Kinetics of quality changes and shelf life estimation of frozen coated Tumpi-Tumpi using accelerated shelf-life testing (ASLT) method with Arrhenius approach

Syahrul¹, R Syarief², J Hermanianto², and B Nurtama²

¹Department of Fisheries, Faculty of Marine Science and Fisheries, Hasanuddin University, Makassar, Indonesia
²Department of Food Science and Technology, IPB University, Bogor, Indonesia.

Email: syahrulpspunhas@gmail.com

Abstract. Quality changes during storage are greatly affected by storage temperatures and food factors. Kinetic quality changes during storage are important to know as one of the parameters in determining the shelf life of a foodstuff. Determination of shelf life can be done by Accelerated Shelf Life Test (ASLT) through a semi-empirical approach with the help of the Arrhenius equation, which is an approach that used kinetics theory which generally has zero-order or first-order reaction for a food product. The kinetics of the frozen coated tumpi-tumpi quality change was assessed by storage at (-10, -5, 0 °C). Observations were made every 7 days until day 35. The quality parameters that were analyzed included the thiobarbituric acid (TBA). This study aims to determine the frozen coated Tumpi-tumpi product quality change at various storage temperatures based on the value of TBA and estimation of shelf life. The frozen coated tumpi-tumpi product quality change parameters based on the changes in the TBA were not yet able to determine the zero-order reaction or first-order kinetics. The results of the activation energy (Ea) calculation of the frozen coated tumpi-tumpi product based on the TBA value critical parameter revealed that the lowest activation energy was 8.537 kcal mol⁻¹, causing this parameter to determine the frozen coated tumpi-tumpi product shelf life. The results of the calculation revealed that the higher the frozen coated tumpi-tumpi storage temperature, the shorter the product shelf life is. The shelf life for the frozen coated tumpi-tumpi at a storage temperature of -18 °C was 284 days.

1. Introduction
Tumpi-tumpi is a traditional/ethnic food from South and West Sulawesi Provinces (Sulselbar), made from a mixture of groundfish meat, shredded coconut, tapioca flour, and spices [1]. Developed a product by producing frozen coated tumpi-tumpi by coating with batter mix dough and breadcrumb [1,2]. After the packaging process, the product is stored at -18 °C freezing. The product presentation is similar to the nugget, which is immediately after being removed from the freezer, fried in hot oil so that it has a crispy texture on the outside and rather chewy on the inside.

Food Law No. 7/1996 and Government Regulation No. 69/1999 are concerning Food Labels and Advertisements, where each food product is obliged to put an expiration date (expired date) on each package of food products. Information about the shelf life (expiration) of food products is very important to include by the manufacturer on the packaging, related to food safety, and provides quality assurance when the product reaches the consumer.

Tumpi-tumpi products are included in the group of food products with a high level of risk because they have aw more than 0.85 and pH more than 4.5. Under these conditions, it is necessary to determine the shelf life. Koswara and Kusnandar [3] stated that the shelf life of food products is between the time of production and consumption, where the product is in satisfactory condition for appearance, taste, aroma, texture, and nutrition. Herawati [4] also states that shelf life is a period of time for products that are sensory and nutritionally acceptable and safe for consumption.
The shelf life of food products can be estimated by two methods, namely Extended Storage Studies (ESS) and the Accelerated Shelf Life Test (ASLT). ESS is called the conventional method of determining expiration by storing a series of products under normal conditions, then observing changes in quality and shelf life. This method requires a very long time. ASLT method is determining the shelf life of products by accelerating changes in quality at critical parameters. This method uses environmental conditions that can accelerate the reaction of a decrease in the quality of food products. Food products are stored in extreme temperature conditions so that the critical parameters decrease in quality due to the influence of heat. In this method, the storage conditions are set outside normal conditions so that the product can be damaged more quickly, and the shelf life can be determined [5].

The shelf life of the product can be estimated in various ways, including using kinetics such as the part-time model and the Arrhenius model [6]. The acceleration method is basically a method adapted for certain food products. The models applied in this acceleration research use two approaches, namely: 1) Critical water content approach with the help of diffusion theory, which is an approach applied to dry products using water content or water activity as an expiration criterion and 2) the semi empirical approach with the help of the Arrhenius equation, which is an approach that uses kinetic theory which generally has a zero or one reaction order for food products. The Arrhenius method is a fairly simple method for estimating shelf life through measurement of the rate of deterioration. Changes in quality during storage are greatly influenced by storage temperature and stored food factors. The kinetics of quality change during storage is important to know as one of the parameters in determining the shelf life of food. This study aims to determine the kinetics of changes in the quality of frozen coated tumpi-tumpi at various storage temperatures based on TBA values and to estimate their shelf life.

2. Materials and methods

2.1. The process of making products of the frozen coated tumpi-tumpi

The recipe used in making products of tumpi-tumpi refers to field references, namely: 30% fish, 45% coconut, 10% tapioca, and 15% spices [1]. The production process follows the following flow (Figure 1).

![Figure 1. Flow chart the production of frozen coated tumpi-tumpi [1,2].](image-url)
2.2. Kinetics of quality change and estimating the shelf life of frozen coated tumpi-tumpi

Kinetics of quality change in frozen coated tumpi-tumpi were carried out using storage at temperatures (-10, -5, 0 °C). Observations were made once every 7 days until the 35th day. The quality parameter analyzed is the thiobarbituric acid (TBA) value. It is estimating the shelf life of the product using the ASLT method with the Arrhenius model. Determination of the critical factors is a preliminary stage carried out to determine the parameters that greatly affect the quality of the product of the blunt product during cold storage. The temperature used in determining the critical factor is the temperature of 0°C; the parameter used is the value of TBA. Every parameter is observed and tested every 7 days. The parameter that most quickly exceeds the standard is the TBA value of 3 mg malonaldehyde kg⁻¹ [7] used to estimate shelf life.

Data on changes in observations during storage are then plotted based on storage time. Then a regression analysis is performed to obtain the slope (k), constant (intercept), and regression coefficient (R²) values of the storage time function (x-axis) to the quality parameters (y-axis) in each storage condition. In the calculation used two relationship models, namely zero-order and first-order models. The model is chosen based on the regression coefficient that is closest to 1.

The value of k (ln k) in the selected model is then regressed with the storage temperature (1/T) so that the slope (-Ea / R), constant (ko) and regression coefficient (R²) is obtained. The values obtained are entered in the Arrhenius formula, ln k = ln ko - Ea / RT where k is the reaction rate constant, ko is the pre-exponential constant, Ea is the activation energy, and T is the absolute temperature. Shelf life is obtained by dividing the quality change that occurs with the value of the reaction speed constant obtained from the Arrhenius formula.

2.3. Measurement of thiobarbituric acid (TBA) numbers [8]

The materials are weighed as much as 10 g, put into a waring blender, added 50 mL of distilled water, and crushed for 2 minutes. Material that has been crushed transferred quantitatively into the distillation flask while being washed with 47.5 mL of distilled water, and added ± 2.5 mL HCl 4 M (up to pH 1.5), boiling stones and froth preventative are added. The distillation flask is mounted on the distillation apparatus and, if available, use an "electric mantle heater." Distillation is carried out by high heating so as to obtain 50 mL of distillate for 10 minutes of heating. The distillate is stirred evenly, piped 5 mL and put into a closed test tube, then added 5 mL of TBA reagent, closed, mixed evenly, then heated for 35 minutes in boiling water. Blanks are made using 5 mL of distilled water and 5 mL of reagents and are performed as a sample determination. The test tube is cooled with cooling water for ± 10 minutes then the absorbance (D) is measured at a wavelength of 528 nm with the blank solution as the zero points. TBA numbers are expressed in mg of malonaldehyde per kg of sample. TBA number = 7.8 D. The TBA number can be determined by the formula:

\[
\text{mg malonaldehyde per kg sample} = \frac{3}{\text{weight of sample}} \times \text{absorbance} \times 7.8
\]  

3. Results and discussion

3.1. Kinetic of changing the value of thiobarbituric acid (TBA) of frozen coated tumpi-tumpi

TBA values have been widely used as parameters to determine the degree of fat oxidation. The development of studies on TBA numbers for mince with washing and without washing was shown to be a significant increase during frozen storage. Tokur et al. [9] conducted a study of fish finger products made from mince with washing and without washing, which showed that fish finger made from mince without washing in the five-month showed a higher value of 0.27 mg malonaldehyde kg⁻¹ compared to washing, i.e., 0.25 mg malonaldehyde kg⁻¹. TBA values have increased very slowly in freezing temperature storage (-18 °C).

Measurement the TBA levels of tumpi-tumpi at -10, -5, 0 °C was observed at intervals of 0, 7, 14, 21, 28 and 35 days. The measurement results have then performed a calculation of the reaction kinetics using the zero-order reaction kinetics and first-order reaction kinetics.
The kinetics curve of the TBA reaction using the zero-order reaction equation is presented in Figure 2a. The calculation results show that all plot line equations at various observational temperatures produce linear curves. The degree of linearity of zero-order reactions is presented in Table 1. The calculation of the kinetics of the TBA reaction is also carried out in the first-order reaction equation (Figure 2b and Table 1).

**Figure 2.** Curve changes in TBA values during storage in zero-order reaction (a) and first-order reaction (b).

The results of the calculation of the value of the TBA reaction constant, both in the zero and first-order reaction kinetics, show that with the higher temperature, the greater the value of the reaction constant is obtained (Table 1). This shows that the change in TBA numbers in frozen coated tumpi-tumpi is a temperature-dependent reaction. Hikmawati [10] states that nugget products made from catfish tend to increase TBA levels during storage, where these changes are faster at higher temperature storage.
Table 1. Constant values and kinetics of zero and first-order reaction kinetics based on critical quality parameters.

| quality parameters | Temperature (°C) | Zero Order | First Order |
|--------------------|------------------|------------|-------------|
|                    |                  | K          | R²          | K            | R²          |
| TBA value          | -10              | 0.0663     | 0.8893      | 0.0299       | 0.7806      |
|                    | -5               | 0.0548     | 0.9581      | 0.0273       | 0.8768      |
|                    | 0                | 0.0304     | 0.9423      | 0.0185       | 0.9215      |

3.2. Determination of the shelf life of frozen coated tumpi-tumpi

The shelf life of food products is the time between the time of production and packaging until the product can no longer be accepted by consumers in certain storage conditions [11]. The parameter used in estimating the storage life of frozen coated tumpi-tumpi is TBA value. The selection of the two attributes is based on the results of a very real test with a high enough $R^2$ (0.78 to 0.97).

Based on the data in Table 1, it is known that the pattern of changes in the quality of TBA can not be determined by the kinetics of zero or first-order reactions. K values at normal storage temperatures can be estimated using the Arrhenius equation: $\ln (K_T) = \ln A_o - \frac{E_a}{RT}$ or $K = K_0 \exp \frac{E_a}{RT}$. Thus, the storage life of frozen coated tumpi-tumpi can be estimated using the equation $t_s = [\ln (N_{O_t} / N_t)] / K_T$ for the first-order reaction rate, while for the zero-order reaction rate, the shelf life can be estimated with the equation $t_s = (N_{O_t} - N_t) / K_T$. Where: $t_s$ = storage time, $N_{O_t}$ = value of quality parameters at $t_o$ (initial storage), $N_t$ = quality parameter values after storage time $t$ (critical limit), $K_T$ = value of $K$ at storage temperature $T$.

3.3. Determination of reaction constants at various storage temperatures

The value of the reaction constant can be determined by entering the storage temperature value in either the zero-order reaction or the first-order reaction obtained on the Arrhenius curve. Arrhenius curves are obtained by connecting the $\ln K$ (natural logarithm) start of the reaction rate constant at the observed temperature with $1 / T$ (observing temperature in Kelvin units).

Arrhenius equation curves for zero and first-order reactions based on critical quality parameters of TBA values are presented in Figure 3. Activation energy (Ea) values and the line equation of the Arrhenius curve for various critical quality parameters are presented in Table 2.

Figure 3. Relationship between the value of $1 / T$ to $\ln k$ for the TBA value.
Table 2. The line equation of the Arrhenius curve and activation energy (Ea) values on critical quality parameters.

| Quality parameter | Line equations          | Activation Energy (cal mol⁻¹) |
|-------------------|-------------------------|------------------------------|
|                   | Zero Order               | First Order                  |
| TBA value         | y = 6364.9x – 26.796     | y = 4298.8x – 19.75          | 12 640.69 | 8 537.42 |

The line equation obtained in Table 2 above is based on zero and first-order reactions, then the reaction constant values can be determined on all quality parameters. The temperature value (1 / T) in the Kelvin unit is entered in the line equation, and by performing mathematical adjustments, the reaction rate constants will be obtained (Table 3).

Table 3. The value of the TBA quality parameter reaction rate constants at various storage temperatures using the equation of zero-order and first-order reactions.

| Quality parameter | Storage temperatures | Reaction rate constants (K) |
|-------------------|----------------------|-----------------------------|
|                   | °C       | 1/T (°K) | Zero order | First order |
| TBA value         | -18      | 0.003922 | 0.005599   | 0.003557    |
|                   | -10      | 0.003802 | 0.013498   | 0.010463    |
|                   | -5       | 0.003731 | 0.020228   | 0.013750    |
|                   | 0        | 0.003663 | 0.030766   | 0.018252    |

Table 3 shows the results of research on the value of the reaction rate constant at several storage temperatures. It can be seen that the speed of quality change based on the TBA value parameter increases with increasing temperature. In the Arrhenius model, the temperature is a very influential factor in the decline in the quality of food products. The higher the temperature, the higher the reaction rate. In other words, the higher the T, the higher the k value. This relationship is based on the theory of activation, that a change reaction will begin to take place if given a minimum amount of energy called activation energy (Ea) stated in the equation [12].

\[
\ln k = \ln k_0 - \frac{E_a}{T}
\]

Where, \(E_a\) is the activation energy, the value of which is considered constant (fixed) over a certain temperature range, \(R\) is the gas constant (1,986 cal/mol K), \(T\) is the temperature expressed in Kelvin (K). In this study, the value of \(\ln\) at several temperature levels is related to the storage temperature in Kelvin (K), which is plotted consecutively as ordinate and abscissa (Figure 3).

3.4. The shelf life of the frozen coated tumpi-tumpi
The reaction kinetics of changes in TBA values in previous experiments based on correlation values indicate that the change in TBA values between the kinetics of zero and first-order reactions is almost the same, so the reaction kinetics cannot be determined. Reaction constant values are based on the results of the calculation of the tumped TBA value (Table 3). Determination of storage life of frozen coated tumpi-tumpi is obtained by entering the value of the reaction rate constant in the equation of
the zero-order and first-order reaction rates. The critical quality limit value of TBA is 3 mg malonaldehyde kg\(^{-1}\) sample so that the storage life of frozen coated tumpi-tumpi at -18 °C based on the TBA value parameter is 341.10 days for zero-order and 284.63 days for first-order reactions (Table 4).

| Quality parameter | Storage temperature | Shelf life (day) |
|-------------------|---------------------|-----------------|
|                   | °C  | °K  | 1/T (°K) | Zero order | First order |
|                   |-18 | 255 | 0.003922 | 341        | 284         |
|                   |-10 | 263 | 0.003802 | 141        | 96          |
|                   |-5  | 268 | 0.003731 | 94         | 73          |
| TBA value         | 0  | 273 | 0.003663 | 62         | 55          |

Estimated shelf life, the frozen coated tumpi-tumpi, is calculated using a linear regression equation of parameters that have the lowest activation energy value [13]. The equation obtained to estimate the shelf life the frozen coated tumpi-tumpi \( y = 4298.8x - 19.75 \) with the activation energy \( (E_a) \) changes in TBA value of 8 537.42 cal mol\(^{-1}\) so that the shelf life the frozen coated tumpi-tumpi is obtained for 284.63 days (Table 4).

4. Conclusion
Changes in the quality parameters of frozen coated tumpi-tumpi based on changes in thiobarbituric acid (TBA) values cannot yet be determined by the kinetics of zero or first-order reactions. The results of the activation energy \( (E_a) \) calculation of the frozen coated tumpi-tumpi based on critical parameters of TBA values have the lowest activation energy of 8 537.42 cal mol\(^{-1}\) so that they serve as parameters determining the shelf life of the frozen coated tumpi-tumpi. The calculation results show that the higher the storage temperature of the frozen coated tumpi-tumpi, the shorter shelf life of the product. The shelf life of the frozen coated tumpi-tumpi at a storage temperature of -18 °C is 284 days.

References
[1] Syahrul, Syarief R, Hermanianto J, Nurtama B 2016 Oil content response of tumpi-tumpi to frying process condition International Journal of ChemTech Research. 9 569-574.
[2] Syahrul, Syarief R, Hermanianto J, Nurtama B 2017 The optimization of the frying process of tumpi-tumpi from milkfish used response surface methodology JPHPI. 20 432-445.
[3] Koswara S, Kusnandar F 2004 Case study for estimating the shelf life of food products. Training on Estimating the Expiration Time of Materials and Food Products. Bogor, 1-2.
[4] Herawati H 2008 Determination of shelf life in food products Journal of Agricultural Research and Development. 27 124-130.
[5] Arpah M, Syarief R 2000 Evaluate models of estimating food shelf life from the diffusion of Unidirectional Fick Law Food Industry Technology Bulletin. 11 11-16.
[6] Dermensonlouglo E K, Pougouri S, Taoukis P S 2008 Kinetic study of the effect of the osmotic dehydration pre-treatment to the shelf life of frozen cucumber Innovative Food Science and Emerging Technologies. 9 542-549.
[7] Das A K, Anjaneyulu A SR, Gadekar Y P, Singh R P, Pragati H 2008 Effect of full-fat soy paste and textured soy granules on quality and shelf-life of goat meat nugget in frozen storage Journal Meat Science. 80 607-614.
[8] Apriyantono A, Fardiaz D, Puspitasari N L, Sedarnawati, Budiyanto S 1989 Food Analysis
Laboratory Instructions. Department of food science and technology. IPB University.

[9] Tokur B, Ozkutuk S, Atici E, Ozyurt G, Ozyurt CE 2006 Chemical and sensory quality changes of fish fingers, made from mirror carp (Cyprinus carpio L., 1758), during frozen storage (-18°C) Food Chemistry. 99 335–341.

[10] Hikmawati M 2012 Characteristics of fish nuggets from African catfish (Clarias sp) with fillers and coatings from Bogor taro. Thesis. IPB University.

[11] Ellis M J, Man C M D 2000 The methodology of shelf-life determination. In: Man CMD, Jones AA, editor. Shelf-life Evaluation of Foods. Ed ke-2. (Maryland (US): Aspen) 22-33.

[12] Hariyadi P 2004 Principles for determining and estimating expiration periods and efforts to extend shelf life. Department of Food and Nutrition Technology, Faculty of Agricultural Technology, IPB University.

[13] Haryati, Estiasih T, Heppy F, Ahmadi K 2015 Estimating shelf life using the accelerated shelf-life testing (ASLT) method with the Arrhenius approach to Mojokerto's typical black sticky tape products from sterilization Journal of Food and Agro-Industry. 3 156-165.