Shelf life prediction of apple brownies using accelerated method

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Abstract. The aim of this research was to determine shelf life of apple brownies. Shelf life was determined with Accelerated Shelf Life Testing method and Arrhenius equation. Experiment was conducted at 25, 35, and 45°C for 30 days. Every five days, the sample was analysed for free fatty acid (FFA), water activity (\(A_w\)), and organoleptic acceptance (flavour, aroma, and texture). The shelf life of the apple brownies based on FFA were 110, 54, and 28 days at temperature of 25, 35, and 45°C, respectively.

1. Introduction
Brownies are foods from Western countries and now very popular in Indonesia which is actually a kind of pastry. There is one of SMEs (Small and Medium Enterprise) that produce apple brownies in the city of Batu East Java Indonesia. The problem in this SMEs is the industry received many returned brownies products from sales outlets because it has been damaged before expired date. The shelf life is very important as expiring date has to be included on the packaging label. Therefore a re-analysis of the appropriate apple brownies shelf life is required.

Apple Brownies produced by SMEs in the city of Batu contains fat and has a dry texture. According to [1], rancidity is the main problem encountered in foods containing high fat. In addition, degradation mechanism of dry food quality is started by the absorption of water vapour in products [2]. The increasing water content in food lead to deterioration reactions that are mediated by the \(A_w\) product [3]. As a result, dried food such as apple brownies becomes moist, loses vitamins and loses aroma causing damage and is no longer acceptable by the consumers [4].

One method used in determining the shelf life of a product is Accelerated Shelf Life Testing (ASLT). The food product damage will be accelerated by placing products in unnormal conditions for establishing the rate of degradation. In this method the Arrhenius approach is used to know the relationship between storage time and temperature, where this linear equation is considered most appropriate for use at high storage temperatures.

2. Method
2.1 Determination of Initial Characteristics of the apple brownies
Preparation of dried apple brownies to be used in the research. apple brownies are needed as many as 18 boxes, each box containing 8 pieces of apple brownies.
• Preparation and storage of dried apple brownies in 3 storage boxes with temperature 25°C (298K), 35°C (308K), and 45°C (318K).
• Before storage, FFA, A_w and organoleptic test of apple brownies as initial data were performed. Organoleptic tests performed are aroma, taste, and texture using hedonic scale test model.

2.2 Quality Decrease Rate Parameter Selection and Shelf Life Determination of Apple Brownies
• During storage, observations are performed every 5 days for 30 days. Observations were made by taking samples on different packs for each observation and testing the parameters affecting the quality of apple brownies such as; FFA, A_w and organoleptic (flavour, taste and texture).
• The data obtained of FFA and A_w from apple brownies were plotted against time and three equations for different product storage temperatures Y = bx + a will obtained, where x is the storage time (day), Y represents the characteristic value of apple brownies, a is the initial characteristic value of brownies apple, and b is the rate of characteristic change (slope).
• From every linear regression equation is obtained the value of quality decrease rate (k).
• Then the ln k value is plotted with 1/T (K^-1), and the intercept and slope value of the linear regression equation ln k = ln k_o - (E / R) (1 / T) was obtained.
• After the activation energy characteristic of the apple brownies and the constant value k_o is obtained, the Arrhenius equation is calculated by the formula:
  \[ k = k_o e^{(E / R)T} \] ........................................... (1)
Where:
  \( k \) = quality degradation constant
  \( k_o \) = constant (independent of temperature)
  E = activation energy
  T = absolute temperature (K)
  R = gas constant (1.986 cal / mol K)

With using Arrhenius equation, the rate of reaction (k) from the changes characteristic of apple brownies at a predetermined temperature (T) can be calculated. Shelf life determination of apple brownies is done by choosing parameters that have the highest correlation coefficient (R^2). Furthermore, the value of k obtained is entered into the order equation of the reaction:

  \[ A_T = A_o + kt \] ........................................... (2)
Where:
  \( A_o \) = A value at the beginning of shelf life
  \( A_T \) = A value at end of shelf life
  t = shelf life
  k = quality degradation constant

Shelf life of apple brownies for each specified temperature will be obtained.

3. Result and Discussion
3.1. Kinetics of Quality Decrease Rate of Apple Brownies Against Free Fatty Acid (FFA)
Free Fatty Acid (FFA) is one of the parameters used to determine the rate of decline in the quality of apple brownies. FFA shows the amount of free fatty acids in a product. Fig. 1 shows that the FFA value of apple brownies increases with the length of storage time at all three storage temperatures. According to [5], an increase in FFA percentage due to oxidation of the product. The oxidation reaction of apple brownies is caused by the contact of oxygen with fat containing in the apple brownies. Fat is derived from margarine, eggs, and chocolate that being composition of apple brownies.
The choice of the reaction order kinetics from decreasing moisture content is done by comparing the value of $R^2$ in each linear regression equation at the same temperature on order reaction of zero and first order. The chosen reaction order is a reaction order with a larger $R^2$ value. Table 1 shows that the decreasing rate of apple brownies on FFA based on zero order reaction. This is shown from the value $R^2$ zero order > $R^2$ first order at 35°C and 45°C.

Table 1. Linear regression equation for FFA value parameter of apple brownies.

| Storage (°C) | Linear Regression Equation | R² |
|-------------|---------------------------|----|
| Zero Order  | First Order               |    |
| 25          | $y = 0.0122x + 0.1382$    | 0.9680 |
| 35          | $y = 0.0289x + 0.1229$    | 0.9890 |
| 45          | $y = 0.0479x + 0.1321$    | 0.9984 |

3.2. Kinetics of Quality Decreasing of Apple Brownies Against $A_w$

The $A_w$ of apple brownies is directly proportional to the water content analysis. It because the relationship between water content and $A_w$ is indicated by the tendency that higher water content the higher $A_w$. Fig. 2 shows that there is a decrease in the value of apple brownies with the length of storage time in three storage temperature conditions. This is appropriate with $A_w$ analysis conducted by [6], against dried apple snack, which also decreased with length of storage time. According to [7], the value of water content is directly proportional to the value of $A_w$.

Figure 1. FFA value of apple brownies at three storage temperature conditions

The determination of the reaction order kinetics from decreasing moisture content is done by comparing the value of $R^2$ in each linear regression equation at the same temperature on order reaction of zero and first order. The chosen reaction order is a reaction order with a larger $R^2$ value. Table 2
shows that the $A_w$ decrease rate of apple brownies based first order reaction. It is shown from the value of $R^2$ first order > $R^2$ of zero order at temperature 25°C and 45°C.

### Table 2. Linear regression equations for the value parameter of the apple brownie $A_w$

| Storage (°C) | Linear Regression Equation | $R^2$ | First Order | Zero Order |
|--------------|-----------------------------|-------|-------------|------------|
| 25           | $y = -0.0044x + 0.5277$     | 0.6945| 0.7163      |
| 35           | $y = -0.0044x + 0.517$      | 0.8771| 0.8689      |
| 45           | $y = -0.0043x + 0.5082$     | 0.8686| 0.9024      |

### 3.3. Shelf Life Determination of Apple Brownies

Shelf life determination of apple brownies was done based on the parameter of quality which experienced the fastest decline (the highest correlation coefficient ($R^2$) value). Table 3 shows that the largest parameter of $R^2$ is the FFA, with the value $R^2 = 0.9830$ and the activation energy of 12903.836 cal/mol. Therefore, the main parameters in determining the shelf life of apple brownies are measured by FFA value.

### Table 3. The Arrhenius equation: correlation coefficient value ($R^2$) of the apple brownies degradation parameter.

| No | Parameter | Arrhenius equation | $R^2$ |
|----|-----------|--------------------|-------|
| 1  | FFA       | $\ln k = -6496.4 (1/T) + 17.444$ | 0.9830 |
| 2  | $A_w$     | $\ln k = -809.35 (1/T) - 1.9455$ | 0.9052 |

### Table 4. The results of calculating the shelf life of apple brownies store at various temperatures with FFA value parameters.

| Storage (°C) | $k$ value | Shelf Life |
|--------------|-----------|------------|
|              |           | Days       | Month     |
| 25           | 0.012830  | 110.68     | 3.20      |
| 35           | 0.026038  | 54.54      | 1.24      |
| 45           | 0.054300  | 28.09      | 0.94      |

Table 4 shows that the shelf life of apple brownies stored at 25°C, 35°C and 45°C are 3 months 20 days, 1 month 24 days, and 28 days, respectively. Therefore, the best way to store apple brownies is at 25°C.

In addition, it is better if the shelf life or expiration date that listed by SMEs on apple brownies is revised to be 3.20 months because the average of temperature in that city is 25°C. The apple brownies on the outlet should be placed away from sunlight to prevent the damage of apple brownies due to light and solar heat. On the other hand, if the producer want to sell apple brownies in areas or cities that have higher temperatures, then the length of shelf life may be modified according to the average temperature in the area. This can help the SMEs expanding market share of apple brownies.

### 3.4. Quality Decrease of Apples Brownies Organoleptically

The overall result of apple brownies organoleptic test showed that the panelist preferences for taste, aroma, and texture of apple brownies had decreased with the length of storage time at all three temperatures. This is related to the increasing FFA and the decreasing $A_w$ value at storage time. According to [8], decreasing the value of $A_w$ on food affect the process of fat oxidation. Therefore, increased free fatty acids in apple brownies be fathomed make the taste will more not good. This is supported by [5] that the presence of free fatty acids can affect the taste and smell of a product. In addition, it is suspected that the decreasing $A_w$ resulting the harder texture of apple brownies. This is also supported by [7] stated that at high temperature, the water in the product tends to evaporate resulting the harder texture of the product.
Therefore, other alternatives are needed to prevent the decreasing quality of apple brownies and make the product has a longer shelf life. One solution is to add oxygen absorber in the form of a sachet in the apple brownies packaging. Oxygen absorber is generally used to absorb oxygen in food so that the oxidation process can be taken slowly and the shelf life of a product can be extended.

4. Conclusion
The shelf life of apple brownies analysed using ASLT at 25, 35 and 45°C were 110 days, 54 days, and 28 days, respectively.

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