Development of smart TTI label based on kinetics diffusion of vegetable oils blends for cold supply chain monitoring

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Abstract. Time-temperature control is a critical issue in cold supply chain, so it is very important to be tracked. Time-temperature indicator (TTI) label is devices that visually show the cold-chain accumulated history, from both time and temperature fluctuation effects. Diffusion model of TTI’s indicator based on vegetable oils blend (VOB) has been investigated. The VOB indicators were made from canola oil (CA), soybean oil (SB), and olive oil (OV) that have blended with palm oil (PO). Nine formulas of indicator were designed in combination with the oils blendings i.e (A) PO:CA:SB, (B) PO:SB:OV, (C) PO:CA:OV and the combination of various ratio were (1) 50:40:10 %v/v, (2) 50:25:25 %v/v, and (3) 50:10:40 %v/v, then the blendings were added 0.25 %m/v red lake (C.I. 16255). The diffusion kinetics of this TTI indicators have tested on a waterproof hotopaper material and storaged at 4, 18, 29, 37, and 40°C. The result present that the activation energy (Ea) values of indicator were about 28.925 – 40.646 kJ mol⁻¹. The B3 and C indicators have an Ea value which have matched with Ea value of a commercial diffusion-based TTI. Based on Arrhenius equation, the diffusion model (x, m) for B3, C1, C2, and C3, respectively were $x_{B3}^{0.5} = 2t \cdot e^{-4017/(1/T)-4.4053}$, $x_{C1}^{1.5} = 2t \cdot e^{-4124.3/(1/T)-4.0196}$, $x_{C2}^{0.5} = 2t \cdot e^{-4245.1/(1/T)-3.7130}$, and $x_{C3}^{0.5} = 2t \cdot e^{-4888.9/(1/T)-1.6641}$. Overall, the diffusion length of the indicators have significantly correlation with time-temperature changing and this diffusion model established can represented the diffusion behaviour of TTI’s indicators.

Keywords: kinetics diffusion, smart TTI label, supply chain

1. Introduction
Diffusion-based of Time-Temperature indicator (TTI) is one of intelligent packaging innovation in a label formed. TTIs are devices that visually show the cold-chain accumulated history, from both time and temperature fluctuation effects. Temperature fluctuation makes the colored indicator diffuses irreversibly in a medium. This diffusion indirectly indicates the storage time and product quality decreasing (shelf life) based on temperature fluctuation [1].

The TTI and food packages is a system that used to monitors the condition of a product in real time, so it used to give an information about the transport and storage condition of the product and establishes the actual quality before consumption. Overall, the development of TTI head to decreases product waste phenomena and increases a more efficient management of products [2, 3, 4, 5].

The oils and some fatty acids (i.e isopropyl palmitic) have been used as indicator for diffusion based TTI [1, 5, 6]. Octaviasari [6] reports that using palmitic oil as TTI’s indicator was results a typical diffusion length. The diffusible materials for TTI’s indicator must have a specifically activation energy (Ea) value (33–50 kJ mol⁻¹) [7]. The Ea value of palmitic oil as TTI’s indicators was effected by the
reaction (diffusion) rate. In order to decreases the palmitic oil’s Ea value, rate of reaction must be increased. In the case of TTI, reaction rate of indicators was effected by the indicator’s viscosity. The indicator’s viscosity must be decreased to gets an indicator with low Ea. A blends methods between two or more oils which have different viscosities have reported as potential solution for decrease the viscosity and Ea values of final oil blends as TTI’s indicator [8, 9]. Decrease the viscosities have effected by increased the unsaturation fatty acids chain length [9]. For that reasons, PO as potentially material must be blended with some vegetable oils which high in mono or poly-unsaturated fatty acids and low saturated fatty acids, i.e canola oil (CA), soybean oil (SB), and/or olive oil (OV).

The kinetics models of TTI needs to calculated. A systematic kinetic models of a TTI and a targetted product is a prerequisite for aplications the TTI [4]. By using reliable models of the product shelf-life and the kinetics both product and TTI, the effect of temperature can be monitored. For kinetics models, the TTI and product must be storaged under isothermal and/or dynamic temperature condition, for simulates the real storage [4, 10, 11]. The aims of this work were to developed a model for TTI’s indicator diffusion prediction by investigated the indicator’s viscosity and calculated the Ea values by the systematic kinetic models.

2. Experimental Section
2.1. Materials and Instrumentation
Four edible vegetable oils i.e palm olein (PO, PT SMART Tbk, Jakarta, Indonesia), canola oil (CA, Mazola), soybean oil (SB, Happy Soya Oil), and olive oil (OV, Bertolli) and C.I. 16255 red lake (PT Centra Lautan Pewarna) for coloring the indicators were used and purchased from a commercial source. Waterproof photopaper, 10 x 2.0 x 0.01 cm³, respectively (Glossy Photopaper, Printech®), used as diffusion medium.

2.2. Procedures
2.2.1 Indicator preparation. Nine formulas of indicators prepared by blended the (A) PO:CA:SB, (B) PO:SB:OV, and (C) PO:SB:OV in (1) 50:40:10, (2) 50:25:25, and (3) 50:10:40 (%v/v solution) with heating at 40°C using magnetic stirrer, then 0.25% w/v C.I. 16255 red lake added to solution (modification from [12]). Nine (9) formulas of the indicators show in table 1.

| Indicators | Ratio Proportions (%v/v) | C.I 16255 (%m/v) |
|------------|--------------------------|-----------------|
| PO CA SB OV |                          |                 |
| A1         | 50 40 10 -               | 0.25            |
| A2         | 50 25 25 -               | 0.25            |
| A3         | 50 10 40 -               | 0.25            |
| B1         | 50 - 40 10               | 0.25            |
| B2         | 50 - 25 25               | 0.25            |
| B3         | 50 - 10 40               | 0.25            |
| C1         | 50 40 - 10               | 0.25            |
| C2         | 50 25 - 25               | 0.25            |
| C3         | 50 10 - 40               | 0.25            |

2.2.2 Viscosity. The viscosity of indicators determined by viscometer Rotational Dial Reading (Brookfield Engineering Labs Inc, USA) at three different temperatures (18, 29, and 40°C) using 60 RPM (rotation per minutes), spindle number 1 for 29 and 40°C, while spindle number 2 and 3 used for samples at 4°C.

\[
\text{Viscosity (mPas)} = \text{dial reading} \times \text{correction factor}^* \\
\]

*correction factor value based on spindles and speeds used.
2.2.3. Indicator’s diffusion length (x, cm). Photopaper medium dipped in a 2 mL indicator and stored at isothermal temperatures of 4, 18, 29, 37, and 40°C, respectively, using Leec compact incubator and B6200 Heraeus instrument Kelvitron® incubators for 30 hours. When the colored indicator diffuses through the medium, it changes from white to red medium (Figure 1) (Modified from [6]). Data logger has used as the temperatures’s recorder. Each temperature storage needs nine indicators and the experiments performed in triplicate.

![Figure 1](image1.png)

**Figure 1.** Schematic diagram of indicator’s diffusion on photopaper medium before activation (a), on activation (b), and intermediate (c) from top view (A) and side view (B).

2.2.4. Indicators’ diffusion kinetics reaction. Diffusion length value (x, cm) and storage time (t, h) which results from last analyses was used to calculate the diffusion rates (V, cm h⁻¹) (2) and diffusion coefficient value (D, cm² h⁻¹) (4). The diffusion theory of this indicators have established by Fick’s second law (3). An Arrhenius equation used to establishes the activation energy value (Ea, kJ mol⁻¹) and a model of indicator’s diffusion length prediction (5) by plotting the ln D and 1/T.

![Table 2](image2.png)

**Table 2.** Equations used for diffusion-based indicator kinetics.

| Models          | Equations                                      | References               |
|-----------------|------------------------------------------------|--------------------------|
| (1) Diffusion rate | $V = \frac{d}{dx}$                             | [13]                     |
| (2) Fick’s second law | $\frac{\partial T}{\partial x} = \frac{D \partial^2 T}{\partial x^2}$ |                          |
| (3) D Value      | $D = \frac{\eta}{\zeta}$                       | [1, 13, 14, 15]          |
| (4) Modified Arrhenius | $\ln D = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln D_0$ |                          |

Where: $J$: flux per unit area (g cm⁻² s⁻¹); $T$: absolute temperature (K); $t$: time (s); $x$: distance (cm or m); $k$: rate reaction constant; $k_0$, $D_0$: frequency factor; $D$: diffusion coefficient (m² s⁻¹); $E_a$: activation energy (kJ mol⁻¹); $R$: the universal gas constant (8.314 J mol⁻¹ K⁻¹)

2.2.5. Statistic analysis. The Microsoft Office Excel software used to conducted the data analysis. The curve fitting, regression analysis and analysis of variance (ANOVA) were performed according to SPSS statistic program (Version 16.0) software for Windows. Significant differences were determined using Duncan’s multiple range test with P value less than 0.05 were considered statistically significant. All test were conducted in triplicate (n = 3).

3. Results and Discussion

3.1. Viscosities of Indicators
Viscosity (mPas) shows the resistance of fluid to flow, when internal friction was given on started [6]. Figure 2 shows that blended PO with two kinds of other edible vegetable oils was decreases the total viscosities of the oil blends. PO have a higher viscosity than other samples oils. The PO viscosity at 29°C was about 58.333±0.289 mPas. Viscosities of blended oils in A indicators at were about 52 – 54
mPas, viscosities of B indicators were 53.833 – 55.167 mPas, and viscosities of C indicators were about 56.833 – 58.167 mPas.

![Viscosity graph](image)

**Figure 2.** Viscosities of edible vegetable oils blends as TTI’s indicators at (a) 18°C, (b) 29°C, and (c) 40°C.

Edible vegetable oils that have lower viscosity with higher ratios on oils blended method, have effected to decreases the viscosity of oils blends more. Other research reports that blended PO which have more saturated fatty acid (SFA) and high viscosity, with other edible vegetable oils which have unsaturated fatty acid more, can exactly modified the oil blends so it makes the final oil blends more stable when storaged and cooked process [6, 9, 16].

Fluid flow resistance is related to unsaturated and length of the fatty acid at triacylglycerol structures. Breaking of fatty acid in glycerol backbone from tryglyceride molecules was a factor that changes the oil viscosities. Large amount of polyunsaturated fatty acids (PUFAs) leads to low viscosity, conversely, large amount of SFA leads to high viscosity [8, 17]. Kim et al. [9] reported that oil viscosity tended to increase with increasing amount of saturated fatty acids and polymerization, so therefore relates to the melting point of the oil blends as well. Zhang et al. [18] also report that viscosities of oils influenced by oxidation reaction of the oils. When product of primer and secondary oxidation were formed, the
viscosity increased. One of many methods that can decreases the oil viscosity without causing side effect is the blends method.

Other factor that affect the indicators viscosity was temperature storage. Figure 2 shows that temperature storage increased leads to decreases the indicator’s viscosity [6]. Fasina and Colley [19] reported that oils viscosity at 35°C was about 10 to 15 fold of the viscosity at 180°C. Temperature increased leads to molecules modification that reduces the intermolecular pressure so the oil layers passed the other layers which have contributes to viscosity decreases [8, 9]. The diffusion of TTI’s indicator have effected by the oils viscosities. Low viscosities of indicators have diffusion faster than high viscosities indicators, cause the rate diffusion retarded [20, 21].

3.2. Kinetics Diffusion of Indicators
3.2.1. Diffusion Rates of Indicators. Rates of diffusion (V, cm h⁻¹) determined from compared the indicator’s diffusion length (x, cm) at the photopaper medium and the diffusion time (t, h). The results are shows in figure 3. The diffusion rates of indicators increases with increased temperature (T) and decreases as the ratio concentration of high viscosity oils increased. The diffusion rates of indicators at 40°C were fastest than other temperatures, otherwise the diffusion rates was lowest at 4°C. This indicators’s diffusion rates were faster in the beginning but velocity decline with time. Increases the temperature storages changes energy of molecules, from potential to the kinetics energy. The kinetics energy breaks the molecules chain down, leads to molecules distance increases (viscosity decreases) [13].

![Figure 3](image-url)

**Figure 3.** Diffusion rate (V) of indicators at isothermal temperatures.

3.2.2. Indicator’s Diffusion Coefficient Value (D). Indicator’s diffusion coefficient (D, cm²h⁻¹) was determined from compared the squared of indicator’s diffusion length (x², cm²) at the photopaper medium and the diffusion time (t, h) [1, 13]. The length value squared causes D value higher than V value. However, D value have similar behaviour with V value. This values were depends on temperatures storage, the diffusion length, and indicators viscosities. As the decreases the indicators’s viscosity, D value and V value increases with increased the temperature storage (as seen in figure 4) [15, 22]. Overall, the A indicators have highest D and V values, while C indicators have lowest D and V values.
3.2.3. Activation Energy (Ea) of Indicator. This D values of the indicator at isothermal temperatures were used for calculates the activation energy value (Ea, kJ mol\(^{-1}\)). A modified Arrhenius equation was used to calculated Ea value, based on linier gradient resulted by plots of ln D versus 1/T. The slope was used for ln D and 1/T converted to get Ea value (R = 8.314 J mol\(^{-1}\) K\(^{-1}\)). Increased the temperatures storage lead to ln D and Ea values decreases. Moreover, the ANOVA results of all the indicators showed significantly value (0.000) is less than probability value (0.05). Thus, the indicators were correlated with time and temperatures changes.

Table 3. Diffusion kinetics models and Ea values of indicators.

| Indicators (%) | Regression Equations | Ea ± SE (kJ mol\(^{-1}\)) | R\(^2\) | Diffusion prediction models (m) |
|----------------|----------------------|---------------------------|--------|-------------------------------|
| A1             | Ln D = -3479.1 + 5.9526 | 28.925±0.112             | 0.9627 | x = \(\sqrt{\frac{2879.17 - 5.9526}{2879.17}}\) |
| A2             | Ln D = -3801 + 4.9609   | 31.602±0.102             | 0.9943 | x = \(\sqrt{\frac{3801 - 4.9609}{3801}}\) |
| A3             | Ln D = -3844.3 + 4.8515 | 31.962±0.079             | 0.9918 | x = \(\sqrt{\frac{3844.3 - 4.8515}{3844.3}}\) |
| B1             | Ln D = -3779 + 5.1065   | 31.419±0.089             | 0.984  | x = \(\sqrt{\frac{3779 - 5.1065}{3779}}\) |
| B2             | Ln D = -3932.9 + 4.6227 | 32.698±0.070             | 0.9898 | x = \(\sqrt{\frac{3932.9 - 4.6227}{3932.9}}\) |
| B3             | Ln D = -4017.8 + 4.4053 | 33.397±0.105*            | 0.9793 | x = \(\sqrt{\frac{4017.8 - 4.4053}{4017.8}}\) |
| C1             | Ln D = -4124.3 + 4.0196 | 34.289±0.076*            | 0.9899 | x = \(\sqrt{\frac{4124.3 - 4.0196}{4124.3}}\) |
| C2             | Ln D = -4245.1 + 3.713  | 35.294±0.081*            | 0.9765 | x = \(\sqrt{\frac{4245.1 - 3.713}{4245.1}}\) |
| C3             | Ln D = -4888.8 + 1.6641 | 40.646±0.076*            | 0.9865 | x = \(\sqrt{\frac{4888.8 - 1.6641}{4888.8}}\) |

Where: D : diffusion coefficient (m\(^2\) s\(^{-1}\)) ; Ea : activation energy (KJ/mol) ; R\(^2\) : linear regression ; x : distance (m) ; t : time (second) ; e : exponential ; T : absolute temperature (K) ; *selected indicator

The achieved Ea by the diffusion reaction of the indicators values ranged over 28.925-40.646 kJ mol\(^{-1}\). The Ea values from B3, C1, C2, and C3 were have similarity with an Ea values from commercial diffusion-based TTI that have Ea value range over 33 – 50 kJ mol\(^{-1}\) [7, 23]. Overall, the indicators can
be applied as TTI with diffusion-based systems. Based on several researches, the diffusion-based TTI were applied for monitoring microbial quality for perishable food [1, 7].

Ea value of the indicators was the energy for diffusion reaction started. Estimation of Ea values should be preceded since Ea determines the accuracy of food safety and ensures the product quality [1]. The more higher of Ea value, the more sensitive the indicator (caused by temperatures changing). This Ea value was related to D and V value. The Ea value decreases with D and V value increased.

Table 3 shows the Ea values of indicators effected by the indicator’s viscosity. Overall, A indicators which have lowest viscosities, results lowest Ea values than others. While, the C indicators which have highest viscosities results highest Ea values. Wang et al. [24] explains that Ea values reflects the diffusion rates which effected by temperatures. Increases the Ea value relates to increased the effect of temperatures to the diffusion rates (temperatures sensible of the indicators increased). It indicates that C indicators (which have highest Ea) have more sensible than B and A indicators.

Diffusion prediction models used for established the indicators’ diffusion length when the temperature and time of storage were known. Length of the indicator’s diffusion indicates indirectly the product quality decreasing (can be used to established the actual shelf life of a specific product) [1]. The indicators have their diffusion reaction characteristics so this prediction model will be specific just for one indicator respectively. For example, if the shelf life of a specific product was 25 hours (90.000 s) at 29°C (302 K), the diffusion length prediction were 6.06 cm, 6.16 cm, 5.88 cm, and 5.64 cm by using B3, C1, C2, and C3 indicator, respectively.

4. Conclusion
Viscosity of the indicators was affected by the fatty acids components and the temperatures storage. This viscosity relates to the V and D values, and even the Ea value of indicators. The more lowest viscosity, the more higher D value and the more faster diffusion rates, but the Ea will be more decreased. The Ea values of the indicators were about 28.925 – 40.646 Jmol⁻¹. The results shows that the Ea value of B3, C1, C2, and C3 have similarity with Ea value from a diffusion-based TTI commercial. Based on Arrhenius equation, the diffusion model prediction of this selected indicators was established and can be used for predicts the diffusion length of an indicator based on adjustment of specific time and temperature values.

More researches needed to the develop the TTI prototype and studied more about application of this indicators to a specific product. Fatty acids as indicators can be used for next researches to increases their stabilization at lower temperature storage.

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