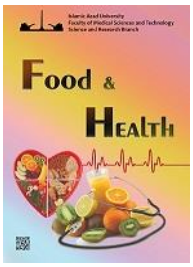

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Evaluation of Oxidative Kinetics of Sunflower Oil Containing Green Tea Extract as a Natural Antioxidant under Rancimat Conditions

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ABSTRACT

This study aimed to compare the antioxidant properties of sunflower oil containing green tea extract (GTE) with the synthetic antioxidant TBHQ by assessing their oxidative stability using the Rancimat method. After 90 days, sunflower oil samples with GTE exhibited enhanced resistance to oxidation, as evidenced by specific fatty acid values indicating saturation and effective prevention of oxidation. Although peroxide values did not differ significantly, suggesting maintained freshness, the PUFA/SFA ratio demonstrated stability in oil containing GTE. The reaction rate increased with temperature; however, oils containing GTE exhibited lower rates due to reduced oxidation, highlighting GTE's ability to enhance sunflower oil's oxidative resistance. The Rancimat method, conducted under isothermal conditions at 120°C and 130°C, enabled the calculation of kinetic parameters, including activation energies (Ea), activation enthalpies (ΔH^{++}), and activation entropies (ΔS^{++}). The Ea, ΔH^{++}, and ΔS^{++} values for sunflower oil with GTE and TBHQ were compared, with GTE exhibiting the highest oxidative resistance. The linear variation of the kinetic rate constant (k) with temperature, along with temperature coefficients (T_{Coff}) ranging from 6.17 to 8.34 ($\times 10^{-2}$ K^{-1}), provided valuable insights into the oxidative stabilities of the samples. The study underscores the synergistic effect of GTE as a natural antioxidant, demonstrating superior stability compared to TBHQ. The derived kinetic parameters offer qualitative consistency and facilitate the evaluation of oxidative stabilities of sunflower oil with GTE at elevated temperatures.

1. Introduction

Lipid oxidation is a significant factor contributing to food quality deterioration. This process can be categorized into autoxidation, photo-oxidation, and enzyme-catalyzed oxidation, each involving distinct reaction mechanisms and influencing factors (1-4). Autoxidation, the most prevalent form of lipid oxidation in food, progresses through initiation, propagation, and termination stages. In the initiation phase, free radicals abstract hydrogen atoms from the methylene group of polyunsaturated fatty acids (3, 4). Subsequently, fatty acid rearrangement stabilizes the fatty acid radical. In the presence of oxygen, these conjugated dienes transform into peroxyl (lipid) radicals with increased reactivity. Lipid oxidation is influenced by various internal and external factors (3, 4). Internally, the fatty acid profile, lipid class, and composition are crucial in determining lipid susceptibility to oxidation. Externally, temperature, light exposure, moisture levels, atmospheric oxygen, and the presence of metals, activators, and inhibitors significantly impact food lipid oxidation (3, 4). These external factors directly influence the quality of the final product and consumer acceptance (5). Oils with significant levels of unsaturated fatty acids are generally more susceptible to oxidation (6, 7). Antioxidants can combat oxidation through various mechanisms, such as reducing agents, free radical scavengers, or inactivators of pro-oxidants like metals (2- 4). Plant antioxidants include polyphenols (anthocyanins, flavonoids, flavones), carotenoids, tannins,

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lignin, phenolic acids, and vitamins. However, these antioxidants may be ineffective under adverse conditions such as high temperatures, extreme pH levels, or intense light exposure (2- 4). The antioxidant capacity of these compounds can be assessed directly by their ability to inhibit lipid oxidation in various food systems. Loi & Paciolla (8) conducted a comprehensive review of various methods to evaluate lipid oxidation and antioxidant capacity in food products, providing an in-depth analysis of their underlying principles and limitations. Several methods have been used to measure various oxidation products. Lipid hydroperoxide is one commonly measured parameter. Traditionally, iodometric titration has been the preferred method for measuring hydroperoxides as peroxide value (PV) (9). Natural antioxidants also provide nutritional value for edible oils and enhance their health status (10). Most natural antioxidants are derived from plant sources such as fruits, vegetables, herbs, and spices. These plant-based antioxidants primarily consist of polyphenols, carotenoids, and vitamins. Alpha-tocopherol, the major tocopherol found in many edible oils like almond, peanut, olive, wheat germ, cottonseed, and sunflower oils, has been effective in delaying oxidation in some oils (11, 12, 3, 4). However, it can act as a pro-oxidant if used in high concentrations. The content of antioxidants decreases during the storage period until it is exhausted, and the food matrix is oxidized (13). Green tea extracts (GTE) are obtained from green tea leaves through various extraction methods (14, 2). The antioxidant activity of GTE is attributed to its content of catechins, which can prevent oxidation by chelating metal ions or donating hydrogen atoms to free radicals, thereby interrupting or slowing down the free radical chain reaction (15, 16, 2). The determination of various kinetic parameters related to the oxidation of vegetable oils can be performed using the Rancimat test. These kinetic data can distinguish the origin of each oil or characterize the differences and similarities between various oils. This information is highly valuable for predicting the oxidative stability of vegetable oils under different heat processing, storage, and distribution conditions (17). While the Rancimat test provides a convenient, rapid, and reproducible method for evaluating oxidative kinetics, this subject has received limited attention, and data on the oxidative degradation kinetics of vegetable oils under Rancimat test conditions are scarce. Therefore, the objective of this work was to determine the relative oxidative stabilities of sunflower oil samples containing GTE as a natural antioxidant, TBHQ as a synthetic antioxidant, and control without antioxidants, as well as to investigate the kinetic parameters of their oxidation under Rancimat test conditions.

2. Materials and methods

2.1. Materials

Refined primary sunflower oil samples were obtained from the Behshahr company (Iran). The oil samples were stored at room temperature until testing. The oil surface was exposed to nitrogen gas at a pressure of 2 bar (2.03944 kg/cm^2). Green tea extract (GTE) in powder form was purchased from Kemin CO. (Belgium). Glacial acetic acid, isooctane, sodium thiosulfate, potassium iodide, sodium sulfate, ethanol, phenolphthalein, and tertiary butylhydroquinone (TBHQ) were purchased from Merck (Germany). All other reagents and chemicals used in this study were of analytical grade and purchased from Sigma-Aldrich (St. Louis, Missouri, United States).

2.2. Preparation of the oil samples

Refined sunflower oils without antioxidants were purchased, and the control sample (T1) contained no antioxidants. Sunflower oil samples treated with 400 ppm GTE (T2) and 75 ppm TBHQ (T3) were prepared. After preparation, the oil samples were packed and labeled in closed containers and evaluated during 90 days of storage at room temperature in a dark place. The kinetic model for the oxidative stability of samples was obtained. All samples were prepared in triplicate, and all measurements were repeated three times for each test.

2.3. Peroxide value (PV)

The PV, which measures primary oxidation products in the oil samples, was determined according to the ISO 3960 (18) method. Determination was conducted by titration of the oil sample dissolved in a solvent mixture containing isooctane: acetic acid (3:2), adding KIO_3 saturated solution to the oil, and titrating with 0.01 N $Na_2S_2O_3$ using starch as an indicator. The PV was calculated using Eq (1):

$$PV = (V2-V1) \times N \times 1000 / m \qquad (1)$$

Where, PV is the peroxide value (meq O_2/kg oil), V2 is the volume of $Na_2S_2O_3$ (mL), V1 is the volume of blank (mL), N is the normality of $Na_2S_2O_3$ (0.01 N), and m is the quantity of oil (g).

2.4. Rancimat test

The oxidative stability of the samples (including sunflower oil samples without antioxidants, with 75 ppm TBHQ, and with 400 ppm GTE) was assessed using a Rancimat apparatus based on the Iranian National Standard (INSO) 3734 (19). The gas diaphragm pump was connected, ensuring a precise flow rate of 20 liters per hour, and the thermal mold temperature was set at 120°C and 130°C. A model 743 Metrohm Rancimat (Herisau, Switzerland) was utilized. Three grams of oil samples were weighed in the test tubes to create air-saturated conditions in the samples, with airflow rates of 20 L/h. Samples were arranged randomly in the heating block for every determination (20). The glassware was thoroughly cleaned between runs to remove any contaminants that might catalyze peroxidation. The tubes were cleaned by boiling for one hour with 2% sodium hydroxide solution, cooled, and then soaked in concentrated hydrochloric acid (21). The clean glassware was fully dried in an oven after rinsing the tubes with distilled water three times to remove the acid.

2.5. Fatty acid profile analysis

The fatty acid composition was analyzed using gas chromatography (GC) equipped with a flame ionization detector (FID) and a CPSIL-88 column (100 m x 250 µm x 0.25 µm), following INSO 13126-2 (22) and 13126-4 (23) protocols with minor modifications. Fatty acid methyl esters (FAMEs) in oil samples with or without antioxidants were determined according to INSO 13126-4. A 2 N potassium hydroxide solution in methanol was prepared. Two grams of each oil sample were weighed in a centrifuge tube, combined with 2 mL of hexane, and vortexed for 2 seconds. Subsequently, 0.2 mL of 2 N potassium hydroxide solution was added, and the tube was vigorously shaken for 60 seconds. The mixture was then centrifuged at 2000 rpm for 5 minutes. The supernatant was separated and injected into the GC-FID. The injection volume was 1 µL with a split ratio of 1:100. Detector and injector temperatures were set at 280°C and 250°C, respectively. The temperature program was as follows: initial temperature of 165°C for 5 minutes, followed by an increase to 210°C at a rate of 5°C/min, and maintained at 210°C for 15 minutes. Fatty acids were identified based on the retention times of standard methyl ester fatty acids (C14:0 to C22:0) and expressed as grams per 100 grams of total acid.

2.6. Evaluation of oxidation kinetic parameters in sunflower oil samples

Oxidation was studied at 120°C and 130°C with a continuous airflow of 20 L/h using a Rancimat device to obtain and calculate kinetic parameters. The effect of temperature (T) on the specific reaction rate (K) was determined using the Arrhenius method and van 't Hoff equation. The specific reaction rate was calculated using the following equation:

$$Ln(K) = Ln(A) - (Ea/RT) \quad (2)$$

Where, K is the reaction rate constant or reciprocal OSI (h^-1), A is the frequency factor (h^{-1}), Ea is the activation energy (kJ/mol), and R is the molar gas constant (8.3443 kJ/mol·K).

Activation energy represents the minimum energy required for a molecule to react. The temperature coefficient (T_{Coeff}) was calculated from the slope of the regression line between Ln(K) and absolute temperature (T) using the following equations:

$$Ln(K) = a(T) + b \quad (3)$$

Where, a and b are equation parameters.

$$Ln(K) = Ln(K_b/h) + (\Delta S^{++}/R) - (\Delta H^{++}/RT) + Ln(T) \quad (4)$$

Where, ΔH^{++} is enthalpy, h is Planck's constant, K_b is Boltzmann's constant, and ΔS^{++} is entropy. The K value was obtained from the reciprocal of the induction period (h^{-1}).

2.7. Statistical analysis

Experiments were performed in triplicate to ensure accuracy and reliability. Statistical analysis was conducted using one-way ANOVA with SPSS software v.26 (IBM Analytics, Armonk, NY, USA). Results are presented as mean values ± standard deviation (SD). Differences were considered statistically significant at $p \leq 0.05$.

3. Results and Discussion

The fatty acid analysis results for all samples are presented in Table 1. The fatty acid profiles of sunflower oil containing GTE and TBHQ were similar to those without antioxidants. All samples' fatty acid profiles were within the standard range specified by INSO 1300 (24). Consequently, it can be inferred that adding GTE did not significantly impact the fatty acid profiles in sunflower oil. However, the oil samples containing GTE and TBHQ exhibited more excellent stability regarding fatty acid changes than those without antioxidants. After 90 days of storage, the amounts of saturated fatty acids (SFA), monounsaturated fatty acids (MUFA), polyunsaturated fatty acids (PUFA), and polyunsaturated fatty acid ratio (PUFA/SFA) in sunflower oil containing GTE were 14.86%, 29.18%, 55.89%, and 3.76%, respectively. These values indicated the oil's saturation, attributable to using oxidation-preventing compounds during storage. Additionally, the peroxide value (PV) indicates the freshness and absence of oxidative activity in vegetable oils. The PV of sunflower oil containing GTE or TBHQ did not differ significantly from sunflower oil without antioxidants. No statistically significant differences were observed in all samples' MUFA and PUFA contents. The ratio of PUFA to SFA is commonly employed to indicate the degree of polyunsaturation in samples (25, 26). This ratio directly correlates with the oil's susceptibility to autoxidation (27). The PUFA/SFA ratio was more consistent across samples, with no statistically significant differences observed. The fatty acid profile of sunflower oil containing GTE was crucial as it demonstrated the oil's stability, resistance to oxidation, and adherence to standard fatty acid ranges, highlighting the potential benefits of using GTE as an antioxidant in sunflower oil products. Table 1 presents the constant values of the reaction speed in different samples at various temperatures. It was observed that, with increasing temperature, the constant reaction rate for all samples increased significantly ($p \leq 0.05$). Lower levels of constant reaction rate in antioxidant-containing oils, particularly the oil containing GTE, are attributed to the presence of antioxidants in the oil, resulting in decreased lipid oxidation at higher temperatures. The PV of all samples was less than 1.5 meq O_2/kg oil, which was lower than the specified value in INSO 1300 (5 meq O_2/kg oil). On the first day of storage, all samples were unoxidized and of high quality, although statistically significant differences were observed (Table 1). The PV, resistance to oxidation, and fatty acid profile are interrelated factors determining sunflower oil samples' oxidative stability and quality. GTE's presence can enhance sunflower oil's oxidative stability by influencing its PV and fatty acid composition, ultimately contributing to improved resistance to oxidation. The k values for lipid oxidation of each sample at each temperature are presented in Table 2. Analysis of lipid oxidation rates in relation to temperature revealed a direct correlation, with increased temperature leading to higher

Table 1. Fatty acids composition of the samples.

Fatty acids (%)	Samples					
	Oil with GTE	Oil with TBHQ	Control	Oil with GTE	Oil with TBHQ	Control
	Day 1			Day 90		
14:0	0.07±0.01^{a}	0.07±0.01^{a}	0.07±0.01^{a}	0.07±0.01^{a}	0.07±0.01^{a}	0.07±0.01^{a}
16:0	6.79±0.24^{a}	6.75±0.23^{b}	6.77±0.23^{c}	6.74±0.22^{d}	6.77±0.21^{c}	6.77±0.20^{c}
16:1	0.50±0.28^{a}	0.51±0.28^{b}	0.52±0.27^{c}	0.52±0.25^{c}	0.50±0.27^{a}	0.53±0.26^{d}
18:0	6.46±-0.07^{a}	6.45±0.08^{b}	6.50±0.07^{c}	6.44±-0.06^{d}	6.46±0.05^{a}	6.49±0.05^{a}
18:1	28.43±0.30^{a}	28.46±0.31^{b}	28.45±0.30^{b}	28.40±0.25^{c}	28.45±0.26^{d}	28.44±0.22^{d}
18:2	55.44±0.07^{a}	55.45±0.07^{a}	55.41±0.07^{a}	55.46±0.06^{b}	55.44±0.06^{b}	55.40±0.05^{c}
18:3	0.41±0.12^{a}	0.42±0.11^{b}	0.41±0.12^{a}	0.43±0.10^{c}	0.42±0.10^{b}	0.41±0.11^{a}
20:0	0.42±0.09^{a}	0.43±0.10^{b}	0.44±0.09^{c}	0.44±0.08^{c}	0.42±0.08^{a}	0.43±0.07^{d}
20:1	0.24±0.10^{a}	0.24±0.10^{a}	0.24±0.10^{a}	0.25±0.09^{b}	0.24±0.08^{a}	0.24±0.10^{a}
22:0	1.23±0.11^{a}	1.22±0.11^{a}	1.20±0.11^{b}	1.24±0.10^{c}	1.22±0.10^{a}	1.21±0.10^{d}
22:1	0.01±0.001^{c}	0.01±0.001^{c}	0.01±0.001^{c}	0.01±0.001^{c}	0.01±0.001^{c}	0.01±0.001^{c}
SFA	14.90	14.85	14.91	14.86	14.87	14.90
MUFA	29.18	29.22	29.22	29.18	29.20	29.22
PUFA	55.85	55.87	55.82	55.89	55.86	55.81
PUFA/SFA	3.74	3.76	3.74	3.76	3.75	3.74
PV (meq O_2/kg oil)	0.88±0.10^{a}	0.99±0.10^{b}	1.09±0.12^{c}	1.48±0.16^{a}	1.96±0.14^{b}	3.44±0.17^{c}

Means within a row with the same lowercase letters are not significantly different at $p<0.05$. SFA, Saturated fatty acid; MUFA, monounsaturated fatty acid; PUFA, polyunsaturated fatty acid. Unsimilar lowercase letters in each row indicate a significant difference ($0.05\geq p$).

oxidation rates. The semi-logarithmic relationship between k and T values in all samples demonstrated a linear dependency with a high correlation of determination (R^2 >0.99). Notably, predicting kinetic rate constants at low temperatures based on accelerated oxidation tests has certain limitations.

Table 2. Constant reaction rate values ($k\times10^3[h^{-1}]$) of samples at different temperatures.

Samples	Temperature (°C)	
	120	130
Control	80.37±-1.89^{Ad}	164.30±-0.48^{Ac}
Oil with TBHQ	79.21±-1.59^{Bd}	159.65±-0.64^{Bc}
Oil with GTE	74.57±-1.07^{Cd}	145.21±-0.71^{Cc}

Means within a column with the same lowercase letters are not significantly different at $p<0.05$; means within a row with the same uppercase letters are not significantly different at $p<0.05$.

The rate constant (k) value at lower temperatures can be influenced by additional factors that may not be fully captured in the Rancimat test. Lipid oxidation at low and high temperatures potentially involves different steps or reaction pathways, depending on the reactivity of metal ions and the effectiveness of antioxidants under varying temperature conditions (28, 29, 30). Fig.1 depicts the logarithmic changes in the constant reaction rate as a function of temperature, exhibiting a linear relationship with a high correlation between variables. The T_{Coff} calculated from Linear Functions in Fig. 1 for samples ranged from 6.17 to 8.34. These values, representing statistically significant differences, could be interpreted as quantities representative of the studied samples. The temperature coefficient of the sunflower oil containing GTE was the highest, while the antioxidant-free oil had the lowest temperature coefficient, indicating differing oxidative stabilities. For comparison, the reported temperature coefficient values for other edible oils were: canola oil (0.072), soybean oil (0.074), sunflower oil (0.0726), corn oil (0.0705), and olive oil (0.0695) (k^{-1}). The higher temperature coefficient of the sunflower oil containing GTE suggested improved oxidative stability compared to the other oils mentioned. This linear relationship between the logarithm of the constant reaction rate and temperature and the differences in temperature coefficients provides insights into the kinetic behavior and oxidative stability of the oil samples under varying thermal conditions (17, 21, 25).

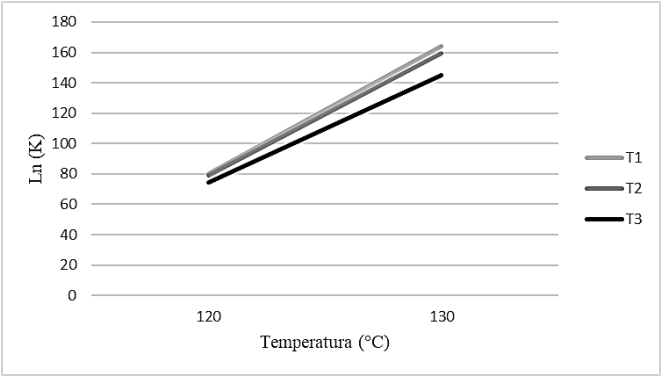

Fig. 1. Semi-logarithmic relation between Constant change rate constant and temperature values for lipid oxidation of samples. T1: Refined sunflower oil without antioxidant, T2: Refined sunflower oil + 75 ppm TBHQ, T3: Refined sunflower oil + 400 ppm GTE.

Table 3 shows the temperature coefficient values and regression functions of different samples. Regression parameters, frequency factor, and activation energy to evaluate the formation of secondary oxidation products (volatile acids, primarily formic acid and smaller amounts of acetic acid, propionic, and other acids) are calculated under the Rancimat test (31).

Table 3. Temperature coefficient and regression functions.

Samples	Ln(K)=a(1/T) +b	R^2	$T_{coff}(\times10^{-2})$ [k^{-1}]
Control	y=0.0635x-24.25	0.9935	6.17
Oil with TBHQ	y=0.0714x-20.74	0.9966	8.31
Oil with GTE	y=0.0728x-20.39	0.9977	8.34

The values of the kinetic parameters for different samples are reported in Table 4. The lowest activation energy was observed in the antioxidant-free oil, while the highest was in the oil containing the free extract of green tea. Regarding the specific constant reaction of the samples, the oil containing

free GTE and antioxidant-free oil exhibited the highest and lowest values, respectively. Furthermore, the GTE oil had the highest enthalpy and entropy values. However, its enthalpy content did not differ significantly from the oil containing the free extract of green tea. These results indicate that the amount and type of volatile acids under Rancimat conditions depend on the concentration of antioxidant compounds that affect oil stability (17, 21, 25). The oils' degree of unsaturation and oxidation stability influence the activation energy. High enthalpy and entropy levels indicate a more significant energy requirement for free radical production at initiating chain reactions and oxidation, which were more pronounced in the antioxidant-containing oil. Rodrigues et al. (32) reported that using antioxidant compounds led to increased activation energy, which aligns with our findings. The kinetic parameters obtained for lipid oxidation of different vegetable oils under Rancimat test conditions varied significantly. This suggests that the production of volatile acids under these test conditions depends on the specific oil source, which affects the assessment of the relative oxidative stability of vegetable oils. The degree of polyunsaturation in vegetable oils influences the activation energy (Ea) value. Previous studies have shown that a higher content of PUFA, such as linoleic and linolenic acids, tends to lower the Ea value for lipid oxidation. Conversely, a higher oleic acid content would increase the Ea value, indicating improved resistance to lipid oxidation. Similarly, increased SFA content has enhanced resistance to lipid oxidation, resulting in a higher Ea value. This is attributed to saturated fatty acids being less susceptible to oxidation than their unsaturated counterparts. These findings highlight the importance of considering the fatty acid composition of vegetable oils when evaluating their oxidative stability and kinetic parameters. The degree of polyunsaturation and the balance between unsaturated and saturated fatty acids can significantly influence the activation energy and, consequently, the overall oxidative resistance of the oils (32). These factors contribute to postponing the initiation of the initial oxidation process, during which bond breakage occurs to generate primary oxidation products. The fatty acid composition of the vegetable oils, as shown in Table 1, partially elucidates the patterns observed in the different activation energies presented in Table 3.

Table 4. Various parameters related to kinetic in samples.

Parameters	Samples		
	Control	Oil with TBHQ	Oil with GTE
Ln(K)=a(1/T) +b			
A	-8.911±0.01	-9.965±0.01	-11.520±0.01
B		31.032±0.28	35.266±0.26
R^2		0.9980	0.9987
Ea(K/T) =A(1/T)		82.852 [a]	95.871 [b]
A[h^{-1}]	1.719×10^{12}	2.999×10^{13}	2.069×10^{15}
Ln(K/T) =a(1/T)			
A	-8.523±65.05	-9.577±74.01	-11.132±79.01
B	21.213±0.31	24.071±0.30	28.306±0.31
R^2	0.9981	0.9978	0.9973
ΔH^{++} [kJ.mol^{-1}]	60.864[a]	75.626[b]	80.928 [c]
ΔS^{++} [J.mol^{-1} K^{-1}]	-21.201[a]	-42.586 [b]	-54.550 [c]

Means within a row with the same lowercase letters are not significantly different at $p<0.05$.

The high correlation coefficient ($R^2\geq0.99$) indicates adequate fit and effective characterization of the temperature dependency of lipid oxidation through the activated complex theory. The ΔH^{++} and ΔS^{++} values for the vegetable oils studied ranged from 83.64 (KJ/mol), and –116.66 (J/mol. K^{-1}) for olive oil to 89.20 (kJ/mol) and 2104.35 (J/mol. K^{-1}) for soybean oil, respectively (33). In this study, the ΔH^{++} and ΔS^{++} values were for control sample 70.864 (KJ/mol) and –21.201 (J/mol. K-1), for sunflower oil with TBHQ, 75.626 (KJ/mol) and -42.586 (J/mol.K^{-1}), and for sunflower oil with green tea extract 80.928 (kJ/mol) and -54.550 (J/mol.K^{-1}). Negative ΔS^{++} values indicate that the active complex was more ordered than the reactant molecule (17). A significant difference in entropy values was observed between sunflower oil without antioxidants and sunflower oil with natural and synthetic antioxidants. In comparable studies on the oxidation stability of sunflower and soybean oils using the Rancimat test, the enthalpy and entropy values, respectively, 84 (KJ/mol) and-8.42 (J/mol. K^{-1}) and 9.74 and 2.70 were reported (33).

4. Conclusions

The results demonstrated that an increase in temperature led to a consistent increase in the reaction rate across all samples, with this increase occurring faster in the control sample. A logarithmic relationship was observed between the reaction rate constant and temperature. Analysis of the oxidation process revealed an increase in oxidation rate corresponding to temperature elevation. The activation enthalpy, activation energy, and entropy were significantly influenced by the type of antioxidants, particularly with the addition of natural antioxidants. These findings provide insights into the thermal behavior and oxidative stability of sunflower oil samples under various conditions and highlight the potential of natural antioxidants, such as green tea extract, in modulating the oxidation kinetics of vegetable oils.

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