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Prediction of Storage Life of Shallot Powder by using Acceleration Method

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ABSTRACT

Scarcity of shallot supply often occurs in Indonesia. Production into powder is one of the solutions to overcome the problem. In the form of powder there is an advantage of having a longer shelf life and ease of use. Storability study is very important especially for new food products from result of research and development activities. The purpose of this study were to learn whether using multivariate principle component analysis is beneficial in prediction of shelf life of shallot; and to predict powder soaked with the two anti-browning ingredients (citric acid 1% and sodium bisulphite 500 ppm) by using an acceleration method. Shallot powder samples packed in alufo bags and stored at temperatures of 20 oC, 30 oC and 40 oC. The shelf life prediction using acceleration method through semi-empirical approach to the Arrhenius equation with the critical parameters of the color values (oHue). Principle component analysis (PCA) has a role in reducing number of component for determination of critical parameter. The storage life results showed that the shallot powder with sodium bisulphite soaking has a longer shelf life by 9.3 months at ambient, compared to soaking with citric acid having 7 months. However at lower temperature storage 15 oC, citric acid treatment has longer shelf life (97.4 month) compared to 77.9 month of sodium bisulphite treatment. Therefore, in prediction of shelf life, the PCA can be used if the reduction of number of parameters for critical determinination is required. For ambient and higher temperature distribution of shallot powder it is recommended to use sodium bisulphite whilst for lower temperature distribution, citric acid is recommended.

Keywords:
Predicted storage life; shallot flour; acceleration method; multivariate

1. Introduction

Onion which is one family with shallot comprise several types of sugars, amino acids, vitamins, sulfur components, enzymes, flavonoids, saponins, and minerals (Soininen *et al*., 2012). The antioxidant especially flavonoid was found in the outer layers of the onion (Cheng *et al*., 2013). Antioxidants activities are *i.e.* inhibit oxidative reactions *in vivo* on enzyme systems and help function of self-defense mechanism in the body's cells (Lu *et al*., 2011).

World onion production is 44 million tons per year. This makes onion is second important horticultural product after tomatoes (Mogren *et al.*, 2006). Indonesian use shallot instead of onion and mainly use it for spices of cooking. Indonesia consider shallot is also important commodity since it induces high inflation rate since the price fluctuate all the time. There was a study connecting Kramat Jati, as Jakarta central market to its supplier such as Brebes, Nganjuk, and Cirebon as suppliers of shallot. It takes 6 to 7 month, to stabilize the fluctuation if there is not any intervention to the market system (Susanawati *et al*., 2015).

For food technologist, to overcome the fluctuation is by providing alternative product that has same function such as shallot flour available in the market. So, the dependence of consumers to fresh shallot is reduced, and price is more stable.

Food safety's factors that warrant product is still safe for consumption is shelf life indicator. Storability determination is very important especially for new products of Research and Development. Date that represent product shelf-life is one of the information that must be placed by the manufacturer on the label of food packages. Inclusion of expiry date becomes very crucial for food safety and also providing quality assurance at the time the product reaches the consumer.

The obligation to state expiry dates on food labels is set in the Indonesian Food Act No.7/1996 and Government Regulation. 69/1999 on Food Labelling and Advertising, where every food industry must include expiration date on every package of food products.

Determination of the shelf life of food products can be done by the method of Extended Storage Studies (ESS) and Accelerated Storage Studies (ASS). ESS method known as the conventional methods is used to determine the expiry date. The measurement is by making a series of product, store them under normal conditions and observed the decline in quality up to achieving the level of quality of unacceptable. This method is accurate and precise, but it takes a long time and the sample number for analyses of parameters are abundant.

ASS method by setting an environmental condition, decrease the time of observation by acceleration, reduce the number of necessary samples. The advantage of the method is a relatively short testing time, but still has a high precision and accuracy. Acceleration method is a kinetic method adapted for certain food products (Syarif and Halid, 1993). However, there was a suggestion that the method is improved by the use of the multivariate system on analysis (Cordovaa *et al*., 2011). The multiple regression has been used also in the analysing data for farmer from coastal and agriculture areas was found powerful (Arsyad *et al*., 2014).

Shallot flour is a new product developed in Indonesia, that will be produced by SME (small and medium enterprises) level, so it is necessary to determine product's expiry date. One of new products of research and development that has been tested before it was being applied in the field is tomato paste (Sukasih *et al*., 2008).

Technology improvements in the manufacturing process of shallot powder, especially the prevention of browning and main-tenance of red color pigment needs to be done so that the shallot powder has long shelf life. Browning prevention material that is often be used to prevent browning and maintain red color are sodium bisulphite (Sukasih and Setyadjit, 2016), and citric acid. On similar product acidification treatment with citric acid to pH 4.4 followed by chilling with air on shallot puree able to extend the shelf life to be 8 weeks (Hasimah *et al*., 2009). However, shelf life of product using both simple chemicals have not been determined yet.

The purpose of this study were

a) To observe the benefit when multivariate analysis would be used in determination of shelf life by using ASS.
b) To predict the shelf life of shallot powder soaked with the two simple anti-browning ingredients (1% citric acid and 500 ppm sodium metabisulphite).

2. Materials and Method

Equipment used were chromameter, analytical balance, brother FC sealer, aluminum foil, shallot slicer, thermometers, incubator (20^{o}C, 30^{o}C, and 40^{o}C). The materials used was the Bima shallot varieties, citric acid and sodium bisulphite technical grade. The study was conducted in the laboratory of Indonesian Centre for Agriculture Postharvest Research and Development in April to August 2013.

2.1. Processing of Shallot Powder

Shallot bulbs sorted from the rotten, then peeled to separate the skin. Bulbs were still in the form of round, then were sliced with a slicer tool. This tool is used by moving the wood part back and forth so that sliced shallot with thickness of ± 3 mm dropped from the opening. Sliced shallots were then soaked into two different solutions, namely soaking solution of 500 ppm sodium bisulphite solution for 10 min and 1% citric acid for 30 minutes. After soaking, sliced shallot were rinsed with clean water twice. Sliced shallot was drained in a small perforated zinc plate for ± 30 minutes. It was done to minimise the use of rinsing water. Drained shallots then were put in the cabinet dryer at temperature of 50°C for 10 hours, then they were weighed with analytical balance. The dried shallots then were blendered until smooth and filtered. Shallots powder were ready to be packaged and tested by using of acceleration method.

Shallot powder were packed in aluminum foil packages with dimension of of 10 cm x 10 cm. After neatly packed, each sample was labelled in accordance with its respective treatment such as soaking treatment, storage temperature and replication. The total samples used were 96 bags of shallot flour. Sampling were done on day 0, 4th, 8th, 12th, 16th, 20th, 24th, 28th, 32nd from 3 different temperatures such as 20 ^{o}C, 30 ^{o}C, and 40 ^{o}C. After taken out samples were analyzed for total phenols (Marinova *et al*., 2005), DPPH (Takaya *et al*., 2003), water activity (AOAC, 2005), and color by chromameter (Li *et al*., 2012).

2.2 Prediction of Storage Life of Shallot Flour

2.2.1 Prediction of Storage Life of Shallot Flour

Multivariate analysis performed included: principal component analysis (PCA). The principal component is a weighted linear combination of parameters that is able to explain the origin of the varians of the maximum data (Adiningsih *et al*., 2004). The principal component of a number p of parameters (variables) can be expressed as:

$y_j = a_{1j}\, x_1 + a_{2j}\, x_2 + \ldots\ldots + a_{pj}\, x_p = \underline{a}'\underline{x}$............(1)

and varians of j principal component is:

$Var\ (y_j) = \lambda_j;\ j=1,2,\ldots,p$ ....(2)

λ1, λ2, ..., λp is the root characteristics obtained from the equation:

$|\sum - \lambda_j I| = 0$

$\lambda_1 \geq \lambda_2 \geq \ldots \geq \lambda_p \geq 0.$

Characteristic vector a as a linear transformation of the variable weighting of origin obtained from the equation:

$|\sum - \lambda_j I|\ \underline{a}_j = 0$

Total varians of principal component:

$\lambda_1+\lambda_2+\ldots+\lambda_p = trace\ (\sum)$..........................(3)

and the percentage of the total varians of data that is able to be explained by j principal component is:

$(\lambda_j/\ trace\ (\sum))\ x\ 100\%$ ....(4)

2.2.2 Testing for storage life of shallot powder using acceleration method

The data from experiment on shallot powder packed in aluminum foil bags and stored at three temperatures, namely 20°C, 30°C, and 40°C, then used for calculation on the shelf life with acceleration method. The steps to estimate storage life by ASS method began by identifying the critical parameters that determine the shelf life of the product. The critical parameters of shallot powder selected is the color (chroma). Thus, the data on total phenol, DPPH, and other color breakdown measured by chromameter were not presented in this paper. The second step was to determine the initial quality and minimum expected value of quality. Minimum limit quality is the value of products quality which is rejected by consumers. Next step was the prediction of the decline in the quality of each critical parameter by plotting the data into a kinetical graph by the zero order 0 first order. To see reaction order one was by looking at the value of correlation (R^2) if it was greater the linear. The decline in the quality of zero order was a constant decline in the quality expressed as the following equation (Labuza, 1982).

At – Ao = -kt ……………………………………(5)

where: At = value A at a time of t
Ao = initial value A
k = rate of quality changes
t = storage time

Plot of the relationship between the reduction in quality with storage time on the reaction zero order can be described as follow. Time was plotted as an horizontal axis and reduction in quality as the vertical axis. The relationship is in the form of straight line which declining with the addition of time.

The decline in the quality of first order is expressed as the following equation.

ln At – ln Ao = -kt .... ………..(6)

Plot of the relationship between the reduction in quality (vertical axis, plotted as Ln At) with storage time (horizontal axis) at first order is also declining with the additional time. However, it is not as a straight line but in the form of curved line, an asymptooth to horisontal axis.

After the reaction order determined, the third step was to set the value of the constant (k) which states the relationship between quality score by long storage at each storage temperature of the second critical parameter was selected, then the value of ln k at each storage temperature was plotted with 1 / T.K. the Arrhenius equation can be obtained as follows:

$\ln k = \ln k0 - \frac{Ea}{R} . 1/T$ ....(7)

Where:
k = contant of rate of reaction
ko = constant of pre-exponential
Ea = activation energy (KJ/mol)
R = gas constant 1.987 (kal/mol)
T = absolute temperature (K)

The next step is to calculate the value of k on temperature storage or distribution desired for predictive storage life. K values of this equation are the rate of decline in every day quality. The shelf life of the product predicted by calculating the difference between the initial score and the score at the time the product is rejected divided by the rate of decline in quality (k) on the predicted storage temperature distribution expressed by the following equation:

$ts = (\ln(N0 - Nt))/KT$, ...(8)

rate of reaction firat order, and

$ts = (N0 - Nt)/KT,$ ....(9)

rate of reaction zero order

where :

ts = storage time

No = value of quality parameter at t_o (initial storage)

Nt = value of quality parameter after certain storage time t (critical limit)

K_T = value K at storage temperature T

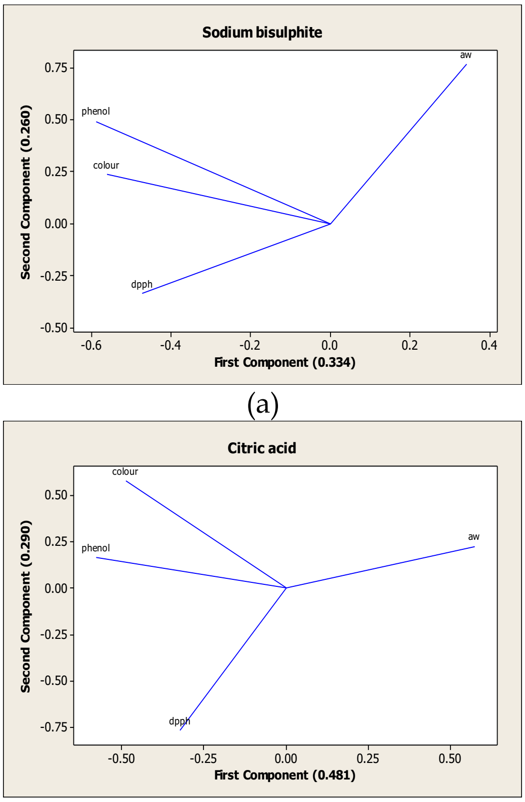
The final step is to set the temperature that we want to know its shelf life.

3. Results and Discussion

3.1. Result

3.1.1 Result of multivariate analysis

Multivariate analysis for all storage conditions (20, 30 and 40 ^{0}C) in the treatment of citric acid and sodium bisulphite were simultaneously analysed using principal component analysis (PCA). PCA results are presented in Figure 1.



(a)

(b)

Figure 1. Loading plot showing the interaction among the quality attributes of 2 PCs a) Citric acid, b) sodium bisulphite

In both citric acid (graph a) and sodium metabisulphite (graph b), it is clear that directions of parameter aw are not the same component to other parameter such as DPPH, phenol and color. Thus, the aw can be excluded from the consideration of critical parameter.

Table 1. Principal components score coefficients

Trt	Var	PC1	PC2	PC3	PC4
C acid	Aw	0.57	0.23	0.66	0.43
	DPPH	-0.58	0.17	0.70	-0.39
	Phenol	-0.58	0.17	0.70	-0.39
	Color	-0.49	0.58	-0.19	0.63
S bisulphite	Aw	0.34	0.77	-0.35	0.41
	DPPH	-0.47	-0.34	-0.69	0.43
	Phenol	-0.59	0.50	-0.21	-0.61
	Color	-0.56	0.24	0.59	0.53

3.1.2. Critical parameter

From some of the results of the observation parameters such as chemical parameters (antioxydants by DPPH assay, total phenols, Aw) and physical parameters (color), in this study defined as the critical parameter is the value of the degree Hoe (color). Selection is based on the stability and consistency of the results obtained data indicated by the highest correlation value. The physical properties measured quantitatively easier than chemical and microbiological properties due to the physical properties tend to be stable. Hoe degrees shallot flour has a correlation value (R^2) which are eligible for a kinetical reaction ($R^2 \geq 0.5$). Hue values range from 60 degrees to 120. Value Hoe of shallot powder with various acceleration treatments such as at different storage temperatures are presented in Table 2.

Table 2. ^{o}Hue of shallot powder on two treatments with three temperature storage acceleration

Storage Temperatur (day)	^{o}Hue		
	20^{o}C	30^{o}C	40^{o}C
Soaking in Sodium bisulphite 500 ppm			
0	85.413	85.413	85.413
4	85.408	85.683	85.738
8	85.351	86.123	95.035
12	85.442	85.536	97.137
16	85.743	87.040	93.342
20	86.047	87.316	99.209
24	86.325	86.847	100.404
28	86.387	87.646	104.422
32	86.611	89.250	106.709
Soaking in Citric acid 1%			
0	79.867	79.867	79.867
4	79.906	78.794	87.026
8	79,807	83.135	91.023
12	79.448	82.335	94.620
16	79.943	81.371	100.822
20	79.747	81.676	110.112
24	80.834	84.122	110.414
28	80.840	83.876	115.415
32	81.300	85.719	118.902

3.1.3. Reaction order

Value decline in the quality of the critical parameters then interpreted using linear regression with the help of Excell program it can be seen the slope, intercept and correlation both on the zero or first order as presented in Table 3.

Table 3. Correlation value of Hue of shallot powder on reaction zero and first order

Treatment/ Storage Temp	Value R^2 Zero Order	Value k	Value R^2 First Order	Value k
Soaking in Sodium bisulphite 500 ppm				
20°C	0.9063	0.043	0.9064	0.0005
30°C	0.814	0.102	0.816	0.001
40°C	0.897	0.642	0.888	0.007
Soaking in Citric acid 1%				
20°C	0.615	0.045	0.614	0.0006
30°C	0.707	0.167	0.705	0.002
40°C	0.983	1.232	0.975	0.012

3.1.4. Result of predicted storage life

Arrhenius equation of storage life of shallot powder on reaction first order as presented in Table 4.

Table 4. Arrhenius equation of storage life of shallot powder on reaction first order

Produce	T (°C)	ln k	T (°K)	1/T (°K)	Linier equation Ln K vs 1/T(°K)	Arrhenius equation Ln K = Ln Ko- Ea/R (1/T)
S Bisulphite 500 ppm	20	-3.150	293	0.0034	Y = -12359X +38.86 R^2 =0.95	Ln K = 38.86 – 12,359 (1/T)
	30	-2.283	303	0.0033		
	40	-0.443	313	0.0032		
Citric Acid 1%	20	-3.093	293	0.0034	Y = -15098X +48.30 R^2= 0.98	Ln K = 48.30– 15,098 (1/T)
	30	-1.793	303	0.0033		
	40	0.208	313	0.0032		

To estimate the shelf life of other storage temperatures such as 25 °C or 35 °C is by inputting the value of the absolute temperature (°K) into the Arrhenius equation to obtain the value of K (constant of decline in quality) then the results are used in the calculation by using equations 8. Estimation results of storability of shallot powder stored on some storage conditions can be seen in Table 5.

Table 5. Predicted storage life of shallot powder stored at various temperatures

Produce	Temperature (^{o}C)	Predicted storage life (months)
Soaked in Sodium Bisulphite 500 ppm	7	265.5
	15	77.9
	25	18.4
	30	9.3
Soaked in citric acid 1%	7	422.5
	15	94.4
	25	16.2
	30	7.0

Remark: Predicted shelf life is based on a critical parameter value which is a hoe critical limit 126 (yellow discoloration limit)

3.2 Discussion

3.2.1 Result of multivariate analysis

Table 1, in this case the model retained 2 PCs. PC 1 (48.1%) and PC 2 (29.0%) which together accounted for 77.1% of the variance for citric acid treatment (Fig 1a). PC 1 (33.4%) and PC 2 (26.0%) which together accounted for 59.4% of the variance for sodium bisulphite treatment (Fig 1b). Aw is inversely proportional to DPPH, phenols and color in the treatment of citric acid and sodium bisulphite (Table 1, Fig 1a and Fig 1b). Dpph, phenol and color directly proportional, so to predict the shelf life can be analysed from one of these variables. In this research, the variables used to estimate shelf life of onion powder is color variable. Cordova *et al*. (2011), suggest that the multivariate is better approach by using a multivariate accelerated shelf-life testing (MAST), since can accomodate all the parameters not only selected one parameter from parameters used. However, whether MAST is better approach compared to the Arrhenius approach for predicting a shelf life is still required to be proven.

3.2.2 Prediction of storage life of shallot powder using accelerated method

Determination of critical parameter

Storage of foodstuffs in certain environmental conditions will cause changes in the food as a result of the process of adjustment to environmental conditions. One of the environmental conditions that affect the change in food is temperature. During storage, shallot flour quality changes such as color changes resulting in lower consumer acceptance. The critical point is determined by the main factors that are very sensitive and can lead to a change in food quality during distribution, storage until ready for consumption.

Color has spectral characteristics which containing 3 main elements, namely the chromatic color (Hue), achromatic or brightness (Value, lightness), and chromatic color intensity (chroma). The level of brightness depends on the intensity of light reflected and absorbed by the sample. If the light is mostly reflected, the sample color tends to white. The intensity of the white color indicates the brightness value. Chromatic color is a color that is produced by the reflection spectrum of colors.

The third dimension is L color that indicates the degree of lightness, the light intensity of the color. L indicates the lightness values, a and b are the chromatical coordinates where a for green color (a negative) to red (a positive) and b for blue (negative b) to yellow (positive b). If the value of L is higher the level of lightness is higher. L-value of 0-100 which represents the chromatic colors white, gray, and black

(Pomeranz and Meloan, 1978). Furthermore, from the values of a and b it can be calculated the formula °Hue: °Hue = tan-1 b / a. Interpretation of the value °Hue presented in Table 6.

Table 6. Interpretation of °Hue value

Result of calculation	Color
18°-54°	Red
54°-90°	Red-yellow
90°-126°	Yellow
126°-162°	Yellow-green
162°-198°	Green
198°-234°	Green-blue
234°-270°	Blue
270°-306°	Blue-purple
306°-342°	Purple
342°-18°	Purple-red

Source : Pomeranz & Meloan 1978.

Hue values range from 60 degrees to 120. Value Hoe of shallot powder with various acceleration treatments such as at different storage temperatures are presented in Table 2. The red color obtained along experiment in the range of degrees Hue value of 18 to 54. Stored shallot flour have a range of 79.86 to 118.9 degrees hue. At the beginning of storage shallot powder with citric acid soaking treatment has Hoe lower value but become opposite at the end of the storage (Table 2). The longer the storage and the higher the storage temperature, the value of the degree of hoe increases and it means leaving red color. This suggests that the higher the storage temperature, the lower the value of L that is visually the colors darker. Dark color is thought to arise due to non-enzymatic browning reactions that occur due to high temperatures.

Determination of reaction order

Determination of the reaction order is a way to predict the degradation behavior in shelf life prediction of shallot powder (Avila, 1999; Lee and Krochta, 2002), mentioned that the reaction to the loss of the quality of food of many reactions described by the order zero and one, and only a few are described by another order. Kinetics of reaction of the decline in the quality usually follows the order of the reaction. Some other reactions that follow the order of the reaction are the oxidative discoloration, rancidity, microbial growth and destruction of vitamins. While that follows the zero order are the enzymatic breakdown, enzymatic browning and oxidation.

The chroma value increased along with the increase in temperature and storage time which indicates the direction of breakdown products *i.e.* the change color (Table 3). The rate of decay of shallot powder during storage is expressed by the value k. The higher the storage temperature, the higher the rate of deterioration due to changes in color, both on the reaction zero and first order. This means that the color change is faster at higher temperatures.

Changes in color values in the shallot powder followed zero-order reaction, because we get a graph that is linear with r values were higher in the zero order than first order (Table 3). Besides the critical factor chroma values have data that consistently decline in the quality with the correlation value (R^2) are comply for reaction kinetics ($R^2 \geq 0.5$).

Correlation values (Table 3) show that there is a tendency the value of R^2 is higher in order zero than order one, although the Sodium bisulphite treatment of 500 ppm at a storage temperature of 30 °C have R^2 values in order zero has only small difference to R^2 value of 0.816 in the order one. The highest value of R^2 was selected to be the reaction order. The difference of R^2 value on research data is not so significant. But still the selection of order is on the linear curve *i.e.* order zero. Zero order is the order in where explains the reaction of enzymatic browning that correspond to the variable used *i.e.* color. Kinetics of enzymatic browning reactions of on onion powder in other study, also follows order zero (Kaymak-Ertekin and Gedik, 2005).

3.2.3 Result of Predicted Storage Life

Production of shallot powder

Shallots are recognized as a major food source containing quercetin such as aglycone and O - glycosylated derivatives. Food industry often process onion using drying and freeze drying technique so that the product has long storage life. The process of making of shallot powder comprises the step of sorting, peeling and slicing, soaking with anti-browning compounds, washing, drying and milling. During the process of peeling and slicing, shallot will release the active compound such as etheric tripropanal sulfoxide which is capable of causing tears. Moreover shallot also produces a distinctive odor emanating from the compound propyl disulfide and propyl - methyl disulphide. This compound serves as a stimulant that stimulates the function of organs so that stimulate nerve sensitivity function and performance of the digestive enzyme (Pérez-Gregorio *et al.*, 2011; Williams *et al.*, 2013). Immersion process aims to prevent browning reactions in the process of making powder. Sodium bisulphite causes sulphitation of the products, thus preventing formation of brown color and then product has long storage life (Adams, 1997).

Citric acid, as a dipping solution, is a tricarboxylic hydroxy acid (2 - hydroxy - 1 ,2,3 - propane tricarboxylic) which can be obtained by extraction of fruit or fermentation process. Citric acid is used as a preservative, preventing damage to the color and aroma, pH regulator, keeping carbonate, flavor boosters, preventing oxidation, giving the cold sensation, and sucrose inverter, as well as produce the dark color of confectionery (Angumeenal and Venkappayya, 2013). Citric acid has a good solubility and stability. Soaking the fruit in a solution of citric acid in the process of semi-wet candied done to lower the pH, color maintenance, improve texture, and flavor addition. The decrease in pH can reduce the rate of reaction. Citric acid can also be used as a chelating agent is a compound which is able to bind divalent metals such as Mn , Mg, and Fe which are needed as catalysts in biological reactions. Preparation of dried shallot for powder for cooking purposes mostly done by industry (Perez-Gregorio *et al.*, 2011).

Prediction value

Shallot powder shelf life is calculated based on the value of ln k of Arrhenius equation. Prediction of shelf life with this equation is following the semi-empirical approach to the method of acceleration. The method uses the kinetic theory which divides the reactions as order zero or one for food products (Syarif and Halid, 1993). Ln k values of the Arrhenius equation is used to predict the shelf life of shallot powder has an invers comparison to storage temperature. If the storage temperature is higher (20°C <30°C <40°C) then the value of ln k in the equation would be lower (Table 4).

Reaction of lost quality in shallot powder explained by a zero order reaction and is only a few explained by other reaction orders. The types of damage of foodstuffs which follow zero order kinetics are enzymatic breakdown reactions, enzymatic browning, and oxidation (Labuza, 1982). The decline in the quality of the zero order reaction is the decrease in quality that is constant in this study only the value of °Hue which is constant and stable.

Arrhenius equation is an equation model used to predict the shelf life of shallot powder. If the k values are applied in the Arrhenius equation, it can be written as follows: ln k = a + b 1/T, so that if any value of k and 1/T is plotted on a graph for each type of shallot powder will be obtained equations as in Table 5. Gradient or slope value (k) states the value of deterioration during storage. Generally speaking, the value of the constants of reaction rate of decrease in quality (K) at each storage temperature can be estimated using the Arrhenius equation is obtained.

Shallot powder products which was prepared with sodium bisulphite treatment, the parameter value Hoe which is decline has equation of Ln K = 38.86-12,359 (1/T), then to predict the shelf life of shallot powder, if kept at a temperature of 15 °C or 288 °K will generate value Ln k = -4.053, meaning that there will be a decrease in chroma value of 0.01736 units per day. The total units of quality until expiry is calculated by subtracting the value of the chroma value of initial of 126 and the critical limit value of 85.413 and resulted in 40.58 absolute unit quality. Estimated shelf life (ts) at 15 °C storage temperature can be calculated with equation 4 to obtain the results of 2337.6 days, equivalent to 77.9 months.

To estimate the shelf life of other storage temperatures such as 25 °C or 35 °C is by inputting the value of the absolute temperature (°K) into the Arrhenius equation to obtain the value of K (constant of decline in quality) then the results are used in the calculation by using equations 8. Estimation results of storability of shallot powder stored on some storage conditions can be seen in Table 5.

The results of this study indicate that the shallot powder with soaking treatment of sodium bisulphite has a longer storage time compared to citric acid when the storage temperature is between 25 °C to 30 °C. Whilst at low storage temperatures from 7 °C to 15 °C, it is showed the opposite (Table 5). Sodium bisulphite is stronger in binding the color while citric acid binding capacity to color of shallot powder not properly maintained along storage.

Onion has sianidin an anthocyanin in the form of 3-glucoside (Rodrigues *et al.*, 2011). Anthocyanins functions as a constituent colors in foodstuffs (Kong *et al.*, 2003). Anthocyanin degradation can occur during extraction, food processing, and storage. Stability and degradation of anthocyanins is influenced by various factors such as light, pH, temperature, sulphite, ascorbic acid, enzymes, etc. Anthocyanin stability can be enhanced by the binding of o-glycosidic, acyl groups on the sugar molecule, metal ion, self association, copigmentation, and encapsulation (Rodriguez *et al.*, 2011).

Storage at low temperatures is essential to prevent the process of discoloration. S - alk (en) ylcysteine sulfoxides produce compound g - glutamyl dipeptide on the catalytically active side GGT (γ - glutamyl transpeptidase), better known as trans - (þ) - S - (1 - propenyl) - L - cysteine sulfoxide (1 - PeCSO) for discoloration process . The process causes the discoloration and the enzyme alliinase located in the vacuole is bonded to the substrate S - alk (en) ylcysteine sulfoxides. The bond formed thiosulfate in the cytosol. Tiosulfinat has a major role in the formation of some amino acids which is the pigment precursor (PP) (Dong *et al.*, 2010). Shallot form pink color is by the contributions tiosulfinat. Ideal circumstances for the stable discoloration or color changes are occurring at acidic pH ranges from 3 to 5. The optimum pH range can accelerate enzymatic and non- enzymatic reactions. The mechanism of color changes in the shallot has not been properly identified so that important contributions of tiosulfinat not entirely known (Zang *et al*., 2013).

This theory supports the results of research on citric acid which is less stable in binding red color of shallot. Citric acid which has a pH of more acidic than sodium bisulphite according to the optimum state of the color change process will accelerate enzymatic and non-enzymatic reaction on shallot powder. The above reaction will accelerate color change. The color stability causes the shelf life of the shallot powder becomes comparable to its color decay. If the color decay is fast then the shelf life will be short.

Shallot flour red color began to fade when acidified and stored at room temperature and more rapidly at elevated temperature. Storage temperature also affects the shelf life. The results of shows the higher the storage temperature of shallot powder then the shorter the shelf life (Table 5). That's because tiosulfinat will be lost during storage so that the amino acids forming the red color will disappear and will form the yellow color. It was the result of non- enzymatic browning reactions. This reaction will cause the interaction of aldehydes, ketones, and reducing sugars by the amino component of amino acids and proteins. This will cause the loss of pink color, flavor, and biological value of protein. Non-enzymatic reaction is also influenced by the temperature setting. Research by (Kaymak-Ertekin and Gedik, 2005), showed that the drying onion powder stored at a temperature of 20 ^{o}C 70 ^{o}C, 30 ^{o}C , and 45^{o}C has a good correlation between tiosulfinat loss and temperature rise. If the storage temperature is higher the value of the lost of tiosulfinat compounds will be higher. The concentration of tiosulfinat which is the constituent of red color in shallot flour will slowly decrease during storage, thus the red color will fade and be replaced with a yellow color.

The use Arrhenius equation on development a kinetic model of quality loss during storage of dried onion slice at various temperature was also reported by (Kaymak-Ertekin and Gedik, 2005). The researcher using various water activity as comparison and using temperature 20^{o}C, 30^{o}C and 45^{o}C as the acceleration conditions whilst at this experiment was used with sodium bisulphite and citric acid were used and the storage temperature used were 20^{o}C, 30^{o}C and 40^{o}C. Thus, the results of both experiments agree that the Arrhenius model is fit for developing a kinetic model. Kaymak-Ertekin and Gedic (2005), however, was using the model for the prediction of the parameter value whilst in this experiment was used to predict the shelf life. Both of the researchers still agree that the Arrhenius model still relevan being used.

4. Conclusion

The use of Multivariate Analyses *i.e.* principal component analysis can reduce the number of parameter prior to critical parameter determination. Color of product such as Hue is the selected critical parameter. Soaking with sodium bisulphite and citric acid have a positive influence on the intensity of the brightness of the color of shallot powder during storage. Both of the preservation methods follow zero order of Arrhenius equation. Soaking with sodium bisulphite have a longer predicted shelf life of shallot powder than the citric acid at higher temperatures for storage such as 25 ^{o}C and 30 ^{o}C. However, at lower temperatures such as 15 ^{o}C and 7 ^{o}C, citric acid treated flour has much longer shelf life prediction. Thus, depend on the market destination and product life expectation, which anti browning is required for production of shallot powder.

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