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COMPARATIVE STUDY OF SPECIFIC HEAT CAPACITIES OF SOME VEGETABLE OILS OBTAINED BY DSC AND MICROWAVE OVEN

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Conventional methods have been proposed to determine thermal properties of edible vegetable oils. The evaluation of the applicability of DSC and microwave oven (MO) methods to determine the specific heat capacities of the edible vegetable oils was performed. It was observed that the specific heat capacities of each edible oil increased as a function of the saturation of the fatty acids.

Keywords: *DSC, edible oils, microwave, specific heat, thermal analysis*

Introduction

It is essential to know the thermal behavior of the edible vegetable oils, their chemical composition and physical properties for a rigorous control of processes and setting up standards for each specific use [1–3]. The specific heat capacity (C_p) can be considered as one of the possible physical properties.

The knowledge of the specific heat capacities of the oils and fats are quite useful to determine their behavior during different technological processes. Despite the specific heat capacities are similar for the triglycerides in their original physical state, they can increase as a function of the unsaturation of the fatty acids in the liquid and also in the solid state. It is important to emphasize that the numerical values of the specific heat capacities of liquid fats are twice larger compared to that of solid fats and also that the α form has a higher heat capacity than the β form exhibits. All these are directly related to the mobility of the oil and fat molecules in the different physical states [4].

The molar heat has a great importance in thermochemical processes and it is related to the heat of transformation, δQ_p, at constant pressure, p, as it is shown below:

$$dH=\delta Q_p \quad (1)$$

δQ_p depends on the heat change and does not depend on the reversibility of these processes. The specific heat capacity (C_p) is calculated by Eq. (2):

$$C_p = \frac{dH}{dT} = \frac{\delta Q_p}{dT} \quad (2)$$

In the last years, new analytical methods have been developed by researchers to characterize the processing and storage conditions. The application of thermoanalytical methods for this study and the characterization of oils and fats has increasing interest. Therefore, using thermoanalytical methods, as TG, DTA and DSC for the characterization of oils and fats has distinguished role in food industry [5–9].

In the present work, the specific heat capacities of some edible vegetable oils were determined by DSC and compared to the results obtained by microwave oven (MO) procedure.

Experimental

Materials

Six edible vegetable oil samples, soybean, olive, rapeseed, rice, corn, sunflower and two mixtures, olive (3%)/soybean (97%) and olive (30%)/sunflower (70%), were used in this study. The composition of edible vegetable oil samples was listed in Table 1.

DSC measurements

A Shimadzu model DSC-50 Differential Scanning Calorimeter was used. The edible vegetable oil samples were placed in aluminum crucibles, heated with β=5°C min^{-1} up to 30°C and were kept for 5 min then heated with β=10°C min^{-1} up to 200°C, under a dynamic atmosphere of nitrogen (50 mL min^{-1}). The initial sample masses were 22.0±0.5 mg. Three mea-

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Table 1 Composition of some edible vegetable oil samples

Edible oils	Fatty acids/%			Artificial antioxidants
	Monounsaturated	Polyunsaturated	Saturated	
Olive	71.3	12.7	16.0	–
Rapeseed	65.0	29.0	5.0	–
Sunflower	23.0	65.0	12.0	–
Corn	33.5	51.0	15.5	citric acid/TBHQ
Soybean	24.3	60.0	15.7	citric acid/TBHQ
Rice bran	40.8	40.1	19.1	–
Soybean/olive	29.2	57.0	13.8	–
Sunflower/olive	41.3	46.7	12.0	citric acid

surements were carried out for each sample: 1) measurements with empty crucible; 2) measurements with a reference material (alumina) with a known specific heat capacity; 3) measurements of the specific heats of the edible oil samples.

Microwave oven measurements

A BRASTEMP model 38MWO microwave oven without any adaptation was used to obtain the specific heat by the microwave oven method. The experiments consisted in monitoring the measurements of the heating temperature of water (used as standard) and of the edible oil samples under controlled conditions (P=900 W, t=30, 60 and 90 s). The sample mass was 150 g and a thermometer was used to measure the temperature periodically.

Results and discussion

DSC measurements

The relationship between the heat capacity of the sample C_s (sample pan support+sample pan+sample), of the reference material C_r (reference material support+reference material pan+reference material) and the heating rate (α) is expressed as:

$$C_S - C_r = \frac{T_S - T_r}{\alpha R} \quad (3)$$

where T_s is the temperature of the oil sample; T_r is the temperature of the reference material; R is the instrument constant (resistance between sample, reference material and furnace) and T_s–T_r is the DSC displacement, which is proportional to the difference between C_s and C_r. If the DSC displacement is S and the proportionality constant is k, the expression will be:

$$C_S – C_r = kS \quad (4)$$

Considering that the heat capacities of the edible vegetable oil sample support and the reference material support can be represented by C_S^h and C_r^h, the specific heat capacities of the reference material and of the oil sample can be represented by c_0 and c, furthermore the mass of the reference material and of the oil sample are m_0 and m, respectively, the following relationships are obtained:

$$C_S^h - C_r^h = kS_1 \quad (5)$$

$$(C_S^h + m_0c_0) - C_r^h = kS_2 \quad (6)$$

$$(C_S^h + mc) - C_r^h = kS_3 \quad (7)$$

where S_1, S_2, S_3 are the thermal displacements of the DSC related to the blank, the reference and the sample. Figure 1 shows the recorded DSC curves for an edible vegetable oil sample and for the blank and reference material.

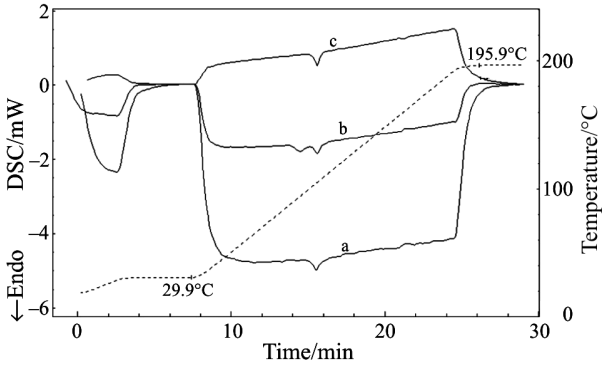

Fig. 1 DSC curves: a – edible oil sample, b – blank and c – reference material

From Eqs (5)–(7) the following equation is obtained:

$$\frac{mc}{m_0c_0} = \frac{S_3 - S_1}{S_2 - S_1} \quad (8)$$

Since the specific heat capacity of the reference material is known, the specific heat capacity of the edible oil samples can be calculated using Eq. (9):

$$c = \frac{m_0 c_0}{m} \frac{S_3 - S_1}{S_2 - S_1} \quad (9)$$

S_1, S_2 and S_3 are continuous functions related to the temperature, consequently the specific heat capacities can be determined continuously [5]. For all the investigated edible oils, the specific heats do not vary substantially and these values can be used for industrial engineering purposes. The specific heat values obtained from the DSC curves of the investigated vegetable edible oils in the range of 40–190°C are listed in Table 2.

In the investigated temperature range, the specific heat capacity values for the olive oil samples and for the mixtures containing olive oil were higher than those of the other oils. These differences can be attributed to a higher concentration of monounsaturated fatty acids are present in the olive oil, as it has been indicated in Table 1 [6]. In general, the results demonstrate that the specific heat capacity probably depends on the unsaturation degree of the analyzed oils.

It can be deduced from the experimental data that for the edible vegetable oils the specific heats did not vary substantially in the studied temperature range. A typical C_p curve obtained for rice and sunflower oils is shown in Fig. 2.

Comparing the results for the edible oil samples with those obtained by other authors [4, 7, 10], a small difference in the specific heat values were observed, which probably can be attributed to the used method.

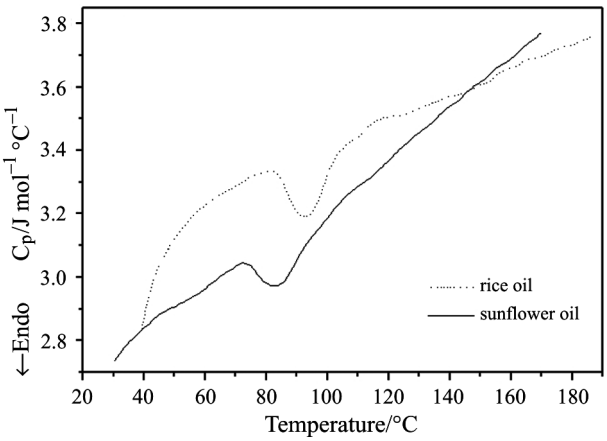

Fig. 2 Specific heat capacity variation of the rice and sunflower oils as a function of temperature

Microwave oven method

The evaluation of the specific heat capacity values was done by calculations which took into account the effectively absorbed power by the samples during heating, as it is shown by Eq. (10):

$$P = \frac{kC_p m\Delta T}{t} \quad (10)$$

Table 2 Specific heat capacities (C_p) of the edible oils between 40–190°C obtained by DSC

Temperature/°C	C_p/J g^{-1} K^{-1}							
	olive	soybean	corn	rice	sunflower	rapeseed	olive/sunflower	olive/soybean
40	2.721	2.269	2.039	1.860	1.833	1.833	2.741	2.731
50	2.820	2.398	2.187	1.980	1.984	1.962	2.844	2.839
60	2.890	2.470	2.250	2.032	2.030	2.008	2.933	2.907
70	2.957	2.495	2.289	2.067	2.056	2.038	2.997	2.962
80	3.052	2.531	2.319	2.089	2.076	2.059	3.057	3.034
90	2.976	2.478	2.273	2.045	2.023	2.007	3.014	2.982
100	3.092	2.547	2.346	2.109	2.070	2.077	3.113	3.052
110	3.197	2.618	2.420	2.180	2.123	2.147	3.208	3.185
120	3.293	2.646	2.462	2.201	2.152	2.165	3.300	3.286
130	3.337	2.669	2.490	2.218	2.164	2.187	3.376	3.368
140	3.483	2.703	2.527	2.238	2.181	2.217	3.483	3.457
150	3.590	2.728	2.561	2.260	2.197	2.240	3.586	3.539
160	3.701	2.756	2.605	2.287	2.219	2.271	3.694	3.615
170	3.778	2.784	2.640	2.310	2.236	2.284	3.765	3.689
180	3.868	2.812	2.673	2.342	2.252	2.319	3.828	3.770
190	3.910	2.780	2.655	2.347	2.241	2.320	3.888	3.546

Table 3 Specific heat capacities (C_p) of the edible vegetable oils

Edible oils	Temperature/°C	C_p/J g^{-1} K^{-1}	
		Microwave oven	DSC
Olive	79	2.575	3.019
	97	2.845	3.009
	110	2.882	3.197
Soybean	76	2.697	2.515
	97	2.892	2.496
	108	2.993	2.611
Corn	77	2.565	2.313
	99	2.821	2.333
	109	2.957	2.420
Rice	78	2.615	2.084
	97	2.899	2.061
	110	2.915	2.180
Sunflower	77	2.615	2.072
	97	2.850	2.036
	110	2.915	2.123
Rapeseed	80	2.481	2.059
	99	2.813	2.060
	110	2.915	2.147
Olive+sunflower	78	2.615	3.047
	101	2.704	3.118
	111	2.849	3.223
Olive+soybean	80	2.454	3.034
	97	2.845	3.004
	109	2.930	3.177

where P is the absorbed power (W), k is the conversion factor from cal/s to watt, C_p is the specific heat of the sample, m is the sample mass and ΔT is the variation of temperature during the exposition time (t) [11].

Before performing the experiments with the vegetable edible oil samples, water was used as [11]. The temperature variation was measured upon furnishing a high power for a defined time interval to 150±1 g of water. Using Eq. (10) and considering that the specific heat of water is 4.18 J g^{-1} K^{-1}, it was possible to calculate the power that the water effectively adsorbed during the microwave treatment. Using the values of the power effectively absorbed by the water and the temperature variation of the oils with the same mass and exposition time, the specific heat capacities of the edible vegetable oils could be determined using Eq. (10).

The specific heat capacity values obtained by the MO method (Table 3) show that there are no significant differences in the values of the edible vegetable oil samples analyzed, indicating the low sensitivity of the method.

Comparing these results with those obtained by DSC, it was observed that specific heat values are higher for all samples, except for these containing olive oil. These differences can be attributed to the amount of the oil samples used in the microwave, which are much higher than that have been used in the DSC experiments.

Conclusions

It was observed that the specific heat capacities of each edible oil increased as a function of the saturation of the fatty acids, despite of being similar for the triglycerides in their original state. Therefore it is concluded that the specific heats of the edible vegetable oils depend on the composition of fatty acids. Thus, it is important to know the specific heats of edible vegetable oils at constant pressure, as these data are helpful during long time of storing, freeze-drying, etc.

The development of an alternative method using DSC technique for determination of specific heat capacities of edible vegetable oils was studied in this work, is different of the methods employed by other researchers. The MO was used as a comparative technique and the results obtained indicated that the microwave oven method is unsatisfactory.

It was concluded, DSC is helpful tool to measure these values, being more rapid than the microwave oven measurements, requiring smaller sample amounts and often yielding greater accuracy.

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References

1 D. Lu and C. P. Wong, J. Therm. Anal. Cal., 59 (2000) 763.
2 J. C. O. Santos, A. V. Santos and A. G. Souza, Eur. J. Pharm. Sci., 13 (2001) S23.
3 M. Welolowski and J. Erecínska, Thermochim. Acta, 23 (1998) 137.
4 N. A. Morad, M. A. A. Kamal, F. Panau and T. W. Yew, J. Am. Oil Chem. Soc., 77 (2000) 1001.
5 J. C. O. Santos, A. G. Souza and I. M. G. Santos, J. Therm. Anal. Cal., 75 (2004) 419.
6 J. C. O. Santos, A. G. Souza and I. M. G. Santos, J. Food Sci., 67 (2002) 1393.
7 T. Kasprzycka-Guttmann and D. Odzeniak, Thermochim. Acta, 191 (1991) 41.
8 G. Litwinienko and T. Kasprzycka-Guttmann, Thermochim. Acta, 319 (1998) 185.
9 B. Kowalski, Thermochim. Acta, 184 (1991) 49.
10 T. Kasprzycka-Guttmann, M. Jarosz-Jarszewska and G. Litwinienko, Thermochim. Acta, 250 (1995) 197.
11 E. Percoraro, M. R. Davolos and M. Jafellici Jr., Quim. Nova, 20 (1997) 89.