Thermal Kinetic Engineering of Virgin Red Palm Oil Beverage Product Quality for Storage Optimization Model Design

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International Journal of Agriculture and Biosciences 2024 13(4): 649-655.
https://doi.org/10.47278/journal.ijab/2024.168

RESEARCH ARTICLE
eISSN: 2306-3599; pISSN: 2305-6622

Thermal Kinetic Engineering of Virgin Red Palm Oil Beverage Product Quality for Storage Optimization Model Design

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ABSTRACT

Palm oil is rich in carotenoids, which give it a distinct reddish hue and contribute to its functional value. The virgin red palm oil emulsion drink is a novel food product that extracts carotenoids and meets the human requirement for pro-vitamin A. The emulsification and stabilization by using carboxymethyl cellulose, resulting in a final look that closely resembles a colloidal suspension. The quality of this beverage is primarily determined by its acid value, an indicator of triglyceride hydrolysis, as the raw, unheated oil is susceptible to lipase enzyme activity. Various oil quality factors, such as peroxide value, iodine value, saponification value, acid value, percentage of oleic free fatty acids (oleic FFA), and percentage of palmitic free fatty acids (palmitic FFA), have been modeled to forecast the shelf life of beverage product. Using the Arrhenius model and accelerated shelf-life testing, the study determined that the product's shelf-life, based on the acid value at 8°C, is 412 hours. The shelf life, determined by the criteria of peroxide value, iodine value, saponification value, oleic FFA, and palmitic FFA, are 363, 398, 419, 398, and 398 hours, respectively. An effective model for optimizing the process of storing products can be developed to generate recommendations for the ideal combination of storage time and temperature, ensuring that the expiration date is not exceeded. Utilizing thermal kinetic engineering and storage optimization models for virgin red palm oil products can make a substantial contribution to modeling other food products, ensuring that they do not exceed the expiration date for different storage temperatures.

Keywords: Arrhenius, Optimization model, Storage, Thermal kinetics, Virgin red palm oil

Article History
Article # 24-790
Received: 01-Sep-24
Revised: 22-Sep-24
Accepted: 01-Oct-24
Online First: 09-Oct-24

INTRODUCTION

Palm oil consists of a variety of beneficial chemicals, with carotenoids and tocopherols being the most abundant (Steffens et al., 2024). β-carotene, being a carotenoid, exhibits potent antioxidant properties that might effectively lower the likelihood of developing certain cardiovascular ailments (Yang et al., 2022). Tocopherol serves as an antioxidant, hence inhibiting the occurrence of degenerative illnesses (Pamunuwa et al., 2023). Currently, there is limited progress in the development of beverage products made from vegetable oil. Palm oil has a comparatively high concentration of carotenoids and tocopherols (Gao et al., 2023). Emulsified palm oil beverages are essential for their high content of pro-vitamin A and vitamin E, which provide significant health benefits (Athanasiadis et al., 2024). Opting for 100% palm oil as the primary ingredient for palm oil beverages is a commendable decision. Palm oil beverage products will retain the purity of newly extracted palm oil, as it contains

Cite this Article as: Yudianto D, Hanafi, Mellisani B, Ulilalbab A, Sibarani RW, Sayekti A and Nainggolan EA, 2024. Thermal kinetic engineering of virgin red palm oil beverage product quality for storage optimization model design. International Journal of Agriculture and Biosciences 13(4): 649-655. https://doi.org/10.47278/journal.ijab/2024.168

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bioactive ingredients with significant potential (Silsia et al., 2021). The high level of carotenoids in palm oil contributes to its authentic red color, which is derived naturally from the fruit of the palm oil tree (Ahmad et al., 2021). This product undoubtedly possesses significant potential to captivate customer interest.

Typically, sterilization is the initial step in the post-harvest treatment of palm oil (Sarah et al., 2023). The term sterilization in this context refers to a heating procedure that is employed to deactivate the lipase enzyme (Wae-hayee et al., 2022). Lipase is an endogenous enzyme that occurs spontaneously in the oil of palm oil fruit (Suwanno et al., 2017). The lipase enzyme exhibits negligible activity when the fruit is unripe. When the palm fruit is fully mature and has a significant amount of triglycerides in palm oil, the lipase enzyme becomes active and breaks down the triglycerides into free fatty acids and glycerol through hydrolysis (Shehu et al., 2019). The enzymatic hydrolysis process is accelerated when the oil palm fruit has been picked and is in a state of readiness for processing (Tan et al., 2023). The implementation of heat to fresh palm oil fruit will undoubtedly impact the bioactive chemicals, particularly carotenoids (Sevindik et al., 2023). Direct exposure of the heating process to oxygen greatly increases the likelihood of oxidation occurring in the fatty acid molecules found in triglycerides (Wang et al., 2023). In addition, heating can potentially harm the beneficial chemicals carotenoids and tocopherols (Souza et al., 2022). The impairment of these bioactive substances will diminish the antioxidant potency of these two constituents, consequently diminishing the functional worth of the product (Marino & Schadt, 2016). The selection of virgin palm oil as the raw material for red palm oil emulsion beverage products is suitable due to the potential harm to triglyceride, carotenoid, and tocopherol components caused by the heating process. Virgin palm oil possesses identical chemical qualities to that of palm fruit, hence enabling the product to accurately manifest the functional worth of the chemical constituents found in fresh palm fruit (Hasibuan & Priyanto, 2021). Nevertheless, virgin palm oil has an inherent enzyme molecule called lipase, which remains functional in breaking down substances through hydrolysis when there is an adequate amount of water to facilitate its action (Martin et al., 2023). The lipase enzyme's activity poses a significant issue in virgin red palm oil beverage products as it leads to the production of free fatty acids, which might diminish the quality of the product (Reyes-Reyes et al., 2022).

The stability of a product can be assessed by examining the rate at which its quality deteriorates until it reaches levels that are considered unsatisfactory or exceeds specified regulatory thresholds (Tarlak, 2023). The stability of the product is crucial as it directly impacts the quality throughout time, ultimately determining if the product has reached its maximum performance level (Duarte et al., 2024). It must be recognized that stores have varying storage conditions for their product. The temperature factor is the primary determinant of variations in environmental circumstances that can impact the pace of quality deterioration in major food products (Dayarathna et al., 2023). Thus, this research specifically examines thermal kinetic engineering to enhance accelerated shelf-life time of virgin red palm oil beverage products. The kinetic data provides a basis for optimizing storage conditions, allowing for precise determination of recommended expiration limits based on storage temperature. The objective of this research was to design an optimal virgin red palm oil beverage shelf life estimation model in various temperature storage conditions based on the kinetics of acid value, peroxide value, iodine value, saponification value, % oleic FFA, and % palmitic FFA as limiting quality parameters for oil deterioration.

MATERIALS & METHODS

Materials

The research utilized virgin red palm oil, fructose, CMC, and citrus flavour as components. The production of virgin red palm oil emulsion drinks utilizes homogenizers. Meanwhile, the examination of these beverages involves the use of analytical balances, spectrophotometers, incubators, beakers, Arlen Meyers, burettes, pipettes, measuring flasks, and hot stoves.

Virgin Red Palm Oil Beverage Production

The virgin red palm oil beverage production was conducted by modification method from Silsia et al. (2021). A total of 30g of virgin red palm oil was thoroughly mixed for 30s. A sugar solution is prepared by combining 60g of water with 4.5g of fructose syrup. The emulsified oil was combined with the prepared sugar solution (64.5g), 0.36g of CMC, and 5.55g of citrus flavour. After combining, thoroughly homogenize for a time of 420s. The product outcome is a virgin red palm oil emulsion beverage.

Evaluation of Kinetics in Product Quality Changes by Temperature Factors

An assessment of the changes in quality during storage will be conducted based on the parameters of peroxide value, iodine value, saponification value, acid value, % oleic FFA, and % palmitic FFA (Patil et al., 2023). The model for the rate of change of each quality will be determined using reaction rates of zero, first, and second orders (Yudianto et al., 2023). The most optimal plot results are observed when the R-square value is at its maximum, which is near 1 (Yudianto et al., 2024). The quality changes are evaluated throughout each time change at three distinct storage temperatures: 25, 35, and 45°C. This evaluation is conducted using the Accelerated Shelf Life Testing (ASLT) method by the Arrhenius model (Calligaris et al., 2022). The storage time was assessed over 96 hours, with samples taken every 24 hours. Nevertheless, because of the possible risk of triglyceride hydrolysis by lipase enzymes, the acid value is the primary factor used to determine the shelf life of the product. The acid value indicates the quantity of fatty acids produced during the triglyceride hydrolysis process. According to the SNI 2901:2021, the Indonesia National Standard, the highest permissible acid value for palm oil is 3.00mg NaOH/g sample. The shelf life estimation will be calculated by approximating the shelf life of the acid value standard, using the parameters of peroxide value, iodine value, saponification value, % oleic FFA, and % palmitic FFA. Shelf life estimation for virgin red palm oil will be conducted at a storage temperature of 8°C, as per the recommended storage reference from Loganathan et al. (2020).

Storage Optimization Model Design

The storage optimization model design was developed using the characteristics of peroxide value, iodine value, saponification value, acid value, % oleic FFA, and % palmitic FFA to determine the shelf life. The product expiration date is determined by considering the temperature and storage time (Laksanawati et al., 2024). A temperature of 8°C is selected as the first reference point. The second point is defined by a change in 1 logarithmic cycle of storage time. By utilizing the Arrhenius model, it is possible to determine the product storage temperature resulting from a 1 log cycle change in the product storage time at a temperature of 8°C for each quality parameter (Yudianto et al., 2023). The storage optimization model's design can be visualized as depicted in Fig. 1 referring to the thermal kinetic data mapping method from Yudianto et al. (2024).

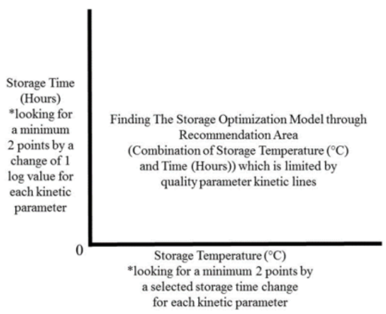

Fig. 1: Design of Storage Optimization Model.

Quality Parameter Determination for Thermal Kinetic Model

Determination of acid value and peroxide value followed the modification methods from Chu et al. (2023). Determination of saponification value followed the modification method from Ivanova et al. (2022). The iodine value determination was conducted by referring to Kucha et al. (2021) modification method. A modification method from Vicentini-Polette et al. (2021) was used to determine % oleic and palmitic FFA.

RESULTS & DISCUSSION

Evaluation of Thermal Kinetics for Product Quality Parameters

The results of the research conducted by Nagy et al. (2024) have a similar basis with this study. Deterioration of food containing oil is based on the formation of free fatty acids from triglycerides consisting of the oil components. In this research, the potential for deterioration due to free fatty acids formation resulting from natural hydrolysis by lipase enzymes in virgin red palm oil beverages can be approached through six general oil deterioration parameters. The evaluation of thermal kinetics for product quality parameter steps aimed to determine the relationship between storage time and quality parameters of virgin red palm oil beverage products. The value of the product quality reduction constant (k) was calculated for each storage temperature. Next, ascertain the sequence that most closely aligns with or adheres to the criteria for reducing quality during storage by examining the R-square value that is highest and approaching 1. Data graphing employs order 0, where the Q value remains unchanged. In contrast, order 1 uses the natural logarithm of the Q value, while order 2 employs the reciprocal of the Q value. Once the order is determined, Arrhenius modeling is performed using the natural logarithm of the k value at each storage temperature as the y coordinate, and the reciprocal of the temperature (in Kelvin) as the x coordinate. The Arrhenius equation is used to determine the values of each parameter. Subsequently, the shelf life is estimated using a linear curve that follows the reaction order of the chemical reaction. The value Q_0 indicates the starting parameter value before storage, whereas Qt represents the final quality parameter value, which is the maximum allowable number of quality parameters in the product for consumption.

Upon examining Fig. 2, it is evident that the highest value of k (slope) is seen for storage at a temperature of 45°C. This is followed by the value of k for storage at temperatures of 35 and 25°C. That chart illustrates the kinetics of quality parameter changes in virgin red palm oil beverage products during storage. The slope seems suitable when considering the storage temperatures of 45, 35, and 25°C since they follow a descending order from the steepest to the least steep. The series of k values indicates that as the storage temperature decreases, the time for the quality parameters to undergo changes increases. As the value of k increases, the rate at which the quality parameter value changes/decreases will also increase (Tong et al., 2022). Both the peroxide value and acid value parameters adhere to a reaction rate equation with a first-order rate constant. The iodine value and saponification value are governed by a reaction rate equation of second order. Finally, the reaction rate equation for the parameters oleic and palmitic follows an order of 0.

Effect of Temperature on Reaction Rate Sensitivity of Product Quality Parameters

The sensitivity experiment examines the impact of temperature variations on the quality parameters of the product. The experimental results are displayed in Fig. 3. Based on this picture, it is evident that increasing the temperature of the product leads to a rise in the value of k. The graph in Fig. 3 is generated by inputting the k-value data corresponding to the temperature shown in the graph. This graph represents the derivative of the reaction rate equation (Tong et al., 2022). The study has graphed

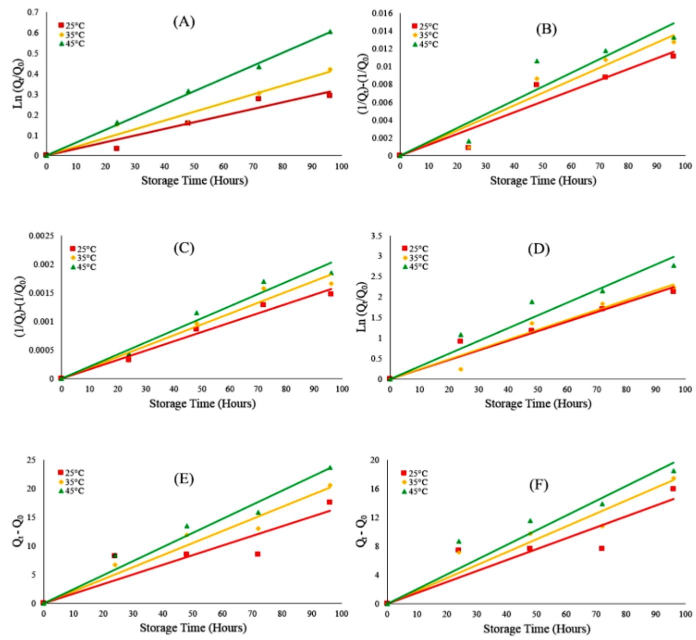

Fig. 2: Thermal Kinetic Model of (A) Peroxide Value, (B) Iodine Value, (C) Saponification Value, (D) Acid Value, (E) % Oleic FFA, and (F) % Palmitic FFA.

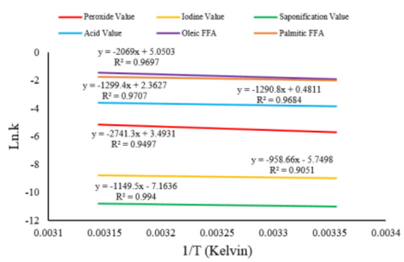

Fig. 3: The Arrhenius Model of Quality Parameters in Virgin Red Palm oil beverage Product.

the kinetics of product quality changes using reaction equations of zero, first, and second orders. The results indicate that the storage temperature treatments exhibit varying R-Squared values, with the maximum value representing the kinetics of six quality changes following zero, first, and second orders. Fig. 3 presents the results of Arrhenius modeling, which indicate that all quality parameters in virgin red palm oil beverages have similar activation energy levels. Fig. 3 demonstrates that the slope level for all quality parameter lines is mostly consistent. This indicates that the sensitivity of all quality metrics to variations in storage temperature is reasonably uniform. The sensitivity of quality parameter kinetics influenced by the change in temperature was also conducted by Shrivastava and Chakraborty (2024). They also used an Arrhenius approach to estimate the parameter kinetics towards the change in temperature condition.

Shelf Life of Virgin Red Palm Oil Beverage Product

Virgin red palm oil derives its name from its minimal processing, which preserves its natural saturated fatty acid components and limits exposure to heat. A closer analysis of the processing procedure reveals that it involves only minimal intervention, ensuring the retention of its beneficial properties. It is believed to induce suboptimal separation of the oxidized oil components, causing them to remain in the product. This results in a somewhat high initial peroxide value, which is even greater when compared to products derived from other vegetable oils. The relatively starting value will gradually and consistently remain high during the storage procedure. Nevertheless, the primary emphasis is assessing the hydrolysis potential when evaluating the shelf life. The shelf life of virgin red palm oil beverage products is determined by the acid value measured at a temperature of 8°C. Table 1 demonstrates that the product's shelf life at 8°C, as per SNI

Table 1: The Shelf Life Calculation of Virgin Red Palm Oil Beverage in 8°C Temperature Storage

Parameter		Peroxide Value	Iodine Value	Saponification Value	Acid Value	Oleic Free Fatty Acid	Palmitic Free Fatty Acid
Best Fitted Order		1	2	2	1	0	0
Arrhenius	Slope	-2741.32	-958.66	-1149.48	-1290.76	-2069.01	-1299.39
	Intercept	3.49	-5.75	-7.16	0.48	5.05	2.36
Q_0		6.10mEq/g	23.92g I_2/100g	183.83mg KOH/g	0.0035326mg NaOH/g	1.78%	1.61%
Qt		12.21mEq/g	11.96g I_2/100g	91.91mg KOH/g	3.00mg NaOH/g	41.21%	43.12%
k value at 8°C		0.001906	0.000105	0.000013	0.016370	0.098991	0.104197
t.8°C (hours)		364	398	420	412	398	398
t. 8°C (days)		15	17	17	17	17	17
t. 8°C (months)		0.50	0.55	0.58	0.57	0.55	0.55

2901:2021, is 412 hours or 17 days. When considering the half-life approach, the peroxide value, iodine value, and saponification value exhibit a shelf life that is comparable to the standard shelf life of the acid value. While there are slight variations, the shelf life of these three parameters are 364, 398, and 420 hours, equivalent to 15, 17, and 17 days, respectively. The observed changes in the oleic FFA and palmitic FFA parameters can be attributed to the hydrolysis process of the oil. The impact of product storage on changes in peroxide value, iodine value, saponification value, and acid value standards is expected to be determined by the % FFA parameters of oleic and palmitic, by the average shelf life. Nevertheless, when considering the possibility of product deterioration caused by lipase enzyme activity, the study of shelf life utilizing the Arrhenius approach method has revealed valuable insights into the very limited longevity of virgin red palm oil beverages. Implementation of the Arrhenius equation for foods and beverages shelf life determination was also recommended by Muniandy et al. (2024). Their research estimates the shelf life of vitamins by the Arrhenius equation. The accuracy of the Arrhenius model depended on the high R-square value of each parameter kinetic to approach 1.

Design of a Model for Optimizing Product Storage

Collecting data on the k values and activation energy values for each quality parameter will assist in the development of product storage optimization models (Deeth, 2017). The optimization model design is conducted by identifying all quality characteristics as constraints for the product storage process (Yudianto et al., 2023). For every quality metric, it is essential to determine the k value when the storage time increases or decreases by a factor of 10 (Hariyadi, 2019a). In an optimal storage method, it is desirable to minimize the alterations in quality parameters, so ensuring that the product storage limitations are effectively adhered to, particularly with regard to the acid value as specified by the SNI 2901:2021 standard. Moreover, a change in storage time of 1 log cycle as a Qt value will allow us to determine the corresponding storage temperature at that specific storage time. Table 2 displays the two combinations of temperature and product storage time values that were determined by analyzing the variations in product storage time by 1 log cycle for all quality criteria.

This experiment has similiar results to the study of Yudianto et al. (2023). They studied the potential deterioration of coconut water drinks during the heating process. The potential deterioration was determined by the phenol and flavonoid as parameters. The duration of the heating process at a certain temperature was limited by the phenol and flavonoids degradation which play a role in limiting the process. The phenol and flavonoid content did not decrease beyond the amount modeled in the kinetic and the Arrhenius equations. Similar to this study, several parameters used as limits for storing the virgin red palm oil beverage products were peroxide value, iodine value, saponification value, acid value,% FFA oleic, and% FFA palmitic. These six parameters could be analogous to phenol and flavonoids in the study of Yudianto et al. (2023). The temperature and duration of coconut water heating were similar to the storage temperature and shelf life of virgin red palm oil beverage products in this study.

Table 2: Calculation of Second Point by 1 Log Cycle of Change in Storage Time

Parameters		First Point	Second Point
Peroxide Value	t (hours)	364	36
	Q_0 (mEq/g)	6.10	6.10
	Qt (mEq/g)	12.21	12.21
	k	0.001906	0.019064
	T (°C)	8	95
Iodine Value	t (hours)	398	40
	Q_0 (g I_2/100g)	23.92	23.92
	Qt (g I_2/100g)	11.96	11.96
	k	0.0001050	0.0010501
	T (°C)	8	591
Saponification Value	t (hours)	420	42
	Q_0 (mg KOH/g)	183.83	183.83
	Qt (mg KOH/g)	91.91	91.91
	k	0.0000130	0.0001295
	T (°C)	8	370
Acid Value	t (hours)	412	41
	Q_0 (mg NaOH/g)	0.00353	0.00353
	Qt (mg NaOH/g)	3.00	3.00
	k	0.0164	0.1637
	T (°C)	8	290
% Oleic FFA	t (hours)	398	40
	Q_0 (%)	1.78	1.78
	Qt (%)	41.21	41.21
	k	0.099	0.990
	T (°C)	8	136
% Palmitic FFA	t (hours)	398	40
	Q_0 (%)	1.61	1.61
	Qt (%)	43.12	43.12
	K	0.104	1,042
	T (°C)	8	287

A line is drawn when each parameter is marked with two points (Hariyadi, 2019b). The storage optimization model, which considers the temperature and storage time, is represented in the graph region below all the quality parameter lines. The formula for determining optimal product storage recommendations is presented in Table 2. Fig. 4 illustrates the storage optimization model, which considers both the storage temperature assigned to the product and the time of storage. Fig. 4 displays the borders that represent recommended areas for product

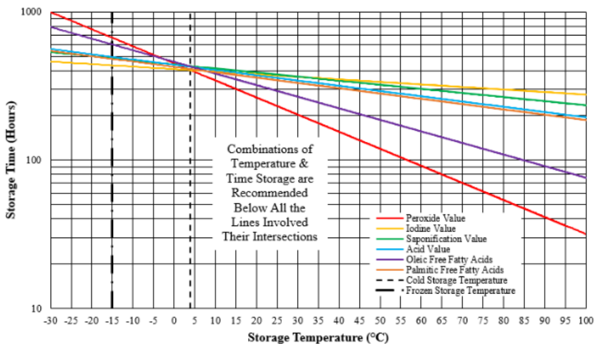

Fig. 4: Storage Optimization Model Design of Virgin Red Palm Oil Beverage Product

storage, such as the thermal process optimization region mentioned in the Deeth (2017) article. The region is depicted below the lowest line, even in the presence of tangents to one or more lines. The line at the bottom is still being used as the limit line.

The study conducted by Yudianto et al. (2024) has also been able to model the concept of thermal kinetic mapping well as in this research. Yudianto et al. (2024) have evaluated the potential for commercial sterilization of butterfly pea flower extract beverages while still considering to the recovery of their functional compounds. The kinetic data of functional compounds of butterfly pea flower extract including; total anthocyanins, red flavylium cation, purple quinonoidal base, blue anionic quinonoidal base, ferulic acid, caffeic acid, p-hydroxybenzoic acid, protocatechuic acid, gallic acid, vanillic acid, vanillin, procyanidin hexamer III, and delphinidin-3-glucose, have been estimated by the Arrhenius equation. This equation would be able to provide an overview of the degradation kinetics of functional compounds which were reduced during the heating process at different temperatures from the commercial sterilization standard. Commercial sterilization is applied to enhance the food shelf life by 12-log cycle inactivation of *Clostridium botulinum* spore using a thermal process (Sayekti et al., 2024). The study from Yudianto et al. (2024) has a similar concept and design results as in this experiment. The parameters of functional compounds in butterfly pea flower extract beverage are similar to the parameters of peroxide value, iodine value, saponification value, acid value, % FFA oleic, and % FFA palmitic as limiting parameters in virgin red palm oil beverages. The heating time and the temperature process selected for sterilizing the butterfly pea flower extract beverage are similar to the shelf life and storage temperature of virgin red palm oil beverage.

Conclusion

According to the findings of this experiment, it can be inferred that there is a positive correlation between the storage temperature of the product and the k value, indicating that as the storage temperature increases, the k value likewise increases. The reaction rates for the parameters peroxide value, iodine value, saponification value, acid value, % oleic FFA, and % palmitic FFA respectively exhibit the sequence 1, 2, 2, 1, 0, and 0 for their reaction order value. The beverage products made with virgin red palm oil have a shelf life of 364, 398, 420, 412, 398, and 398 days accordingly when stored at a temperature of 8°C. Alternatively, the shelf life can be expressed as 15, 17, 17, 17, 17, and 17 days. A robust storage optimization model has been developed to accurately calculate the suggested expiration date for virgin red palm oil beverage products under various storage temperatures. This modeling significantly enhances other food storage models across different businesses by providing knowledge of the expiration date in the event of a change in the applied storage temperature.

Author's Contribution: DY: Project Leader and Thermal Process Engineering Designer. AU, RWS, EAN: Conceived and designed the analysis. H, BM, AS: Collected data and Performed the analysis. All authors critically revised the manuscript and approved the final version.

Acknowledgment: The authors would like to thank the Politeknik AKA Bogor which provides the research funding and laboratory facilities.

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