

Kinetics Study of Time Temperature Indicator Label Based on Red Palm Oil and Soybean Oil Blends

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Abstract. Pasteurized milk is a perishable food. Time Temperature Indicator (TTI) labels can display temperature changes in real time based on variations in storage temperature over a predetermined period of time. The research discussed the time temperature indicator from a mixture of red palm oil (RPO) and soybean oil. The study aimed to determine the ability of the indicator to predict changes in the quality of pasteurized milk and determine the best oil mixture ratio variation that can be used in TTI indicators. The research was conducted with variations in the mixing of RPO and soybean oil, namely A (70%: 30%), B (60%: 40%), C (50%: 50%), D (40%: 60%), and E (30%: 70%) and storage temperatures of 8, 29, 44 and 51°C. Then, the length, rate, and diffusion coefficient and activation energy (Ea) were calculated. Calculation of total microbes in milk samples was done by storing milk at 8, 29, 40°C. Ea values that meet the standard range from 34-50 kJ/mol. The study showed that the selected indicators used were the highest Ea value indicator (E) 41.6889 kJ/mol. and the indicator with the highest percentage of MSM mixture (B) 37.2667 kJ/mol. The Ea value of the pasteurized milk sample is 44.021 kJ/mol, so the difference between the Ea of the product and the Ea of the indicator has met the standard. This means that both indicators are below the maximum Ea difference value limit that is said to be good (<25 kJ/mol). **Keywords:** activation energy, pasteurized milk, red palm oil, soybean oil, time-temperature indicator label.

1 Introduction

One of the basic human needs is food. Food is necessary for human survival and is a key component in improving the quality of human resources. Along with global population expansion, there is a growing demand for fresh and processed food products. Fresh food products typically have a short shelf life, while processed foods have a longer shelf life but still lose quality during storage. Therefore, food product storage management is important to maintain freshness. One way to do this is by storing food products at low temperatures, also known as refrigeration[1].

For food products, namely cow's milk, pasteurization is one way to increase the shelf life of milk without significantly changing its physical properties[2]. In Indonesia, the average shelf life of pasteurized milk products is around 5-7 days. However, storage at low temperatures, below 10°C, has been shown to extend the shelf life of pasteurized milk products compared to storage at room temperature. This is because low temperatures can slow the growth of bacteria that damage the quality of pasteurized milk[3]. Pasteurized milk is more susceptible to bacterial contamination if left at room temperature for extended periods[4]. However, dairy products stored at low temperatures also

require attention. The longer the storage time, the more likely it is that existing bacteria will emerge and reproduce after adapting to the cold temperatures[3].

The changes in storage temperature of a product, especially pasteurized milk, significantly affect its quality and shelf life. Therefore, an indicator is needed that can predict changes in the quality of pasteurized cow's milk and monitor product storage temperatures with appropriate stability. This indicator is one of the inventions in intelligent packaging, namely the Time-Temperature Indicator (TTI) label, which can display temperature changes in real time based on variations in storage temperature over a predetermined period[5].

The stability of the TTI indicator at low temperatures is a critical point of the indicator. This TTI indicator is typically used for food products that require low temperature storage and are perishable. Furthermore, this indicator label is expected to have good sensitivity to increases in storage temperature and be more stable at low temperatures. Therefore, the TTI indicator must use a liquid with a low melting point and stable viscosity.

If palm oil is applied to an indicator, the indicator will work well because palm oil has a characteristic diffusion length[5]. However, room temperature is the only temperature range within which the indicator can be

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applied. This is due to palm oil's poor stability at low temperatures. However, the blending palm oil with other vegetable oils is one way to lower the oil's melting point and viscosity, provided that the oils being blended must have lower melting points and viscosities to achieve stability in the palm oil[6]. Therefore, in this study, the raw materials for making the TTI label indicator will use red palm oil (melting point 20.7°C) and its blend, soybean oil, which has a melting point of -22°C.

There were two objectives of this research. First objective was to identify the ability of TTI label to predict the pasteurized milk quality changes. Second objective was to determine the best ratio of red palm oil and soybean oil that can be used in TTI label.

2 Materials and Methods

2.1 Tools and Materials

The materials used in this research were red palm oil (Salmira, PT. Nutripalma Abadi, Bogor), soybean oil (Sania, PT. Wilmar Nabati Indonesia, Jakarta), waterproof glossy photo paper 10 cm x 2.0 cm x 0,01 cm as the medium of diffusion (Printech).

The tools were incubator oven (Mettler, GmbH), refrigerator Samsung RT20 (Samsung Electronics Co., Ltd), beaker glass 500 mL (Iwaki pyrex), beaker glass 250 mL (Iwaki pyrex), hotplate, and infrared thermometer GM320 (Shenzen Capital Electronics Co., Ltd.)

2.2 Methods

This study was conducted in three stages. First, blending the red palm oil and soybean oil in five different ratios: 70:30 (A), 60:40 (B), 50:50 (C), 40:60 (D), and 30:70 (E). The oil blend was heated in 40 °C with stirring for 10 minutes. Second, diffusion length was measured at four different temperatures (8, 29, 44 and 51 °C). The diffusion length measurement was performed with soaking the photo paper (as medium) in 2 mL of oil blend for 30 hours. The data was used to calculate the diffusion coefficient and kinetics. Diffusion coefficient (D) was calculated by equation: $D = \frac{x^2}{2t}$(1), D was diffusion coefficient (cm²/hour), x was diffusion length (cm), and t was time (hour). Diffusion kinetics was calculated by using first order Arrhenius equation: $\ln D = -\left(\frac{E_a}{R}\right)\frac{1}{T} + \ln D_0$(2), D was diffusion coefficient (m² s⁻¹), E_a was activation energy (KJ mol⁻¹), R was ideal gas constant (8.314 J mol⁻¹ K⁻¹) and T was temperature (K). Third, Activation energy (E_a) comparison between diffusion kinetics with total microbial analysis of pasteurization milk from previous research[7].

2.3 Data Analysis

The statistical analysis was conducted by Analysis of Variance with SPSS v.22. The kinetics was calculated by Microsoft Excel 2019.

3 Result and Discussion

The diffusion coefficient value was calculated based on the square of the diffusion length (x) in the photo paper medium in cm² versus the diffusion time (t) in hours. As can be seen in Figure 1, the diffusion coefficient value showed a higher result or faster diffusion rate as the storage temperature increased.

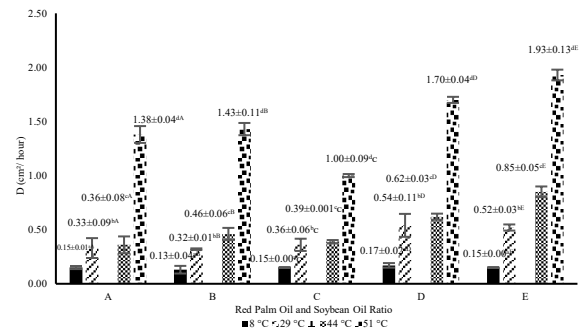


Figure 1. Indicator diffusion coefficient (D) at several storage temperatures

The reaction rate was closely related to the chemical reaction that occur in a substance that forms the reaction products. Chemical reactions occur as a result of collisions between molecules of the reacting substances. Increasing the fraction of molecules with kinetic energy exceeding the activation energy was achieved by increasing the temperature. Therefore, temperature affected the reaction rate, which could increase the rate of the reaction.

The obtained diffusion coefficient values would be used to determine the activation energy (E_a, kJ/mol) of each oil mixing treatment. Activation energy (E_a) is the minimum amount of energy required for a reaction to occur. Activation energy can be calculated using the ln form of the Arrhenius equation[8]. This means the diffusion coefficient values must be translated or converted from the linear form to the ln D form. The ln D values for each indicator type (y-axis) were then plotted against the 1/T value (x-axis), where T (temperature) is first converted from Celsius to Kelvin[9]. The plotting would produce the linear line and a linear regression equation that conforms to the Arrhenius equation (equation 3), or could be simply described by the equation y = a(x)+b. The resulting slope value (E_a/R) could be used to determine the activation energy (E_a), provided the R value is 8.314 J/mol K.

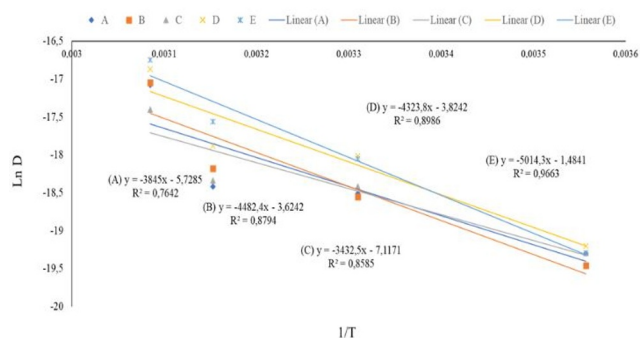


Figure 2. Indicator 1/T and ln D Plot

Figure 2 showed the results of plotting ln D against 1/T. The linear regression equation for each indicator, resulting in an overall indicator Ea value of (A) 31.9673 kJ/mol, (B) 37.2667 kJ/mol, (C) 28.5378 kJ/mol, (D) 35.9481 kJ/mol, and I of 41.6889 kJ/mol. Compared to the commercial Ea values[10], the indicator Ea values that meet the standards are in the range of 34-50 kJ/mol. Therefore, the indicator Ea values that meet the standards were indicators B, D, and E. Indicators A and C did not meet the standards.

Temperature influenced the resulting Ea value and was a reflection of the diffusion rate (reaction rate)[11]. As the activation energy increased, the effect of temperature on the reaction rate became more significant, and the indicator became more sensitive to temperature changes. Based on this statement, if ranked by sensitivity level, indicator E, with the highest Ea value, was the indicator with the highest sensitivity, followed by indicator B, while indicator D had a sensitivity that was not better than indicators B and E.

The activation energy (Ea) values used are Ea indicator B and Ea indicator E. The Ea indicator E value showed the best sensitivity in monitoring product shelf life. Meanwhile, the Ea indicator B value showed the best value when viewed from the use of the main raw material, namely red palm oil, with the highest ratio of 60%. It should be noted that differences in the Ea values of the selected indicators were also influenced by the fatty acid content of the indicator base materials used, namely red palm oil and soybean oil. Based on their chemical structure, fatty acids could be categorized as saturated fatty acids (SFA), or fatty acids without double bonds. Meanwhile, unsaturated fatty acids are fatty acids that contain double bonds. Unsaturated fatty acids are further divided into monounsaturated fatty acids (MUFA), which have one double bond, and polyunsaturated fatty acids (PUFA), which contain one or more double bonds[12]. At room temperature, saturated fatty acids are solid, while unsaturated fatty acids are liquid. PUFAs (polyunsaturated fatty acids) are liquid at room temperature and remain liquid at cold temperatures. Conversely, MUFAs (monounsaturated fatty acids) are liquid at room temperature, but solidify when stored at cold temperatures. This is because PUFAs have a lower melting point than MUFAs or SFAs.

Table 1. Fatty Acids Composition of Red Palm Oil (%w/w) [13]

Fatty Acid	Content
Lauric acid (C12:0)	0.12
Myristic acid (C14:0)	0.61
Pentadecanoic acid (C15:0)	0.03
Palmitic acid (C16:0)	34.05
Palmitoleic acid (C16:1)	0.09
Heptadecanoic acid (C17:0)	0.06
Stearic acid (C18:0)	2.87
Oleic acid (C18:1)	36.39
Linoleic acid (C18:2)	9.13
Arachidonic acid (C20:0)	0.22
Linolenic acid (C18:3)	0.26
Cis-11, 14-Eicosadienoic acid (C20:2)	0.03
Behenic acid (C22:0)	0.03
Lignoceric acid (C24:0)	0.06
MUFA	37.83
PUFA	36.48

Table 1. displayed the fatty acid composition of red palm oil [13] and Table 2 displayed the fatty acid composition of soybean oil[14]. The ratio of red palm oil to soybean oil in indicator B was (60:40) %v/v, while in indicator E was (30:70) %v/v. This ratio indicated that the volume of soybean oil in indicator B was not higher than that in indicator E. This meant that the fatty acid composition, especially polyunsaturated fatty acids (PU), in indicator E was higher than that in indicator B. From this comparison, it could be concluded that the high activation energy value of indicator E was also influenced by the fatty acid composition in the sample. Because at cold temperatures (8°C), indicator E remained liquid and would continue to diffuse, resulting in a higher diffusion coefficient than indicator B.

Table 2. Fatty Acids Composition Soybean Oil (%w/w)[14]

Fatty Acid	Content
Palmitic acid (C16:0)	16.95
Stearic acid (C18:0)	5.15

Oleic acid (C18:1)	16.02
Linoleic acid (C18:2)	47.57
Linolenic acid (C18:3)	12.11
Arachidonic acid (C20:0)	1.40
Eicosenoic acid (C20:1)	0.42
Behenic acid (C22:0)	0.39
SFA	23.89
MUFA	16.44
PUFA	59.68

A good time-temperature indicator is one that has a difference between the activation energy of the product (pasteurized milk sample) and the activation energy of the indicator of ≤ 25 kJ/mol [15]. The difference between the Ea value of pasteurized milk and the Ea value of the selected indicator is shown in Table 3, where the calculation results indicate that the difference is below 25 kJ/mol. This proves that the indicator selected in this study is suitable for monitoring or indicating changes in the quality of pasteurized cow's milk based on microbiological damage. The smaller the difference in Ea value between the product and the indicator, the more similar the pattern between the indicator and the product being measured. Therefore, the indicator's performance will also improve.

Table 3. Activation Energy (Ea) value of Time Temperature Indicator (TTI) and pasteurized milk

Ea value of TTI (KJ/mol)	Ea value of pasteurized milk (KJ/mol)[7]	Ea value of pasteurized milk – Ea value of TTI (KJ/mol)
37.267 (B)	44.021	6.755
41.689 (E)	44.021	2.333

4 Conclusion

A Time-Temperature Indicator label made from red palm oil and soybean oil is capable of predicting the quality of pasteurized cow's milk. It showed by calculating the difference in activation energy of the milk product compared to the selected indicator, which was (B) 6.7550 kJ/mol and (I) 2.3328 kJ/mol, below 25 kJ/mol. The best ratio variations of red palm oil and soybean oil that could be used as TTI label indicators to predict changes in the quality of pasteurized cow's milk are variation B with a ratio of 60%:40% (v/v) and variation E with a ratio of 30%:70% (v/v).

References

1. N. Asiah, L. Cempaka, K. Ramadhan, and S. H. Matatula, Prinsip Dasar Penyimpanan Pangan Pada Suhu Rendah, 1st ed., vol. 1, (CV. Nas Media Pustaka, Makassar, 2020).
2. N. D. Kristanti, Daya Simpan Susu Pasteurisasi Ditinjau dari Kualitas Mikroba Termodurik Dan Kualitas Kimia. *Jurnal Ilmu dan Teknologi Hasil Ternak*. **12** (1), 1–7. (2017).
<https://doi.org/10.21776/ub.jitek.2017.012.01>
3. R. Fauziah, Pengaruh Suhu Pasteurisasi dan Lama Penyimpanan Susu Pasteurisasi di Refrigerator Terhadap Cemaran Bakteri *Staphylococcus aureus* dan Kualitas Susu, Universitas Islam Negeri Maulana Malik Ibrahim Malang, Malang, (2024).
4. L. A. Nababan, I. K. Suada, and I. B. N. Swacita, Ketahanan Susu Segar pada Penyimpanan Suhu Ruang Ditinjau dari Uji Tingkat Keasaman, Didih, dan Waktu Reduktase, *Indonesia Medicus Veterinus*. **3**(4), 274–282. (2014).
5. A. Khairunnisa, N. Edhi Suyatma, and D. Robiatul Adawiyah, “LABEL TIME-TEMPERATURE INDICATOR MENGGUNAKAN CAMPURAN MINYAK NABATI UNTUK MEMONITOR MUTU MIKROBIOLOGI SUSU PASTEURISASI,” *Jurnal Teknologi dan Industri Pangan*, vol. 29, no. 2, pp. 195–200, Dec. 2018, doi: 10.6066/jtip.2018.29.2.195.
6. R. Widyasaputra, M. P. Bimantio, H. Oktavianty, A. Ruswanto, and Ngatirah, “KARAKTERISTIK VISKOSITAS DAN TITIK LELEH PADA CAMPURAN MINYAK SAWIT MERAH DAN MINYAK JAGUNG,” *PROSIDING SEMINAR NASIONAL INSTIPER*, vol. 1, no. 1, pp. 225–232, Jul. 2022, doi: 10.55180/pro.v1i1.258.
7. R. Widyasaputra, R. F. Syah, A. Ruswanto, and M. Y. Fau, “Reliability of Time-Temperature Indicator From Corn and Red Palm Oil Blending For Monitoring Microbial Growth of Pasteurized Milk,” *Food ScienTech Journal*, vol. 5, no. 2, p. 116, Dec. 2023, doi: 10.33512/fsj.v5i2.18094.
8. Q. U. Putri, D. Augustin, and H. Hasanudin, “Kinetika Esterifikasi Asam Lemak Bebas dari Sludge Industri Crude Palm Oil (CPO) Menggunakan Katalis Komposit Montmorillonite/Karbon Tersulfonasi dari Tetes Tebu,” *ALCHEMY Jurnal Penelitian Kimia*, vol. 18, no. 1, p. 48, Feb. 2022, doi: 10.20961/alchery.18.1.50470.48-57.
9. R. Widyasaputra, A. Ruswanto, N. Ngatirah, and S. Sunardi, “DEVELOPMENT OF TIME-TEMPERATURE INDICATOR FROM RED PALM OIL AND MAIZE OIL BLENDING,” *Jurnal Pangan dan Agroindustri*, vol. 10, no. 3, pp. 151–157, Jul.

- 2022, doi:
<https://doi.org/10.21776/ub.jpa.2022.010.03.3>.
10. M. F. F. Poças, T. F. Delgado, and F. A. R. Oliveira, “Smart Packaging Technologies for Fruits and Vegetables,” in *Smart Packaging Technologies for Fast Moving Consumer Goods*, John Wiley & Sons, Ltd, 2008, ch. 9, pp. 151–166. doi:
<https://doi.org/10.1002/9780470753699.ch9>.
 11. R. A. Hurley, A. Ouzts, J. Fischer, and T. Gomes, “Effects of Private and Public Label Packaging on Consumer Purchase Patterns,” *Packaging Technology and Science*, vol. 26, no. 7, pp. 399–412, 2013, doi:
<https://doi.org/10.1002/pts.2012>.
 12. R. A. D. Sartika, “Pengaruh asam lemak jenuh, tidak jenuh dan asam lemak trans terhadap kesehatan,” *Kesmas*, vol. 2, no. 4, pp. 154–160, 2008.
 13. A. Marliyati and R. Harianti, “KARAKTERISTIK FISIKOKIMIA DAN FUNGSIONAL MINYAK SAWIT MERAH,” *Jurnal Gizi Masyarakat Indonesia*, vol. 10, no. 1, p. 83, 2021, [Online]. Available:
<https://www.researchgate.net/publication/353175127>
 14. A. Metalisa, “EVALUASI PEMBERIAN MINYAK NABATI TERHADAP PROFIL LIPIDA DARAH SECARA IN VIVO,” Universitas Jember, Jember, 2018.
 15. H. R. Park, K. Kim, and S. J. Lee, “Adjustment of Arrhenius activation energy of laccase-based time–temperature integrator (TTI) using sodium azide,” *Food Control*, vol. 32, no. 2, pp. 615–620, Aug. 2013, doi:
10.1016/J.FOODCONT.2013.01.046.