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Green extraction and valorization of olive pomace using limonene: A kinetic modeling and thermodynamic approach

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Abstract: This work explores the extraction of oil from olive pomace using limonene as a green solvent, with particular emphasis on the effects of temperature on yield, kinetics, and thermodynamics. Results show that oil recovery increases with time and temperature, following a two-stage mechanism: a rapid washing phase dominated by surface oil removal, and a slower diffusion-controlled stage. Kinetic modeling revealed that the Patricelli model best fits the process ($R^2 > 0.99$), while mass transfer coefficients confirm the predominance of washing at lower temperatures. The relatively low activation energy (16.98 kJ·mol^{-1}) suggests a diffusion-limited process that is thermally accessible and suitable for industrial application. Thermodynamic parameters support this interpretation, with negative Gibbs free energy values confirming spontaneity, an endothermic enthalpy change (ΔH = 1.68 kJ·mol^{-1}), and positive entropy (ΔS = 17.39 J·mol^{-1}·K^{-1}) reflecting increased molecular disorder during extraction. Overall, limonene demonstrates high efficiency and sustainability, offering a viable alternative to hexane in line with green chemistry principles.

Keywords: oil recovery; alternative solvent; azeotrope distillation; activation energy; process efficiency; spontaneous extraction.

INTRODUCTION

Olive pomace, alternatively termed olive mill cake or foot cake, represents a solid byproduct resulting from oil extraction processes. This residue comprises pulp, skins, endocarp fragments, and water following olive processing. Its chemical profile typically features elevated moisture (40–60%), organic constituents including cellulose, hemicellulose, lignin, and residual lipids (2–8%), alongside various phenolic compounds, minerals, nitrogenous substances, and

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trace fatty acids.[1,2] From an environmental standpoint, olive foot cake offers distinct challenges and opportunities.[3] Negatively, its substantial organic load and phytotoxic phenolic constituents hinder biodegradation; improper management may trigger pollution, offensive odors, and soil or water contamination.[3,4] Conversely, effective valorization enables diverse sustainable applications. It serves as combustible biomass or a substrate for biogas production via anaerobic digestion[1]. Following specific treatments, it functions as a soil conditioner or livestock feed, although phenolic concentrations restrict immediate utilization. Furthermore, high-value components, including polyphenols and antioxidants, are extractable for integration into cosmetic, food, and pharmaceutical industries.[5]

Olive mill residue is convertible into biochar or activated carbon for environmental remediation purposes.[6,7] This solid byproduct retains significant residual oil, typically 5% to 10% by mass, representing a lucrative secondary source for edible and industrial applications[8]. Valorizing olive cake via oil recovery facilitates waste mitigation and environmental sustainability while simultaneously bolstering the economic viability of olive oil manufacturing. Various solvent-based techniques are utilized for extraction, differing in efficiency and ecological footprints. Conventionally, hexane remains the predominant solvent owing to its superior lipid solubility and capacity for maximizing residual oil yields[8]. Nonetheless, increasing apprehensions concerning its toxicity, flammability, and overall environmental impact have catalyzed research into greener alternatives. Ethanol, a bio-based and less hazardous solvent, has emerged as a viable substitute, offering good extraction performance while being safer and more environmentally friendly.[9] Additionally, limonene—a natural solvent sourced from citrus rinds—has garnered significant interest recently due to its biodegradability, minimal toxicity, and exceptional solvating capacity for non-polar substances like vegetable lipids[10]. Comparative studies have shown that while hexane may achieve slightly higher yields, ethanol and limonene offer more sustainable solutions, especially when combined with process optimization strategies such as temperature control, solvent recycling, and pre-treatment of the biomass.[11]

Modeling olive pomace oil recovery using limonene as a sustainable solvent has attracted significant interest as a promising alternative to conventional hexane. Mathematical frameworks are widely used to describe extraction kinetics, providing valuable insights into mass transfer mechanisms and the influence of process variables on extraction yield, thereby facilitating process optimization.[9,12,13] Numerous models have been proposed to explain solvent extraction from oilseeds and agro-industrial by-products, allowing the estimation of extraction rate constants, equilibrium yields, and model coefficients for process prediction and optimization.[6] Recent studies have further highlighted the growing interest in green extraction technologies and bio-based solvents for olive pomace

valorization.[14–16] In particular, Pagliaro *et al.*[17] reviewed the application of limonene as a renewable and recyclable solvent for natural product extraction, including its successful use in microwave-assisted olive pomace oil extraction. However, despite these advances, quantitative investigations describing the extraction mechanism of olive pomace oil using limonene under conventional heating conditions remain scarce. In particular, studies combining kinetic modelling, mass-transfer analysis, activation energy determination, and thermodynamic evaluation have rarely been reported. Therefore, this study employed limonene to recover residual lipids from olive pomace under conventional heating conditions and provides a comprehensive kinetic and thermodynamic assessment of the extraction process, enabling a quantitative understanding of the extraction mechanism and the feasibility of limonene as a sustainable extraction solvent.

EXPERIMENTAL

Raw materials

The olive pomace was sourced from a modern oil mill located in Tizi Ouzou (Northern Algeria). Its initial moisture content of 46.9% was reduced to 5.4% by oven-drying (Memmert, model 854 Schwabach) at 103 °C. The resulting olive cake was used in its raw state, without further grinding. All extraction procedures were performed using limonene with a purity of 97%.

Oil extraction

Extractions were conducted in a double-walled glass reactor with a capacity of 5×10^{4} m^3, equipped with a mechanical stirrer to ensure homogeneity. For each experiment, 5×10^{-2} Kg of olive pomace was mixed with 1.5×10^{-4} m^3 of limonene, maintaining a liquid-to-solid (L/S) ratio of 3×10^{-3} $m^3 kg^{-1}$. The mixture temperature was kept constant via water circulation within the reactor jacket. Oil yield kinetics were investigated at four temperatures (25, 35, 45, and 65 °C) for durations ranging from 5 to 60 minutes, with a constant stirring velocity of 450 rpm.

Limonene, with an average density of 0.84 kg m^{-3} at 20 °C, was used as the solvent. Each result reported represents the average of three replicates for both the kinetic and equilibrium studies. The total oil content of the samples was determined via exhaustive extraction for 24 hours, in accordance with the NF V03-924 standard. For each procedure, a constant mass of 5×10^{-2} kg of olive cake was used. Following extraction, the solid and liquid phases were separated by vacuum filtration using a BUSCH pump (model RB 0004 B NF0), and the oil was subsequently recovered through distillation.

Following the extraction step, the separation of limonene from the extracted oil was performed via vacuum distillation. Due to the relatively high boiling point of limonene (175 °C at atmospheric pressure[18]) direct distillation requires elevated temperatures that may induce the thermal degradation of thermo-sensitive components within the oil.[19] To mitigate this and lower the distillation temperature, distilled water was added to the limonene–oil mixture to promote the formation of a heteroazeotropic system. This azeotrope exhibits a boiling point of approximately 97.4 °C,[10] which is significantly lower than that of pure limonene. The formation of this azeotrope stems from the non-ideal behavior of the mixture; specifically, positive deviations from Raoult's law resulting in a minimum-boiling point.[18] Operating under reduced pressure further decreases the boiling point, facilitating efficient separation under mild thermal

conditions. This strategy prevents the decomposition of heat-sensitive constituents while improving the overall energy efficiency of the process.[20]

After azeotropic distillation, the limonene and extracted oil were recovered separately. The oil and water remaining in the distillation flask were separated by decantation, and any residual water was removed by oven-drying at 103 °C. The limonene in the distillate was similarly recovered through decantation. The oil yield was determined using Equation (1) :

$$Oil\ yield\ (\%) = \frac{mass\ of\ oil\ (g)}{mass\ of\ olive\ pomace\ sample(g)} * 100 \quad (1)$$

Kinetic models

Various mathematical models, traditionally used to describe the falling-rate period in drying processes, were adapted to characterize the of the oil extraction kinetics. In this study, the Patricelli, Peleg, diffusion, and logarithmic models were evaluated (Table I). For each model, R represents the yield (g oil/100 g solid), t is the contact time (min), k is kinetic constant (min^{-1}), and a, b are model-specific constants, R_w and R_d : extraction yields associated with the washing and diffusion stages, respectively, while K_w and K_d : rate constants. The parameters k_1 and k_2 are the Peleg model constants, and k, a, and b are empirical constants of the diffusion and logarithmic models.

Table I. Mathematical model

Name	Model	
	$R = \frac{t}{(k_1 + k_2 t)}$	(3)
	$R = a\,exp(-kt) + (1-a)exp(-kbt)$	(4)
Logarithmic model	$R = aLogt + b$	(5)

The goodness-of-fit was assessed using several statistical indicators, the coefficient of determination (R^2), the chi-square statistic (χ^2), and the mean square error (MSE). These criteria provide a quantitative basis for comparing model performance. Following established methodologies,[13,21] the optimal model was identified by the highest R^2 and the lowest χ^2 and MSE values. The statistical parameters were calculated using the following equations:

$$Residual = \sum_{i=1}^{N}\left(R_{exp,i} - R_{the,i}\right) \quad (6)$$

$$\aleph^2 = \frac{\sum_{i=1}^{N}(R_{exp,i} - R_{the,i})^2}{N - z} \quad (7)$$

$$MSE = \left(\frac{1}{N}\sum_{i=1}^{N}(R_{the,i} - R_{exp,i})^2\right)^{\frac{1}{2}} \quad (8)$$

R_{exp} experimental value, R_{the}: calculated (predicted) value, N: number of observations, Z: number of constants.

RESULTS AND DISCUSSION

Oil extraction yield

Figure 1 illustrates the evolution of oil yield as a function of time across various extraction temperatures. A detailed kinetic analysis reveals two distinct phases: a rapid initial extraction rate followed by a plateau, or a significantly slower rate, after approximately 30 minutes. Notably, at a constant extraction time of 15 minutes, the oil yield rose from 12% to 37% when the temperature was increased from 25 °C to 65 °C. In comparison, at a constant temperature of 25 °C, extending the extraction time from 5 to 60 minutes resulted in a more substantial yield increase—approximately 87%. This behavior suggests that the extraction process is initially driven by the solubilization of surface oil, followed by a diffusion-controlled mechanism that prevails as the easily accessible oil is depleted. Notably, these findings indicate that extraction time exerts a more pronounced influence on oil yield than temperature, particularly during the early stages. This trend aligns with the observations of Meziane *et al*.,[9] regarding hexane extraction from olive pomace, where a rapid initial phase was followed by a slower, diffusion-limited stage.

Similar results were reported by Chemat *et al.*[22] regarding the microwave-assisted extraction of essential oils, where the bulk of the oil was recovered within the first few minutes, with extended times duration yielding only marginal improvements. In this context of supercritical CO_2 extraction of rapeseed oil, it was also noted[23] that extraction time exerted a more pronounced effect on recovery than moderate variations in pressure or temperature, particularly during the initial phase dominated by external mass transfer. Likewise, Soxhlet extraction studies of peanut and sesame oil by Luque-Garcia *et al.*[24] demonstrated that yield increases significantly with time up to a threshold, beyond which a plateau is reached regardless of further temperature increments. Collectively, these findings underscore the dominant role of extraction time in oil recovery kinetics, especially in solid–liquid systems where rapid initial solubilization is followed by slow diffusion from internal cellular structures.

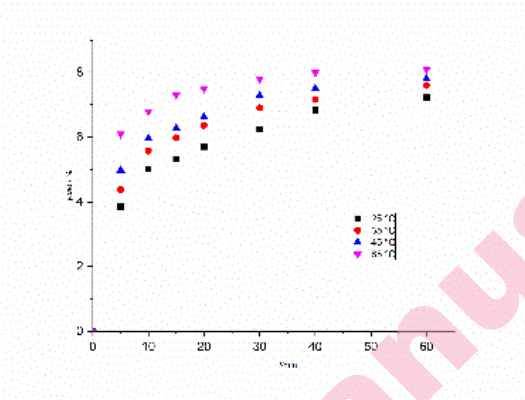

Fig. 1. Evolution of the efficiency according to time (L/S=3, V=450 rpm), temperatures 25, 35, 45 and 65°C.

Results modeling

The experimental data showing in Fig. 1 were fitted to the mathematical models listed in Table I with the resulting model constants for each temperature summarized in Table II. Nonlinear regression analysis was performed using Statistica 7 software to estimate the parameters, providing a quantitative description of the extraction kinetics across the investigated thermal conditions.

Figure 2 (a–d) shows the comparison between the experimental extraction yields and the values predicted by the different kinetic models at each temperature. All models demonstrated a strong agreement with the experimental data, as evidenced by the close overlap between the predicted and experimental curves. This strong correlation, further supported by Fig. 3 (a–d), indicates that each model accurately captures the extraction kinetics across the entire temperature range studied.

The coefficients of determination *(R^2),* chi-square (χ^2) values, and mean square errors *(MSE)* calculated for each model at the different extraction temperatures are summarized in Table II.[25,26]. Among the tested models, the diffusion model shows the weakest agreement with the experimental data, with R^2 values ranging from 0.969 to 0.997. In contrast, the Patricelli and Peleg models demonstrate superior fits, with R^2 values between 0.991 and 1, indicating a much closer correspondence with the observed data.

The use of multiple statistical indicators strengthens the evaluation of model performance. While R^2 provides a general measure of fit quality, the χ^2 and *MSE* values are more sensitive to discrepancies between observed and predicted values. The fact that the Patricelli model performs best across all three indicators reinforces its validity and suitability for representing the extraction process. This makes it a reliable tool for further kinetic modeling and potential scale-up of the extraction process.

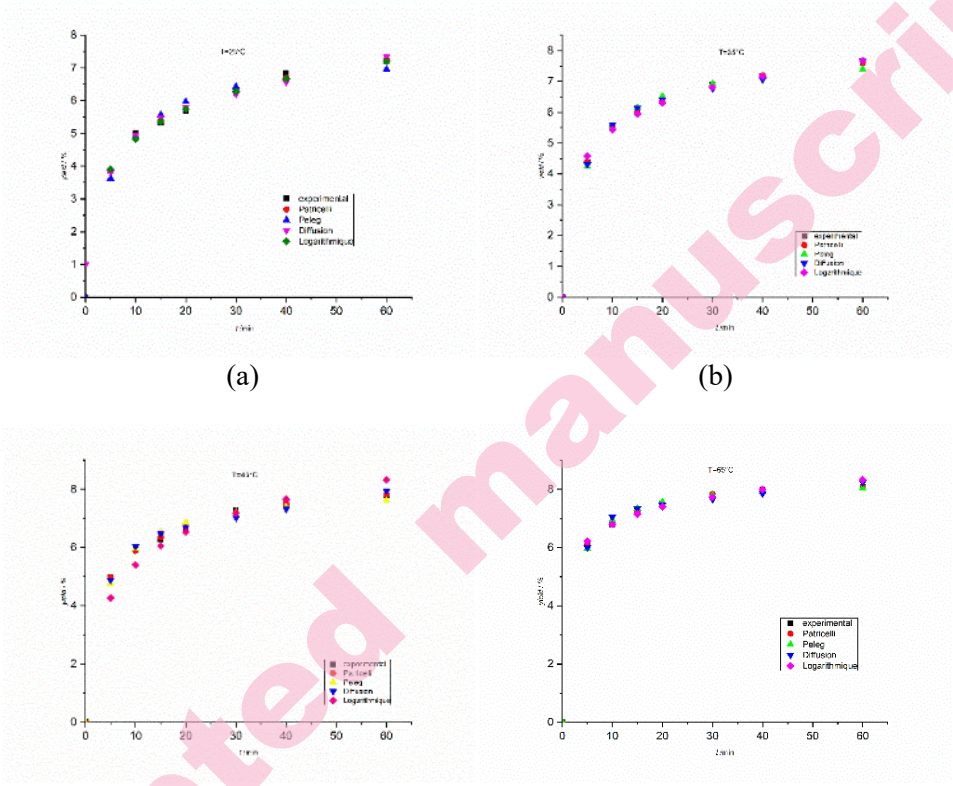

Fig. 2. Time-courses of the experimental and calculated values of yield for the various temperatures. (a) 25 ˚C; (b) 35 ˚C; (c) 45 ˚C; and (d) 65 ˚C.

Evaluation of the Patricelli model

Oil extraction from oleaginous seeds, fundamentally based on lipid solubilization within a solvent, is primarily governed by diffusive mechanisms. The proposed mathematical model characterizes the extraction as a dual-stage process:

(i) Surface Wash: An initial rapid removal of accessible surface oil via immediate solvent contact;

(ii) Internal Diffusion: A subsequent recovery of intra-cellular lipids occurring through a biphasic diffusion process. This internal phase comprises a relatively slow, unhindered diffusion from ruptured cells (Step 1), followed by a significantly more constrained diffusion from intact cellular structures (Step 2).

The extraction of oil from olive cake is fundamentally governed by the solvent's capacity to solubilize lipophilic compounds sequestered within the solid matrix. Various kinetic models have been developed to characterize this

phenomenon; among them, the Patricelli model has proven particularly robust, especially in applications involving olive oil recovery.[9]

Table II. The values of the model constants for temperatures 25, 35, 45, and 65 °C. The values of the comparison criteria χ^2, *CME*, and R^2 of the different models.

Model	Constants	*Temperature*/ °C			
		25	35	45	65
Patricelli	R_w	4.063	4.724	4.695	5.367
	Rd	3.943	3.274	3.348	2.752
	k_w	0.356	0.341	0.501	0.731
	kd	0.028	0.035	0.045	0.076
	R^2	0.999	1	0.999	1
	X^2	0.01050	0.00200	0.00625	0.00175
	CME	0.07246	0.03162	0.05590	0.02958
Peleg	k_1	0.720	0.549	0.430	0.234
	k_2	0.132	0.126	0.124	0.120
	R^2	0.991	0.997	0.995	0.999
	X^2	0.01946	0.05383	0.03750	0.00917
	CME	0.12081	0.20094	0.16771	0.08292
Diffusion	*k*	0.196	0.205	0.256	0.324
	a	-4.259	0.205	-5.192	-6.118
	b	-0.028	-0.020	-0.016	-0.008
	R^2	0.969	0.974	0.973	0.997
	X^2	0.22696	0.21297	0.23858	0.22824
	CME	0.37663	0.36483	0.38615	0.37769
Logarithmic	*a*	3.053	2.866	3.756	1.953
	b	1.780	2.577	1.647	4.857
	R^2	0.991	0.989	0.799	0.966
	X^2	0.01237	0.01272	0.19607	0.01719
	CME	0.09632	0.09767	0.38347	0.11354

In the current study, the application of the Patricelli model demonstrated high fidelity to the experimental results, validating its predictive accuracy under the investigated parameters. These findings exhibit strong congruence with the work of Meziane *et al.*,[9] who similarly observed a high degree of correlation between empirical data and model simulations during hexane-based extraction.

Consequently, the present results not only substantiate the validity of the Patricelli model for olive cake extraction but also underscore its robustness and versatility across diverse solvents and operational parameters. The extraction yield is thus defined by the equation 2.

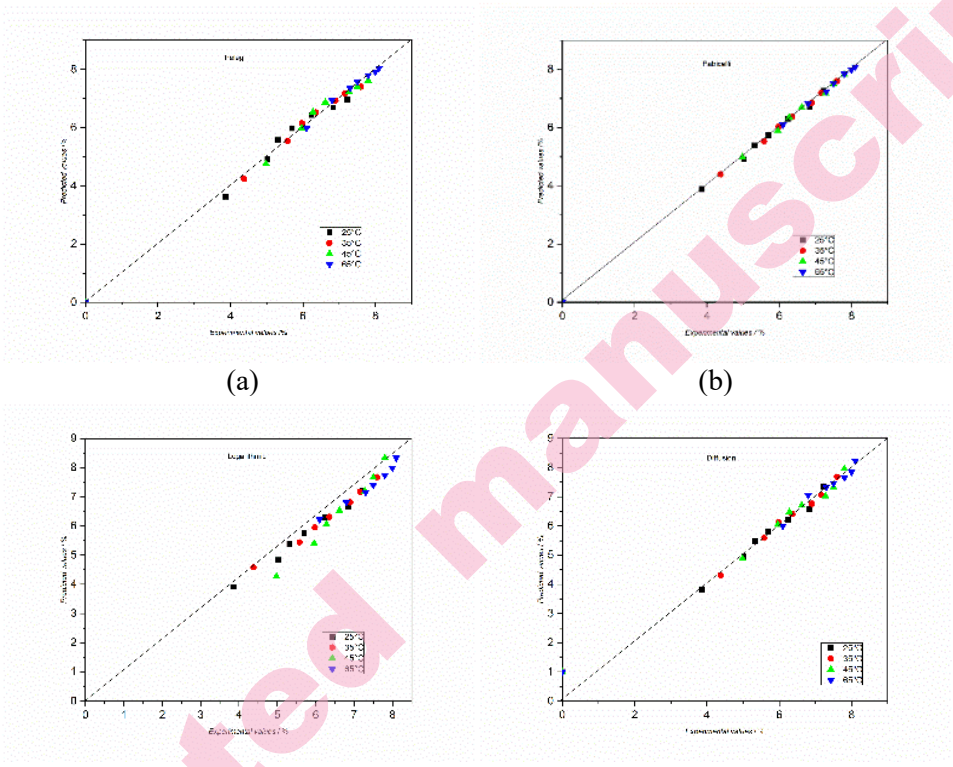

Fig. 3. Comparison between experimental and calculated values for the various considered models: (a) Patricelli;(b) Peleg; (c) Diffusion model and (d) Logarithmic model

The mass transfer coefficients k_w and k_d and equilibrium oil yields R_w and R_d were numerically determined using a non-linear least-squares fitting method via Statistica software. Table II summarizes these kinetic parameters across the investigated temperature range. At all temperatures, the yield attributed to the washing stage consistently exceeded that of the diffusion phase. Notably, at 65 °C, the washing yield was approximately double that of the diffusion yield, underlining the predominance of surface oil removal during the initial extraction phase.

The calculated mass transfer coefficients further corroborate this trend. At 25 °C, the washing coefficient *(k_w)* was approximately 12-fold higher than the diffusion coefficient *(k_d),* reflecting the rapid desorption of accessible surface oil. Both coefficients exhibited a linear temperature dependence, indicating that thermal energy enhances both surface washing and internal diffusion mechanisms. However, while *(k_w)* roughly doubled between 25 °C and 65 °C, the diffusion coefficient increased by a factor of three. This disparity suggests that temperature

exerts a more pronounced influence on internal mass transfer resistance than on surface washing kinetics.

Extraction kinetic rate

The kinetic behavior is further elucidated by the extraction profiles. As illustrated in Figure 1, the oil yield exhibits a sharp initial increase followed by an asymptotic plateau, signifying the transition from the rapid washing phase to the rate-limiting diffusion-controlled phase. This kinetic pattern is corroborated by the extraction rate calculations derived from Equation 4. The data in Table III indicate that the initial extraction rate (V_0) is highest at the onset of the process but undergoes a rapid exponential decay over time. Furthermore, the natural logarithm of the initial rate ($ln\ V_0$) displays a linear correlation with temperature. This relationship confirms that mass transfer processes are thermally activated, following a temperature-dependent acceleration consistent with Arrhenius-type behavior.

Table III. Variation of the extraction rate with time

Time / min	Rate of extraction / %.min^{-1}			
	25 °C	35 °C	45 °C	65 °C
0	1.55761	1.72547	2.50257	4.13347
5	0.33927	0.38901	0.31343	0.24443
10	0.12414	0.13398	0.11225	0.10043
15	0.07921	0.07746	0.07820	0.06696
20	0.06407	0.05866	0.06140	0.04575
30	0.04765	0.04016	0.03893	0.02139
40	0.03605	0.02826	0.02473	0.01001
60	0.02066	0.01403	0.00998	0.00219

The extraction rate is determined by the first derivative of the Patricelli equation with respect to time (Equation 9):

$$V = \frac{dR}{dt} = k_w R_w\, exp(-k_w t) + k_d R_d\, exp(-k_d t) \tag{9}$$

The initial extraction rate, is defined at t = 0 and can be expressed as follows (Equation 10) :

$$V_0 = \left(\frac{dR}{dt}\right)_{t=0} = k_w R_w + k_d R_d \tag{10}$$

Parameter of the Arrhenius equation

The activation energy for the extraction process was calculated using rate constants derived from mass transfer coefficients via the Patricelli model (Equation 11). These constants served to evaluate the Arrhenius equation parameters.[27]

$$k = A\, exp\left(\frac{-E_a}{RT}\right) \tag{11}$$

Where k is the rate constant (min^{-1}), Ea the activation energy ($J.mol^{-1}$), A the frequency factor (min^{-1}), R is the universal gas constant ($J.mol^{-1}. K^{-1}$), T the absolute temperature (K).

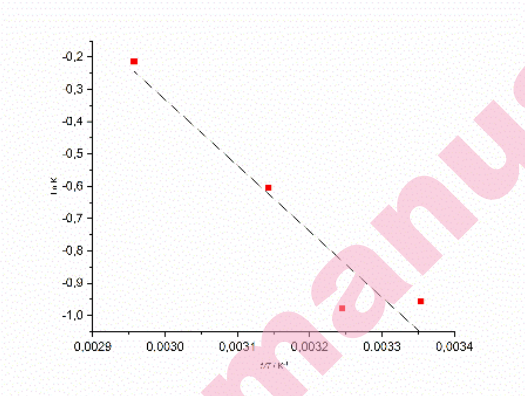

Fig. 4. Arrhenius plot of the extraction rate constant as a function of reciprocal temperature

The linear Arrhenius equation facilitates the determination of activation energy from the slope ($-E_a/R$) of the ln k versus (1/T) (Fig. 4), while the intercept yields ln A. Analysis produced an activation energy of 16.98 $kJ \cdot mol^{-1}$. This relatively low value carries significant implications for process design and industrial scalability. Primarily, it suggests that the rate-limiting step is governed by physical phenomena—such as solvent penetration, lipid solubilization, and matrix diffusion—rather than chemical transformations. From a process engineering perspective, this is advantageous, as physical mechanisms are generally more predictable and easier to optimize than chemically controlled reactions. Furthermore, this low energy barrier indicates reduced sensitivity to temperature fluctuations, potentially enhancing operational stability and minimizing energy consumption in large-scale applications. Consequently, moderate temperatures can be effectively utilized to achieve high extraction efficiencies, supporting the economic and technical feasibility of using limonene as a sustainable alternative.

In this study, the activation energy was determined to be 16.98 kJ. Mol^{-1}, indicating a diffusion-controlled mechanism. This result aligns closely with literature values for solvent-based lipid recovery from oleaginous matrices. For instance, Meziane *et al.* reported an Ea of approximately 17.4 kJ. Mol^{-1} for olive pomace extraction using hexane, which is highly comparable to the current findings.[9] Conversely, Usenu *et al.* identified Ea values of 6 508 kJ. Mol^{-1} for palm kernel oil,[28] while Perez *et al.* documented ranges between 11 and 33 kJ. Mol^{-1} for soybean oil, depending on specific conditions.[29] Furthermore, Baidoo *et al.*, observed activation energies near 60 $kJ.mol^{-1}$ during oil extraction from cashew

kernels, confirming that such processes are predominately governed by internal mass transfer (diffusion).[30] The strong correlation between our data and established values further validates the experimental methodology and supports the applicability of the kinetic framework employed in this research.

Thermodynamic study

The Gibbs free energy change (ΔG) associated with the oil extraction process was calculated using the following thermodynamic relation:

$$\Delta G = -RT\, lnKe \tag{12}$$

where R is the universal gas constant (J·mol^{-1}·K^{-1}), T is the absolute temperature (K), and K_e is the equilibrium constant, which quantifies the distribution of oil between the solvent (miscella) and the solid phase at equilibrium. The equilibrium constant K_e is defined by:

$$K_e = \frac{R_{miscella}}{R_{solid}} \tag{13}$$

Here, $R_{miscella}$ represents the equilibrium yield of oil extracted at a given temperature, while R_{solid} is the residual oil content remaining in the solid matrix at equilibrium, also at the same temperature. The residual oil content was calculated based on the initial oil content of the sample, determined to be 9.94 %, through exhaustive extraction using 97 % limone.

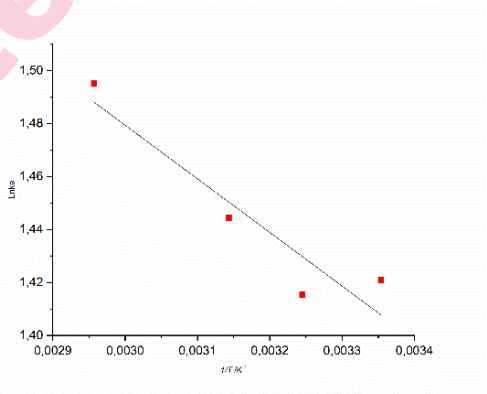

Fig.5.Van't Hoff plot used to determine the enthalpy (ΔH) and entropy (ΔS) changes of the extraction process.

The ΔG values presented in Table IV provide critical insights into the spontaneity of the extraction process. Negative ΔG values demonstrate that oil recovery occurs spontaneously under the investigated conditions. Elevated temperatures generally yield more negative ΔG values, reflecting improved solubilization and accelerated mass transfer. Similar trends were documented by Meziane et al., for olive cake extraction with hexane, where ΔG decreased from –

4.52 to –6.80 kJ. Mol^{-1} between 30 and 60 °C.[9] Dagostin *et al.*[30] reported ΔG values ranging from –0.41 to –15.86 kJ. Mol^{-1} for soybean oil extraction using ethanol between 25 and 55 °C. Similarly, Sunday et al. observed negative ΔG values (–1.37 to –3.61 kJ. Mol^{-1}) for neem oil recovery between 50 and 74 °C. Collectively, these findings confirm that lipid extraction is thermodynamically spontaneous and enhanced at elevated temperatures due to improved diffusivity and solute–solvent interactions. To further elucidate the thermodynamic behavior of the system, enthalpy (ΔH) and entropy (ΔS) changes were determined utilizing the Van't Hoff equation, expressed as follows:

$$lnK_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (14)$$

The linear relationship observed in the ln Ke versus 1/T plot (Fig. 5) aligns with the Van't Hoff equation, where the slope represents *(−ΔH/R)* and the intercept denotes *ΔS/R*. Linear regression analysis yielded an enthalpy change *(ΔH)* of 1.68 kJ·mol^{-1}, and an entropy change *(ΔS)* of 17.39 J·mol^{-1}·K^{-1}.

The positive ΔH value indicates that olive pomace oil extraction is an endothermic process requiring thermal input. The positive ΔS reflects heightened molecular disorder resulting from matrix disruption and oil diffusion into the liquid phase. Thermodynamic parameters (ΔH, ΔS) thus clarify the extraction mechanism. Comparable behavior was reported by Liauw *et al.*[31] for neem oil extraction using hexane (ΔH = 25.33 kJ. Mol^{-1}; ΔS = 0.09 kJ. K^{-1}·mol^{-1}), confirming an endothermic and irreversible process. Dagostin *et al.* similarly observed elevated ΔH (95 kJ. Mol^{-1}) and ΔS (320 kJ. K^{-1}· Mol^{-1}) values during soybean oil recovery [30]. Furthermore, Meziane and Kadi reported a ΔH of 12.91 kJ. Mol^{-1} for olive pomace oil with hexane, indicating substantial energy requirements. Collectively, these investigations confirm that lipid extraction is generally endothermic and thermodynamically favored at increased temperatures due to accelerated diffusion and enhanced solute–solvent interactions.

Table IV. Thermodynamic parameters and equilibrium constants for olive pomace oil extraction using limonene.

T /°C	K_e	ΔG /kJ
25	4.14	-3.53
35	3.10	-3.62
45	4.24	-3.83
65	4.46	-4.21

CONCLUSION

This investigation evaluated olive pomace oil recovery using limonene, specifically examining temperature's influence on yield, kinetics, and thermodynamic properties. Findings indicated that oil yields correlate positively with both duration and temperature. The process follows a biphasic progression:

an initial rapid "washing" stage characterized by surface oil removal, followed by a protracted diffusion-limited phase. Statistical evaluation of various kinetic frameworks revealed that the Patricelli model offered the most accurate representation of experimental observations. This was rigorously validated by high correlation coefficients ($R^2 > 0.99$) and minimal error metrics (χ^2 and MSE), confirming its suitability for predicting extraction behavior

Calculated mass transfer coefficients confirmed that the washing mechanism dominates early extraction stages, especially at lower temperatures, whereas both washing and diffusion rates enhance near-linearly with thermal increase. The determined activation energy (16.98 $kJ \cdot mol^{-1}$) is relatively low, indicating a physical extraction process that is diffusion-limited and thermally accessible—essential characteristics for industrial scalability. Thermodynamic evaluation yielded negative Gibbs free energy values (ΔG), confirming process spontaneity which intensifies at higher temperatures. The extraction was identified as endothermic ($\Delta H = 1.68\ kJ \cdot mol^{-1}$) and characterized by a positive entropy change ($\Delta S = 17.39\ J \cdot mol^{-1} \cdot K^{-1}$), suggesting increased molecular disorder as lipids transition from the solid matrix into the solvent phase. These parameters collectively validate limonene as an efficient, thermodynamically favorable green alternative for the sustainable recovery of residual olive oil. In summary, limonene demonstrates efficacy as an environmentally benign solvent for olive pomace oil recovery, achieving performance comparable to hexane while adhering to green chemistry principles. The process is thermodynamically favorable and kinetically predictable, exhibiting significant potential for sustainable industrial integration as a viable alternative to conventional, petro-based extraction methods.

И З В О Д

ЗЕЛЕНА ЕКСТРАКЦИЈА И ВАЛОРИЗАЦИЈА КОМИНЕ МАСЛИНЕ ПРИМЕНОМ ЛИМОНЕНА: ПРИСТУП ЗАСНОВАН НА КИНЕТИЧКОМ МОДЕЛОВАЊУ И ТЕРМОДИНАМИЧКОЈ АНАЛИЗИ

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У овом раду извршено је експериментано испитивање екстракције уља из комине маслине применом лимонена као зеленог растварача, са посебним нагласком на утицај температуре на принос, кинетику и термодинамику процеса. Резултати показују да се искоришћење уља повећава са временом и температуром, пратећи двостепени механизам: брзу фазу испирања, којом доминира уклањање површинског уља, и спорију фазу контролисану дифузијом. Кинетичко моделовање је показало да Патричелијев модел најбоље описује процес ($R^2 > 0,99$), док коефицијенти преноса масе потврђују доминацију механизма испирања на нижим температурама. Релативно ниска енергија активације (16,98 $kJ \cdot mol^{-1}$) указује на процес ограничен дифузијом, који је термички приступачан и погодан за индустријску примену. Термодинамички параметри потврђују овакво тумачење:

негативне вредности Гибсове слободне енергије потврђују спонтаност процеса, ендотермна промена енталпије (ΔH = 1,68 kJ·mol^{-1}) и позитивна вредност ентропије (ΔS = 17,39 J·mol^{-1}·K^{-1}) указују на повећање молекулског нереда током екстракције. У целини посматрано, лимонен показује високу ефикасност и одрживост, представљајући одрживу алтернативу хексану у складу са принципима зелене хемије.

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