IOP Conf. Series: Earth and Environmental Science **122** (2018) 012082 doi:10.1088/1755-1315/122/1/012082

Estimation of shelf life of wikau maombo brownies cake using Accelerated Shelf Life Testing (ASLT) method with Arrhenius model

S Wahyuni, Holilah, Asranudin and Noviyanti

Department of Food Science and Technology, Faculty of Technology and Agricultural Industry, Universitas Halu Oleo, Indonesia
Email : sriwahyuni_aan@yahoo.com

Abstract. The shelf life of brownies cake made from wikau maombo flour was predicted by ASLT method through the Arrhenius model. The aim of this study was to estimate the shelf life of brownies cake made from wikau maombo flour. The storage temperature of brownies cake was carried out at 20°C, 30°C and 45°C. The results showed that TBA (*Thio Barbaturic Acid*) number of brownies cake decreased as the storage temperature increase. Brownies stored at 20°C and 30°C were overgrown with mold on the storage time of six days. Brownies product (WT0 and WT1) had shelf life at 40°C approximately six and fourteen days, respectively. Brownies made from wikau maombo and wheat flour (WT1) was the best product with had the longest of shelf life about fourteen days.

1. Introduction

Brownies are one of the most popular cake-based wheat flour, a chocolate cake with attractive colors, a delicious aroma, and a less-fluffy texture [1]. During this time, production of brownies cake using wheat flour. To reduce the dependence on wheat flour and the food development based local resource, substitution of wheat flour is needed in production of brownies cake. One example of local food that can be used to substitute wheat flour is wikau maombo flour. Wikau maombo flour produced from varieties of cassava ie. *Manihot utillisima* and *Manihot esculenta* Crantz, respectively [2-3].

Production of wikau maombo flour is through the process of immersion in sea water, fermentation, drying and milling [2]. Wikau maombo flour has similar characteristics of wheat flour can be seen from the color and texture of flour. Compared with ordinary cassava flour, wikau maombo flour has a better appearance ie. whiter, soft and odorless. Wikau maombo flour has a different content with wheat flour [3]. The fundamental difference in content is that wikau maombo flour does not contain gluten. One of the requirements for the industrialization of brownies cake should have nutritional value information and have information of the shelf life of product.

Based on the description, it is necessary to study the proximate analysis of brownies cake from wikau maombo flour and to estimation of the product shelf life using ASLT (Accelerated Shelf Life testing) with Arrhenius model. So it is known deadline brownies cake that safe to be consumed by society. The ASLT method is a method of estimating shelf life by conditioning food products above normal storage conditions [4]. In the ASLT method the temperature acts as a key parameter determining food damage, because the higher the temperature, the food damage will be faster [5]. The correlation between temperature and speed of deterioration can be seen using the Arrhenius equation.

2. Materials and Methods

2.1 Materials

Cassava (*Manihot esculenta* Crantz) roots were obtained from Buton island, Southeast Sulawesi, Indonesia. Wheat flour, sugar, egg, margarine, vanilla, chocolate powder, dark chocolate and skim milk were purchased from traditional market, Kendari, Southeast Sulawesi. All materials used in this work were analytical grade. Hydrogen chloride (HCl, ≥37%) was purchased from Merck, Germany. Acetic acid (CH_3COOH, ≥99%) and Thiobarbituric Acid ($C_4H_4N_2O_2S$, ≥98%) were purchased from Sigma-Aldrich, Singapore.

2.2 Preparation of Wikau maombo flour

Preparation of Wikau maombo flour used is according to the procedure that have been conducted by Wahyuni *et al.* [2]. Cassava roots were manually peeled, washed with tap water and chipped using a manual chipper. The pieces then immersed in seawater for 3 h. In order to remove mucus formed during immersion, cassava was washed with fresh water. Cassava was fermented for 3 days. Fermentation of cassava was conducted by storing of cassava in closed condition. After fermentation was completed and then dried in oven at 60°C for 24 h. And then the dried cassava millded into powder, sieved (70 mesh) and dried at 60°C for 2 h.

2.3 Preparation of brownies cake

Preparation of brownies cake was carried out by shaking the mixture of egg and sugar until expands for 15 minutes. And then little by little wikau maombo flour that sieved and roasted added. Vanilla, TBM, skim milk, cocoa powder and salt were also added. The dough is stirred until blended well. The melted margarine and chocolate are added to the dough and stir until blended. The dough is then poured into the mold. After that, baked at 160°C for 45 minutes. Production of brownies cake with the addition of wheat flour of 0% and 25% were denoted with WT0 and WT1 samples, respectively.

2.4 Estimation of shelf life of brownies cake

The estimation of shelf life of brownies cake using ASLT method wuth Arrhenis model. Storage of the product was carried out at 20°C, 30°C, 40°C. The test at various temperatures were used to estimate the shelf life from rancidity rates of product through the test of TBA content. Determination of the initial TBA number is the TBA number of product after the production, the initial TBA content of the product is measured before it is placed at various temperature. Determination of critical of TBA number was conducted over a period of time which determined in accordance with Table 1.

Table 1. Parameters for determination of critical TBA number.

Temperature (°C)	Time (day)
20	20
30	10
40	5

3. Results and Discussion

3.1 Determination of k parameter

From observation of brownie cake to time can be plotted and got 3 regression equation obtained from three temperature (20, 30, 40°C) of different storage. From each equation obtained the value of the slope (b) and the constant (k). Determination of the reaction order to be used is the order reaction of zero which is the relationship between the value of k with the time of storage and reaction order of one which the relationship between ln k with the time of storage. From the two equations obtained the largest R^2 selected as the reaction order. For Arrhenius approach the value of k is plotted by 1/T through the linear regression equation ln k = ln k - (E/R) (1/T) with ln ko is intercept and E/R is slope.

Ea is the activation energy and R is the ideal gas constant of 1.986 cal/mol.K (Figure 1). After coefficient values obtained are the pre exponential factor and the activation energy value of the change reaction on the characteristic of brownies where EA = E, Arrhenius equation is obtained which the equation of reaction rate of characteristic change in brownies with the equation k -ko.e-E / RT with T is the storage temperature. From the Arrhenius equation is obtained, it can be calculated Arrhenius constant value in each storage temperature. The parameters that have the lowest activation energy value are the key parameters [8]. The shelf life was calculated using the reaction equation based on the reaction order. To estimate the shelf life of brownies by entering the temperature value into the equation ln k = ln ko - (E/R) (1/T). The obtained k values are included in equation of the reaction order to obtain the shelf life of brownies. Summary of shelf life prediction of brownies (WT0 and WT1) is shown in Table 2.

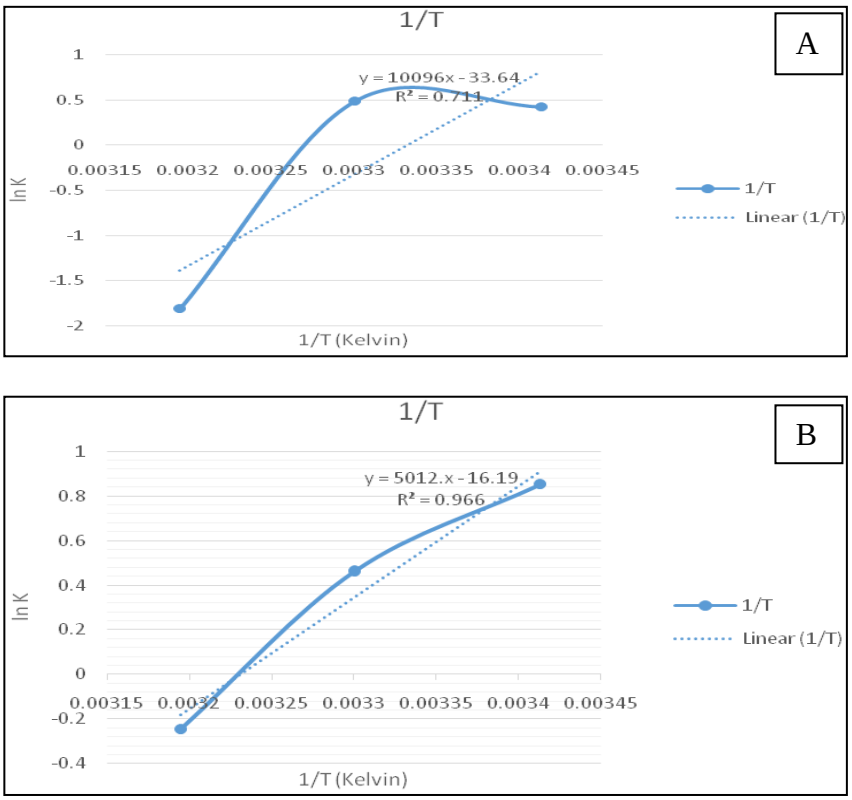

Fig. 1. The relationship of storage temperature (1/T) and In K on WT1 (A) and WT0 (B) samples.

Table 2. Parameters of shelf life prediction of brownies (WT0 and WT1).

Sample	T (K)	K	Initial TBA number	ct/co	Ln ct/co	Shelf life (day)
WT1	313	0.24	0.08	34.96	3.55	14.27
	303	0.72	0.08	34.96	3.55	4.92
	293	2.25	0.08	34.96	3.55	1.57
WT0	313	0.83	0.01	192.30	5.25	6.30
	303	1.41	0.01	192.30	5.25	3.71
	293	2.48	0.01	192.30	5.25	2.11

3.2 Estimatioon of shelf life of brownies using Arrhenius model

Arrhenius model was applied of food products that easily damaged by the result of chemical reaction, such as fat oxidation, Maillard reaction, denaturation of proteins, and so on. In general, the rate of chemical reactions will accelerate at higher temperatures, which means the decrease in product quality is faster [6]. Storage by acceleration method is done to accelerate the process of damage including oxidation reactions that cause rancidity in the product. Acceleration method can be done by raising the storage temperature. In this study, variations of three storage temperatures are used ie temperature 20°C, 30°C and 40°C. During storage, measurement of TBA number was performed. The graph of TBA number for 30 days storage for brownies cake is presented in Figure 2.

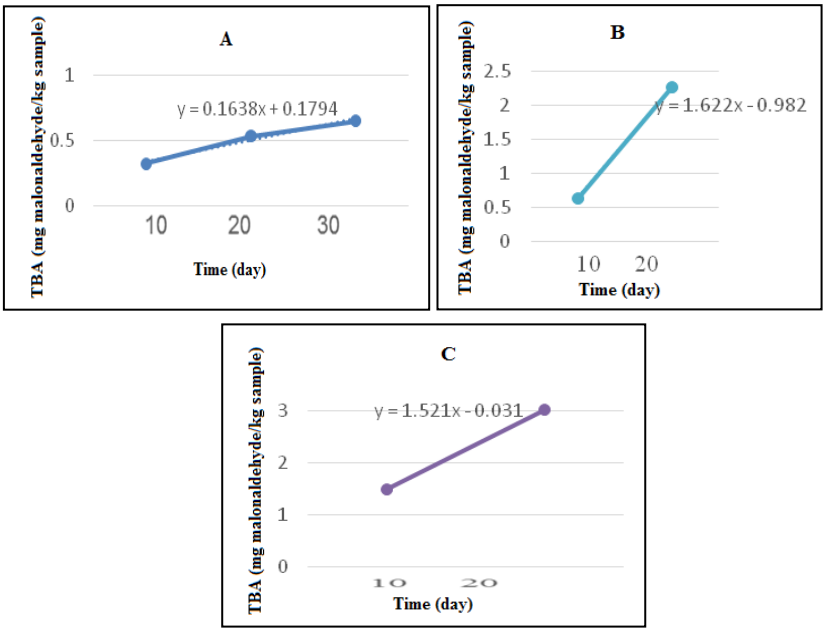

Fig. 2. TBA number of WT1 sample at 40°C (A), 30°C (B) and 20°C (C).

Based on the number of TBA in WT1 sample showed that the value of TBA decreased based on the increase of storage temperature. The storage at 40°C (days 5) showed a TBA number of 0.32 mg/kg sample. While storage days 10 and 15 showed TBA number of 0.53 mg/kg and 0.65 mg/kg sample, respectively. The number of TBA in the sample increases as storage time increases. TBA number at 30°C on days 10 and 20 ie. 0.71 and 2.30 mg/kg smple, respectively. TBA number at 20°C on days 15 and 30 are 1.48 and 3.01 mg/kg samples, respectively. Determination of shelf life of brownies can be estimated through the Arhennius equation at each storage temperature. Temperature increases (20, 30 and 40°C) showed an increase of shelf life of 1.57; 4.9 and 14 days.

WT0 sample (composition of wikau maombo flour 100% and wheat flour 0%) showed that the number of TBA at 40°C with the storage of 5; 10 and 15 days ie. 0.28; 0.58 and 1.84 mg/kg samples, respectively. TBA number increases with the increasing of storage time. Based on the equation of y = 0.7839x-0.663, the estimated of shelf life of WT0 is 6 days. The number of TBA at 30°C with storage time of 10 and 20 days are 0.71 mg/kg and 2.30 mg/kg sample, respectively. While TBA number at 20°C on storage time of 15 and 30 days are 2.32 mg/kg sample and 4.67 mg/kg sample, respectively. The shelf life of brownies on storage temperature of 30 and 20°C ie 4 and 2 days. Determination of shelf life of both brownies formulas through the reaction order of one approach. Figure 3 shows the number of TBA in WT0 sample at different storage temperatures.

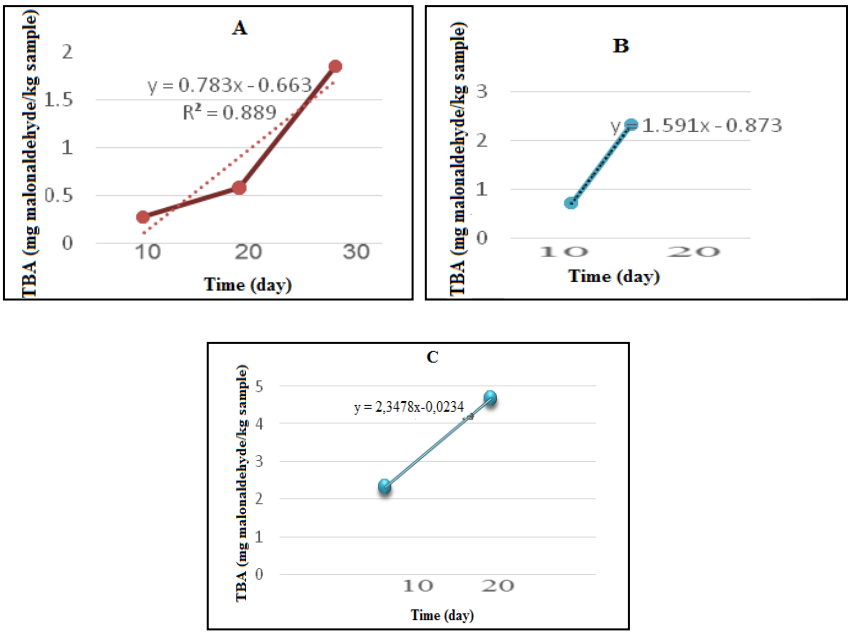

Fig. 3. TBA number of WT0 sample at 40ºC (A), 30ºC (B) and 20ºC (C).

Figures 2 and 3 showed that the increase of brownie storage temperature causes an increase in the number of TBA. TBA number indicates the amount of malonal aldehyde produced due to the fat oxidation reaction. Fat oxidation will gradually produce aldehyde compounds such as (E/Z) hexenal. The shelf life is relatively short because the product is a very rich product of fat and sugar so it is susceptible to damage due to thermal treatment and yeast contamination. To increase the resistance of food products from physical, chemical or biological damage can use various antioxidants and antimicrobials of food grade standard. The use of an additive in food can be a natural or synthetic substance that safe for humans [10-11].

3.3 Parameter of shelf life of selected brownies sample

Characteristics of quality brownies stored at different storage temperatures are significantly altered when storage time of 20 days. Basically, brownie cake products are dark brown as they are influenced by the addition of dark chocolate and cocoa powder. Brownies were stored at room temperature and at 20°C overgrown with mold after storage time of 6 days. Decrease in quality occurs due to oxidation reactions that can cause changes in color, aroma, and texture of the product. In addition, the oxidation process that occurs is also caused by the growth of microbes in large numbers resulting in damage to food characteristics. While the product storage at 40°C until 20 days has not been covered with mold. The storage results of brownies are shown in Figure 4.

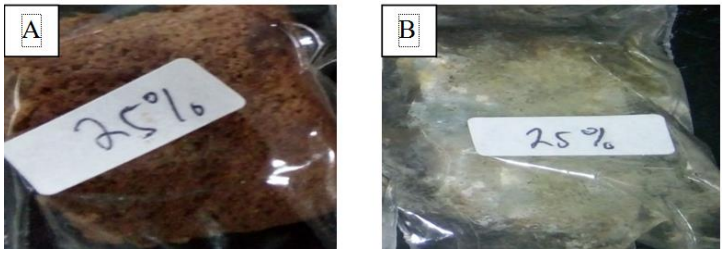

Fig. 4. Brownies before storage process (A) and brownies overgrown with white mold after 6 days storage at 20°C (B).

The extreme temperatures will accelerate the occurrence of product degradation and are often identified as the testing temperature of product shelf life [7]. Temperature control, humidity, and poor physical handling can be categorized as an abnormal food distribution condition. Distribution and temperature conditions will determine the shelf life of food products [8].

Based on the research results of Kusumo [5] has been reported that the shelf life of corn cookies product by Accelerated Shelf Life Test (ASLT) method, Arrhenius model with several parameters ie TBA, hardness, water content and Aw. Dry corn cookies was stored for 6 weeks, the sample is packaged in two different packages (metalized plastic and OPP-PP plastic with a thickness of 60 μm) and stored at 25°C, 35°C, and 45°C. The results showed that the estimation of shelf life, corn cookies packaged in plasticized metal has longer shelf life (2.4 months) than packaged in OPP-PP plastic (2 months). The TBA number (rancidity) is a major indicator in the destruction of corn cake quality. In addition, the shelf life of spirulina biscuit products by Arrhenius method, storage is done at 25ºC and 35ºC with observation interval is 5 days for 30 days. The parameters observed were fat content and peroxide number. The results showed that based on the parameters of packaging fat content that can maintain the quality of spirulina biscuits is packed aluminum foil when stored at 35ºC that can last for 52 days 4 hours 49 minutes [9].

The use of room temperature can lead to greater reaction rate with increasing TBA numbers. If the reaction rate gets faster, then the product will be more quickly damaged which affects of the shelf life. Thus the good shelf life used from the results of this study is storage of WT1 sample at 40ºC because the shelf life of the product the longer the 14 days.

The change of nutritional value such as fat during storage can form rancidity in foodstuffs. According to Ketaren [10], the change of peroxide numbers that occur during storage can suppress the rate of increase in the TBA number. The number of TBA is the most important for determining the degree of damage to fats and oils. The results showed that the number of TBA in brownies increased during storage of seven days at 30°C and 20°C. Bith temperature are suitable for mesophilic microbial growth that can accelerate the damage of brownies. The storage at higher temperature is suitable for WT0 and WT1 samples.

4. Conclusions

Rancidity is a critical quality parameter that affects the damage of brownies. In this study showed that the shelf life of brownies with wheat flour substitution has a longer shelf life at 40°C.

References

[1] Edma AV, Pratjojo W and Budisusatyo E 2015 Indo. Uji proksimat dan organoleptik brownies dengan subtitusi tepung *MOCAF* (Modified Cassava Flour) (Proximate analyses and organoleptic of brownies with *MOCAF* substitution) *Indo Journal of Chemical Sci*ence **4(3)** 168-171.

[2] Wahyuni S, Ansharullah, Saefuddin, Asranudin and Holilah 2017 Physico-chemical properties of Wikau maombo flour from cassava (*Manihot esculenta* Crantz) *Journal of Food Measurement and Characterization*. **11** 329–336.

[3] Wahyuni S, Ansharullah, Saefuddin, Asranudin and Holilah 2016 Characterization of Wikau maombo Flour from Fermented Cassava (*Manihot utilissima*) *International Journal of Chemical, Environmental and Biological Sciences (IJCEBS).* **4(2)** 134-137.
[4] Labuza TP and Riboh D 1982 Theory and Aplication Of Arrhenius Kinetics to The Prediction of Nutrien Losses in Food *Journal of Food Technology*. **36** 66-74.
[5] Kusumo ME 2013 Shelf Life Estimation Of Corn Cookies Packed In OPP-PP And Metalized Plastic Using Accelerated Shelf-Life Testing Method-Arrhenius Equation. [Skripsi]. Program Studi Teknologi Pangan. Fakultas Teknologi Pertanian. Universitas katolik Soegijapranata Semarang.
[6] Hariyadi P dan Andarwulan N 2006 Perubahan Mutu (Fisik, Kimia dan Mikrobiologi) Produk Pangan Selama Pengolahan dan Penyimpanan (Quality changes (Physical, Chemical, Microbiological) in Food Products during Processing and Storage). Di dalam: Modul Pelatihan Pendugaan dan Pengendalian Masa Kadaluarsa Bahan dan Produk Pangan. Departemen Ilmu dan Teknologi Pangan dan Seafast Center IPB, Bogor.
[7] Hariyadi P 2004 Prinsip-prinsip pendugaan masa kedaluwarsa dengan metode Accelerated Shelf Life Test (Principles in determining life-shelf using Accelerated Shelf Life Test method). Pelatihan Pendugaan Waktu Kedaluwarsa (Self Life). Bogor, 1−2 Desember 2004. Pusat Studi Pangan dan Gizi, Institut Pertanian Bogor.
[8] Dewi R 2010 Pendugaan Umur Simpan Keripik Cakar Ayam (ceker) Menggunakan Metode Accelerated Shelf Life Testing Dalam Berbagai Bahan Pengemas [Skripsi] (Determining chicken feet chips shelf-life using Accelerated Shelf Life Testing in various packing materials [Essay]). Fakultas Teknologi Pertanian Universitas Brawijaya Malang.
[9] Astari MD 2015 Pendugaan Umur Simpan Biskuit Spirulina dengan Jenis Kemasan yang Berbeda (Determining Spirulina Shelf-life with different packing materials) *Jurnal Online Mahasiswa (JOM) Bidang Perikanan dan Ilmu Kelautan*. **2(2)** 1-7.
[10] Ketaren S 1986 *Pengantar Teknologi Minyak dan Lemak Pangan (Introduction to Oil and Fat)*. Edisi 1. Jakarta: UI-Press.
[11] Sunaryo E 2002 Pengolahan produk dan biji-bijian. [Skripsi] (Product and cereals processing [Essay]. Jurusan Teknologi Pangan dan Gizi, FakultasTeknologi Pertanian. IPB. Bogor.

Acknowledgments

The authors would like to acknowledge the Directorate General of Strengthening Research and Development, Ministry of Research, Technology and Higher Education, Indonesia for financial support under “MP3EI” grant research.