Estimating the Shelf Life of Balado “DR” Cassava Chips Based on Free Fatty Acid Parameters with the Accelerated Shelf-Life Test Method Arrhenius Model

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Abstract

Balado cassava chips are one of the processed cassava chips wrapped with Balado seasoning. Balado cassava chips “DR” is one of the cassava chips produced in Sleman, Yogyakarta. The Balado “DR” cassava chip product that has been marketed to shops does not include an expiration date. Whereas information about the shelf life of a food product is one of the important details to be included on the label or packaging. It aims to ensure the quality and safety of a food product when it reaches consumers. During storage, Balado cassava chips can experience a decrease in quality in the form of rancidity caused by the fat content in Balado seasoning due to the hydrolysis process. Free fatty acid analysis or FFA can be used to measure quality degradation caused by the hydrolysis process. The purpose of this study was to estimate the shelf life of Balado “DR” cassava chips based on FFA parameters. The method of estimating the shelf life used is the Accelerated Shelf-Life Test (ASLT) Arrhenius Model. The test parameter used is Free Fatty Acid (FFA). Observations were made every 5 days at 40°C for 20 days and every 7 days at 30°C and 50°C for 28 days. The results showed that the higher the temperature and storage time, the higher the FFA contents. So that the quality of cassava chips decreases with increasing FFA value. Based on FFA analysis, the estimated shelf life of Balado “DR” cassava chips at storage temperatures of 30°C, 40°C and 50°C, respectively, is 20 days, 18 days and 16 days.

Introduction

Cassava chips are snacks made from thinly sliced cassava which is fried, with spices or not (Koswara, 2013). Cassava chips are not a new product for people in Indonesia. With the increasing public interest in these processed products, cassava chips are processed with various flavors. In the research of Harsita and Amam (2019), consumer attitudes towards various processed cassava products are positive or well-accepted. The highest positive value is found in cassava chips because they are considered delicious, practical, and suitable as a snack. Due to increasing customer demand, cassava chips are currently being developed with different flavors. Balado cassava chips are one of them, which are snack products that are widely consumed by consumers because of their spicy and crunchy taste and affordable prices.

Balado cassava chips “DR” is one of the producers of cassava chips for the small and medium-scale food industry (SME) in Sleman, Yogyakarta. Balado “DR” cassava chips do not include an expiration date on the product packaging label. This is because the shelf life of the product has not been estimated scientifically, only from the experience of the manufacturer. To fulfill the obligations of Government Regulation No. 28 of 2004 concerning Food Safety and Government Regulation, based on No. 69 of 1999 concerning Food Labels and Advertisements, all food and beverage manufacturers must ensure that every product sold has an expiration date. This is because it is one of the food information provided by producers to consumers and is a form of health protection for consumers (Indriani, 2020).

The type of packaging used by balado “DR” cassava chips is polypropylene (PP) plastic. However, because
the product was not packaged using a vacuum during packaging, there was still air in the package when it was closed. According to Fajriyani et al. (2019), oxygen in packaging can also affect the process of rancidity. The imperfect packaging process results in chips that are easier to go rancid and sluggish (Afriyanti, 2017). This can also reduce the shelf life of cassava chip products and damage due to air entry (Kusuma, 2015).

According to the Institute of Food Science and Technology, food shelf life is the amount of time between manufacture and consumption when the product is in an acceptable condition taking into account factors such as appearance, taste, aroma, texture, and nutritional content (Swadana & Yuwono, 2014). Therefore, cassava chips outside these conditions can be declared unfit for consumption. According to Nursiti (2017), products that are no longer suitable for consumption are those that have undergone physical and chemical degradation. Quality degradation of cassava chips occurs during storage. At the time of the store, cassava chip products were often placed in places that are not ideal, thus accelerating the decline in product quality. On the other hand, storage and packaging conditions during the shelf life are the main functions that protect the product from physical and non-physical deterioration (Sumiyarto et al., 2013). A decrease in product quality can also be the cause of a decrease in product shelf life (Suwita et al., 2012).

Balado seasoning mixed with cassava chips also contains fat which can make cassava chips susceptible to fat oxidation during storage. This is the result of auto-oxidation of unsaturated fatty acids in fat. Free radicals generated by light, heat, fat peroxide or hydrogen peroxide, heavy metals including Cu, Fe, Co, and Mn, and lipoxidase enzymes can accelerate the auto-oxidation process (Winarno, 2004). This change can make food unetable and classify it as expired material (Arpah, 2001).

The main damage to fats is a rancid taste and odor, a process called rancidity caused by hydrolysis or oxidation. FFA analysis can be used to measure how much food products have been harmed by the hydrolysis process (Winarno, 1997). A high FFA content indicates poor product quality. Food products that become rancid can be identified by the increase in the amount of free fatty acids. By keeping the sample outside of normal conditions so that the product can be degraded faster and its shelf life can be calculated, the Accelerated Storage Life Test (ASLT) method can be used to estimate the shelf life of foodstuffs (Anggraini et al., 2019). The ASLT approach was chosen because it produces excellent accuracy quickly. The critical moisture content approach model and the Arrhenius approach can both be used to implement the ASLT technique. The critical moisture content approach model based on diffusion theory, which is often used in the dry food industry, is based on expiration criteria for changes in moisture content and water activity. Usually, the Arrhenius method model is used to calculate the shelf life of goods that are susceptible to chemical processes such as fat oxidation (Palupi et al., 2011). Therefore, to determine the shelf life of cassava chips balado “DR” in this study used the FFA test parameters with the ASLT method using the Arrhenius approach.

**Materials and methods**

**Materials**

The study was conducted in June-September 2022. This study used cassava chips with balado flavor variants obtained from cassava chips UKM “DR” Sleman, Yogyakarta which were packaged in PP (polypropylene) plastic with a thickness of 0.8 mm. The materials used for the FFA test were 96% alcohol, 0.1 N NaOH, filter paper and 1% PP indicator. The tools used include an incubator (Memmert), digital scale (I-3000), burette, static and valve, electric stove (Maspion), blender (Phillips), beaker (100 ml), measuring cup (50 ml), Erlenmeyer (100 ml), wire gauze, dropper, small jar, funnel, and stirrer.

**Test Sample Preparation**

Balado-flavored cassava chips obtained from the company “DR” which have been packaged in PP plastic are stored in an incubator with different temperatures, namely 30°C, 40°C and 50°C and the FFA content test treatment is carried out with each storage time of every 5 once a day at 40°C for 20 days and once every 7 days at 30°C and 50°C for 28 days.

**FFA Analysis**

The FFA analysis in this study used the AOAC (2005) method. The mashed balado cassava chip sample weighed 5 g and then put into a beaker. 50 ml of 96% alcohol was added to neutralize the sample or dissolve the fat, then the sample solution was filtered with filter paper, and boiled for 10 minutes while stirring. The triglycerides in the sample are hydrolyzed to form free fatty acids on heating after the addition of alcohol. Then 5 drops of PP indicator were added after the sample had cooled. 0.1N NaOH solution was used to titrate the sample, which resulted in a pink color change (not disappearing for 30 seconds). Titration is used to measure the amount of FFA. In this titration method, phenolphthalein (PP) indicator is used because the pH range is alkaline, tends to be colorless, and makes it easier to observe color changes. On the other hand, because NaOH has a strong alkaline tendency, it is used for titration. Then the FFA content can be calculated using the following formula:

\[
\% \text{ FFA} = \frac{BM \times V \times N}{W \times 1000} \times 100\%
\]

**Information:**

- BM FFA = Molecular Weight of FFA (lauric acid = 200)
- V = Volume of NaOH after titration (ml)
- N = Normality of NaOH (N)
- W = Sample weight (g)

**Shelf-Life Calculation**

From three different storage temperatures, three regression equations will be obtained to determine the effect of temperature and storage time of cassava chips, with each equation obtaining the following values:

\[
Y = ax + b
\]

**Information:**

Y = Analysis value
a = intercept  
\( x \) = storage time (days)  
b = slope = quality degradation constant (k) at each storage temperature

Order one, or the relationship between ln k and storage time, and order zero, or the relationship between the value of k and storage time, is used to determine the reaction order to be used. Order selection is determined by taking the value of \( R^2 \) with the highest value from the three regression equations (Herawati et al., 2017).

Order zero:  
\[ t = \frac{At - A_0}{k} \]

Order one:  
\[ t = \frac{\ln \left( \frac{A_0}{A} \right)}{k} \]

Information:
\[ t \] = storage time  
\[ At \] = critical quality  
\[ A_0 \] = initial quality

For the Arrhenius approach, the value of k is written as 1/T and ln k which is the intercept and slope of the linear regression equation:
\[ \ln k = \ln k_0 - \frac{E}{R} (1/T) \]

Information:
\[ \ln k_0 \] = intercept value  
\[ E/R \] = slope value  
\[ R \] = gas constant (1.986 cal/mol.K)  
\[ T \] = storage temperature (273+°C)  
\[ E \] = activation energy value

The Arrhenius equation which is the rate of change of the balado cassava chips will be obtained after obtaining the value of \( k_0 \), which is the pre-exponential factor \( \ln k_0 \) and the activation energy value of the change in the quality of balado cassava chips where \( E = E_a \) with the following equation:
\[ k = k_0 \cdot e^{E_a/RT} \]

The value of the Arrhenius constant at each storage temperature can be calculated using the Arrhenius equation that has been obtained. Based on the reaction order, the reaction equation is used to calculate shelf life. The reaction order equation combines the calculated k values to determine the shelf life of balado cassava chips (Swadana & Yuwono, 2014).

Results and Discussion

FFA content
Based on the results of the study in Table 1, the contents of FFA in cassava chips stored at temperatures of 30°C, 40°C and 50°C increased. The highest contents of FFA were found in cassava chips stored at 50°C. According to SNI-01-4305-1996, regarding the quality requirements of cassava chips, it is stated that the free fatty acid content in cassava chips is a maximum of 0.7%. cassava chips maximum 0.7%. So, the acceptance of cassava chips has reached a critical limit because it has passed the maximum FFA content on day 28 for a temperature of 30°C, on day 20 for a temperature of 40°C and on day 21 for a temperature of 50°C.

Increased contents of FFA are also a sign that cassava chips are undergoing a process of rancidity. The increase in the FFA value also indicates the occurrence of an adverse hydrolysis process. Food products undergo a hydrolysis process when water molecules break down fats or triglycerides to form FFA and glycerol (Ketaren, 2008). Therefore, it can be said that the moisture content of cassava chips also increased with the increase in FFA contents. The oil will be hydrolyzed in water, causing the carbon chains to separate and the formation of free fatty acids (Fajiyani et al., 2019).

| Storage Time (days) | FFA Content Test Results at 30°C | FFA Content Test Results at 50°C |
|---------------------|---------------------------------|---------------------------------|
| 0 (control)         | 0.36                            | 0.36                            |
| 7                   | 0.39                            | 0.47                            |
| 14                  | 0.43                            | 0.69                            |
| 21                  | 0.69                            | 0.79                            |
| 28                  | 0.80                            | 0.95                            |

Table 2. FFA Content Test Results at 40°C

| Storage Time (days) | Average %FFA at 40°C |
|---------------------|----------------------|
| 0 (control)         | 0.36                 |
| 5                   | 0.41                 |
| 10                  | 0.45                 |
| 15                  | 0.60                 |
| 20                  | 0.73                 |

In line with the research of Nurminabari et al. (2022), that fat hydrolysis occurs because fat contains a certain amount of water which breaks down fat into free fatty acids and glycerol. In addition, Wulandari and Fatmaryanti (2021), support the idea that hydrolysis can cause loss of nutritional value and produce unpleasant odors in food products. As a result, the quality of cassava chips decreases with increasing FFA value (Silalahi et al., 2017).

Kinetics of Quality Deterioration of Balado "DR" Cassava Chips During Storage Based on FFA Value

The rate of change in the content of free fatty acids or FFA of cassava balado chips during storage at various temperatures is depicted in Figure 1 which is also a linear regression graph for order zero and for order one shown in Figure 2. By choosing the value of the coefficient of determination (\( R^2 \)) which is greater between zero and first order, the order of the reaction can be determined. Because the value of \( R^2 \) on the zero order is greater than the first order, it can be shown in Figures 1 and 2 that the estimated shelf life of "DR" cassava chips follows the zero order. Because higher contents of \( R^2 \) produce more precise analytical results (Nurminabari et al., 2022).

Based on Table 3, which is a comparison of the value of \( R^2 \) on the order of zero and order one, it can be concluded that the value of \( R^2 \) on the order of zero is greater than the value of \( R^2 \) of order one, so that the estimation of the shelf life of cassava chips balado "DR" based on the analysis of FFA contents using zero order. After determining the reaction order to predict shelf life, the Arrhenius equation can also be determined to calculate the reaction rate constant (k) at the storage temperature of the product used.
Based on linear regression analysis of the relationship between 1/T and ln k, the Arrhenius equation is obtained, namely $y = -1149.1x - 0.3069$. Where the slope value (b) of the equation is the value $-E/R = -1149.1$. Then the value of $Ea$ (activation energy) = 2282,1126 cal/mol.K. so to start the damage reaction of cassava chips balado “DR” requires energy of 2282,1126 cal/mol.K. Then the value of ln $k_0$ is also obtained which is the intercept (a) of the Arrhenius equation ln $k_0 = -0.3069$ and the value of $k_0$ is the pre-exponential factor of ln $k_0$, namely $k_0 = 0.7357$.

After obtaining the value of $k_0$, then the rate of increase in the contents of FFA (k) can be determined by the following Arrhenius equation:

$$k = k_0 e^{Ea/(RT)}$$

The results in Table 5 show that temperature affects the k value of balado “DR” cassava chips when stored. The value of product k increases with increasing storage temperature. The value of k shows how the FFA content of the product changes over time. A higher k value causes the quality to decline faster (Putri, 2016).

**Shelf-Life Calculation**

Based on the first-order quality deterioration equation and the quality degradation reaction kinetics determined in the previous stage, the shelf life of Balado “DR” cassava chips can be estimated. Day-0 of the trial (control) resulted in the initial FFA content of Balado “DR” cassava chips, which was 0.36%. The calculation of shelf life also requires a critical value of FFA contents in addition to the initial quality. The critical value of FFA contents was obtained from the maximum FFA value of the quality requirements of SNI-01-4305-1996 cassava chips, which was 0.7%. So, it can be seen the shelf life of Balado “DR” cassava chips in Table 6 with the first order reaction equation, namely:

$$t = \frac{A_t - A_0}{k} \quad \text{or:} \quad \text{Shelf life} = \frac{(\text{Critical FFA} - \text{Early FFA})}{\text{FFA improvement rate}}$$

### Table 3. Comparison of $R^2$ Values in Order Zero and Order One

| $T$ (°C) | $R^2$ (order zero) | $R^2$ (order one) |
|----------|-------------------|-------------------|
| 30       | 0.8873            | 0.9102            |
| 40       | 0.9955            | 0.9885            |
| 50       | 0.9882            | 0.9696            |

### Table 4. Calculations with the Arrhenius equation

| Temperature | $T$ (°C+273) | 1/T | Slope | ln k  |
|-------------|--------------|-----|-------|-------|
| 30          | 303          | 0.0033 | 0.0169 | -4.0804 |
| 40          | 313          | 0.0032 | 0.018  | -4.0174 |
| 50          | 323          | 0.0031 | 0.0214 | -3.8444 |

The value of the reaction rate constant (k), which can be used to determine the Arrhenius equation, is shown in Table 4. as the slope of the linear regression equation at three storage temperatures. Then plot the Arrhenius equation by plotting the values of 1/T and ln k on the rate of change of FFA contents in Figure 3.

**Table 5. Rate of Increase in FFA Contents of Balado Cassava Chips “DR”**

| Temp (°C+273) | $k_0$ | $e^{Ea/RT}$ | k   |
|---------------|-------|--------------|-----|
| 30            | 0.7357 | 0.0225412    | 0.0165841 |
| 40            | 0.7357 | 0.0254447    | 0.0187203 |
| 50            | 0.7357 | 0.0285076    | 0.0209737 |

The value of $k_0$ of balado “DR” cassava chips, which was 0.36%. The calculation of shelf life also requires a critical value of FFA contents in addition to the initial quality. The critical value of FFA contents was obtained from the maximum FFA value of the quality requirements of SNI-01-4305-1996 cassava chips, which was 0.7%. So, it can be seen the shelf life of Balado “DR” cassava chips in Table 6 with the first order reaction equation, namely:
The shelf life of cassava chips is affected by the increase in free fatty acid contents that occurs due to the increase in water content during storage, which causes a reaction with triglycerides and produces fatty acids and glycerol. The rates of hydrolysis and breakdown of lipids are both accelerated by increasing water content. An increase in water content will also result in a higher concentration of free fatty acids, which are rapidly oxidized and cause rancidity of the product (Hanifah, 2016). Fatty acids undergo reorganization because of complex reactions in the oil, which produce free fatty acids. This allows an increase in free fatty acids through the frying process which can harm fried foods and cause rancidity (Rismariani, 2015). According to Rismariani (2015), the formation of free fatty acids increases with the duration of use of oil for frying.

Conclusion

The shelf life of Balado “DR” cassava chips based on FFA parameters using the Arrhenius model ASLT method at temperatures of 30°C, 40°C and 50°C are 20 days, 18 days, and 16 days, respectively.

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Table 6. Results of Estimating the Shelf Life of Balado Cassava Chips “DR”

| Temp (°C) | Critical Early k | Shelf Life (days) |
|----------|-----------------|-------------------|
| 30       | 0.7             | 0.36              | 0.0166 | 20.50 |
| 40       | 0.7             | 0.36              | 0.0187 | 18.16 |
| 50       | 0.7             | 0.36              | 0.0210 | 16.21 |
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