EFFECT OF TEMPERATURE ON THE DENSITY AND THE COEFFICIENT OF THERMAL EXPANSION OF OLIVE OIL

César Augusto Canciam[1]

Resumo

A massa específica e o coeficiente de expansão térmica são usados na caracterização dos materiais e são dependentes da temperatura e da pressão. O objetivo desse trabalho foi avaliar o efeito da temperatura sobre a massa específica e o coeficiente de expansão térmica do azeite de oliva, entre 313,15 e 373,15 K e pressão de 1 atm, por meio da determinação da energia de ativação. A energia de ativação é um parâmetro que pode ser relacionado com a susceptibilidade térmica, de maneira que, materiais que apresentam baixos valores da energia de ativação são considerados menos susceptíveis à variação de temperatura. Utilizando uma equação do tipo Arrhenius e os dados experimentais da massa específica em função da temperatura, o valor encontrado para a energia de ativação foi de 718,3022 J mol-1. A partir da energia de ativação, foi encontrada uma expressão do coeficiente de expansão térmica em função desta grandeza e da temperatura absoluta. Na literatura, não foram encontrados valores experimentais da energia de ativação do azeite de oliva, o que dificultou a comparação.

Palavras-chave: energia de ativação; susceptibilidade térmica; dilatação.

Abstract

The density and the coefficient of thermal expansion are used to characterize the materials and are dependents on temperature and pressure. The objective of this work was to evaluate the effect of temperature on the density and the coefficient of thermal expansion of the olive oil, between 313.15 and 373.15 K and pressure of 1 atm, by determining the activation energy. Activation energy is a parameter that can be related to thermal susceptibility, so that, materials with low activation energy values are considered less susceptible to temperature variation. Using an Arrhenius-type equation and the experimental data of density in function of temperature, the value obtained for the activation energy was 718.3022 J mol-1. From the activation energy, an expression of the coefficient of thermal expansion as a function of this magnitude and the absolute temperature was found. In the literature, there are no experimental values of the activation energy of the olive oil, which complicated the comparison.

Keywords: activation energy; thermal susceptibility; dilatation.

1 Introduction

Density, heat capacity, thermal diffusivity, viscosity and thermal conductivity are considered as thermophysical properties of materials (MAGERROMOV *et al.*, 2008). Density is defined as the ratio between the mass of the material and its occupied volume. Data on this property are necessary to design and evaluate equipment such as evaporators, pumps, filters and mixers, and serve as a quality index for the final product (ALVARADO and ROMERO, 1989).

[1] Doutor em Engenharia Química pela Universidade Estadual de Maringá-UEM, professor titular da Universidade Tecnológica Federal do Paraná-UTFPR, câmpus Ponta Grossa. E-mail: canciam@utfpr.edu.br.

The knowledge of the thermophysical properties of materials is important from a thermodynamic and heat transfer point of view. Incropera and Dewitt (2019) comment that knowledge of thermophysical properties is essential for the efficient and economical design of processing operations involving heat transfer. Failures in equipment or in the design of processes can be attributed to the lack of this information due to the inadequate selection of values for the thermophysical properties used in the initial analysis of the systems under study.

Determining the density of liquids is useful in many industrial processes. In the food industry, it is common to use density as a process control parameter (ARAUJO, 2008). Parameters such as acidity index, saponification index, peroxide index, refractive index and density are used in the quality control of vegetable oils. Quality control is a measure adopted by organizations with the aim of uniformly defining standards in procedures, policies and actions (CARVALHO, 2017).

Almeida and coauthors (2011) comment that the determination of density in the food industries allows verifying if there was adulteration in the products. In Brazil, food fraud is established as adulteration and forgery. It is estimated that 98 % of frauds are motivated by economic gains, being carried out through processes that aim to attribute to the products qualities and requirements that do not have or hide poor structural and/or sanitary conditions (CARVALHO, 2017).

In November 2020, the Civil Police of the State of Espírito Santo (Brazil), through the Consumer Defense Police (Decon), dismantled a criminal organization specialized in the counterfeiting of olive oil. According to the investigation, the products sold as extra virgin olive oil were actually soy oil (BUISSINNE, 2020).

The density of a liquid reflects the degree of packing of its chemical species, which is a result of the intensity of the interactions between them. Volume and density are inversely proportional quantities. The stronger the interactions, the more packed the chemical species are and thus, volume will be smaller and, consequently, density will be greater (BROWN and HOLME, 2014).

Vegetable oils consist mainly of lipid structures, such as triacylglycerols and, in smaller amounts, of free fatty acids, monoacylglycerols and diagylglycerols, which are formed from degradation processes. In addition to having other components in small amounts, which vary according to the types of oils, such as sterols, tocopherols, phospholipids. Olive oil has mostly a fatty acid composition formed by oleic acid (55 - 83 %), linoleic acid (3.5 - 21.0 %), palmitic acid (7.5 - 20 %), stearic acid (0.5 - 5 %) and palmitoleic acid (0.3 - 3.5 %) (TONIN *et al.*, 2018).

The coefficient of thermal expansion is considered a thermal property of materials and it is related to the response of materials to temperature variation (CALLISTER, 2008). In general, when a material is heated, its dimensions increase. This dilation process occurs due to the increase in the degree of agitation of the chemical species that make up the material. When heating the material, the more agitated chemical species tend to move away, leading to an increase in the distance between them. This greater spacing is manifested through the increase in the dimensions of the material (BROWN and HOLME, 2014; HALLIDAY *et al.*, 2016).

The objective of this work was to evaluate the effect of temperature on the density and the coefficient of thermal expansion of olive oil, between 313.15 and 373.15 K and pressure of 1 atm. Therefore, a linear regression analysis of experimental data of the density of olive oil as a function of absolute temperature was performed.

2 Influence of temperature on the density e the coefficient of thermal expansion

Arrhenius-type equations allow verifying the effect of temperature on a physicochemical parameter, in addition to allowing its mathematical modeling (TSEN and KING, 2002; GIAP, 2010). Equation (1) corresponds to an Arrhenius-type equation and relates the density (ρ) with the absolute temperature (T) (TSEN and KING, 2002).

$$\rho = \rho_\infty \cdot \exp\left(\frac{E_a}{R \cdot T}\right) \tag{1}$$

Where ρ_∞ is density when the temperature tends to infinity (kg m^{-3}), E_a represents activation energy (J mol^{-1}) and R is the gas constant (J·mol^{-1}·K^{-1}).

The values of ρ_∞ and E_a can be obtained by the method of linearization of curves proposed by Freund (2004). Thus, Equation (1) is rewritten in the form of:

$$\ln \rho = \ln \rho_\infty + \left(\frac{E_a}{R}\right) \cdot \frac{1}{T} \tag{2}$$

The activation energy indicates the dependence of the density on the absolute temperature. In other words, materials with high activation energy present a great variation in the density as a function of the absolute temperature (TSEN and KING, 2002). Activation energy is a parameter that be related to thermal susceptibility, that is, it reflects the sensitivity of a material to temperature variations. Thus, materials with higher activation energy values are considered more susceptible to temperature variations (CANCIAM, 2014a; CANCIAM *et al.*, 2017).

The coefficient of thermal expansion (β) indicates the density variation caused by the temperature variation, while the pressure remains constant, thus is defined as (AMORIM, 2007):

$$\beta = \left(\frac{-1}{\rho}\right) \cdot \left(\frac{\partial \rho}{\partial T}\right)_P \tag{3}$$

In Equation (3), the negative sign corrects the expression, as the density variation in relation to the temperature variation is negative, that is, the final density is less than the initial density, after heating (AMORIM, 2007).

The volumetric expansion is variable and presents a direct relationship with chemical composition (JERÔNIMO *et al.*, 2012). Canciam (2014b) studied the influence of total solids content on the coefficient of thermal expansion of soursop juice and found that an increase in the total solids content caused a decrease in the coefficient of thermal expansion of soursop juice. The same behavior was observed in the work by Canciam (2012) who studied the influence of total solids content on the coefficient of thermal expansion of pineapple juice.

Canciam (2013) studied the effect of concentration of ethanol on the coefficient of thermal expansion of aqueous ethanol mixtures and observed that as the concentration of ethanol in the mixture increased, the value of the coefficient of thermal expansion for this mixture increased.

Santos and Vieira (2010) comment that the coefficient of thermal expansion is related to the chemical bond energy between chemical species, so that materials in which the chemical bonds are strong, the coefficient of thermal expansion is small.

Considering Equation (1), Equation (4) provides the coefficient of thermal expansion as a function of activation energy and absolute temperature.

$$\beta = \frac{E_a}{R \cdot T^2} \tag{4}$$

3 Materials and methods

Dikko (2015) experimentally determined the density of olive oil between 313.15 and 373.15 K and 1 atm. Table 1 lists the experimental data on the density of olive oil as a function of absolute temperature.

Table 1- Experimental values of the density of olive oil as a function of absolute temperature

T (K)	ρ (kg m^{-3})
313,15	888,89
323,15	882,47
333,15	876,12
343,15	870,34
353,15	863,71
363,15	856,60
373,15	850,15

Source: DIKKO (2015).

Equations (5), (6) and (7) are part of the linear regression analysis of the paired data of $\ln\rho$ and $\frac{1}{T}$. Equations (5) and (6) determine, respectively, the values of $\left(\frac{E_a}{R}\right)$ and $\ln\rho_\infty$, while Equation (7) determines the value of the linear correlation coefficient (r^2). Equations (5), (6) and (7) were adapted from the works of Triola (2017) and Canciam *et al*. (2017).

$$\frac{E_a}{R}=\frac{\left\{n\cdot\left[\sum_{i=1}^{n}\left(\frac{1}{T_i}\right)\cdot\ln\rho_i\right]-\left[\sum_{i=1}^{n}\left(\frac{1}{T_i}\right)\cdot\sum_{i=1}^{n}\ln\rho_i\right]\right\}}{\left\{n\cdot\left[\sum_{i=1}^{n}\left(\frac{1}{T_i}\right)^2\right]-\left[\sum_{i=1}^{n}\left(\frac{1}{T_i}\right)\right]^2\right\}} \tag{5}$$

$$\ln\rho_\infty=\frac{\left\{\left(\sum_{i=1}^{n}\ln\rho_i\right)-\left(\frac{E_a}{R}\right)\cdot\left(\sum_{i=1}^{n}\frac{1}{T_i}\right)\right\}}{n} \tag{6}$$

$$r^2=\frac{\left\{n\cdot\sum_{i=1}^{n}\left\{\left(\frac{1}{T_i}\right)\cdot(\ln\rho_i)\right\}-\left\{\left[\sum_{i=1}^{n}\left(\frac{1}{T_i}\right)\right]\cdot\left[\sum_{i=1}^{n}\ln\rho_i\right]\right\}\right\}}{\left\{\left\{\left[n\cdot\sum_{i=1}^{n}\left(\frac{1}{T_i}\right)^2\right]-\left[\sum_{i=1}^{n}\left(\frac{1}{T_i}\right)\right]^2\right\}^{1/2}\cdot\left\{\left[n\cdot\sum_{i=1}^{n}(\ln\rho_i)^2\right]-\left[\sum_{i=1}^{n}\ln\rho_i\right]^2\right\}^{1/2}\right\}} \tag{7}$$

In Equations (5), (6) and (7), n corresponds to the number of paired data of $\ln\rho$ in function of $\frac{1}{T}$, which is equivalent to 7, according to Table 1.

Based on the data indicated in Table 1, the values of $\left(\frac{E_a}{R}\right)$ and $\ln\rho_\infty$ were obtained from the linear regression analysis of the values $\ln\rho$ as a function of $\frac{1}{T}$.

The coefficient of thermal expansion of olive oil was determined from Equation (4). In the calculation to determine the activation energy and the coefficient of thermal expansion, it was considered that the value of the gas constant (R) is equivalent to 8.314 J mol^{-1} K^{-1} (LIAO *et al.*, 2021).

Equation (8) calculates the percentage value ($V\%$) between the coefficient of thermal expansion at the initial temperature ($\beta_{initial}$) and the coefficient of thermal expansion at the final temperature (β_{final}).

$$V\% = \frac{\left(\beta_{final} - \beta_{initial}\right)\cdot 100}{\beta_{initial}} \tag{8}$$

Equation (8) was adapted from the work of Lessa (2021).

4 Results and discussion

Table 2 lists the results obtained through Equations (5), (6) and (7). It can be seen in Table 2 that the linear correlation coefficient (r^2) is close to unity. Regarding this coefficient, Pinheiros and coauthors (2009) comment that this parameter measures the linear interdependence between the variables and assesses the quality of the adjustment, that is, the closer the linear correlation coefficient is to the unit, the better the adjustment of the straight line in relation to the points of dispersion.

Table 2 - Results obtained from linear regression analysis

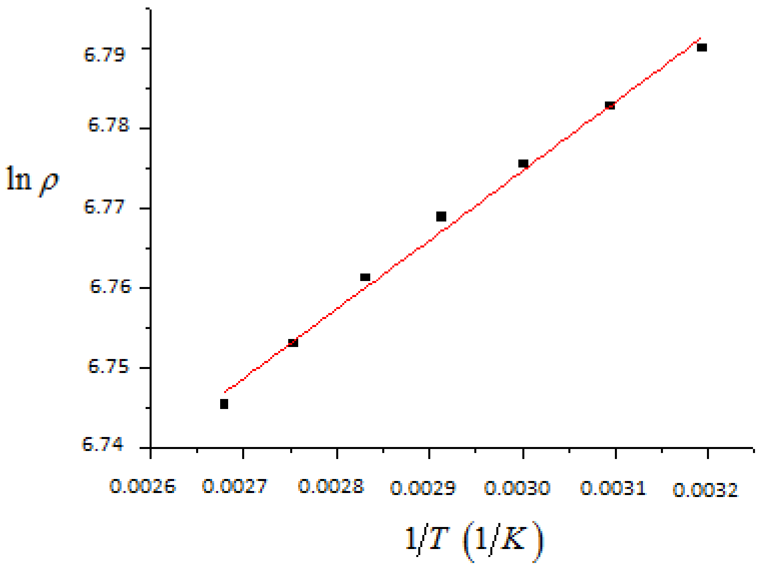
$\left(\frac{E_a}{R}\right)$	$\ln \rho_{\infty}$	r^2
86.3967	6.5155	0.9929

Source: Elaborated by the author.

Carvalho (2005) comments that the linear correlation is classified as very strong when the values of the linear correlation coefficient are greater than or equal to 0.90 and less than 1.0. Thus, the linear correlation is classified as very strong.

Figure 1 illustrates the graph of $\ln \rho$ versus $\frac{1}{T}$ for olive oil.

Figure 1 - Graph of $\ln \rho$ a function of $\frac{1}{T}$ for olive oil



Source: Elaborated by the author.

Based on Table 2, the value obtained for the activation energy (E_a) is equivalent to 718.3022 J mol^{-1} and value of the density when the temperature tends to infinity (ρ_∞) is 675.5316 kg m^{-3}.

Table 3 lists the analysis of variance (ANOVA) of the linear regression analysis performed for olive oil. In this table, GL and SQM correspond to degrees of freedom and the sum of mean squares, respectively. QM is mean square and $Fcal$ is the calculated F value. Included in this table, is the $p-value$.

According to Triola (2017), in the simple linear regression model, the function of the F test is to test the significance of the effect of X on Y, that is, to test the significance of the effect of temperature on the density. Considering a significance level of 5 %, the $Ftab$ value equivalent to 6.61. In Table 3, the $Fcal$ value is greater than the $Ftab$ value, the ANOVA results suggest that the linear regression as a whole makes sense, that is, the explanatory variable "temperature" globally influences the explained variable "density".

Table 3 - ANOVA and $p-value$ for linear regression analysis

Source of variation	GL	SQM	QM	$Fcal$	$p-value$
Regression	1	0.0015	0.0015	842.3930	9.0993x10^{-7}
Residual	5	9.0775x10^{-6}	1.8155x10^{-6}		
Total	6	0.0015			

Source: Elaborated by the author.

Ara and coauthors (2003) comment that the $p-value$ varies between zero and one. It is assumed as a critical value, values less than or equal to 0.05. Thus, 5 % chance of error is assumed as a safety margin, or a 95 % chance of being right. In Table 3, it can be seen that the $p-value$ is small, suggesting that the error safety margin is small.

Searching in the literature for works associated with the effect of temperature on the density of the olive oil by determining the activation energy, it was found that this study was absent; which made the analysis of the results obtained in this work difficult.

Canciam (2014a) studied the effect of temperature on the density of methyl biodiesels from different sources and observed that the activation energy (E_a) of methyl castor bean biodiesel was equality 722.279 J mol^{-1}. This value is close to the value found for the activation energy of olive oil (718.3022 J mol^{-1}).

From the activation energy, Equation 8 indicates the effect of temperature on the coefficient of thermal expansion of olive oil.

$$\beta = \frac{86.3967}{T^2} \tag{9}$$

Table 4 lists the results obtained through Equation (9). It can be seen in this table, which as the temperature increases, the coefficient of thermal expansion decreases.

Based on Table 4, Figure 2 illustrates the graph of the coefficient of thermal expansion (β) of olive oil in function of absolute temperature.

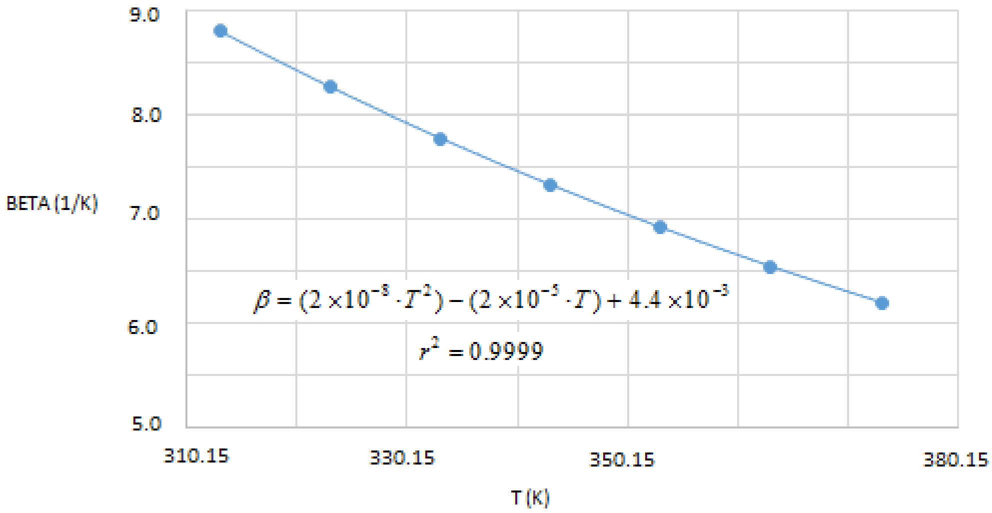
The curve depicted in Figure 2 indicates that the coefficient of thermal expansion of olive oil decreases with squared absolute temperature.

Table 4 - Calculated values of the coefficient of thermal expansion of olive oil as a function of absolute temperature

T (K)	β (K^{-1}) x 10^{-4}
313,15	8,8103
323,15	8,2735
333,15	7,7843
343,15	7,3372
353,15	6,9275
363,15	6,5513
373,15	6,2048

Source: Elaborated by the author.

Figure 2 - Graph of β as a function of absolute temperature



Source: Elaborated by the author.

The percentage value ($V\%$) between the coefficient of thermal expansion at the initial temperature ($\beta_{initial}$) and the coefficient of thermal expansion at the final temperature (β_{final}) is equivalent to -29.57 %. This means that the value of the coefficient of thermal expansion at the final temperature (β_{final}) decreased by 29.57% of the value of the coefficient of thermal expansion at the initial temperature ($\beta_{initial}$).

Similarly, for the density of olive oil, the percentage value between the density at the initial temperature and the density at the final temperature is equivalent to -4.36 %. This means that the value of the density at the final temperature decreased by 4.36 % of the value of the density at the initial temperature.

5 Conclusion

Using an Arrhenius-type equation, the found value of activation energy for the density of olive oil was 718.3022 J mol^{-1} and linear regression analysis revealed that the linear correlation was classified as very strong.

In the literature, no result was found for this parameter, which made the comparison difficult. Comparing with values found in the literature, it was observed that the activation energy of olive oil is close to the activation energy of methyl castor bean biodiesel.

The results suggest that the coefficient of thermal expansion of olive oil decreases with squared absolute temperature and that value of the coefficient of thermal expansion at the final temperature decreased by 29.57 % of the value of the coefficient of thermal expansion at the initial temperature.

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