Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 261–272

CONSTRUCTION OF AN ISOPERIBOL CALORIMETER TO MEASURE THE SPECIFIC HEAT CAPACITY OF FOODS BETWEEN 20 AND 90°C

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Abstract

A simple isoperibol calorimeter, using the modified method of mixtures, was developed to measure the average specific heat capacity of different dough types between 20 and 90°C. The method consisted of encapsulating the sample in a copper cylinder and immersing the capsule in water at a different temperature. The procedure was tested for reliability with distilled water and whole fat milk before applying it to five dough types of varying moisture and fat contents. Mean values of $4.176\pm0.008 \text{ kJ kg}^{-1} \text{ K}^{-1}$ and $3.942\pm0.034 \text{ kJ kg}^{-1} \text{ K}^{-1}$ were obtained for distilled water and milk respectively, which agree within 0.23 and 0.34% from reported values. The specific heat values for the five dough types were found to range between $2.15-2.68 \text{ kJ kg}^{-1} \text{ K}^{-1}$ between $2.35-3.10 \text{ kJ kg}^{-1} \text{ K}^{-1}$ and between $2.40-3.19 \text{ kJ kg}^{-1} \text{ K}^{-1}$ at the three temperature levels studied. The specific heat capacity was found to depend not only on the moisture level but also on the fat content, especially for dough types with a high percent of fat. Regression analysis was then used to correlate these values and develop a set of empirical equations. The results were used to assist in energy balance calculations in backing oven for industrial purposes.

Keywords: calorimeter, dough, method of mixtures, specific heat capacity

Introduction

The specific heat capacity of a substance plays a central role in all processes involving the uptake, release or transfer of heat energy. With respect to the food processing industries, major unit operations involve the heating and cooling of foods which includes thermal processing (e.g. sterilisation, pasteurisation, drying, etc.) refrigeration and freezing. The design of equipment for such processes requires exact knowledge of the thermal properties of the product; in particular heat loads, processing time and equipment size depend to a large extent on the product's calorimetric properties [1].

Data on the thermal properties of natural and synthetic foods are numerous since each food has its own physical structure and composition. To facilitate any systematic analysis and/or study of operation and design it is therefore desirable to reduce the amount of data so that a few sets of equations can be used to assist process compu-

1418–2874/2001/ \$ 5.00 © 2001 Akadémiai Kiadó, Budapest Akadémiai Kiadó, Budapest Kluwer Academic Publishers, Dordrecht tation [2]. Several authors have proposed various models to calculate the specific heat capacity of foods based on empirical equations.

Siebel [3], Mohsenin [4], Rice *et al.* [5] and Gupta [6], among others, proposed linear models based on the moisture content. In addition, other models were proposed by Riedel [7], Heldman and Singh [8], Thomareis and Hardy [9] and Choi and Okos [10]. A compilation of such formulae used for the calculation of the thermal properties of simple foods has been published by Miles *et al.* [11].

The objective of this research is the construction of a fluid type calorimeter to measure the specific heat capacity of dough in the temperature range of 20 to 90°C, using the modified method of mixtures. The specific heat capacity of five dough types is analysed at three temperature levels and regression analysis is used to correlate the results and develop a set of empirical equations. These equations can be used to predict the specific heat capacity under the given conditions.

Theory

The average specific heat capacity is defined by:

$$c_{t_0}^{t} = \frac{1}{m(t-t_0)} \int_{t_0}^{t} Cdt \text{ or } c_{t_0}^{t} = \frac{1}{(t-t_0)} \int_{t_0}^{t} Cdt$$
(1)

The energy equivalent of the calorimeter is the amount of heat energy needed to raise the temperature of the calorimeter (fluid) by 1°C. To this end a copper block of known mass and specific heat capacity is heated to a certain temperature and then lowered into the calorimeter container. The tabulated value for the specific heat capacity of copper (c_u) is 386.656 J kg⁻¹ K⁻¹ from which the heat capacity can be calculated:

$$C_{\rm cu} = mc_{\rm u}$$
 (2)

The heat capacity of the calorimeter (C_{cal}) is then given by the following equation:

$$C_{\rm cal} = \frac{C_{\rm cu}\Delta T_1}{\Delta T_2} = \frac{C_{\rm cu}(t_{\rm ic} - t_{\rm e})}{(t_{\rm e} - t_{\rm c})}$$
(3)

The heat capacity of the sample container which also takes part in the heat exchange process, can thus be calculated as follows:

$$C_{\rm G} = \frac{C_{\rm cal}\Delta T_2}{\Delta T_1} = \frac{C_{\rm cal}(t_{\rm e} - t_{\rm c})}{(t_{\rm isc} - t_{\rm e})} \tag{4}$$

The average specific heat of a substance, can be calculated by use of the values obtained for the heat capacity of the empty sample container (C_G) and the energy equivalent of the calorimeter (C_{cal}):

$$c_{p_{t_{e}}^{t_{i}}} = \frac{\frac{C_{cal}(t_{e} - t_{c})}{t_{is} - t_{e}} - C_{G}}{\frac{m_{A}}{m_{A}}}$$
(5)

Materials and methods

Apparatus

The schematic set-up of the calorimeter is shown in Fig. 1. It consists of a wooden cupboard fitted with a platform 35.8 cm above the cupboard base. The electric heater is fixed outside the cupboard to minimise heat generation and to keep the distance between the heater and calorimeter as small as possible. The cupboard is fitted with a door kept in place with four removable screws. The interior of the cupboard is insulated on all sides by a 5 cm thick foam insulation.



Fig. 1 Calorimeter (upper section)

Two containers, made of stainless steel, serve as the calorimeter container and an outer container respectively. Foam insulation is used between the two containers, which are placed on the platform in the upper section of the cupboard. The sample container (Fig. 2), made of brass, is heated in the electric resistance heater (Fig. 3). After a steady reading is recorded at the required temperature, the sample container is lowered, by means of a pulley, into the calorimeter container which is filled with water. A stirrer (~200 rpm) passes through the top section of the cupboard into the calor



Fig. 2 Sample container



Fig. 3 Electric heater

rimeter container ~20 mm from the base. A wooden sliding lid serves to insulate the calorimeter contents from the surroundings. Two platinum resistance thermometers (Pt-100) to measure the sample temperature and the temperature of the calorimeter fluid are used. The sample container consists of a cylindrical pipe (8 mm in diameter) passing through its centre for the uptake of the thermometer. The second thermometer passes through the lid and insulation in the top cover of the cupboard. Both thermometers are connected to a data logger which registers the change in temperature during a measurement with an accuracy of $\pm 0.01^{\circ}$ C.

Experimental procedure

The sample is weighed and then preheated in an oven for about two hours, to ensure uniform temperature distribution at the required temperature. The electric heater is switched on approximately 30 min before the start of a measurement. The sample container is then placed in the electric resistance heater and the temperature allowed to equilibrate for about 15 min. The calorimeter container is filled with approximately 6 kg of water and is placed in the second container. The two containers are placed on the wooden platform in the cupboard and the door is shut. The stirrer is put in place and the calorimeter is then ready for a measurement. The actual heat exchange lasts between 30–100 min depending on the sample type. The temperature is recorded at a rate of 1 reading/10 s and can be checked on the digital display of the data logger. The temperature of the water bath increases steadily during the heat exchange while that of the sample decreases. The rate of heat exchange gradually decreases as the sample and water approach equilibrium. The temperature is then recorded for a further 10–15 min, after which a measurement is completed.

Measurements and calorimeter control

The initial measurements were all taken between 20–50°C. For this temperature interval three platinum resistance thermometers (Pt-100) were calibrated in a commercial calibration device, between 22–50°C at 2°C intervals with an accuracy of ± 0.01 °C. For the higher temperature range three platinum resistance thermometers

$T_{\rm initial}/^{\circ}{\rm C}$	$T_{\rm equil}/^{\circ}{ m C}$	$T_{\rm iw}$ /°C	ΔT_2	ΔT_1	Sp. Ht./ kJ kg ⁻¹ K ⁻¹
54.10	26.95	24.29	2.66	27.15	4.20
53.26	22.38	19.36	3.02	30.88	4.19
53.06	26.86	24.31	2.55	26.20	4.16
52.32	27.00	24.52	2.48	25.32	4.19
53.20	27.00	24.44	2.56	26.20	4.18
50.84	25.38	22.90	2.48	25.46	4.17
				Ν	Mean=4.17±0.01

Table 1 Specific heat capacity of distilled water

 Table 2 Specific heat capacity of distilled water (second set of results)

$T_{\rm initial}/^{\rm o}{\rm C}$	$T_{\rm equil}/^{\circ}{\rm C}$	$T_{\rm iw}$ /°C	ΔT_2	ΔT_1	Sp. Ht./ kJ kg $^{-1}$ K $^{-1}$
49.25	24.00	26.23	23.02	2.23	4.18
52.92	22.85	25.51	27.41	2.66	4.19
51.37	22.90	25.41	25.96	2.51	4.17
52.84	22.61	25.28	27.56	2.67	4.18
				ו	Mean=4.18±0.01

 Table 3 Specific heat capacity of milk (3.6% fat)

$T_{\rm im}/^{\circ}{\rm C}$	$T_{\rm iw}/^{\rm o}{\rm C}$	$T_{\rm equil}/^{\circ}{\rm C}$	ΔT_1	ΔT_2	Sp. Ht./ kJ kg ⁻¹ K ⁻¹
46.19	23.96	25.88	20.31	1.92	3.89
50.94	21.82	24.36	26.58	2.54	3.95
53.23	20.55	23.41	29.82	2.86	3.96
45.84	22.08	24.16	21.68	2.08	3.97
					Mean=3.94±0.03

Table 4 Specific heat capacity of baking fat

$T_{ m if}$ /°C	$T_{\rm iw}/^{\circ}{\rm C}$	$T_{\rm equil}/^{\rm o}{\rm C}$	ΔT_1	ΔT_2	Sp. Ht./ kJ kg ⁻¹ K ⁻¹
63.00	18.96	21.62	2.66	41.38	2.59
73.62	14.05	17.68	3.63	55.94	2.63
74.31	19.40	22.74	3.34	51.57	2.64
					Mean=2.64

Mass/g	$T_{\rm id}/^{\rm o}{\rm C}$	$T_{\rm iw}/^{\rm o}{\rm C}$	$T_{\rm equil}/^{\circ}{\rm C}$	ΔT_1	ΔT_2	Sp. Ht./ kJ kg ⁻¹ K ⁻¹
656	46.67	22.55	24.30	1.75	22.37	2.63
635	47.95	23.17	24.96	1.79	22.99	2.70
651	48.43	23.67	25.48	1.81	22.95	2.68
651	49.89	24.22	26.12	1.90	23.77	2.70
					Mean=2	2.68±0.03
606	65.86	21.85	25.15	3.30	40.71	3.02
650	77.14	20.85	25.46	4.61	51.68	3.19
649	77.95	21.57	26.18	4.61	51.77	3.19
608	87.47	22.43	27.52	5.09	59.95	3.19

Table 5 Specific heat capacity of dough type-A

Table 6 Specific heat capacity of dough type-B

Mass/g	$T_{\rm id}/^{\rm o}{\rm C}$	$T_{\rm iw}/^{\rm o}{\rm C}$	$T_{\rm equil}/^{\circ}{\rm C}$	ΔT_1	ΔT_2	Sp. Ht./ kJ kg ⁻¹ K ⁻¹
664	47.86	25.47	26.98	1.51	20.88	2.34
633	47.40	19.97	21.78	1.81	25.62	2.37
660	46.28	21.94	23.60	1.66	22.68	2.39
620	48.56	23.79	25.40	1.61	23.16	2.37
					Mean=2	2.37±0.02
605	73.76	21.44	24.80	3.36	48.96	2.47
588	77.82	21.79	25.48	3.69	52.34	2.49
589	78.57	20.76	24.58	3.82	53.99	2.57
575	88.02	22.12	26.44	4.32	61.58	2.62

Table 7 Specific heat capacity of dough type-C

Mass/g	$T_{\rm id}/^{\rm o}{\rm C}$	$T_{\rm iw}/^{\rm o}{\rm C}$	$T_{\rm equil}/^{\circ}{\rm C}$	ΔT_1	ΔT_2	Sp. Ht./ kJ kg ⁻¹ K ⁻¹
650	48.05	21.29	23.04	1.75	25.01	2.28
658	47.81	21.91	23.59	1.68	24.22	2.23
681	47.09	22.36	24.06	1.70	23.03	2.34
688	48.98	23.16	24.92	1.76	24.06	2.29
					Mean=2	2.28±0.05
660	65.39	20.78	23.82	3.04	41.57	2.42
671	67.54	22.50	25.64	3.14	41.90	2.45
663	84.26	22.36	26.68	4.32	57.58	2.50
655	90.19	19.64	24.56	4.92	65.63	2.51

Mass/g	$T_{\rm id}/^{\circ}{\rm C}$	$T_{\rm iw}$ /°C	$T_{\rm equil}/^{\circ}{\rm C}$	ΔT_1	ΔT_2	Sp. Ht./ kJ kg ⁻¹ K ⁻¹
563	50.41	25.73	27.15	1.42	23.26	2.17
565	50.28	26.22	27.61	1.39	22.67	2.17
555	47.79	25.52	26.77	1.25	21.02	2.11
550	48.69	23.54	24.95	1.41	23.74	2.13
					Mean=	2.15±0.03
566	61.84	19.72	22.26	2.54	39.58	2.35
536	67.74	21.35	24.06	2.71	43.68	2.35
562	94.04	22.18	26.56	4.38	67.48	2.40
560	97.57	25.00	29.47	4.47	68.10	2.45

Table 8 Specific heat capacity of dough type-D

Table 9 Specific heat capacity of dough type-E

Mass/g	$T_{\rm id}/^{\rm o}{\rm C}$	$T_{\rm iw}$ /°C	$T_{\rm equil}/^{\circ}{\rm C}$	ΔT_1	ΔT_2	Sp. Ht./ kJ kg ⁻¹ K ⁻¹
659	46.00	23.23	24.79	1.56	21.21	2.41
649	46.11	22.40	24.02	1.62	22.09	2.44
647	49.78	21.68	23.61	1.93	26.17	2.46
					Mean=	$2.44{\pm}0.03$
650	67.27	20.95	24.12	3.17	43.15	2.47
642	77.19	22.51	26.25	3.74	50.94	2.48
618	93.51	24.71	29.38	4.67	64.13	2.55

were calibrated between $0-100^{\circ}$ C at 10° C intervals. To speed up the measurement procedure two sample containers were used. The heat capacity of each container at the three temperature levels was determined. The mass of water in the calorimeter container was kept constant at 6.614 kg. The volume was chosen so that the sample container is fully immersed. The calorimeter was calibrated between 20–50, 20–70 and 20–90°C. In order to test the calorimeter performance several control runs using distilled water, whole fat milk and skimmed milk were carried out between 20–50°C. The main sources of errors include thermal leakage, the problem of mixing and energy added by stirring. The results for the control runs are given in Tables 1–4 and for the dough samples in Tables 5–9.

Moisture and fat contents

The moisture content (wet basis) of each dough type for each measurement was determined (Table 10). This was done by weighing before and after drying. The fat content was also calculated.

Attempt No.	Dough type-A	Dough type-B	Dough type-C	Dough type-D	Dough type-E
			M wb		
1	37.93	18.99	10.68	15.91	9.091
2		15.38	14.89	13.64	12.24
3	32.60		12.77	13.64	
4			17.14		
Average	35.27	17.18	13.87	14.40	10.67

Table 10 Moisture content wet basis (wb)
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Results and discussion

Analysis

As can be seen from the results the specific heat of the five dough types increases with temperature. As opposed to models where the specific heat is moisture dependent, the results obtained in the present work show that the change of specific heat capacity could not be explained by the moisture content alone. However, a correlation was found to exist between the specific heat capacity and the sum of the mass fractions of moisture and fat (Fig. 4).



Fig. 4 Relationship between the specific heat capacity and the sum of the mass fractions of moisture and fat

Prediction of the specific heat capacity

By plotting the sum of the mass fraction of the moisture and fat content (x_{F+M}) vs. the specific heat capacity three empirical equations were obtained. The equations obtained were used to predict the specific heat capacity and the values compared to the actual experimental values.

Between 20 and 50°C:

$$c=1.56653+2.84334 x_{\text{F+M}} \text{ kJ kg}^{-1} \text{ K}^{-1}$$
 (6)

The correlation coefficient is 0.9957 showing a very strong relationship between the two variables, and R^2 =99.16%.

Between 20 and 70°C

$$c=1.36084+4.31415 x_{F+M} \text{ kJ kg}^{-1} \text{ K}^{-1}$$
 (7)

 R^2 =0.9052 or 90.52%, and x_{F+M} is as defined above. The correlation coefficient is 0.951435 showing a strong relationship between the two variables.

Between 20 and 90°C

$$c=1.47104+4.21742 x_{F+M} \text{ kJ kg}^{-1} \text{ K}^{-1}$$
 (8)

 R^2 =92.57%, and $x_{\text{F+M}}$ is as defined above. The correlation coefficient is 0.962107 showing a strong relationship between the two variables.

The specific heat capacity of distilled water and milk were determined and the values obtained compared to standards. The specific heat capacity of distilled water between 20 and 50°C in this work was found to have an average value of $4.18\pm 0.01 \text{ kJ kg}^{-1} \text{ K}^{-1}$. The documented value for the specific heat capacity of whole fat milk is given as 3.9679 kJ kg⁻¹ K⁻¹ [13]. The experimental value obtained was 3.94 kJ kg⁻¹ K⁻¹ between 20–50°C, which deviates from the documented value by 0.66%.

The specific heat capacity of the five dough types tested were found to lie in the range of 2.15–2.68 kJ kg⁻¹ K⁻¹ between 20–50°C, 2.35–3.13 kJ kg⁻¹ K⁻¹ between 20–70°C and 2.46–3.19 kJ kg⁻¹ K⁻¹ between 20–90°C. Between 20 and 50°C four trials were performed for each dough type. At the higher temperatures the temperature was more difficult to regulate, thus two attempts were performed for each dough type. The specific heat capacity for each dough type was found to increase with temperature. It was found that the specific heat values obtained did not correlate when moisture was taken to be the only independent variable. This is contrary to the results obtained for moisture rich foods such as fruit pulps where the bulk of the food consists of water with a mostly sugar based solid content [12]. Likewise the values did not show any direct correlation with the fat content. This is to be expected since dough has a relatively low moisture content and is composed of several ingredients.

By comparing the specific heat values of the different ingredients used in making the dough types to the specific heat values obtained for the dough in this work,

one can assume the amount of water (moisture) and fat to be two determining factors affecting the specific heat capacity values. Using regression analysis, three equations are proposed to predict the specific heat capacity at the three temperature levels studied, where the independent variable is taken to be the sum of the mass fractions of moisture and fat. It is interesting to note that at higher temperatures, the curves take an upward turn which could be explained by chemical interactions due to leavening.

The equations are proposed for the temperature intervals between 20 and 50, between 20 and 70, and between 20 and 90°C. The models show a statistically significant relationship between the dependent and independent variables at the 99, 95 and 99% confidence levels respectively. The *R*-squared statistic indicates that the models explain 99.16, 90.52 and 92.57% respectively of the variability of the dependent variable. The correlation coefficients 0.9959, 0.9514 and 0.9621 respectively indicate a very strong relationship between the variables in the models.

Dough type	Mass fraction/M+fat	Predicted value/ kJ kg ⁻¹ K ⁻¹	Experimental value/ kJ kg ⁻¹ K ⁻¹
50°C			
А	0.3883	2.6673	2.6750
В	0.2819	2.3671	2.3663
С	0.2424	2.2549	2.2840
D	0.2091	2.1603	2.1459
E	0.3110	2.4497	2.4351
70°C			
А	0.3883	3.0302	3.1306
В	0.2819	2.5727	2.4824
С	0.2424	2.4028	2.4300
D	0.2091	2.2596	2.3450
E	0.3110	2.6978	2.5948
90°C			
А	0.3883	3.1096	3.1912
В	0.2819	2.6606	2.5985
С	0.2424	2.4939	2.5013
D	0.2091	2.3540	2.4277
E	0.3110	2.7834	2.6788

Table 11 Predicted and experimental specific heat capacity values (using the fitted models)

The models were used to predict the specific heat capacity and the results were compared to the actual experimental values at each temperature level (Table 11).

Notation

C=specific heat capacity (kJ kg⁻¹ K⁻¹) C=heat capacity (J K⁻¹) c_u =specific heat capacity of copper (386.656 kJ kg⁻¹ K⁻¹) $c_{p_{t_o}^{t_i}}$ =specific heat capacity at constant pressure between the temperatures t_e and t_i (kJ kg⁻¹ K⁻¹) $C_{\rm G}^{\circ}$ =heat capacity of the empty sample container (J K⁻¹) $C_{\rm cu}$ =heat capacity of copper (J K⁻¹) C_{cal} =heat capacity of the calorimeter (J K⁻¹) db=dry basis m, m_d =mass and mass of dough respectively (g) M=moisture Sp. Ht=specific heat $(kJ kg^{-1} K^{-1})$ t=temperature at time t (K) t_0 =initial temperature at time zero (K) $t_{\rm c}$ =initial temperature of water in calorimeter (K) $t_{\rm e}$ =equilibrium temperature (K) t_{ic}=initial temperature of the copper block after heating (K) $t_{\rm isc}$ =initial temperature of the sample container (K) t_{is} =initial temperature of sample (K) x_{F+M} =sum of the mass fraction of moisture and fat T_{initial} =initial temperature (°C) T_{equil} =equilibrium temperature (°C) T_{iw} =initial temperature of water (°C) $T_{\rm im}$ =initial temperature of milk (°C) T_{if} =initial temperature of baking fat (°C) T_{id} =initial temperature of dough (°C) wb=wet basis.

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