Research Article

On the Thermal Effusivity of Bovine Milk

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Thermal diffusivity, conductivity, and effusivity are parameters that can be measured using photoacoustic techniques. Both thermal diffusivity and conductivity have already been measured for bovine milk. To complete its thermal characterization, this paper deals with the thermal effusivity of commercial bovine milk with a different fat content. The thermal effusivity ε obtained for skimmed, partly skimmed, and whole milks is $0.153 \text{ W cm}^{-2} \text{ s}^{1/2} \text{ K}^{-1}$, $0.144 \text{ W cm}^{-2} \text{ s}^{1/2} \text{ K}^{-1}$, and $0.140 \text{ W cm}^{-2} \text{ s}^{1/2} \text{ K}^{-1}$, respectively, with the uncertainty being less than 5%. It was observed that the thermal effusivity decreases with the increase in the fat content. For the first time, it is observed that the thermal effusivity is a linear function of the logarithm of the fat content. The comparison of our results with previous results for milk from Slovakia revealed different thermal effusivity values. This might be due to regional differences in the milk composition and could be used as a criterion to identify the milk provenience.

1. Introduction

The thermal conductivity k ($\text{W cm}^{-1} \text{ K}^{-1}$), thermal diffusivity α ($\text{cm}^2 \text{ s}^{-1}$), and thermal effusivity ε ($\text{W cm}^{-2} \text{ s}^{1/2} \text{ K}^{-1}$) are three dynamic thermophysical parameters unique to each material and related among them through the relation $\varepsilon = k/\alpha^{1/2}$. Thermal effusivity ε , also termed thermal impedance, measures the ability of matter to exchange heat with its environment [1]. These thermal parameters present high sensitivity to changes in microstructural variables, composition, temperature, and specific processing conditions. Handling these thermal parameters data contributes to refinements in optimization of food processing conditions, techniques, and equipment, resulting in improved quality and storage of foods as milk.

Milk is a complex, nutritious liquid that contains several substances that are either in solution, suspension, or emulsion in water. The fat and fat soluble vitamins in it are in the form of an emulsion. The casein micelles and the fat globules are responsible for most of its physical characteristics. The composition of milk varies considerably with the breed of cow and other factors. The nutritional value of milk as a

whole is greater than the value of its individual nutrients because of its unique nutritional balance. The amount of water in milk reflects that balance [2].

Thermal properties have been measured in the past for milk with a different fat content. Spells [3] measured the thermal conductivity for different liquids of biological interest, as human blood, rat blood, cow's milk, skimmed milk, egg white, and egg yolk. Spells reported that, at about 35°C , the thermal conductivity for cow's milk (4.42% fat content) is 0.532 W/(mK) and for skimmed milk (1.4% fat content) is 0.574 W/(mK) . In that report, it is also correlated the thermal conductivity to the water content of the biological fluids measured, and he observed a linear correlation above 50% water content.

Bozikova [4] measured the thermal conductivity and diffusivity for several foods, in function of temperature, using an instrument Isomet. Milk samples with a different fat content were also measured. For 20°C , thermal conductivity (W/mK) and diffusivity ($10^{-8} \text{ m}^2/\text{s}$) were 0.592 and 12.9 for 0.5% fat content, 0.556 and 13.45 for 1.5% fat content, and 0.54 and 13.86 for 3.5% fat content. It was also observed in that report that thermal conductivity decreases when fat

content increases, but thermal diffusivity increases when fat content increases.

Gustavsson and Gustafsson [5] also measured the thermal conductivity for milk as a function of fat content. As the content of water is higher for several biological fluids, they assume that the specific heat per unit volume (ρC_p) must be fairly close to that of pure water for the calculation of milk thermal conductivity. In that report, the milk was purchased on the local market and the fat concentrations were (a) less than 0.1%, (b) 0.5%, (c) 1.5%, and (d) 3%. The thermal conductivities (W/mK) reported were (a) 0.564, (b) 0.556, (c) 0.549, and (d) 0.536. The last three values follow a linear dependence with the fat content, with the first one above the linear prediction (see Figure 4 at [5]). Interestingly, when Gustavsson and Gustafsson data are plotted in function of water content, a linear dependence is observed as Spells [3] showed. It looks like thermal conductivity k is more sensible to water content than to fat content of milk.

The relation among these parameters is $k/\alpha = \rho C_p$. If ρC_p is constant for milk, in this case the one for water 4.17 MJ/(m³K), then α can be estimated from the k values. Doing this for the Gustavsson and Gustafsson [5] data it is observed that the thermal diffusivity decreases when fat content increases, a result that is contrary to that of Bozikova [4]. So, the assumption of ρC_p of milk similar to that one of water must be reviewed to resolve that discrepancy.

The photothermal (PT) methods are classes of nondestructive analytical techniques, capable of determining both thermal and optical properties of any material based on the interaction of modulated light with matter. They offer a wide range of detection schemes and hence permit the selection of the detection technique to suit the material demands [6–9].

Among many PT methods, the most widely used are those based on the photoacoustic (PA) effect, described by Rosencwaig and Gersho [10], and several of its variants [11, 12]. The PA effect consists in the transformation of pulsed electromagnetic energy (chopped light) into mechanical energy (sound). The relation among the pulse frequency and the sound amplitude and phase permits the determination of the thermal diffusivity, conductivity, and effusivity. The PA methodology was explored for determining the iron content of milk protein concentrates [13], for studying the extent of adulteration of powdered skimmed milk with whey powder under controlled thermal treatment [14], and also for a direct determination of the phenolic content in red sorghum flours [15].

The closed PA cell technique applied to liquid samples allows the direct determination of the thermal effusivity ε [16]. For milk samples, as the thermal diffusivity and conductivity have been measured [3–5], the thermal effusivity can be estimated through the relation among them. A direct determination of the parameter ε eliminates the error propagation associated to the mathematical calculus. The main goal of the present study was to determine experimentally, for the first time, the thermal effusivity ε of three different kinds of commercial bovine milk with a different fat content, using the conventional closed PA cell technique.

FIGURE 1: Diagram of the experimental setup of the closed photoacoustic cell.

2. Theory

The methodology used to determine the thermal effusivity was similar to the one reported by Balderas-Lopez et al. [16]. The diagram of the PA experimental setup is shown at Figure 1, corresponding with that reported by Rosencwaig and Gersho [10] (also termed the RG model). The PA cell used has two faces, one of them closed with a glass window and the other side closed with a black-painted aluminum (Al) foil. The incident light geometry used was the frontal one, with the chopped light first hitting the glass window and just after the surface of the Al foil. The fundamental idea of determining the thermal effusivity of liquid by the closed PA cell technique is to measure the PA signal when the sample holder is empty (air) and when it is filled with the liquid sample. Both PA signals are used to calculate the appropriate normalized PA signal that must be analyzed to calculate the thermal effusivity, as discussed below.

Once the thermal diffusion process is the main source of the acoustic signal generation, the complete solution to the PA signal following the RG model is given by [10]

$$Q = \frac{Y}{a_g(\beta^2 - \sigma_s^2)} \times \left(\frac{(r-1)(b+1)\exp(\sigma_s l) - (r+1)(b-1)\exp(-\sigma_s l)}{(g+1)(b+1)\exp(\sigma_s l) - (g-1)(b-1)\exp(-\sigma_s l)} + \frac{2(b-r)\exp(-\beta l)}{(g+1)(b+1)\exp(\sigma_s l) - (g-1)(b-1)\exp(-\sigma_s l)} \right), \quad (1)$$

where the indexes s , g , and b are related, respectively, to sample, gas, and backing; $Y = (\beta I_0 \gamma P_0) \cdot (2^{3/2} k_s l_g T_0)^{-1}$; β is the optical absorption coefficient of the light absorbing sample; I_0 is the incident radiation intensity; γ is the adiabatic coefficient of the gas; P_0 and T_0 are, respectively, the ambient pressure and temperature in the PA chamber; l_g is the gas chamber length; $r = (1-j)\beta/(2a_s)$ is the thermo-optical coupling of the sample and $j = (-1)^{1/2}$ is the imaginary unit; $\sigma_s = (1+j)a_s$ is the complex thermal diffusion coefficient, where $a_i = (\pi \cdot f/\alpha_i)^{1/2}$ is the thermal diffusion coefficient; and finally $b = \varepsilon_b/\varepsilon_s$ and $g = \varepsilon_g/\varepsilon_s$ estimate the thermal couplings between the neighbor mediums.

In this study, the black-painted Al foil is placed as the light absorbing sample and can be considered an optically opaque material ($\beta l_s \gg 1$, or $\exp(-\beta l_s) \approx 0$). As the gas chamber is filled with air $g = 2.4 \times 10^{-4} \ll 1$. The thickness of the Al foil used in this paper was $46 \mu\text{m}$ and in this case, as $\alpha_{\text{Al}} = 0.98 \text{ cm}^2/\text{s}$, the cutting frequency $f_c = \alpha_s/(\pi \cdot l_s^2)$, as defined by the RG model [10], would be 14.7 KHz. Using measuring frequencies up to 150 Hz, the thermal regime must be thermally thin ($f \ll f_c$, or $1/a_s \gg l_s$) and the following approach is valid: $\exp(\pm \sigma_s l_s) \approx 1 \pm \sigma_s l_s = (1 \pm a_s l_s) \pm j a_s l_s$. Also the expression $a_s l_s$ can be written as $(f/f_c)^{1/2}$, presenting relative values between the experimental frequencies and the cutting frequency. Equation (1) can be written as

$$Q = \frac{Y}{a_g(\beta^2 - \sigma_s^2)} \times \left(\frac{(r-1)(b+1)(1+\sigma_s l_s) - (r+1)(b-1)(1-\sigma_s l_s)}{(b+1)(1+\sigma_s l_s) + (b-1)(1-\sigma_s l_s)} \right). \quad (2)$$

Under the optically opaque and thermally thin conditions $r-1 \approx r+1 \approx r$.

In the absence of any sample, we have the reference measurement (Q_{ref}) and in this case $b = g \ll 1$. So, rewriting (2) and taking $x = a_s l_s$, we defined the normalized signal Q_N as the quotient among the reference and liquid signals $Q_N = Q_{\text{ref}}/Q_{\text{liq}}$, leading to

$$Q_N = \frac{1/\sigma_s l_s}{(1+\sigma_s l_s)/(b+\sigma_s l_s)} \approx \frac{b+\sigma_s l_s}{\sigma_s l_s} = 1 + \frac{b}{(1+j)x} \quad (3)$$

$$= 1 + (1-j) \frac{b}{2x} = \left(1 + \frac{b}{2x}\right) - j \frac{b}{2x}.$$

The amplitude of the normalized signal is

$$|Q_N|^2 = 2 \left(\frac{b}{2x} \right)^2 + 2 \left(\frac{b}{2x} \right) + 1. \quad (4)$$

Equation (4) shows that to measure b , the square modulus $|Q_N|^2$ must be fitted to a parabola as function of $(f/f_c)^{-1/2}$ if $(f/f_c) \ll 1$. Once the Al foil is placed as the sample and the liquids are placed as the backing, the parameter b can be written as $b = \varepsilon_{\text{liq}}/\varepsilon_{\text{Al}}$. So, to determine ε_{liq} it is necessary to calculate the parameter b from the fitted experimental data.

3. Materials and Methods

The PA experimental setup was composed of a commercial diode laser (405 nm, 100 mW) used as the light source, a homemade two-beam PA cell coupled with an electret microphone (Sennheiser, model KE-4-211-2), and a dual-phase lock-in amplifier (Stanford Research System, model SR-530). Light was chopped in the range of 10–150 Hz using a mechanical chopper (Benthan, model 218) and directed to the PA chamber. All measurements were performed at room temperature. For each frequency, the data were collected

during 20 s (about one datum per second) and averaged to improve the signal to noise ratio, using always the same experimental conditions.

As previously described in Figure 1, the PA cell used has two faces, one of them closed with a glass window and the other side closed with an Al foil ($46 \pm 1 \mu\text{m}$) with just one black-painted surface, responsible for the absorption of the chopped light and consequently the generation of the PA signal, that is recorded by the lock-in amplifier. A thin vacuum grease layer placed between the closed PA cell housing, the glass window and the Al foil are enough to provide adequate sealing of the air chamber, where the generated PA signal is detected by a coupled microphone, avoiding leakages. The liquid was placed in a cylindrical plastic holder (10 mm height and 8 mm diameter) over the Al foil, ensuring a full coverage of the illuminated sample area. The thermal effusivity was estimated in distilled water and three types of commercial UHT (ultra-high temperature) milks with different fat concentrations (skimmed, less than 0.1% fat; partly skimmed, 1.0% fat; and whole, 3.0% fat), produced by *Elegê* (BRF, Brasil Food Inc., Brazil, <http://www.elege.com.br/>) and purchased at the local market.

4. Results and Discussion

The experimental setup was calibrated by measuring the thermal effusivity of distilled water. The PA signal produced by the empty sample holder and that obtained after filling the holder with distilled water are measured as a function of the light modulation frequency. It was observed that the amplitude of the PA signal produced by the empty sample holder is greater than that of sample holder containing any liquid. This indicates that the liquid sample is acting as a heat sink, where some part of the thermal energy generated by the aluminum is absorbed by the liquid.

The thermal effusivity ε was calculated from the plots shown in Figure 2, showing the variation of $|Q_N|^2$ as a function of $(f/f_c)^{1/2}$ and (4) was used to fit the data and calculate the adjustable parameter $b = \varepsilon_{\text{liq}}/\varepsilon_{\text{Al}}$. The measured value of the thermal effusivity for distilled water was $(0.157 \pm 0.0003 \text{ W cm}^{-2} \text{ s}^{1/2} \text{ K}^{-1})$ and is in a good agreement with reported values [16].

Since bovine milk is largely composed of water (about 90%), its thermal effusivity is expected to be very close to that of distilled water. In Table 1, values of the fitted parameters b obtained and the calculated thermal effusivity of the distilled water and milk samples are summarized, with the averaged error estimated to be less than 5%. These effusivity values of the bovine milk samples are in accordance with the effusivity values estimated from thermal diffusivity and conductivity values taken from the report by Bozikova [4]. From that report, the estimated values for ε are 0.164, 0.153, and $0.145 \text{ W cm}^{-2} \text{ s}^{1/2} \text{ K}^{-1}$, respectively, for 0.5%, 1.5%, and 3.5% fat content (temperature of 20°C). Comparing these values with the ones reported in Table 1, we observe that they are of the same magnitude order but greater than ours. This difference can be associated with regional differences in

FIGURE 2: Q_N^2 versus $(f_c/f)^{1/2}$ for the black-painted aluminum foil using as backing distilled water, skimmed milk, partly skimmed milk, and whole milk.

TABLE 1: Calculated thermal effusivity ε ($\text{W cm}^{-2} \text{s}^{1/2} \text{K}^{-1}$) for distilled water, skimmed milk, partly skimmed milk, and whole milk. ε_{ref} taken from Balderas-Lopez et al. [16].

Liquid sample	b	ε
Distilled water ($\varepsilon_{\text{ref}} = 0.1582$)	0.0655	0.1572
Skimmed milk	0.0638	0.1531
Partly skimmed milk	0.0601	0.1442
Whole milk	0.0583	0.1398

the milk content, as the milk analyzed by us is from Brazil and the ones analyzed by Bozikova [4] are from Slovakia, or can be associated to common variations in the thermal parameters of similar samples. More studies are necessary to elucidate the source of these differences.

Figure 3 shows a linear dependence of the thermal effusivity on the log of the fat content $\log_{10}(X_{\text{fat}})$, providing an equation for the linear regression as it follows:

$$\varepsilon = 0.144 - 0.009 * \log_{10}(X_{\text{fat}}) \quad (R = -0.99). \quad (5)$$

A similar linear regression can be obtained for Bozikova [4] data:

$$\varepsilon = 0.157 - 0.022 * \log_{10}(X_{\text{fat}}) \quad (R = -0.99), \quad (6)$$

where the main difference between these equations is that (6) was obtained from values estimated using the expression $\varepsilon = k/\alpha^{1/2}$ while (5) was obtained directly from our experimental data. Equations (5) and (6) are better than a linear relation in (X_{fat}) because they include the ε value for skimmed milk. Different to the thermal conductivity k , the thermal effusivity does not follow a linear dependence on the milk water content.

A similar correlation can be also observed with the energy content but it is more interesting to correlate with some

FIGURE 3: Thermal effusivity as a function of fat content (X_{fat}) for three commercial bovine milk samples. The axis of fat content is in decimal logarithm scale. Dot symbols: data calculated from the thermal diffusivity and conductivity in Bozikova [4]. Star symbol: data from Table 1. In both cases the line results from the linear fit.

specific content of the milk, since the energy content is associated with the composition of the food (fats, protein, carbohydrates, etc.). The decrease of thermal effusivity with the increase in the milk fat content has been observed also among the thermal effusivity and fat content in sour cream and mayonnaise [17]. In all these, cases the thermal conductivity and effusivity decrease when the fat content increases. This must happen because fat is a good thermal insulator and its increase in the milk or other media impede heat transport and exchange.

5. Conclusion

To complete the milk thermal characterization, since its thermal diffusivity and conductivity have been measured previously, thermal effusivity values of three bovine milk samples with different fat contents were directly measured using a PA technique for the first time. From this paper, it is concluded that the thermal effusivity decreases with increase in the fat content, similar to the thermal conductivity. For the first time, it is observed that the thermal effusivity is a linear function of the logarithm of the fat content. It was observed that results with milk from a different region (Slovakia) produced effusivity values different for the milk from Brazil. This might be due to regional differences in the milk composition and could be used as a criterion to identify the provenience of the milk.

Conflict of Interests

The authors declare that they do not have any financial relation with BRF (Brasil Food Incorporated).

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