The Shelf-life Prediction of Sweet Orange Based on Its Total Soluble Solid by Using Arrhenius and Q 10 Approach

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Abstract. The information about shelf-life of sweet orange is necessary for its post-harvest handling to reduce the loss facing by farmers and sellers. The study aimed to observe if the Arrhenius and Q 10 models can be used to predict the shelf-life of sweet orange based on its total soluble solid (TSS). The fresh sweet oranges obtained from the market were stored at three extreme temperatures i.e. 55, 65, and 70°C. During the storage, the TSS was analyzed every hour, until the sweet oranges quality had decreased. The TSS was observed by using a hand digital refractometer. The TSS change in linear model was chosen to perform the Arrhenius model since its R-square value was higher than that of exponential model. The study had proved that there was a possibility of using the Arrhenius and Q 10 models to predict the shelf-life of sweet oranges based on its TSS contents. The Arrhenius model of TSS change was and the Q 10 value was 1.92. The real shelf-life of sweet orange at storage temperature 10°C was 18 days. The shelf-life of sweet orange at any storage temperatures can be predicted by, and as the results of drawing this prediction, the shelf-life of sweet orange can be simply calculated by, for more comfortable and easy purposes. However, the shelf-life prediction model of sweet orange should be improved by further study since it contains a relative error above 2%. For further study it is suggested to assure the TSS change at temperature 55°C as well as the ascorbic acid change in order to improve the shelf-life prediction of sweet oranges.

Keywords: Sweet orange, Shelf-life, Total soluble solid, Arrhenius, Q10

1. Introduction

The sweet orange (Citrus sinensis) is one of potential fruits produced in Aceh Province, Indonesia. The central production of sweet orange is Bireuen District with share about 77% of whole production in Aceh Province (Zikria, 2015). Therefore, it is necessary to predict the shelf-life of this product with the objective of to reduce the loss facing by farmers and sellers. The information of shelf-life of sweet orange can be used to organize its post-harvest handling method, and maintain its quality. The farmers can use this information to maintain the production while the sellers can use this information for controlling their stock in the market. method (simulation). One of the simulation methods that can be used to predict the shelf-life of the product is the Arrhenius Model [3-6]. The Arrhenius Model is based on some assumptions i.e. the quality change is caused by a specific reaction during constant temperature without the influence of previous process [7]. The further study of Arrhenius Model is the Q_{10} model provided the more convenient results of the prediction [8]. Therefore, the combination use of Arrhenius and Q_{10} Models is applied to predict the shelf-life of sweet orange.
Since the change of total soluble solid (TSS) values were indicated to the decreased quality of sweet orange [9-11], the study aimed to predict the shelf-life of sweet orange by using Arrhenius and Q\textsubscript{10} models based on its TSS contents.

2. Methodology
The study was conducted at Laboratory of Postharvest Technology, Department of Agricultural Engineering, Faculty of Agriculture, University of Syiah Kuala, Banda Aceh, Indonesia from Mei to October, 2018. The instruments used were refractometer DBR 85 and oven. About 10 kg of sweet oranges were observed.

The fruits were selected based on its size and colour to have the same maturity index. The selected sweet oranges were stored at three extreme temperatures i.e. 55, 65, and 70 °C. During the storage, the total soluble solid (TSS) was observed hourly until the quality of the fruit had decreased indicated by the colour and texture changes. The TSS was measured by using a hand digital refractometer. After calibrated to zero by using distilled water at 20°C, the juice of sweet oranges was placed a few drops on the prism window. Then, by a single press on “meas” button, the instrument starts to test in a few second.

The TSS changes were analysed by using linear model in equation 1 and exponential model using equation 2. The model with the higher R-square was chosen for the next calculation. The rate constant of TSS changes was determined as the slope of the model (k). Furthermore, the slope was calculated as the natural logarithm (ln k) and the temperature in degree Centigrade was transformed to Kelvin as 1/T. The trend line of this curve was used to determine the Arrhenius model. The Arrhenius model is written as equation 3 and the Q\textsubscript{10} is written as equation 4. Finally, the shelf-life of sweet orange was predicted by using equation 5. Previously, another separated experiment by storing the fruits at temperatures 10°C was applied to find out the real shelf-life of this fruits as t\textsubscript{sT2}/g1827=/g1827/g2868−/g1863/g1872.

Where; A is the TSS content of sweet oranges (% brix), A\textsubscript{0} is the initial TSS content of sweet oranges (% brix), t is Storage time (hour), k is rate constant of quality change, k\textsubscript{0} is rate constant without temperature influence, E is the activation energy (cal/mol), T is temperature (K), R is Gas constant (1.986 kal/mol K), t\textsubscript{sT1} is the shelf-life of sweet oranges at estimated temperature (day), t\textsubscript{sT2} is the shelf-life of sweet oranges at temperature basis (day) and T+10 is the storage temperature at 10°C higher.

3. Results and Discussion
3.1. The TSS change of sweet oranges at extreme temperature
Results of TSS changes of sweet oranges during storage at three extreme temperatures can be seen in figure 1-3. The initial TSS content was about 9 to 10 %brix. During the storage, the TSS content had fluctuated irregularly. The final TSS content was between 3 to 5%brix at temperature 65 and 70°C, which cut off more than 50% of its initial values. However, the final TSS content at 55°C was approximately 7% brix. The linear and exponential models of TSS changes are shown in table 1.
Generally, the figures 1-3 explain that during storage, there was a decrease trend of TSS values. The highest rate constant of this changes was observed at temperature 65 °C, while the lowest rate constant was found at temperature 55 °C. According to the R-square values, the models of TSS changes in sweet oranges at temperature 65 and 70 °C are better than the model of TSS change in sweet oranges at temperature 55 °C. On the other word, it is important to repeat the experiment at temperature 55 °C to improve the model. In fact, the linear model of TSS changes of Sweet oranges is better than that of the exponential model recognized by the higher R-square. Therefore, the linear model of TSS changes was used to determine the Arrhenius model.

| Storage Temperature (°C) | Linear Model      | R-square | Exponential Model | R-square |
|--------------------------|-------------------|----------|------------------|----------|
| 55                       | $y = -0.1673x + 8.3182$ | 0.2372   | $y = 8.1741e^{-0.02x}$ | 0.19     |
| 65                       | $y = -0.6555x + 9.8409$ | 0.9014   | $y = 10.507e^{-0.106x}$ | 0.86     |
| 70                       | $y = -0.3755x + 8.0409$ | 0.6354   | $y = 7.9798e^{-0.057x}$ | 0.65     |
| Average                  | 0.591             |          |                  | 0.57     |

However, the results were in contrast as reported by Adnan. He had found that the slight increase of TSS content of sweet oranges during storage had contributed to their broken quality [10]. Similarly,
Aborisade and Sakhale had also confirmed about a slight increase of the TSS content at ambient temperature [9,12]. This difference probably was caused by the extreme temperature applied in this study leaded to the higher TSS changes.

3.2. The Arrhenius Model Based on the TSS changes

The rate constant (k-value) of TSS changes of sweet oranges was recognized from the slope values of those models (figure 1-3). The lists of rate constants can be seen in table 2. The rate constant of TSS change at temperature 55°C was 0.167. As the temperature increased to 65°C, the rate constant also increased to 0.665, corresponded to almost 4 times higher. However, at temperature 70°C, the rate constant of TSS change was lower than that of at temperature 65°C, but it was almost double if it was compared to the rate constant of TSS change at temperature 55°C.

### Table 2. The rate constant value and its natural logarithm of TSS changes of sweet oranges.

| No | Storage Temperature (°C) | Storage Temperature (K) | 1/T (K⁻¹) | k   | ln k           |
|----|--------------------------|-------------------------|-----------|-----|----------------|
| 1. | 55                       | 328                     | 0.003049  | 0.167 | -1.78976       |
| 2. | 65                       | 338                     | 0.002959  | 0.655 | -0.42312       |
| 3. | 70                       | 343                     | 0.002915  | 0.375 | -0.98083       |

**Figure 4.** The plot of ln k and 1/T from the linear TSS model of sweet oranges.

\[
y = -7456x + 21.112
\]

By plotting the natural logarithm of rate constant value (ln k) and 1/T in degrees of K on a graph (figure 4), the Arrhenius model is determined as equation 6. Later, the Arrhenius model can be used to determine the rate constant of TSS changes at any storage temperatures. In addition, the model also explains about the activation energy needed to this reaction. The activation energy of the TSS changes was 14,807 cal/mol. The activation energy of TSS changes in soft drink was also confirmed about 13,030 cal/mol [12].
The comparison of rate constant values between the experiment and the prediction results are shown in table 3. It can be seen that the predicted rate constant follows the theory that the higher the storage temperatures the higher the rate constant values. Now, it can be inferred that if it is compared to the rate constant at temperature 55°C, the rate constant at temperature 65°C is two-fold, whereas at temperature 70°C it is almost three-fold.

| No | k\_experiment | k\_prediction |
|----|---------------|---------------|
| 1. | 0.167 | 0.197 |
| 2. | 0.655 | 0.386 |
| 3. | 0.375 | 0.533 |

Table 3. The comparison of rate constant value between the experiment and the prediction results

3.3. The Q\(_{10}\) approach and shelf-life prediction

By using equation 4, it was found that the Q\(_{10}\) value was 1.92. The real shelf-life of sweet oranges at storage temperature 10°C was found about 18 days (according to the real observation through direct method). Recently, the equation 5 can be written as equation 7. The results of shelf-life prediction of sweet orange can be seen in table 4 estimated by using equation 7. Sakhale and Kapse had determined that the shelf-life of sweet oranges at temperature 30°C was about 5-7 days, whereas the shelf-life prediction of sweet oranges at temperature 30°C was 4.9 days [11]. It means that there is a relative error between 2 and 30%.

\[ t_{s_{\text{T,1}}} = 18 \times 1.92^{(10-\text{T})/10} \]  

(7)

Table 4. The shelf-life prediction (days) of sweet oranges based on its TSS contents.

| No | Storage Temperature (°C) | ts (day) |
|----|--------------------------|---------|
| 1  | 35 | 3.5 |
| 2  | 30 | 4.9 |
| 3  | 25 | 6.8 |
| 4  | 20 | 9.4 |
| 5  | 15 | 13.0 |
| 6  | 10 | 18.0 |

The prediction of sweet oranges shelf-life by using this approach is very important in corresponding to the increase average daily temperature due to the climate change since the prediction can be done at any storage temperature. The relationship of shelf-life and temperature as the results of prediction by using equation 7 is shown in figure 5. It explains that the shelf-life of sweet orange follows the logarithmic model and now it can be written as equation 8. It is suggested that the equation 8 can be used to simply predict the shelf-life of sweet orange rather than equation 7, for more comfortable and easy use purposes.

There is a possibility to extend the shelf-life of sweet orange by the application of technology such as the use of 100 ppm of gibberelic acid, 500 ppm of bavistin and wrapped in LDPE bags of 20% vents [11], curing in hot air at 37°C [9] and dipping in hot water at 45°C for 15 minutes [13]. The prediction
for shelf-life model in this study only can be used for the untreated fruits. In the other words, there is a chance to develop the prediction model for the manipulated fruits following the same approach.

\[ ts = 34.56 \times e^{-0.06T} \]  

(8)

Figure 5. The predicted shelf-life of sweet orange in corresponding the temperature change.

4. Conclusion
The study had proved that there was a possibility of using the Arrhenius and Q_{10} models to predict the shelf-life of sweet oranges based on its TSS contents. The Arrhenius model was performed by using the linear model of TSS change because it was better than that of the exponential model recognized from its high R-square value. The Arrhenius model was \( k = 1.4 \times 10^7 \times e^{-7.456/T} \) and the \( Q_{10} \) value was 1.92. The real shelf-life of sweet oranges at storage temperature 10°C was 18 days. The activation energy of TSS change was about 14,807 cal/mol. The shelf-life of sweet oranges can be predicted at any storage temperatures by equation 7, \( ts_{r1} = 18 \times 1.92^{(10-T)/10} \), and it is suggested to use the equation 8, \( ts = 34.56 \times e^{-0.06T} \), for more comfortable and easy purposes. However, the equation 7 should be improved by further study since it contains a relative error above 2%. For further study, it is suggested to assure the TSS change at temperature 55°C as well as the ascorbic acid change in order to improve the shelf-life prediction of sweet oranges.

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