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Study of Solid–Liquid Extraction Kinetics of Oil from Dried Avocado (*Persea Americana*) Flesh Using Hexane as A Solvent

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Abstract. In the present study, solid–liquid extraction of dried avocado flesh was investigated using hexane as a solvent for three pre-treatment methods (uncooked, cooked with $CaCO_3$, and cooked with water) and two material sizes (8 mm × 5 mm × 5 mm and ≤1.19 mm). Based on the highest yield of avocado oil obtained, the kinetics of oil extraction for a material size of ≤1.19 mm for the various pre-treatment methods was studied. Two stages, namely rapid oil extraction and slow oil extraction, were observed. Three kinetics models (Peleg, power law, and unsteady-state diffusion model) were used to describe the extraction of avocado oil. At conditions with the highest oil yield, the Arrhenius equation was used to calculate the activation energy at three different temperatures (25, 40, and 50°C). Based on the R^2 value obtained, the unsteady-state diffusion model (R^2 = 0.6236–0.8752) is most suitable to describe the avocado oil extraction process. A positive value of the activation energy (47.51 kJ/mol) confirmed that the avocado oil extraction process is endothermic.

Keywords: Avocado oil; Kinetics model; Pre-treatment; Solid–liquid extraction

1. Introduction

Avocado (*Persea americana*) belongs to the Lauraceae family and originated in Mexico. It is widespread and farmed around the world in tropical and subtropical climates. Avocados are edible, and their oil yield is significantly higher than that of other edible oil crops, including rapeseed, sunflower, sesame, and jatropha (Satriana *et al*., 2019). Avocados have the potential to produce valuable and useful products, one of which is avocado oil. Avocado oil finds common use in both food and non-food industries, such as cooking oil and cosmetic formulations. It contains a high level of monounsaturated and polyunsaturated fatty acids, making it a natural ingredient suitable for various applications (Ge *et al*., 2021). Avocado oil contains a mixture of compounds, including antioxidants, vitamins, and phytosterols, that are beneficial for a healthy diet (Satriana *et al*., 2019). Demand for avocado oil has grown significantly over time as consumers have become aware of its health advantages.

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Several studies report that the development of extraction techniques can produce avocado oil with a high content of bioactive compounds in addition to maintaining its properties and nutritional value after extraction and during storage (Satriana *et al*., 2019; dos Santos *et al*., 2014). Avocado oil has characteristics similar to olive oil (Barros *et al*., 2016) and is extracted from the dried fruit's fleshy pulp. Although solvent-free extraction is a currently trending environmentally-friendly process, the traditional lipid extraction method of solid-liquid solvent extraction is still widely applied in industrial-scale processes due to its efficiency (Mgoma, Basitere, and Mshayisa, 2021). This method involves the penetration of the solvent into the lipid membrane while matching the polarity of the target chemicals. However, since the solvents come into direct contact with the lipids, it is necessary to pre-treat the raw material before adding the solvent to improve the extraction yield.

Pre-treatment, including size reduction and heat treatment, of raw material is one of the primary methods for enhancing oil recovery during the extraction process. Size reduction is used because the contact area between the material and the solvent increases as the size of the material decreases (Yusuff, 2021). Heat treatment, on the other hand, increases the yield of extracted oil by destroying the oil cells, thereby lowering the viscosity and moisture content of the oil and causing the flour proteins to coagulate. It also inactivates enzymes in ingredients that may affect the quality of the extracted oil (Evangelista, Isbell, and Cermak, 2012). Treatment with water combined with processing aids, such as enzymes and calcium carbonate ($CaCO_3$), also weakens the oily cell walls and helps prepare the plant matrix for optimal oil extraction (Satriana *et al*., 2019). Squeo *et al*. (2016) reported that $CaCO_3$ could be used as a coadjuvant to increase the extraction yield of extra virgin olive oil. However, there was no clear trend regarding the impact on oil quality. More recently, Arpi *et al*. (2023) reported the effect of a precooking treatment with water and $CaCO_3$ on the properties of dried avocado pulp and its oil extract.

Solid–liquid extraction of avocado oil is a multiphase and unsteady-state mass transfer process in which the solute concentration in the solid is continuously varied. A model of avocado oil extraction and an estimate of its extraction rate is necessary for analyzing and designing extraction processes on an industrial scale. The available literature contains limited information on the kinetics of avocado oil extraction. This is likely due to the fact that many avocado oil manufacturers still rely on traditional technology and may not prioritize process optimization. Mgoma, Basitere, and Mshayisa, (2021) studied the kinetics and thermodynamics of oil extraction of Hass avocados from South Africa. Arimalala, Hervé, and Rafihavanana (2022) reported that the second-order kinetics model provides a good representation of the experimental results of the oil extraction of avocados from Madagascar. Understanding the kinetics of avocado oil extraction is essential for conducting technical and economic analyses of the process. Kinetic knowledge aids in fundamental comprehension of the process, allowing for better process control and higher efficiency. Additionally, studying kinetics is crucial for scaling up the process, as noted by Prihutami *et al*. (2021).

Previous studies suggested that avocado oil extraction could be improved using various pre-treatment methods (Arpi *et al*., 2023; Santana *et al*., 2015). The novelty of this work resides in the investigation of the kinetics of avocado oil extraction using raw material cooking pre-treatment and the addition of a coadjuvant. To the best of the authors' knowledge, there is little information in the published literature about the pre-treatment of raw material using coadjuvant in avocado oil extraction processes. The primary goal is to examine the solid–liquid extraction yield and kinetics of oil from dried avocado flesh using hexane as a solvent. The experimental data obtained will be compared to published kinetics models.

2. Methods

2.1. Materials

A fully ripe Hass avocado fruit was obtained from agricultural resources in Central Aceh, Indonesia. Analytical-grade hexane and $CaCO_3$ of 99.95% purity were procured from Merck (Indonesia). All compounds were utilized without further purification.

2.2. *Experimental Procedure*

The experimental procedure is presented in Figure 1. The experiments were conducted on a laboratory scale.

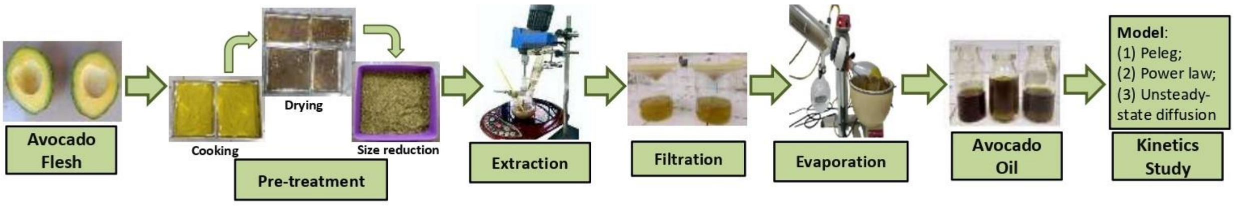

Figure 1 Schematic of the experimental procedure.

2.2.1. Sample Preparation

The experiment required approximately 8 kilograms of ripe avocado. Three different pre-treatment methods, as reported by Arpi *et al.* (2023), were applied to the avocado flesh. In the first sample group, the avocado flesh was cooked in water. In the second sample group, the avocado flesh was cooked with water containing 5% $CaCO_3$ (w/w of flesh). The last sample group was uncooked as a control. After completing the three pre-treatment methods, the resulting dried avocado was shaped into two sizes: 8 mm × 5 mm × 5 mm and ≤1.19 mm.

2.2.2. Avocado Oil Extraction

The material was extracted at a material-to-solvent ratio of 1:15 (g/mL) using hexane as a solvent. Extraction was carried out in a 1 L round-bottom flask placed in a water bath. The extraction process was conducted at the specified temperature for 30 min at a stirring speed of 400 rpm. The resulting avocado oil was recovered using a rotary evaporator after the extra solvent was distilled. The extraction products were provided as avocado oil yields (Equation 1). The experiment was repeated twice to ensure the reproducibility of the data and to assess the mean of the measured data. The experimental error detected across the experiments was less than 5%, which is negligible for data collected under identical conditions (Supardan *et al*., 2019).

$$\text{Oil yield (\%)} = \frac{\text{Oil weight (g)}}{\text{Dried flesh weight (g)}} \times 100 \qquad (1)$$

The influence of the three pre-treatment methods (uncooked, cooked with $CaCO_3$, and cooked with water) and two material sizes (8 mm × 5 mm × 5 mm and ≤1.19 mm) on the avocado oil yield were investigated in the first series of trials. Evaluation of the extraction kinetics was carried out based on the highest yield of avocado oil obtained in the first series of trials for the various pre-treatment methods. The influence of temperature (25, 40, and 50°C) on the extraction yield was investigated using the highest avocado oil yield obtained in the first series of trials.

2.3. Kinetic Model of Avocado Oil Extraction

Various kinetic models have been developed to describe the oil extraction mechanism. The phenomena of mass transfer through solid plant materials and from their surfaces into the bulk of the solvent are the basis for physical kinetic models. Several kinetic models for avocado oil extraction have been reported, including second-order, Peleg, logarithmic (Arimalala, Hervé, and Rafihavanana 2022), first-order reaction, Fick's law, and Van't Hoff's (Mgoma, Basitere, and Mshayisa, 2021). The most frequently used models are based on film theory and the concept of unsteady-state diffusion through particles. The Peleg model is an empirical and classical hyperbolic model that was initially designed to describe moisture sorption curves. The Peleg model has been modified and applied to represent the solid–liquid extractions of numerous plant metabolites in general and in phenolics, particularly due to the similarity between the extraction and sorption curves (Milićević *et al.*, 2021).

2.3.1. Peleg Model

The Peleg model can provide an accurate estimation of the kinetics of the solid–liquid extraction process (Liao, Guo, and Yu, 2021). The mathematical model introduced by Peleg (Equation [2]) was adopted as the kinetic model for the extraction of plant material.

$$C_t = C_0 + \frac{t}{k_1+k_2} \tag{2}$$

In Equation (2), t is the extraction time (min), C_0 is the initial concentration of avocado oil (g/g), C_t is the concentration of avocado oil at t (g/g), k_1 is Peleg's rate constant (min.g/g), and k_2 is Peleg's capacity constant (g/g). The constants k_1 and k_2 indicate the initial extraction rate and the maximum solute concentration achieved during the process, respectively (Anbalagan *et al.*, 2019). A modified Peleg equation to plot solute concentration in the extraction solvent is presented in Equation (3).

$$C_t = \frac{t}{k_1+k_2} \tag{3}$$

2.3.2. Power Law Model

The power law model (Equation [4]) has previously been applied to the extraction process (Natolino and Porto, 2020; Alara and Abdurahman, 2019).

$$C_t = Bt^n \tag{4}$$

In Equation (4), C_t is the concentration (g/L) of avocado oil at any time t (s), B denotes the extraction coefficient (L/g.s), and n denotes the power law exponent. Equation (4) can be further simplified to Equation (5).

$$\ln C_t = \ln B + n \ln t \tag{5}$$

Plotting ln C_t against ln (t) gives n and ln B as the slope and intercept, respectively.

2.3.3. Unsteady-state Diffusion Model

The unsteady-state diffusion model was developed based on a solvent extraction technique that included concurrent evaporation and diffusion processes. The model defined by Equation (6) contains two parameters: the quick oil extraction stage, represented by b (evaporation coefficient), and the slow oil extraction stage, represented by k (diffusion coefficient). This model can be applied to simulate the oil extraction kinetics of any plant material.

$$\frac{q_0 - q}{q_0} = (1-b)\cdot e^{-kt} \tag{6}$$

In Equation (6), q_0 represents the initial oil content (g/g), q represents the oil yield (g/g) at time t, b represents the evaporation coefficient, k represents the diffusion coefficient (1/min), and t represents the extraction period (min). The linearized form of Equation (7) can be used to determine b and k.

$$\ln\left(\frac{q_0 - q}{q_0}\right) = \ln(1-b) - kt \tag{7}$$

Plotting $\ln\left(\frac{q_0 - q}{q_0}\right)$ against time t gives $-k$ and ln $(1-b)$ as the slope and intercept, respectively.

2.4. Activation Energy (Ea)

The activation energy (Ea) is the minimum energy required to initiate the extraction process (Abed *et al*., 2019), and it can be calculated using the Arrhenius equation. Equation (8) presents the correlation between the extraction rate constant (k) and the temperature of extraction (T).

$$k = Ae^{-Ea/RT} \tag{8}$$

where k represents the diffusion coefficient (min^{-1}), Ea represents the activation energy (kJ/mol), A represents the Arrhenius constant (s^{-1}), T represents the absolute temperature (K), and R represents the universal gas constant (kJ/mol.K). A linear relationship between ln k and $1/T$ can be obtained (Equation 9).

$$\ln k = \ln A + \frac{-E_a}{R}\frac{1}{T} \tag{9}$$

Plotting ln k against $1/T$ gives $-Ea/R$ and ln A as the slope and intercept, respectively.

3. Results and Discussion

3.1. Influence of Process Variables

The avocado oil obtained from each experiment was similar in appearance; it was dark green and had a distinctive viscosity. The avocado oil yield was significantly affected by extraction time. Figure 2 depicts the influence of time on the oil yield for each pre-treatment method and material size. There was a marked correlation between extraction time, pre-treatment method, material size, and oil yield under the given conditions.

The avocado oil yield increased as the extraction time increased. This was because longer extraction times led to longer contact between the solvent and plant material, thereby increasing mass transfer. The yield of oil increased significantly initially, then gradually decreased as the extraction progressed. As shown in Figure 2, increasing the extraction time after approximately 30 min did not further increase the oil yield. It may be inferred that 30 min after extracting the material, the remaining oil in the avocado was reduced to a minimum value. Many studies have observed similar trends, such as in the extraction of alpha-glucosidase inhibitors from lemongrass (Widiputri *et al*., 2020) and the extraction of bioactive compounds from avocado seeds (Corral-Pérez, and Almajano, 2016).

As expected, the yield increased as the material size decreased. The oil yield obtained by material size ≤1.19 mm was higher than that obtained by the 8 mm × 5 mm × 5 mm material. By reducing the size of the materials, the surface area increases, which increases the mass transfer of the active principle from the plant material to the solvent and makes extraction more efficient. In addition, the extraction yield increases because the dispersion distance of the solute in the solid decreases when the particle size is small; therefore, a shorter time is required for the solute to reach the surface. It should also be noted that very small particle sizes can cause difficulties during the screening process (Makanjuola, 2017). Santos *et al.* (2015) discovered a similar pattern when using ethanol as a solvent to extract oil from *Jatropha curcas* L. However, as the size of the material increased, the influence of pre-treatment on oil yield became more significant. It has been suggested that pre-treatment of the material provides several advantages, such as easier penetration of the solvent into the plant cell to release the oil from the cell (Arpi *et al.*, 2023).

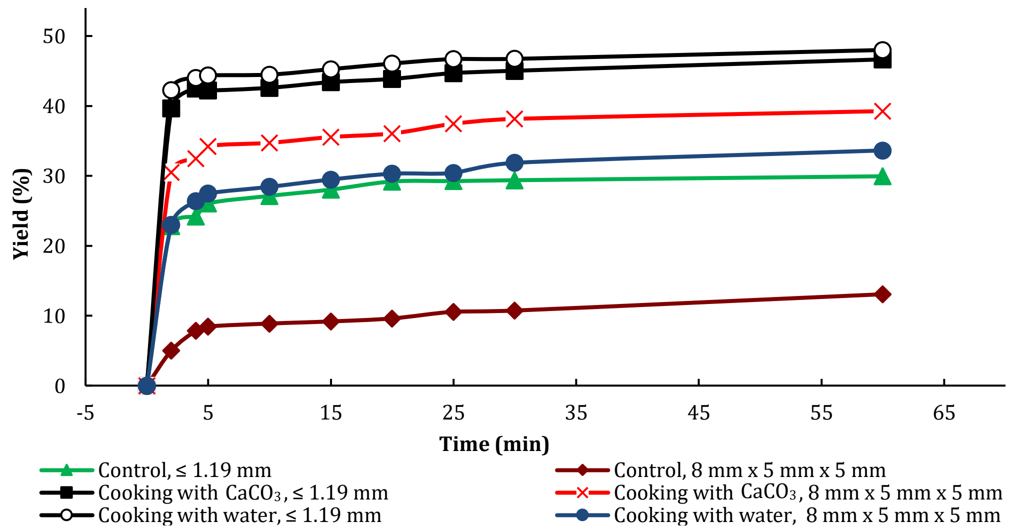

Figure 2 Influence of extraction time on avocado oil yield at various extraction conditions (extraction temperature of 25°C; a solid-to-solvent ratio of 1:15 g/mL; 400 rpm).

Figure 3 depicts the influence of temperature on avocado oil yield. Extraction temperature was critical to maximize the extraction yield, and the results obtained indicate that the amount of oil extracted increased with extraction temperature. This relationship was predicted because the driving force for extraction increases as temperature increases. As the temperature increases, oil solubility and solvent diffusivity increase, and the viscosity of both solute and solvent decreases, facilitating mass transfer processes and resulting in a change in oil yields (Mgoma, Basitere, and Mshayisa, 2021; Anbalagan *et al.*, 2019). Moreover, increased temperature promotes the spread of oil and reduces its viscosity (Meziane and Kadi, 2008).

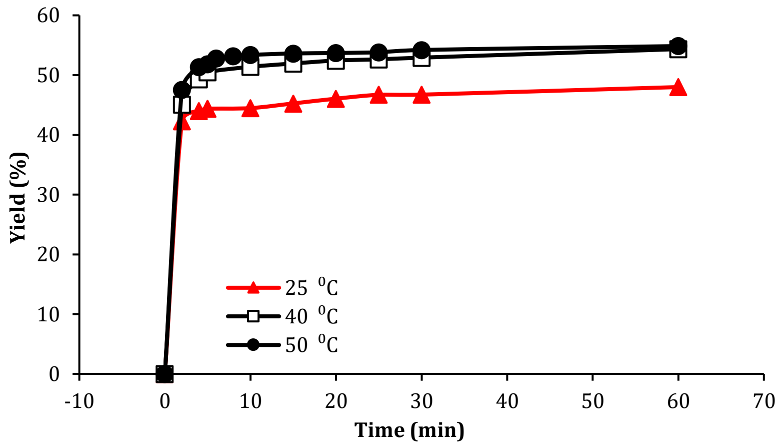

Figure 3 Influence of temperature on avocado oil yield (experimental conditions: cooking pre-treatment with water and material size ≤1.19 mm).

Figures 2 and 3 depict the time course of the change in avocado oil yield during the extraction process for various process variables. There is a typical curve for extracting oil from plants. Avocado oil extraction can be divided into two stages: rapid oil extraction and slow oil extraction. The rapid oil extraction stage occurred during the early stages of extraction, during which oil was rapidly released and evaporated from the outer surface of the plant material. During this time, the yield of avocado oil increased rapidly. As the extraction process progressed, the extraction rate decreased until a nearly constant oil yield was reached. During the slow oil extraction stage, oil extraction was followed by slow molecular diffusion of the oil from the undamaged cells to the surfaces of the plant materials. Oil production slowed down because the oil spread slower. This mechanism was critical for further extraction kinetics modeling. Some researchers, including Anbalagan *et al*. (2019) in the mangiferin extraction from *Mangifera indica* leaves and Santos *et al*. (2015) in the oil extraction from *Jatropha curcas*, reported a similar trend.

3.2. Kinetic Model of Avocado Oil Extraction

The kinetic model is a method used to describe the process of mass transfer and diffusion in the extraction process (Alara and Abdurahman, 2019). Figure 4 displays graphs of the kinetics of the Peleg, power law, and unsteady-state diffusion models for various cooking pre-treatment methods. The slope and intercept of each curve were utilized to calculate the kinetic parameters of each model and are presented in Table 1.

The coefficient of determination (R^2) was used to select the best mathematical model for avocado oil extraction (Arimalala, Hervé, and Rafihavanana, 2022). In the present study, the unsteady-state diffusion model had the highest R^2 value, indicating that this model provided the most accurate prediction of the results of the extraction process. Both kinetic parameters of the unsteady-state diffusion model were greater for the cooking pre-treatment than for the control sample. These results are in line with the obtained oil yield trend. It was also discovered that the value of k was less than the value of b for all experimental variables, implying that the slow oil extraction stage influenced the process rate. The coefficients for the rapid oil extraction periods were 86–120 times larger than those for the slow oil extraction periods, indicating that diffusion is much slower than evaporation. This trend has also been reported for oil extraction from avocado seeds (Segovia, Corral-Pérez, and Almajano, 2016) and sunflower seeds (Perez, Carelli, and Crapiste, 2011). The performance of an extraction process can be represented by the k value. It was observed that the increase in temperature led to an increase in extraction rate. The k value obtained was comparable to those published in the available literature for avocado oil extraction (Table 2).

Table 1 Kinetic parameter for Peleg, power law, and unsteady-state diffusion models.

Kinetics Model	Pre-treatment	Y	R^2	k_1 (min.g/g)	k_2 (g/g)
Peleg's	Control	0.1073x + 25.290	0.6009	0.0395	9.3197
	Cooking with $CaCO_3$	0.0985x + 41.532	0.8019	0.0241	10.1522
	Cooking with water	0.0859x + 43.687	0.8038	0.0229	11.6414
		Y	R^2	B (L/g.s)	n
Power law	Control	0.0587x + 2.789	0.6107	16.2599	0.0587
	Cooking with $CaCO_3$	0.0517x + 3.366	0.7979	28.9711	0.0517
	Cooking with water	0.044x + 3.479	0.8228	32.4532	0.0440
		Y	R^2	b	k (min^{-1})
Unsteady-state diffusion	Control	-0.0038x – 0.611	0.6236	0.4573	0.0038
	Cooking with $CaCO_3$	-0.0087x – 1.378	0.8752	0.7479	0.0087
	Cooking with water	-0.0089x – 1.548	0.8663	0.7872	0.0089

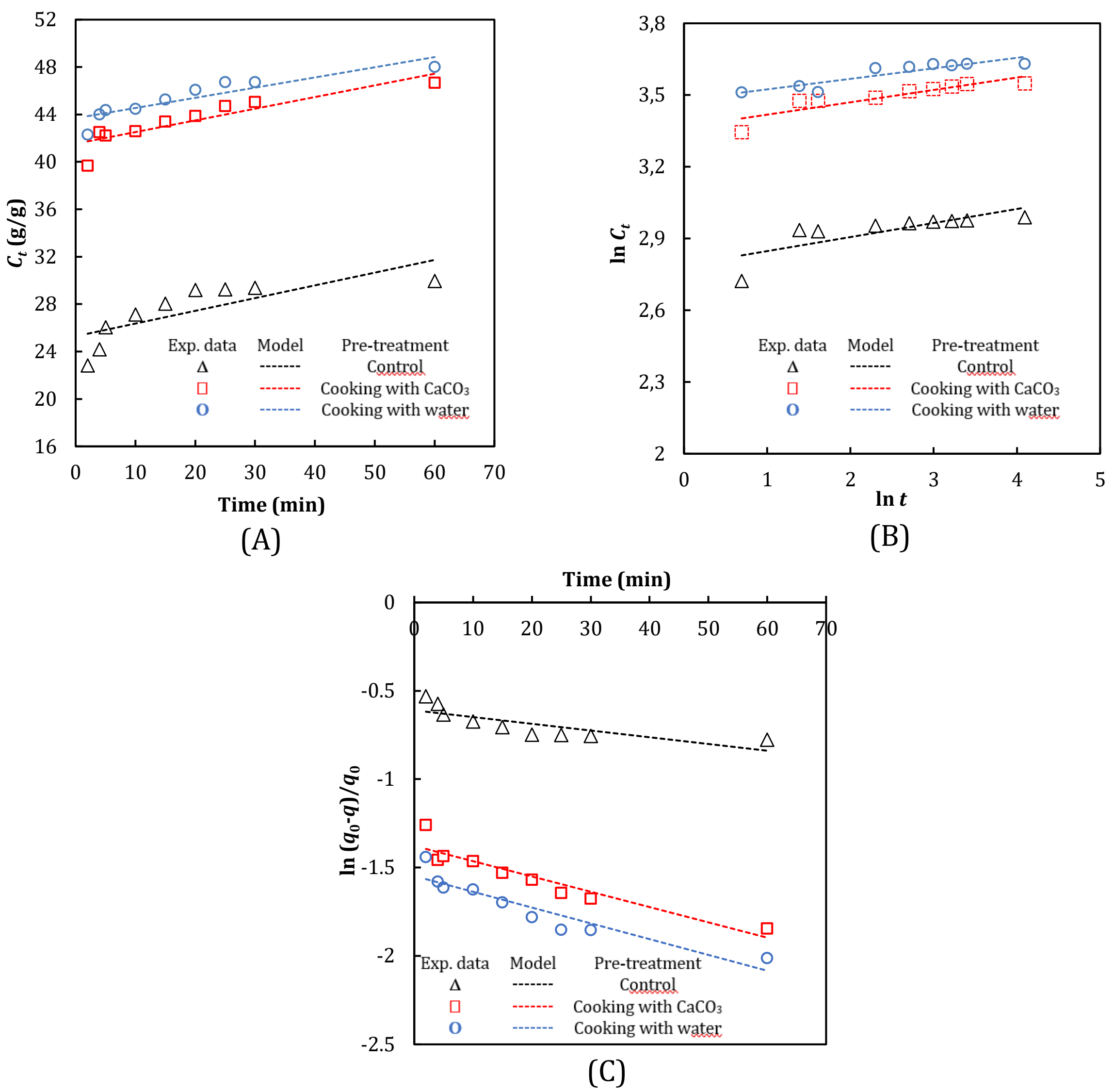

Figure 4 (A) Peleg model, (B) power law model, and (C) unsteady-state diffusion model (experimental conditions: material size ≤1.19 mm and extraction temperature of 50°C).

Table 2 Comparison of kinetic model parameters for avocado oil extraction.

Reference	*k*	Temperature (°C)
This study	0.0038–0.0089 min^{-1}	25, 40, 50
Mgoma, Basitere, and Mshayisa (2021)	0.0015–0.1382 min^{-1}	40, 50, 60, 70
Arimalala *et al.* (2022)	0.374 $mLg^{-1}min^{-1}$	70

3.3. Activation Energy

Figure 5 depicts the relationship between k and $1/T$. The estimated Arrhenius parameters are presented in Table 3. The value of R^2 from the graph of ln k versus $1/T$ in Figure 5 is 0.9014, and the value of Ea was calculated from the linear correlation between ln k and $1/T$. The Arrhenius parameters of the process for material size ≤1.19 mm and the cooking pre-treatment with water were 47.51 kJ/mol and 21,111,692 min^{-1} for Ea and A, respectively. Table 3 provides a comparison of Ea values for various vegetable oils. It can be observed that the value of Ea obtained is low and reasonable compared with the value reported in the literature. A high Ea reduces the extraction process rate, while a low Ea helps to increase the extraction process rate. The lower the Ea value, the less energy is required for oil extraction to begin (Ramesh, Yasin, and Arshad, 2020). Furthermore, a positive *Ea* indicates that the process is endothermic (Rahma and Hidayat, 2023). The energy required to overcome the endothermic nature of the process is provided by heating during extraction. Previous work has demonstrated that *Ea* values of certain vegetable oils are in the range of 79 to 104 kJ/mol, indicating that they have varying fatty acid profiles (Tan *et al*., 2001). Oils with lower *Ea* values are expected to require higher temperatures to trigger certain changes to the oxidation rate (Aktar and Adal, 2019).

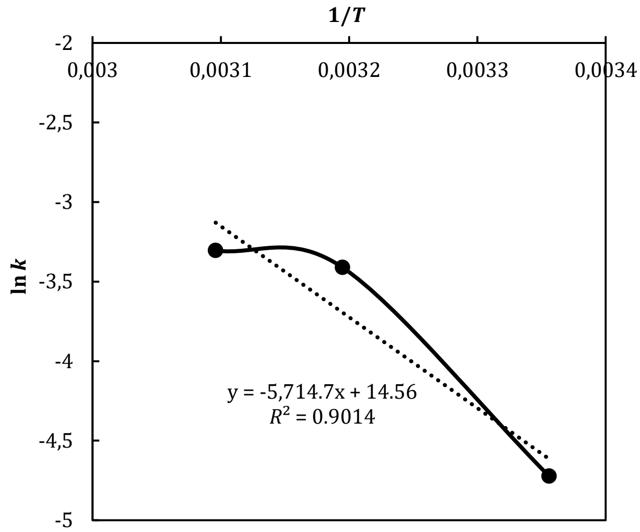

Figure 5 Plot of ln k against $1/T$ to determine the activation energy.

Table 3 Comparison of the estimated activation energy of various vegetable oils.

Reference	*Ea* (kJ/mol)	Remark
Ramesh Yasin, and Arshad (2020)	39.66	Oil extraction from *Chlorella vulgaris*
This study	47.51	Oil extraction from avocado flesh
Abed *et al*. (2019)	55.11	Oil extraction from peppermint leaves
Tan *et al*. (2001)	79–104	Oil extraction from 10 different vegetable oils
Aktar and Adal (2019)	99.60	Avocado oil under rancid conditions

4. Conclusions

Kinetic studies contribute to a fundamental understanding of the process and enable better process control and process scaling. In this study, the solid-liquid extraction kinetics of dried avocado flesh using hexane as a solvent was investigated. Experimental results showed that there was a clear correlation between extraction time, pre-treatment method, material size, extraction temperature and oil yield. Avocado oil extraction can be divided into two stages, rapid oil extraction and slow oil extraction. The coefficients for the rapid oil extraction stages were 86–120 times larger than those for the slow oil extraction stages, suggesting that diffusion is much slower than evaporation. Based on the magnitude of R^2 values, the unsteady-state diffusion model was shown to adequately represent the rate of avocado oil extraction. A positive *Ea* value of 47.51 kJ/mol was obtained, indicating that the extraction process is endothermic. This research is necessary to develop and implement a complete and improved industrial avocado oil extraction process.

Acknowledgments

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