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Non-Isothermal Thermal Degradation Kinetics of Cerbera odollam Seed Oil

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Abstract

The thermal degradation kinetics of refined non-edible Cerbera odollam seed oil were investigated under non-isothermal conditions using thermogravimetric analysis (TGA) and the Advanced Vyazovkin isoconversional method. TGA measurements were conducted at nominal heating rates of 5, 10, 15 and 20 °C min^{-1} over the investigated temperature range. Increasing the heating rate progressively shifted the principal degradation region toward higher temperatures, with the DTG peak temperature increasing from 310 °C at 5 °C min^{-1} to 340 °C at 20 °C min^{-1}. The Advanced Vyazovkin objective functions exhibited well-defined approximately parabolic profiles with distinct minima at the investigated conversion levels, confirming the suitability of numerical minimization for determining the apparent activation energy. The apparent activation energy decreased with increasing conversion, with representative values of approximately 115.17 kJ mol^{-1} at $\alpha = 0.20$, 97 kJ mol^{-1} at $\alpha = 0.50$ and 88 kJ mol^{-1} at $\alpha = 0.80$. This progressive decrease demonstrates that the apparent kinetic barrier for degradation is conversion dependent rather than constant throughout the degradation process. The results establish a non-isothermal thermal degradation profile and conversion-dependent kinetic fingerprint for C. odollam seed oil, providing useful thermal kinetic information for its consideration as a non-edible industrial feedstock and for subsequent thermally processed applications.

Keywords: Cerbera odollam seed oil; thermogravimetric analysis; thermal degradation; isoconversional kinetics; Advanced Vyazovkin; activation energy; non-isothermal kinetics.

1. Introduction

Vegetable oils are increasingly being investigated as renewable alternatives to petroleum-derived feedstocks because their triglyceride structures contain fatty-acid chains with functional groups and unsaturation that can participate in chemical modification and conversion into value-added materials. Their use as industrial raw materials extends beyond biofuels to polymeric materials, coatings, resins and other bio-based products. For such applications, understanding the thermal behaviour of the oil is important because extraction, processing, chemical modification and subsequent thermal treatment may expose the material to elevated temperatures. Thermal stability and degradation kinetics are therefore important parameters in assessing the suitability of oil-based feedstocks for thermally demanding industrial processes.

Cerbera odollam (sea mango) is a tropical oil-bearing plant belonging to the family Apocynaceae, and its seeds contain a substantial quantity of non-edible oil. Unlike edible vegetable oils commonly investigated for food and industrial applications, C. odollam is associated with toxic seeds and is consequently considered a non-edible feedstock. Its oil has nevertheless attracted attention as a potential industrial resource because the seed contains appreciable oil and the material does not directly compete with conventional edible oil resources. Recent studies have characterized *C. odollam* seed oil as a non-edible plant-derived oil with potential for industrial applications. Madiebo et al. (2024) reported that the refined oil is dominated by oleic and palmitic acids, with linoleic and stearic acids also present, providing a chemically reactive triglyceride structure relevant to industrial conversion. Consequently, the non-edible character of C. odollam seed oil, together with its fatty-acid composition, makes it a relevant renewable feedstock for investigations involving thermal processing and conversion

Previous work has established that C. odollam seed oil possesses measurable thermal stability but also undergoes substantial mass loss at elevated temperatures. Rosli et al. (2023) reported that the oil remained comparatively stable below approximately 200 ^{o}C, followed by substantial mass loss at higher temperatures, with the principal degradation behaviour occurring at elevated temperature. Their study employed thermogravimetric analysis

primarily to determine the thermal stability and decomposition characteristics of the extracted oil. These findings are useful for identifying the practical thermal range of the oil; however, a degradation temperature or mass-loss profile obtained from a conventional TGA experiment does not, by itself, provide a complete description of the kinetics governing the degradation process. In particular, the temperature at which a degradation event appears depends on experimental conditions such as heating rate, and therefore a single-heating-rate TGA curve cannot adequately establish how the apparent energetic barrier changes as degradation progresses.

Non-isothermal kinetic analysis using multiple heating rates provides a means of obtaining more detailed information from thermogravimetric data. In isoconversional analysis, temperatures corresponding to the same conversion are compared across different heating rates, allowing the apparent activation energy to be evaluated as a function of conversion without requiring the degradation process to conform to a predetermined reaction model. This feature is particularly relevant to complex organic feedstocks such as *C. odollam* seed oil, whose thermal decomposition may involve contributions from triglycerides containing different fatty-acid structures and potentially overlapping degradation processes. The use of a conversion-dependent activation energy, E_α, therefore provides more information than assigning a single activation energy to the overall degradation process.

Among the available model-free approaches, the Advanced Vyazovkin isoconversional method provides a rigorous numerical procedure for determining activation energy from non-isothermal thermogravimetric data acquired at multiple heating rates. The method evaluates an objective function derived from the temperature integral of the Arrhenius equation and determines the activation energy at each conversion level through numerical minimization. Vyazovkin's isoconversional framework was developed specifically to evaluate activation energies for thermally stimulated processes under arbitrary temperature variation, while subsequent developments provided the Advanced Vyazovkin formulation for improved numerical treatment of non-isothermal kinetic data (Vyazovkin, 2015). Drozin et al. (2020) subsequently implemented the Advanced Vyazovkin procedure as a computational tool for determining kinetic parameters from thermal-decomposition data, providing a practical framework for numerical evaluation of the method. The Arrhenius temperature integral required in the calculation can also be efficiently approximated using the rational approximations developed by Senum and Yang (Budrugeac, 2016), which were specifically formulated for kinetic analysis of thermogravimetric data.

Although C. odollam seed oil has previously been investigated for extraction (Lim et al., 2023), biodiesel production (Ang et al., 2015), alkyd resin synthesis (Madiebo et al., 2024), chemical characterization and general thermal stability (Rosli et al., 2023), the available literature identified in this study does not provide a detailed conversion-dependent Advanced Vyazovkin kinetic profile of its non-isothermal thermal degradation. Existing TGA work has primarily established thermal stability and decomposition temperature rather than systematically determining the evolution of apparent activation energy over the conversion range. This creates an opportunity to extend the thermal characterization of this non-edible oil from a descriptive assessment of mass loss to a quantitative kinetic description of the degradation process.

Hence, this study seeks to determine the non-isothermal thermal degradation kinetics of Cerbera odollam seed oil using the Advanced Vyazovkin isoconversional method and to evaluate the variation of apparent activation energy with conversion. TGA data obtained at multiple heating rates were transformed into conversion-dependent kinetic parameters, with the Advanced Vyazovkin objective function numerically optimized to determine E_α over the investigated conversion range. The study addresses the identified gap in the literature by providing a detailed conversion-dependent activation-energy profile for the non-isothermal degradation of C. odollam seed oil, rather than relying solely on degradation temperatures or mass-loss characteristics. The innovative aspect lies in applying the Advanced Vyazovkin isoconversional framework to establish this conversion-dependent kinetic fingerprint for the oil, thereby providing a more quantitative description of its thermal degradation behaviour and a basis for assessing its suitability as a non-edible renewable feedstock for thermally demanding industrial applications.

2.0 Materials and methods

2.1 Methods

Refined Cerbera odollam seed oil was used as the test material. The oil was previously extracted from *C. odollam* seeds and refined following the procedure reported by Madiebo et al. (2024). The previously prepared refined oil was stored in sealed glass containers prior to analysis. No further chemical modification of the oil was performed before thermogravimetric analysis. Because C. odollam is a toxic, non-edible plant, the oil and seed-derived materials were handled using laboratory safety procedures.

2.2 Thermogravimetric Analysis

The thermal degradation behaviour of the refined C. odollam seed oil was investigated using thermogravimetric analysis (TGA) under non-isothermal conditions. Approximately 6 mg of oil was accurately weighed into the TGA sample pan and heated from 25 to 600 °C under a controlled nitrogen atmosphere at a constant gas flow rate of 20 mL min^{-1}. Four heating rates of 5, 10, 15 and 20 °C min^{-1} were employed. The same sample mass range, atmosphere, gas flow rate and temperature programme were maintained for all experiments to ensure comparability of the thermogravimetric curves. The recorded sample mass was expressed as a function of temperature and used to determine the thermal degradation profile of the oil. The derivative thermogravimetric (DTG) curve was obtained from the first derivative of mass with respect to temperature DTG = dm/dT, to identify the principal mass-loss region and the corresponding maximum degradation temperature. The onset temperature, peak degradation temperature and final degradation temperature were determined from the TGA/DTG curves. These parameters were used to describe the thermal stability and principal degradation characteristics of the refined oil

2.3 Computational Processing and Conversion-Temperature Extraction

TGA data processing was executed using Visual Studio Code (version 1.134.0) with Python 3.10.9. The workflow utilized a custom Python script incorporating NumPy and pandas for numerical calculations and structured data manipulation, SciPy for numerical optimization and interpolation routines, and Matplotlib for generating data visualizations. Recorded mass loss values were first converted into fractional conversion (α) using Eq. (1). For each heating rate, the conversion values were arranged in ascending order, and the corresponding temperature array was interpolated using shape-preserving piecewise cubic Hermite interpolating polynomials (scipy.interpolate.PchipInterpolator). This allowed extraction of the conversion-dependent temperature array, $T_{\alpha,i}$, across a grid of $\alpha = 0.10\text{-}0.90$ at intervals of 0.01.

The Advanced Vyazovkin objective function was subsequently calculated at each conversion increment using the four interpolated temperatures corresponding to heating rates of $5{,}10{,}15$, and $20\ ^{\circ}\mathrm{C} \cdot \mathrm{min}^{-1}$. The apparent activation energy (E_α) was determined via bounded Brent scalar minimization using scipy.optimize.minimize_scalar (method='bounded'). Optimization was performed over a broad search range of 1.0×10^3 to $5.0 \times 10^5\ \mathrm{J} \cdot \mathrm{mol}^{-1}$ (1-500 $\mathrm{kJ} \cdot \mathrm{mol}^{-1}$), ensuring full coverage of typical thermal degradation energy barriers without edge-boundary constraints. Uniform optimization bounds and a scalar tolerance of $1.0 \times 10^{-6}\ \mathrm{J} \cdot \mathrm{mol}^{-1}$ were applied independently across all evaluated conversion levels ($\alpha = 0.10\text{-}0.90$).

2.4 Thermal Degradation Kinetic Framework

The thermal degradation of Cerbera odollam seed oil under a programmed temperature increase can be represented as the progressive conversion of the initial oil into lower-molecular-weight and volatile degradation products as heat is continuously supplied to the sample:

$$\text{C. odollam oil} \xrightarrow[\beta = dT/dt]{\text{heat}} \text{degradation products}$$

where $T$is the absolute temperature and β is the heating rate. Because vegetable oil is a chemically complex material containing triglycerides with fatty-acid chains of different structures, the degradation process is treated as an overall conversion process rather than as the decomposition of a single pure compound. Thermogravimetric analysis therefore provides the experimental basis for following the progress of degradation through the change in sample mass.

The extent of conversion, α, is obtained from the measured mass loss according to

$$\alpha = \frac{m_0 - m_T}{m_0 - m_f} \tag{1}$$

where m_0, m_T, and m_f are the initial mass, mass at temperature T, and final mass, respectively, over the selected degradation interval. Thus, $\alpha = 0$ represents the initial state and $\alpha = 1$ represents completion of the degradation interval. This conversion variable transforms the experimentally measured thermogravimetric mass-loss curves into a form suitable for kinetic analysis.

The general rate equation for a thermally activated conversion process can be written as

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \tag{2}$$

where $f(\alpha)$represents the conversion-dependent reaction function and $k(T)$is the temperature-dependent rate constant. Following the Arrhenius relationship,

$$k(T) = A\exp\left(-\frac{E_\alpha}{RT}\right) \tag{3}$$

where $A$is the pre-exponential factor, $E_\alpha$is the apparent activation energy at conversion α, $R$is the universal gas constant, and $T$is absolute temperature. The use of E_α, rather than a single constant E, is appropriate for an isoconversional treatment because the apparent kinetic barrier may vary as the degradation proceeds.

Under the non-isothermal conditions employed in TGA, the heating rate is

$$\beta = \frac{dT}{dt} \tag{4a}$$

and is maintained approximately constant for each experiment. Hence,

$$dt = \frac{dT}{\beta} \tag{4b}$$

Combining the rate equation with the Arrhenius relationship and the non-isothermal heating condition gives

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E_\alpha}{RT}\right)f(\alpha) \tag{5}$$

which establishes the relationship between the experimentally measured conversion, temperature and heating rate. This formulation is also the basis of the kinetic framework presented by Drozin et al. for thermal-decomposition analysis.

For a model-free isoconversional analysis, a particular form of $f(\alpha)$is not required. Instead, the principle of isoconversion is applied: at a fixed conversion α, the reaction rate is governed by temperature, and the temperatures corresponding to the same conversion can therefore be compared across experiments conducted at different heating rates.

Accordingly, TGA measurements are performed at several heating rates,

$$\beta_1, \beta_2, \dots, \beta_n,$$

and for a selected conversion α, the corresponding temperatures are obtained as

$$T_{\alpha,1}, T_{\alpha,2}, \dots, T_{\alpha,n}.$$

The activation energy is then determined independently at successive conversion levels, for example over

$$0.10 \le \alpha \le 0.90. \tag{6}$$

The Advanced Vyazovkin method (Santhosh et al., 2025) determines the apparent activation energy at each conversion level by minimizing an objective function constructed from the temperature integrals obtained at different heating rates. The formulation used in the present study is given by Eqs. (7)–(12);

$$\Omega(E_\alpha) = \sum_{i=1}^{n}\sum_{\substack{j=1 \\ j\neq i}}^{n}\frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} \tag{7}$$

Where i and j denote the heating rates employed, n is the total number of heating-rate experiments and $I(E_\alpha, T_{\alpha,i})$ is the Arrhenius temperature integral evaluated at the temperature corresponding to conversion α for experiment i. The temperature integral is expressed as

$$I(E_\alpha, T_{\alpha,i}) = \int_{T_0}^{T_{\alpha,i}}\exp\left(-\frac{E_\alpha}{RT}\right)dT \tag{8}$$

and is evaluated using the substitution

$$x = \frac{E_\alpha}{RT} \tag{9}$$

The integral can consequently be written in the form

$$I(E_\alpha, T_{\alpha,i}) = \frac{E_\alpha}{R}p(x) \tag{10}$$

where $p(x)$is a rational approximation to the Arrhenius temperature integral expressed as fourth-order Senum–Yang approximation (Budrugeac, 2016)

$$p(x) = \frac{e^{-x}(x^3 + 18x^2 + 88x + 96)}{x(x^4 + 20x^3 + 120x^2 + 240x + 120)} \tag{11}$$

With x evaluated with Eq. 9.

The apparent activation energy at each conversion is finally obtained by numerical minimization of the Vyazovkin function in Eq. 9:

$$E_\alpha = \Omega(E) \tag{12}$$

such that the value of E producing the minimum of $\Omega(E)$is assigned as the activation energy corresponding to that conversion.

In the present work, this minimization was implemented in Python using Brent's method, which is a bounded one-dimensional scalar optimization algorithm. This method is appropriate because only one parameter, E_α, is optimized at each conversion level, while the physically meaningful search interval can be explicitly bounded. The optimization was repeated at each selected conversion level to obtain the conversion-dependent activation-energy relationship depicted in Eq. 13.va

$$E_\alpha = f(\alpha) \tag{13}$$

which constitutes the principal kinetic output of the analysis. The resulting $E_\alpha - \alpha$ profile provides a direct assessment of whether the apparent energy barrier for degradation remains approximately constant or changes as conversion progresses. Significant variation in E_α with conversion can indicate conversion-dependent kinetics and may be consistent with overlapping or competing degradation processes**.** Thus, the complete kinetic framework analysis flow diagram of the experimental thermal response of C. odollam seed oil to a model-free determination of its conversion-dependent degradation kinetics is depicted in Figure 1:

$$m(T) \rightarrow \alpha(T) \rightarrow \frac{d\alpha}{dT} \rightarrow T_{\alpha,i} \rightarrow I\left(E_\alpha, T_{\alpha,i}\right) \rightarrow \Omega(E_\alpha) \rightarrow \min \Omega \rightarrow E_\alpha$$

Fig. 1: TGA-to-kinetics framework for Advanced Vyazovkin analysis.

The final output adapted from Eq.13 is given as E_α versus α represents the kinetic fingerprint used to characterize the non-isothermal thermal degradation behaviour of C. odollam seed oil.

3. Results and Discussion

3.0 Result and Discussion

3.1 Thermogravimetric and derivative thermogravimetric behaviour

The thermogravimetric profiles of refined Cerbera odollam seed oil obtained at heating rates of 5, 10, 15 and 20 °C min^{-1} are presented in Figure 2, while the corresponding derivative thermogravimetric (DTG) profiles are presented in Figure 3. The TGA curves exhibit a relatively gradual mass loss at temperatures below approximately 240-250 °C, followed by a pronounced reduction in mass over the subsequent temperature range. The principal degradation event becomes progressively displaced toward higher temperature as the heating rate increases.

At the lowest heating rate of 5 °C min^{-1}, the rapid degradation region begins at approximately 250–260 °C and the DTG maximum occurs at about 310 °C. Increasing the heating rate to 10, 15 and 20 °C min^{-1} shifts the corresponding DTG maxima to approximately 320, 330 and 340 °C, respectively. Thus, a systematic increase of approximately 10 °C in the peak degradation temperature occurs for every increase in heating rate used in the present study. The corresponding DTG peak magnitude decreases from approximately -1.25 % $°C^{-1}$ at 5 °C min^{-1} to -0.95 % $°C^{-1}$ at 20 °C min^{-1}, indicating that the apparent rate of mass loss expressed per unit temperature interval becomes less concentrated as the heating rate increases.

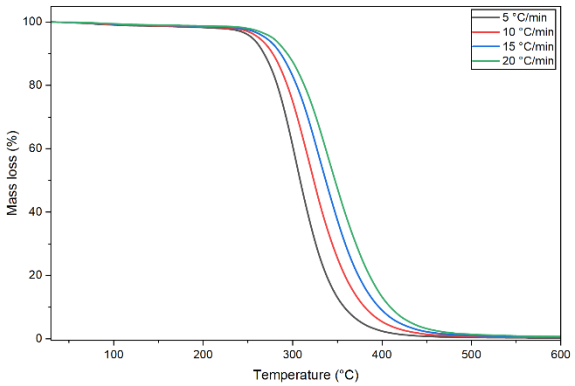


Figure 2. Thermogravimetric (TGA) curves of Cerbera odollam seed oil at different heating rates.

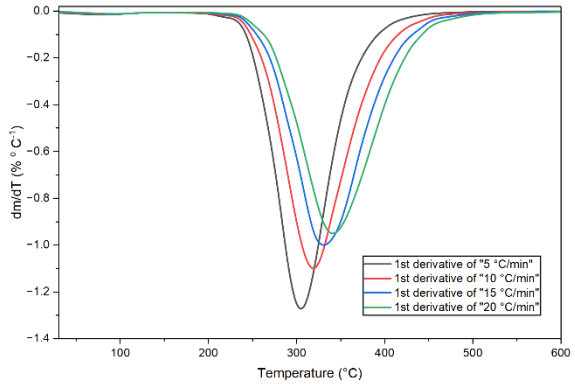


Figure 3. Derivative thermogravimetric (DTG) curves of Cerbera odollam seed oil at different heating

This displacement of the degradation region toward higher temperatures with increasing heating rate is characteristic of non-isothermal thermogravimetric measurements. Under faster heating, the sample experiences less time at each temperature, and consequently a higher temperature is required to attain a particular extent of conversion. Similar heating-rate dependence has been reported for vegetable oils(Li et al., 2018; Sarker et al., 2025), where the thermal degradation/oxidation characteristics and characteristic temperatures shift with heating rate.

The present results are also consistent with the available TGA study of C. odollam seed oil by Rosli et al. (2023) who reported that the oil remained comparatively stable below approximately 200 °C before undergoing substantial mass loss at higher temperature. Their experiment was conducted under nitrogen from room temperature to 800 °C at 10 °C min^{-1}. The present results extend that observation by demonstrating how the principal degradation temperature changes systematically when the heating rate is varied.

Table 1. Preliminary TGA/DTG characteristics of refined C. odollam seed oil

Heating rate (°C min^{-1})	$T_{(5\%)}$(°C)	T_{max}(°C)	$T_{(95\%)}$(°C)	Residue at 600 °C (%)
5	254.8	310	376.2	0.25
10	262.3	320	400.1	0.40
15	269.9	330	415.9	0.55
20	277.4	340	428.3	0.70

The calculated mass loss over the complete experimental temperature interval was approximately 99.3–99.8%, with only 0.25-0.70% residual mass at 600 °C. This indicates that the refined oil undergoes almost complete volatilization/decomposition under the employed TGA conditions. The TGA curves in Figure 1 show that only minor mass loss occurred before the principal degradation region, with rapid mass loss occurring predominantly at temperatures above approximately 250 °C. The main degradation event was therefore clearly separated from the low-temperature region, indicating that the oil undergoes substantial thermal decomposition only at relatively high temperatures under the experimental conditions. The progressive shift of the degradation region toward higher temperatures with increasing heating rate is characteristic of non-isothermal TGA and is subsequently considered in the kinetic analysis. The slight increase in residual mass with increasing heating rate is not interpreted as a direct indication of improved thermal stability, since the final residue can be influenced by the thermal history and time available for decomposition during the programmed heating experiment. The observed thermal behaviour demonstrates that C. odollam seed oil undergoes its principal mass-loss process within a high-temperature region,

with the exact degradation temperature depending on the applied heating rate. These observations provide the experimental basis for the subsequent isoconversional kinetic analysis.

3.2 Effect of heating rate on degradation conversion

To quantitatively evaluate the progression of degradation, the TGA mass-loss data were transformed into fractional conversion using Eq. 1. The resulting conversion-temperature relationships are shown in Figure 4. A clear separation of the four curves is observed throughout the principal degradation region. At a given conversion, the temperature required to achieve the conversion increases systematically with heating rate.

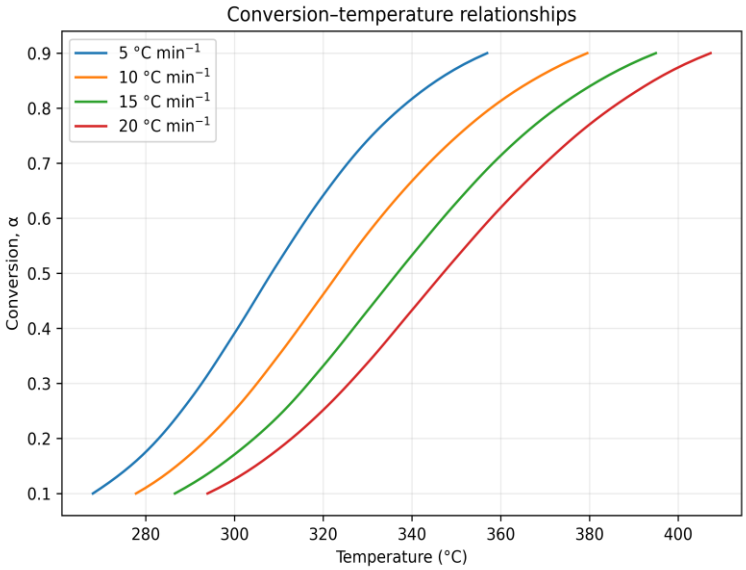


Figure 4. Conversion–temperature profiles of Cerbera odollam seed oil at different heating rates.

At $\alpha = 0.50$, the temperatures obtained from the 5, 10, 15 and 20 °C min^{-1} experiments are approximately 308.3, 323.4, 336.7 and 347.0 °C, respectively. Thus, increasing the heating rate from 5 to 20 °C °C min^{-1} increases the temperature corresponding to 50% conversion by approximately 39 °C. The same trend is observed at other conversion levels as shown in Table 2.

Table 2 Temperatures corresponding to selected conversion levels

α	5 °C/min	10 °C/min	15 °C/min	20 °C/min
0.10	268.1	277.8	286.6	293.9
0.20	282.9	294.0	304.4	312.9
0.30	292.6	305.1	316.7	325.8
0.40	300.7	314.5	326.8	336.6
0.50	308.3	323.4	336.7	347.0
0.60	316.4	332.7	346.9	357.8
0.70	325.5	343.8	358.2	370.0
0.80	337.5	357.8	372.6	384.9
0.90	357.0	379.5	395.0	407.3

The different heating rates provide the temperature values required for the isoconversional analysis. At each selected conversion, the corresponding temperatures from the four heating rates were compared and used in the Advanced Vyazovkin calculation. Thus, the use of multiple heating rates was necessary to determine how the apparent activation energy changed with conversion. The shift in the degradation profiles with increasing heating rate agrees with recent observations reported for plant-derived oils. Sarker et al. (2025) reported a rightward shift in the TGA/DTG profiles of vegetable oils and their modified derivatives as the heating rate increased, indicating that higher temperatures were required to initiate thermal devolatilization at higher heating rates. A comparable heating-rate effect is observed for the non-edible *Cerbera odollam* seed oil in the present study. The resulting differences in degradation temperature at a given conversion provide the temperature data required for the Advanced Vyazovkin calculation of E_α.

3.3 Advanced Vyazovkin Objective-Function Analysis

Figure 4 presents the Advanced Vyazovkin objective function, Ω(Eα), as a function of trial activation energy at selected conversion levels of α = 0.20, 0.50 and 0.80. The three profiles exhibit a distinct, approximately parabolic dependence on the trial activation energy and possess well-defined minima. The observed behaviour is consistent with recent thermokinetic investigations of vegetable oils using Advanced Vyazovkin analysis. Ramírez-Verduzco and Torres-García (2024) in a comparative study of palm and soybean oils, reported multiple degradation stages

and substantial variation in activation-energy barriers and related this behaviour to triglyceride composition and the degree of fatty-acid unsaturation. This provides a relevant basis for interpreting the conversion-dependent E_α profile observed for *C. odollam* seed oil, although the present TGA analysis does not by itself permit assignment of individual kinetic features to specific fatty-acid constituents. This interpretation is also supported by Li et al. (2018), who demonstrated through TGA analysis of vegetable oils and their constituent fatty acids that thermal stability varies with fatty-acid structure and degree of unsaturation, with more highly unsaturated fatty acids exhibiting lower thermal-oxidative stability.The present results therefore support the applicability of the Advanced Vyazovkin approach to the thermal degradation analysis of non-edible *Cerbera odollam* seed oil

The position of the minimum of each objective-function curve represents the optimum apparent activation energy, Eα, corresponding to that particular conversion level. In the present study, the minima occur at approximately 115 kJ mol⁻¹ at α = 0.20, 97 kJ mol⁻¹ at α = 0.50 and 88 kJ mol⁻¹ at α = 0.80. The progressive displacement of the minima toward lower activation energies with increasing conversion therefore indicates that the apparent activation energy decreases as thermal degradation proceeds. The Advanced Vyazovkin implementation reported by Drozin et al. (2020) similarly determines Eα by locating the minimum of the Vyazovkin objective function through numerical optimization.

The decrease in Eα from approximately 115 kJ mol⁻¹ at α = 0.20 to 88 kJ mol⁻¹ at α = 0.80 corresponds to an approximate reduction of 23.5%. This conversion dependence indicates that the degradation of the refined Cerbera odollam seed oil cannot be adequately described by a single conversion-independent activation energy over the investigated degradation interval. Such behaviour is expected for complex organic materials because the apparent activation energy obtained by an isoconversional method represents the overall kinetic response of the material at a particular stage of conversion rather than the activation energy of a single elementary reaction.

The well-defined minima observed for all three representative conversion levels also demonstrate the numerical stability of the optimization procedure used in the present study. At each conversion level, the activation energy was obtained by identifying the value of E that minimizes the objective function, such that:

$$E_\alpha = \arg\min \Omega(E) \tag{14}$$

where Ω(E) is the Advanced Vyazovkin objective function and E_α is the activation energy corresponding to the selected conversion. The representative objective-function curves in Figure 5 therefore provide the direct numerical basis for the activation-energy values obtained at the selected conversion levels. The optimization was subsequently repeated at each conversion level over the selected conversion range to obtain the complete E_α–α relationship shown in Figure 5. The resulting relationship provides a direct representation of the variation in the apparent activation energy as the thermal degradation of the oil progresses.

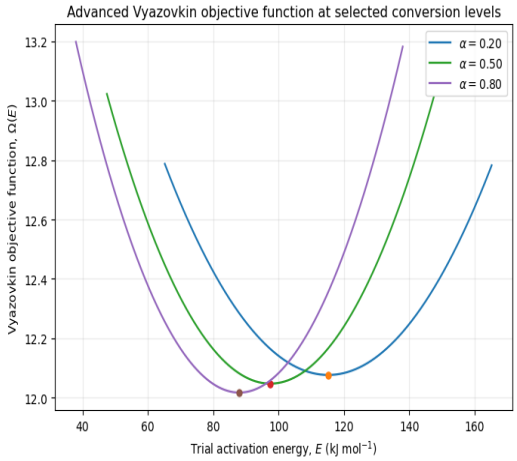


Figure 5. Advanced Vyazovkin objective functions at selected conversion levels.

The conversion-dependent apparent activation energy obtained using the Advanced Vyazovkin isoconversional method is presented in Figure 6. The calculated activation energy does not remain constant throughout the degradation process. Instead, $E_\alpha$decreases progressively with increasing conversion during the early and intermediate stages of degradation, followed by a tendency toward stabilization and a slight increase at the highest conversion investigated.

At $\alpha = 0.10$, the calculated apparent activation energy is approximately 127.4 kJ mol^{-1}. It decreases to approximately 115.17 kJ mol^{-1} at $\alpha = 0.20$, 107.49 kJ mol^{-1} at $\alpha = 0.30$, 102.35 kJ mol^{-1} at $\alpha = 0.40$, and 97.46 kJ mol^{-1} at $\alpha = 0.50$. The decrease continues through $\alpha = 0.60$ and 0.70, reaching approximately 93.4 and 90.0 kJ mol^{-1}, respectively. The lowest value occurs around $\alpha = 0.80$, where E_α is approximately 88.0 kJ mol^{-1}, followed by a small increase to approximately 88.1 kJ mol^{-1} at $\alpha = 0.90$.

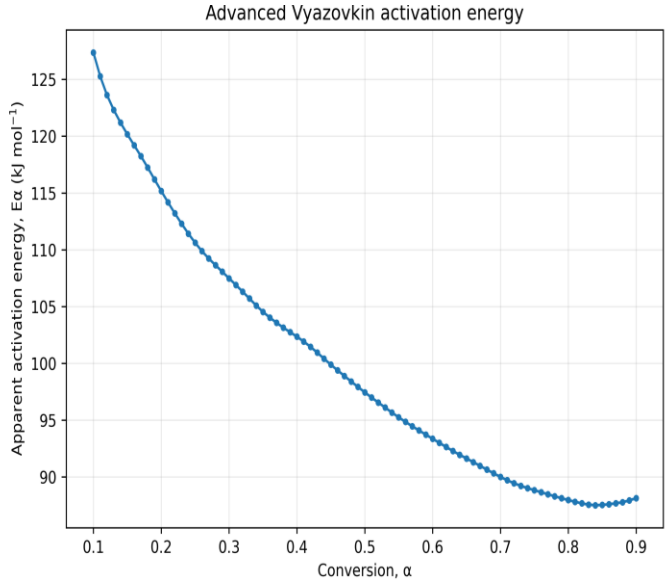


Figure 6. Apparent activation energy as a function of conversion for Cerbera odollam seed oil.

The decrease of E_α with conversion is the most important kinetic result of the study. It indicates that the thermal degradation of the refined *C. odollam* oil cannot be adequately represented by a single conversion-independent activation energy. Instead, the apparent kinetic barrier changes as degradation proceeds. This behaviour is physically plausible for vegetable oils because the material is not a single chemical species but a mixture of triglycerides containing fatty-acid chains with different degrees of unsaturation and different thermal reactivities. Previous thermogravimetric studies have similarly associated the degradation of vegetable oils with contributions from fatty-acid components having different degrees of unsaturation. Studies using conventional kinetic approaches have reported multiple degradation contributions associated with polyunsaturated, monounsaturated and saturated components.

The present E_α profile provides a stronger indication of this conversion dependence than a single average activation energy would. Advanced isoconversional analysis was specifically developed to determine activation energy as a function of conversion without requiring prior selection of a particular reaction model. Drozin et al. (2020). describe this as one of the principal advantages of the Vyazovkin approach for complex thermal decomposition processes. Isoconversional activation energy is therefore best interpreted as a kinetic descriptor of the overall degradation process rather than as the activation energy of one uniquely identified elementary reaction. Interestingly, the magnitude of the present activation energies is within the general range reported for thermal decomposition of various vegetable-oil-derived materials, although direct numerical comparison should be made cautiously because reported values depend strongly on atmosphere, sample composition, heating rates, conversion range and kinetic method. For example, recent thermogravimetric investigations of chemically modified vegetable oils have reported substantially higher average activation energies under oxidative conditions, demonstrating how strongly chemical modification and atmosphere influence the apparent kinetic barrier.

The present study therefore provides a conversion-resolved kinetic description specifically for refined C. odollam seed oil, rather than assuming that values reported for soybean, sunflower, palm or other oils are transferable to C. odollam.

Table 3. Advanced Vyazovkin kinetic parameters

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E_α(kJ mol^{-1})	127.36	115.17	107.49	102.35	97.46	93.37	90.01	87.97	88.14

3.4 Kinetic interpretation and implications for industrial utilization

The combined TGA and kinetic results demonstrate that refined C. odollam seed oil possesses a comparatively stable region below approximately 250 °C under the conditions investigated, followed by a pronounced degradation process extending through approximately 250–430 °C depending on heating rate. The shift in degradation temperature with heating rate and the systematic variation of E_α with conversion demonstrate that its thermal degradation is both heating-rate dependent and conversion dependent. This finding has practical relevance to the use of C. odollam oil as a non-edible industrial feedstock. The oil has previously been investigated as a precursor for alkyd-resin synthesis, demonstrating that its fatty-acid functionality can be exploited in polymeric materials. The present results add an important thermal-kinetic dimension to that application by establishing the temperatures and apparent energy barriers associated with progressive thermal degradation.

The results are particularly useful for defining the distinction between processing temperature and degradation temperature. Temperatures substantially below the principal degradation region provide a considerably greater thermal margin for handling and processing the oil, whereas exposure to the rapid degradation region would result in significant mass loss and chemical transformation. The previous C. odollam TGA study similarly reported stability below approximately 200 °C, providing independent support for the lower-temperature stability observed in the present work.

From an industrial processing perspective, the identified degradation profile provides useful guidance for establishing temperature limits during oil storage, pre-treatment, blending, and other thermal processing operations. Industrial processes involving prolonged exposure of the oil to temperatures approaching the principal degradation region should be avoided where preservation of the original oil composition is required. The heating-rate dependence also indicates that degradation cannot be evaluated solely from a single characteristic temperature; both the imposed thermal history and the extent of conversion should be considered when assessing thermal exposure. The conversion-dependent kinetic parameters obtained in this study can therefore provide input for thermal-risk assessment and for the development of process-specific thermal models for C. odollam-based feedstock utilization.

The kinetic results further demonstrate why the use of a single activation energy would provide an incomplete description of the oil. The decrease from approximately 127.36 kJ mol^{-1} at 10% conversion to approximately 88 kJ mol^{-1} near 80–90% conversion indicates that the apparent resistance to thermal degradation decreases as conversion proceeds. Consequently, the thermal degradation of refined C. odollam oil is better represented by the relationship depicted in Eq. 13 than by a single global value of E.

This conversion-dependent kinetic description can potentially be incorporated into subsequent thermal modelling of C. odollam-based alkyd or biodiesel systems, although the kinetic parameters obtained here should not be transferred directly to the cured alkyd resin or biodiesel. Resin and biodiesel formation changes the molecular structure, molecular weight distribution and crosslinking behaviour of the material and therefore requires independent thermal characterization.

4.0. Conclusion

The non-isothermal thermal degradation behaviour of refined Cerbera odollam seed oil was successfully investigated using TGA at heating rates of 5, 10, 15 and 20 °C min^{-1} and analysed using the Advanced Vyazovkin isoconversional method. The study established that the thermal degradation of the oil is both heating-rate dependent and conversion dependent and therefore cannot be adequately represented by a single conversion-independent activation energy. The TGA/DTG results showed a clear dependence of the degradation temperature on heating rate, with the principal DTG peak shifting from 310 to 340 °C as the heating rate increased from 5 to 20 °C min^{-1}. The Advanced Vyazovkin objective functions displayed distinct approximately parabolic minima, providing well-defined activation-energy values at the selected conversion levels. The apparent activation energy decreased progressively with conversion, from approximately 115.17 kJ mol^{-1} at α = 0.20 to 97.46 kJ mol^{-1} at α = 0.50 and 88.14 kJ mol^{-1} at α = 0.80.

These findings demonstrate the conversion-dependent nature of the overall thermal degradation kinetics of the oil and provide a useful kinetic fingerprint for non-edible C. odollam seed oil. The study also demonstrates the applicability of the Advanced Vyazovkin isoconversional approach for its conversion-dependent kinetic characterization. The resulting thermal and kinetic information provides a quantitative basis for assessing the thermal processing window of C. odollam oil and can support future investigations involving its processing, storage, thermal modelling, and utilization as a non-food industrial feedstock.

5.0 Recommendation

Future work should extend the kinetic analysis through complementary chemical characterization of the degradation products to further elucidate the molecular processes underlying the observed conversion-dependent activation-energy behaviour.

Nomenclature

α = Fractional conversion

E_α = Apparent activation energy at conversion, kJ mol^{-1}

A = Pre-exponential (frequency) factor, min^{-1}

R = Universal gas constant, J mol^{-1} K^{-1}

β = Heating rate, $^{\circ}C\ min^{-1}$

$T_{\alpha,i}$ = Absolute temperature corresponding to conversion at heating rate i, K

$I(E_\alpha, T_{\alpha,i})$ = Temperature integral used in the Vyazovkin objective function, K

$\Omega(E_\alpha)$ = Advanced Vyazovkin objective function

m_0 = Initial sample mass, mg
m_T = Sample mass at temperature, mg
m_f = Final sample mass, mg
$f(\alpha)$ = Reaction model/function describing the dependence of conversion rate on conversion
n = Number of heating-rate experiments
i, j = Indices representing individual heating-rate experiments
$p(x)$ = Senum–Yang fourth-order approximation function for the temperature integral
t = Time, min
T = Absolute temperature, K
$k(T)$ = Temperature-dependent reaction-rate constant
DTG = Derivative thermogravimetry; rate of mass loss with temperature, % /°C
E = Trial activation energy used during numerical optimization, J mol^{-1}
$\mathrm{d}\alpha/\mathrm{d}t$ = rate of conversion, min^{-1}
$\mathrm{d}\alpha/\mathrm{d}T$ = Rate of conversion rate with respect to temperature, K^{-1}

Code Availability; The Python code developed for the kinetic calculations is available from the corresponding author upon reasonable request.

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