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Thermal Diffusivity and Specific Heat of Bovine Milk Affected by Temperature and Composition

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Abstract

The sizing of equipment used in food processing, particularly heat exchangers and other equipment that require pumping of products, requires accurate data of thermophysical properties. Milk is one of the most processed liquid food fluids in the world and currently data on its thermophysical properties are limited. In a previous paper (Alcântara et al., 2010) density and dynamic viscosity data of bovine milk were presented and how these properties are affected by temperature and composition, in ranges commonly encountered in food processing. Here the thermal diffusivity and specific heat data for milk are presented, evaluating the effect of composition (moisture, fat, lactose, protein and minerals contents) and temperature (only for thermal diffusivity). Linear regression was used and the best models were selected based on the determination coefficient (R^2), lack of fit, significance parameters and root mean square error (RMSE) values. Predictive ability of fitted models was compared with Choi and Okos (1986) correlations. Thermal diffusivity ranged from (1.00 to 9.03) × 10-7 m2•s-1 and specific heat from (3.078 to 4.121) kJ•kg-1•K-1. Thermal diffusivity presented a polynomial quadratic behavior affected by temperature and composition, except for lactose concentration which showed no significant effect ($p>0.05$). For specific heat, increase in the moisture content led to an increase in the specific heat while elevations in fat, protein, lactose and mineral contents promoted a decrease of this property. In both cases the fitted models showed satisfactory R^2 values, non-significant lack of fit ($p>0.05$) and significant parameters ($p<0.05$), with RMSE values lower than Choi and Okos (1986) correlations. From the properties presented here and in the earlier paper, accurate calculations can be made for correct sizing and adaptation of equipment, as well as provide information of other thermophysical properties such as thermal conductivity and thermal expansion coefficient.

KEYWORDS: modeling, thermophysical properties, major constituents, milk

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1. Introduction

Milk plays an important in human diet due to its high nutritional value, providing almost all the macro and micronutrients in considerable quantities. It is basically composed of water (87% w/w), proteins (3.5% w/w), lipids (3.0% w/w) and lactose (4.5% w/w), which also makes it a favorable environment for the development of spoilage microorganisms, requiring conservation methods such as refrigeration and pasteurization (Minim et al., 2002). Many products can be made from fresh milk which require a great number of industrial processes including pumping, concentration, thermal treatment, cooling and others. In these processes the composition and temperature suffers significant variations, changing the physical properties of milk (Alcântara et al., 2012).

The knowledge of thermal properties is crucial for designing efficient and economical equipment for food processing operations involving heat transfer, making it of extreme importance to obtain accurate data regarding properties such as thermal diffusivity and specific heat and to understand how these properties behave during specific processes as functions of temperature and food composition (Guimarães et al., 2009). Equipment failures or poor process design can be attributed to lack of information when selecting values for key properties used in the initial analysis of the systems under study (Incropera and Dewitt, 2003).

Although milk is likely the most processed liquid food in the world and has been studied since 19^{th} century, information about its thermophysical properties are still limited, prejudicing the calculations for sizing and adaptation of equipments (Cochran, 1893; Whitnah, 1962; Minim et al., 2002; Flauzino et al., 2009).

In a previous work (Alcântara et al., 2012) density and dynamic viscosity values of bovine milk affected by temperature and composition were presented, contributing to provide knowledge in this area. Now in this paper an investigation was performed on the thermal diffusivity and specific heat values over a large range of milk constituents including moisture, fats, lactose, proteins, minerals and temperature, based on typical processing values. Simple correlations for predicting these properties were also proposed for practical applications, besides a comparison with traditional used correlations.

2. Materials and Methods

2.1. Materials

Three lots of whole milk powder, skim milk powder and fresh milk cream were acquired from a local dairy industry (Itapetinga, BA Brazil). Physical-chemical analyses were performed in triplicate according to the AOAC (1996), where the compositions (mass fraction) of the whole milk powder, skimmed milk powder and fresh milk cream are presented in Table 1 (Alcântara et al., 2012). Lactose, casein and tricalcic phosphate ($Ca_3(PO_4)_2$) were of analytical grade (Vetec, São Paulo, SP, Brazil).

Table 1. Composition (mass fraction) of whole milk powder (WMP), skimmed milk powder (SMP) and fresh milk cream (FMC) used in the experiments (Alcântara et al., 2012).

	WMP	**SMP**	**FMC**
Moisture	0.038±0.002	0.033±0.002	0.361±0.012
Fat	0.253±0.003	0.009±0.002	0.593±0.051
Lactose	0.420±0.041	0.549±0.053	0.024±0.004
Protein	0.228±0.003	0.333±0.015	0.016±0.005
Minerals	0.059±0.002	0.072±0.008	0.003±0.001

2.2. Experimental Design.

To obtain thermal diffusivity data, experiments were conducted in a completely randomized design with three repetitions. Temperature was studied on a range of 275.15 K to 355.15 K at 20 K intervals, totaling five temperatures. In order to evaluate the effect of each milk component, five sub-experiments were conducted in a 5^2 factorial design, composed of five temperature values and five respective component values. The effect of moisture (x_w) on the thermophysical properties was investigated in samples with moisture contents ranging from 0.60 to 0.99 (mass fraction). These were obtained by the mixing of whole milk powder with the respective amount of distilled water. The effect of fat (x_f) was studied in samples with fat concentrations ranging from 0.001 to 0.20 (mass fraction), obtained by mixing skimmed milk powder with distilled water followed by the addition of fresh milk cream if necessary. To study the effect of the lactose (x_l), protein (x_p) and mineral (x_m) contents, lactose, casein and tricalcic phosphate were added, respectively, to reconstituted whole milk powder. Samples with concentrations ranging from 0.05 to 0.25 (mass fraction) for lactose, 0.03 to 0.15 (mass fraction) for protein and 0.008 to 0.048 (mass fraction) for minerals were obtained. The values used herein were the same as those of Alcântara et al. (2012).

To obtain data on specific heat, experiments were conducted in a completely randomized design with three repetitions and five replicates each. In order to evaluate the effect of each milk component, the composition values used were the same as in thermal diffusivity experiments and equilibrium temperature was maintained near 293.15 K.

Multiple linear regressions and simple linear regressions were performed to adjust the models to the diffusivity and specific heat data. Fit of the model to the experimental data was evaluated by the coefficient of determination (R^2), non-significant lack of fit (p>0.05), and root mean square error (RMSE) values. The significance of the regression coefficients was evaluated via the Student's t-test. For each parameter estimated in the models, a test of significance was performed. Parameters with less than 95% significance (p>0.05) were pooled into the error term. The model was further validated by an analysis of variance (ANOVA). All statistical analyses were performed using the SAS v.9 software (SAS, 2008). Experimental data and fitted models were compared with data obtained by Minim et al. (2002) and by correlations from Choi and Okos (1986), using RMSE to evaluation.

2.3. Apparatus and Methods

(a) Thermal diffusivity

For determination of thermal diffusivity a method adapted from Dickerson (1965) was used, utilizing a metallic capsule constructed of stainless steel (3.8 cm of diameter, 25.5 cm of height and 1.0 mm of thickness) with two copper-constantan thermocouples, one on the external surface of the capsule and the other exactly at its the center, and a kinematic bath (Fontan et al., 2009; Silva et al., 2010; Souza et al., 2010). In order to calculate the thermal diffusivity of the sample the following equation was used:

$$\alpha = \frac{A \cdot R^2}{4\left(T_e - T_{\mathrm{i}}\right)} \tag{1}$$

where α is the thermal diffusivity ($m^2 \cdot s^{-1}$), A is the rate of heating of the thermal bath (K/min), R is the inner radius of the cell (m) and ($T_{\mathrm{ext}} - T_{\mathrm{int}}$) is the difference between the external temperature and the temperature inside the capsule (K).

(b) Specific heat

The average specific heat of samples, at an equilibrium temperature or roughly 293.15 K, was determined by using a previously calibrated mixture calorimeter (Hwang and Hayakawa, 1979; Fontan et al., 2009; Silva et al., 2010; Souza et al., 2010). The specific heat of the samples was calculated using the following equation:

$$c_p = \frac{(c_w \cdot m_w + C_{cal})(T_{eq} - T_0)}{m_s(T_s - T_{eq})} \tag{2}$$

where c_p is the specific heat of the sample ($kJ \cdot kg^{-1} \cdot K^{-1}$), c_w is the specific heat of water, C_{cal} is the heat capacity of the calorimeter ($kJ \cdot K^{-1}$), m_w is the mass of water inside the calorimeter (kg), m_s is the mass of sample, T_0 is the initial temperature of the calorimeter with water (K), T_s is the initial temperature of sample and T_{eq} is the temperature inside the calorimeter with water and the sample when equilibrium is reached (K).

3. Results and Discussion

Experimental results for thermal diffusivity and specific heat of bovine milk with respective deviations at different temperatures and compositions are presented in Tables A.1 and A.2 (see Appendix).

A multiple linear model (Eq. 3) was fitted to the experimental thermal diffusivity data in order to explain the effect of temperature and composition on this property within the ranges under study. A simple linear model (Eq. 4) was fitted to experimental data of specific heat.

$$\alpha \cdot 10^7 = \beta_0 + \beta_1 \cdot x_i + \beta_2 \cdot T + \beta_3 \cdot x_i^2 + \beta_4 \cdot T^2 + \beta_5 \cdot x_i \cdot T \tag{3}$$

$$c_P = \beta_0 + \beta_1 \cdot x_i \tag{4}$$

where α is the thermal diffusivity ($m^2.s^{-1}$), c_p is the specific heat ($kJ.kg^{-1}.K^{-1}$), x_i is the mass fraction of the studied constituent i, T is the temperature (K), and β_0, β_1, β_2, β_3, β_4 and β_5 are fitted parameters of the models.

The models fit well to the experimental data presenting adequate R^2, non-significant lack of fit ($p>0.05$), significant parameters ($p<0.05$) and low RMSE values. This information indicates that the models are suitable for predicting the behavior of thermal diffusivity and specific heat within the ranges of temperature and composition studied. Fitted parameters and R^2 values are shown in Tables 2 and 3 for the thermal diffusivity and specific heat models, respectively.

Thermal diffusivity ranged from 1.00×10^{-7} $m^2 \cdot s^{-1}$ to 9.03×10^{-7} $m^2 \cdot s^{-1}$. Minim et al. (2002) studied the effect of temperature (275.15 K to 344.15 K), moisture (0.72 to 0.92 mass fraction) and fat (0.0044 to 0.0771 mass fraction) contents in density, specific heat and thermal conductivity of milk. From the obtained values it was verified that thermal diffusivity ranged from $1.27 \times 10^{-7}\ m^2 \cdot s^{-1}$ to $1.58 \times 10^{-7}\ m^2 \cdot s^{-1}$, inside the range obtained in the present work. This property presented a polynomial quadratic behavior similar to that observed by Silva et al. (2010) and Souza et al. (2010), who studied the effect of moisture content and temperature on the thermophysical properties of genipap and umbu pulps, respectively. Temperature and major constituents concentrations affected this property, except for the lactose which presents no significant effect (p>0.05). When compared with the studied constituents, temperature appears to have the greatest effect on thermal diffusivity.

Specific heat values ranged from $3.078\ kJ \cdot kg^{-1} \cdot K^{-1}$ to $4.121\ kJ \cdot kg^{-1} \cdot K^{-1}$. These values are on the same order those reported by other authors working with different foodstuffs (Minim et al., 2002; 2009; Tansakul and Chaisawang, 2006; Fontan et al., 2009). For milk with different moisture and fat contents Minim et al. (2002) found values between $3.369\ kJ \cdot kg^{-1} \cdot K^{-1}$ and $4.124\ kJ \cdot kg^{-1} \cdot K^{-1}$.As expected, an increase in moisture content results in increased specific heat (Souza et al., 2010; Silva et al., 2010). On the other hand, increases in the other constituents promoted a decrease in this property. Similar behavior was found by Minim et al. (2002) and Tansakul and Chaisawang (2006) studying thermophysical properties of milk and coconut milk, respectively.

Table 2. Estimated parameters, R² and RMSE values of the thermal diffusivity model (Eq. 3) for each studied constituent.

coefficients	**milk constituents**				
	moisture	**fat**	**lactose**	**protein**	**minerals**
β_0	101.1034	63.2843	52.0350	119.7768	119.4939
β_1	37.0221	-15.9815	---	-90.3133	203.1283
β_2	-0.7277	-0.4044	-0.3452	-0.75538	-0.807811
β_3	-26.3004	74.5757	---	365.8553	2452.8191
β_4	0.00119	0.00067	0.00059	0.00126	0.00140
β_5	---	---	---	---	-1.1184
R²	0.75	0.85	0.90	0.84	0.89

Table 3. Estimated parameters, R² and RMSE values of the specific heat model (Eq. 4) for each studied constituent.

coefficients	**milk constituents**				
	moisture	**fat**	**lactose**	**protein**	**minerals**
β_0	1.3220	3.9465	3.6999	4.1685	4.0096
β_1	2.7520	-2.5867	-1.8353	-7.4733	-13.1467
R²	0.99	0.99	0.99	0.98	0.99

Correlations proposed by Choi and Okos (1986) were used to compare the predictive ability of the fitted models. RMSE values to both were shown in Table 4. As could be seen, the Choi and Okos (1986) correlations always presented superior RMSE values when compared to fitted models. Besides, at studied conditions, Choi and Okos (1986) correlations for specific heat tends to overestimate this property at studied conditions, while the correlations for thermal diffusivity tends to underestimate the same ones. So, fitted models are more adequate to predict these properties of bovine milk.

Table 4. RMSE values of fitted models and Choi and Okos (1986) correlations for specific heat and thermal diffusivity for studied constituent.

milk constituents	**specific heat**		**thermal diffusivity**	
	fitted models	**Choi and Okos (1986) correlations**	**fitted models**	**Choi and Okos (1986) correlations**
moisture	0.2214	0.2854	2.09E-7	3.23E-7
fat	0.0813	0.0832	1.02E-7	1.11E-7
lactose	0.1424	0.2662	6.61E-8	1.23E-7
protein	0.1175	0.3562	1.36E-7	2.71E-7
minerals	0.1254	0.2621	1.55E-7	3.22E-7

The properties studied in this work, associated to properties studied in a previous paper for the same ranges of temperature and composition (Alcântara et al., 2012) allow for understanding the behavior of other important thermophysical properties necessary in sizing and development of equipments from simple equations, such as thermal conductivity and the thermal expansion coefficient (Zuritz et al., 2005, Fontan et al., 2009; Muramatsu et al., 2010).

4. Conclusions

The effect of temperature and milk constituent concentrations on thermal diffusivity and specific heat were investigated within ranges commonly employed by the dairy industries. Composition and temperature had a significant effect on the evaluated properties, except for lactose which had no significant effect on thermal diffusivity. Multiple linear models were fitted to the thermal diffusivity experimental data and simple linear models were fitted to specific heat data. The models selected for both thermophysical properties present non-significant lack of fit, significant parameters, good R^2 and low RMSE values. Based on these results, the proposed equations can be used for the calculation of thermal diffusivity and specific heat of bovine milk, considering the information available on its composition. Moreover, from data of thermophysical properties studied in this work and in a previous paper, the behavior of other properties as conductivity and thermal expansion coefficient could be evaluated from simple equations.

Appendix

Table A.1. Experimental values of thermal diffusivity for bovine milk in the ranges of temperature and composition under study.

moisture variation		
T (K)	x_w (mass fraction)	$10^7\ \alpha$ ($m^2 \cdot s^{-1}$)
275.15	0.600	1.57 ± 0.12
	0.700	1.81 ± 0.97
	0.800	3.37 ± 2.26
	0.900	3.91 ± 2.79
	0.990	4.22 ± 0.76
295.15	0.600	1.21 ± 0.09
	0.700	1.63 ± 0.24
	0.800	2.18 ± 0.74
	0.900	2.12 ± 0.91
	0.990	2.82 ± 0.37
315.15	0.600	1.35 ± 0.13
	0.700	1.62 ± 0.28
	0.800	2.38 ± 0.09
	0.900	2.52 ± 0.86
	0.990	2.41 ± 0.33
335.15	0.600	1.97 ± 0.23
	0.700	2.29 ± 0.56
	0.800	4.25 ± 0.42
	0.900	3.70 ± 3.39
	0.990	2.98 ± 0.72
355.15	0.600	3.09 ± 0.38
	0.700	3.36 ± 0.51
	0.800	7.12 ± 1.29
	0.900	3.94 ± 1.58
	0.990	4.53 ± 1.50
fat variation		
T (K)	x_f (mass fraction)	$10^7\ \alpha$ ($m^2 \cdot s^{-1}$)
275.15	0.001	2.82 ± 0.41
	0.050	2.11 ± 0.38
	0.100	1.90 ± 0.97

	0.150	2.81 ± 1.50
	0.200	1.94 ± 1.35
295.15	0.001	2.01 ± 0.28
	0.050	1.84 ± 0.26
	0.100	1.53 ± 0.90
	0.150	1.79 ± 1.14
	0.200	1.72 ± 0.78
315.15	0.001	2.46 ± 0.49
	0.050	1.88 ± 0.09
	0.100	1.52 ± 1.02
	0.150	1.46 ± 1.29
	0.200	1.91 ± 0.77
335.15	0.001	3.82 ± 0.29
	0.050	2.30 ± 0.20
	0.100	1.87 ± 1.32
	0.150	1.81 ± 1.79
	0.200	2.41 ± 1.31
355.15	0.001	5.09 ± 1.34
	0.050	2.88 ± 0.51
	0.100	2.58 ± 1.80
	0.150	2.85 ± 2.66
	0.200	3.22 ± 2.38
lactose variation		
T	**x_l**	**$10^7\ \alpha$**
(K)	**(mass fraction)**	**($m^2 \cdot s^{-1}$)**
275.15	0.050	1.73 ± 0.22
	0.100	1.51 ± 0.41
	0.150	1.49 ± 0.18
	0.200	1.52 ± 0.22
	0.250	1.33 ± 0.62
295.15	0.050	1.26 ± 0.26
	0.100	1.18 ± 0.16
	0.150	1.30 ± 0.41
	0.200	1.15 ± 0.42
	0.250	1.50 ± 0.13
315.15	0.050	1.72 ± 0.27
	0.100	1.24 ± 0.65
	0.150	1.77 ± 0.78

	0.200	1.14 ± 0.59
	0.250	1.84 ± 0.08
335.15	0.050	1.99 ± 0.74
	0.100	2.09 ± 1.17
	0.150	2.90 ± 0.98
	0.200	1.54 ± 0.72
	0.250	2.37 ± 0.09
355.15	0.050	2.76 ± 0.39
	0.100	3.95 ± 1.77
	0.150	4.64 ± 1.11
	0.200	2.43 ± 0.83
	0.250	3.47 ± 0.36
	protein variation	
T	**x_p**	**$10^7\,\alpha$**
(K)	**(mass fraction)**	**($m^2 \cdot s^{-1}$)**
275.15	0.030	4.35 ± 0.27
	0.060	2.30 ± 0.49
	0.090	1.77 ± 0.35
	0.120	2.21 ± 0.59
	0.150	2.13 ± 0.60
295.15	0.030	3.40 ± 1.48
	0.060	1.95 ± 1.42
	0.090	1.00 ± 0.03
	0.120	1.38 ± 0.11
	0.150	1.14 ± 0.26
315.15	0.030	3.86 ± 2.42
	0.060	2.48 ± 2.24
	0.090	9.59 ± 0.04
	0.120	1.72 ± 0.25
	0.150	9.95 ± 0.13
335.15	0.030	5.74 ± 3.10
	0.060	3.89 ± 2.96
	0.090	1.64 ± 0.12
	0.120	3.24 ± 0.16
	0.150	1.69 ± 0.19
355.15	0.030	9.03 ± 3.53
	0.060	6.16 ± 3.57
	0.090	3.04 ± 0.54

	0.120	5.92 ± 1.17
	0.150	3.23 ± 0.45
minerals variation		
T	***x_m***	***10^7 α***
(K)	**(mass fraction)**	**($m^2 \cdot s^{-1}$)**
275.15	0.008	2.78 ± 0.77
	0.018	1.88 ± 1.54
	0.028	2.40 ± 0.22
	0.038	3.43 ± 1.24
	0.048	4.99 ± 0.77
295.15	0.008	2.36 ± 0.73
	0.018	2.39 ± 1.19
	0.028	1.62 ± 0.30
	0.038	2.58 ± 0.74
	0.048	2.92 ± 1.01
315.15	0.008	2.38 ± 1.51
	0.018	3.64 ± 1.78
	0.028	1.81 ± 0.38
	0.038	3.00 ± 0.92
	0.048	2.00 ± 1.08
335.15	0.008	4.24 ± 2.13
	0.018	4.11 ± 2.93
	0.028	2.35 ± 0.82
	0.038	5.17 ± 1.57
	0.048	2.63 ± 1.52
355.15	0.008	8.27 ± 2.59
	0.018	4.98 ± 4.35
	0.028	4.01 ± 1.68
	0.038	8.08 ± 2.33
	0.048	6.47 ± 2.71

Table A.2**.** Experimental values of specific heat for bovine milk in the ranges of composition under study.

moisture variation		**fat variation**	
x_w (mass fraction)	c_p (kJ·kg^{-1}·°C^{-1})	x_f (mass fraction)	c_p (kJ·kg^{-1}·°C^{-1})
0.600	3.021 ± 0.106	0.001	3.904 ± 0.101
0.700	3.270 ± 0.053	0.050	3.769 ± 0.108
0.800	3.553 ± 0.286	0.100	3.694 ± 0.042
0.900	3.639 ± 0.437	0.150	3.632 ± 0.125
0.990	4.121 ± 0.261	0.200	3.472 ± 0.097
lactose variation		**protein variation**	
x_l (mass fraction)	c_p (kJ·kg^{-1}·°C^{-1})	x_p (mass fraction)	c_p (kJ·kg^{-1}·°C^{-1})
0.050	3.556 ± 0.078	0.030	3.968 ± 0.072
0.100	3.646 ± 0.233	0.060	3.728 ± 0.106
0.150	3.424 ± 0.143	0.090	3.550 ± 0.174
0.200	3.411 ± 0.176	0.120	3.214 ± 0.183
0.250	3.328 ± 0.200	0.150	3.078 ± 0.086
minerals variation			
x_m (mass fraction)	c_p (kJ·kg^{-1}·°C^{-1})		
0.008	3.963 ± 0.241		
0.018	3.792 ± 0.054		
0.028	3.692 ± 0.151		
0.038	3.568 ± 0.168		
0.048	3.354 ± 0.065		

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