

Kinetic Study of the Oxidative Degradation of Choibá Oil (*Dipteryx oleifera* Benth.) with Addition of Rosemary Extract (*Rosmarinus officinalis* L.)

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Abstract

Choibá (*Dipteryx oleifera* Benth.) is a promising source of edible oil with high nutritional quality and a significant content of oleic acid (52% - 54%). To promote Choibá as source of edible oil is necessary to ensure its stability along the time of production, distribution and storage. Loss of nutritional and organoleptic quality in lipids is mainly due to lipid peroxidation reactions. The aim of this research was to evaluate the oxidative stability of Choibá oil at 100°C ± 1°C with aeration (1150 mL air/min) supplemented with rosemary extract (*Rosmarinus officinalis* L.), at 1000 mg/L (RE1000) and 1500 mg/L (RE1500), and with BHT (200 mg/L) and from this results to evaluate the degradation kinetics and shelf-life of Choibá oil at 35°C, 45°C and 55°C without addition of antioxidants (Control) and with addition of best concentration of rosemary extract obtained from previous study. Progress in oil oxidation was measured through the extent of oxidation products: peroxide value (PV) and thiobarbituric acid reactive substances (TBARS). Results revealed that the addition of rosemary extract at 1500 mg/L significantly reduced de formation of hydroperoxides (PV), more than BHT. Through correlations between concentrations of antioxidant (including control without antioxidant) with peroxide values, the kinetics of degradation and shelf-life of Choibá oil with predictive models are evaluated in real time and accelerated (35°C, 45°C and 55°C) using the Arrhenius equation. In addition, the oxidation reactions of this oil follow a first order kinetic model for PV and zero order kinetic model for TBARS. The rate of formation of PV was dependent on the storage temperature, according to the Arrhenius equation with the activation energy of 4611.5071 J/mol for Control and 7409.5771 J/mol for RE1500 treatment. The result of

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TBARS didn't adjust to Arrhenius model, thus measurement of malondialdehyde (MDA) wasn't a useful parameter for shelf-life determination of Choibá oil.

Keywords

***Dipteryx oleifera*, Oxidative Stability, Shelf-Life, *Rosmarinus officinalis*, Lipid Peroxidation, Arrhenius**

1. Introduction

The increased demand for health food in recent decades, has promoted the study of new sources of vegetable oils with considerable content of unsaturated fatty acids, as oleic and linoleic. These fatty acids have been attributed health benefits, specifically protective effect against cardiovascular disease by lowering LDL cholesterol and triglycerides [1] [2]; further contribute to decreased risk of breast and colon cancer [3] [4].

Choibá oil (*Dipteryx oleifera* Benth.) with an oleic acid content of about 52% is an important source of omega 9 (ω 9) with high nutritional quality [5]. However, to promote the consumption of this vegetable oil is necessary to ensure the quality of the product throughout the marketing process. Therefore, it is important to note the various reactions that occur during storage and can lead to loss of quality of fats and oils. Quality is a complex and dynamic attribute of food, which directly influences the degree of consumer acceptance. Foods with high lipid content are susceptible to oxidation reactions of unsaturated fatty acids and determine the deterioration of lipids during the stages of production, storage and distribution [6] [7].

Autoxidation, which lead to loss of nutritional value, is the main cause of deterioration in edible fats and oils [7]. It consists in a series of chain reactions, that not only generate the appearance of unpleasant odors and flavors, but it also leads to accumulation of compounds that can be harmful to human health [8] [9]. To retard the rancidity process, the lipids are supplemented with synthetic antioxidants such as Butylated Hydroxytoluene (BHT) and Butylated Hydroxyanisole (BHA); this compounds have the capacity to act through the stabilization of free radicals formed during the autoxidation, but because of their recognized adverse health effects [10] [11], they have begun to be substituted with antioxidant compounds from natural sources such as plant extracts and spices [12] [13].

Several studies have evaluated the effect of the addition of rosemary extracts (*Rosmarinus officinalis* L.) on the oxidative stability of vegetable oils, finding similar results or better than commonly used synthetic antioxidants, especially at elevated temperatures such as those reached during frying processes [14]-[16]. Other advantage of natural antioxidants is their relative security. In October of 2010, Rosemary extract was classified as food additive (as antioxidant) by European Commission Directive 2010/69/EU [15].

Monitoring the appearance of intermediate and products of oxidation, is a quantifiable index of the fast deterioration of fats and oils and can monitor the shelf-life of fats and oils during storage [17]. Therefore, from experimental data it is possible to determine the kinetic equations describing the behavior of oil deterioration and different Arrhenius model parameters evaluating the effect of temperature on the rate of deterioration. The extrapolation of the descriptors together allows determining the shelf-life of the oil at any temperature [7] [18].

Lipid peroxidation reactions occur slowly at room temperature; then, usually accelerated stability test that establish shelf-life in less time are used. Temperature is the commonly used parameter to accelerate lipid oxidation because the reaction rate increases exponentially [7] [8]. Different methods have been implemented for determining the shelf-life of lipids, which are induced or accelerated tests such as AOM (Active Oxygen Method) test oven (Oven Test), Oxygen Pump, Rancimat, among others. These methods provide an estimate of the oxidative stability, but not necessarily have a high correlation with the shelf-life of the product [12] and may lead to underestimation or over-estimation of the time stability of oils [19]. Furthermore, the mechanism of oxidation of edible oils changes when the temperature rises above 60°C, whereby the application of stability studies under controlled conditions employing temperatures between 40°C and 60°C is recommended, and the extrapolation of the results to ambient conditions may provide acceptable results to some extent [7].

In addition, there are few studies on Choibá oil [5]; therefore, the aim of this study was to evaluate the kinetics of degradation Choibá oil, supplemented with rosemary extract at a concentration of 1500 mg/L and un-supplemented by linearized Arrhenius model.

2. Materials and Methods

2.1. Preparation of Rosemary Extract (*Rosmarinus officinalis* L.)

Dried rosemary leaves cultivated in the Region of Tolima (Colombia), were sprayed in industrial food processor (Ika-Werk®); then, they were subjected to extraction by percolation using ethanol as solvent, in a relation 1: 5. The extract was filtered through Whatman paper (GF/A, 110 mm) and the percolate was vacuum distilled at 40°C in a rotary evaporator (Heidolph®). Finally, the extract was dried in a vacuum oven at 30°C for 2 hours to remove any residual solvent. The extract obtained was dark green, which was dissolved in glycerol, and stored under refrigeration at 4°C prior to use.

2.2. Antioxidant Capacity, Carnosic Acid and Rosmarinic Acid Content of Rosemary Extract

To determine the antioxidant activity, and carnosic acid (AC) and rosmarinic acid (AR) content of rosemary extract, 50 µL taken from the original sample and dissolved in 950 µL of ethanol. From this solution, it was prepared the dilutions for the different assays.

2.2.1. Oxygen Radical Absorbance Capacity (ORAC) Assay

The ORAC assay was determined using the following methodology: 3 ml was prepared from the following solution: 21 µl of a 10 µM solution of fluorescein, 2899 µl of 75 mM phosphate buffer (pH 7.4), 50 µl of 600 mM 2,2'-Azobis(2-amidinopropane) dihydrochloride (AAPH) and 30 µl of extract. Fluorescence was recorded on a Perkin Elmer LS45 spectrofluorometer with a thermostated multicell. The ORAC value µmol Trolox/g was calculated by a calibration curve using different concentrations of Trolox® [16] [20].

2.2.2. Evaluation of Free Radical-Scavenging Activity by DPPH Assay

A method improved by Rojano *et al.* (2008) was used. This procedure was performed using 10 µL of the extract and 90 µL of the methanolic DPPH-solution (20 mg/L). After 30 minutes of reaction at room temperature in the dark, the absorbance was read at 517 nm. For each studied sample, the percentage inhibition of the radical was calculated and the results were expressed as TEAC values (Trolox Equivalent Antioxidant Capacity) by the construction of a standard curve, using several concentrations of the TROLOX® antioxidant [20] [21].

2.2.3. Total Phenolic Content TPC

The concentration of total phenols in the extracts was determined using the Folin-Ciocalteu reagent and external calibration with gallic acid [22]. Briefly, 50 µL of extract solution, 425 µL distilled water and 125 µL of Folin-Ciocalteu reagent was added and mixed thoroughly. After 6 minutes, 400 µL of 7% NaCO₂ was added and then the mixture was allowed to stand for 1 hour at room temperature. The absorbance was measured at 760 nm using a Thermo Scientific, Multiskan Spectrum spectrophotometer. The TPC was determined as mg of gallic acid equivalent (GAE) using an equation obtained from the external galic acid calibration curve.

2.2.4. Determination of Carnosic and Rosmarinic Acid Content

Preliminary studies in different rosemary extracts have reported carnosic acid and rosmarinic acid as compounds with high antioxidant activity [13]-[16]. The content of carnosic acid (CA) and rosmarinic (AR) of the rosemary extract was determined by HPLC analysis according to the modified protocol of Martinez *et al.* (2013) [23]. The ethanol extract of rosemary was filtered through a 0.45 µm pore size and dilutions were made in HPLC grade ethanol before injection to the chromatograph. A liquid chromatograph (Shimadzu LC-20AD), equipped with a SIL-20A auto injector/HT, a communication module and CBM-20A (PDA) SPD-M20A calibrated at 284 nm was used. Quantification of both acids was performed on a LiChrospher® 100RP-18 column (5 M) 250 × 4. The mobile phase was program as a linear gradient from 95% A (water 840 mL, 150 mL of acetonitrile and 8.5 ml of acetic acid) and 5% B (methanol) to 100% B in 40 minutes with a flow of 0.6 ml/min and an injection volume of 20 µL. The identification of both acids was performed by comparison of retention times with those of pure standards.

2.3. Extraction of Choibá Oil (*Dipteryx oleifera* Benth.)

Choibá's seeds (*Dipteryx oleifera* Benth.) were obtained from fallen fruit and collected from the ground at ran-

dom, in the Region of Antioquia (Colombia), ensuring that they were in good shape, without any physiological damage. Once the fruits were selected, they were stored in plastic bags and taken to the laboratory of Food Science at Universidad Nacional of Colombia in Medellin, where almonds were subsequently dried to proceed with the extraction of oil.

Oil extraction was performed according to the method reported by Thiex *et al.* [24], the technique used for extracting oils from grains and seeds employed the Soxhlet apparatus and volatile solvents to extract the fat present in the seeds. The solvent used was hexane due to its good yields in the extraction of vegetable seed oils [25].

2.4. Fatty Acid Composition of Choibá Oil (*Dipteryx oleifera* Benth.)

To determine the fatty acid profile of Choibá oil a gas chromatograph Agilent 6890N GC coupled to an Agilent 5973N MS selective detector and equipped with a split/splitless injector was used. The injector temperature was $300^{\circ}\text{C} \pm 1^{\circ}\text{C}$. Samples previously derivatized to facilitate their detection as methyl esters (FAME) were automatically injected in the splitless mode. An HP-5 MS (5% phenylmethylsiloxane) 30 m, 0.25 mm column 0.25 μm a film thickness and a maximum temperature of 325°C was used. To identify the type of fatty acid present 98 base NIST data was used [5].

2.5. Oxidative Stability and Shelf-Life Determination of Choibá Oil (*Dipteryx oleifera* Benth.)

Oxidative stability: In this case was used the Active Oxygen Method (AOM). To 30 mL of Choibá oil was added rosemary extract until a final concentration of 1000 mg/L (RE1000) and 1500 mg/L (RE1500) in the oil. As positive control Butylated Hydroxytoluene (BHT) at 200 mg/L and as negative control (Control) oil without addition of extract were used. Progress in oil oxidation, at $100^{\circ}\text{C} \pm 1^{\circ}\text{C}$ with aeration (1150 mL air/min) was evaluated through the measurement of peroxide value (PV).

Shelf-life determination: In this stage was chosen the best concentration of rosemary extract for shelf-life determination of Choibá oil. These values are incorporated in an experimental design (multilevel design with 3 experimental factors and 2 blocks, which furnish protection against the effect of hidden variables).

To 30 mL of Choibá oil was added rosemary extract until a final concentration of 1500 mg/L in the oil (RE1500). As negative control was used Choibá oil without addition of extract (Control). The samples were stored in dark bottles at $35^{\circ}\text{C} \pm 1^{\circ}\text{C}$, $45^{\circ}\text{C} \pm 1^{\circ}\text{C}$ y $55^{\circ}\text{C} \pm 1^{\circ}\text{C}$ in accelerated chambers with 15% to 95% RH and temperature control since 10°C to $60^{\circ}\text{C} \pm 2^{\circ}\text{C}$ (humidification by evaporation, Platinum sensor 100 (dry bulb) and dehumidification by condensation).

In order to calculate the parameters of the kinetic model of oil deterioration and the Arrhenius equation, which takes into account the effect of temperature on the rate of degradation; it was followed intermediate and final oxidation products that appeared during the process such as peroxide value (PV) and thiobarbituric acid reactive substances (TBARS).

2.5.1. Peroxide Value (PV)

Peroxide value was measured according to the method described for Shantha & Decker [26] with some modifications. This method is based on the ability of lipid peroxide to oxidize the Fe^{2+} to Fe^{3+} ; 0.03 g of sample were added to 3.5 mL of a solution of chloroform: methanol (7:3), the mixture was stirred for 10 seconds.

To 1 mL of the above solution were added 50 μL of solution ($\text{FeSO}_4 \cdot 0.144 \text{ M}$ and BaCl_2 in HCl 0.4M) and 50 μL of a solution of NH_4SCN (0.44 M), this mixture was incubated for a period of 20 minutes in the darkness; after this time the absorbance was determined at a wavelength of 510 nm in a spectrophotometer Jenway[®] 6405 UV/Vis. Results were expressed as milliequivalents of oxygen per kilogram of oil (meq. Oxygen/kg of oil).

2.5.2. Thiobarbituric Acid Reactive Substances (TBARS)

The final lipid peroxidation product malonaldehyde (MDA), reacts with 2-thiobarbituric acid (TBA) to produce a fluorescent complex that can be measured at 500 nm excitation and 520 nm emission wavelengths and the fluorescence was read by a Perkin-Elmer LS-55 spectrofluorometer (Perkin-Elmer, Beaconsfield, UK). To 500 μL of oil it was added to 80 μL of trichloroacetic acid (TCA 1%) and 160 μL of thiobarbituric acid (TBA 6%); this mixture was incubated for a period of 20 minutes at 90°C and then it was submerged in cold water for 10 mi-

minutes. After this period, 600 μL of butanol were added to it. This sample was stirred and the respective measurements were taken. TBARS values were expressed as nmol of malondialdehyde per millilitre of oil (nmol MDA/mL of oil) using a calibration curve with malondialdehyde (MDA) as standar substance [27].

2.6. Kinetic Study of Lipid Peroxidation of the Choibá Oil (*Dipteryx oleifera* Benth.)

A change in the quality of lipids can be measured by the appearance or disappearance of one or more quantifiable indices, symbolized by A (PV and TBARS); the rate of appearance or disappearance of A can be represented by the Equation (1).

$$r_A = -\frac{dA}{dt} = K[A]^m \quad (1)$$

where K is the rate constant and m is the apparent order of reaction. Then when m is 0, 1 and 2 the rate equation become in Equations (2)-(4) respectively.

$$A = A_0 - Kt \quad m = 0 \quad (2)$$

$$A = A_0 e^{-kt} \quad m = 1 \quad (3)$$

$$\frac{1}{A} = \frac{1}{A_0} - Kt \quad m = 2 \quad (4)$$

In order to establish the order of reaction, the value of A (PV and TBARS) was plotted as a function of time [6], and it was obtained by linear regression the most useful mathematical model that represents the degradation kinetics of Choibá oil.

2.7. Effect of Temperature on the Rate of Degradation of Choibá Oil (*Dipteryx oleifera* Benth.)

The Arrhenius relation has been used to describe the effect of temperature on the rate of several reactions of quality loss as follows Equation (5)

$$K = K_A \exp\left(\frac{-E_A}{RT}\right) \quad (5)$$

Or in its linearized form Equation (6)

$$\ln(K) = \ln(K_A) - \frac{E_A}{RT} \quad (6)$$

where K is the rate constant, K_A represents the Arrhenius equation constant and E_A is the activation energy. R is the universal gas constant (8.3144 J/mol K) and T is the absolute temperature (K). To estimate the effect of temperature on the reaction rate of a specific quality deterioration mode, values of K was calculated at different temperatures in the range of interest, and $\ln(K)$ is plotted against $1/T$ in a semilogghrap. A straight line is obtained with a slope of $-E_A/R$. Also the temperature acceleration factor, known as the Q_{10} number, was calculated from the parameters of Arrhenius model [28].

2.8. Statistical Analysis

Initially is conceived a principal component analysis (PCA) in order to reduce the dimensionality of the variables related to each other, had the main impact on the involvement of responses variables.

All experiments were carried out over triplicate samples and their mean values reported. Statistically significant differences between treatments were estimated by analysis of variance (ANOVA) for the evaluated variables, with a significance level of 95% ($p < 0.05$). Data from experiments have been adjusted to kinetic models through a linear regression analysis, and the values of R-squared have been reported. Statgraphics Centurion XVI was used for statistical analysis.

3. Results and Discussion

3.1. Antioxidant Capacity, Carnosic Acid and Rosmarinic Acid Content of Rosemary Extract

The results revealed a total phenol content of 91.01 mg GAE/g extract, and rosmarinic acid 20466.89 mg AR/L, comparable with those obtained by Erkan *et al.* (2008) and Hernández-Hernández *et al.* (2009) who reported total phenol content of 162.00 and 109.50 mg GAE/g extract, respectively, and rosmarinic acid content 37525.00 mg AR/L in different ethanolic extracts of rosemary; however, the content of carnosic acid in rosemary extract obtained is much lower than previously reported in some rosemary extracts from other latitudes [29] [30].

This difference in the concentration of rosmarinic acid and carnosic rosemary extract may be due to different factors such as the region of origin and environmental conditions (altitude and latitude) and extraction method that affects its antioxidant properties [31].

The results obtained by DPPH assay for rosemary extract, showed higher antioxidant activity (557.47 $\mu\text{mol Trolox/g}$ extract) than reported in previous studies for ethanol extracts of *Mutisia acuminata* (414.70 $\mu\text{mol Trolox/g}$ extract), *Aloysiatriphylla* (512.80 $\mu\text{mol Trolox/g}$ extract) and *Melissa officinalis* (253.80 $\mu\text{mol Trolox/g}$ extract).

A similar behavior was observed in the results of scavenging capacity of oxygen radicals, wherein the rosemary extract with an ORAC value of 3440.00 $\mu\text{mol Trolox/g}$ of extract, has a higher activity than extracts *Mutisia acuminata* (2326.20 $\mu\text{mol Trolox/g}$ of extract), *Aloysiatriphylla* (1175.00 $\mu\text{mol Trolox/g}$ of extract) and *Melissa officinalis* (476.60 $\mu\text{mol Trolox/g}$ of extract), spices with comparable total phenol content, measured by the Folin-Ciocalteu [32].

3.2. Fatty Acid Composition of Choibá Oil

The extent and rate of degradation of lipids, not only depends on the temperature and oxygen exposure; but also the composition of the oil. For example, the degree of unsaturation is a factor that directly affects the kinetics of degradation reactions [33]-[36]; edible oils with a high content of unsaturated fatty acids, especially polyunsaturated fatty acids are more susceptible to oxidation thus, the type and concentration of fatty acids present in the oil is an important quality parameter in the selection of vegetable oils [37].

Table 1 shows the percentage of fatty acids of Choibá oil. The results revealed that the oil is constituted by a 54.03% oleic acid, 11.27% palmitic acid with lesser amounts of linoleic acid (1.09%); values similar to those previously reported by Zapata-Luján *et al.* [5]. The amount of oleic acid found in Choibá oil is comparable with that reported for oils like olive oil (60% - 70%) and mid-oleic sunflower (50% - 70%) [38].

3.3. Oxidative Stability of Choibá Oil

The susceptibility of lipids to oxidation is often evaluated by measuring the concentration of intermediate and final oxidation products, after incubation of the sample under certain storage conditions for a period of time [39]. One of the most important products of lipid peroxidation is hydroperoxides [40]; These compounds are formed

Table 1. Percentages of fatty acids of Choibá oil.

Fatty Acid	%
Lauric (C12:0)	2.59
Myristic (C14:0)	9.09
Stearic (C18:0)	3.88
Oleic (C18:1)	54.03
Linoleic (C18:2)	1.09
Arachidonic (C20:0)	0.92
Gondoic (C20:1)	4.11
Behenic (C22:0)	9.07

a. Chemical characterization of Choibá oil. Percentaje % of fatty acids in the oil.

during the early stages of oxidation and they are important parameters in the determination of the oxidative stability and shelf-life of lipids [39].

Figure 1 shows the behavior of the formation of hydroperoxides in Choibá oil supplemented with rosemary extract at 1000 mg/L (RE1000) and 1500 mg/L (RE1500), BHT (200 mg/L) and without addition of antioxidants (Control).

The concentration of hydroperoxides increases mildly during the first six hours of the test, corresponding to the period of induction of lipid peroxidation, and from seven hour, markedly increased during the period of propagation of lipid peroxidation reactions. See **Figure 1**.

The comparison between treatments at each time studied, showed that from the ninth hour the treatment RE1500 has the highest protective effect on Choibá oil, with a reduction in hydroperoxides production of 60.91% versus the control treatment, compared with RE1000 and BHT samples, which reduced the content of hydroperoxides by 30.17% and 21.54% respectively.

Previous studies about the effectiveness of different extracts of rosemary in the oxidative stabilization of lipids have shown that rosemary extracts reduced to 50% the rate of formation of hydroperoxides in animal fats and vegetable oils like sunflower and corn. Additionally, these extracts are more effective than commercial mixtures of synthetic antioxidants such as Butyl Hydroxytoluene (BHT), Butyl Hydroxyanisole (BHA) and Propyl Gallate (PG) in stabilizing vegetable oils [14] [41].

3.4. Shelf Life Determination of Choibá Oil

Based on the previous results 1500 mg/L (RE1500) was selected as the most suitable concentration of rosemary extract for the shelf-life determination of Choibá oil. **Figure 2** shows the behavior of the formation of hydroperoxides in Choibá oil with and without addition of rosemary extract at 35°C, 45°C and 55°C, respectively.

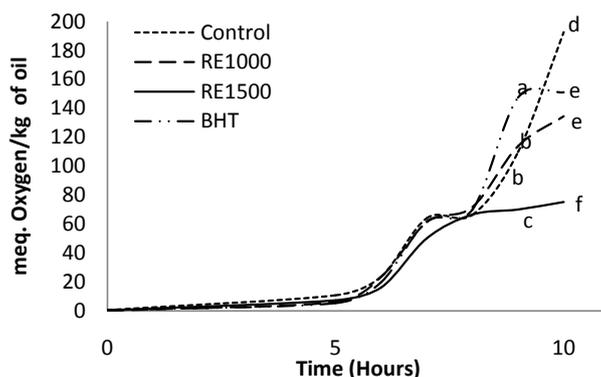


Figure 1. Evolution of hidroperoxyde formation in Choibá oil ($100^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and 1150 ml Air/min). Means from 9 hour with different letters indicate that there are statistical differences between treatments ($p < 0.05$; $n = 3$).

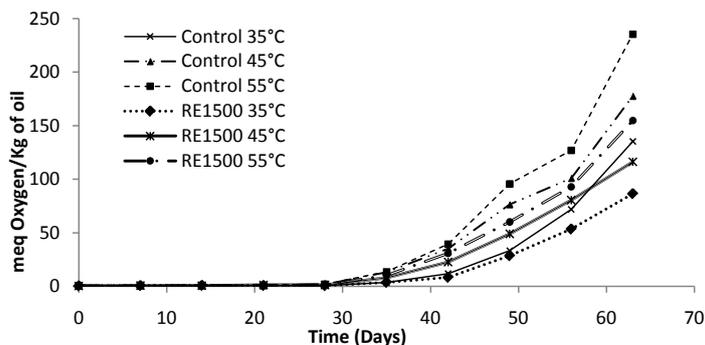


Figure 2. Formation of hydroperoxides in Choibá oil with rosemary extract at 1500 mg/L at 35°C, 45°C y 55°C. Reported values are expressed such as mean of triplicate assays.

During the early stages, lipid peroxidation starts at a slow rate, even more in the presence of antioxidants because they effectively quench most of the free radicals produced. In consequence, the level of these compounds remains low until the antioxidant is almost consumed completely; once this happens, reaction rates increases exponentially until there are no more oxidizable substrates [39] [42].

In order to estimate the shelf-life of Choibá oil, in terms of the appearance of hydroperoxides, it was proceeded to determine the parameters of the kinetic model that fit better the experimental data. Initially, the apparent order of reaction of the formation of these compounds was determined through a linear regression analysis. Most of the reactions responsible for food quality loss have been classified as zero, first and second order [43]. These kinetic equations are specific for each food and for each temperature studied [6].

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According to the coefficients of linear regression (r^2), the kinetic model that adjusted the results from the degradation of Choibá oil corresponds to a first order model Equation (7) for all treatments (Control and RE1500).

$$\ln(PV) = \ln(PV_0) - K_{PV} \times t \quad (7)$$

where K_{PV} is the rate constant for hydroperoxides formation (meq. Oxygen/Kg-day), t is the reaction time and PV_0 represents the peroxide value at time zero of reaction.

Table 2 shows the coefficients of linear regression (r^2) and the parameters of the kinetic model of first order obtained, K_{PV} y $\ln(PV_0)$. The previously mentioned data emphasize the effects of temperature on the rate of reaction during the lipid peroxidation of Choibá oil. For instance, as it was increased the temperature testing, the constant rate also increased.

To determine the entity of dependency between constant rate and temperature, it was drawn Arrhenius plot, $\ln(K_{PV})$ Vrs $1/T$, as it can see in **Figure 3**, for Control and RE1500 treatments, respectively. For these calculations, it was taken into account the values of constant rate of formation of hydroperoxides (K_{PV}) that were obtained from kinetic models of first order in each temperature tested.

Data obtained from both procedures (Control and RE1500) adjust to linear model of Arrhenius. With the results obtained at 35°C, 45°C and 55°C is possible to extrapolate the rate constant value and shelf-life of Choibá oil at any other temperature [28] [44].

The concentration of hydroperoxides in fats and oils has been regulated by legislation; however the rancidity defined as lipids organoleptic impairment, is only detectable once the decomposition of hydroperoxides has started during the last stages of oxidation and plays a significant role on consumer rejection of products [7] [8] [39]. As general rule, the secondary products of oxidation are the result of impairment of hydroperoxides when

Table 2. Parameters of the first order kinetic model for the formation of hydroperoxides in Choibá oil.

Treatment	Temperature °C	r^2	K_{PV}	$\ln(PV_0)$
Control	35	0.913978	0.1037	-0.7790
	45	0.953495	0.1142	-1.7689
	55	0.948943	0.1157	-1.6573
RE1500	35	0.892329	0.0966	-1.8790
	45	0.945623	0.1070	-1.7955
	55	0.947013	0.1152	-2.0033

a. Linear correlation coefficient (r^2), rate constants K_{PV} (meq. Oxygen/kg-day) and $\ln(PV_0)$ (meq. Oxygen/kg of oil), for Control and RE1500 treatments at 35°C, 45°C y 55°C.

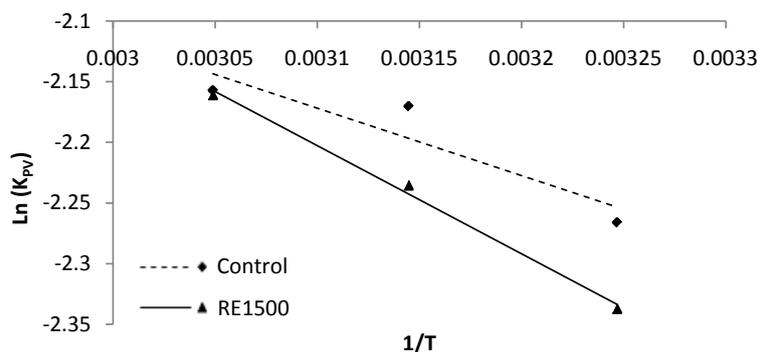


Figure 3. Effect of temperature on the reaction rate of formation of hydroperoxides in Choibá oil with and without addition of rosemary extract (Control and RE1500).

they reach a value of 20 meq Oxígeno/Kg of oil [19] [45], and for this reason, this value was set as the limit to determine the shelf-life of Choibá oil at 25°C.

In **Table 3**, it is reported. As result from data adjustment to Arrhenius linear model, the coefficient of linear regression (r^2), energy activation values E_A , rate constant (K_{PV25}) at ambient temperature (25°C), and shelf-life of Choibá oil at the same temperature for the tests Control and RE1500, with 20 meq Oxígeno/kg of oil as maximum limit allowed of hydroperoxides. The factor of acceleration, Q_{10} , for the formation of hydroperoxides was also calculated.

Energy activation values obtained for Control and RE1500 treatments are lower than values obtained in the study of stability of seeds of Coroba palm and crude oil of Abadejo. These values are under the lowest range estimated for lipids rancidity reactions [18] [44]. Choibá oil with addition of rosemary extract (RE1500), showed an energy activation value that rises approximately in 60% in comparison with Choibá oil without antioxidant (Control). According to kinetic theory, the activation energy, defined as average energy needed by molecules in order to take part in a reaction [46], remains constant as far as the reaction mechanism does not change. Addition of antioxidants, variation in partial pressure of oxygen, and other factors may alter the reaction mechanism and as result the activation energy [39] [47]. An increase in E_A implies an improve in the resistance to the lipid oxidation [48], so the raising in activation energy within the treatment RE1500 indicates that addition of rosemary extract to Choibá oil, reduces its oxidation rate, this is reflected over the shelf-life calculated at 25°C, that increased over 45.16% the shelf-life of the product.

Different studies on the lipids stability have indicated that there is not a relationship between the initial value of hydroperoxides and the shelf-life of oils. However, due to the higher lipids instability at higher temperatures, the energy needed during the impairment process is triggered, therefore the formation of final products of oxidation and even more radicals are accelerated during the propagation stage of lipid peroxidation, and this increases the impairment rate and reduces the value of the energy needed to produce the reaction. In consequence, it should be expected that a reduction of starting hydroperoxides and other compounds of the oxidation reaction, that are present within crude oils in a considerable number, may contributes to increase oxidative stability and shelf-life of this kind of products [49].

The magnitude of the temperature effect on the oxidation rate of Choibá oil, in terms of PV, was evidenced by Q_{10} values. The addition of rosemary extract decreased the Q_{10} in 1.37% compared with the Control sample. In general a higher Q_{10} number implies that a smaller temperature change is needed to induce a certain change in the rate of lipid peroxidation [48].

One of the main products of impairment of hydroperoxides is malondialdehyde (MDA) and it is easily quantified through the technique TBARS [40]. In order to estimate the shelf-life of Choibá oil, in terms of presence of TBARS, it was determined the parameters of kinetic model in analogous way to the study on formation of lipid peroxides.

Figure 4 shows the behavior of formation of MDA within both, the crude sample of Choibá oil (Control) and the stabilized sample with addition of rosemary extract (RE1500) at 35°C, 45°C y 55°C respectively.

The linear regression analysis indicated that the kinetic model that best fitted the data corresponds to a zero-order model Equation (8).

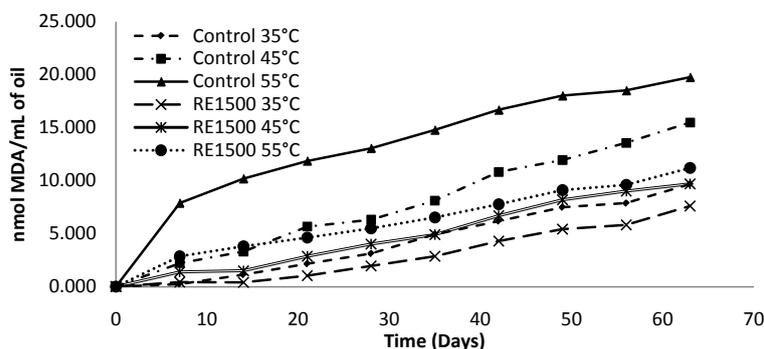


Figure 4. Evolution of thiobarbituric acid reactive substances formation (TBARS) in crude Choibá oil (Control) and with addition of rosemary extract (RE1500) at 35°C, 45°C y 55°C. Reported values are expressed such as mean.

Table 3. Parameters of Arrhenius model for the formation of hydroperoxides and malondialdehyde in Choibá oil.

Parameter	Treatment	r^2	E_A	$K_{25^\circ\text{C}}$	Shelf-life	Q_{10}
VP	Control	0.8520	4611.5071	0.0989	38.17	2.6482
	ER1500	0.9950	7409.5771	0.0880	55.40	2.6118
TBARS	Control	0.8990	21233.3979	0.1277	53.48	2.3745
	ER1500	0.7464	11304.2582	0.1105	61.82	2.5415

a. Activation energy E_A (J/mol), rate constants K_{PV25} (meq. Oxygen/Kg-day) and $K_{TBARS25}$ (nmol MDA/mL-day), estimated shelf-life (days) at 25°C, and Q_{10} number, in terms of the formation of hydroperoxides (PV) and thiobarbituric acid reactive substances (TBARS) for Control and RE1500 treatments

$$TBARS = TBARS_0 - K_{TBARS} \times t \quad (8)$$

where, K_{TBARS} is the rate constant for the formation of MDA (nmol MDA/mL-day), t is the reaction time and $TBARS_0$ are the nmol of MDA/mL of oil at time zero of reaction.

Table 4 shows the coefficients of linear regression (r^2) and the parameters, K_{TBARS} y $TBARS_0$, of kinetic model of zero order that were obtain for each treatment at every temperature studied. From data of kinetic model of zero order, it was drawn Arrhenius plot shown in **Figure 5**. Researches on oxidative stability in fried food and meat products, have found that levels of malondialdehyde (MDA) over 1 mgMDA/Kg (5.97 nmolMDA/mL), are indicators of rancidity [50]-[52].

In **Table 3**, it is presented the coefficient of linear regression (r^2), that was obtained from adjustment of data to Arrhenius linear model; values of activation energy E_A , rate constant value ($K_{TBARS25}$) was estimated at ambient temperature (25°C), along with shelf-life of Choibá oil, at same temperature, for the Control and RE1500 samples, taking 5.97 nmol MDA/mL of oil as cutoff parameter.

A value close to 1 within the coefficient of linear regression (r^2) indicates that Arrhenius model is applicable to experimental data obtained, and that the activation energy (E_A) remains constant within the range of temperature studied. As it can be notice within linear model (r^2), the level of adjustment of experimental data to Arrhenius model, for the sample that contained rosemary extract added at 1500 mg/L (RE1500), was low ($r^2 = 0.7464$). The previous information can be corroborated from the rate constants obtained for temperatures of 45°C and 55°C within the treatment RE1500, because it was not observed any effect of temperature on malondialdehyde (MDA) rate formation. Despite this, estimated shelf-life at 25°C (298 K) for control was 15.59% less than RE1500 sample, and Q_{10} number for control sample was lower than ER1500 sample. This last result is due to the activation energy for the formation of TBARS in ER1500 sample was lower than control treatment. However, this result could be erroneous due to the low adjustment mentioned above.

This behavior is probably resulted of a change in the mechanism of reaction at the studied temperatures, and/or that other reactions gain importance during the process and then influence the rate of formation of this compound [47] [53]. Within the studied case, it was observed that Control sample (oil without additives) adjusts

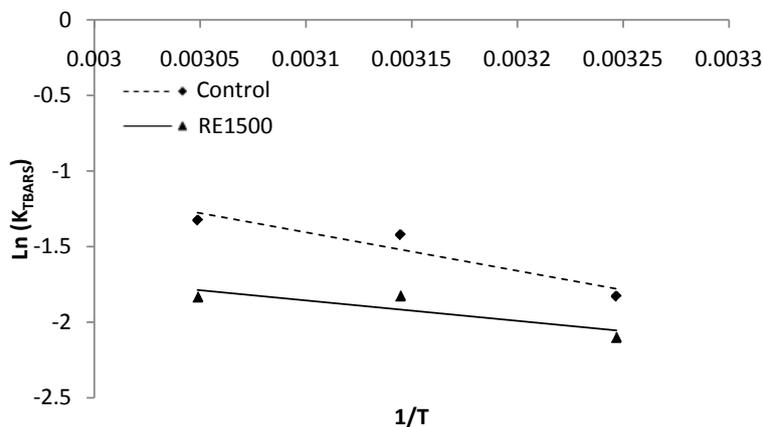


Figure 5. Effect of temperature on the reaction rate of formation of thiobarbituric acid reactive substances formation (TBARS) in Choibá oil with and without addition of rosemary extract (Control and RE1500).

Table 4. Parameters of the zero order kinetic model for the formation of malondialdehyde in Choibá oil.

Treatment	Temperature °C	r^2	K_{TBARS}	$TBARS_0$
Control	35	0.9836	0.1609	-0.8612
	45	0.9944	0.2415	0.1482
	55	0.8892	0.2659	4.6998
RE1500	35	0.9514	0.1226	-0.8612
	45	0.9855	0.1612	-0.2368
	55	0.9761	0.1601	1.0754

Linear correlation coefficient (r^2), rate constant K_{TBARS} (nmol MDA/mL-day) and $TBARS_0$ (nmol MDA/mL), for the formation of thiobarbituric acid reactive substances (TBARS) in Choibá oil, for Control and RE1500 treatments at 35°C, 45°C y 55°C.

well to Arrhenius model ($r^2 = 0.8990$). This suggests that addition of antioxidants may alter the process of oxidation, leading to wrongful data regarding activation energy and shelf-life. In consequence, studying MDA that have appeared during the process was not a useful parameter to determine the extent of shelf-life of Choibá oil supplemented with rosemary extract.

4. Conclusions

Although, the study of secondary oxidation products through TBARS technique is not relevant to measure the extent of shelf-life of Choibá oil for Control and RE1500 treatments, data obtained from hydroperoxides measurement constitute a useful parameter to determine the oxidative stability and shelf-life of this oil.

Within the research on formation of hydroperoxides in the Choibá oil, it is possible to find that data adjusted closer to Kinetic model of first order. Furthermore, the results have revealed that lipid peroxidation rate depends on temperature, and this is described closely by Arrhenius linear model.

Finally, within the Choibá crude oil without antioxidant additives (Control) the extent of shelf-life estimated at 25°C, in terms of formation of hydroperoxides, is approximately 38 days, while in Choibá oil with addition of rosemary extract (RE1500) is 55 days. Therefore, the results of this research suggest that addition of rosemary extract increases the oxidative stability of Choibá oil, through the stabilization of free radicals forms during the initial stages of the peroxidation process; this ratifies the possibility of using these kinds of extracts to stabilize edible oils.

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