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THE SHELF-LIFE PREDICTION OF SWEET SOY SAUCE USING ASLT METHOD WITH ARRHENIUS MODEL

Sudarminto Setyo Yuwono, Fasandra Novi Liyundzira*, Eka Shinta Wulandari

Department of Food Science and Biotechnology, Faculty of Agricultural Technology, Universitas Brawijaya
Veteran Street, Malang 65145 East Java Indonesia
*Corresponding Author, Email: fasandra24@student.ub.ac.id

ABSTRACT

Sweet soy sauce is a typical Indonesian soy sauce. One of soy sauce producers in Malang Regency is Jawa Sehati Mulia SMEs. This SMEs has not yet estimated the shelf life of sweet soy sauce product so that the current shelf life refers to other commercial products. The purposes of this study were to determine the characteristics quality and to estimate the shelf life of Tugu Jawa sweet soy sauce. The product was stored at 31, 34, and 37 °C and the organoleptic, microbiological, physical, and chemical characteristics were analysed every seven days. The result showed that the critical parameter was pH because it has the lowest activation energy value. Changes in pH parameter values follow first order with a linear regression equation y = -4.115,68x + 7,33 so that the estimated shelf life of sweet soy sauce was 127,92 days or 4,26 months at room temperature (25 °C).

Keywords: Arrhenius, ASLT, Shelf-life, Sweet Soy Sauce

INTRODUCTION

Sweet soy sauce is a typical Indonesian soy sauce that is used to add aroma and flavor to dishes. In 2019, the total production of sweet soy sauce was 100,424,912 liters (BPS, 2019). One of the soy sauce producers in Malang Regency is the Jawa Sehati Mulia SMEs. However, this SMEs have never estimated the shelf life of their products and the expiration date used currently refers to other commercial products, which is one year. Based on Prasetyawati (2006), the estimated shelf life of sweet soy sauce using the Arrhenius model with treatment temperatures of 27, 42, and 55 °C is 2.5 years with critical parameters of pH changes. Meanwhile, Ginting's (2015) research on the alleged shelf life of Kecap Sari Kecap products produced by PT Lombok Gandaria using the Arrhenius model with treatment temperatures of 27, 45, and 55 °C is 3.12 months with critical parameters of salt content. The difference in the estimated shelf life of sweet soy sauce is influenced by the different ingredients and processes of each producer. Therefore, Tugu Jawa sweet soy sauce produced by Sehati Mulia SMEs needs to be estimated with the Accelerated Shelf-Life Test (ASLT) method of the Arrhenius model.

METHODOLOGY

Materials

The main ingredient was sweet soy sauce brand Tugu Jawa from Jawa Sehati Mulia SMEs packaged in 250 ml bottles. Other ingredients were potato dextrose agar (PDA), buffered peptone water, chloramphenicol, and tartaric acid ($C_4H_6O_6$), 0.1 N NaOH, oxalic acid dihydrate ($C_2H_2O_4.2H_2O$), and phenolphthalein (PP) indicator.

Tools

The main tool used was a Memmert incubator at 31, 34, and 37 °C. Other tools used were laminar air flow (LAF) for mold and bacteria, autoclave (GEA), electric stove (Maspion), supporting glassware, viscometer (Elcometer), hand refractometer (Atago), color reader (Konica Minnolta), vacuum oven (Vacucell), desiccator (Nalgene), burette (Pyrex), and pH meter (Seinz).

Research Design

This research was conducted in two stages. First, determining the initial and final quality characteristics of the product by organoleptic testing every seven days with four panels of sensory experts. Microbiological (total mold and total plate count (TPC)), physical (total soluble solids, viscosity, and color), and chemical (moisture content, total acid, and pH) analyses were conducted on day 0 and on the day the kecap manis product was rejected by the panel of sensory experts to obtain the initial and final quality of kecap manis. In this first stage, the soy sauce was stored at 37 °C. Secondly, data were collected on the quality change of the soy sauce to model the kinetics of quality deterioration during storage at the experimental temperatures. Soy sauce was stored at 31, 34, and 37 °C. Microbiological, physical, and chemical parameters were observed once every seven days until a minimum of five observation points were obtained.

Research Stages

1. Determination of initial and final quality characteristics of Java Monument sweet soy sauce:

Tugu Jawa sweet soy sauce used to determine initial and final quality characteristics was soy sauce stored at a critical temperature of 37 °C. Before storage began, microbiological, physical and chemical tests were conducted as initial values (A0). Then, sensory analysis was conducted every seven days until the sensory expert panel rejected the product. The expert panel amounted to four people who were the owners and employees of Jawa Sehati Mulia SMEs. After the sweet soy sauce product was rejected, microbiological, physical, and chemical analysis is carried out as the final value (A).

2. Estimation of shelf life of Tugu Jawa sweet soy sauce with Arrhenius model:

Sweet soy sauce packed in PET bottles was stored at three temperatures, i.e. 31 °C (304 K), 34 °C (307 K), and 37 °C (310 K). The determination of this storage temperature was based on the level of damage to sweet soy sauce suspected to be caused by microbiological factors (validated by the initial TPC value of sweet soy sauce which was 3.9 x 103). Therefore, the storage temperature method used for acceleration is the optimum temperature for microorganism growth (31, 34 and 37 °C).

Observations of microbiological, physical and chemical parameters were made every seven days until a minimum of five observation points were obtained. The observation results of each parameter were plotted with time (days) to obtain three linear regression equations obtained from three different storage temperatures with the equation y = a + bx, where y = characteristic value of sweet soy sauce, x = storage duration (days), a (intercept) = characteristic value of sweet soy sauce at the beginning of storage, and b (slope) = rate of quality deterioration reaction. In addition, the equation can also produce an R2 value which is used as a determinant of the reaction order used. The reaction order chosen is the larger reaction order. Then, the Arrhenius approach is carried out by converting the value of k into ln k and T into 1/T (K-1) then the two values are plotted to obtain a linear regression equation ln k = ln A - (Ea/R) (1/T) where ln A = intercept, Ea/R = slope, Ea = activation energy, and R = ideal gas constant (1.986 cal/(mol·K)). The reaction rate value (k) can also be obtained from the Arrhenius equation. Then the shelf life of soy sauce is calculated with the reaction kinetics equation based on the reaction order. If the reaction order = 0, then the reaction equation used is A = A0 - kt. If the reaction order = 1, then the reaction equation is ln A = ln A0 - kt where A0 is the product characteristic at t = 0 (the beginning of storage), A is the product characteristic at the end of the shelf life, and t is the shelf life.

Methods

Estimation of the shelf life of Tugu Jawa sweet soy sauce was carried out using the Accelerated Shelf-Life Test (ASLT) method where the product to be estimated is stored at a temperature above room temperature. The analysis conducted includes microbiological, physical, and chemical analysis. The prediction of the reaction of each analysis was approximated by the Arrhenius model.

Analysis Procedure

Organoleptic testing was carried out by assessing the attributes of aroma, taste, viscosity, color, and appearance. Microbiological tests was carried out in determining the initial and final quality characteristics are total plate count (TPC) and total mold. For estimating shelf life with the Arrhenius model, microbiological tests include total mold. Physical tests conducted were total soluble solids, viscosity, and color (L*, a*, b*). Meanwhile, chemical tests carried out were water content, total acid, and pH.

RESULTS AND DISCUSSIONS

1. Initial and Final Quality Characteristics of Sweet Soy Sauce

Based on the test, sweet soy sauce products stored at a critical temperature of 37°C was rejected when entering the 70th day. The average results of the organoleptic test during storage until rejection were listed in Table 1.

Table 1. Average Product Acceptance Test during Storage at Critical Temperature (37°C)

Day-	A	B	C	D	E	Revenue (%)
0	9.01	8.94	8.94	8.59	8.68	100
70	6.36	5.65	6.15	6.18	6.90	0

Table 2. Initial (A0) and Final (A) Quality Characteristics of Sweet Soy Sauce

No.	Analytical Parameter	A_0	A
1	Total plate count (TPC) (CFU/g)	3.9×10^3	4.1×10^4
2	Total mold (colonies/g)	5	0
3	Total soluble solids (oBrix)	74.67	75.27
4	Viscosity (cP)	1300	1187
5	Color		
	Brightness level (L*)	27.1	28.97
	Green-red color intensity (-a* and a*)	-0.7	-1.03
	Yellow color intensity (-b* and b*)	4.2	4.03
	Color change (⊗E)	0.0	1.92
6	Moisture content (% wet basis)	23.52	22.97
7	Total acid (%)	0.68	0.61
8	pH	5.80	4.77

According to the expert panel of Jawa Sehati Mulia SMEs, the factor that caused the rejection of sweet soy sauce in the organoleptic test on the 70th day was the change in taste attributes where a salty taste appeared. The salty taste is thought to be caused by an increase in the number of certain compounds as a result of microorganism activity during storage that can increase the perception of salty taste even though the compounds themselves do not have a salty taste, such as amino acids, dipeptides, and organic acids. Based on Table 2, sweet soy sauce contains mold and other microorganisms shortly after production. These contaminant microorganisms are thought to continue the fermentation activity, increasing the value of amino acids such as arginine. According to Ohta *et al.* (2003), arginine can increase the perception of salty-taste enhancer. In addition, some dipeptides resulting from microorganism hydrolysis in soy sauce that were found to have a positive correlation with salty taste were His-Leu, Leu-Arg, Phe-His, Phe-Ile, and His-Val (Yamamoto et al., 2014). Then, organic acids such as lactic acid as a result of microorganism metabolites can also increase the intensity of saltiness in NaCl (Frankowski et al., 2014). The initial (day 0) and final (day 70) quality characteristics of sweet soy sauce stored at 37 °C are listed in Table 2.

The difference in number between TPC and mold in A0 and A is because the TPC test counts the number of bacteria, molds, and yeasts. Meanwhile, the mold test only counts the number of molds. The difference in trend between TPC and mold is thought to be caused by increased growth of other microorganisms besides mold and the activity of these microorganisms (bacteria) is thought to be antagonistic to mold growth.

2. Reaction Kinetics of Each Analysis Parameter

The reaction kinetics of each analysis parameter were calculated from each product stored at 31, 34, and 37 °C. Furthermore, each reaction kinetics of each parameter was predicted for shelf life by determining the use of zero order or first order. Temperature conversion from °C to K was done for calculation purposes.

2.1 Total mold

SNI 3543.1:2013 regulates that the microbiological contamination of mold in sweet soy sauce is a maximum of 50 colonies/g. The results of observations of mold growth in sweet soy sauce products can be seen in Table 3.

Table 3. Changes in Total Mold at Three Storage Temperatures

	Total mold (colonies/g)		
Time (days)	**Temperature 31 °C**	**Temperature 34 °C**	**Temperature 37 °C**
0	5	5	5
7	10	5	15
14	20	15	50
21	5	5	5
28	5	0	5
42	0	0	0

The increase in total mold until day 14 is due to favorable environmental conditions where one of the influencing factors is temperature. In general, molds grow in a wide temperature range (0-60°C) and grow well at room temperature. According to Lacey (1994), the optimum temperature for growth of *Aspergillus restrictus* species is 30 °C, A. *chevalieri* is 30-35°C, A. *vitis* is 33-35°C, A. *candidus* is 25-32°C, A. *ochraceus* is 24-31°C, and A. *flavus* is 35-37°C.

Meanwhile, mold growth decreased to 0 colonies/g on day 42 and day 70 (based on Table 2). This is suspected to be the presence of anti-mold compounds such as chitinase produced by contaminant bacteria such as *Bacillus sp.* The presence of these bacteria is supported by the TPC test results (Table 2) where on the day of rejection, the TPC value was 4.1x104. According to Muzuni *et al.* (2021), *Bacillus sp.* can produce the enzyme chitinase, which is amycolytic enzyme that can breakdown the main component of the cell wall of fungi, namely chitin. The growth of total mold, which decreased and amounted to 0 colonies/g on the 42^{nd} day, caused this parameter not to be used as a basis for predicting the shelf life of sweet soy sauce because organoleptic analysis Table 1 of sweet soy sauce products stored at critical temperature (37°C) on the 42^{nd} day had not been rejected so the research was still continuing. Therefore, total mold was not calculated using reaction prediction for determining the shelf life of sweet soy sauce.

2.2 Total Dissolved Solids (TDS)

TDS is a parameter that measures the combined content of all inorganic and organic substances contained in foodstuffs. The observation results of changes in the TPT value of sweet soy sauce can be seen in Table 4.

Table 4. Changes in TPT Value at Three Storage Temperature Conditions

	TDS (°Brix)		
Time (days)	**Temperature 31°C**	**Temperature 34°C**	**Temperature 37°C**
0	74.67	74.67	74.67
7	74.77	74.73	74.90
14	74.90	74.83	74.97
21	74.87	74.93	75.00
28	74.93	75.00	75.00
42	74.97	75.07	75.17

The TDS value of sweet soy sauce increases with the length of storage time. The increase in TPT is thought to occur due to the breakdown of complex compounds such as polysaccharides and proteins by enzymes produced by microbes into simple water-soluble compounds. According to Nangin and Sutrisno (2015), amylase enzymes produced by various types of microbes, including *Aspergillus niger* (mold), can catalyze the process of starch hydrolysis to produce glucose, maltose, and dextrin. According to Rahmawati and Yunianta (2015), the sugar component formed from starch hydrolysis has water-soluble properties. In addition, *Bacillus sp.* bacteria and molds (*Aspergillus sp., Penicillium sp., Rhizopus sp., Mucor sp.*) can also produce protease enzymes as protein hydrolysis catalysts that produce water-soluble peptides and amino acids (Yusriah and Kuswytasari, 2013).

Table 5. Predicted Reactions for TDS Parameters

Temperature (K)	Reaction Equation		R^2	
	Order Zero	**Order One**	**Order Zero**	**Order One**
304	y = 0.00673x + 74.72429	y = 0.00009x + 4.31381	0.81168	0.81140
307	y = 0.01007x + 74.68429	y = 0.00013x + 4.31327	0.95839	0.95818
310	y = 0.01000x + 74.76333	y = 0.00013x + 4.31433	0.84691	0.84627

Based on Table 5, the reaction prediction for the TDS parameter follows zero order because the coefficient of determination of the zero order reaction equation is higher than that of first order (R2 zero order > R2 first order).

2.3 Viscosity

Soy sauce is a thick liquid product. This is due to the high carbohydrate content in soy sauce. The observation results of changes in the viscosity value of sweet soy sauce against time at three storage temperatures are presented in Table 6.

The viscosity value of sweet soy sauce decreased with storage time. This phenomenon is inconsistent with the results of changes in total soluble solids (TPT) Table 4 and water content Table 11. Low viscosity can be caused by low TPT and high-water content (Fibrianto *et al.,* 2020). The phenomenon of decreasing viscosity with increasing TPT value is thought to occur due to an increase in the number of low molecular weight compounds such as glucose, maltose, peptides, amino acids, and short-chain fatty acids as a result of hydrolysis of complex compounds such as polysaccharides, proteins, and fats by enzymes produced by microbes such as molds. This is supported by Mauer and Ozon (2004), explaining that one of the factors affecting the viscosity of a solution is molecular weight, so that where the more compounds that have low molecular weight, the viscosity of the solution will decrease.

Table 6. Changes in Viscosity Value at Three Storage Temperatures

	Viscosity (cP)		
Time (days)	**Temperature 31ºC**	**Temperature 34ºC**	**Temperature 37ºC**
0	1300.00	1300.00	1300.00
7	1360.00	1403.33	1423.33
14	1253.33	1310.00	1336.67
21	1183.33	1220.00	1240.00
28	1057.67	1133.33	1200.00
42	1153.33	1210.00	1220.00

Based on Table 7, the reaction prediction for the viscosity parameter follows first order because the coefficient of determination of the zero order reaction equation is lower than that of first order (R2 zero order < R2 first order).

Table 7. Reaction Predictions for Viscosity Parameters

Temperature (K)	**Reaction Equation**		**R^2**	
	Order Zero	**Order One**	**Order Zero**	**Order One**
304	y = -5.63129x + 1323.06190	y = -0.00463x + 7.18797	0.61217	0.59953
307	y = -4.45578x + 1345.95238	y = -0.00353x + 7.20454	0.50734	0.50746
310	y = -3.97959x + 1360.95238	y = -0.00308x + 7.21564	0.51022	0.52321

2.4 Color (L*)

In color measurement with the CIELAB system, the notation L* indicates brightness; a* indicates green-red intensity; b* indicates blue-yellow intensity; and ΔE* indicates the magnitude of the color difference. The observation results of changes in the color value of sweet soy sauce against time at three different storage temperatures can be seen in Table 8.

Table 8. Changes in Color Value at Three Storage Temperatures

	Color (L*a*b*□E)											
	Temperature 31 ºC				**Temperature 34 ºC**				**Temperature 37 ºC**			
Time (days)	**L***	**a***	**b***	**ΔE***	**L***	**a***	**b***	**ΔE***	**L***	**a***	**b***	**ΔE***
0	27.10	-0.67	4.17	0.00	27.10	-0.67	4.17	0.00	27.10	-0.67	4.17	0.00
7	27.00	-1.23	3.77	0.91	26.37	-1.23	4.27	1.00	26.97	-1.23	4.43	1.03
14	25.73	-1.37	4.40	1.85	24.60	-1.30	4.43	2.60	24.30	-1.23	3.93	2.96
21	24.63	-1.13	3.60	2.63	24.47	-1.83	3.60	3.06	24.90	-1.13	3.57	2.60
28	24.00	-1.40	3.53	3.30	24.50	-1.37	3.73	2.76	24.93	-1.27	3.60	2.42
42	22.34	-1.70	2.87	5.07	22.57	-1.80	3.83	4.51	23.00	-1.57	3.63	4.07

Table 9. Coefficient of Determination (R2) of Each Color Notation (L*a*b*⊗E*)

	Coefficient of Determination (R2)		
Color Notation	**Temperature 31ºC**	**Temperature 34ºC**	**Temperature 37ºC**
L*	0.97995	0.91417	0.78947
a*	0.72461	0.65574	070186
b*	0.70096	0.38807	0.62318
⊗E*	0.99813	0.86520	0.71543

Based on Table 9, the L* notation has the highest R2 value compared to the other notations so it was chosen to be the parameter used to estimate the shelf life based on color parameters. Table 8 explains that sweet soy sauce changes in brightness with the length of storage. On day 0 to day 42, there was a decrease in the brightness of soy sauce products which was thought to be caused by the production of pigment compounds by molds. This is supported by Ashok *et al.* (2014) that *Aspergillus sp*. and *Penicillium sp.* can produce melanin which is a dark brown to blackish pigment. However, the final value of L* notation in the quality of sweet soy sauce Table 2 has a value of 29.0, resulting in an increase in brightness after the 70^{th} day of storage. This phenomenon can be explained by the degradation of the dominant pigment of sweet soy sauce, melanoidin, as a result of the Maillard reaction during cooking, which contributes to the dark brown color by the metabolites of contaminant bacteria such as *Bacillus sp.* According to Det-Udom *et al.* (2019), *Bacillus amyloliquefaciens* is capable of de-browning using enzymes. This tanning reduction activity is due to the degradation, depolymerization, and breaking of large amounts of C=C, C=O, and C≡N bonds in melanoidin by the enzyme laccase.

Table 10. Predicted Reaction for Brightness Parameter (L*)

Temperature (K)	**Reaction Equation**		**R^2**	
	Order Zero	**Order One**	**Order Zero**	**Order One**
304	y = -0.12088x + 27.39095	y = -0.00488x + 3.31303	0.97995	0.98102
307	y = -0.10143x + 26.82667	y = -0.00409x + 3.29087	0.91417	0.91897
310	y = -0.09306x + 26.93714	y = -0.00371x + 3.29436	0.78947	0.79348

Based on Table 10, the reaction prediction for the brightness parameter (L*) follows first order because the coefficient of determination of the zero-order reaction equation is lower than that of first order (R2 zero-order < R2 first-order).

2.5 Moisture Content

Moisture content is an important parameter because it is one of the factors to determine food durability or stability. The observation results of changes in the water content value of sweet soy sauce can be seen in Table 11.

Table 11. Changes in Moisture Content Value at Three Storage Temperatures

Moisture Content (% wet basis)			
Time (days)	**Temperature 31ºC**	**Temperature 34ºC**	**Temperature 37ºC**
0	23.52	23.52	23.52
7	23.43	23.46	23.31
14	23.31	23.37	23.25
21	23.34	23.28	23.21
28	23.28	23.21	23.21
42	23.25	23.15	23.06

Table 12: Predicted Reactions for Moisture Content Parameters

Temperature (K)	**Reaction Equation**		**R^2**	
	Order Zero	**Order One**	**Orde Zero**	**Order One**
304	y = -0.00626x – 0.00626	y = -0.00027x – 0.00027	0.81168	0.81251
307	y = -0.00936x – 0.00936	y = -0.00040x – 0.00040	0.95839	0.95902
310	y = -0.00930x – 0.00930	y = -0.00040x – 0.00040	0.84691	0.84882

Based on Table 12, the reaction prediction for the moisture content parameter follows first order because the coefficient of determination of the zero order reaction equation is lower than that of first order (R2 zero order < R2 first order).

2.6 Total Acidity

According to Lioe *et al.* (2012), lactic acid is the most dominant organic acid in soy sauce. The observation results of changes in the total acidity value of sweet soy sauce can be seen in Table 13.

Table 13. Changes in Total Acidity Value at Three Storage Temperatures

	Total Acid (%)		
Time (days)	**Temperature 31ºC**	**Temperature 34ºC**	**Temperature 37ºC**
0	0.68	0.68	0.68
7	1.05	1.12	1.15
14	0.70	0.77	0.84
21	0.65	0.67	0.67
28	0.52	0.55	0.56
42	0.35	0.38	0.40

The increase in total acidity up to day 7 is due to the formation of organic acids produced by microorganisms such as molds where on day 7 the total number of molds has increased Table 3. According to Yang *et al.* (2016), metabolites in the form of organic acids produced by *Aspergillus niger* are citric and gluconic acids, A. *terreus* produces itaconic acid, and A. *oryzae* produces kojic and malic acids. *Penicillium sp.* molds can also produce oxalic and propionic acids (Wang *et al.,* 2022).

Then, the decrease in total acidity after day 7 can be caused by the neutralization reaction of organic acids by alkaline compounds such as ammonia (NH3+). Ammonia comes from the hydrolysis of amino acids such as asparagine and glutamine catalyzed by bacterial enzymes such as *Bacillus subtilis* and other contaminant bacteria (Liu *et al.,* 2022). Prihanto *et al.* (2020) reported that *Bacillus subtilis* can produce L-asparaginase to hydrolyze the amide bond of L-asparagine into aspartic acid and ammonia. In addition, Yulianti *et al.* (2012) stated that L-glutaminase can be produced by bacteria, yeasts, and molds to hydrolyze the gamma-amido bond of the amino acid glutamine into glutamic acid and ammonia.

Table 14. Reaction Prediction for Total Acidity Parameters

Temperature (K)	Reaction Equation		R^2	
	Order Zero	**Order One**	**Order Zero**	**Order One**
304	y = -0.01196x + 0.88157	y = -0.02039x – 0.33952	0.60590	0.71935
307	y = -0.01206x + 0.92014	y = -0.01924x – 0.35966	0.54116	0.65848
310	y = -0.01216x + 0.94371	y = -0.01867x – 0.37281	0.51051	0.62239

Based on Table 14, the reaction prediction for the total acid parameter follows first order because the coefficient of determination of the zero order reaction equation is lower than that of first order (R2 zero order < R2 first order).

2.7 pH

According to SNI 3543.1:2013 on sweet soy sauce, the quality requirements for the pH of sweet soy sauce range from 3.5-6.0. The observation results of changes in the pH value of sweet soy sauce at three different storage temperatures can be seen in Table 15.

The pH value decreases with the length of storage time. This is caused by the formation of organic acids produced by the growth of microorganisms such as molds and bacteria. Molds such as *Aspergillus sp.*, *Penicillium sp.*, and *Rhizopus sp.* which are contaminants in sweet soy sauce products can produce organic acids such as citric, gluconic, itaconic, kojic, malic, oxalic, and propionic acids (Wang *et al.,* 2022). Although based on Table 3 the molds amounted to 0 colonies/g on day 42, other contaminant microorganisms such as bacteria are also capable of producing organic acids that contribute to the decrease in pH of sweet soy sauce. According to Yan *et al.* (2013), *Bacillus sp.* such as B. *lichenformis* and B. *subtilis* can produce malic, lactic, acetic, citric, succinic, propionic, and butyric acids.

Table 15. Changes in pH Value at Three Storage Temperatures

	pH		
Time (days)	**Temperature 31 °C**	**Temperature 34 °C**	**Temperature 37 °C**
0	5.80	5.80	5.80
7	5.51	5.49	5.48
14	5.39	5.38	5.46
21	5.33	5.29	5.30
28	5.40	5.35	5.34
42	5.23	5.20	5.10

Tabel 16. Prediksi Reaksi untuk Parameter pH

Suhu (K)	Persamaan Reaksi		R^2	
	Orde Nol	**Orde Satu**	**Orde Nol**	**Orde Satu**
304	y = -0.01122x + 5.65286	y = -0.00204x + 1.73202	0.73972	0.74937
307	y = -0.01208x + 5.64386	y = -0.00221x + 1.73040	0.75486	0.76574
310	y = -0.01441x + 5.68229	y = -0.00266x + 1.73771	0.87090	0.88079

Based on Table 16, it can be seen that the reaction prediction for the pH parameter follows first order because the coefficient of determination of the zero-order reaction equation is lower than first order (R2 zero order < R2 first order).

2. Estimation of Sweet Soy Sauce Shelf Life with Arrhenius model

In this study, the parameters used to predict shelf life were TPT, viscosity, brightness, moisture content, total acid, and pH. Table 17 is a linear regression equation plotting 1/T and ln k which is the Arrhenius equation for each parameter.

Table 17. Arrhenius Equation for Each Parameter

No.	Analysis Parameters	The Arrhenius Equation
1	Total dissolved solids (oBrix)	y = -6.297,77x + 15.56
2	Viscosity (cP)	y = 5.458,74x – 16.25
3	Brightness (L)	y = 4.327,27x – 19.57
4	Moisture content (% wet basis)	y = -6.295,26x + 12.55
5	Total acidity (%)	y = -56.132,37x + 181.28
6	pH	y = -4.115,68x + 7.33

The activation energy (Ea) is obtained from the Arrhenius equation by examining the slope of the line, where the slope is equal to Ea/R, with R having a value of 1.986 cal/(mol·K). Therefore, the value of Ea can be obtained by multiplying the slope value by the value of R.

Table 18. Activation Energy (Ea) Values for Each Parameter

No.	Parameter Analisis	Energi Aktivasi (kal/(mol·K))
1	Total padatan terlarut (TPT) (°Brix)	12372.31
2	Viskositas (cP)	10841.07
3	Kecerahan (L)	8593.95
4	Kadar air (% basis basah)	12502.39
5	Total asam (%)	111478.88
6	pH	8173.74

The parameter used to estimate the shelf life of sweet soy sauce is the parameter with the lowest activation energy (Ea), which is the pH value. According to Hariyadi (2019), the Ea value represents the minimum energy level required to initiate a change reaction. The rate constant (k), which indicates the rate of deterioration, can be obtained from the Arrhenius equation using the pH parameter and is used to calculate the shelf life of sweet soy sauce at different temperatures.

Table 19. Calculation Results of Shelf Life at Various Temperatures with pH Value Parameters

Temperature		**Value of k**	**Shelf life (t) (days)**
ºC	**ºK**		
21.0	0.003401	0.00127	154.36
25.0	0.003356	0.00153	127.92
28.3	0.003319	0.00178	109.96

The various temperatures in Table 9 are the retail storage temperatures of sweet soy sauce such as in supermarkets and other convenience stores. According to Halim and Kattu (2020), the average supermarket temperature is 21°C so that sweet soy sauce stored at supermarket temperatures has a shelf life of approximately 154.36 days. The temperature in convenience stores is assumed to follow the average temperature of the marketing area where sweet soy sauce is currently marketed in several areas such as DKI Jakarta and Surabaya. According to the Meteorology and Geophysics Agency (BMKG) (2023), the average temperature of DKI Jakarta Province and Surabaya City in 2022 is 28.3°C so that the estimated shelf life of sweet soy sauce is 109.96 days. However, the shelf life stated on the soy sauce label can only refer to one temperature, namely room temperature (25°C). Therefore, the shelf life of sweet soy sauce is 127.92 days or 4.26 months.

CONCLUSION

Determination of the shelf life of sweet soy sauce using pH parameters and reaction kinetics used to predict shelf life is first order. The linear regression equation from the Arrhenius plot of the pH parameter was y = -4.115.68x + 7.33 with R2 = 0.94395. The activation energy value obtained was 8.173,74 cal/(mol·K) and the rate of deterioration (k) was 0.00153. The shelf life of sweet soy sauce stated on the label uses a reference room temperature of 25°C with a shelf life of 127.92 days or 4.26 months

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