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Kinetics of the oxidation of oils derived from Peruvian foods rich in ω-3 and ω-6 fatty acids using the Rancimat method

Cinética de la oxidación de aceites derivados de alimentos peruanos ricos en ácidos grasos ω-3 y ω-6 mediante el método Rancimat

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ABSTRACT

Peru has several foods with high lipid content (especially oils), rich in omega fatty acids (ω-3 and ω-6) that are widely studied for their anti-inflammatory (ω-3) and pro-inflammatory (ω-6) effects. However, ω-3 and ω-6 are susceptible to oxidation resulting in accelerated deterioration of the oils. The objective of this work was to determine the oxidative stability index (OSI) of vegetable (seeds) and animal (anchoveta) oils from Peru, with high ω-3 and ω-6 contents, in order to compare oxidation kinetic parameters and shelf life. For this purpose, the Rancimat accelerated oxidation method was used, whose working parameters were: air flow (F = 25 L/h), sample weight (M = 3 g) and temperature range (T = 60-140 °C). The results indicated that the OSI values, as well as the shelf-life projection (T = 25°C) were in the following order: olive oil > chestnut > sesame > sacha inchi > flaxseed > chia > fish. The kinetic parameters of rate constant (k), activation energy (Ea), enthalpy (ΔH), entropy (ΔS) and temperature acceleration factor (Q_{10}) varied significantly among the oils ($p < 0.05$). The comparison of the kinetic behavior of the studied samples is key for the development of new products with longer shelf life and increased nutritional value.

***Keywords*:** Vegetable oils; oxidative stability; omegas; autoxidation; rancimat.

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RESUMEN

Perú posee varios alimentos con alto contenido lipídico (especialmente aceites), ricos en ácidos grasos omega (ω-3 y ω-6) que son ampliamente estudiados por sus efectos antiinflamatorios (ω-3) y proinflamatorios (ω-6). Sin embargo, los ω-3 y ω-6 son susceptibles a la oxidación, lo que provoca un deterioro acelerado de los aceites. El objetivo de este trabajo fue determinar el índice de estabilidad oxidativa (OSI) de aceites vegetales (semillas) y animales (anchoveta) del Perú, con altos contenidos de ω-3 y ω-6, para comparar parámetros cinéticos de oxidación y vida útil. Para ello, se utilizó el método de oxidación acelerada Rancimat, cuyos parámetros de trabajo fueron: flujo de aire (F = 25 L/h), peso de la muestra (M = 3 g) y rango de temperatura (T = 60-140 °C). Los resultados indicaron que los valores de OSI, así como la proyección de la vida útil (T = 25°C) seguían el siguiente orden: aceite de oliva > castaña > sésamo > sacha inchi > linaza > chía > pescado. Los parámetros cinéticos de constante de velocidad (k), energía de activación (Ea), entalpía (ΔH), entropía (ΔS) y factor de aceleración de la temperatura (Q_{10}) variaron significativamente entre los aceites ($p < 0,05$). La comparación del comportamiento cinético de las muestras estudiadas es clave para el desarrollo de nuevos productos con mayor vida útil y mayor valor nutritivo.

***Palabras clave*:** Aceites vegetales; estabilidad oxidativa; omegas; autooxidación; rancimat.

INTRODUCCIÓN

Oils from vegetable seeds and marine sources are indispensable in the human diet, since many of them contain essential fatty acids, which means that this type of raw material represents more than 75% of the total lipids consumed in the world (Jinadasa et al., 2022). Among the functions of oils are to provide energy, maintain normal body temperature, protect body tissues, transport fat-soluble vitamins, among other functions (Orsavova et al., 2015). With population growth and economic development, edible vegetable oils have experienced a remarkable increase due to their important roles in health protection and disease prevention (Yang et al., 2018). Between January and August 2021, Peru exported 566,337 kilos of vegetable oils for an FOB value of US$ 6,196,604. These figures reveal a moderate increase from the 464,672 kilos exported in the same period of 2020 for US$ 5,405,797 (Ramos, 2021). The main destination of these shipments was France, including avocado, sacha inchi, walnut, Palo de Rosa, chia and jojoba oils. The Netherlands followed with US$1,126,902, Taiwan with US$ 747,663, Malaysia with US$ 571,537, Spain with US$ 569,584, Germany with US$ 308,866, the United Kingdom with US$228,487, the United States with US$ 145,007, Colombia with US$11,118, and others with smaller amounts that together totaled US$ 455,358 (Ramos, 2021). On the other hand, oils of marine origin such as fish oil differ from other vegetable and animal oils due to their high content of polyunsaturated fatty acids (PUFAs) (Özyurt et al., 2020). Peru produces on average 230 000 tons of fish oil per year, representing ~23% of the world production (Fréon et al., 2017). It has been reported that ω-3 fatty acids, especially EPA (eicosapentaenoic acid, C20:5, ω-3) and DHA (docosahexaenoic acid, C22: 6, ω-3), tend an anti-inflammatory role allowing it to develop an important role in the prevention of coronary artery disease, some types of cancer, rheumatoid arthritis, cellular aging, and improvement of neurological functions in children (Bi et al, 2019; Rahmawaty & Meyer, 2020; Shahidi & Ambigaipalan, 2018).

In the human body, dietary linoleic acid (ω-6) is converted into arachidonic acid (ω-6), which is an essential part of membrane phospholipids. These molecules are then converted to prostaglandin H_2 by the enzyme's cyclooxygenase-1 (COX-1) and cyclooxygenase-2 (COX-2). The conversion of prostaglandin H2 to PGE2 as a proinflammatory eicosanoid contributes to the development of metastasis and tumor growth through a different mechanism, including inhibition of apoptosis, cell proliferation and invasion. For example, high levels of PGE_2 have been demonstrated in malignant prostate cancers (compared to their benign counterparts) (Kobayashi et al., 2006). Recent studies indicate that linoleic acid, at least in part, may be influencing the inhibition of expression of two genes (WIF-1 and WT1) involved in the Wnt signaling pathway as the molecular basis for the formation and progression of many types of cancer (Mohammadihaji et al., 2022). The rancimat method is an accelerated deterioration (oxidation) test carried out by heating samples in test tubes at elevated temperatures. With the aid of an air flow into the tubes, the samples undergoing oxidation are bubbled and volatile chemicals such as acetic acid and formic acid are withdrawn into a container of distilled water through an outlet duct. This process changes the conductivity of the distilled water and allows the products of the oxidation process to be monitored. The oxidation stability of part of the

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samples can be correlated with the so-called induction time or oxidative stability index (OSI), measured in hours, which elapses from the start of the test until the secondary oxidation products increase the conductivity dramatically in the vessel containing the distilled water (Bär et al., 2021).

The great variety of lipid raw materials in Peru and the possibility of deepening studies linked to PUFAs, especially ω-3 and ω-6, for their wide nutritional benefits, implies comparing them at a chemical level (deterioration) for future technological applications in the food industry. The objective of this work was to determine and OSI of edible oils derived from Peruvian foods rich in ω-3 and ω-6 fatty acids, such as those derived from vegetable seeds and marine source such as anchoveta oil, to compare their oxidation kinetic parameters and shelf life using the accelerated rancimat oxidation method.

METHODOLOGY

Samples and preparation of blends

Vegetable seeds were obtained from different regions of Peru. Sacha inchi (*Plukenetia volubilis* L, variety - Peanut INCA-1) was harvested from the San Martin Region, Lamas province (06°25′00‴S altitude and 76°32′00‴W latitude); Chia (*Salvia hispanica* L., variety - Black) was obtained from Ancash region, Yungay province (09° 08′ 20″ S altitude and 77° 44′ 40″ W latitude); Chestnut (*Bertholletia excelsa* H.B.K) was from Madre de Dios Region in the forests of De Las Piedras district in Tambopata (12°35' 36" S altitude and 69° 10' 35" W latitude); Linseed (*Linum usitatissimum* L., variety - Brown) was obtained from Ancash Region, Corongo province (8°30′34″S altitude 77°54′37″W latitude); Sesame (*Sesamun indicum* L., Variety - Venezuela 51) was obtained from San Martin Region, Tarapoto district (6°29′39″S altitude and 76°22′11″W latitude). The oil from the mentioned seeds was obtained by cold pressing (SEW-EURODRIVE press model FA57/G, Germany) with a screw speed of 40 rpm and maximum temperature of 40°C, the seeds had a humidity between 9 - 11 % (Figure 1 and 2). The oil was kept for 30 days in a dark flask under nitrogen atmosphere in a refrigerator (BOSCH, model KAN58A, South Korea) at a temperature of (5.00 ± 0.5°C) at the facilities of the Agroindustrial Technological Research Institute of the Universidad Nacional del Santa.

Regarding the olive oil (*Olea Europea*), they were obtained from fruits "olives" (Variety - Criolla) harvested in the Tacna Region, province of La Yarada - Los palos (18°17′08″S altitude and 70°26′20″W latitude). The conventional method of extra virgin olive oil extraction was used, which consisted of three main processes, which were crushing, malaxation and centrifugation. Subsequently, stored under refrigeration at a temperature of 5.0 ± 0.5°C. The fish oil was from the anchoveta species (Engraulis ringens), provided by the fish processing company CFG-COPEINCA S.A.C. Chimbote, Peru.

Physico-chemical characterization

The acid number (*AV*) was determined by the titration method defined in the official methods Cd 3d-63 of the American Oil Chemists' Society (AOCS, 1993). 7Titration of the oil samples (10 g) dissolved in 50 mL of previously neutralized chloroform–ethanol medium (50:50 v/v) was applied, using a 0.1 N potassium hydroxide (KOH) ethanolic solution as standard reagent to a phenolphthalein endpoint. *AV* was expressed as milligrams of KOH required to neutralize the free fatty acids present in 1 g of the oil sample (mg KOH/g).

$$AV = G \times N \times 56.1 / w \quad (1)$$

Where: *G* is the titratable volume of KOH (mL), *N* is the normal of KOH (0.1 N) and *w* is the weight of the sample (g).

The refractive index (*RI*) was measured according to method 921.08 (AOAC International, 2019) working at 25 °C and using a digital A 24051 refractometer (Rudolph Research Analytical, NJ, USA) kept at 20 °C.

The iodine value (*IV*) was determined by the Wijs method, in accordance with method 993.20 (AOAC International, 2019), 0.2 g of oil was dissolved with 10 mL of chloroform and 15 mL of Wijs reagent, after 45 min of rest 10 mL of potassium iodide 15% in 50 mL of distilled water was added, proceeded to titrate with sodium thiosulfate (0.1 N) with a brown to yellow color change, 1 mL of 1% soluble starch was added and titrated again with 0.1 N sodium thiosulfate until the color changed from blue to white. *IV* was expressed as mg I_2/g.

$$IV = (B - M) \times N \times 12.65 / w \quad (2)$$

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Where: *B* and *M* are the titratable volumes of sodium thiosulfate (mL) for the blank and oil sample, respectively. N is the sodium thiosulfate normal (0.1 N) and w is the sample weight (g).

The peroxides value (PV) was determined following the Cd 8-53 method (AOCS, 1998) with modifications, where 5 g of oil were dissolved in 30 mL of acetic acid-chloroform solution (60/40 v/v), added 0. 5 mL of saturated potassium iodide was added and allowed to stand for 1 min in the dark, then 30 mL of distilled water was added and stirred for 5 min. Finally, 0.5 mL of 1% starch solution was added and titrated with 0.01 N sodium thiosulfate solution. PV was expressed in milliequivalents of active oxygen present in 1 kg of oil ($mEqO_2/kg$).

$$PV = G \times N \times 1000 / w \quad (3)$$

Where: *G* is the titratable volume of sodium thiosulfate (mL), *N* is the normal of sodium thiosulfate (0.01 N) and *w* is the weight of the sample (g).

The p-anisidine (*p-AV*) value was monitored using the Cd 18-90 method (AOCS, 1998) with modifications, two reagent dilutions were prepared, the first consisted of the oil/isooctane mixture (0.5 g/25mL), and the second was anisidine reagent/acetic acid (0.025 g/25 mL). Subsequently, the absorbances of the dilutions were measured at 350 nm, according to the following description:

$$p\text{-}AV = 25 \times (1.2 \times As - Ab)/w \quad (4)$$

Where: *As* is absorbance of oil/isooctane minus absorbance of pure isooctane. *Ab* is absorbance of the oil/isooctane diluted in anisidine/acetic acid (1/1, v/v) minus the absorbance of the anisidine/acetic acid diluted in isooctane (1/1, v/v). *w* is the weight of the oil (g).

Finally, the total oxidation value (*TotOX*) has been determined as:

$$TotOX = 2PV + p\text{-}AV \quad (5)$$

Fatty acid profile

The fatty acid composition of the oils was determined according to the fatty acid methyl ester method n. 991.39 (AOAC,2005), which consisted of weighing 0.025 g of oil and reacting with 1.5 mL of NaOH 0.5 N at 90°C in a water bath (Foos, mode-loWB1024) for 5 min, then cooling to 30°C and adding 2. 0 mL of boron trifluoride (BF_3) heated to 100°C for 30 min, again cooled by adding 1 mL of iso-octane and 5 mL of saturated NaCl solution, all under stirring and constantly covered with nitrogen. Identification of the components was determined on gas chromatograph (Shimadzu, model GC-2010, Japan), equipped with a flame ionization detector (FID) and a Shimadzu AOC-20Si autosampler. An SP Rt™ -2560 silica capillary column (100 m x 0.25 mm with 0.20 µm film) was used helium as carrier gas at a flow rate of 30 mL/min and pressure of 261.5 kPa. Injection volume was 1 µL. Injector temperature was programmed at 225°C (Split mode) and detector at 250°C. Oven temperature was programmed: initial temperature 100°C for 4 min, then at 240°C with a rate of 3°C/min for 10 min.

Oxidative stability index (OSI) and shelf-life

The accelerated stability test was carried out in a Rancimat equipment (Metrohm, model 743, Switzerland) to evaluate the OSI (hours) of the samples according to the AOCS Cd 12b-92 method. Rancimat parameters were programmed at three different reaction temperatures (100, 110 and 120 °C) with an air flow (15 L/h) and constant sample weight (3.00 ± 0.1 g). The temperatures were selected according to the oxidation resistance of AO and VOO (Jiang et al., 2020; Farhoosh et al., 2013). The OSI values were inversely proportional to the temperatures values and related according to the equation proposed by Heidarpour and Farhoosh (2018):

$$\text{Log (OSI)} = \alpha(T) + \beta \quad (6)$$

Shelf-life prediction (OSI_{25}) was determined by extrapolating the temperature to 25°C.

Autooxidation kinetics

The activation energy (Ea) was determined according to:

$$\text{Ln(OSI)} = \text{Ln}\left(\frac{-\text{Ln}(1-\alpha^*)}{Z}\right) + \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \quad (7)$$

Where: R=8.314 J/mol K (universal gas constant), α* is the degree of transformation of unsaturated molecules and Z is factor of Arrhenius equation.

The entropy (ΔS^{++}) and enthalpy (ΔH^{++}) were obtained by regressing Log (k/T) versus (1/T), equation derived from the activated complex theory, according to Heidarpour and Farhoosh (2018):

$$\text{Log}\left(\frac{K}{T}\right) = \left[\text{Log}\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^{++}}{2.303R}\right)\right] - \left(\frac{\Delta H^{++}}{R}\right)\left(\frac{1}{T}\right) \quad (8)$$

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Where: k_B=1.380658 x 10-23 J/K (Boltzmann constant), h=6.6260755 x 10-34 Js (Planck's constant) and K = 1/OSI. The Gibbs free energy (ΔG^{++}) was calculated according to equation:

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

The value of Q_{10} was determined according to Farhoosh (2007):

$$Q_{10} = \frac{\text{OSI at time T}}{\text{OSI at T +10 °C}} \quad (10)$$

Statistical analysis

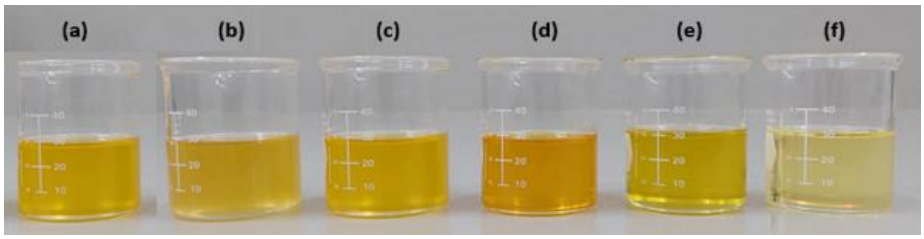
Data processing was performed in Minitab statistical software version 18 (Softonic, USA). Analysis of variance (ANOVA) was used to determine significant differences between treatment means using Tukey's test ($p<0.05$). Means were calculated by triplicate analysis of the samples.

Figure 1

Raw materials derived from vegetable seeds and fish

Figure 2

Vegetable seed oils from Peru: (a)chestnut, (b) sesame, (c) chia, (d) flaxseed, (e) olive and (f) sacha inchi



Physico-chemical characterization of Peruvian oils

The physical and chemical characteristics of the oils are presented in Table 1, the composition of fatty acids of unsaturated nature was presented mostly in chia, sacha inchi, flaxseed and anchovy oils, these oils are referenced for their high content of α-linolenic for those of vegetable origin and DHA + EPA for those of marine origin (Rodriguez et al., 2020; Aguirre et al., 2021; Alonso et al., 2023; Suri et al., 2023). Anchoveta oil presented 37.57% of PUFAS, among which DHA (22.6%) and EPA (13.6%) stood out; these results were similar to those presented by Alonso et al. (2023). Chestnut and sesame oil are characterized by high linoleic fatty acid contents (~42%), this is confirmed by España et al. (2011) and Teklu et al. (2022), respectively. Olive oil presented a majority of oleic acid, the main component of MUFAS. On the other hand, olive oil presented 15.48% PUFAS, mainly composed of linoleic acid (ω-6), both fatty acid profiles were confirmed by the reports of Özyurt et al. (2020) and Xiang et al. (2017), respectively.

Regarding the chemical characteristics of the oils, the PV in all cases were less than 15 meqO2/kg, recommended by the Codex Alimentarius (2015). The VA values for the various oils are similar to those presented by: Özkan and Özcan (2016) for olive oil (0.11 mg KOH/g); Alonso et al. (2023) for anchoveta oil (0.43 mg KOH/g); Rodriguez et al. (2022) for sacha inchi oil (1. 1 mg KOH/g); Tańska et al. (2016) for Flaxseed oil (0.5 mg KOH/g); Rodriguez et al. (2020) for chia oil (0.43 mg KOH/g) and sesame (0.61 mg KOH/g). The p-AV of the vegetable oils were lower than the values of the anchoveta oil, this is explained

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by the greater deterioration of the unsaturated acids (ω-3) specific to anchoveta oil, which generates chemical compounds of late stages in a lower proportion than the vegetable oils presented in this study. As a consequence, the TotOx value of anchoveta oil was higher compared to the other samples, presenting statistically significant differences ($p < 0,05$).

Oxidative stability index and shell life

The OSI of vegetable oils and anchoveta oil were compared at a temperature of 100°C (Table 2), because at this temperature all oils presented OSI results within the range of analysis. The analysis temperatures depend on the chemical nature of the oils, which translates into oxidation resistance time (Rodríguez et al., 2020). According to the fatty acid profile, oils with higher PUFAS content presented lower OSI values than those with higher SFA values, in the order of: olive > chestnut > sesame> flaxseed > chia > sacha inchi > anchovy.

Table 1

Physicochemical characteristics of Peruvian oils

Profile	Oils						
	Olive	Chestnut	Sesame	Flaxseed	Sacha inchi	Chia	Anchovy
C14:0	0.048 ± 0.006^{b}	nd	nd	nd	nd	nd	8.877 ± 0.076^{a}
C16:0	15.980 ± 0.028^{b}	12.918 ± 0.006^{c}	11.083± 0.091^{d}	6.522 ± 0.047^{f}	3.933 ± 0.125^{g}	6.900 ± 0.041^{e}	20.453 ± 0.066^{a}
C16:1	nd	2.723 ± 0.032^{b}	nd	nd	nd	nd	9.818 ± 0.026^{a}
C18:0	1.950 ± 0.024^{f}	nd	6.253 ± 0.111^{a}	5.124 ± 0.061^{b}	2.528 ± 0.056^{e}	4.593 ± 0.042^{d}	4.810 ± 0.054^{c}
C18:1	66.100 ± 0.050^{a}	34.868 ± 0.327^{c}	38.653 ± 0.129^{b}	20.617 ± 0.104^{d}	8.893 ± 0.051^{f}	6.817 ± 0.058^{g}	15.717 ± 0.189^{e}
C18:2 (ω-6)	15.467 ± 0.047^{d}	42.668 ± 0.115^{a}	42.649 ± 0.119^{a}	13.678 ± 0.096^{e}	36.552 ± 0.073^{b}	19.950 ± 0.082^{c}	1.277 ± 0.125^{f}
C18:3 (ω-3)	0.013 ± 0.005^{e}	6.533 ± 0.096^{d}	0.315 ± 0.018^{e}	53.193 ± 0.223^{b}	48.085 ± 0.084^{c}	61.100 ± 0.455^{a}	0.125 ± 0.019^{e}
C20:0	0.140 ± 0.014^{d}	0.233 ± 0.010^{c}	0.335 ± 0.011^{b}	0.130 ± 0.020^{d}	nd	nd	1.797 ± 0.037^{a}
C20:5 (ω-3, EPA)	nd	nd	nd	nd	nd	nd	22.490 ± 0.029
C22:6 (ω-3, DHA)	nd	nd	nd	nd	nd	nd	13.687 ± 0.119
SFA	18.370 ± 0.057^{b}	13.151 ± 0.015^{d}	17.671 ± 0.031^{c}	11.776 ± 0.099^{e}	6.462 ± 0.070^{g}	11.493 ± 0.033^{f}	35.937 ± 0.078^{a}
MUFAS	66.100 ± 0.041^{a}	37.591 ± 0.235^{c}	38.653 ± 0.105^{b}	20.617 ± 0.085^{e}	8.893 ± 0.042^{f}	6.817 ± 0.047^{g}	25.535 ± 0.172^{d}
PUFAS	15.480 ± 0.050^{g}	49.201± 0.203^{d}	42.963 ± 0.115^{e}	66.872 ± 0.189^{c}	84.636 ± 0.061^{a}	81.050 ± 0.374^{b}	37.578 ± 0.227^{f}
ω-6	15.467 ± 0.047^{d}	42.688 ± 0.115^{a}	42.649 ± 0.119^{a}	13.678 ± 0.096^{e}	36.552 ± 0.073^{b}	19.950 ± 0.082^{c}	1.277 ± 0.125^{f}
ω-3	0.013 ± 0.005^{f}	6.533 ± 0.096^{e}	0.315 ± 0.018^{f}	53.193 ± 0.223^{b}	48.085 ± 0.084^{c}	61.100 ± 0.455^{a}	36.302 ± 0.108^{d}
ω-3/ω-6	0.001 ± 0.000^{c}	0.153 ± 0.002^{c}	0.007 ± 0.000^{c}	3.889 ± 0.039^{b}	1.316 ± 0.004^{bc}	3.063 ± 0.035^{bc}	28.688 ± 2.593^{a}
Acidity (%)	0.910 ± 0.008^{b}	0.900 ± 0.022^{b}	0.350 ± 0.041^{e}	0.487 ± 0.009^{d}	1.083 ± 0.025^{a}	0.777 ± 0.021^{c}	0.927 ± 0.005^{b}
Iodine (mg I_2/g)	89.783 ± 0.883^{f}	160.833 ± 1.008^{d}	123.167 ± 1.778^{e}	183.667 ± 1.190^{b}	191.867 ± 1.915^{a}	176.533 ± 1.310^{c}	178.327 ± 1.605^{c}
PV (meq O_2/kg)	1.840 ± 0.008^{c}	0.487 ± 0.009^{f}	1.223 ± 0.021^{e}	1.790 ± 0.008^{d}	2.023 ± 0.012^{b}	1.987 ± 0.009^{b}	4.870 ± 0.008^{a}
***p*-AV**	1.110 ± 0.008^{b}	1.140 ± 0.014^{b}	1.340 ± 0.014^{b}	1.093 ± 0.090^{b}	1.410 ± 0.008^{b}	1.027 ± 0.052^{b}	13.067 ± 1.144^{a}
TotOx	4.790 ± 0.132^{bc}	2.113 ± 0.029^{d}	3.787 ± 0.053^{c}	4.673 ± 0.098^{bc}	5.457 ± 0.021^{b}	5.000 ± 0.049^{bc}	22.807 ± 1.156^{a}

**Equal letters in the same row do not show significant difference ($p<0.05$). nd: not detected.*

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Olive, chestnut and sesame oils were the only ones that did not show a significant difference (p<0,05) at 100°C; however, as the temperature increased, it became evident that chestnut oil presented a higher resistance to oxidation (higher OSI) than olive and sesame oils. Table 3, shows the shelf life of the oils.

As expected, the highest projection values corresponded to olive oil, approximately one year, while chestnut and sesame oil presented less than half a year, with no significant difference (p<0,05). The Q10 values obeyed the principle of doubling of the reaction rate for each 10°c increase in temperature.

Table 2

Oxidative stability index (OSI) of oils

Oils	Temperature (°C)							
	60	70	80	90	100	110	120	130
Oliva	-	-	-	-	18.626±0.089[a]	7.529±0.021	3.528±0.016	1.527±0.019
Chestnut	-	-	-	-	18.700±0.283[a]	9.777±0.020	4.400±0.041	2.207±0.025
Sesame	-	-	-	-	18.333±0.125[a]	9.450±0.041	3.747±0.041	1.700±0.014
Flaxseed	-	-	-	12.767±0.034	6.220±0.022[b]	2.567±0.009	1.050±0.040	-
Chia	-	-	-	6.187±0.025	3.027±0.021[d]	1.500±0.008	0.797±0.021	-
Sacha inchi	-	-	7.480±0.016	3.533±0.025	1.567±0.012[c]	0.523±0.021	-	-
Anchovy	5.333±0.125	2.400±0.082	1.167±0.047	0.513±0.009	0.317±0.012[e]	-	-	-

**Equal letters in the same row do not show significant difference (p<0,05), OSI in horas (h).*

Autooxidation kinetic parameters

The kinetic parameters of the oils were presented in Table 4, showing the high susceptibility of anchovy oil to oxidation compared to vegetable oils, as can be seen in the Ea value, which indicates the behavior of the autooxidation reaction. High Ea values are due to a higher content of saturated fatty acids in the oil matrix; on the contrary, unsaturated fatty acids mostly reduce Ea values (Adhvaryu et al., 2000).

Anchoveta oil presented the lowest Ea value, compared to vegetable oils, this was lower than 82.84-96.97 kJ/mol, presented by Yang & Chiang (2017). Olive oil presented the highest Ea value (103.27 kJ/mol), this was similar to the 101.87 kJ/mol, found by Alonso et al. (2023).

In the case of sacha inchi oil, the value was lower (115.13 kJ/mol) presented by Rodríguez et al. (2022).

The enthalpy of all samples was endothermic in nature, as the values were positive (ΔH^(++) > 0) (Farhoosh & Hoseini-Yazdi, 2013). Regarding the entropy, negative values (ΔS^(++)< 0) were obtained in all samples, this suggests that the activated complexes are more ordered than their reactants. In other words, the activated complex will have a slower oxidation reaction rate (Rodríguez et al., 2020). Regarding the Q10 values for all oils ranged from 1.982 - 2.306, these values indicate that for every 10 °C increase in temperature the reaction rate doubles (Redondo-Cuevas et al., 2018).

Table 3

Shelf life (OSI_{25}) and Q_{10} of oils

Oils	α	β	R^2	OSI_{25} (meses)	Q_{10}
Olive	-0.035 ± 0.000	4.846 ± 0.025	0.995 ± 0.000	12.366 ± 0.555[a]	2.306 ± 0.007[b]
Chestnut	-0.031 ± 0.000	4.413 ± 0.041	0.998 ± 0.000	5.943 ± 0.441[b]	2.043 ± 0.004[b]
Sesame	-0.035 ± 0.001	4.440 ± 0.101	0.998 ± 0.030	5.170 ± 0.936[b]	2.228 ± 0.015[a]
Flaxseed	-0.036 ± 0.000	4.405 ± 0.047	0.991 ± 0.000	4.351 ± 0.344[c]	2.308 ± 0.281[b]
Sacha inchi	-0.041 ± 0.001	4.264 ± 0.170	0.998 ± 0.000	2.498 ± 0.072[d]	2.457 ± 0.044[b]
Chia	-0.029 ± 0.000	3.462 ± 0.032	0.999 ± 0.000	0.727 ± 0.040[e]	1.982 ± 0.031[b]
Anchovy	-0.034 ± 0.000	2.743 ± 0.049	0.999 ± 0.010	0.111 ± 0.009[f]	2.186 ± 0.064[b]

**Equal letters in the same row do not show significant difference (p<0,05)*

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Table 4

Kinetic parameters of oils

Oils	Ea (kJ/mol)	ΔH^{++} (kJ/mol)	ΔS^{++} (J/mol K)	ΔG^{++} (kJ/mol)
Olive	103.271± 0.677[a]	100.067 ± 0.677[a]	2.808 ± 1.777[b]	- 98.950 ± 1.384[a]
Chestnut	90.039 ± 1.025[b]	86.832 ± 1.025[b]	38.723 ± 2.646[a]	- 71.421 ± 2.078[b]
Sesame	100.736 ± 2.998[a]	97.531 ± 2.998[a]	10.132 ± 6.955[b]	- 93.500 ± 6.153[a]
Flaxseed	99.262 ± 1.316[a]	96.140 ±1.316[a]	4.008 ±3.025[b]	- 94.545 ± 2.737[a]
Sacha inchi	98.607 ± 1.385[a]	95.569 ± 1.385[a]	6.835 ± 3.855[b]	- 92.848 ± 0.149[a]
Chia	81.291 ± 0.858[c]	78.166 ± 0.858[c]	46.425 ± 2.309[a]	- 59.689 ± 1.777[c]
Anchovy	77.776 ± 1.315[c]	74.900 ± 1.315[c]	35.022 ± 3.698[a]	- 60.961 ± 2.784[c]

CONCLUSIONS

Various foods native to Peru are known for their nutritional and bioactive properties. Oils derived from vegetable and marine sources are rich in omegas (ω-3 and ω-6), which are important for human health. However, the deterioration of the raw materials studied in this work presents substantial differences due to their chemical structure.

The use of the rancimat equipment allowed comparing the oxidation resistance times or oxidative stability indexes (OSI) under accelerated deterioration conditions, determining that the order of deterioration of the oils were: olive < chestnut < sesame < sacha inchi < flaxseed < chia < anchoveta.

The oxidation kinetics allowed characterizing thermodynamic properties (k, Ea, ΔH, ΔS and Q_{10}), which would help in quality control and development of new products.

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