# Enthalpy and heat capacity of bread dough at freezing and refrigeration temperatures

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**Abstract.** *The thermophysical properties (unfreezable water, enthalpy of fusion and apparent specific heat) of bread dough were measured at temperature range from -40 V to 35 V using a differential scanning calorimetry and the initial freezing point calculated by water activity determination. Dough samples with water contents 0.42, 0.43 and 0.44 kg/ kg of product were studied.*

*The apparent specific heat and enthalpy varied as function of temperature, specific heat in freezing region varied from 1.7-1.8 to 21.4-23.1 Jg$^{1}$* C"' *and it was practically constant after freezing (2.7 J g$^{-1}$ ℃ -$^{1}$). These results are in agreement with those reported by Rask (1989) where the heat capacity for bread dough was 1.8 J g -$^{1}$ ℃ -$^{1}$ at -43.5 ℃ and 2.8 J g-$^{1}$ ℃$^{-1}$ at 21 ℃.*

*The amount of unfreezable water varied from 0.388 to 0.431 kg/kg of total water for bread dough with water content of 0.44 and 0.42 kg/kg of product.*

*The aim of this work is to determine unfreezable water, enthalpy, ice content and apparent specific heat of bread dough in different temperatures and water content. These properties are very important to model the heat transfer phenomena as freezing and thawing.*

*Regression models to describe the variation of enthalpy, apparent specific heat and ice content should be developed for experimental data and other thermophysical properties as apparent density, thermal diffusivity and thermal conductivity determined to complete this study.*

**Keywords.** Specific heat capacity, enthalpy, bread dough, differential scanning calorimetry.

## Introduction

French bread is the most consumed bread in Brazil, its production represents 85 % of the total amount of bread produced in the country and it is responsible for incoming about U$ 11 billion/year (Nutrinews, 1999; ABIP, 2005). The consumption of bread produced from frozen dough is increasing due to economic attraction of centralized manufacturing and distribution that generates attractive prices, not specialized workers and the availability of "fresh" bread in shorter time at store (Klimaquip, 2003).

Thermophysical properties at freezing temperatures are essential to make an efficient design and selection of process and equipment of freezing and refrigeration, to estimate the freezing and thawing time of food product in an accurate manner and to control operating costs. The use of accurate values of thermal and physical properties of bread is essential and depends strongly of temperature and composition (Tocci, Flores & Mascheroni, 1997; Ngadi, Chinnan & Mallikarjuan, 2003; Handami, Monteau & Le Bail, 2004; Cogné, Andrieu, Laurent, Besson & Nocquet, 2003).

Measured values of thermal properties of bakery products have been correlated by some authors. However, data on the thermophysical properties of dough and bakery products below freezing point are scarce as compared to other food products and due to the great variation in composition it is often necessary to make measurements for each case (Lind, 1991; Rask, 1989; Handami etal., 2004).

Differential Scanning Calorimetry (DSC) has been used by many researchers to measure the enthalpy of fusion, apparent specific heat and unfreezable water content of food materials such sweet potato (Fasina, 2005), ice cream (Cogné et al., 2003), partly baked bread (Handami et al., 2004), fried shrimp (Ngadi et al., 2003), boneless mutton (Tocci et al., 1997) and surimi (Wang & Kolbe, 1991).

The advantages of DSC are rapid and simple measurement and much information can be obtained by a single thermogram (Cogné et al., 2003). Nevertheless, Wang & Kolbe (1991) reported a distorted apparent specific heat curve near to the initial freezing point and it restricted the application of DSC in this field.

The initial freezing point can also be determined by experimental water activity above initial freezing point measurement and freezing point depression equation (Equation 1) if the following assumptions are made: food is a heterogeneous system in a state of thermodynamic equilibrium at constant pressure, system is above the eutectic point, Raoult's law is applicable, thermal capacity of solution phase is a linear function of concentration and it is independent of temperature, thermal capacity of solid phase is constant (Barlett, 1944 apud Chen, 1985).

$$\frac{d(\ln a_w)}{dT} = \frac{M_w L}{R T^2} \qquad (1)$$

where $a_w$ is the water activity, $T$ the temperature, $M_w$*the* water molecular weight, L the water latent heat of fusion and R the ideal gas constant.

Enthalpy is used for calculating the total heat to be removed and to determine the rate removal during refrigeration and freezing of food products. Unfreezable water is the amount of water unavailable for freezing in a food product at reference temperature of -40 ℃ (Fasina, 2005).

In this study the bread dough thermophysical properties of interest are unfreezable water content, enthalpy of fusion and apparent specific heat at temperature range from -40 ℃ to 35 ℃ using DSC and the initial freezing point calculated by water activity determination. The aim of this work is to determine thermophysical properties of bread dough in different temperatures and water content. These properties are very important to model the heat transfer phenomena as freezing and thawing.

## Materials and Methods

### *Bread dough preparation*

Three formulations with different water content of French bread dough were made from commercial bakers' flour *(water content 14.20 %, protein 9.15 %, ash 0.6% and farinograph water absorption 64.60% - AACC 54-21),* 2% salt, 1 % vegetable shortening, 0.3% polysorbate, 0.2% DATEM (diacetyl-tartaric acid ester of monoglycerides) and water (57, 60 and 63%). All ingredients quantities were calculated based on wheat flour basis. Yeast was not added.

All ingredients, except the salt, were mixed *(Kitchen aid, model BEA 52A, USA)* for complete water absorption at low speed. After that, salt was added and the dough was mixed, at a high speed until its complete development. The ingredients and final temperatures of the dough were monitored.

Fresh dough samples were collected for water content, DSC and water activity analysis.

#### ***Water content ($x_{water}$)***

The water content of bread dough produced for DSC analysis was determined, in replicates, at 105 °C for at least 16 hours.

#### ***Water activity ($a_w$) and Initial freezing point** ($T_f$)*

The water activity of each bread dough sample was determined in triplicate using Novasina equipment *(model AW-Center Series AWC 500, Switzerland)* at 25 °C. The initial freezing point was determined by the relation presented in Equation 1.

#### ***Thermophysical properties determination***

The thermal properties of bread dough were measured in triplicate for each formulation using a differential scanning calorimeter *DSC 2010 (TA Instruments, USA)* calibrated with indium (melting point 156.61 °C; heat of fusion 28.54 J $g^{-1}$). Nitrogen gas was continuously flushed through the cell to avoid water condensation. The samples (12-16 mg) were placed in an aluminum pan (20 pL) and frozen inside the calorimeter with liquid nitrogen until -50 °C. An identical empty pan, used as a reference, was exposed to the same heating rate of 5 °C $min^{-1}$ until the temperature reach 40 °C. The apparent specific heat *($Cp_{app}$)* and enthalpy *(H)* were calculated by the software *Universal V2.5H* provided by manufacturer using sapphire as a reference material for calculations.

Distilled water was also scanned using the same program to verify equipment calibration.

The heating rate could generate temperature lags (Fasina, 2005), which can be correct according to Wang & Kolbe (1991). The authors reported that Cp curve was distorted to the right because of slow time response of dynamic calorimetry and they proposed the following modification of first-order correction (Equation 2).

$$Cp_{app}(T) = Cp^{*}_{app}(T) + \tau \frac{d\, Cp^{*}_{app}(T)}{dt} \quad (2)$$

Where $Cp_{app}$* is the $Cp_{app}$ value determined in DSC analysis, τ describes the delay of the sample response and it was determined by an iteration of the integral assuming that the experimental must be the same of corrected enthalpy. It was considered the initial freezing point determined from water activity measurement.

Unfreezable water *(ufw),* at -40 ℃, was considered the difference between total water content and the amount of water detected by DSC fusion endotherm (Cogné et al., 2003; Hamdami et al., 2004).

$$ufw = x_{water} - \frac{H_{Fusion}}{L} \quad (3)$$

where $H_{Fusion}$ is the enthalpy of water fusion (J $g^{-1}$) and $L$ is the ice fusion latent heat (J $g^{-1}$).

From enthalpy curves (Figure 2), it was observed a linear region until about -20 ℃ that was correlated by a linear regression. The line can be extrapolated at higher temperatures, $H_{ext}$, rrelatedbyalinearregression.Thelinecanbeextrapolatedathighertemperarepresenting a virtual solid state of the material. Thus, the isothermal enthalpy variation *(tures,H -HH$_{ex}$text)* corresponds to the latent variation, $H_S$ (Cogné et al., 2003). The ice fraction, or amount of frozen water, can be determined by Equation 4.

$$x_{ice} = (1 - ufw) - \left( \frac{H_S(T)}{L(T)} \frac{100}{x_{water}} \right) \quad for\ (T < T_f) \quad (4)$$

### *Statistical analysis*

Analysis of variance (ANOVA) was applied using a statistical software, Statgraphics v 4.0 for Windows, within 95 % confidence interval, to the results obtained for water content, unfrozen water content and enthalpy of fusion (Manugistics, 1994).

## Results and Discussion

The results for total water content *($x_{water}$),* enthalpy of fusion *($H_{Fusion}$),* unfreezable water content *(ufw),* water activity (aw) and initial freezing point ($T_f$) are given in Table 1. The water content of each formulation was significantly different ($p < 0.05$).

The water activity, which was not influenced significantly by the amount of water in bread dough, is the only parameter that influenced the initial freezing point calculation (Equation 1). Thus the initial freezing point was considered -5 ℃ for all formulations and it is the same peak temperature from DSC thermogram.

The fusion enthalpy of formulation FI and FIII are significantly different due to water content of the bread dough. The value obtained is in agreement with reported by Matuda, Romeu, Trigilio, Parra, Lugão & Tadini (2005) that found enthalpy of fusion varying from 86 to 89 J $g^{-1}$ for the correspondent water content (0.44 kg/ kg of product) bread dough.

The unfreezable water varied from 0.388 kg/kg of total water for formulation FIII to 0.431 kg/ kg of total water for formulation FI. These values are little higher than those reported in previous studies (Matuda, Parra, Lugão & Tadini, 2005; Matuda, et al., 2005) and also by Laaksonen & Roos (2000). The difference among the values should be attributed to the composition of bread dough and to the different procedures in the studies.

Table 1. Water content $(x_{water})$, enthalpy of fusion $(H_{Fusion})$, unfreezable water content (ufw), water activity ^,) and initial freezing point $(T_f)$ of French bread dough with different water content.

| Properties | F I | FII | FIII | Tukey HSD 5% |
|---|---|---|---|---|
| *Water activity* $x_{water}$ (kg/ kg total product) | 0.422[a] | 0.433[b] | 0.443[c] | 0.002 |
| $a_w$ | 0.949[a] | 0.950[a] | 0.952[a] | 0.008 |
| $T_f$(°C) | -5.26 | -5.23 | -5.02 | |
| *DSC* $H_{Fusion}$ (J $g^{-1}$ °$C^{-1}$) | 80.55[a] | 85.60[ab] | 90.23[b] | 5.20 |
| *ufwFusion(kg/* kg total water) | 0.431[a] | 0.407a[b] | 0.388[b] | 0.036 |

*Averages with the same letter, in the same line, are not significantly different at 95% confidence interval.

The apparent specific heat of French bread dough with 0.42, 0.43 and 0.44 kg of water/ kg of product as a function of temperature is given in Figure 1, the enthalpy in Figure 2 and amount of ice content in Figure 3. The shape of enthalpy and specific heat curves obtained in this study are typical of results reported in the literature for bread dough by Lind (1991).

In these properties, the curves for all formulations were very similar and the main difference were apparent specific heat peak value at $T_f$, the final enthalpy at 30 °C and the amount of frozen water.

The apparent specific heat increase from 1.69,1.62 and 1.54 J $g^{-1}$ °$C^{-1}$ at -40 °C to 21.34,22.07 and 23.10 J$g^{-1}$ °$C^{-1}$ at peak value $(T_f)$ and above $T_f$, specific heat is almost constant around 2.73, 2.71 and 2.71 J $g^{-1}$ °$C^{-1}$ for 0.42, 0.43 and 0.44 kg of water/ kg of product respectively. It is clear that water content used in this work did not influence little much on specific heat above $T_f$ (Figure 1).

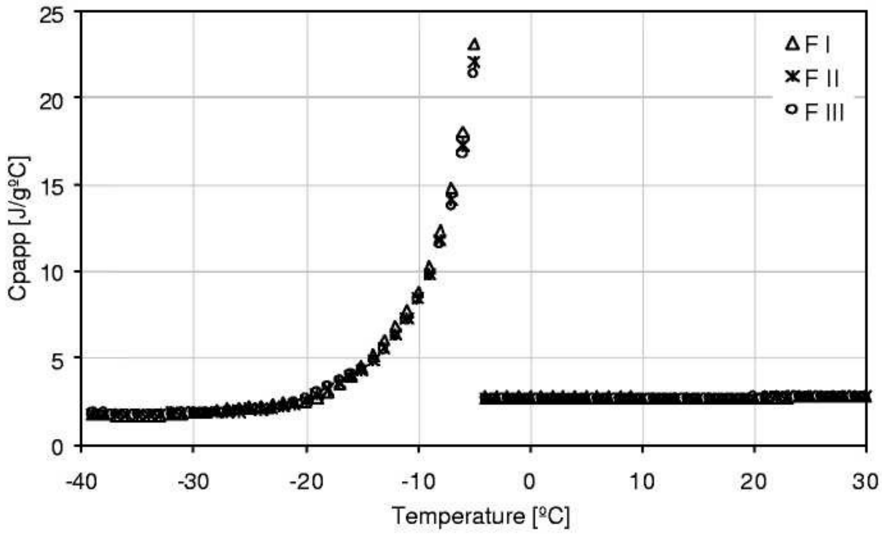


Figure 1. Experimental data of bread dough apparent specific heat for formulations with different water content. FI (A): 0.42; FII (*): 0.43; FIII (O): 0.44.

The enthalpy values varied from 0 J $g^{-1}$ at -40 °C (reference temperature) to about 260 J $g^{-1}$ at 30 °C depending on bread dough water content. There was a rapid non-linear increase in enthalpy until $T_f$ (Figure 2). Above $T_f$, change in enthalpy results is a linear increase. Formulation FIII shows the highest final enthalpy value as expected because of higher water content.

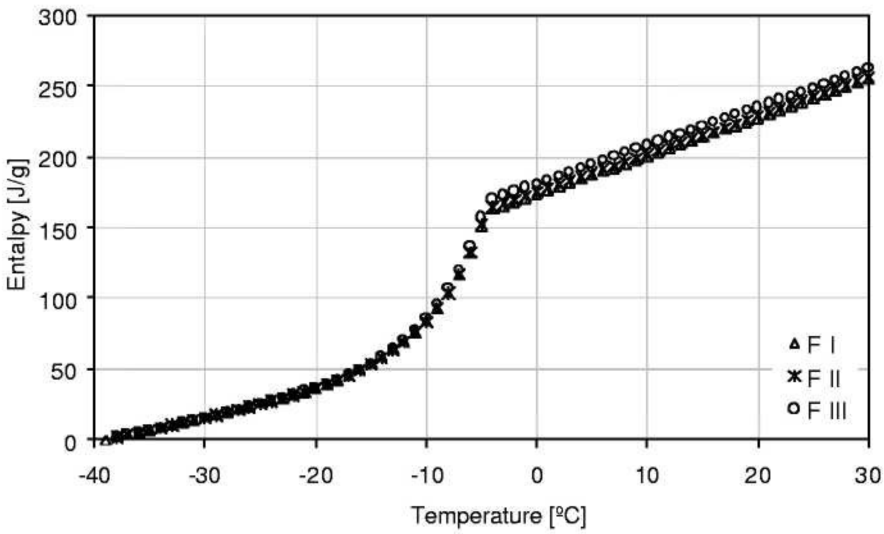


Figure 2. Experimental data of bread dough enthalpy for formulations with different water content. FI (A): 0.42; FII (*): 0.43; FIII (O): 0.44.

The ice fraction varied as expected. Formulation with higher water content presents the higher initial of amount of frozen water as showed in Figure 3. The curves are in agreement with those reported for dough by Lind (1991), which have total amount of frozen water between 60 and 70 %.

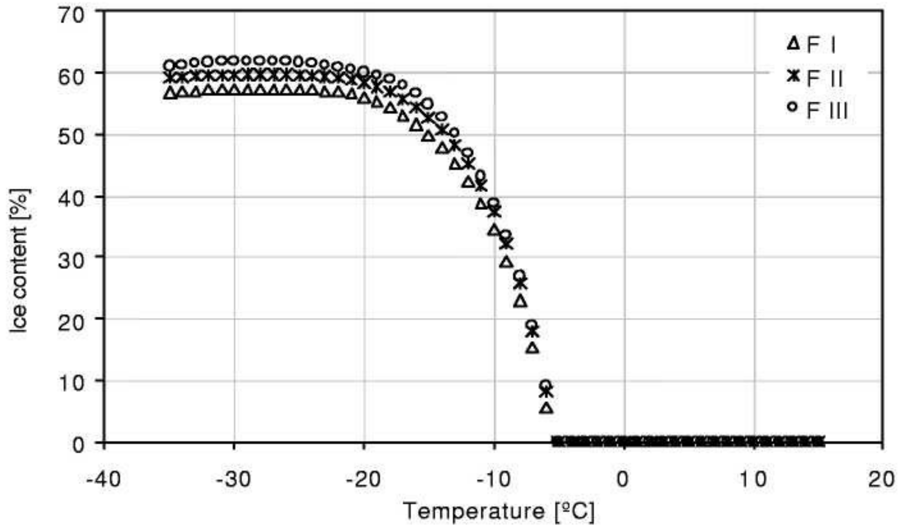


Figure 3. Ice content of bread dough for formulations with different water content. FI (A): 0.42; FII (*): 0.43; FIII (O): 0.44.

## Conclusions

Initial freezing point can be determined by DSC thermogram but also by experimental water activity determination and freezing point depression equation. The second option is probably the best because DSC thermogram indicates a distortion due to slow time response of dynamic calorimetry. However the values obtained for enthalpy of fusion are confident.

The use of DSC and the correction proposed by Wang & Kolbe (1991) could be adequate to determine apparent specific heat and enthalpy. However, future studies with lower heating rate on DSC should be done to verify the correction used in this work. The lower the heating rate the lower is the difference between experimental and corrected specific heat.

Regression models to describe the variation of enthalpy, apparent specific heat and ice content should be done for experimental data to complete this study.


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## Nomenclature

| | |
|---|---|
| $a_w$ | Water activity |
| $Cp_{app}$ | Dynamic corrected apparent specific heat [J g$^{-1}$ °C$^{-1}$] |
| $Cp_{app}^*$ | Uncorrected $Cp_{app}$value determined by raw data from DSC analysis [J g$^{-1}$ °C$^{-1}$] |
| $H$ | Enthalpy [J g$^{-1}$] |
| $HFusion$ | Enthalpy of water fusion [J g$^{-1}$ ] |
| $H_{ext}$ | Extrapolated enthalpy [J g$^{-1}$] |
| $H_s$ | Enthlapy for ice melting *($H$-$H_{ext}$)* [J g$^{-1}$] |
| $L$ | Ice fusion latent heat [J g-$^{1}$ ] |
| $M_w$ | Molecular weight of water [kg mol$^{-1}$] |
| $R$ | Ideal gas constant [J mol$^{-1}$ °C$^{-1}$] |
| $t$ | Time [s] |
| $T$ | Temperature [°C] or [K] |
| $Tf$ | Initial freezing point *[°C]* |
| $x$ | Time constant in Equation 2 [s] |
| $ufw$ | Unfreezable water [kg/ kg total water] |
| $x_water$ | Water content [kg/ kg total water] |
| $xice$ | Ice content [kg/ kg total water] |

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