (un-fried *kemplang*) from Palembang get from the local food industry owned by Mrs. Hasanah in Palembang South Sumatra Indonesia, *Wijen Nasional* 1 (Winas 1) sesame seeds variety is which obtained from Crops Research Institute Sweeteners and Fiber of Indonesia (*Balai Penelitian Tanaman dan Serat* / Balittas) under the Ministry of Agriculture of the Republic of Indonesia, regular palm oil (local brand) purchased from the local market, the polypropylene plastic packaging material, and all materials which is needed for packaging and storage. The chemical reagents used for proximate analysis with AOAC method (1995) [11], chemical reagents for thio-batbituricacid analysis based on Ottolenghi (1959) [12], and chemicals reagents for lignan sesame analysis based on Rangkadilok, et. al., (2010) [13].

Some research tool used in this research was Coffee Roaster RK - 28 - RCg with additional thermal data logger tool to record actual temperature in roaster tube to roasting the sesame seed, hydraulic pressure to get the sesame oil, frying pan to fry the fish cracker, and some tools for packaging purposes. The incubator also used as a storage place for samples with different temperature conditions.

2.2. Preparation of Fish Cracker Frying Oil

Sesame oil was obtained from Winas 1 sesame seed varieties which already roasted at 200° C for 15 minutes using Lee et. al., (2009) [14] method to increase the antioxidant activity. Roasted sesame seeds grounded by using a special tool to extract oil from roasted sesame seed. The extracted oil then filtered and collected in a clean container for the next use as a stuff to make a mixed oil as a frying medium of fish crackers. The yield of extracted sesame oil ranges from 30 - 45%. This sesame oil then mixed with regular palm oil which commonly used as a frying medium of fish cracker in many fish cracker home industry in Palembang, South Sumatra Indonesia. The mixing ratio between palm oil and sesame oil was 90: 10 (v/v) (Table 1). The mixed oil is then stored in a clean container for use as a frying medium for fish crackers and will be compared to fish crackers fried with palm oil only as a control variable.

2.3. Fish Cracker Frying Process with Palm Oil (Control) and Mixed Oil

To make a ready to eat fish crackers we need to fry fish cracker in 2 times frying processes. The first frying process use palm oil as a frying medium with a temperature of about 110° C for ± 45 seconds while in the second frying process use palm oil with a frying temperature of about 200° C for ± 30 seconds. In this research we use the second frying process oil medium to compare between palm oil as a control and mixed oil of palm oil and sesame oil. We use a temperature control device in both of frying process so that the frying temperature in each process can be monitored and controllable. Raw fish crackers that will be fry will be uniformly in weight, shape, diameter, and thickness, which derived from a similar manufacturing process in the fish cracker industry of Palembang. The volume of oil used in the first and second frying process is surely covering all the fish crackers at both stage. The ratio between fish crackers and frying oil is 1:20 (weight/volume). The fryer tools used a 35 cm diameter pan and stove powered by liquid petroleum gas, each stove and pans in each frying process was added an automatic temperature control unit on each frying medium which controlled by a series of temperature regulators (consisting of thermostat and thermo couple) and selenoid valve (Figure 1).

The volume of oil used in the first and second fryers is 2 liters each. The amount of crackers fried in a single process of frying amounted to 15 raw crackers with a weight per pieces ± 6 g, thickness ± 0.5 cm, and ± 3 cm in diameter. Fried fish crackers have a thickness of ± 0.7 cm, diameter ± 6 cm, and weight per cracker ± 5 g. Crackers are then selected which are uniform in size and packaged according to the type of frying oil used and directly tested for shelf-life at a later stage. Figure 16 shows the flowchart of fish cracker frying process.

Table 1: Treatment of fish crackers frying oil medium on the second frying process

Treatment	Palm Oil: Sesame Oil Comparison		Frying Temperature (°C)	Frying Time (second)
	Palm Oil	Sesame Oil		
Control	10	0	200	±30
Fried with mixed oil	90	10	200	±30

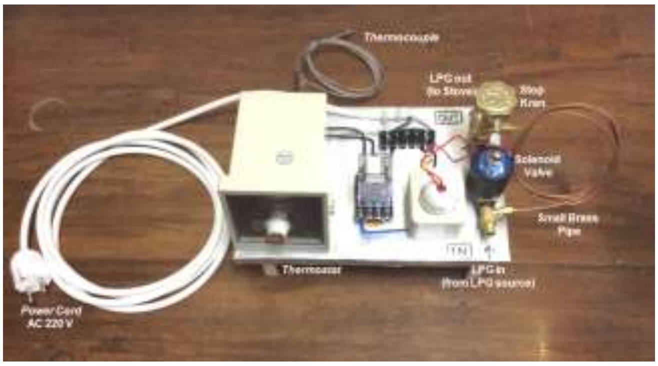


Figure 1: Automatic frying temperature control set circuit

2.4 Determination of Shelf-life

The shelf-life of fish crackers is determined by the Accelerated Shelf-Life Test (ASLT) method using the Arrhenius equation. Fish crackers that have been fried in the previous stage selected in uniform size (weight ± 5 g, diameter ± 6 cm, and thickness ± 0,7 cm). This selected cracker samples packed with polypropylene packaging. The size of the packaging made in equal size, i.e. 270 cm^2 (15 x 18 cm) with the weight of each pack is ± 30 g (contains 6 pieces of crackers). The packaged sample inserted into some sealed container in which has an installed saturated salt buffer (BaCl2.2H2O) salt for make a uniform RH storage space. Each container stored at different temperatures, i.e. 25 °C, 35 °C, and 45 °C, and observed on day 0, day 3, day 6, day 9, day 12, and the 15th day. The observations variable of oxidation are the number of TBA which refers to the method Maqsood (2010). The obtained TBA number data were averaged, then plotted in the form of a graph of the relationship between storage duration and the number of TBA and obtained by the reaction rate constant (k) or degradation value for each experimental temperature with its R value. The plot of k value against the experimental temperature according to the Arrhenius equation the form of equation 2 with the slope is -Ea / R and intercept ln-k_0. With the known activation energy (Ea) and k_0 it will obtain the equation of reaction rate at the tested storage temperature (30 °C). The reaction rate constant is used to calculate the estimated shelf-life of fish cracker by using equation (1) of reaction of order 0 as below:

$$t = \frac{Qt - Q0}{k} \qquad (1)$$

Where:
Q0 = initial quality storage value
Qt = quality value at time t
k = constant rate of reaction / degradation at temperature T
t = storage time (day)
Qt in this case is the critical value of the rancidity of fish crackers with the TBA rate of 1.28 obtained from the previous test.

3. Result and Discussion

3.1. Changes of Fish Frying Chicken Figures During Storage

Determining the shelf-life of fish crackers can be calculated by calculating reaction kinetics at each storage temperature until Arrhenius equation is obtained at each temperature. The obtained Arrhenius equation is used to predict the shelf-life of fish crackers. The shelf-life of fish crackers can be known from the initial quality values, end point values, and kinetic constants at storage temperatures. The change of TBA number during the determination of shelf-life using ASLT Arrhenius method can be seen in Table 2.

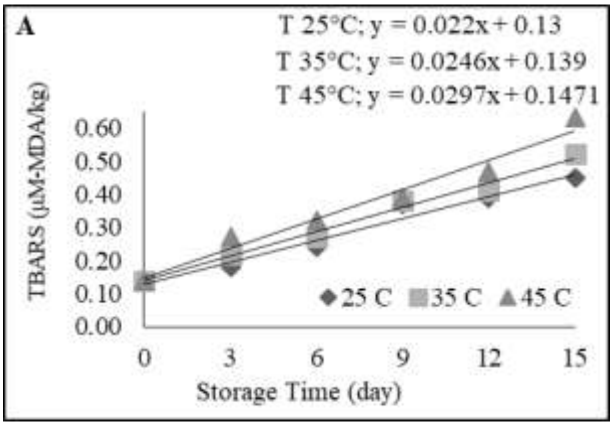
3.2. Determination Shelf-Life of Fish Crackers Control and Fish Crackers Fried with Mixed Oil (Palm Oil: Sesame Oil)

To determine the reaction rate (k) at each storage temperature, we need to plot the data from Table 2 on the storage time curve and the TBA number. The resulting plotting and linear equations for each storage temperature for fish crackers control and fish crackers fried with mixed oil are respectively seen in Figures 2.A and 2.B. From both graphs it is seen that the higher the storage temperature, the constant of the reaction velocity (k) shown by the slope becomes higher. The graphs also show that the reaction speed of the fish cracker control is higher than that of fried fish crackers with mixed oil. According to Lundberg (1962), the fat oxidation reaction is influenced by temperature, light and oxygen concentration. Any temperature increase of 10 °C will result in a reaction rate of up to 2 - 3 times. The increase of k value from fish crackers control following by increase of temperature at 10 °C was slightly lower than Lundberg's research (1962).

The resulting of reaction rate values in fish cracker control and fish crackers fried with mixed oil for each temperature tabulated into Table 3. This result are used to determine the kinetic reaction value at the storage temperature by making the graph of the relationship between 1/T as the x-axis and ln-k as the y-axis. Graph of plotting result of fish cracker control and fish cracker fried with mixed oil are shown in Figure 3.A and 3.B.

The graph is a linear line equation as Equation 2 of Arrhenius derivative with slope is -Ea / R and intercept is ln k. From the fish cracker control (Figure 4.A), the linear line is shown by equation 2 below:

$$y = -1417.5x + 0.9261 \qquad (2)$$



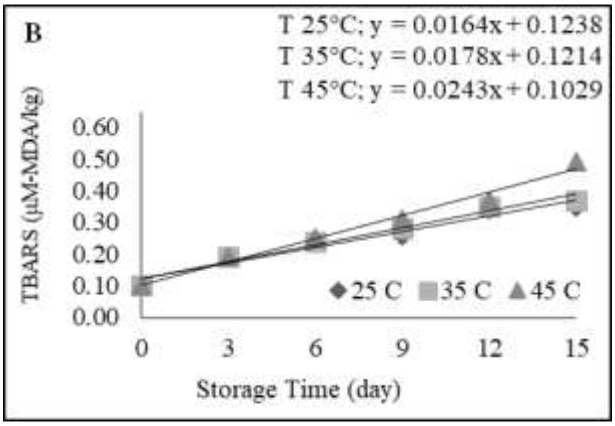


Figure 2: Long duration of storage with TBA number of fish crackers; (A) fish cracker control and (B) fish crackers fried with mixed oil.

Table 2: Changes in TBA number of fish cracker control and fish crackers fried with mixed oil for 15 days storage at various test temperatures.

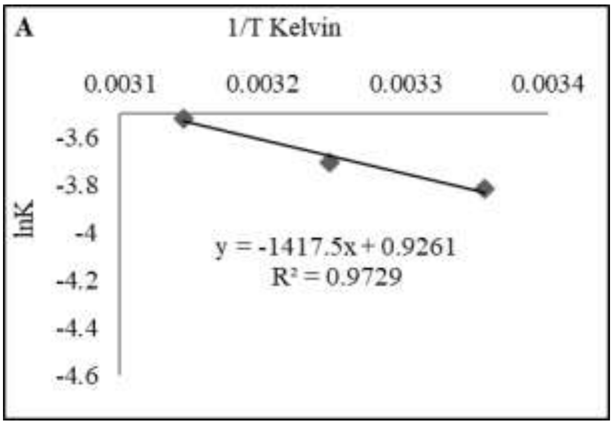
Fish cracker frying oil medium	Temp. Storage (° C)	TBA value (µM-MDA/kg)					
		Day 0	Day 3	Day 6	Day 9	Day 12	Day 15
Palm oil only (Control)	25	$0,14^{a}$ ± 0,07	$0,18^{a}$ ± 0,21	$0,24^{a}$ ± 0,04	$0,37^{a}$ ± 0,11	$0,39^{a}$ ± 0,07	$0,45^{a}$ ± 0,31
	35	$0,14^{ab}$ ± 0,09	$0,22^{ab}$ ± 0,11	$0,27^{ab}$ ± 0,21	$0,38^{ab}$ ± 0,04	$0,41^{ab}$ ± 0,03	$0,52^{a}$ ± 0,49
	45	$0,14^{bc}$ ± 0,07	$0,27^{abc}$ ± 0,14	$0,32^{abc}$ ± 0,21	$0,39^{abc}$ ± 0,09	$0,47^{abc}$ ± 0,36	$0,63^{a}$ ± 0,39
Mix palm oil : Sesame oil (90:10) v/v	25	$0,10^{a}$ ± 0,13	$0,19^{a}$ ± 0,09	$0,24^{a}$ ± 0,23	$0,26^{a}$ ± 0,27	$0,34^{a}$ ± 0,06	$0,35^{a}$ ± 0,01
	35	$0,10^{b}$ ± 0,06	$0,19^{ab}$ ± 0,24	$0,24^{ab}$ ± 0,08	$0,28^{ab}$ ± 0,05	$0,35^{ab}$ ± 0,28	$0,37^{ab}$ ± 0,12
	45	$0,10^{bc}$ ± 0,11	$0,19^{bc}$ ± 0,03	$0,25^{abc}$ ± 0,15	$0,31^{abc}$ ± 0,26	$0,37^{abc}$ ± 0,14	$0,49^{ab}$ ± 0,18

Data is shown in ± SD, the same letter at the same temperature indicates significantly different, with P> 0.05.

In other words, the graph is the equation of the relationship of ln k versus 1/T i.e. ln k = -1417.5 (1/T) + 0.9261 with the value R2 = 0.97. High correlation coefficient (R^2) indicates that the Arrhenius equation is valid enough to test the reaction kinetics due to temperature.

Table 3: Changes in kinetics of reaction rate of fish cracker control and fish crackers fried with mixed oil at 25 °C, 35 °C and 45 °C storage temperature.

Fish cracker frying oil medium	T (° K)	K	1/T	lnK
Palm oil only (Control)	298	0.022	0.003356	-3.81671
	308	0.0246	0.003247	-3.70501
	318	0.0297	0.003145	-3.51661
Mix palm oil : Sesame oil (90:10) v/v	298	0.0164	0.003356	-4.11047
	308	0.0178	0.003247	-4.02856
	318	0.0243	0.003145	-3.71728



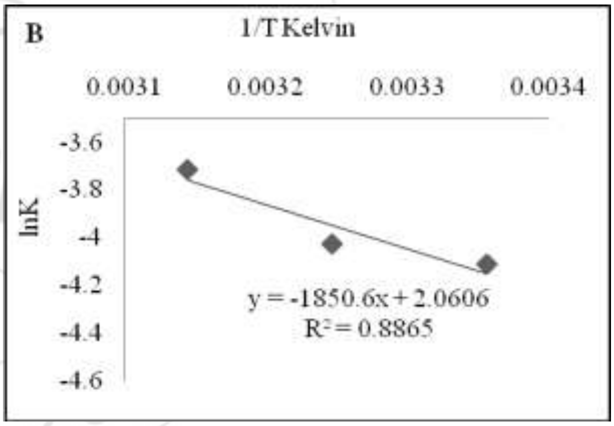


Figure 3: Relationship 1/T with ln k from storage of fish crackers; (A) control and (B) fish crackers fried with mixed oil.

The equation then used to calculate the value of k on the projection of the fish cracker control storage temperature. In this product, the product is assumed to be stored at 30 °C, then from the equation we get the value of ln k = -6.22814 or k = 0.023468 TBA per day (increase of TBA by 0.023468 per day). With the critical value of TBA is 1.28 and the initial TBA sample number is 0.14 then it can be determined the estimated shelf-life of the fish cracker control using equation 3, i.e.;

$$Shelflife = \frac{1.28 - 0.14TBA}{0.023468TBA / day} = 48.57 day \quad (3)$$

The results of this calculation is more than the shelf-life of fish crackers in previous research that is only about 37 days

[2]. Different estimates of shelf-life due to different approach of methods, in previous research the variable of oxidative deterioration based on daily sampling by relying on acid numbers while this study used the Arrhenius kinetics approach referring to the TBA number. The graph of a 1/T relationship with ln k of fish crackers fried with mixed oil (Fig. 4.B) is also a linear line equation as shown in equation 4 below;

$$y = -1850.6x + 2.0606 \quad (4)$$

The graph is an equation of the relationship of ln k versus 1/T, i.e. ln k = -1850.6 (1/T) + 2.0606; with the value of R^2 = 0.8865. With a high correlation coefficient value (0.88) indicates that the Arrhenius equation is valid enough to be used for calculating the oxidation reaction kinetics due to temperature. The equation is then used to calculate the value of k in the projection of food storage temperature as in the control fish crackers. So from fitting data the value of ln k = -4.04699 or k = 0.017475 TBA per day (increase of TBA by 0.0174 per day). By using the critical value of TBA equal to the control sample (0.90) and the initial TBA sample number is 0.1 then it can be determined the estimated shelf-life of the fish cracker fried with mixed oil, that is;

$$Shelflife = \frac{1.28 - 0.1TBA}{0.0174TBA/day} = 67.52day \quad (5)$$

The results showed that the treatment of fish cracker fried with oil mixture of palm oil and sesame oil with ratio of 90: 10 could extend the shelf-life of control fish cracker from 48 days to 67 days, or delayed 19 days expiry. Similar results shown on fish crackers packed with polypropylene packaging can resist fish crackers from oxidative damage for 38 days [2]. The presence of lignans in sesame oils that function as antioxidants is a major factor in the prevention of oxidation damage of fish crackers, thereby reducing the increase in the number of TBA and ultimately reducing the aroma of rancidity. With limited rancid reactions, the mix oil of palm oil and sesame oil as a medium fryer of fish cracker can extend the shelf-life of fish crackers itself.

4. Conclusion

Accelerated Shelf-Life Test (ASLT) method with Arrhenius model can be used to estimate the shelf-life of fish crackers fried with mix oil of palm oil and sesame oil with ratio of palm oil and sesame oil 90:10 (v/v) caused by oxidation reaction. The retention time of control fish cracker is 48 days and the shelf-life of fish cracker fried with mix oil is 67 days. Frying fish crackers with mixed oils of palm oil and sesame oil proved to extend shelf-life to 19 days with its role in suppressing rancid reactions.

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