Research Article

Model of Degradation Kinetics for Coconut Oil at Various Heating Temperatures

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Abstract

This study was aimed to investigate the model of degradation kinetics for coconut oil at various heating temperatures. The oxidative stability of coconut oil at temperature variations between 130 and 200 °C was investigated by UV absorbance measurement. The induction times (time-to-abrupt change) were determined from the curves between the absorbance at 270 nm, related to amount of secondary oxidation products, and time. The model of degradation kinetics was empirically estimated using non-linear regression. From the obtained model, coconut oil degraded via at least two different pathways while being heated, i.e., autocatalysis and first order reactions. This model could describe the entire degradation curve including the induction time behavior of coconut oil at heating temperatures below 150 °C. However, at higher heating temperatures, the other pathways of degradation might occur which could not be explained by the proposed model.

Key Words: Degradation kinetics; Oxidative stability; Induction time; Coconut oil

Introduction

Coconut oil has a long history for providing human with several applications in daily life. It has found use in foods (e.g., cooking oil), cosmetics (e.g., spa oil) and industries (e.g., lubricant). Coconut oil is classified to unique group of vegetable oils called lauric oils since its main composition is lauric acid (Jayadas and Nair, 2006). Although most compositions of coconut oil are saturated fatty acids, its minor unsaturated fatty acids (oleic and linoleic acids) can lead to oil rancidity because of lipid oxidation. Generally, lipid oxidation is described by a free-radical chain mechanism involving three steps, i.e., (i) initiation or formation of initial free radicals ($RH \rightarrow R^\bullet + H^\bullet$), (ii) propagation of the free radicals and formation of primary oxidation products such as hydroperoxide ($R^\bullet + O_2 \rightarrow ROO^\bullet$, $ROO^\bullet + RH \rightarrow ROOH + R^\bullet$) and (iii) termination and formation of secondary oxidation products such as carbonyl compounds ($R^\bullet + R^\bullet \rightarrow R\text{-}R$, $R^\bullet + ROO^\bullet \rightarrow ROOR$, $ROO^\bullet + ROO^\bullet \rightarrow O_2 + ROOR$) (Kanner and Rosenthal, 1992; Gonzaga and Pasquini, 2006). Oxidative stability is represented by the time in which an oil sample resists to oxidation. This time, called induction time or induction period, can be determined by heating the oil sample to a constant temperature and then measuring a parameter of the degree of oxidation with time. Several physical and chemical parameters can be used to elucidate the degree of oxidation of the oil sample. The parameters related to degree of oxidation remains practically constant during the stability period of the oil. Afterwards, it begins changing resulting in determination of the induction time (Gonzaga and Pasquini, 2006). Many experimental techniques have been applied to investigate degree of oxidation of an oil sample, e.g., thermo-analytical method, electron spin resonance spectroscopy, near infrared emission spectroscopy, Fourier transform Raman spectroscopy, conductivity measurement, fast ultrasound-assisted method and UV absorbance measurement (Kanner and Rosenthal, 1992; Halbaut et al., 1997; Vieira and Regitano-d´Arce, 1998; Rudnik et al., 2001; Guillén and Cabo, 2002; Cañizares-Macías et al., 2004; Gomez-Alonso et al., 2004; Oliveira and Regitano-d´Arce, 2004; Velasco et al., 2004; Muika et al., 2005; Gonzaga and Pasquini, 2006; Jayadas and Nair, 2006). Among these techniques, UV absorbance measurement for performing amounts of the secondary oxidation products with time seemed to be a convenient method in order to elucidate the induction time of an oil sample, coconut oil. In addition, the obtained data could be further studied for the model of degradation kinetics.

The aim of this work was to investigate the model of degradation kinetics for coconut oil at various heating temperatures.

Materials and Methods

Materials

Coconut oil was prepared in house by cold process without refining, bleaching and deodorization. This process is a common way of producing commercial virgin coconut oil. Briefly, the gratings of fresh and mature coconut were prepared using a rotating grater. The wet gratings were put in a net and extracted for coconut milk by squeezing. The obtained milk was mixed with the coconut water and allowed to settle through a process called culturing. Afterwards, a three-layer mixture was obtained. Protein contents rose up to the surface while oil and water contents were in the middle and the lowest layers, respectively. The oil was collected and filtered. The gained oil was clear liquid with mild coconut flavor. Chloroform was purchased from Lab-Scan Analytical Science (Bangkok, Thailand) and used as received without further purification.

Heating Coconut Oil at Various Temperatures

The 40 ml of coconut oil was heated at the various temperatures of 130, 140, 145, 150 and 200 °C using a hot plate with a thermocouple for controlling the temperature in an ambient condition. The heated oil was taken and measured by UV absorbance spectroscopy for its secondary oxidation products occurring during 10 studying hours until the color change from colorless to brown was observed (Vieira and Regitano-d´Arce, 1998; Oliveira and Regitano-d´Arce, 2004). The initial time (minute 0) started when the oil reached to the determined temperature. At each sampling time, 300 µl heated coconut oil was taken. After the oil sample was allowed to cool down to room temperature, it was mixed with 3 ml chloroform. The heating experiment was done in duplicate for each heating temperature. Afterwards, the absorbance of each sample was measured in duplicate using UV spectrophotometer (Spectronic Genesys 5, Milton Roy, Ivyland, PA, USA) at the wavelength of 270 nm while chloroform was used as a blank. The studied wavelength was 270 nm since changing in absorbance from the spectrum of UV-scans between 200 to 400 nm of heated coconut oil in the preliminary study was observed at 270 nm (data not shown). This result was in accordance with the report of Vieira and Regitano-d´Arce (1998) who found that molecular friction during microwave heating of refined canola, corn and soybean oils could promote the formation of secondary oxidation products (trienes and unsaturated ketones or aldehydes) exhibiting absorption at 270 nm.

Estimation of the Empirical Model of Degradation Kinetics

The obtained data were analyzed to estimate the empirical model in order to explain the degradation kinetics of coconut oil. Due to the complexity of the differential equation model and the data structures, the non-linear regression of the differential equation was manually performed in Microsoft Excel™. Although this method was inferior to using standard software since it did not provide confidence interval, it was suffice to elucidate the possible kinetic model.

The finite differences numerical method was used for numerically solving differential equation. In this study, Euler method (order 1) was selected (Wylie and Barrett, 1982). The time step used in the Euler method was arbitrarily assigned and adjusted until stable and converged prediction result was provided. Afterwards, it was implemented as a user-defined function in visual basic code for Microsoft Excel™ to calculate the incremental change described by the differential equation for any time interval $t_1 \rightarrow t_2$. The criterion for performing non-linear regression was to minimize Sum of Square Error (SSE) of the prediction. The parameters of kinetics (degradation rate constants) for each temperature were manually adjusted until measurement data from all temperatures could be simultaneously described by the differential equations at each temperature, sharing only the initial condition parameters (i.e., initial concentrations).

Results and Discussion

As shown in Figure 1, the absorbance values of coconut oil heated at 130, 140, 145, 150 and 200 ˚C were low and almost constant during the induction time (i.e., 420, 210, 240, 120 and 15 min, respectively). After the induction time, the absorbance values abruptly increased due to the formation of secondary oxidation products (Vieira and Regitano-d′Arce, 1998). In addition, higher slope of absorbance-heating time curves during oxidation period at higher heating temperature was observed in Figure 1. This suggested that the heating temperature influenced not only the oil stability, a decrease of the induction time, but also the oxidation rate after the induction time (Gonzaga and Pasquini, 2006).

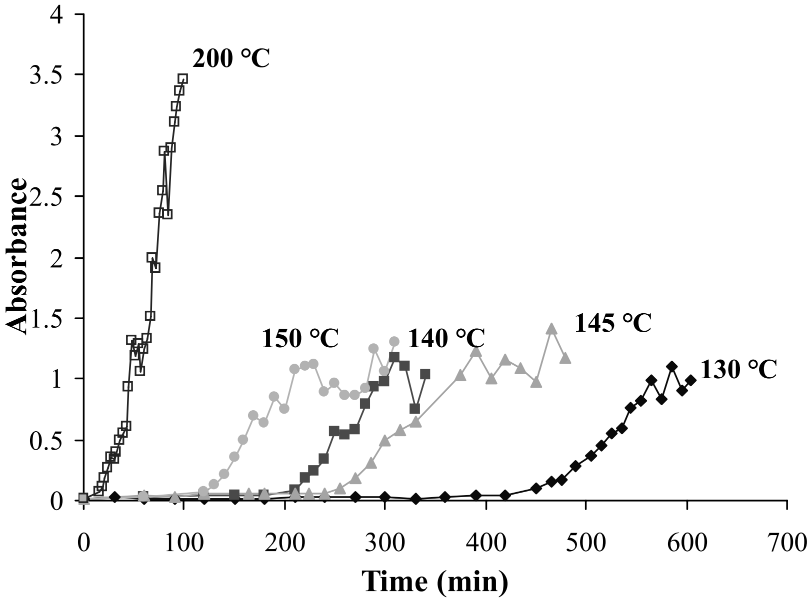

Figure 1 Absorbance at 270 nm of coconut oil samples heated at various temperatures between 130 and 200 ˚C as a function of time.

The model was empirically constructed from the results in Figure 1 by data fitting with various scenarios and each scenario had its own specific sets of differential equations to explain the degradation kinetics of coconut oil as shown in Figure 2. Due to the biphasic behavior in logarithmic scale, the degradation of coconut oil could be described by two simplified pathways, i.e., changing from non-degraded coconut oil (A) to first (B) and second (C) degradation products, respectively. The first pathway (A → B) was called autocatalysis reaction since the degradation product (B) could catalyze its own rate of formation (i.e., positive feedback for its own destruction). The autocatalysis model suggested that oxidation possibly involved in degradation pathway of coconut oil. The second pathway (A → C) was simple first order reaction. These degradation pathways could thus be described with the following equations (Martin, 1993):

$$d[A]/dt = -k_1[A][B]-k_2[A] \quad (1)$$

$$d[B]/dt = k_1[A][B] \quad (2)$$

$$d[C]/dt = k_2[A] \quad (3)$$

where [A] was concentration of non-degraded coconut oil; [B] and [C] were concentrations of degradation products of coconut oil; k_1 and k_2 were rate constants of autocatalysis and first order reactions, respectively. The concentration could be expressed as UV absorbance; therefore absorbance values were used instead of concentration throughout this experiment.

The obtained data from the experiment were compared with the calculated data as presented in Figure 3. The measured and predicted values were in the same tendency while the heating temperatures were lower than or equal to 150 °C. Hence, the proposed model could properly explain the degradation of coconut oil in the range of low

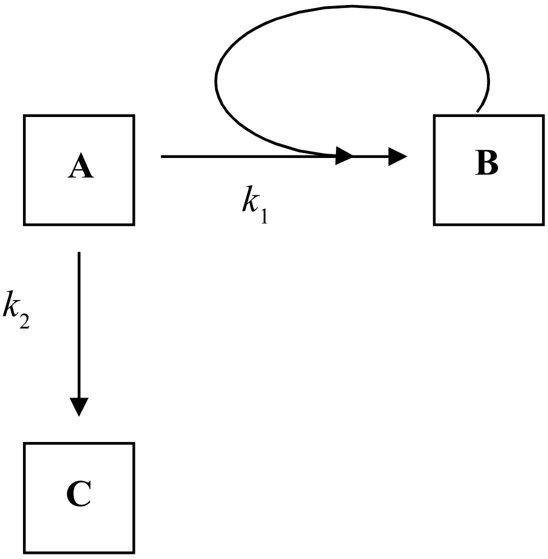

Figure 2 Model of degradation kinetics of coconut oil. A refers to non-degraded coconut oil. B and C refer to degradation products of coconut oil. The k_1 and k_2 refer to rate constants.

temperature (≤150 °C). However, the model could partially explain the data at higher heating temperature (200 °C) in first 60 minutes since there might be further degradation that contributed to absorbance far exceed that found in lower temperature range. This result suggested that degradation of coconut oil at high heating temperature (200 °C) may occur in different pathways from that at low heating temperature (≤150 °C).

The best-fit values of k_1 and k_2 could be found by manual optimization in Microsoft Excel™ Worksheet. All the regression parameters were manually optimized to achieve the best fit criterion (i.e., minimize SSE) for each and all particular temperatures. The initial values of all components (i.e., A_o, B_o, C_o) were fixed as the same values for all temperature data and varied particular sets of k_1 and k_2 for each temperature.

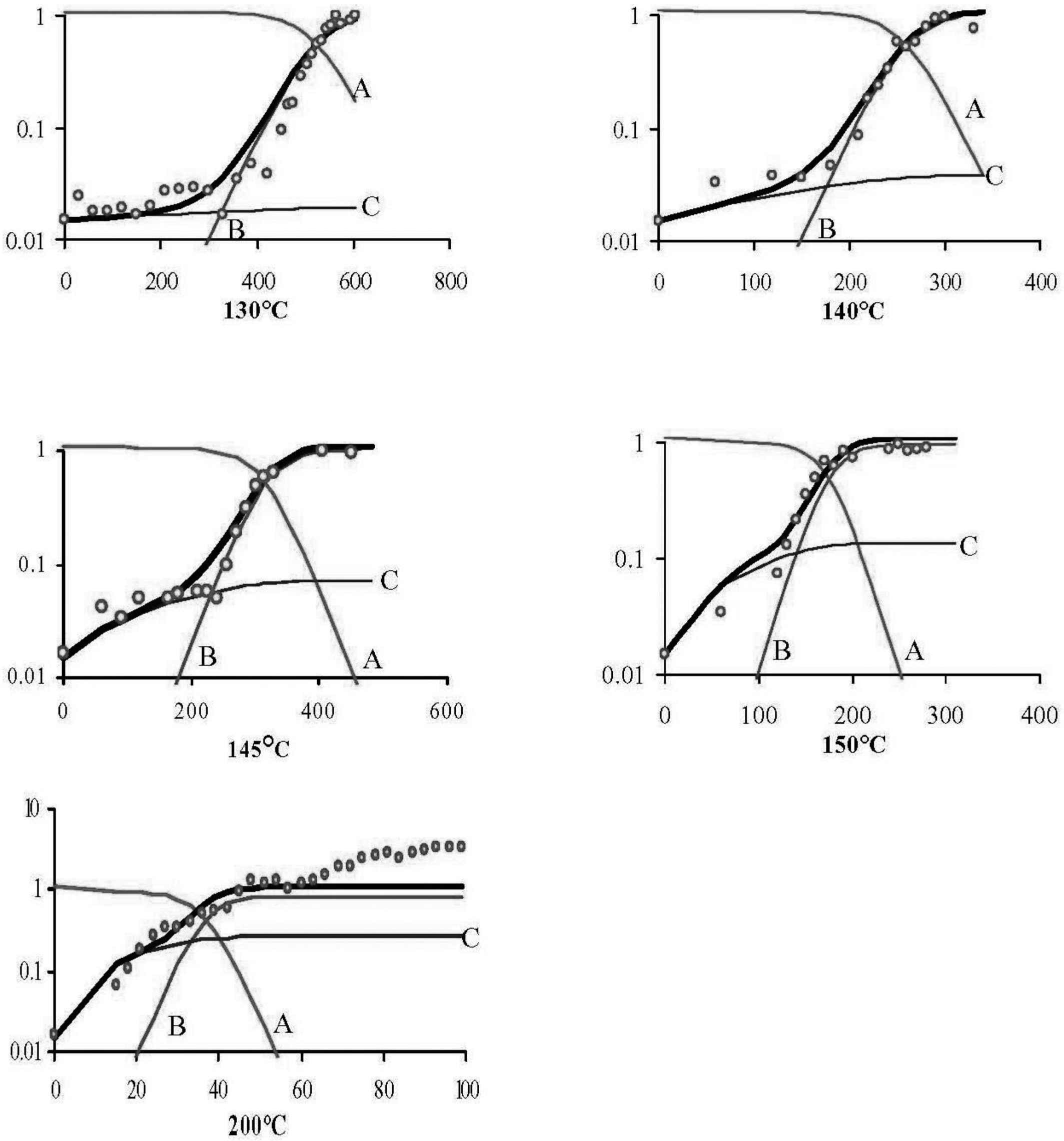

Figure 3 Plot of relationship between log (absorbance) of heated coconut oil samples (y axis) at various temperatures and time (x axis). The dotted and hard lines represent the measured and predicted values, respectively. The light lines show the partial effect of A, B and C estimated from the nonlinear regression of the model.

The induction time could be roughly estimated via graphical method. However, in order to standardize the data interpretation process, the degradation profile was simulated to predict induction time. Before the induction time, the slope was low (non-zero slope) and could be approximated by a constant slope. After the induction time, the slope was at its highest and could be approximated by another constant slope. From this observation, the derivative of the slope (i.e., the second derivative of the concentration with time) should be highest at the induction time. We simulated the system and computed second derivative of the degradation curve in respect to the heating time; the time to reach the highest second derivative of the simulated concentration of the degradation products was the induction time in this study.

Table 1 The rate constants (k_1 and k_2), predicted induction time and percentage of prediction error of coconut oil degradation at various heating temperatures.

Heating Temperature (°C)	k_1 (absorbance^{-1} min^{-1})	k_2 (min^{-1})	Predicted Induction Time (min)	% Prediction Error
130	0.019	7.9×10^{-6}	467	11.19
140	0.039	8.1×10^{-5}	234	11.43
145	0.030	1.7×10^{-4}	282	17.50
150	0.060	6.7×10^{-4}	157	30.83
200	0.300	7.0×10^{-3}	37	146.67

The summary of predicted k_1, k_2 and induction time values at various heating temperatures are shown in Table 1. From the obtained model, it could be estimated from linear regression between temperature and logarithm of induction time that induction time decreased approximately by half for every increase of 14 °C in the heating temperature. In previous study, Gonzaga and Pasquini (2006) found that the induction time of canola oil decreased approximately by half for every increase of 10 °C in the heating temperature. This model was not suitable for describing the degradation of coconut oil at high heating temperature (200 °C) due to different degradation behavior. It could be noted in Table 1 that higher values of percentage of prediction error for induction time compared to the experimental data in Figure 1 were observed at higher heating temperatures. Theoretically, the k_1 and k_2 could be further used to predict the shelf-life of the sample using Arrhenius equation (Martin, 1993). However, the actual kinetic processes were suspected to be more complex than described by UV measurement in this study. Hence, only induction time extrapolation was used in this study.

Conclusions

The obtained empirical model suggested that there were at least two types of degradation pathways involved while coconut oil was heated. The first-type of pathway was autocatalysis (second order kinetics) due to positive feedback from the primary oxidation products. The second-type of pathway was first order kinetics. Each pathway might consist of various smaller kinetic processes of the same nature. From simulation study, autocatalysis was found to be very slow in the beginning and very fast after reaching critical level at induction period. Since autocatalysis was positive feedback process (i.e. self-destruct feedback), preventing its initiation should also prevent its destruction process.

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