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# Specific heat of vegetable oils as a function of temperature obtained by adiabatic scanning calorimetry

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**Abstract** Vegetable oils can undergo changes in their physical and chemical properties when they are subjected to processes such as extraction, purification, cooking, frying, or chemical modifications that are required depending on their application in the food industry. In the present research, different methods were used to determine physical, chemical, and thermal properties of avocado, sesame, extra virgin flaxseed, extra virgin olive, and grape seed oils, in order to evaluate and compare the compositional effects of each vegetable oil. By using an adiabatic scanning calorimeter, an alternative calorimetric method, the specific heat of five vegetable oils was obtained as a function of the temperature, in the range of 25–90 °C. The fatty acid profile was determined via gas chromatography. Monounsaturated acids present in avocado and extra virgin olive oil cause higher specific heat values in these oils, and the presence of polyunsaturated acids, contained mainly in extra virgin flaxseed oil, reduces the specific heat values. We found an almost linear behavior of vegetable oil specific heats, as a function of the temperature, and the slopes of these linear fits depend on the contained percentage of polyunsaturated fatty acids in the vegetable oil. The unsaturated acids are an important factor to analyze the behavior of specific heat of vegetable oils. The obtained specific heat values were compared with the estimation from the Rowlinson–Bondi equation, for specific heat of vegetable oils, giving a very good adjustment, mainly in a temperature range near to the room temperature.

## Introduction

Lipids, proteins, and carbohydrates constitute the principal structural components of foods. Lipids are heterogeneous organic molecules, formed by carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulfur to a lesser extent; due to the formation of its hydrocarbon chain, they are insoluble in water and soluble in organic solvents. The main sources of lipids are animal fats and oils in seeds. The difference between fats and oils lies in the proportion of the present fatty acids [1].

Composition of vegetable oils includes complex mixtures of triacylglycerols (TAGs) which are esters derived from glycerol and three fatty acids. TAGs represent from 95 to 98 % of composition of these oils, which also are composed by minor amounts of diacylglycerols, free fatty acids, phospholipids, carotenoids, chlorophylls, sterols, tocopherols/tocotrienols, phytosterol esters/phytosterols, proteins, resinous and mucilaginous materials, and oxidative products (usually <5 %) [2–4]. All fatty acids are synthesized from palmitic acid through of elongation and desaturation processes. Seeds from some plants contain enzymes capable of stopping the elongation process, resulting in fatty acids of medium or short chain incorporated in idioblasts stored as oil [5].

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The fatty acids in nature are classified as saturated, monounsaturated, and polyunsaturated according of the number of double bonds in their fatty acid chains. In turn, the polyunsaturated fatty acids can be classified in omega-3 and omega-6 fatty acids (Table 1), according to the position of the first double bond site or the furthest terminal carbon from the functional group of carboxylic acid (omega-carbon). The most prominent omega-6 fatty acids, in the human diet, are arachidonic acids from animal origin, and also linoleic acid present in vegetables, seeds, and nuts. The main sources of omega-3 fatty acids are fish that contains eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA); as well as nuts, seeds, and vegetable oils containing α-linolenic acid (ALA), which is the precursor of omega-3 fatty acids [5–10].

Other omega fatty acids that are not considered essentials are the omega-7 and omega-9 series or palmitoleic acid; which are monounsaturated fatty acids. The omega-7 can be found in animal oils, marine oils, and vegetable oils [11]. One of the main natural sources of omega-9 is the extra virgin olive oil, rich in oleic acid; other sources of omega-9 are walnuts, hazelnuts, peanuts, mustard seed, canola, and avocado oil [8, 12].

Edible oils extracted from plant and animal sources have a very important role in food products worldwide, because they provide flavor and texture, to taste them, as well as provide energy and vitamins, which help to the growth and keep good health [13–15], also these oils are used in different food industries, cosmetics, pharmaceutical, and lubricants [16, 17]. It is indispensable to know their chemical composition, physical properties, and thermal behavior, in order to evaluate the quality for each specific use of the edible vegetable oils.

Fatty acid composition and minor components of vegetable oils can be characterized by chromatographic technique, which gives good quantitative information about each oil component. Different methodologies have been proposed to know some parameters in order to evaluate quality in vegetable oils such as iodine index, peroxide index, and saponification index, among others [18, 19].

It is essential to know the chemical composition and physical properties of vegetable oils, but the knowledge about their thermal behavior is also very important. In food research, several thermal analysis techniques have been developed to study the vegetable oil components [20] and during several years different calorimetric techniques with varying degrees of accuracy and precision have been developed. Thermal mechanical analysis (TMA), thermogravimetric analysis (TG), differential thermal analysis (DT), and differential scanning calorimetry (DSC) are the most common thermal analysis techniques; the last one is the most usual technique used by researchers to

**Table 1** Unsaturated fatty acids

| Common name | Systematic name | General formula | Numerical symbol | Omega family |
|---|---|---|---|---|
| Palmitoleic | (Z)-9-hexadecenoic | $C_{16}H_{30}O_2$ | 16:1 | 7 |
| Oleic | (Z)-9-octadecenoic | $C_{18}H_{34}O_2$ | 18:1 | 9 |
| Elaidic | (E)-9-octadecenoic | $C_{18}H_{34}O_2$ | 18:1 | 9 |
| Petroselinic | (Z)-6-octadecenoic | $C_{18}H_{34}O_2$ | 18:1 | 12 |
| Vaccenic | (E)-11-octadecenoic | $C_{18}H_{34}O_2$ | 18:1 | 7 |
| Gondoic | (Z)-11-eicosenoic | $C_{20}H_{38}O_2$ | 20:1 | 9 |
| Erucic | (Z)-13-docosenoic | $C_{22}H_{42}O_2$ | 22:1 | 9 |
| Nervonic | (Z)-15-tetracosenoic | $C_{24}H_{46}O_2$ | 24:1 | 9 |
| Linoleic | (Z,Z)-9,12-octadecadienoic | $C_{18}H_{32}O_2$ | 18:2 | 6 |
| α-Linolenic | (Z,Z,Z)-9,12,15-octadeca-trienoic | $C_{18}H_{30}O_2$ | 18:3 | 3 |
| γ-Linolenic | (Z,Z,Z)-6,9,12-octadeca-trienoic | $C_{18}H_{30}O_2$ | 18:3 | 6 |
| Cis-linolenic | (E,E,E)-9,12,15-octadeca-trienoic | $C_{18}H_{30}O_2$ | 18:3 | 3 |
| Punicic | (Z,E,Z)-9,11,13-octadeca-trienoic | $C_{18}H_{30}O_2$ | 18:3 | 5 |
| Oleostearynic | (E,E,E)-9,11,13-octadeca-trienoic | $C_{18}H_{30}O_2$ | 18:3 | 5 |
| Arachidonic | (All-Z)-5,8,11,14-eicosate-traenoic | $C_{20}H_{30}O_2$ | 20:4 | 6 |
| Timnodonic | (All-Z)-5,8,11,14,17-icosapentaenoic | $C_{20}H_{30}O_2$ | 20:5 | 3 |
| Clupanodonic | (All-Z)-4,8,12,15,19-docosapentaenoic | $C_{22}H_{34}O_2$ | 22:5 | 3 |
| Docosahexaenoic | (All-Z)-4,7,10,13,16,19-docosahexaenoic | $C_{22}H_{32}O_2$ | 22:6 | 3 |
| Ricinoleic | (R)-12-hydroxy-(Z)-9-octa-decenoic | $C_{18}H_{34}O_3$ | 18:1 | 9 |

determining thermal parameters of vegetable oils [21–24]. Despite the common use of DSC technique, there are disadvantages that can affect the accuracy of the obtained results [25]. An alternative calorimetric technique is an adiabatic scanning calorimeter (ASC), which is based on the idea of surrounding a measuring cell by a shell exactly the same temperature as the cell, eliminating all unwanted heat exchange with the environment and provides the cell with a system to supply or subtract heat. To maintain exactly the same temperature between the cell and the shell is necessary to take into account the accuracy of the temperature sensors and the fast response of the control system. It is also important to reduce conduction and convection heat transport in order to achieve an adiabatic environment. A typical ASC has one or more additional shields surrounding the first shield, all with their own temperature sensors and control systems. Due to its characteristics are achieved scanning rates of the order of a few mK min$^{-1}$. For heating runs a constant power is continuously applied to (or extracted from) the cell by an electrical heater. ASC has been applied to study different kind of materials with high temperature resolution and high accuracy, such as liquid crystals, liquid mixtures, and starches, among others [26–28].

In the present study, ASC was used as an alternative method to determine the specific heat, which is one of the main thermal properties of the liquids. Also physical and chemical characterizations, by using different methods including gas chromatography, and determination of peroxide index, iodine index, and saponification index were obtained in order to characterize some edible vegetable oils.

## Materials and methods

Five commercial edible vegetable oils, see Table 2, were used in this study (avocado, pure sesame, extra virgin flaxseed, extra virgin olive, and grape seed; AO, PSO, EVFO, EVOO, and GSO, respectively). Then the chemical, physical, and thermal characterizations mentioned above were performed on these oil samples.

**Table 2** Studied vegetable oils

| Vegetable oil | Brand | Origin |
| --- | --- | --- |
| AO | Ahuacatlán | México |
| PSO | Borges | Spain |
| EVFO | Lee Kum Kee | USA |
| EVOO | Inés Aceites naturales | México |
| GSO | Borges | Spain |

## Chemical and physical characterization

The fatty acid content was determined via gas chromatography (PerkinElmer, model Autosystem, USA) equipped with a flame ionization detector (FID) and a column Zebron FFAP 25 m × 0.25 mm, d.i. 5 μm after derivatization as methyl esters. The column temperature started at 100 °C for 5 min and then increased to 200 °C at the rate of 5 °C min$^{-1}$ and held for 3 min and finished at 2 °C held for 10 min. Standards for identification of fatty acids were prepared for myristic, oleic, palmitic, palmitoleic, stearic, oleic, and linoleic. The experimental results are reported in percentage (%), the conventional quantification used for fatty acid contents.

The acid index was determined by titration in accordance to NMX-F-101-1987 [29]; the peroxide index was obtained by NMX-F-154-1987 [30], PANREAC [31], and Qian and Pike [32]; the iodine index was obtained by Hannus method (NMX-F-408-S-1981) [33], and the saponification index was determined using the method described in NMX-F-174-S-1981 [34] and Qian and Pike [32]. All determinations were performed in triplicate.

## Thermal characterization

### Adiabatic scanning calorimeter (ASC)

The used adiabatic scanning calorimeter was developed and constructed at KU Leuven, Belgium. The ASC consists of three different stages: (1) the sample cell (holder), (2) inner shield, and (3) the outer shield immersed in a temperature-controlled water bath (Fig. 1). Temperatures of the three stages play an important role to keep adiabatic conditions (temperatures with differences <1 mK). In heating runs, a constant heating power $P$ is continuously supplied electrically to the resistive heater on the sample cell, and the temperature evolution as a function of time $T$
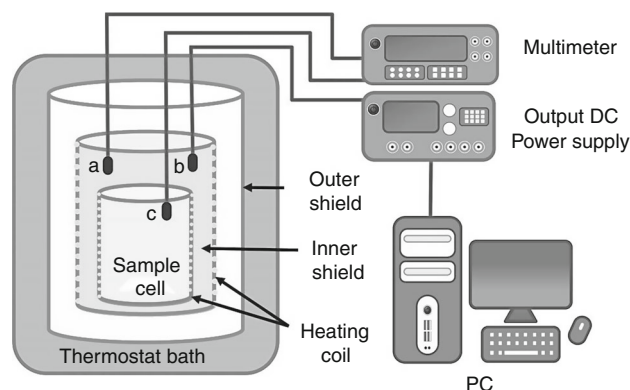


**Fig. 1** Adiabatic scanning calorimeter. **a** Shield thermistor, **b** shield platinum thermistor and **c** cell thermistor

(t) of the sample is measured with a thermistor on the sample holder. The total heating capacity is given by the following equation [35]:

$$C = C_s + C_h = P/(dT/dt) \qquad (1)$$

where $C_s$ and $C_h$ are the heat capacity of the sample and of the sample holder, respectively. $dT/dt$ is the time derivative of the sample temperature $T(t)$.

The specific heat [J (kg K)$^{-1}$] of each edible vegetable oil was obtained by dividing $C_s$ by the total mass of the sample (after subtracting $C_h$). All ASC measurements were done by duplicate, and the mean values are showed.

## Results and discussion

### Chemical and physical characterization

The fatty acid compositions of vegetable oils are shown in Table 3. The fatty acid with higher content in all samples was oleic acid (C18:1) with 68.94, 49.21, 38.65, 76.73, and 29.87 % for AO, PSO, EVFO, EVOO, and GSO, respectively. Linoleic acid (C18:2) was the second fatty acid in content, which is negatively correlated to the stability, because it is more susceptible to oxidation. The ratio of oleic to linoleic acids has great importance because of the nutritional properties as well as the high oxidative stability, which occurs when the content of oleic acid is higher when compared with linoleic acid content [36]. Therefore, EVOO has greater oxidative stability because it shows a good ratio of 76.73–5.42 %, and the worst oxidative stability comes from GSO with a ratio of 29.87–26.71 % for oleic to linoleic acid, respectively. Flaxseed oil becomes rancid quickly because of its high

linolenic acid content (21.71 %), since the polyunsaturated fatty acids (linoleic and linolenic) have lower oxidative stability. The percentage of saturated fatty acids in all oil samples is small when compared with the percentage of unsaturated fatty acids. Palmitic acid was the saturated fatty acid with higher percentage in the samples, ranged from 7.11 (AO) to 11.66 % for GSO. The fatty acid compositions of the AO, PSO, EVFO, EVOO, and GSO analyzed vary slightly from those published in the literature [37–42], which may differ oil to oil, depending on the place of production, latitude, climate, variety, and stage of fruit maturity or seed [43].

Table 4 summarizes the physical–chemical properties of the studied samples. The acid index is a measure of the free fatty acids (FFA) content in oils. All vegetable oils show minimal formation of FFA. The acid values ranged from $0.0659 \pm 0.0032$ to $1.1112 \pm 0.0155$ (oleic acid percentage) for AO to PSO, respectively. The high percentage of acid index in PSO ($1.1112 \pm 0.0155$), it could be due to the process to obtain this vegetable oil, through solvent extracting or mechanically pressing, as well as the contain of impurities, moisture, fungal invasion, and other factors that contribute to hydrolysis of TAGs and cause increases in FFA [43]. Higher values of FFA for sesame oil were found by Elleuch et al. [44], ranged from 2.37 to 10.73 as oleic acid percentage; however, in this article is not specified the purity of the samples.

Table 5 shows the standard values established for vegetable oils. The iodine index indicates the degree of oil unsaturation. The higher the iodine value, the greater unsaturation and susceptibility to oxidation, so that AO and EVOO ($92.22 \pm 0.0550$ and $92.30 \pm 0.8600$, respectively) are more saturated than PSO, EVFO, and GSO [4]. Only two oil samples are within established ranges for iodine

**Table 3** Fatty acids composition of vegetable oil samples

| Fatty acids | | Vegetable oils | | | | |
|---|---|---|---|---|---|---|
| | | AO/% | PSO/% | EVFO/% | EVOO/% | GSO/% |
| Lauric | (C12:0) | –[a] | 0.61 | –[a] | –[a] | 0.93 |
| Myristic | (C14:0) | 0.51 | 1.52 | 1.84 | 0.03 | 3.84 |
| Palmitic | (C16:0) | 7.11 | 11.29 | 8.96 | 9.64 | 11.66 |
| Palmitoleic | (C16:1) | 1.53 | 1.53 | 0.25 | 0.79 | 0.31 |
| Stearic | (C18:0) | 2.21 | 7.19 | 8.27 | 3.27 | 7.89 |
| Oleic | (C18:1) | 68.94 | 49.21 | 38.65 | 76.73 | 29.87 |
| Linoleic | (C18:2) | 13.25 | 21.1 | 11.62 | 5.42 | 26.71 |
| Linolenic | (C18:3) | 2.29 | –[a] | 21.71 | 0.54 | –[a] |
| Saturated | | 11.85 | 23.94 | 21.16 | 14.24 | 30.33 |
| Unsaturated | | 88.14 | 76.05 | 78.84 | 85.76 | 69.67 |

[a] It was not determined

**Table 4** Vegetable oil quality indexes

| | Vegetable oils | | | | |
|---|---|---|---|---|---|
| | AO | PSO | EVFO | EVOO | GSO |
| Acid index/% oleic acid | $0.0659 \pm 0.0032$ | $1.1112 \pm 0.0155$ | $0.6640 \pm 0.0120$ | $0.2259 \pm 0.0214$ | $0.0797 \pm 0.0031$ |
| Iodine index/gI$_2$ 100 g$^{-1}$ | $92.22 \pm 0.0550$ | $95.42 \pm 0.1400$ | $103.95 \pm 3.0100$ | $92.30 \pm 0.8600$ | $104.16 \pm 6.0900$ |
| Peroxide index/meq O$_2$ kg$^{-1}$ | $4.403 \pm 0.2440$ | $0.741 \pm 0.0870$ | $0.847 \pm 0.0580$ | $8.069 \pm 0.4330$ | $2.898 \pm 0.1570$ |
| Saponification index/mg KOH g$^{-1}$ | $162.942 \pm 0.4220$ | $158.652 \pm 0.5840$ | $160.610 \pm 1.1670$ | $164.283 \pm 0.4000$ | $160.963 \pm 0.1090$ |
| Unsaponifiable matter/% | $2.572 \pm 0.0270$ | $5.930 \pm 0.0450$ | $3.979 \pm 0.0850$ | $2.361 \pm 0.1470$ | $3.393 \pm 0.9800$ |
| Sg (est.) | 0.90929 | 0.90845 | 0.91024 | 0.90971 | 0.91037 |

**Table 5** Physical and chemical standard properties for the studied vegetable oils

| | Vegetable oils | | | | |
|---|---|---|---|---|---|
| | AO [48, 49] | PSO [38, 50] | EVFO [51–53] | EVOO [39] | GSO [50, 54] |
| Acid index/% oleic acid | $\leq 1.5$ | $\leq 0.05$ | 0.304 | 0.13–0.20 | 0.37–1.47 |
| Iodine index/gI$_2$ 100 g$^{-1}$ | 85–90 | 104–120 | 155–205 | 75–94 | 103–135 |
| Peroxide index/meq O$_2$ kg$^{-1}$ | $\leq 10$ | $\leq 2 - \leq 10$ | $\leq 2$ | $\leq 20$ | $\leq 10$ |
| Saponification index/mg KOH g$^{-1}$ | 177–198 | 186–195 | 188–195 | 184–196 | 187–195 |
| Unsaponifiable matter/% | 1–1.5 | $\leq 2 - \leq 20$ g kg$^{-1}$ | $\leq 1.5$ | $\leq 15$ g kg$^{-1}$ | $\leq 1.5 - \leq 28$ g kg$^{-1}$ |

index (EVOO and GSO). Lower iodine values, ranged from 119.1 to 119.8 and 81.87 for SO and EVOO, respectively, were reported by Yermanos et al. [45], and Henna Lu and Tan [46].

Elevated peroxide values indicate that lipid oxidation has taken place, and it is measured as reactive oxygen content in terms of milliequivalents per 1000 g of fat. All of vegetable oils studied are within the established range (Table 5), despite the high peroxide value of EVOO ($8.069 \pm 0.4330$), remains within the range published by the International Olive Oil Council (for EVOO, $\leq 20$) and it is similar to that reported by Gutfinger [47].

Saponification index provides the information of the average molecular weight of all fatty acids present. The saponification value is expressed as the amount of potassium hydroxide (KOH) in milligrams required to saponify 1 g of fat or oil under the specified conditions. From molecular point of view, one mole of oil requires three moles of KOH to complete saponification, because there are three ester bonds in one oil molecule, i.e., the oils with high molecular weight have lower saponification values than those with low molecular weight. The obtained saponification values are similar between the studied vegetable oils, $162.942 \pm 0.4220$, $158.652 \pm 0.5840$, $160.610 \pm 1.1670$, $164.283 \pm 0.4000$, and $160.963 \pm 0.1090$ for AO, PSO,

EVFO, EVOO, and GSO, respectively. Low saponification values were observed in all samples when compared with the established ranges for each type of oil (Table 5).

Unsaponifiable matter includes sterols, hydrocarbons, tocopherols, pigments, and other components of higher molecular weight which are insoluble in water and also cannot be saponified by alkalis. The level of unsaponifiable matter of all studied vegetable oils was higher than the established standards for each kind of vegetable oil (Table 5).

Specific gravity was estimated from saponification and iodine indexes of the different vegetable oils. The method to estimate the specific gravity for vegetable oils was developed by Lund [43]. The relation is:

$$sg(15°) = 0.8475 + 0.00030\text{SV} + 0.0014\text{IV} \qquad (2)$$

where $sg$ is the specific gravity of the vegetable oil, compared to water at 15 °C, SV and IV are the oil saponification and iodine indexes, respectively. The estimated $sg$ values for the studied oils are shown in Table 4.

**Thermal characterization**

From the ASC data, specific heat was obtained for the studied vegetable oils. Figure 2 shows the temperature dependence of the specific heat as calculated from Eq. (1)
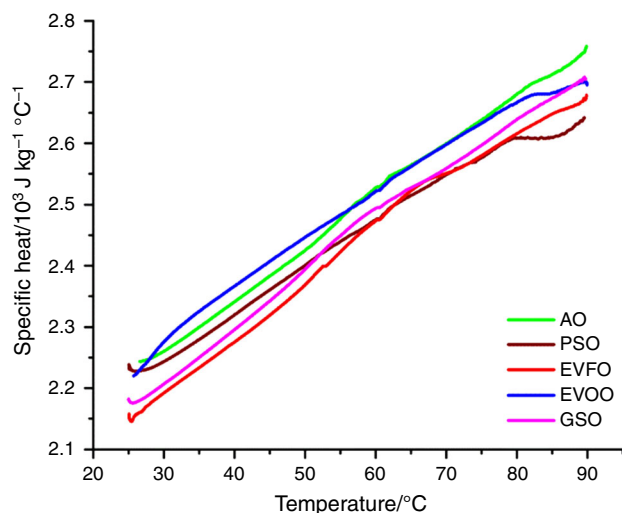
**Fig. 2** Specific heat of vegetable oils measured by ASC

and divided by the total mass of each vegetable oil in the temperature range from 25 to 90 °C. Table 6 shows the specific heat values at different temperatures.

Figure 2 shows that as oleic acid content (monounsaturated fatty acid) is higher, the specific heat values in the oil samples are higher; i.e., the specific heat increases to a higher degree of unsaturation [55]. AO and EVOO showed a high specific heat related with the degree of unsaturated acid (88.14 and 85.76 %, respectively). Samyn et al. [56] studied the quality of some vegetable oils by modulated DSC, they reported lower values of specific heat than traditional calorimetric measurements (at 50 °C), 1.49, 1.58, 1.63, 1.85, and 3.2 J (g °C)$^{-1}$ for castor oil, palm oil, canola oil, corn oil, sunflower oil, and soy oil, respectively. Also they concluded that specific heat depends on the unsaturation degree.

A particular case was observed, EVFO that has higher unsaturated fatty acid content (78.84 %) than PSO and GSO (76.05, 69.67 %, respectively), it is expected that its specific heat was higher than PSO and GSO; however, specific heat of EVFO is slightly lower compared with these oils. The low specific heat could be related to the fact that the percentage of polyunsaturated acids (C18: 2, C18: 3; 11.62 %, 21.71 %, respectively) is higher than the

**Table 6** Specific heat and slope values of vegetable oils

| $T/°C$ | Specific heat/$10^3$ J kg$^{-1}$ °C$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | AO | | PSO | | EVFO | |
| | $c_p$ (exp.) | $c_p$ (est.) | $c_p$ (exp.) | $c_p$ (est.) | $c_p$ (exp.) | $c_p$ (est.) |
| 25 | 2.2091 ± 0.04 | 2.2495 | 2.2166 ± 0.02 | 2.2318 | 2.1223 ± 0.02 | 2.1952 |
| 30 | 2.2293 ± 0.03 | 2.2603 | 2.2306 ± 0.01 | 2.2430 | 2.1663 ± 0.02 | 2.2066 |
| 40 | 2.3095 ± 0.03 | 2.2825 | 2.3070 ± 0.01 | 2.2658 | 2.2490 ± 0.02 | 2.2299 |
| 50 | 2.3963 ± 0.02 | 2.3053 | 2.3942 ± 0.01 | 2.2892 | 2.3307 ± 0.03 | 2.2537 |
| 60 | 2.4860 ± 0.04 | 2.3286 | 2.4842 ± 0.01 | 2.3131 | 2.4208 ± 0.05 | 2.2780 |
| 70 | 2.5621 ± 0.03 | 2.3524 | 2.5567 ± 0.01 | 2.3375 | 2.4944 ± 0.05 | 2.3027 |
| 80 | 2.6420 ± 0.03 | 2.3765 | 2.6336 ± 0.02 | 2.3622 | 2.5702 ± 0.04 | 2.3277 |
| 90 | 2.7034 ± 0.05 | 2.4009 | 2.6923 ± 0.06 | 2.3872 | 2.6406 ± 0.03 | 2.3530 |
| Slope | 0.00828 | $R^2 = 0.9978$ | 0.00746 | $R^2 = 0.9982$ | 0.00839 | $R^2 = 0.9910$ |

| $T/°C$ | Specific heat/$10^3$ J kg$^{-1}$ °C$^{-1}$ | | | |
|---|---|---|---|---|
| | EVOO | | GSO | |
| | $c_p$ (exp.) | $c_p$ (est.) | $c_p$ (exp.) | $c_p$ (est.) |
| 25 | 2.2261 ± 0.01 | 2.2661 | 2.1844 ± 0.01 | 2.1687 |
| 30 | 2.2652 ± 0.01 | 2.2768 | 2.2191 ± 0.01 | 2.1811 |
| 40 | 2.3515 ± 0.01 | 2.2988 | 2.2987 ± 0.01 | 2.2065 |
| 50 | 2.4316 ± 0.01 | 2.3215 | 2.3840 ± 0.02 | 2.2323 |
| 60 | 2.5119 ± 0.01 | 2.3446 | 2.4751 ± 0.01 | 2.2586 |
| 70 | 2.5905 ± 0.01 | 2.3683 | 2.5471 ± 0.01 | 2.2852 |
| 80 | 2.6602 ± 0.01 | 2.3923 | 2.6243 ± 0.01 | 2.3121 |
| 90 | 2.6969 ± 0.01 | 2.4166 | 2.6750 ± 0.02 | 2.3393 |
| Slope | 0.00788 | $R^2 = 0.9989$ | 0.00811 | $R^2 = 0.9953$ |

percentage of polyunsaturated acids contained in PSO and GSO, since the increase in double bonds in the fatty acid chains causes a decrease in the specific heat of the oil [43]. Another way to observe the unsaturation or presence of double bonds is through the iodine index; a high value indicates a large number of double bonds in the structure of the fatty acids in the vegetable oil, and therefore EVFO and GSO with the higher iodine values, $103.95 \pm 3.01$ and $104.16 \pm 6.09$ (gI$_2$/100 g), respectively, show low specific heat values due to percentage of polyunsaturated fatty acids [43].

A similar thermal study of vegetable oils were reported by Pardauil et al. [57], they found that the melting enthalpy is related with the saturation and unsaturation degree of oils studied, and Li et al. [58] obtained by DSC different endothermic and exothermic peaks for camellia oil linked with the content of saturated and unsaturated TAG and fatty acids, which show that thermal behavior is related with fatty acids composition of vegetable oils.

A linear fit to the curves of specific heat for each vegetable oil studied was performed. Figure 3 shows the linear fit to the specific heat curve of AO. The slopes of each linear fit are shown in Table 6. The oils with a higher slope were GSO and EVFO, which could be related to the polyunsaturated fatty acids contained in them. A higher slope indicates that it requires a further increase in energy to raise the temperature of a vegetable oil, in this case in a temperature ranging from 25 to 90 °C. Despite the high percentage of linoleic acid (C18: 2, 21.1 %) for PSO, its slope had the lower value, which could be related to the high content of unsaponifiable matter ($5.930 \pm 0.0450$ %), also is one of the oils with high amount of lignans, such as
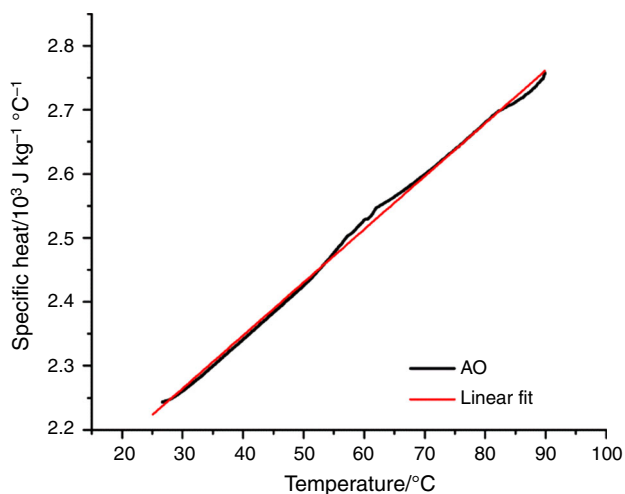
sesamol, sesamin and sesamolin, which act as natural antioxidants [59, 60].

The specific heat of oils has often been observed to increase linearly, as a function of the temperature, but nonlinear behavior at higher temperatures ($T > 70$ °C) has been observed by some researchers [13]. Then the oil specific heat ($c_p$) has been estimated by using the mixture properties corresponding to the fatty acid compositions to estimate $c_p$ for pure fatty acids by using the Rowlinson–Bondi (RB) equation [61]:

$$\left(c_p - c_p^0/R\right) = 1.45 + 0.45(1 - T_r)^{-1} + 0.25\omega\left[17.11 + 25.2(1 - T_r)^{1/3} T_r^{-1} + 1.742(1 - T_r)^{-1}\right]$$

(3)

where $c_p^0$ is the ideal gas specific heat capacity, $T_r$ is the reduced temperature, which was calculated as $T_r = T/T_c$ ($T_c$, critical temperature), and $\omega$ is the acentric factor, a parameter widely used as a measure of the complexity of a molecule with respect to both geometry and polarity. $c_p^0$ was calculated using the method of Rihany and Doraiswamy [62]:

$$c_p^0 = \Sigma a + T\Sigma b + T^2\Sigma c + T^3\Sigma d$$

(4)

The constants a, b, c, and d for several chemical groups were used to calculate the ideal gas capacity for pure fatty acids (FA) [63]. The $T_c$ and $\omega$ constants values of the FA of oils are listed in Table 7. To estimate $c_p$ must be considered the mixture of different fatty acids contained in each vegetable oil. Therefore, any parameter in the equation for oil can be replaced by the sum of the products of fatty acid molar percentages and the corresponding parameter for fatty acid [20].

The estimated values of $c_p$ for the oil samples at temperatures between 25 and 90 °C are shown in Table 6.



**Fig. 3** Linear fit to specific heat curve of AO

**Table 7** Primary properties of fatty acids [20]

| Fatty acids | $T_c$ | $\omega$ |
|---|---|---|
| Lauric | 756.21 | 0.8422 |
| Myristic | 779.07 | 0.9760 |
| Palmitic | 799.88 | 1.1087 |
| Palmitoleic | 800.34 | 1.0524 |
| Stearic | 819.00 | 1.2369 |
| Oleic | 819.14 | 1.1850 |
| Linoleic | 819.82 | 1.1294 |
| Linolenic | 820.23 | 1.0724 |

The error, between experimental and estimate values, in the range of 25–30 °C was $\pm 0.3$ % for AO, PSO, EVFO, and EVOO. In the case of GSO, this oil has an error of 1 % at 30 °C. The difference between the estimate and experimental values increases for higher temperatures (>30 °C), so the equation Rowlinson–Bondi is adjusted to specific heat of temperatures between 25 and 30 °C approximately. The differences between Rowlinson–Bondi equation of $c_p$ and those obtained experimentally by ASC could be due to the differences of heating scan rate; meanwhile, in the ASC the scan rate is around 100 mK min$^{-1}$, and in the case of DSC, the most common calorimetric technique to obtain $c_p$ is of the order of 10 K min$^{-1}$. Values of specific heat of PSO, EVOO, and GSO are higher than published by Fascina and Colley [15] and lower values for EVOO compared with the reported values of Santos et al. [55].

## Conclusions

The physical–chemical properties of AO, PSO, EVFO, EVOO, and GSO vary slightly from those published in the literature, and they are agreed with the values expected for oils with their fatty acid composition. Vegetable oil properties depend on many factors as geographic region, climate, process of oil production, and the characteristics of soil.

It was shown that the ASC technique is an effective tool to study, with high temperature resolution and high accuracy, the specific heat of vegetable oils.

Specific heat increases with the degree of monounsaturated acid (higher chain length; oleic fatty acid) but decreases with the degree of polyunsaturated acid (higher double bonds; Linoleic and Linolenic fatty acids) contained in vegetable oils, and there is a progressive increase in specific heat with increasing temperature.

The slope of specific heat curve fit could be related to the polyunsaturated fatty acids contained in them. The greater the slope the higher content of unsaturated acids present in the oil. The estimation of $c_p$ by the Rowlinson–Bondi equation for the studied oils agrees very well with the experimental data obtained by ASC mainly in temperature range of 25–30 °C.

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