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Research Note

Specific heat of apple at different moisture contents and temperatures

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This work discusses results of experimental investigations of the specific heat, C, of apple in a wide interval of moisture contents (W = 0–0.9) and temperatures (T = 283–363 K). The obtained data reveal the important role of the bound water in determination of $C(W,T)$ behaviour. The additive model was applied for description of $C(W)$ dependence in the moisture range of $0.1 \leqslant W < 1$, where the apple was considered as a mixture of water and hydrated apple material (water plasticised apple) with specific heat C_h. The difference between C_h and specific heat of dry apple, $\Delta C_b = C_h - C_d$, was proposed as a measure of the excess contribution of bound water to the specific heat. The estimated amounts of bound water W_b were comparable with the monolayer moisture content in the apple.

1. Introduction

The moisture (W) and temperature (T) dependences of the apparent specific heat C of apples are very important for control and evaluation of the quality of apples during their storage and processing. These dependences can be roughly evaluated using the additive model (Ginzburg and Gromov, 1987)

$$C = C_w + (C_w - C_d)(W - 1), \quad (1)$$

where W is the moisture content (g H_2O/g total), C_w and C_d are specific heats of water (W = 1, $C_w \approx 4.187$ kJ kg^{-1} K^{-1} at T = 273–373 K) and dry matter (W = 0), respectively.

This model was applied for estimation of the moisture dependence of C in apples at temperatures close to the ambient (Singh and Lund, 1985). The temperature dependence (in the range of 272 K < T < 363 K) of C in fresh apples was approximated by linear relation (Ramaswamy and Tung, 1981). More general $C(W,T)$ dependences were also estimated within the ranges W = 0.3–0.9 and T = 303–363 K on the basis of additive model and data on specific heat of fresh apples and of apple juice (Ginzburg and Gromov, 1987). These estimations are indirect and their applicability under the question. Moreover, the additive model supposes that water and dry matter are inert to each other and their mixing or separation is not accompanied by the thermal effect that can be wrong for the real food systems.

The present work experimentally studies $C(W,T)$ dependencies of apples in the wide intervals of moisture content (W = 0–0.9) and temperature (T = 283–263 K). The role of bound water in determination of $C(W,T)$ behaviour is discussed.

2. Materials and methods

Fresh "Delikates" apples, obtained from the local market (Kyiv, Ukraine), were used throughout this study. The round slices of ≈6 mm in diameter and thickness 1–2 mm were cut parallel to the apple axis. The specific heat was measured using the differential scanning calorimeter (DSM), equipped with data logger and data treatment software (DSM-2M, Specialized Design Office of Instrument Making, Pushchino, Russia). The samples were dehydrated in a flow of dry air at 343 K for reaching the desirable moisture content (W = 0–0.9). Then samples were sealed in hermetic aluminium pans. For a totally dehydrated sample, (W = 0) the decapsulated pan was used and the supplementary drying inside the calorimeter at 378 K in the atmosphere of dry helium was applied. The drying was controlled by the drift of the DSC curve, i.e., stability of the calorimeter "zero" in the isothermal regime. During the DSC measurements, the unit was blown by dry helium to avoid moisture condensation in the calorimetric cells. Samples were heated at 8 K/min in the temperature range of 283–363 K. Finally, the moisture content was determined after DSC measurements. For this purpose, the pans were decapsulated and placed into an oven, where they were kept at 378 K until less than 0.5% variation of consecutive weightings, made at 1 h intervals.

Each experiment was repeated, at least, three times. The error bars, presented on the figures, correspond to the standard deviations.

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3. Results and their discussion

Fig. 1 shows specific heat of apple C versus water content, W, (Fig. 1a) and temperature, T (Fig. 1b). It is remarkable that $C(W)$ dependencies were practically linear at $W \geqslant 0.1$ and non-linear at small humidity ($W \leqslant 0.1$). The linear contribution to the specific heat, C_l, can be described as

$$C_l = C_w + (C_w - C_h(T))(W - 1), \tag{2}$$

where C_h is the value of $C_l(W)$ intercept.

The observed behaviour is not surprising accounting for the fact that water in apples has heterogeneous structure and can be divided into intercellular or capillary water (free water), multilayer water (weakly bound water), and monolayer water (tightly bound to the polar sites of apple tissues) (Okos et al., 1992). A characteristic jump in $C(T)$ at certain critical temperature, $T \approx 290$ K and small water content (including ≈ 0.02–0.03 of bound water) (Fig. 1b) can reflect the transition from a relatively stable glassy state to a metastable rubbery state. The glass transition temperature T_g increases with decrease of moisture content and the value of $T_g \approx 290$ K at $W = 0.023$ is in correspondence with $T_g(W)$ dependencies, previously reported for apple (Mrad et al., 2012).

The observed linear behaviour of specific heat in the moisture range of $0.1 \leqslant W < 1$ evidences applicability of the additive model for the mixtures of water and hypothetic hydrated apple material (water plasticised apple) with the specific heat C_h. At small moisture content, the systematic deviation between linear contribution $C_l(W)$ and measured value of $C(W)$ was observed. It reached maximum, $\Delta C = \Delta C_b = C_h - C_d$, in completely dried apple (at $W = 0$). The measured values of C always noticeably exceeded predictions of the additive model, Eq. (1), (see, e.g., deviations between data point and solid line for $T = 283$ K in Fig. 1a). It evidences a noticeable supplementary contribution of the, so called, bound water to the specific heat of hydrated apple. The value of ΔC_b characterises the excess contribution of interactions between water and dry matter and the effect of water confinement in the pores of an apple. The concept of bound water is widely accepted and accounts for the possibility of structural changes in the regular structure of water in hydration shells (Okos et al., 1992).

The temperature dependences of the specific heat components C_h, C_d and ΔC_b are shown in Fig. 2. Note that contributions C_h, C_d grow and the excess contribution ΔC_b decreases as temperature increases. The observed decrease of ΔC_b with temperature evidences diminution of the excess contribution of bound water and can be explained by the damage of the specific structure of bound water. The excess values ΔC_b were rather small (0.25–0.8 kJ kg^{-1} K^{-1}) in comparison to that of free H_2O ($C_w \approx 4.187$ kJ kg^{-1} K^{-1}). However, the contribution of bound water was crucial for violation of the additive model.

Usually, the additive model is applied for estimation of the effective specific heat of bound water C_b^e. The additive approximation for evaluation of C_b^e may be rewritten as (Suurkuusk, 1974)

$$C/(1 - W) = C_d + C_b^e(W/(1 - W)) \tag{3}$$

The plot of experimental data, presented as $C/(1–W)$ against $W/(1–W)$, gives the C_b^e value as a slope of the curve (Fig. 3). These dependencies are noticeably nonlinear at small moisture content (see insert in Fig. 3). So, it is evident that results of C_b^e estimation can be strongly dependent on the choice of interval of moisture content. In principle, the direct calculation of the effective specific heat of water C_b^e using the additive model can result in significant

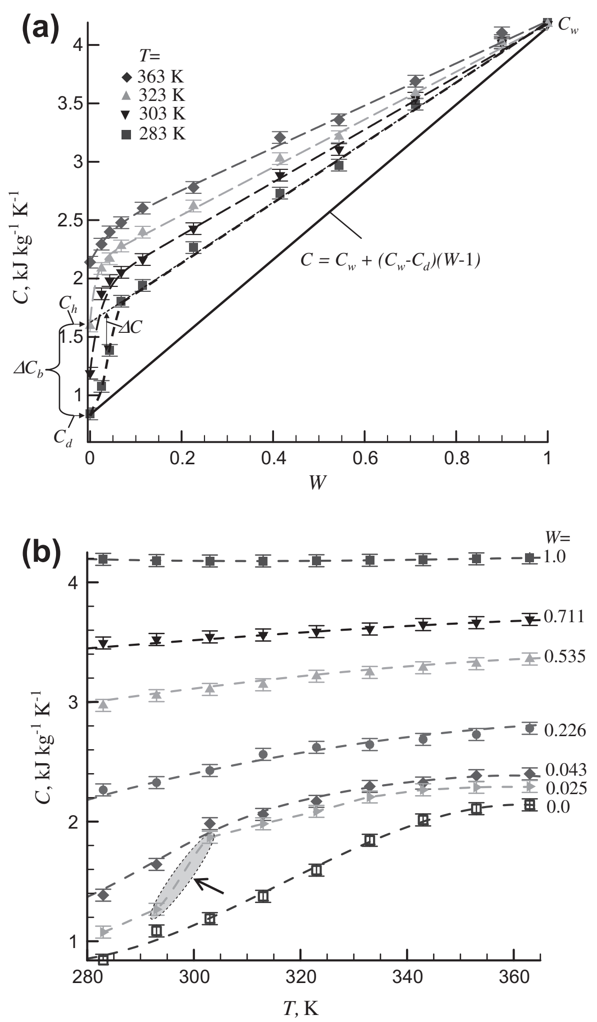

Fig. 1. Specific heat of apple C versus the moisture content W (a) and temperature T (b). The example of $C(W)$ data analysis at $T = 283$ K is presented in (a). The solid line corresponds to the additive model of specific heat. Here, C_h, C_d, and C_b are the contributions of hypothetic hydrated tissue, completely dried tissue, and interactions between water and dry matter of apple, respectively; ΔC is the difference between linear contribution $C_l(W)$ and measured value of $C(W)$. Arrow in (b) shows the change in curve inclination at $T \approx 300$ K.

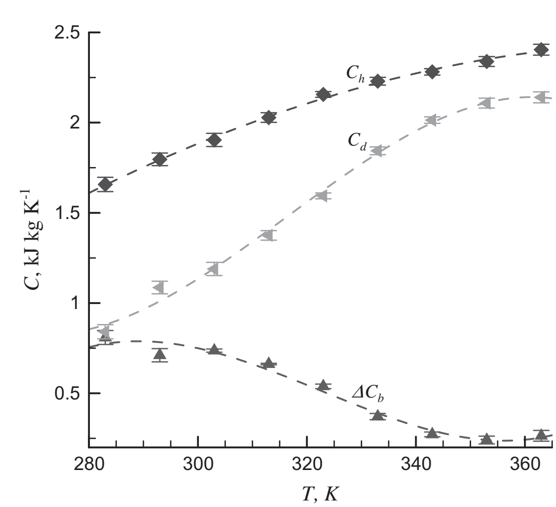

Fig. 2. The temperature dependences of different specific heat components C_h, C_d and ΔC_b, related to contributions of hypothetic hydrated tissue, completely dried tissue and bound water, respectively.