GRASAS Y ACEITES 74 (4)
October-December 2023, e532
ISSN-L: 0017-3495
https://doi.org/10.3989/gya.0675221

Kinetic and thermodynamic parameters of curcumin in edible oils with different degrees of unsaturation

P. Ramezani[a], A. Rafati[b,✉], M.R. Toorani[c] and M.T. Golmakani[c,✉]

[a]Division Food Science & Nutrition, Sarvestan Branch, Islamic Azad University, Sarvestan, Iran.
[b]Division Pharmaceutical Chemistry & Food Science & Nutrition, Sarvestan Branch, Islamic Azad University, Sarvestan, Iran.
[c]Department of Food Science and Technology, School of Agriculture, Shiraz University, Postal Code 71441-65186, Shiraz, Iran.
✉Corresponding authors: alireza_rafati57@yahoo.com; rafati@iausarv.ac.ir; golmakani@shirazu.ac.ir

Submitted: 10 July 2022; Accepted: 27 June 2023; Published online: 26 December 2023

SUMMARY: The antioxidant activity of curcumin (0.02–0.1%) was evaluated in olive, sesame, and safflower oils at 373, 383, and 393 K. The results were examined in contrast to the effects of tocopherol (0.1%) and BHT (0.02%), so that the inhibitory function of curcumin was evaluated comparatively. The activation energy of oxidation was determined for olive (82.94 kJ·mol^{-1}), sesame (77.39 kJ·mol^{-1}) and safflower oils (74.42 kJ·mol^{-1}). Adding curcumin (0.1%) enhanced the activation energy by 26.26, 26.64, and 38.81% in the case of olive, safflower, and sesame oils, respectively. Based on Gibbs free energy, curcumin functioned more effectively in olive oil at 373 K (growth coefficient: 1.52%), compared to the action of the other two antioxidants, namely tocopherol (1.43%) and BHT (1.39%). The efficiency of curcumin was lower in oils which had a higher degree of polyunsaturation due to the disproportionation of the hydrogen-donating mechanism and the rate of free-radical formation in these oils.

KEYWORDS: *Activated complex theory; Antioxidant activity; Curcumin; Hydrogen donating mechanism; Lipid oxidation; Thermodynamic parameters.*

RESUMEN: ***Parámetros cinéticos y termodinámicos de la curcumina en aceites comestibles con diferentes grados de insaturación.*** La actividad antioxidante de la curcumina (0,02–0,1 %) se evaluó en aceites de oliva, sésamo y cártamo a 373, 383 y 393 K. Los resultados se contrastaron con los efectos del tocoferol (0,1 %) y del BHT (0,02%), por lo que se evaluó comparativamente la función inhibitoria de la curcumina. Se determinó la energía de activación de la oxidación para los aceites de oliva (82,94 kJ·mol^{-1}), sésamo (77,39 kJ·mol^{-1}) y cártamo (74,42 kJ·mol^{-1}). La adición de curcumina (0,1 %) mejoró la energía de activación en un 26,26 %, 26,64 % y 38,81 % en el caso de los aceites de oliva, cártamo y sésamo, respectivamente. Según la energía libre de Gibbs, la curcumina funcionó de manera más eficaz en aceite de oliva a 373 K (coeficiente de crecimiento: 1,52 %), en comparación con la acción de los otros dos antioxidantes; es decir, tocoferol (1,43 %) y BHT (1,39 %). La eficiencia de la curcumina fue menor en los aceites que tenían un mayor grado de poliinsaturación debido a la desproporción del mecanismo de donación de hidrógeno y la tasa de formación de radicales libres en estos aceites.

PALABRAS CLAVE: *Actividad antioxidante; Curcumina; Mecanismo de donación de hidrógeno; Oxidación de lípidos; Parámetros termodinámicos; Teoría del complejo activado*

Citation/Cómo citar este artículo: Ramezani P, Rafati A, Toorani MR, Golmakani MT. 2023. Kinetic and thermodynamic parameters of curcumin in edible oils with different degrees of unsaturation . *Grasas Aceites* **74** (4), e532. https://doi.org/10.3989/gya.0675221

Copyright: ©2023 CSIC. This is an open-access article distributed under the terms of the Creative Commons Attribution 4.0 International (CC BY 4.0) License

1. INTRODUCTION

Antioxidant addition is among the most effective strategies which can assist researchers and producers in preventing the chemical spoilage of vegetable oils. In fact, antioxidants are inhibitors of oxidation chain reactions which have different functions which emanate from their structural nature. In recent research, natural antioxidants have received a great deal of attention because of their safe applicability which entrusts public awareness and serves as reliable alternatives to the possible carcinogenicity of synthetic antioxidants. Curcumin (diferuloylmethane), has two phenolic rings and a beta-diketone part which is known as a natural antioxidant originating from saffron, clove, and turmeric. The antioxidant activity of this compound has been frequently reported by many researchers (Aliabbasi *et al.*, 2021; Barzegar, 2012; Hewlings and Kalman, 2017; Kumar *et al.*, 2016). In addition, curcumin plays a valuable role in the treatment and prevention of various types of diseases such as inflammatory, anti-cancer, anti-blood pressure, anti-fungal, anti-viral, anti-fibrotic, anti-ulcer, and anti-toxic activities. Also, curcumin plays important roles in food technology, including stability improvement, quality enhancement, and decreasing lipid oxidation (Mandal *et al*., 2023; Hewlings and Kalman, 2017). In general, antioxidant activity can be potentially related to the presence of phenolic groups in the chemical structure of antioxidants (Frankel, 2012). Two mechanisms of hydrogen donating and electron transfer are effective in the occurrence of antioxidant activity. Curcumin is assumed to have desirable antioxidant activity which can be attributed to having two phenolic rings. However, the antioxidant activity of curcumin can be affected by the presence of methoxy groups in the ortho position of benzene rings (in the proximity of hydroxyl groups) due to the high electronegativity of these groups (Barzegar, 2012).

Curcumin shows low bioavailability due to its high hydrophobicity. It is very common to use carriers to solve this defect and also to inhibit degradation caused by oxidation, or protection against environmental factors such as pH changes. On the other hand, the amount of its dissolution in vegetable oils is adequate. However, the log p of this antioxidant is 1.945, which is considered a relatively non-polar antioxidant due to the many functional groups in its structure. Different researchers have reported that antioxidants show good antioxidant activity in opposite environments in terms of polarity. In this way, the performance of curcumin in vegetable oils is expected to be favorable (Jokar *et al.*, 2022; Malik *et al*., 2016; Malik *et al*., 2020; Waraho, *et al*., 2011).

Lipid oxidation is one of the main causes of quality loss in lipid systems. This reaction is accompanied by the production of harmful products that tend to threaten human health (Shahidi, 2005). The rate of this reaction is affected by temperature at an exponential rate, revealing an interdependence which is well explained by the Arrhenius equation (Farhoosh and Hoseini-Yazdi, 2014; Shim and Lee, 2011). In fact, this equation is part of the collision theory, based on which, effective collisions should take place between reactant molecules before a chemical reaction could occur. An effective collision occurs when the reactant molecules hit each other with sufficient energy and at the right angle. Specifically, it is the number of collisions within a certain timeframe that controls the reaction rate. Therefore, the reaction rate can change by any factor affecting the collision of reactants (e.g. temperature) (Kamal-Eldin and Yanishlieva, 2005). The increase in temperature can change the pathways of oxidation reactions and may cause performative defects in the occurrence of antioxidant activity. It should be noted that antioxidants can reduce effective collisions between oxidation reactants, although an important question is how much the performance of natural antioxidants can be affected by the operating conditions and by high temperatures, even as the antioxidants contain diverse functional groups (such as curcumin).

Hydroperoxides are among the most important precursors of the oxidation reactions of oils. Different oils produce different hydroperoxides, depending on the degree of unsaturation of their constituent fatty acids, which create several diverse secondary products, depending on oxidation reactions. Oils with more oleic acid, such as olive oil, produce more stable hydroperoxides, and oils such as sesame contain more linoleic acid, which generates more unstable hydroperoxides which break down more quickly into secondary oxidation products. Depending on their natural chemical structures, antioxidants indicate different functions against hydroperoxides. Thus, the performance of an antioxidant can be different in various oils (Laguerre *et al.*, 2020, Toorni and Golmakani, 2022).

Nevertheless, the present research aimed to investigate the potential application of a natural, available and inexpensive antioxidant such as curcumin. This research was planned in several sections. First, the performance of curcumin was investigated in various oils with different degrees of unsaturation. Second, the changes in the antioxidant activity of curcumin were checked by increasing concentration, and the best concentration was also determined. The effectiveness of curcumin was evaluated by increasing temperature, especially at temperatures above 100 °C. Furthermore, the efficacy of curcumin was compared to synthetic antioxidants in order to replace them. These sections have been established in order to develop detailed instructions so that this valuable antioxidant could be used effectively. In practice, different concentrations of curcumin were added to olive, sesame, and safflower oils, and the antioxidant activity of curcumin was measured by kinetic and thermodynamic equations, according to data obtained from the Rancimat device at different temperatures. To evaluate the inhibitory power of curcumin, its effectiveness was compared to natural (tocopherol) and synthetic (BHT) antioxidants.

2. MATERIALS AND METHODS

2.1. Materials

Refined, bleached, and deodorized safflower, sesame and olive oils which did not contain any added synthetic antioxidants were supplied by the Narges and Golbarg-e-Baharan companies. The oils were stored at -18 °C. Curcumin (CAS No. 458-37-7) was purchased from Sigma-Aldrich (St. Louis, MO). All other chemicals were of analytical grade, and standard markers were supplied by Sigma-Aldrich (St. Louis, MO) and Merck (Darmstadt, Germany). The antioxidant capacity of curcumin was measured by the DPPH assay according to the method described by Sanchez *et al*., (1998). The amount of IC_{50} for curcumin was 23.61 ± 3.45 µM.

2.2. Fatty acid composition

Fatty acid composition was determined by gas-liquid chromatography (Hewlett-Packard, 5890, Palo Alto, CA) according to the AOCS official method Ce 2-66 (Firestone, 2009). For this purpose, oils (0.3 g in 7 mL n-hexane) were converted into their corresponding fatty acid methyl esters by mixing with a solution of methanolic potassium hydroxide (2 mL of 7 N) for 15 min at 65 °C. The gas chromatography device was equipped with a flame ionization detector and a CP-FIL 88 column (with 60 m length, 0.22 mm internal diameter, and 0.2 µm film thickness) (Supelco Inc., Bellefonte, PA). The injector, detector, and oven temperatures were set at 225, 265, and 195 °C, respectively. Nitrogen gas was applied as carrier gas at a flow rate of 1 mL·min^{-1}.

2.3. Induction period

A Rancimat device (Methrom, model 743 Herisau, Switzerland) was used for determining the induction periods (IPs) of the oils under study. In brief, a batch of 3 ± 0.001 g per oil, containing 0.02, 0.06, or 0.1% (w/w) curcumin, 0.1% (w/w) tocopherol, or 0.02% (w/w) BHT was weighed in separate reaction vessels and placed into the heating channel of the Rancimat. The airflow rate was regulated on 20 L·h^{-1}, and the temperature inside the conductivity tube was constantly maintained at 25 °C. The oxidative stability of the oils was automatically determined at 373, 383, and 393 K by Apparatus software.

2.4. Analysis of kinetic and thermodynamic data

Temperature coefficient (T_C, 1/K) was calculated by the slope (parameter a) of the curve which fitted as follows:

$$\text{Log IP} = \text{T}_\text{C}.\text{T} + \log \text{IP}_0 \quad \text{Eq. (1)}$$

where T is temperature (K), and IP_0 is IP at a reference temperature. The temperature acceleration factor was embodied in the Q_{10} number, showing the increase in reaction rate due to a 10 °C rise in temperature, as obtained from Eq. (2).

$$Q_{10} = \frac{\text{IP at T °C}}{\text{IP at (T+10) °C}} \rightarrow Q_{10} = 10^{-10T_\text{C}} \quad \text{Eq. (2)}$$

According to Eq. (3) (Arrhenius equation), the activation energy (E_a) and frequency factor (A) of the secondary oxidation products were calculated by plotting the natural logarithm of k (1/IP) vs the 1/RT.

$$\ln k = -\left(\frac{E_\text{a}}{R\text{T}}\right) + \ln A \quad \text{Eq. (3)}$$

where R and T represent the molar gas constant (8.3143 J/mol K) and temperature (K), respectively.

According to Eq. (4) and Eq. (5), the Arrhenius equation parameters were calculated using the obtained slope (a) and intercept (b) from Eq. (3).

$$E_{\mathrm{a}} = -a \quad \text{Eq. (4)}$$

$$A = \exp{(b)} \quad \text{Eq. (5)}$$

Enthalpy (ΔH^{++}) and entropy (ΔS^{++}) of activation were determined by the Eyring equation (Eq. (6)) via drawing ln (k/T) against 1/RT.

$$\ln\left(\frac{k}{\mathrm{T}}\right) = \ln\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^{++}}{R}\right) - \left(\frac{\Delta H^{++}}{R\mathrm{T}}\right) \quad \text{Eq. (6)}$$

where k_B and h are the Boltzmann constant (1.380658 × 10^{-23} J K^{-1}) and Planck's constant (6.6260755 × 10^{-34} J s), respectively. The values for enthalpy and entropy were calculated using the slope and intercept related to the mentioned relationship, according to Eq. (7) and Eq. (8).

$$\Delta H^{++} = -a \quad \text{Eq. (7)}$$

$$\Delta S^{++} = \left[b - \ln\left(\frac{k_B}{h}\right)\right] \times R \quad \text{Eq. (8)}$$

ΔH^{++} and ΔS^{++} were used to determine the Gibbs free energy equation according to Eq. (9).

$$\Delta G^{++} = \Delta H^{++} - \mathrm{T}\Delta S^{++} \quad \text{Eq. (9)}$$

The percentage of changes (C%) in the kinetic parameters, relevant to inhibited oxidation, were compared to non-inhibited and were calculated according to the following equation:

$$\mathrm{C\%} = \left(\sum_{i=1}^{3}([\mathrm{AH}]_i(\mathrm{X_i} - \mathrm{X_c})100/\mathrm{X_c}) \Big/ \sum_{i=1}^{3}[\mathrm{AH}]_i\right) \quad \text{Eq. (10)}$$

where X_i and X_c are kinetic parameters in the presence and absence of the antioxidant, respectively.

The percentage of changes in ΔG^{++} due to temperature variations was determined using linear regression between the natural logarithm of changes (%) in ΔG^{++} and temperature. A decrease in the effectiveness of antioxidants (Ef_d) due to an increase in temperature of 10 °C was measured by the slope (a) of said relationship according to Eq. (11).

$$\mathrm{Ef_d} = \exp{(10a)} \quad \text{Eq. (11)}$$

2.5. Statistical analysis

All evaluations were carried out in triplicate, and the analysis of variance (ANOVA) of the results was performed by SPSS Software. Significant differences among means were compared by Duncan's statistical test ($P < 0.05$).

3. RESULTS AND DISCUSSION

3.1. Oxidative potential of oils

The fatty acid composition of each oil showed a significant difference from other oils in terms of linoleic (C18:2), oleic (C18:1), and palmitic (C16:0) acids (Table 1). The highest amount of saturated fatty acids was found in olive oil, followed by sesame and safflower oils. The highest value for monounsaturated fatty acids, an important symbol of oxidative stability, was observed in olive oil; whereas no significant difference was observed between safflower and sesame oils in this respect. As expected, the highest

TABLE 1. Fatty acids composition (%) of different vegetable oils.

Fatty acid	Safflower	Sesame	Olive
C12:0	0.04 ± 0.00^{b}*	0.12 ± 0.01^{a}	0.08 ± 0.01^{a}
C14:0	0.07 ± 0.01^{a}	0.07 ± 0.00^{a}	0.03 ± 0.00^{b}
C16:0	5.74 ± 0.11^{c}	8.28 ± 0.16^{b}	13.43 ± 0.06^{a}
C16:1	0.12 ± 0.13^{b}	0.17 ± 0.01^{b}	0.91 ± 0.02^{a}
C18:0	2.55 ± 0.19^{b}	4.56 ± 0.18^{a}	2.49 ± 0.09^{b}
C18:1	32.91 ± 0.37^{b}	32.67 ± 0.13^{c}	69.33 ± 0.13^{a}
C18:2	58.06 ± 0.27^{a}	53.36 ± 0.11^{b}	12.44 ± 0.13^{c}
C18:3 (n-3)	0.06 ± 0.01^{b}	0.20 ± 0.14^{b}	0.62 ± 0.02^{a}
C18:3 (n-6)	0.17 ± 0.02^{b}	0.17 ± 0.01^{b}	0.27 ± 0.01^{a}
C20:1	0.28 ± 0.02^{b}	0.41 ± 0.01^{a}	0.41 ± 0.00^{a}
SFA **	8.40 ±0.20^{c}	13.03 ± 0.04^{b}	16.02 ±0.12^{a}
MUFA	33.30 ±0.40^{b}	33.25 ± 0.13^{b}	70.66 ±0.15^{a}
PUFA	58.30 ±0.55^{a}	53.72 ± 0.16^{b}	13.32 ±0.13^{c}

* All experiments were performed in triplicate. The results were checked using ANOVA and were compared by Duncan's test ($P < 0.05$). In each row, averages (± standard deviation) with different lowercase letters are statistically different.
** Saturated fatty acids; Monounsaturated fatty acids; Polyunsaturated fatty acids.

and lowest polyunsaturation degrees (presented as the nutritional index of the oils) belonged to safflower and olive oils, respectively. Since the average relative rates of oxidation, pertaining to linolenic, linoleic, oleic, and stearic fatty acids were 2500, 1200, 100, and 1, respectively (Hsieh and Kinsella, 1989). The results provided information on the antioxidant activity of curcumin in the diverse lipid systems and in terms of degree of unsaturation.

3.2. Curcumin and oxidative stability period

The absolute values for the oxidation IPs are shown in Table 2. As predicted, the control samples exhibited different levels of oxidative stability. Even though the oxidative stabilities of the oils were not doubled compared to each other, this trend was somewhat maintained as temperatures rose from 373 to 393 K. The results showed that the addition of curcumin increased the oxidative stability of the oils. Despite the fact that increasing the concentration of curcumin improved the oxidative stability of the oils, the growth slope of the IP was unique for each oil (Figure 1a). Such contradictory behavior of curcumin can be attributed to the occurrence of complex chemical reactions. These reactions are most likely due to the residual radical of curcumin after releasing $[H]^+$ and by the excitation of oxidation chain reactions, whereby lipid substrates are attacked (Fennema, 1996). Thus, the best and most economical concentration of curcumin was 0.02% in the bulk oils of this study. Also, the growth slope of IPs, due to increasing temperature eventuated in a significant decrease which appeared more noticeable in the sesame oil. By comparing the performance of the antioxidants in sesame oil, the presence of curcumin at a concentration of 0.02% could be seen as a competitive approach in comparison with the function of tocopherol and BHT. Nonetheless, the behavioral pattern of curcumin requires further discussion on specific measurements and detail in comparison with other antioxidants so as to elucidate the inhibitory mechanism of this valuable natural antioxidant.

TABLE 2. Induction periods (IPs) and thermal kinetic parameters of olive, sesame, and safflower oils in the presence of different concentrations of curcumin, tocopherol, and BHT and at different temperatures.

Oil	AO	*C* (%)	IP (h)			T_C (×10-2)	Q_{10}
			373 K	383 K	393 K		
Safflower	Con	-	4.02 ±0.08^{o}*	2.15 ±0.04^{l}	1.19 ±0.02^{m}	-2.65 ±0.07^{j}	1.84 ±0.03^{j}
	CUR	0.02	6.93 ±0.03^{n}	3.52 ±0.10^{k}	1.65 ±0.03^{k}	-3.12 ±0.05^{f}	2.05 ±0.02^{f}
	CUR	0.06	7.42 ±0.03^{m}	3.66 ±0.03^{k}	1.59 ±0.04^{k}	-3.35 ±0.06^{de}	2.16 ±0.03^{de}
	CUR	0.10	7.96 ±0.06^{k}	3.64 ±0.03^{k}	1.70 ±0.05^{j}	-3.36 ±0.05^{d}	2.17 ±0.02^{d}
	TCP	0.10	9.07 ±0.03^{i}	3.94 ±0.03^{j}	1.72 ±0.02^{j}	-3.61 ±0.01^{c}	2.30 ±0.01^{c}
	BHT	0.02	8.44 ±0.06^{j}	4.15 ±0.03^{i}	1.45 ±0.05^{l}	-3.82 ±0.06^{a}	2.41 ±0.03^{a}
Sesame	Con	-	7.81 ±0.03^{l}	3.81 ±0.10^{j}	2.20 ±0.03^{i}	-2.75 ±0.02^{i}	1.89 ±0.01^{i}
	CUR	0.02	15.36 ±0.04^{h}	7.16 ±0.04^{g}	2.83 ±0.03^{h}	-3.67 ±0.02^{b}	2.33 ±0.01^{b}
	CUR	0.06	16.50 ±0.08^{g}	7.31 ±0.03^{f}	2.98 ±0.07^{fg}	-3.72 ±0.06^{b}	2.35 ±0.03^{b}
	CUR	0.10	16.64 ±0.24^{g}	6.63 ±0.09^{h}	2.86 ±0.06^{g}	-3.83 ±0.07^{a}	2.41 ±0.04^{a}
	TCP	0.10	13.93 ±0.03^{b}	7.09 ±0.02^{g}	3.10 ±0.03^{f}	-3.26 ±0.03^{e}	2.12 ±0.01^{e}
	BHT	0.02	16.99 ±0.07^{f}	7.39 ±0.09^{f}	3.51 ±0.04^{e}	-3.42 ±0.03^{d}	2.20 ±0.03^{d}
Olive	Con	-	15.41 ±0.08^{h}	7.31 ±0.04^{f}	3.96 ±0.04^{d}	-2.95 ±0.02^{h}	1.97 ±0.01^{h}
	CUR	0.02	22.38 ±0.08^{e}	9.84 ±0.05^{e}	4.23 ±0.03^{c}	-3.62 ±0.02^{c}	2.30 ±0.01^{c}
	CUR	0.06	25.98 ±0.02^{d}	11.07 ±0.03^{d}	4.92 ±0.04^{b}	-3.61 ±0.2^{c}	2.30 ±0.01^{c}
	CUR	0.10	27.86 ±0.06^{a}	11.89 ±0.07^{b}	5.00 ±0.06^{b}	-3.73 ±0.02^{b}	2.36 ±0.01^{b}
	TCP	0.10	27.16 ±0.05^{b}	13.21 ±0.04^{a}	6.72 ±0.03^{a}	-3.03 ±0.01^{g}	2.01 ±0.01^{g}
	BHT	0.02	26.52 ±0.04^{c}	11.49 ±0.08^{c}	4.99 ±0.02^{b}	-3.63 ±0.00^{c}	2.31 ±0.00^{c}

* All experiments were performed in triplicate. The results were checked using ANOVA and were compared by Duncan's test ($P < 0.05$). Means ± SD (standard deviation) within a column with the same lowercase letters are not significantly different.
AO: antioxidant; *C*: antioxidant concentration; Con: control sample; CUR: curcumin; TCP: tocopherol; BHT: butylated hydroxytoluene; T_C: temperature coefficient (K^{-1}); Q_{10}: temperature acceleration factor.

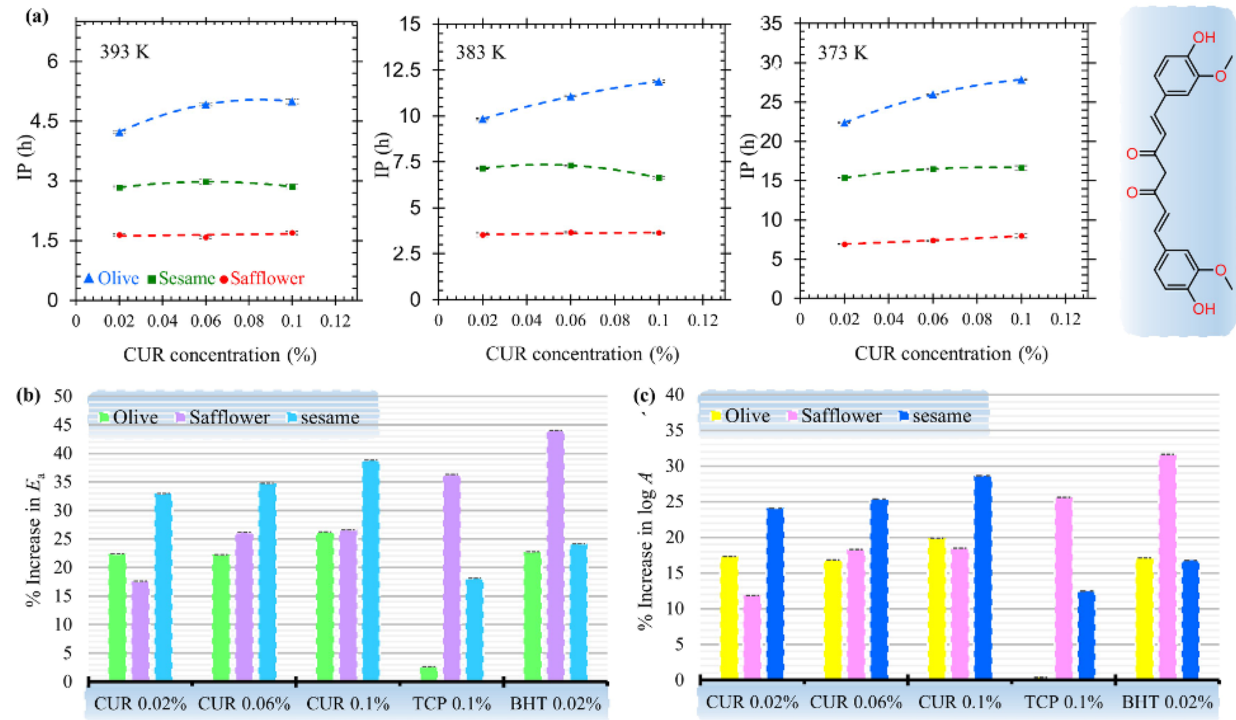

Figure 1. (a) Relationship between curcumin (CUR) concentration and induction period (IP) for the oxidation of different vegetable oils at 373, 383, and 393 K. **(b,c)** Percentage of increase in activation energy (E_a) or logarithm of frequency factor (Log A) compared to the control samples for the oxidation of different vegetable oils in the presence of various concentrations of curcumin (CUR), tocopherol (TCP), and butylated hydroxytoluene (BHT) at 373, 383, and 393 K. All experiments were performed in triplicate. The results were checked using ANOVA and were compared by Duncan's test ($P < 0.05$).

3.3. Temperature and curcumin function

It is clear that the rise in temperature is a critical parameter in consideration when monitoring the performance of antioxidants. The role of heat is important in two aspects. First, there are the potential effects on the mechanistic pathway of the oxidation process. It has been confirmed that the general trend of the oxidation process tends to change at temperatures higher than 60 °C (Zheng *et al.*, 2020). Although the reaction rate also increases, the effect of the pathway change is much higher than the reaction rate (Keramat *et al.*, 2021). Second, the effects of temperature on antioxidant molecules which can cause decomposition or evaporation. Meanwhile, heat can convert the antioxidants into per-oxidant compounds. The T_c and Q_{10} indices are considered very important tools for evaluating the performance of antioxidants against temperature rise. The percentage of changes in these parameters was lower in olive oil, with the highest amount of oleic acid, compared to the sesame and safflower oils (Table 2). The occurrence of such changes is likely related to the higher resistance of oleic acid at high temperatures.

In general, according to the data in Table 2, it was revealed that the shelf-life of oils in the presence of curcumin has no significant differences with the samples containing synthetic antioxidants. The observation of such effects reveals the favorable inhibitory power of curcumin.

3.4. Parameters of Arrhenius model

Oxidation reactions of the unsaturated oils tend to occur under any circumstances, while heat accelerates the rate of these reactions like a catalyst. The parameters of the Arrhenius equation actually represent the relationship between temperature and the occurrence of chemical reactions. This relationship has been frequently used in predicting the behavior of reactants and in estimating how many reaction products can be produced (Golmakani *et al.*, 2020a; Toorani and Golmakani, 2022; Zheng *et al.*, 2020). Since the amount of secondary oxidation products was a criterion for estimating Arrhenius parameters such as E_a, the measured parameter was introduced as the "activation energy of curcumin". In fact, the term refers to a rise in the required energy, created by

Table 3. Thermal kinetic parameters of olive, sesame, and safflower oils in the presence of different concentrations of curcumin, tocopherol, and BHT at different temperatures (373, 383, and 393 K).

Oil	AO*	C (%)	Arrhenius equation parameters		Eyring equation parameters		Gibbs free energy at 373–393 K		
			E_a	log A	ΔH^{++}	ΔS^{++}	ΔG^{++}_{373}	ΔG^{++}_{383}	ΔG^{++}_{393}
Safflower	Con	-	74.4±.0^{j}†	13.4±.3^{j}	71.2±2.0^{j}	-135.5±0.0^{j}	121.8±0.0^{o}	123.1±0.0^{m}	124.5±0.1^{n}
	CUR	0.02	87.5±.4^{f}	15.0±.2^{f}	84.3±.4^{f}	-105.1±.7^{f}	123.5±0.0^{n}	124.6±0.0^{l}	125.6±0.1^{kl}
	CUR	0.06	93.9±.6de	15.8±0.2^{de}	90.7±.6de	-88.6±.2de	123.7±0.0^{m}	124.6±0.0^{l}	125.5±0.1^{l}
	CUR	0.10	94.2±.3^{d}	15.8±.2^{d}	91.0±.3^{d}	-88.1±.6^{d}	123.9±0.0^{l}	124.8±0.0^{k}	125.6±0.1^{kl}
	TCP	0.10	101.4±.4^{c}	16.8±.1^{c}	98.2±.4^{c}	-69.9±.1^{c}	124.3±0.0^{j}	125.0±0.0^{j}	125.7±0.0^{k}
	BHT	0.02	107.1±.6^{a}	17.6±.2^{a}	103.9±.6^{a}	-54.4±.3^{a}	124.2±0.0^{k}	124.6±0.0^{k}	125.3±0.0^{m}
Sesame	Con	-	77.4±.5^{i}	13.5±.1^{i}	74.2±.2^{i}	-132.9±.2^{i}	123.7±0.0^{m}	125.1±0.0^{i}	126.4±0.0^{j}
	CUR	0.02	102.9±.6^{b}	16.8±.1^{b}	99.7±.6^{b}	-70.5±.6^{b}	126.0±0.0^{g}	126.7±0.0^{h}	127.4±0.0^{i}
	CUR	0.06	104.3±.6^{b}	16.9±.2^{b}	101.1±.6^{b}	-67.3±.3^{b}	126.2±0.0^{f}	126.9±0.0^{g}	127.6±0.1^{h}
	CUR	0.10	107.4±.0^{a}	17.4±.3^{a}	104.2±.0^{a}	-58.8±.4^{a}	126.1±0.0^{f}	126.7±0.0^{h}	127.3±0.1^{i}
	TCP	0.10	91.4±.8^{e}	15.2±.1^{e}	88.2±.8^{e}	-100.5±.1^{e}	125.7±0.0^{i}	126.7±0.0^{h}	127.7±0.0^{g}
	BHT	0.02	96.1±.9^{d}	15.8±.13^{d}	92.9±.9^{d}	-89.3±.5^{d}	126.2±0.0^{f}	127.1±0.0^{f}	128.0±0.0^{f}
Olive	Con	-	82.9±.6^{h}	14.0±.1^{h}	79.7±.6^{h}	-123.7±1.5^{h}	125.9±0.0^{h}	127.1±0.0^{f}	128.3±0.0^{e}
	CUR	0.02	101.5±.5^{c}	16.4±.1^{c}	98.3±.5^{c}	-77.2±.3^{c}	127.1±0.0^{e}	127.9±0.0^{e}	128.7±0.0^{d}
	CUR	0.06	101.4±.5^{c}	16.3±.1^{c}	98.2±.5^{c}	-78.6±.2^{c}	127.5±0.0^{d}	128.3±0.0^{d}	129.1±0.0^{c}
	CUR	0.10	104.7±.6^{b}	16.8±.6^{b}	101.5±.6^{b}	-70.4±.5^{b}	127.8±0.0^{a}	128.5±0.0^{b}	129.2±0.0^{b}
	TCP	0.10	85.1±.3^{g}	14.0±.0^{g}	81.9±.3^{g}	-122.7±.9^{g}	127.7±0.0^{b}	128.9±0.0^{a}	130.1±0.0^{a}
	BHT	0.02	101.8±.1^{c}	16.4±.0^{c}	98.6±.1^{c}	-77.8±.2^{c}	127.6±0.0^{c}	128.4±0.0^{c}	129.2±0.0^{b}

† All experiments were performed in triplicate. The results were checked using ANOVA and were compared by Duncan's test ($P < 0.05$). Means ± SD (standard deviation) within a column with the same lowercase letters are not significantly different.
AO: antioxidant; C: antioxidant concentration; Con: control sample; CUR: curcumin; TCP: tocopherol; BHT: butylated hydroxytoluene; E_a: activation energy (kJ·mol^{-1}); log A: logarithm of frequency factor (h^{-1}); ΔH^{++}: activation enthalpy (kJ·mol^{-1}); ΔS^{++}: activation entropy (J mol^{-1}); ΔG^{++}: Gibbs free energy (kJ·mol^{-1}).

curcumin or other antioxidants, for lipid oxidation to occur less easily. The results of E_a showed that curcumin desirably increased the oxidative resistance of all oils even at 393 K (Table 3). One of the concerns before starting the research was the thermal degradation of curcumin and the destruction of its inhibitory function at high temperatures due to the presence of many functional groups in the chemical structure of curcumin. However, the results showed that this antioxidant is highly capable of resisting 393 K. The highest value for E_a was observed in sesame oil when using 0.1% curcumin, which was higher than in samples with any other antioxidant.

Compared to the control samples, the percentage of increase in E_a by curcumin ultimately led to finding the optimal performance of this antioxidant in the lipid systems under study (Figure 1b). The highest amount of this parameter was found in sesame oil – in response to different concentrations of curcumin. It has been proven that this factor cannot be considered exclusively as an appropriate criterion for predicting the intensity of antioxidant activity (Toorani *et al.*, 2021). It is clear that the function of an antioxidant is affected by both factors of the Arrhenius equation, namely E_a and A. The results of the A parameter (log A) showed that this factor increased significantly in the presence of curcumin. A powerful antioxidant is characterized by a high E_a and a low A value. Since the trend of changes in these two parameters was incremental, it became difficult to judge the optimal performance of curcumin. The percentage of increase in A showed a noticeable growth in all samples (Figure 1c). However, the lowest growth percent was observed in the safflower oil with a maximum amount of PUFA. It is clear that the variations in A values per antioxidant were proportional to the changes in E_a, so that a decrease in A significantly reduced the E_a value. The A value was mathematically defined as serving a reaction rate whereby all reactants have enough energy for a chemical reaction to occur (i.e. $E_a = 0$) or in a case where the temperature inclines to infinity ($T \rightarrow \infty$) (Toorani and Golmakani, 2022). In fact, A is a criterion of reaction rate, showing the reactivity of lipid systems against oxidation. Therefore, considering the two Arrhenius parameters together is the most reliable way to understand how fast a reaction proceeds.

3.5. Thermodynamic indices

According to the activation complex theory, the reactants should form an intermediate compound by interconnection and structural rearrangement to facilitate the production of the final product. As an activated complex, it has more energy than the reactants and the products, thereby defining the overall rate of chemical reactions. The stored energy (ΔH^{++}) in this structure is consumed, while changing the length and angles of reactant bonds, thereby causing structural integrity and molecular rearrangement (Atkins *et al.*, 2014). ΔS^{++} is a symbol of environmental disorder and indicates an associative mechanism in which the reactants create an intermediate complex (Espenson, 1995). Higher values for ΔS^{++} show an increase in the possibility of creating activated complexes. In fact, the reaction is likely to occur by participating the fewer molecules of reactants. A lower ΔS^{++} value (more negative) and higher ΔH^{++} value are indicative of the high stability of lipid systems against temperature changes. According to Table 3, the highest and the lowest amount of ΔH^{++} among lipid systems in the non-inhibited condition was observed in olive and safflower oils, (79.7 vs. 71.2 kJ mol^{-1}), respectively. In the presence of curcumin (0.1%), however, maximum ΔH^{++} was observed in sesame oil (104.2 kJ mol^{-1}). The highest and lowest ΔH^{++}, considering all concentrations of curcumin, were observed in sesame and safflower oils, respectively. This can be attributed to a mismatch between the produced hydroperoxides and the function of inhibitory mechanisms of antioxidants (Toorani and Golmakani, 2021). As the precursor of oxidation products, the generated hydroperoxides in safflower oil were very unstable due to noticeable amounts of linoleic acid and the presence of allylic and bis-allylic carbons in its acyl chain. On the other hand, the presence of a methoxy group in the vicinity of the antioxidant agent (-OH), due to high electronegativity, decreased the rate of hydrogen release into the medium, thereby preventing quench free radicals (Barzegar, 2012). Thus, the tendency of curcumin to trap extremely active hydroperoxides is practically negligible.

The results indicated that adding curcumin to the oils increased ΔS^{++} in all samples. The highest and lowest values for ΔS^{++} were observed in sesame oil with 0.1% curcumin and in safflower oil with 0.02% curcumin, respectively. However, none of the parameters of the Eyring equation alone could predict the optimal performance of curcumin or any other antioxidant.

An analysis of the results showed that variations in the Eyring and the Arrhenius parameters were interdependent. Two appropriate linear models were obtained between the parameters of the Eyring and Arrhenius equations (Figure 2a and Figure 2b). These relationships were identical in the case of each oil with different unsaturation degrees. The obtained experimental models were quite similar to the equations reported by Farhoosh and Hoseini-yazdi (2014). Specifically, the slopes were identical, whereas the intercepts were slightly different. According to the transition state theory, the Eq.s (12) and (13) show the involved variables for converting the parameters of Eyring and Arrhenius models to each other.

$$A = \left(\frac{Tk_b}{h}\right) + exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \quad \text{Eq. (12)}$$

$$E_a \sim \Delta H^{++} \quad \text{Eq. (13)}$$

3.6. Curcumin performance based on Gibbs free energy

It is proven that ΔG^{++} is a suitable parameter for the purpose of comparing the oxidative stability of oils (Golmakani *et al.*, 2020b; Veloso *et al.*, 2020). Higher values for ΔG^{++} indicate higher stability of the lipid systems against oxidation reactions. In olive and sesame oils, the ΔG^{++} values showed that curcumin performance was better than tocopherol and BHT at 373 K (Table 3). However, higher temperatures slightly reduced the effectiveness of curcumin, since the ΔG^{++} was more affected by ΔS^{++} values than by ΔH^{++}. Accordingly, more negative ΔS^{++} values further increased the ΔG^{++}, which means an increase in oxidative stability. In safflower oil, curcumin was less effective than tocopherol and BHT in enhancing oxidative stability at 373 K.

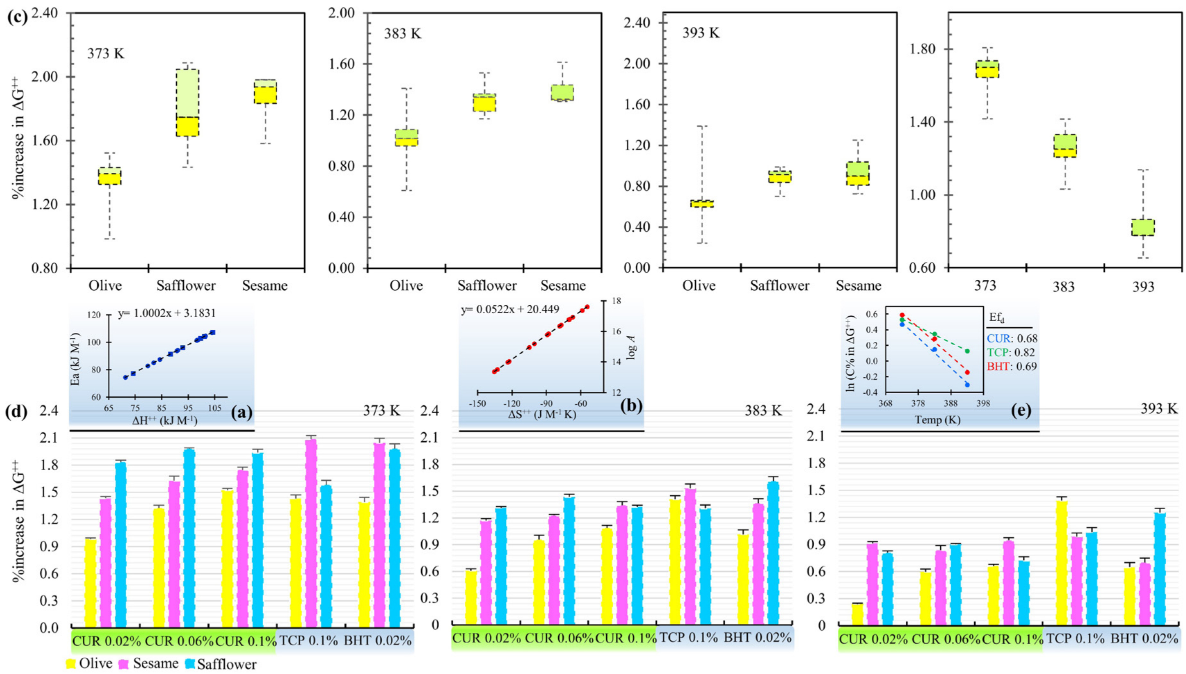

FIGURE 2. (a,b) Linear relationships between the changes in activation energy (E_a) and activation enthalpy (ΔH^{++}) or logarithm of frequency factor (log A) and activation entropy (ΔS^{++}) for the oxidation of olive, sesame, and safflower oils in the presence of various concentrations of curcumin, tocopherol, and butylated hydroxytoluene (BHT) at 373, 383, and 393 K. **(c)** Scattering curve of increase in Gibbs free energy (ΔG^{++}) for the oxidation of different vegetable oils in the presence of various concentrations of curcumin at 373, 383, and 393 K, and scattering curve of increase in Gibbs free energy (ΔG^{++}) for all oils at 373, 383, and 393 K. **(d)** Percentage of increase in ΔG^{++} compared to the control samples for the oxidation of different vegetable oils in the presence of various concentrations of curcumin (CUR), tocopherol (TCP), and butylated hydroxytoluene (BHT) at 373, 383, and 393 K. **(e)** A decrease in the effectiveness of antioxidants (Ef_d) under study due to temperature increase. All experiments were performed in triplicate. The results were checked using ANOVA and were compared by Duncan's test ($P < 0.05$).

Nonetheless, this trend changed at higher temperatures (383 and 393 K) and made curcumin show no significant difference in function compared to the other two antioxidants. While increasing the temperature enhances the effect of entropy coefficient in the equation of ΔG^{++} (Eq. (9)), changes in this index are further revealed at higher temperatures. In safflower oil, ΔH^{++} was much lower than in the other two oils, and the curcumin effect was more apparent in ΔS^{++}. It should be noted that the increase in ΔG^{++}, due to rising temperatures, arose from the endothermic nature of the active complex taking form during the oxidation reactions (Toorani and Golmakani, 2022).

The changes in ΔG^{++} at different temperatures indicated a lower dispersion of data pertaining to various lipid systems (Figure 2c). A lack of outlier data reflected the accuracy of the calculations and normality of the data. Also, the size of the box plots of the lipid systems was different, meaning that the growth coefficient in curcumin efficiency differed per oil when the curcumin concentration increased. Furthermore, the distribution of data indicated an increase in their dispersion, parallel to the increase in temperature. This can be attributed to a high degree of antioxidant susceptibility to heat, the decomposition caused thereof, and/or loss via volatilization, which is known as the carry-through property (Dugan and Kraybill, 1956).

Based on the percentage of increase in ΔG^{++}, the best performance of curcumin was observed in sesame oil, where its efficiency was higher than tocopherol but not significantly different from BHT (Figure 2d). Surprisingly, curcumin (0.02%) showed optimal performance, although the antioxidant activity of curcumin was less than that of the other two antioxidants in olive and safflower oils. The difference in the function of curcumin in various oils is likely due to a difference in the types of active radicals which were produced and of the hydroperoxides in these oils, which were not well adapted to the inhibitory mechanisms of this antioxidant. In all samples containing curcumin, the results showed that the percentage of growth in ΔG^{++} decreased in a consistent manner when the temperature increased. Also, a similar trend was observed in the case of tocopherol, but the decline in growth was lower in the presence of

BHT, possibly because of the high resistance of BHT to evaporation and thermal degradation. It is clear that an increase in temperature reduced the effectiveness of all antioxidants. The Ef_d of curcumin was 0.68 by an increase of 10 K (regardless of oil type and antioxidant concentration) (Figure 2e).

3.7. Relationship between IP and ΔG^{++}

As can be seen in Figure 3, power equations with high correlations ($R^2 > 0.99$) can properly describe the relationship between the values for IP and ΔG^{++}. The obtained nonlinear relationships indicated that the inhibitory power of phenolic antioxidants did not increase linearly by an increase in their concentration. This approach did not change fundamentally by increasing the temperature. On the other hand, the obtained exponential equations enable predictions of ΔG^{++} using simple data such as IP. It is clear that the estimation of ΔG^{++} at various temperatures can enable suitable assessments of the efficiency of antioxidants.

4. CONCLUSIONS

This research revealed that curcumin is substantially capable of antioxidant activity and can compete with synthetic antioxidants such as BHT. Also, curcumin showed different abilities to inhibit the oxidative reactions in different lipid systems. While curcumin showed appropriate antioxidant activity in lipid systems with higher unsaturation degrees, a maximum achievable efficiency was not observed. This result was attributed to a mismatch between the hydrogen donating mechanism of curcumin and the rate of hydroperoxide production by polyunsaturated systems, which were likely caused by the presence of methoxy groups in the benzene rings of the chemical structure of curcumin. Since the hydroxyl group in the phenolic ring is directly responsible for showing antioxidant activity, the presence of the methoxy group in its vicinity increases the energy required for separating hydrogen from the hydroxyl group. This phenomenon can be related to the high electronegativity of the methoxy group. As a result, the hydrogen donating mechanism was impaired in its function of quenching more reactive radicals produced by polyunsaturated fatty acids. Therefore, it is suggested that this natural antioxidant can be used in bulk oils with lower unsaturation degrees like olive or sesame oils in a concentration of 0.1% to achieve maximum antioxidant capacity. Furthermore, the results of the present study proved that curcumin is not thermally decomposed in the temperature range of 373-393 K, and that its antioxidant activity does not undergo fundamental changes. The results of this project do not necessarily suggest that synthetic antioxidants such as BHT can be generally replaced with curcumin, but that replacing a portion of synthetic antioxidants with this valuable herbal compound can be useful.

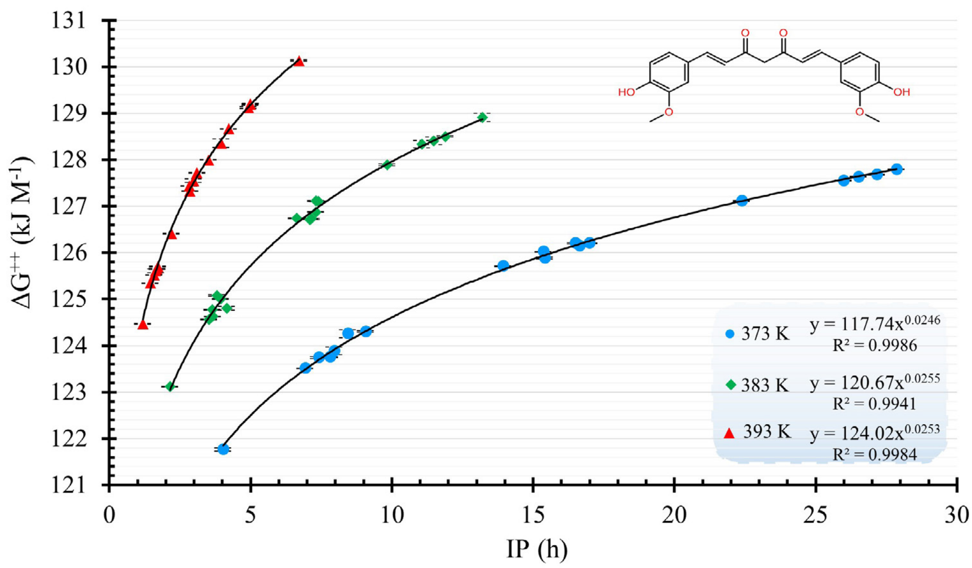

Figure 3. Relationship between Gibbs free energy (ΔG^{++}) of the activated complex formation and induction period (IP) for the oxidation of different vegetable oils in the presence of different concentrations of curcumin at 373, 383, and 393 K. All experiments were performed in triplicate. The results were checked using ANOVA and were compared by Duncan's test ($P < 0.05$).

5. ACKNOWLEDGMENTS

This work was financially supported by Shiraz University and Islamic Azad University.

6. REFERENCES

Aliabbasi N, Fathi M, Emam-Djomeh Z. 2021. Curcumin: A promising bioactive agent for application in food packaging systems. *J. Environment. Chem. Eng.* **9**, 105520. https://doi.org/10.1016/j.jece.2021.105520.

Atkins P, Atkins P W, Paula J. 2014. *Atkins' physical chemistry,* Oxford university press.

Barzegar A. 2012. The role of electron-transfer and H-atom donation on the superb antioxidant activity and free radical reaction of curcumin. *Food Chem.* **135**, 1369-1376. https://doi.org/10.1016/j.foodchem.2012.05.070.

Dugan J L, Kraybill H. 1956. Tocopherols as carry-through antioxidants. *J. Am. Oil Chem. Soc.* **33**, 527-528. https://doi.org/10.1007/BF02638480.

Espenson J H. 1995. *Chemical kinetics and reaction mechanisms,* Citeseer.

Farhoosh R, Hoseini-Yazdi S Z. 2014. Evolution of oxidative values during kinetic studies on olive oil oxidation in the Rancimat test. *J. Am. Oil Chem. Soc.* **91**, 281-293. https://doi.org/10.1007/s11746-013-2368-z.

Fennema O R. 1996. *Food chemistry,* CRC Press.

Firestone D. 2009. *Official methods and recommended practices of the AOCS,* AOCS.

Frankel E N. 2012. Chapter 9 - Antioxidants. In *Lipid Oxidation (Second Edition)*, Frankel, E. N. (ed.). Woodhead Publishing; 209-258.

Golmakani M-T, Keramat M, Zare Darniyani L. 2020a. A kinetic approach to the oxidation of linseed oil as influenced by fruit peel and seeds of pomegranate. *Eur. J. Lipid Sci. Technol.* **122**, 1900084. https://doi.org/10.1002/ejlt.201900084.

Golmakani M T, Soltani A, Hosseini S M H, Keramat M. 2020b. Improving the oxidation kinetics of linseed oil using the blending approach. *J. Food Process. Preserv.* **44**, e14964. https://doi.org/10.1111/jfpp.14964.

Hewlings S J, Kalman D S. 2017. Curcumin: A review of its effects on human health. *Foods* **6**, 92. https://doi.org/10.3390/foods6100092.

Hsieh R, Kinsella J. 1989. Oxidation of polyunsaturated fatty acids: mechanisms, products, and inhibition with emphasis on fish. *Adv. Food Nutr. Res.* **33**, 233-341. https://doi.org/10.1016/S1043-4526(08)60129-1.

Jokar M, Nateghi L, Golmakani M-T, Berenji SH. 2022. Effects of polyglycerol polyricinoleate on the antioxidant pathways of curcumin during the peroxidation of canola oil. *LWT*. **162,** 113455. https://doi.org/10.1016/j.lwt.2022.113455.

Kamal-Eldin A, Yanishlieva N. 2005. Kinetic analysis of lipid oxidation data. *Anal. lipid oxidat.* 234–263. https://doi.org/10.1201/9781439822395.ch10.

Keramat M, Golmakani M T, Toorani M R. 2021. Effect of Interfacial Activity of Eugenol and Eugenol Esters with Different Alkyl Chain Lengths on Inhibiting Sunflower Oil Oxidation. *Eur. J. Lipid Sci. Technol.* **123**, 2000367. https://doi.org/10.1002/ejlt.202000367.

Kumar A, Singh M, Singh P P, Singh S K, Raj P, Pandey K D. 2016. Antioxidant efficacy and curcumin content of turmeric (Curcuma-longa L.) flower. *Int. J. Current Pharmace. Res.* 112–114.

Laguerre M, Tenon M, Bily A, Birti´c S. (2020). Toward a spatiotemporal model of oxidation in lipid dispersions: A hypothesis-driven review. *Eur. J. Lipid Sci. Technol.* **122,** 1900209. https://doi.org/10.1002/ejlt.201900209.

Malik P, Singh M, Ameta R K. 2020. Advances in oxidative stability mechanisms of emulsions. (Chapter-9) In: Emulsion-based Encapsulation of Antioxidants, Editor: Mohammad Ali Aboudzadeh, *Springer Publications*. https://doi.org/10.1007/978-3-030-62052-3_9.

Malik P, Ameta R K, Singh M. 2016. Physicochemical study of curcumin in oil driven nanoemulsions with surfactants. *J. Mol. Liq.* **220,** 604–622. http://dx.doi.org/10.1016/j.molliq.2016.04.126.

Mandal D, Sarkar T, Chakraborty R. 2023. Critical Review on Nutritional, Bioactive, and Medicinal Potential of Spices and Herbs and Their Application in Food Fortification and Nanotechnology. *Biotechnol. Appl. Biochem.* **195**, 1319–1513. https://doi.org/10.1007/s12010-022-04132-y.

Sanchez-Moreno C, Larrauri J A, Saura-Calixto F. 1998. A procedure to measure the antiradical efficiency of polyphenols. *J. Sci. Food Agric.* **76**, 270–276. https://doi.org/10.1002/(SICI)1097-0010(199802)76:2<270::AIDJSFA945>3.0.CO;2-9.

Shahidi F. 2005. *Vol. 1: Edible oil and fat products: chemistry, properties, and health effects,* Hoboken: Wiley-Interscience.

Shim S D, Lee S J. 2011. Shelf-life prediction of perilla oil by considering the induction period of lipid oxidation. *Eur. J. Lipid Sci. Technol.* **113**, 904–909. https://doi.org/10.1002/ejlt.201000325.

Toorani M R, Farhoosh R, Golmakani M T, Sharif A. 2021. Thermal antioxidative kinetics of sesamol in triacylglycerols and fatty acid methyl esters of sesame, olive, and canola oils. *J. Am. Oil Chem. Soc.* **98**, 871–880. https://doi.org/10.1002/aocs.12520.

Toorani M R, Golmakani M-T. 2021. Investigating relationship between water production and interfacial activity of γ-oryzanol, ethyl ferulate, and ferulic acid during peroxidation of bulk oil. *Sci. Rep.* **11**, 1–14. https://doi.org/10.1038/s41598-021-96439-9.

Toorani M R, Golmakani M-T. 2022. Effect of triacylglycerol structure on the antioxidant activity of γ-oryzanol. *Food Chem.* **370**, 130974. https://doi.org/10.1016/j.foodchem.2021.130974.

Veloso A C, Rodrigues N, Ouarouer Y, Zaghdoudi K, Pereira J A, Peres A M. 2020. A Kinetic□Thermodynamic Study of the Effect of the Cultivar/Total Phenols on the Oxidative Stability of Olive Oils. *J. Am. Oil Chem. Soc.* **97**, 625–636. https://doi.org/10.1002/aocs.12351.

Waraho T, Mcclements D J, Decker E A. 2011. Impact of free fatty acid concentration and structure on lipid oxidation in oil-in-water emulsions, *Food Chem.* **129,** 854–859. https://doi.org/10.1016/j.foodchem.2011.05.034.

Zheng L, Jin J, Karrar E, Wang X, Jin Q. 2020. Activated complex theory is a classical theory suitable for food science with appropriate use. *Food Chem.* **332**, 127486. https://doi.org/10.1016/j.foodchem.2020.127486.