Food Research 7 (3) : 227 - 232 (June 2023)
Journal homepage: https://www.myfoodresearch.com

FOOD RESEARCH

FULL PAPER

The effect of natural antioxidant from clove (*Syzygium aromaticum L.*) on the oxidative stability of crude oil produced by the traditional wet rendering process of coconut (*Cocos nucifera L.*)

[1,*]Lestari, D., [2]Suluhingtyas, L.C. and [2]Ariono, D.

[1]*Department of Food Engineering, Institut Teknologi Bandung, Jl. Let. Jend. Purn. Dr. (HC) Mashudi No.1, Sumedang 45363, West Java, Indonesia*

[2]*Department of Chemical Engineering, Institut Teknologi Bandung, Jalan Ganesha 10 Bandung 40132, West Java, Indonesia*

Article history:
Received: 11 November 2021
Received in revised form: 13 December 2021
Accepted: 23 March 2022
Available Online: 30 June 2023

Keywords:
Coconut oil,
Oxidative stability,
Clove's natural antioxidant,
Artificial Neural Network,
Arrhenius kinetics

DOI:
https://doi.org/10.26656/fr.2017.7(3).852

Abstract

Coconut oil produced by the traditional wet rendering process may contain free fatty acids and water which lead to rancidity and shorter shelf life. Previous studies proved that cloves (Syzygium *aromaticum L.*), as a natural source of antioxidant eugenol, can increase coconut oil oxidation stability. This research aimed to investigate the effects of clove addition during the wet rendering process on the Peroxide Value of coconut oil and to estimate shelf life using Accelerated Shelf Life Testing (ASLT) and Artificial Neural Network (ANN). Clove powder was added into coconut milk prior to oil rendering or into coconut oil, followed by oil storage at 28, 63, and 100°C. ASLT method predicted that adding 1 g clove/kg coconut milk and 5 g clove/kg coconut oil gave the best result by improving oil shelf life from approximately 11 days (control) to 14 days, while the ANN method predicted that adding 10 g clove/kg coconut milk gave the best result by improving estimated oil shelf life to 47 days at 28°C. Coconut oil produced from clove-treated coconut milk had the best oxidative stability during storage. Activation energies and activation enthalpies of coconut oil oxidation increased due to clove addition and therefore, improved stability during storage.

1. Introduction

The utilization of coconut oil from traditional home industries using the wet rendering process is decreased due to impurities which leads to fast rancidity and shorter shelf life. Coconut oil or lauric oil is mainly composed of medium to long saturated fatty acids, such as lauric acid (44-52%-wt.), myristic acid (13-19 %-wt.), palmitic acid (7-10 %-wt.), and a minor amount of unsaturated long fatty acids, such as oleic acid (5-8 %-wt.) and linoleic acid (1.5-2.5 %-wt) (Jayadas and Nair, 2006). Coconut oil contains 84 %-wt triglycerides with three saturated fatty acids, 12 %-wt. triglycerides with two saturated fatty acids, and 4 %-wt. triglycerides with one saturated fatty acid (Ketaren, 1986). Traditional (unrefined) coconut oil also contains phosphatides, gums, sterols (0.06 – 0.08 %-wt.), tocopherols (0.003 %-wt.), a small amount of protein and carotene, and a significant amount of free fatty acids (approximately 5% -wt.). Unsaturated fatty acids and free fatty acids content in unrefined coconut oil can still undergo lipid oxidation which leads to oil rancidity.

Several previous studies were conducted to improve the oxidative stability of coconut oil, indicated by peroxide values, by adding additives such as antioxidants from cloves (*Syzygium aromaticum L.),* one of the natural sources of antioxidant eugenol, into coconut oil to increase resistance to oxidation (Lee and Shibamoto, 2001; Laitupa and Susane, 2010; Nurjannah *et al.* 2013). Antioxidants can bind to the peroxide compounds' double bond and stabilize it so that the peroxide number in oil is reduced and the shelf life is increased (Gordon, 1990). Nurjannah *et al.* (2013) conducted a study to test the antioxidant activity of clove bud oil and standard eugenol against corn oil irradiated by UV light and using Electron Spin Resonance. The results showed that the addition of clove essential oil, with eugenol as an active compound, effectively trapped alkyl free radicals up to 60%, hydroxyl radicals up to 48%, and peroxyl radicals up to 36%. Despite the potential, clove essential oil extraction involves a tedious and high-energy process, which might be less feasible for home industries. Therefore, a more simple method, such as the direct

*Corresponding author.
Email: *dianika@che.itb.ac.id*

eISSN: 2550-2166
Published by Rynnye Lyan Resources

addition of clove bud powder as a processing aid during the wet rendering process or as additives in coconut oil products needs to be investigated to improve oil stability, especially those produced by traditional coconut oil home industries.

Shelf-life testing of products can be conducted using the kinetic approach by observing parameter changes during storage at elevated temperatures or Accelerated Shelf Life Testing (ASLT) method (Gómez-Alonso *et al.,* 2004; Calligaris *et al.*, 2019). This method is commonly used and already proven, but it might be less feasible and more time-consuming, especially for small or home industries. Another emerging method to estimate product shelf life is the Artificial Neural Networks (ANN) method. ANN is a model that works based on the human neuron system, which has several advantages such as being capable of handling incomplete data and non-linear problems, and once the supervised learning process is completed, ANN can make faster predictions based on given input data (Przybylski and Zambiazi, 2000; Dehghani *et al.*, 2012; Tan *et al.,* 2012). Utilization of ANN with various algorithms including intelligent computational methods of ANN *linear layers* and *time-delay* and *central nervous system* had been conducted for various applications, such as to predict the shelf life of *soft mouth melting milk cakes* stored at 6°C, cascade feedforward or backpropagation model to predict the sensory quality of sterile drinking instant coffee and to predict the shelf life of processed cheese and dairy products (Goyal and Goyal, 2011; Goyal, 2012; Goyal and Goyal, 2012). The application of ANN in the engineering field is interesting and continues to increase. However, ANN has not been used yet to estimate the shelf life of coconut oil produced from the traditional wet rendering process.

To improve traditional coconut oil quality and stability, a simple treatment of adding clove bud powder as a processing aid during the wet rendering process or as additives in coconut oil products and the use of ANN emerging method to estimate coconut oil shelf life compare to ASLT method needed to be explored. Therefore, the objective of this research was to investigate the effect of clove powder addition during the wet rendering process on the oxidative stability of coconut oil and to estimate the oil shelf life using Accelerated Shelf Life Testing (ASLT) and Artificial Neural Network (ANN) methods.

2. Materials and methods

Raw materials used in this study were fresh coconut milk bought directly from local traditional markets in Bandung, Indonesia. Dried clove bud powder was obtained from traditional markets in Bandung. The chemicals used for analysis were $Na_2S_2O_3$ solution, glacial acetic acid, chloroform, KI, Na_2HCO_3, KOH, HCl and 1% starch solution from Sigma Aldrich or Merck.

2.1 Coconut oil production by the wet rendering process

Extraction of coconut oil was conducted using the wet rendering method (Seneviratne and Dissanayake, 2008). Fresh coconut milk was divided into three different treatments of clove additions: 1) clove added to coconut milk as a processing aid during wet rendering, 2) clove added to freshly extracted coconut oil after the wet rendering of coconut milk, and 3) coconut milk as raw material for wet rendering without clove addition (control). Briefly, fresh coconut milk was boiled to separate oil from the water phase and insoluble proteins. About 1, 5, or 10 g of cloves were added and mixed into 1 kg of coconut milk or coconut oil. Next, extracted coconut oil from three different treatments was divided into containers for storage. During storage, extracted coconut oil was analysed for peroxide values, which were used for shelf life estimation using Accelerated Shelf Life Testing (ASLT) and Artificial Neural Network (ANN) methods.

2.2 Accelerated shelf-life testing method of coconut oil

Oxidative stability of the investigated coconut oil samples to determine shelf life was conducted by using *Schaal oven test* to facilitate accelerated lipid oxidation (Antolovich *et al.*, 2002). Briefly, coconut oil samples from the three treatments were kept in a 1 L Erlenmeyer flask without closure and stored in an incubation oven at a constant temperature of 28, 63, or 105°C for 7 days. All variations were conducted in duplicates. Peroxide values of oil samples were analysed at days 0, 1, 2, 3, 4, 5, 6, and 7 of storage.

2.3 Peroxide value analysis

Peroxide values of the coconut oil samples were analysed on a daily basis (days 0, 1, 2, 3, 4, 5, 6, and 7) during storage following the method from Indonesian National Standardization Board (BSN-Indonesia, 1992). Briefly, about 2.5 g oil sample was weighed and mixed with a 15 mL mixture of acetic-chloroform acid (3:2). Samples were added with a saturated KI solution, stirred well, and allowed to stand. Next, distilled water then added to the previous sample solution, stirred well, and titrated with sodium thiosulfate. About 0.25 mL of starch solution was added to the oil samples solution and the titration was continued until the blue colour disappeared.

2.4 Shelf-life estimation using Artificial Neural Network

The peroxide value of coconut oil from experimental data was used to develop the ANN model to estimate the shelf life of traditional manufactured coconut oil according to the algorithm in Figure 1. ANN algorithm was developed based on the study of Przybylski and Zambiazi (2000) with modifications and computed using MATLAB software. This experiment was carried out through 144 observations for each input and output parameter. The input and output parameters are used to develop the ANN model. Experimental data of peroxide value were separated into three sets: 1) training data set, 2) validation data set, and 3) test data set to predict values. The amount of clove addition, substrate added (coconut milk or coconut oil), and temperature were used as input data (predictors), while the values of peroxide values served as outputs. Various combinations of internal parameters, consisting of a number of hidden layers and the number of neurons in each hidden layer were explored in order to optimize the predictive ability of the model. The algorithm used is the backpropagation algorithm, with neurons in each hidden layer varying from 1 to 5. These neural networks were trained until they reached a stable condition. Networks were trained with single or multiple hidden layers. The transfer function for the hidden layers was sigmoid, while the output layer used pure linear functions. Networks were trained by using training and dataset validation, then the neural network model was used to simulate new data using MATLAB.

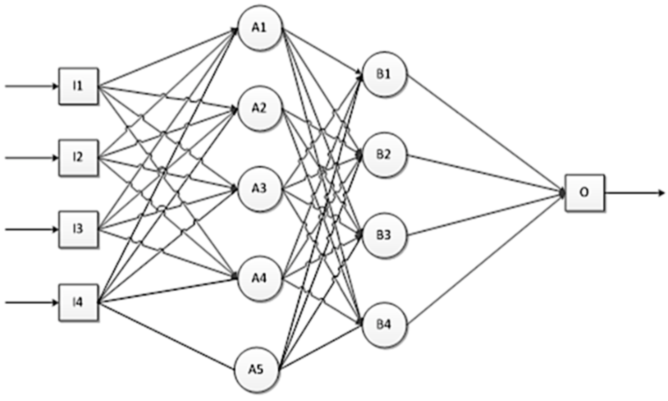

Figure 1. ANN configuration results of the training process, where I1 is the storage period (days); I2 is the clove mass added (g); I3 is the storage temperature (°C); I4 is whether clove is added to the raw material or product (-1/1); and O is the predictive value of the peroxide number.

2.5 Kinetic data analysis

Peroxide values were plotted against storage times following the first-order reaction rate (Equation 1) based on several studies on lipid stability and oxidation mechanisms. Further, the reaction rate constants from the reaction rate equation were used to calculate kinetic data, such as activation energy (Ea), frequency factors (A), activation enthalpies (ΔH^{++}), and activation entropies (ΔS^{++}) from Arrhenius correlation and the activated complex theory (Tan *et al.,* 2001; Besbes *et al.,* 2004; Farhoosh *et al.*, 2008; Sahin, 2019).

$$PV_t = PV_0\, exp(-kt) \qquad (1)$$

Where PV_t = peroxide value at day t; PV_0 = peroxide value at day 0; k = reaction rate constant (day^{-1}); and t = storage time (day). The reaction rate constant, k (day^{-1}) was determined from the coefficient of temperature in Equation 1.

The activation energy (*Ea, kJ/mol*) and the pre-exponential or frequency factors (*A, day^{-1}*) were calculated using Equation 2, derived from the regression line of ln (k) vs. 1/T plotting based on the Arrhenius equation.

$$ln\ (k) = ln\ (A) - (Ea/RT) \qquad (2)$$

Where k = reaction rate constant; R = molar gas constant (8.3143 J/mol K). The value of *Ea* was calculated from the slopes, while *A* was calculated from the intercepts.

Enthalpies (ΔH^{++}) and entropies (ΔS^{++}) of activation were determined from the regression line of ln (k/T) vs. 1/T plotting based on equation derived from the activated complex theory of Equation 3.

$$ln\ (k/T) = ln\ (k_B/h) + (\Delta S^{++})\ /R) - (\Delta H^{++}/RT) \qquad (3)$$

Where: k_B = Boltzmann constant of 1.38^{-23} J/K and h = Planck's constant of 6.63^{-34} J.s. The value of ΔH^{++} was calculated from the slopes while ΔS^{++} were calculated from the intercept.

3. Results and discussion

3.1 Effect of clove addition on coconut oil initial peroxide values

Before storage, the initial peroxide number of coconut oil from different treatments was analysed to determine the effect of clove addition into coconut milk as a processing aid on the quality of fresh coconut oil. During the wet rendering process, coconut milk was heated to break the emulsion and separate the oil from the water phase. Peroxide number is an important quality parameter of oil degradation due to lipid primary oxidation. Therefore, the initial peroxide value of coconut oil indicated the degree of lipid oxidation during the wet rendering process (Seneviratne and Dissanayake, 2008; Wongpoowarak *et al.*, 2009; Laitupa and Susane, 2010; Tan *et al.,* 2012; Subajiny *et al.*, 2018; Ramos *et al.,* 2019). The initial peroxide numbers of fresh coconut oil is shown in Table 1.

Coconut oil produced from the wet rendering process with various treatments had an initial peroxide value between the range of 0.92 to 1.29 (control), which was still within the range of National Indonesian Standards

https://doi.org/10.26656/fr.2017.7(3).852

Table 1. Initial peroxide value (meq O_2/kg oil) of traditional manufactured coconut oil.

Initial condition at 28°C	Control	Clove added to coconut milk (g clove/kg)			Clove added to coconut oil (g clove/kg)			Codex Standard
		1	5	10	1	5	10	
Peroxide Value (meq O_2 /kg)	1.29	1.07	0.92	0.98	1.29	1.29	1.29	Crude Oil <1 Frying Oil <15

(BSN-Indonesia, 1992) and the International Codex (Codex Alimentarius, 1999). Peroxide value is one of the most common methods to detect oxidative degradation and measure antioxidant activity. Peroxide number (expressed as meq O_2/kg of oil) is used to measure peroxide radicals (ROOH*) or other compounds similar to peroxides, such as hydroperoxides which formed through oil oxidation during oil processing and storage. Not only be used as a measure of the degree of oxidation, but peroxide value is also a measure of the degree of rancidity. According to the International Codex (Codex Alimentarius, 1999), processed coconut oil must have a peroxide value less than 15 meq O_2/kg oil, while the Indonesian standard expected that crude coconut oil must have a peroxide value less than 5 meq O_2/kg oil (BSN-Indonesia, 1992).

Experimental data in Table 1 showed that crude coconut oil without clove treatment (control) had a peroxide value of < 5 meq O_2/kg oil which fulfilled the standard requirement. On the other hand, coconut oil which is produced from the wet rendering of clove powder treated - coconut milk had lower initial peroxide value (0.92-1.07 meq O_2/kg oil) than coconut oil control (1.29 meq O_2/kg oil). Clove addition of 5 and 10 g clove/kg coconut milk gave the lowest peroxide value of the extracted crude oil into less than 1 meq/kg oil. During the wet rendering process, heat was applied to denature protein and destabilize the oil-in-water emulsion to separate oil from the water phase. This heat treatment during wet rendering might cause hydrolysis of oil into free fatty acids, which was oxidized quite easily and led to hydrolytic rancidity. In addition, coconut oil which was produced from the wet rendering process might contain high moisture content which also facilitates enzymatic oil hydrolysis (Penet *et al.*, 2010; Marasabessy *et al.*, 2010; Nurah *et al.*, 2017). Furthermore, heat treatment during the oil extraction process can reduce the natural antioxidant content of the coconut oil (Seneviratne and Dissanayake, 2008), and therefore, clove addition into coconut milk seemed to replace or add antioxidant activity of the coconut oil during wet rendering. Briefly, the addition of clove powder into coconut milk as a processing aid proved to reduce oil oxidation during the high-temperature wet rendering process.

3.2 Effects of clove addition on coconut oil peroxide values during storage

In general, adding cloves into coconut milk during wet rendering or into coconut oil products proved to inhibit the increase of peroxide value during storage at various temperatures. Figure 2 shows that the peroxide value of coconut oil increased gradually during storage following the 1st order reaction rate equation. The effect of clove addition was more significant by the increase of temperatures, which indicated that clove natural antioxidants increased coconut oil oxidative stability at elevated temperatures. Antioxidants are substances that in small amounts will disrupt the normal oxidation process in oils and fats. A low concentration of antioxidants can inhibit or prevent the auto-oxidation reaction of fat and oil at the initiation and propagation stages (Chandran *et al.*, 2017; Laitupa and Susane, 2010; Nurjannah *et al.,* 2013; Seneviratne and Dissanayake, 2008). Antioxidant radicals (A) formed in the reaction are relatively stable and do not have enough energy to react with other lipid molecules to form new lipid radicals (Gordon, 1990).

The effect of clove powder addition to coconut milk and coconut oil on peroxide value changes during storage is shown in Figure 2. In general, the peroxide value of all coconut oil increases gradually during storage. The increased peroxide value during storage indicated the formation of hydroperoxide compounds due to primary oxidation (Ketaren, 1986). In general, coconut oil control had the most significant increase in peroxide value throughout the 7-day storage compared to clove powder-treated coconut oil. The addition of antioxidants will result in the separation of free radicals so that they can suppress the oxidation process. This is possible because eugenol has an OH group in one of its bonds. This OH group has a weak bond that the H atom in the OH group that is in the eugenol compound can be given to free radicals before the free radicals attack lipid compounds, in this case, the free fatty acids contained in coconut oil, so that the oxidation of coconut oil hampered (Lee and Shibamoto, 2001).

The primary oxidation reaction rate constant of coconut oil produced by various treatments with clove powder is shown in Table 2. The higher the oxidation reaction rate constant, the lower the oxidative stability of the coconut oil. At ambient temperature (28°C) storage, coconut oil produced by the wet rendering of coconut

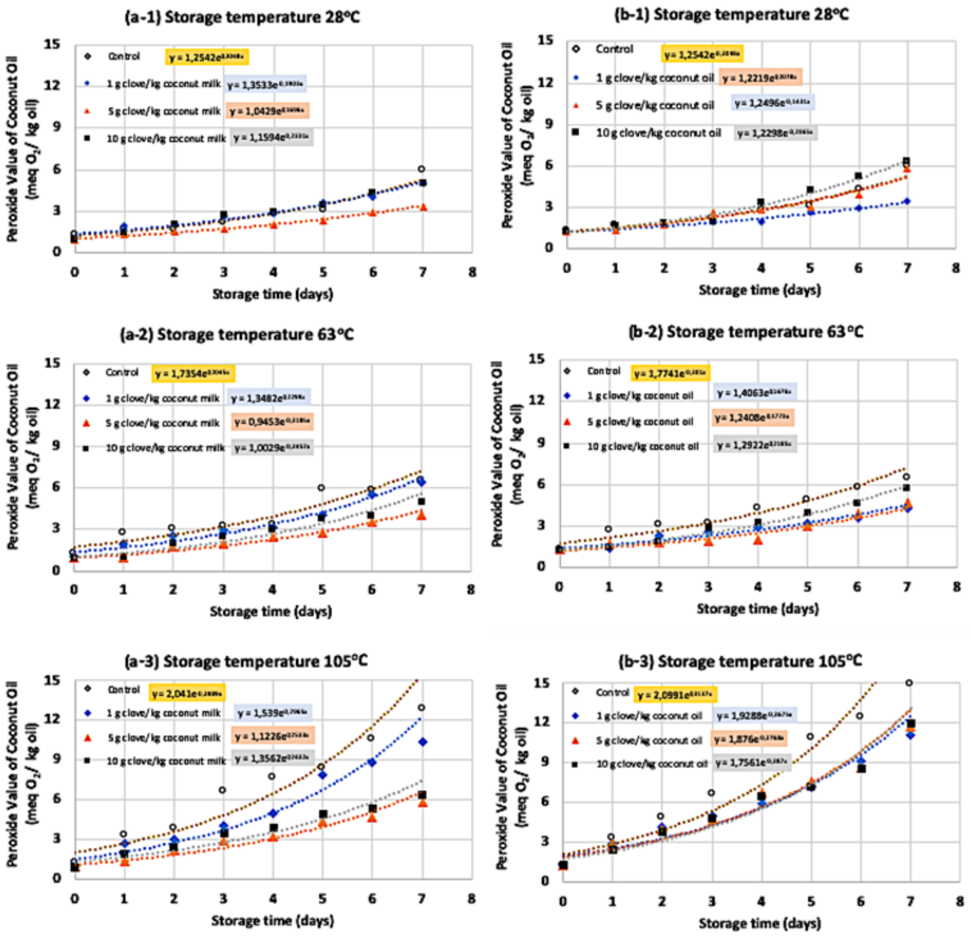

Figure 2. Effect of clove addition to coconut milk (a) or to coconut oil (b) on coconut oil oxidation stability (peroxide value) at various temperature

Table 2. Primary oxidation reaction rate constant at various temperature for coconut oil produced from wet rendering process with different clove treatment.

Temperature Kelvin (°C)	1st Order Reaction Rate Constant, k (day^{-1})						
	Control	Clove added to coconut milk (g clove/kg coconut milk)			Clove added to coconut oil (g clove/kg coconut oil)		
		1	5	10	1	5	10
301 (28)	0.201	0.190	0.170	0.223	0.168	0.143	0.219
336 (63)	0.205	0.230	0.219	0.243	0.208	0.177	0.237
378 (105)	0.314	0.297	0.253	0.246	0.268	0.277	0.287

milk added with a clove of 1 and 5 g clove/kg coconut milk had an oxidation reaction rate constant of approximately 5 and 16% lower than coconut oil control, respectively. On the other hand, coconut oil added with cloves of 1 and 5 g clove/kg coconut oil had a reaction rate constant of approximately 17% and 29% lower than coconut oil control, respectively. On the contrary, adding 10 g clove per 1 kg coconut oil increased the oxidation rate constant during storage of approximately 9 to 11% compared to that of coconut oil control. These results indicated that active compounds in clove at a higher concentration of 10 g per kg coconut oil acted as pro-oxidant, which well corresponded to the result from Seneviratne (2008). However, coconut oil added with 10 g clove/kg oil or coconut oil produced from coconut milk added with 10 g clove /kg milk had the least increase of reaction rate constant of 30% and 10%, respectively by the increase of temperature from 28 to 105°C, which indicated better stability at elevated temperature compared to coconut oil control and other clove powder treated-coconut oil.

Table 2 shows that the primary oxidation reaction rate constant increased with the increase in temperature. This well corresponded to the previous study which showed that the oxidative stability of processed vegetable oils tends to decrease with the increase in temperature, oxygen intake, and time (Koelsch *et al.* 1991; Tan *et al.,* 2001; Gómez-Alonso *et al.,* 2004; Farhoosh *et al.,* 2008; Sahin, 2019). At 63°C, almost all clove-treated coconut oil had higher reaction rate constants than the control, except for coconut oil treated with the addition of 5 g clove/kg coconut oil. On the other hand, all clove-treated coconut oil had lower

https://doi.org/10.26656/fr.2017.7(3).852

reaction rate constants than the control at a higher temperature of 105°C. These results indicated that clove powder treated - coconut oil showed better stability at high temperatures. This result was well correlated to the result from Farhoosh *et al.* (2008), who stated that added antioxidants compound of several vegetable oils affected its resistance to oxidative degradation to varying extents.

In general, clove powder added into coconut milk before oil rendering resulted in a lower peroxide value of coconut oil than clove powder added directly into coconut oil product (after rendering). This result showed that the addition of cloves to the raw material (coconut milk) proved to be a more effective treatment to inhibit oxidation reactions, not only during the wet rendering process but also during storage. This may be contributed by early stabilizations of radicals during the rendering process which inhibits the formation of radicals and free fatty acids, which were reactants for lipid oxidation reactions.

3.3 Kinetic parameter of coconut oil derived from ASLT method and Arrhenius approach

ASLT method combined with Arrhenius kinetic approach is commonly used to estimate the shelf life of a product in a specific temperature based on reaction rate constants at various temperatures. Table 3 shows the Arrhenius kinetic parameters for coconut oil produced by different treatments. ASLT method combined with Arrhenius kinetic approach is commonly used to estimate the shelf life of a product based on reaction rate constants correlations at various temperatures. Based on the coconut oil oxidation rate constants (k) presented in Table 2, it is observed that the rate of coconut oil oxidation was increased as temperature increased, with *ln(k)* showing a linear correlation with (1/T). Prediction of coconut oil oxidation rate constants at lower temperature based on ASLT combined with Arrhenius kinetics approach might encounter some limitations, which may be due to the possible difference between lipid oxidation mechanism at low and high temperatures (Hagenmaier *et al.,* 1972*;* Tan *et al.,* 2001; Farhoosh *et al.,* 2008). Therefore, reaction rate constants predictions were only considered as approximate values. In addition, different types and different concentrations of antioxidants may have different effects on the lipid oxidation mechanism (Seneviratne and Dissanayake, 2008; Chandran *et al.*, 2017).

Arrhenius kinetic parameters for coconut oil produced by different treatments were calculated from the regression parameters between *ln(k)* vs. *(1/T)* following Arrhenius correlation (Equation 1). Table 3 shows the calculated Arrhenius kinetic parameters for coconut oil oxidation, such as frequency factors *(A)*, activation energies *(Ea)*, and Q_{10}. The addition of clove powder of low to moderate concentrations (1 and 5 g clove/kg), both into coconut milk or into coconut oil, increased *Ea* compare to coconut oil control, which indicated better resistance to lipid oxidation. Clove addition variations of 1 g clove/kg coconut milk and 5 g clove/ coconut oil resulted in the highest and second-highest increase of oxidation *Ea* of approximately 1.75-fold and 1.6-fold than *Ea* of coconut oil control (3.1 kJ/ mol). On the contrary, clove addition of 10 g clove/kg coconut milk and 10 g clove/ coconut oil reduced oil oxidation *Ea* of approximately 0.4-fold and 0.6-fold than *Ea* of coconut oil control, which confirmed the possible pro-oxidant activity of clove powder at the stated

Table 3. Arrhenius kinetics parameter for oxidation reaction of coconut oil produced from wet rendering process with different clove treatment.

Arrhenius Parameters	Control	Processing Treatment: Clove added to coconut milk (g clove/kg coconut milk)			Clove added to coconut oil (g clove/kg coconut oil)		
		1	5	10	1	5	10
ln(k) = -a(1/T) + b							
a	374.40	654.41	539.81	143.41	437.33	597.50	244.89
b	-0.29	0.50	0.21	-1.01	-0.29	-0.21	0.20
R^2	0.599	0.9904	0.9812	0.8383	0.9408	0.8491	0.8209
Ea (J/mol)	3112.76	5440.76	4487.98	1192.31	3635.96	4967.62	2036.02
A_0 (day^{-1})	0.75	1.65	1.24	0.36	0.81	1.22	0.52
Q_{10}	1.04	1.07	1.06	1.02	1.05	1.07	1.03
ln(k/T) = -a(1/T) + b							
a	316.63	317.97	257.37	-193.03	353.88	653.68	65.16
b	-6.78	-6.32	-6.61	-7.83	-6.32	-5.57	-7.03
R^2	0.4568	0.9727	0.8838	0.8717	0.9928	0.9108	0.3351
ΔH^{++} (J/mol)	1414.88	2643.60	2139.77	1604.85	2942.16	5434.70	541.74
ΔS^{++} (J/mol.K)	-253.94	-250.09	-252.48	-262.68	-250.11	-243.89	-255.98

concentration. Frequency factors, *A*, showed a similar trend to that of the *Ea* values. Clove addition of 1 to 5 g per kg coconut milk or coconut oil increased frequency factors, while clove addition of 10 g per kg coconut milk or coconut oil reduced frequency factors compare to coconut oil control. On the other hand, Q10 values depicted the magnitude of the temperature effect on coconut oil oxidation rate, where a higher Q10 value indicates that only a small temperature change is needed to give rise to the changes in lipid oxidation rate (Gómez -Alonso *et al.,* 2004; Farhoosh *et al.*, 2008; Chandran *et al.*, 2017). As shown in Table 3, Q10 values of coconut oil control and other clove-treated coconut oils were almost similar between the range of 1.02 to 1.07, which may represent the thermal independence characteristic of the coconut oil–eugenol system.

Values of ΔH^{++} and ΔS^{++} for all coconut oil variations were estimated based on the activated complex theory, in which the corresponding regression parameters are shown in Table 3. The high correlation of determination for most of all coconut oil variations (R^2 of 0.772 - 0.993), with the exception for coconut oil control and 10 g clove/kg substrate variations (R^2 of 0.335 - 0.457), indicated that only the system of coconut oil and low-to-moderate concentration of clove antioxidant were sufficiently fit for the temperature dependence of lipid oxidation using the activated complex theory.

Based on the stated correlation, coconut oil control had ΔH^{++} value of approximately 1.4 kJ/mol and DS^{++} value of approximately -0.25 kJ/mol K. These values were much lower than the values of several vegetable oils studied by Kowalski (1991) using Rancimat methods, such as rapeseed oil (82 kJ/mol and –52.7 J/mol K), sunflower oil (84 kJ/mol and –42.8 J/mol K), and soybean oil (74.9 kJ/mol and –70.2 J/mol K).

Evaluation of vegetable oil oxidative stability using DSC by Tan *et al.* (2001) stated that ΔH^{++} and ΔS^{++} values were higher for oil with high unsaturated fatty acids content and lower for oil with high saturated fatty acids content. Negative values for ΔS^{++} in all the coconut oil variations indicated that entropy decreased or become more ordered during lipid oxidation, which illustrated an associative mechanism of two radicals to form a single activated complex (Espenson, 1995).

3.4 Comparison of ASLT-Arrhenius and ANN method to predict peroxide value changes during storage

Experimental data of peroxide values were used as *training data* to find the appropriate ANN model to predict coconut oil peroxide value based on several inputs such as initial peroxide value, clove addition treatments, storage time, and temperature. The next step was finding the best configuration of the number of *hidden layers* and the number of *neurons* in each *hidden layer*. To find the best ANN configuration, *training* and *testing* of various ANN configurations were conducted using experimental data. Some experimental data were used as *validators* to calculate the resulting *error* value. Various ANN configuration experiments were performed using *backpropagation* algorithm (Levenberg-Marquardt) with a *sigmoid* transfer function. The best ANN configuration is given by the 5-4 configuration (5 *neurons* in the first *hidden layer*, and 4 *neurons* in the second *hidden layer*) with MSE 0.151. Prediction of peroxide value profile using ANN compare to ASLT – Arrhenius approach for coconut oil after various treatments is shown in Figure 3.

Based on the peroxide value profile in Figure 3, both ASLT-Arrhenius approach and ANN methods showed a similar trend for control and 1 g clove/kg coconut milk or coconut oil variations from day 1 to day 10. After 10 days, the increase of peroxide value predicted by ASLT-Arrhenius method for variations of clove addition of 5 and 10 g clove/kg coconut milk or coconut oil continued to follow the 1st order kinetic reaction rate equation, while the ANN method predicted the second lag phase where peroxide value was temporarily plateau before it increased again. There was a possibility that the Arrhenius kinetic model only applied for one of the specific stages or mechanisms of the studied coconut oil oxidation, specifically the initial oxidation stage or induction period, while ANN could predict the changes after the induction period stage. Xu *et al.* (2017) compared the Arrhenius model and the radial basis function neural network (RBFNN) model to predict the quality changes of frozen shrimp (*Solenocera melantho*) and found that although most of the indicators were well-fitted to the Arrhenius model, this model had lower accuracy to predict quality indicators in the later storage days. On the other hand, the RBFNN model showed consistently high accuracy for all indicators throughout the studied storage time. *Wang et al.* (2022) also showed that while both Arrhenius and ANN models could accurately predict the changes during storage of tilapia at 233-265 K up to about 14 weeks of storage, the accuracy of the Arrhenius model was reduced significantly in the later stage of storage, while the ANN prediction on the quality changes was consistently accurate throughout the period of storage of 16 weeks. These results indicated that the neural network might be more adaptable to the changes in reaction mechanism at the extended storage period.

https://doi.org/10.26656/fr.2017.7(3).852

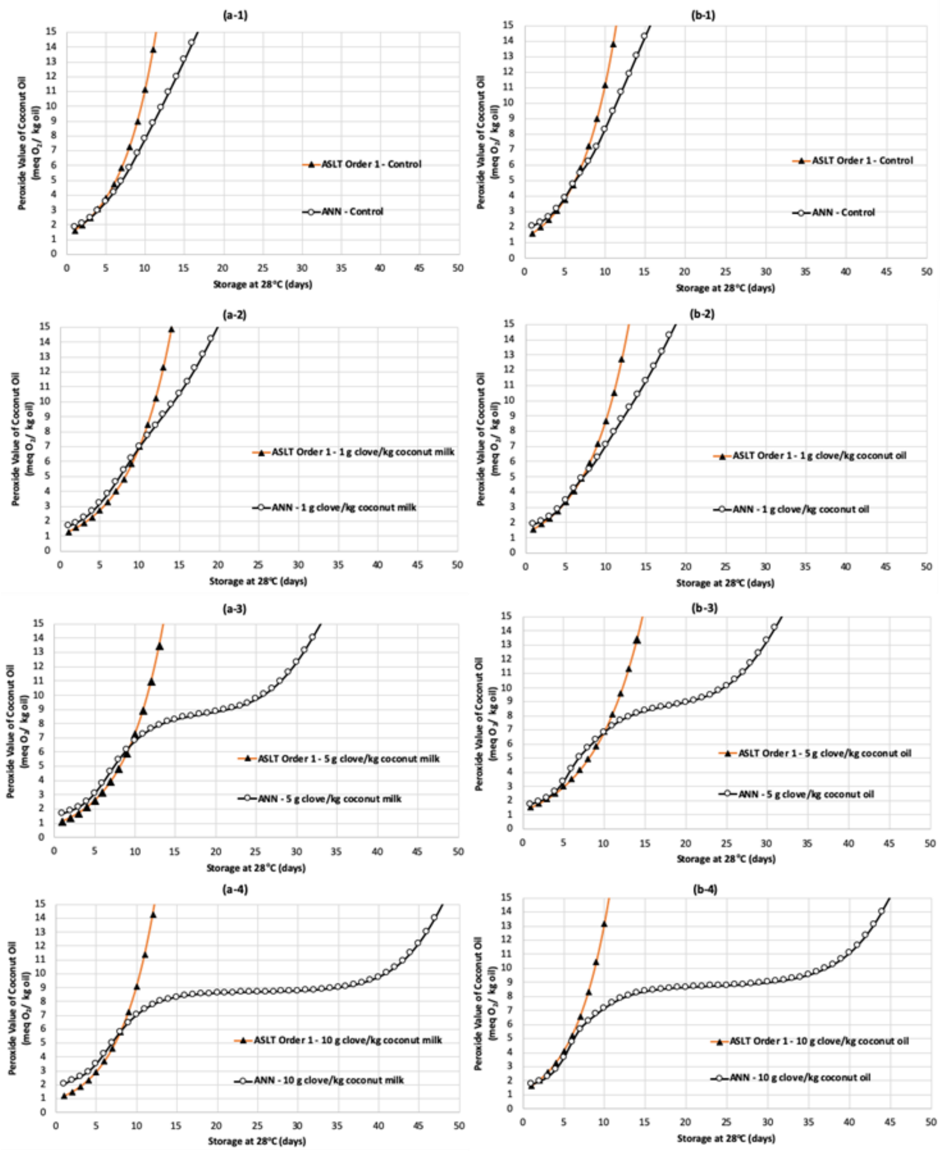

Figure 3. Peroxide value prediction at 28°C the value of rancidity using ASLT-Arrhenius and ANN method for coconut oil produced through wet rendering with clove addition (a) into coconut milk as processing aid, and (b) into coconut oil as additive with clove addition of (1) 0 (control), (2) 1 g clove/ kg, (3) 5 g clove/ kg, and (4) 10 g clove/ kg.

3.5 Comparison of coconut oil shelf life estimation using ASLT-Arrhenius and ANN method

ASLT method combined with Arrhenius kinetic approach can be used to estimate shelf life based on reaction constant at wider temperature range outside experimental data. This estimated shelf life and the time required for coconut oil to reach the peroxide value limit of 15 meq/kg (t) were then plotted as a function of temperature (T) following exponential regression in Equation 4:

$$t = a \exp(bT) \text{ or } \ln(t) = \ln(a) + b \ln(T) \qquad (4)$$

Where t (days) is the time required to reach the upper limit of peroxide value (15 meq O_2/ kg of oil) at a specific temperature of T (°C); with *a* and *b* are constants. The plot in Figure 4 can be used empirically to predict the time required for the studied coconut oil to reach the defined upper limit of peroxide values at various temperatures. This estimate may be useful to predict coconut oil stability at various temperature ranges, not only during storage but also during cooking or processing, such as baking, frying, or chilling. While the lower amount of clove addition into coconut milk as processing air or into coconut oil product resulted in longer shelf life in room temperature storage, the addition of 10 g clove into 1 kg of coconut milk during oil rendering gave the highest stability of coconut oil on high temperature, which will ensure the oil stability in the processed product after expose in high temperature processing such as baking or frying.

Shelf life estimation of coconut oil using ANN compared to ASLT – Arrhenius approach for coconut oil after various treatments is shown in Figure 5. In general, clove addition either as a processing aid in coconut milk or as additive in coconut oil improved the shelf life of coconut oil compared to the control. At 28°C storage, the ASLT method predicted that coconut oil control had an estimated shelf life (reached the limit peroxide value of 15 meq O_2 /kg) of approximately 11 days. This result well corresponded to the result from Laitupa and Susane

https://doi.org/10.26656/fr.2017.7(3).852

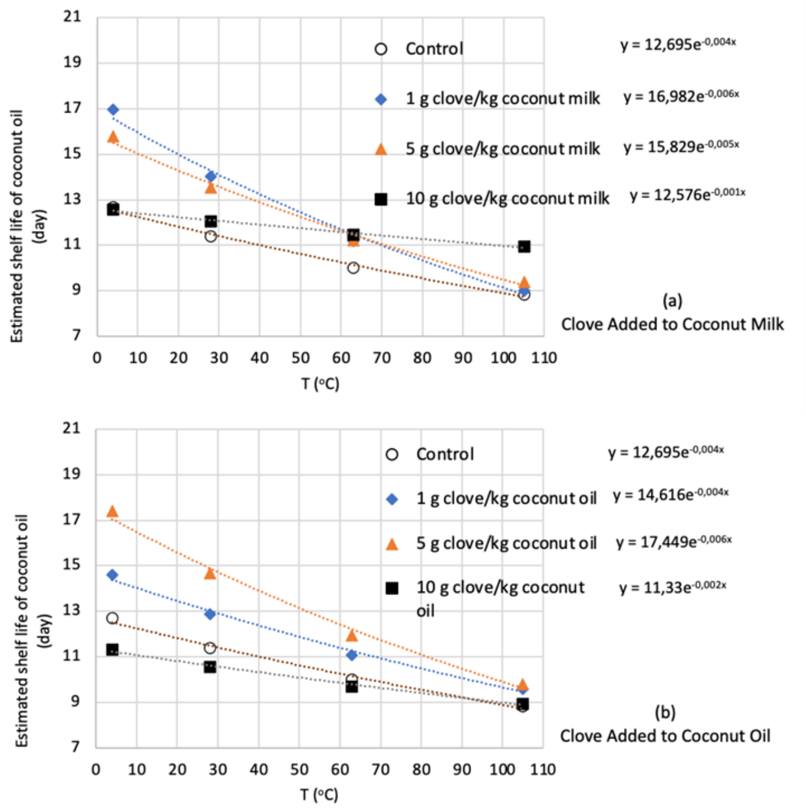

Figure 4. Shelf life of coconut oil produced through wet rendering with clove addition into (a) coconut milk as processing aid and (b) coconut oil as additive, as temperature function derived from ASLT-Arrhenius method.

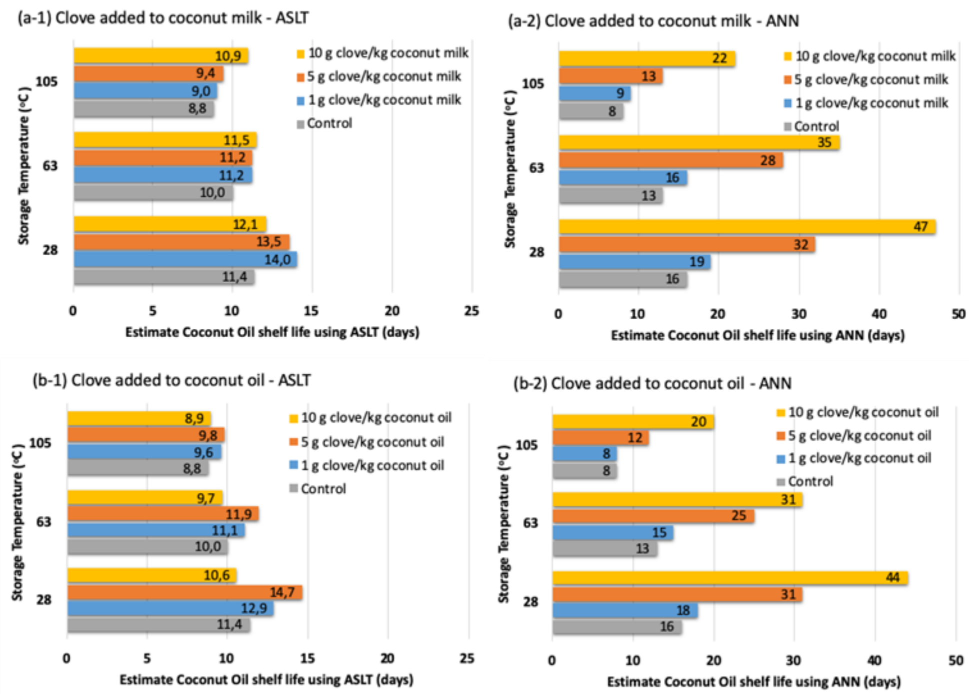

Figure 5. Shelf life estimation at various oxidation temperature until the value of rancidity for coconut oil produced through wet rendering with clove addition (a) into coconut milk as processing aid, and (b) into coconut oil as additive using (1) ASLT-Arrhenius and (2) ANN method.

(2010), which showed that crude coconut oil produced by traditional wet rendering reached a peroxide value of 15 meq/kg oil after 12 days of storage at ambient temperature. Adding 1 g clove/kg coconut milk and 5 g clove/kg coconut oil gave the best result by improving coconut oil shelf life to 14 days while adding 10 g clove per kg coconut oil showed the opposite effect by slightly reducing shelf life compared to control. However, at higher temperatures, adding 10 g clove per kg coconut milk as processing aid improved shelf life from approximately 10 days (control) to 11.5 days at 63°C and from approximately 9 days (control) to 11 days at 105°C. ANN method showed a different trend than Arrhenius kinetics, where the increase of clove addition amount from 1 to 10 g clove/kg coconut milk or coconut oil improved shelf life of approximately 1.2-times to 3-times

https://doi.org/10.26656/fr.2017.7(3).852

longer than coconut oil control. Based on ANN method predictions at 28°C, adding 10 g clove/kg coconut oil improved the estimated oil shelf life to 35 days, while 10 g clove/kg coconut milk improved the estimated oil shelf life to 47 days. In general, the shelf-life prediction of various studied coconut oil by using ANN was approximately 1.5 to 4-times higher than ASLT-Arrhenius approach, and the difference was more distinguished by the increase of clove amount addition. The estimated shelf life until the clove treated-coconut oil reach a peroxide value of 15 meq O_2/ kg of oil was between 12 to 15 days by using the Arrhenius model and between 19 to 47 days by using the ANN model. These estimated values were much lower than the result from Perera *et al.* (2020), who studied the effect of incorporating bioactive compounds in selected spiced (ginger, garlic, nutmeg, cloves, pepper, and cinnamon) on the peroxide value of the flavoured coconut oil, where the oil peroxide values were far below 15 meq O_2/ kg of oil after 12 weeks of storage. This study showed that the flavoured coconut oil contained a high amount of phenolic content and DPPH free radical scavenging activity, which inhibited peroxide formation by neutralizing the pre-formed free radicals. This inhibition of peroxide formation in the later stage of secondary lipid oxidation may not be accommodated by using only Arrhenius models, especially based on the peroxide value in the earlier stage of storage, in which the primary oxidation mainly occurs.

4. Conclusion

This research shows that clove addition during the wet rendering process increases the oxidative stability of coconut oil products. The addition of clove powder into coconut milk as a processing aid proved to reduce oil oxidation during the heated wet rendering process. ASLT-Arrhenius approach and ANN method resulted in similar predictions of peroxide value changes on day 1 to day 10 of storage, but start to show different trends of peroxide value changes after day 10. In general, the ASLT-Arrhenius method gave a shorter estimated shelf life than the ANN method. The peroxide value predictions with ANN method were still partially fitted with the common knowledge on primary lipid oxidation mechanism, while ASLT-Arrhenius approach seems to be more suitable for predicting the shelf life of the coconut oil produced by the wet rendering process in this study. However, the ANN model is a promising and convenient tool to predict the quality changes of traditional coconut oil throughout the longer storage period. Therefore, further study needs to be conducted to verify other indicators of oil stability, such as total oxidation and antioxidant activity, throughout a longer storage time by using the ANN method.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

This research was partially funded by ITB Research Grant 2021 provided by Institut Teknologi Bandung, Indonesia.

References

Antolovich, M., Prenzler, P.D., Patsalides, E., McDonald, S. and Robards, K. (2002). Methods for testing antioxidant activity. *Analyst*, 127(1), 183–198. https://doi.org/10.1039/b009171p

Besbes, S., Blecker, C., Deroanne, C., Lognay, G., Drira, N.E. and Attia, H. (2004). Quality characteristics and oxidative stability of date seed oil during storage. *Food Science and Technology International*, 10(5), 333–338. https://doi.org/10.1177/1082013204047777

BSN-Indonesia. (1992). Indonesian National Standardization of Crude Coconut Oil, SNI 01-2902-1992. Jakarta, Indonesia: BSN.

Calligaris, S., Manzocco, L., Anese, M. and Nicoli, M. C. (2019). Accelerated shelf-life testing (Chapter 12). In Galanakis, C.M. (Ed). Food Quality and Shelf Life, p. 359-392. USA: Academic Press. https://doi.org/10.1016/B978-0-12-817190-5.00012-4

Chandran, J., Nayana, N., Roshini, N. and Nisha, P. (2017). Oxidative stability, thermal stability, and acceptability of coconut oil flavored with essential oils from black pepper and ginger. *Journal of Food Science and Technology*, 54(1), 144–152. https://doi.org/10.1007/s13197-016-2446-y

Codex Alimentarius. (1999). Codex Standard for Named Vegetable Oils (Codex Stan 210-1999). Geneva, Italy: Codex Alimentarius.

Dehghani, A.A., Mohammadi, Z.B., Maghsoudlou, Y. and Mahoonak, A.S. (2012). Intelligent Estimation of the Canola Oil Stability Using Artificial Neural Networks. *Food and Bioprocess Technology*, 5(2), 533–540. https://doi.org/10.1007/s11947-009-0314-8

Espenson, J.H. (1995). Chemical Kinetics and Reaction Mechanism. 2nd ed., p. 1–281. USA: McGraw-Hill Education.

Farhoosh, R., Niazmand, R., Rezaei, M. and Sarabi, M. (2008). Kinetic parameter determination of vegetable oil oxidation under Rancimat test conditions. *European Journal of Lipid Science and Technology*, 110(6), 587–592. https://doi.org/10.1002/ejlt.200800004

Gómez-Alonso, S., Mancebo-Campos, V., Salvador, M.D. and Fregapane, G. (2004). Oxidation kinetics in olive oil triacylglycerols under accelerated shelf-life testing (25-75°C). *European Journal of Lipid Science and Technology*, 106(6), 369–375. https://doi.org/10.1002/ejlt.200300921

Gordon, M.H. (1990). The Mechanism of Antioxidant Action *in Vitro*. In Hudson, B.J.F. (Eds.) Food Antioxidants. Elsevier Applied Food Science Series, p. 1-18. Dordrecht, Netherlands, Springer. https://doi.org/10.1007/978-94-009-0753-9_1

Goyal, S. (2012). Predicting shelf life of dairy product by using artificial neural networks (ANN) and statistical computerized methods. *International Journal of Computer Engineering Research,* 3(2), 20–24. https://doi.org/10.5897/IJCER12.008

Goyal, S. and Goyal, G.K. (2011). Simulated Neural Network Intelligent Computing Models for Predicting Shelf Life of Soft Cakes. *Global Journal of Computer Science and Technology*, 11(14), 29-33.

Goyal, S. and Goyal, G.K. (2012). Estimating Processed Cheese Shelf Life with Artificial Neural Networks. *IAES International Journal of Artificial Intelligence (IJ-AI)*, 1(1), 19–25. https://doi.org/10.11591/ij-ai.v1i1.336

Hagenmaier, R., Cater, C.M. and Mattil, K.F. (1972). Critical unit operations of the aqueous processing of fresh coconuts. *Journal of the American Oil Chemists Society*, 49(3), 178–181. https://doi.org/10.1007/BF02633790

Jayadas, N.H. and Nair, K.P. (2006). Coconut oil as base oil for industrial lubricants-evaluation and modification of thermal, oxidative, and low temperature properties. *Tribology International*, 39 (9), 873–878. https://doi.org/10.1016/j.triboint.2005.06.006

Ketaren, S. (1986). Pengantar teknologi minyak dan lemak pangan. Jakarta, Indonesia: UI-Press. [In Bahasa Indonesia].

Koelsch, C.M., Downes, T.W. and Labuza, T.P. (1991). Hexanal Formation via Lipid Oxidation as a Function of Oxygen Concentration: Measurement and Kinetics. *Journal of Food Science*, 56(3), 816–820. https://doi.org/10.1111/j.1365-2621.1991.tb05389.x

Kowalski, B. (1991). Thermal-oxidative decomposition of edible oils and fats. DSC studies. *Thermochimica Acta*, 184(1), 49–57. https://doi.org/10.1016/0040-6031(91)80134-5

Laitupa, F. and Susane, H. (2010). Pemanfaatan eugenol dari minyak cengkeh untuk Mangatasi Ranciditas Pada Minyak Kelapa. *Jurusan Teknik Kimia, Fakultas Teknik. Universitas Diponegoro.*, (24), 1–10. [In Bahasa Indonesia].

Lee, K.G. and Shibamoto, T. (2001). Antioxidant property of aroma extract isolated from clove buds (*Syzygium aromaticum L.*). et Perry. *Food Chemistry*, 74(4), 443–448. https://doi.org/10.1016/S0308-8146(01)00161-3

Marasabessy, A., Moeis, M.R., Sanders, J.P.M. and Weusthuis, R.A. (2010). Coconut oil extraction by the traditional Java method: An investigation of its potential application in aqueous Jatropha oil extraction. *Biomass and Bioenergy*, 34(8), 1141–1148. https://doi.org/10.1016/j.biombioe.2010.03.005

Nurah, T.O., Fernando, W., Coorey, R., Gold, I. and Jayasena, V. (2017). Effect of extraction techniques on the quality of coconut oil. *African Journal of Food Science*, 11(3), 58–66. https://doi.org/10.5897/AJFS2016.1493

Nurjannah, D.A., Retnowati, R. and Juswono, U.P. (2013). Aktivitas Antioksidan dari Minyak Bunga Cengkeh (*Syzygium aromaticum*) Kering berdasarkan Aktivitas Antiradikal yang ditentukan menggunakan Electron Spin Resonance. Indonesia: Universitas Brawijaya, BSc. Thesis. [In Bahasa Indonesia].

Penet, C., Birschbach, P., Glatz, S.E., Glatz, C.E., Johnson, L.A., Lamsal, B.P., Zhang, C. and Wu, J. (2010). Enzyme-assisted de-emulsification of aqueous lipid extracts. U.S. Patent No. 0227042. Washington, DC, USA: U.S. Patent and Trademark Office.

Perera, D.N., Hewavitharana, G.G., Navaratne, S.B. (2020). Determination of Physicochemical and Functional Properties of Coconut Oil by Incorporating Bioactive Compounds in Selected Spices. *Journal of Lipids*, 2020, 8853940. https://doi.org/10.1155/2020/8853940

Przybylski, R., and Zambiazi, R.C. (2000). Predicting oxidative stability of vegetable oils using neural network system and endogenous oil components. *Journal of the American Oil Chemists' Society*, 77 (9), 925. https://doi.org/10.1007/s11746-000-0146-x

Ramos, T.C.P.M., de Souza, E.F., Santos, M.N., Fiorucci, A.R., Cardoso, C.A.L. and da Silva, M.S. (2019). Evaluation of antioxidant potential and chemical composition blends of sunflower oil (*Helianthus annuus l.*) with coconut oil (*Cocos nucifera L.*). *Orbital*, 11(4 Special Issue), 246–252. https://doi.org/10.17807/orbital.v11i4.1226

Sahin, S. (2019). Evaluation of Stability against Oxidation in Edible Fats and Oils. *Journal of Food Science and Nutrition Research*, 2(3), 283–298.

https://doi.org/10.26502/jfsnr.2642-11000027

Seneviratne, K.N. and Dissanayake, D.M.S (2008). Variation of phenolic content in coconut oil extracted by two conventional methods. *International Journal of Food Science and Technology*, 43(4), 597–602. https://doi.org/10.1111/j.1365-2621.2006.01493.x

Subajiny, S., Dilini, B. and Terrence, M. (2018). A comparative study on stability of different types of coconut (*Cocos nucifera*) oil against autoxidation and photo-oxidation. *African Journal of Food Science*, 12(9), 216–229. https://doi.org/10.5897/AJFS2018.1695

Tan, C.P., Che Man, Y.B., Selamat, J. and Yusoff, M.S.A. (2001). Application of Arrhenius kinetics to evaluate oxidative stability in vegetable oils by isothermal differential scanning calorimetry. *Journal of the American Oil Chemists' Society*, 78(11), 1133–1138. https://doi.org/10.1007/s11746-001-0401-1

Wang, H., Zheng, Y., Shi, W. and Wang, X. (2022) Comparison of Arrhenius model and artificial neuronal network for predicting quality changes of frozen tilapia (*Oreochromis niloticus*). *Food Chemistry*, 372, 131268. https://doi.org/10.1016/j.foodchem.2021.131268

Wongpoowarak, W., Pichayakorn, W., Oungbho, K., Boontaweesakul, W. and Sirivongmongkol, S. (2009). Model of Degradation Kinetics for Coconut Oil at Various Heating Temperatures. *Science*, 2(2), 43–49.

Xu, Z., Liu, X., Wang, H., Hong, H., and Luo, Y. (2017). Comparison between the Arrhenius model and the radial basis function neural network (RBFNN) model for predicting quality changes of frozen shrimp (*Solenocera melantho*). *International Journal of Food Properties*, 20(11), 2711-2723. https://doi.org/10.1080/10942912.2016.1248292

