Research Paper

Modeling temperature in chocolate mass to predict tempering quality

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A computational model is developed to predict the temperature in chocolate as a function of space and time during a new tempering process where pellets of seed crystals of form V are added to the melted chocolate. The model, a refined version of a previous one (Debaste *et al.*, *J Food Eng.* 2008, 88, 568–575) including a new expression for the heat sink, is based on the energy equation, simplified by the use of an effective thermal conductivity. A shrinking core model is used to express the heat sink term associated with the melting of pellets. The width of the limit layer around the pellets is the fitting parameter. The model is validated on experimental temperature profiles in bowls and compared to a previous kinetic model. The quality of tempering is then assessed by differential scanning calorimetry. Combining this information with the model, the quality of tempering based on the initial experimental conditions is predicted.

Keywords: Chocolate tempering / Differential scanning calorimetry / Heat transfer

Received: December 12, 2008; accepted: February 16, 2009

DOI 10.1002/ejlt.200800290

1 Introduction

Cocoa butter, the main ingredient of chocolate, crystallizes in six different polymorphs, each with specific properties. Only one crystalline form, form V, is preferred in the final product as its melting point gives a firm and glossy chocolate at room temperature and at the same time a chocolate that melts in the mouth. Chocolate with cocoa butter crystallized in form V has a higher capacity to resist to "fat bloom", which gives a non-attractive aspect of chocolate, and also leads to a high volumetric contraction during solidification, which facilitates the demolding stage [1]. Tempering of chocolate is therefore needed to crystallize cocoa butter in the right crystalline form.

The objective of the tempering process is to bring seed crystals of form V into the melted chocolate to secure crystallization of chocolate in the preferred form. The common tempering process submits chocolate to a complex temperature profile over time [2]. A new patented tempering process on pre-crystallization for use by professional pastry chefs has been developed by Belcolade [3]. It is based on the introduction of solid pellets of cocoa butter into melted chocolate at a temperature such that the melting of the pellets results in seed crystals. The pellets are added to the melted chocolate at a temperature low enough not to melt completely (leading to untempered chocolate), yet high enough to generate seed crystals with appropriate dimensions allowing induction of crystal growth (leading to well-tempered chocolate after solidification). The advantages of this new process are ease of use and saved time.

This process has been developed based on experimental observations. It is therefore useful to develop a mathematical model in order to enhance the understanding and control of the process. Such a model is used to make the process less empirical and to determine the temperature of the melted chocolate at which the pellets have to be introduced to lead to a well-tempered product.

The developed model is based on the numerical resolution of a heat transport equation in the bulk of the melted chocolate. It is based on a previously published model by Debaste *et al.* [4] studying the tempering process in a stirred bowl using a two-dimensional axisymmetric geometry. In this first paper, the heat sink produced by the melting of the cocoa butter pellets was modeled by an experimentally fitted kinetics. Although the temperature profile of the chocolate during most of the experiment was correctly predicted by this model, the temperature profile in the chocolate in the first minutes after

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the seeding was significantly different. As this initial period might play a key role for the tempering quality prediction, a more detailed model had to be developed. In this paper, the melting kinetics is expressed as a shrinking core model of the melting particle. Consequently, the resulting kinetics has a strong physical meaning. Moreover, the obtained curves are correlated with the quality of the tempering as measured by differential scanning calorimetry (DSC) measurements. Therefore, the final model predicts the quality of tempering based on the initial experimental conditions.

2 Materials and methods

2.1 Tempering experiment

The tempering experiments were done under the conditions of the new patented process. A mass of chocolate (1, 2 or 3 kg) was heated to 323 K. The bowl containing this chocolate was then placed in an air-conditioned room and the melted chocolate was cooled by manual mixing. At a given temperature, solid seeds of cocoa butter (5–10 mm diameter spherical pellets) were added to the chocolate. The bowl used for experiments was made of plastic, axisymmetric, shaped as a flat-bottom half sphere, with a depth at the center of 7 cm and a diameter at the upper surface of 20 cm. Two type K thermocouples, located at the center of the chocolate at a depth of 3 cm, were connected to a data acquisition system from Agilent Technology (Diegem, Belgium) recording the temperature every second. All the experimental results presented were obtained using dark chocolate (composed of 50% cocoa mass and 50% sugar, with a total fat content of 27–28%) produced by Belcolade (Erembodegem, Belgium) and using spherical cocoa butter particles as solid pellets (obtained from tempered Pure Prime Pressed cocoa butter deposited on a moving belt and solidified in a cooling tunnel).

2.2 Quality of the tempering analysis

A differential scanning calorimeter (DSC821e) from Mettler-Toledo (Zaventem, Belgium) was used to analyze the tempering of the chocolate during the experiments. Samples of chocolate (between 5 and 25 mg) were taken from the bowl at different times during an experiment and placed in a DSC pan (40 μL in aluminum). The pans were rapidly analyzed on the differential scanning calorimeter with the following short program: starting at 298 K for 1 min, heating to 313 K at 5 K/min, isothermal period of 1 min at 313 K. The melting curves recorded give the fusion enthalpy that is proportional to the amount of crystals present in the chocolate. In that way it was possible to evaluate the quality and the speed of crystallization of chocolate as a function of the conditions of tempering.

2.3 Mathematical model

A mathematical model of the temperature fields in the chocolate mass during a tempering experiment was developed. A detailed description of the heat transfer equation can be found in Debaste *et al.* [4]. The idea was to include the contribution of conductive and convective terms on heat transfer in one single term, expressed as a conductive term with an effective thermal conductivity coefficient. The assumption made is that convective terms can be expressed as conductive terms. This approach simplifies the transient heat balance equation to the following expression [5]:

$$\rho_l C_p \frac{\partial T}{\partial t} - k_{eff} \nabla^2 T = -Q \tag{1}$$

where ρ_l is the volumetric mass of the liquid chocolate (kg/m^3), C_p is the heat capacity (J kg^{-1} K^{-1}), T is the temperature (K), t is the time (s), k_{eff} is the effective thermal conductivity (W m^{-1} K^{-1}) and Q is the volumetric rate of heat taken by the melting of seeds (W/m^3).

Equation (1), considering a known sink term, can be solved in combination with boundary conditions for conductive and radiative heat transfer from the surrounding air [6]:

$$-k_{eff} \left.\frac{\partial T}{\partial x}\right|_{x_L} = h(T - T_{ext}) + \sigma \varepsilon_S \left(T^4 - T_{ext}^4\right) \tag{2}$$

where h is a heat transfer coefficient for the combination of the inner wall of the bowl, its outer wall and the conductive resistance (W m^{-2} K^{-1}), σ is the Planck constant (W m^{-2} K^{-4}), ε_s is the bowl emissivity and T_{ext} is the ambient temperature. Details on the values of the coefficients for the boundary conditions can be found in Debaste *et al.* [4].

In the previous study, the sink term had the form of a kinetic reaction; its parameters were identified from an adiabatic melting experiment. In the present work, a model based on mass and energy balances was set up to express the heat sink term.

It is assumed that the pellets are uniformly dispersed in the whole chocolate mass due to the stirring. The heat needed to bring the pellets of seed crystals from their initial temperature to their melting temperature is assumed to be transferred instantaneously to the pellets. Upon pellets introduction into the chocolate mass, the chocolate temperature is uniformly lowered to compensate this transfer of energy. The solving of a complementary transport equation for the pellets temperature is therefore avoided. Analytical calculations using a conduction equation in a pellet submitted to an abrupt change of temperature can assess the validity of this hypothesis [6]. A time of 9 s is needed to reduce the temperature gradient in the pellet to 4% of its initial value. This time is of smaller order of magnitude than the characteristic time for the pellets melting, which is a few minutes.

The heat sink term can therefore be expressed as the product of a melting kinetics and the latent heat of fusion:

$$Q = L\frac{dc}{dt} \tag{3}$$

where L is the latent heat of fusion (J/kg) and c is the concentration of solid pellets (kg/m^3).

The kinetics of melting of solid pellets is built on mass and conductive and convective energy balance equations on a solid pellet and on the molten chocolate surrounding it. The pellets are assumed to be spherical. Figure 1 presents a schematic view of a pellet of radius R surrounded by a layer film of thickness ΔR. The detailed derivation of the heat sink term is given in Appendix A. The final expression is given by

$$Q = -\frac{3c_0 kL}{R_0^2 \rho_S}\left(\left(1+\frac{R}{\Delta R}\right)(T - T_m)\right)\sqrt[3]{\frac{c}{c_0}} \tag{4}$$

where ρ_s is the volumetric mass of the solid pellets (kg/m^3), c is the concentration of solid pellets (kg/m^3), c_0 is the initial concentration of pellets (kg/m^3), R_0 is the initial radius of a solid pellet (m) and T_m is the melting temperature of the solid pellets (K).

Equations (5) and (6) form a system of non-linear partial differential equations:

$$\rho_l C_p \frac{\partial T}{\partial t} = k_{eff}\Delta T - \frac{3c_0 k}{R_0^2 \rho_s}\left(\left(1+\frac{1}{f}\right)(T - T_m)\right)\sqrt[3]{\frac{c}{c_0}} \tag{5}$$

$$\frac{dc}{dt} = -\frac{3c_0 k}{R_0^2 L \rho_S}\left(\left(1+\frac{1}{\mathrm{f}}\right)(T - T_m)\right)\sqrt[3]{\frac{c}{c_0}} \tag{6}$$

where f is the ratio of the layer thickness ΔR and the radius of the pellet.

Simulations are started when solid pellets are added to the chocolate. The initial condition for the simulations is a uniform temperature considering the cooling induced by the fact that pellets are not added at their melting temperature. Mathematically, this is expressed as follows:

$$T(t=0) = T_{ci} - \frac{C_{pp} c_0}{\rho_l C_p}(T_m - T_{bi}) \tag{7}$$

where T_{ci} is the temperature of chocolate at which solid pellets are added (K), T_{bi} is the initial temperature of the solid pellets (K), C_{pp} is the specific heat of the pellets (J kg^{-1} K^{-1}).

The above system of non-linear partial differential equations with boundary conditions is solved by the finite elements method using the commercial package COMSOL® 3.4 (Comsol, Sweden). In this method, the studied geometry is meshed, *i.e.* divided into polygonal elements. For each element, the solution of the equations is approached by a polynomial function. The computational domain for the simulations includes the chocolate mass only. The domain is divided into triangular elements. Figure 2 shows the geometry and the corresponding mesh, composed of 1440 elements. This corresponds to the coarsest mesh where the simulation results do not depend on elements size and number. Evolution of the temperature over 200 s has been simulated using the time-dependent iterative non-linear solver already implemented in the Chemical Engineering Module of COMSOL.

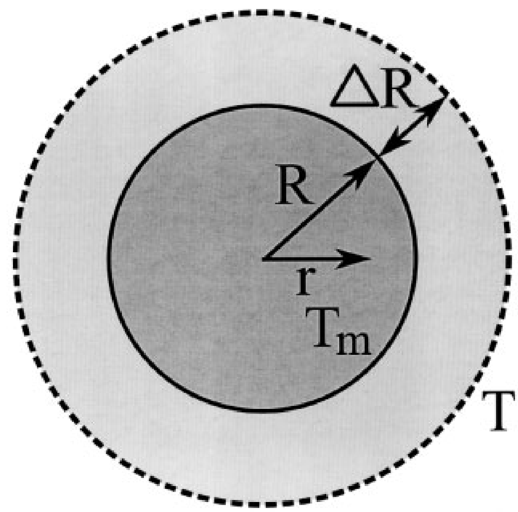

Figure 1. Schematic drawing of a spherical pellet of radius R melting surrounded by a heat transfer layer zone of ΔR thickness. r is the radial coordinate. The surface of the pellet is assumed to be at the melting temperature T_m while the bulk temperature is T.

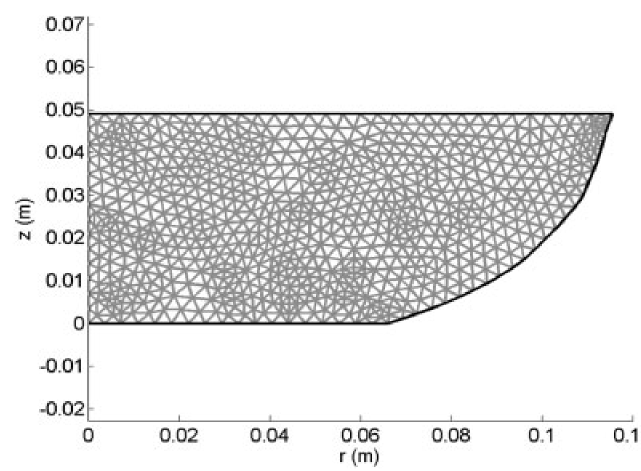

Figure 2. Axisymmetric section of the bowl with mesh, implemented in COMSOL, for 2 kg of chocolate.

3 Results

3.1 Measured and modeled temperature evolution in the bowl

A comparison between experimentally measured values of temperature and calculated values obtained from the model was made to validate the computational model.

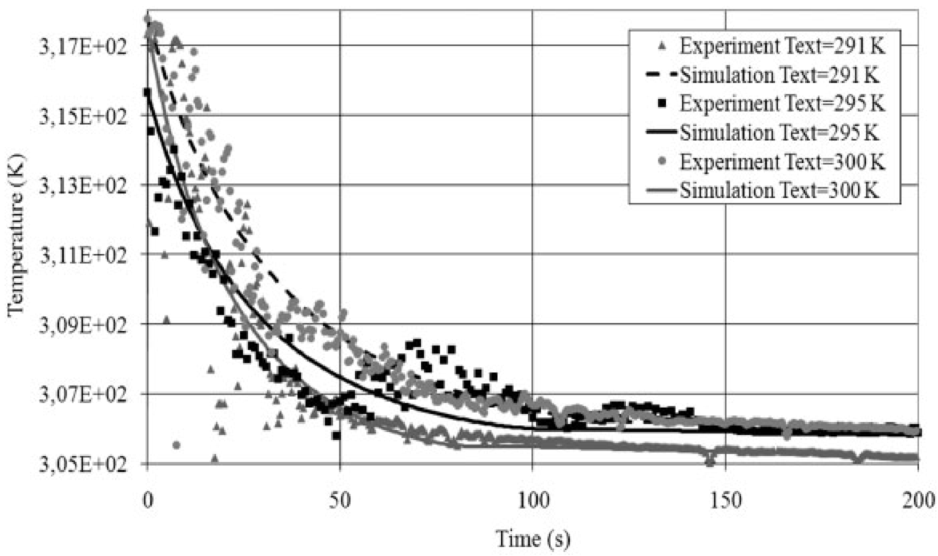

Figure 3. Modeled and measured temperature in the bulk of chocolate as a function of time for three different ambient temperatures. 2 kg of chocolate were used. T_{ext} is the ambient temperature.

Figure 3 shows the evolution of the temperature of the chocolate obtained from experiments and from the model with 2 kg of dark chocolate at three different ambient temperatures. The model parameters are summarized in Table 1. The value of the parameter $f = 1.3$ has been determined so that the simulated temperature evolution during time in the tempering process at a temperature of 295 K fits in sense of least squares to the experimental data based on the first 200 s. This short period is crucial for melting of the seeds. Moreover, the previously developed model, presented by the dashed line, based on an empirical kinetic equation for the sink term, presented a too fast cooling during this initial period. Enhancement due to the new expression of the heat sink can therefore be highlighted in this initial period. After 200 ms, the model is the same as the one validated by Debaste *et al.* [4].

The evolution of the chocolate temperature during the tempering process can be explained by the physical phenomena happening. When the pellets are introduced into the molten chocolate, the melting of the pellets, an endothermic phenomenon, induces a rapid decrease of the chocolate temperature. The melting ends when the temperature of the chocolate is lower than the melting temperature of the pellets. If the chocolate is well tempered, there should remain some seeds of pellets in the chocolate. Then, only the exchange of heat with ambient air still occurs and leads to further cooling of the chocolate. This cooling is slower. The slope of the evolution of temperature along time changes at around 100 s. Before this change of slope, experimental fluctuations of temperature are observed. Small non-uniformities of temperature exist in the stirred chocolate, for example, when a melting solid seed comes close to a thermocouple. Except for these oscillations, the model shows a fairly good match with the experiments. The physical interpretation of the value of $f = 1.3$ is that, at any time, the order of width of the heat limit layer is the same as the radius of the grain. While such a value does not seem to be unrealistic, we cannot assure its physical validity. However, a parametric study, such as presented in Fig. 4, highlights a low influence of f on the temperature evolution. The low sensitivity of the equation system to the value of f is partially mathematically explained by the fact that f appears in Eqs. (5) and (6) in a term having the form of $\left(1+\frac{1}{f}\right)$. For $f >>1$ this term reduces to 1 and is therefore independent of f. The dotted curve, for $f = 3.3$ is therefore really similar to those obtained for any upper value.

Table 1. Values of parameters used in the model and sources. (*) corresponds to data from this work. (**) corresponds to data from Debaste *et al*. [4]. (***) stands for values measured at the beginning of the experiment. (****) are adjusted values.

Parameter	Value	Source
C_p	1580 J kg^{-1} K^{-1}	(*)
C_{pp}	2010 J kg^{-1} K^{-1}	(*)
c_0	129 kg/m^3	(***)
ε_s	0.93	(**)
f	1.3	(****)
h_{out}	6 W m^{-2} K^{-1}	(**)
k	0.2 W m^{-1} K^{-1}	(**)
k_{eff}	10.7 W m^{-1} K^{-1}	(**)
L	157000 J/kg	(**)
R_0	0.0015 m	(*)
ρ_l	1290 kg/m^3	(**)
ρ_s	990 kg/m^3	(**)
T_{bi}	277 K	(***)
T_{ci}	315.5 K	(***)
T_{ext}	295 K	(***)
T_m	306 K	(*)

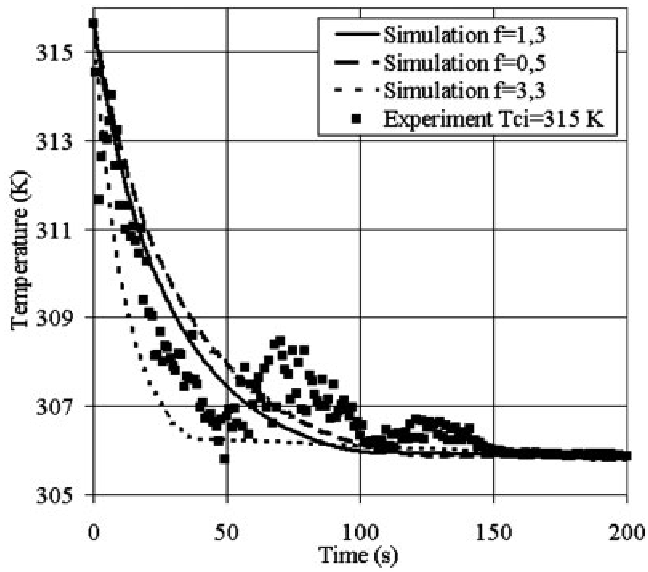

Figure 4. Sensitivity analysis on the value of *f*. T_{ci} is the initial temperature of the chocolate.

3.2 DSC measurement

Two peaks are observed in a typical DSC curve of the melting of a sample of chocolate during a tempering experiment (Fig. 5). The first one around 300.8 ± 0.8 K corresponds to the melting of form IV crystals, the second one, around 304.2 ± 0.4 K, corresponds to the melting of form V crystals [7]. In order to assess the quality of the tempering and the amount of crystals present during the process, the area of the second peak is plotted as a function of time during the tempering. Figure 6 presents results for five different experiments. Two distinct behaviors are observed:

(1) Form V appears since the beginning of the experiment. The amount of crystals grows fast and viscosity rises rapidly. The chocolate is over-tempered and cannot be further used. This is due to a too large quantity of form V seeds. The pellets are not completely melted.

(2) An induction period of 50 min appears before growth of the form V crystals. The chocolate is well tempered.

A third behavior, not plotted, corresponds to untempered chocolate, without form V crystals due to a complete melting of the seeds. Figure 6 also shows that very small variations of conditions can modify the tempering quality.

3.3 Tempering quality prediction

The high sensitivity of the result to the ambient conditions complicates the systematic determination of conditions leading to a well-tempered chocolate. To limit the number of experiments required, it is proposed to define a criterion of good tempering based on the measured temperature in the chocolate. Such a criterion is based on the temperature reached shortly after the end of the melting of seeds. At that time, the temperature is characteristic of the melting and not of recrystallization. This criterion is a small (~1 K) interval of temperature after a fixed given time.

It is then possible to use the presented model to predict the tempering quality. This was done for three chocolates of Belcolade. For each of these chocolates, an interval of temperature leading to well-tempered chocolate was identified combining tempering experiments and DSC. Using the model, it was possible to predict the temperature of addition of the pellets to have a well-tempered chocolate for a wide range of room temperatures (from 291 to 301 K). The simulations were realized for various masses of chocolate in the bowl (from 1 to 3 kg).

4 Discussion

Combination of the model with this criterion represents a powerful tool, as it can be used to determine the initial tem-

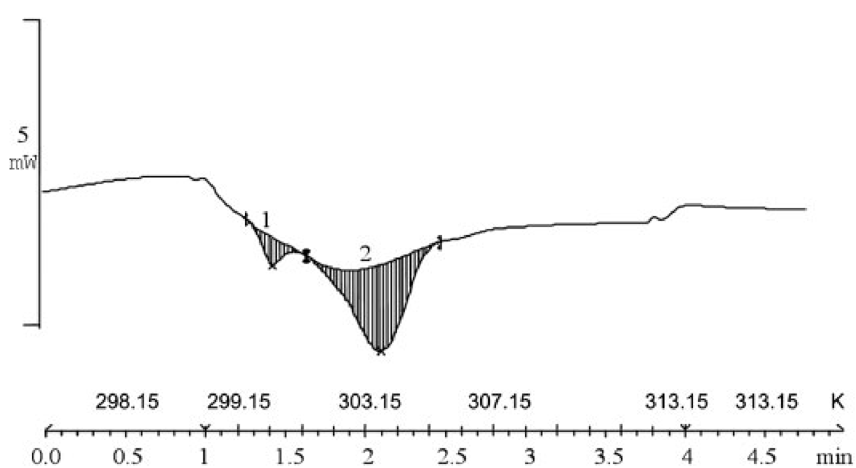

Figure 5. Typical DSC curve.

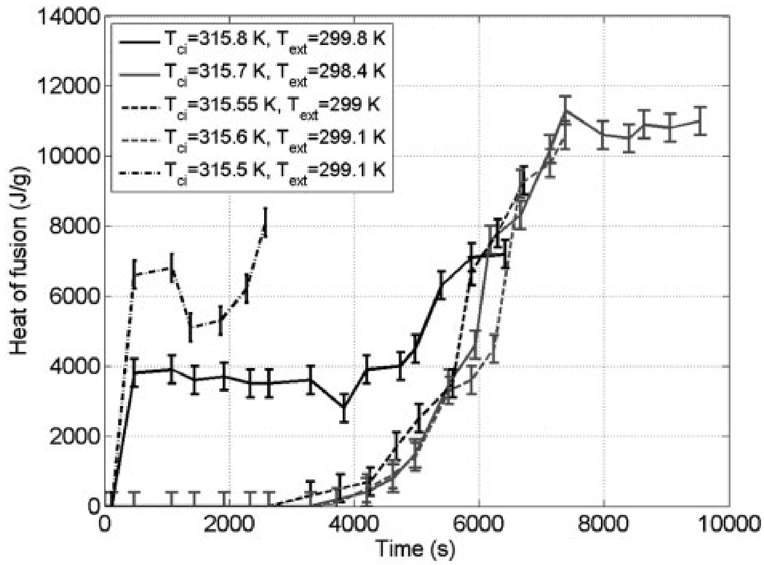

Figure 6. Evolution of the form V heat of fusion as a function of time for five different experiments. T_{ext} and T_{ci} are the ambient temperature and the initial temperature of the chocolate, respectively.

perature of melted chocolate at which pellets of seed crystal have to be introduced to give a well-tempered chocolate over a wide range of operating conditions, mass of chocolate and bowl geometries. In this way, it is possible to minimize expensive and time-consuming pilot tests and to have good indications on the quality of the final products.

The presented model is a refined version of a previous one [4]; the heat sink term is changed to explicitly consider the transport phenomena. This improvement clearly enhances the fitting quality of the model for the initial period where the seeds are melting. As this period is the key one for the tempering criterion, using this new sink term offers a significant improvement to predict the tempering quality.

The model can be improved in particular by looking for a more reliable determination of heat transfer layer thickness. In this model, the ratio between the layer thickness and the pellet radius is kept to the constant value *f*. Using a more complex relationship between layer thickness and pellet radius, for example using classical correlation or computational fluid dynamics around a pellet, might improve the model. However, the main challenge is the change of the criterion of good tempering from a temperature determined empirically to a criterion relying on the kinetics of crystallization of the form V.

Although this model was developed for a particular patented process, the principle of the modeling of the melting could be used in any other process where the heat transport phenomenon is limiting the melting.

Appendix A: Derivation of the sink term Eq. (4)

Firstly, mass balance applied to a solid pellet expresses the balance between the solid mass lost during melting and the liquid mass formed during melting.

$$\frac{d}{dt}\left(\rho_s \frac{4}{3}\pi R^3\right) = -4\pi R^2 \mathcal{J} \qquad (8)$$

where $\mathcal{J}$ is the melting rate per surface unit (kg m^{-2} s^{-1}).

Mass balance on a solid pellet leads to

$$\mathcal{J} = -\rho_s \frac{dR}{dt} \qquad (9)$$

Secondly, energy balance applied to the melting front of a solid pellet states that heat transported by conduction from molten chocolate to the external surface of the pellet is used integrally to melt the solid pellet:

$$4\pi R^2 \mathrm{k} \left.\frac{dT}{dr}\right|_{\mathrm{R}} = 4\pi R^2 \mathcal{J} L \qquad (10)$$

where r is the radial position (m).

Thirdly, with the assumption of quasi stationary conditions, mass balance applied on a liquid volume of chocolate leads to

$$4\pi \mathrm{v}(r) r^2 = \frac{4\pi R^2 \mathcal{J}}{\rho_l} - \frac{4\pi R^2 \mathcal{J}}{\rho_s} \qquad (11)$$

where $v(r)$ is the radial velocity of liquid chocolate (m/s) and ρ_l is the volumetric mass of liquid chocolate (kg/m^3). Equation (11) expresses the mass flux of liquid resulting from the melting of the chocolate due to a difference of volumetric mass between the solid and the liquid. As the liquid is denser than the solid, the melting of the pellets leads to a local mass flow in the direction of the pellets. This movement generates a convective heat transfer.

Fourthly, a steady-state energy balance applied to a liquid volume (thus without sink term) included between position r and position $r + dr$, considering conductive heat transfer (lefthand side) and local convective terms due to the liquid velocity (right-hand side), leads to

$$k\frac{d}{dr}\left(r^2\frac{dT}{dr}\right) = \rho_l C_p r^2 v\frac{dT}{dr} \tag{12}$$

Combining Eqs. (7) and (8) gives

$$k\frac{d}{dr}\left(r^2\frac{dT}{dr}\right) = \rho_l C_p R^2 \mathcal{J}\left(\frac{1}{\rho_l}-\frac{1}{\rho_s}\right)\frac{dT}{dr} \tag{13}$$

The solution of this equation at $r = R$ is

$$\left.\frac{dT}{dr}\right|_R = \frac{1}{R}\left(\frac{1}{f}(T-T_m)+T-T_m\right) \tag{14}$$

Combining Eqs. (9), (10) and (14) gives

$$\frac{dR}{dt} = -\frac{k}{RL\rho_s}\left(\frac{1}{f}(T-T_m)+T-T_m\right) \tag{15}$$

Finally, it can be shown that the radius of solid pellets is associated with the concentration of solid pellets in the chocolate mass. This concentration can be expressed as the ratio of the mass of pellets added to the molten chocolate and the chocolate volume.

$$c(t) = \frac{N_p M_p(t)}{\mathrm{V}} \text{ and } c_0 = \frac{N_p M_p(0)}{V} \tag{16}$$

where N_p is the number of pellets, M_p is the mass of one pellet (kg) and V is the volume of chocolate (m^3).

Moreover, the mass of one pellet is expressed as a function of its radius through

$$M_p(t) = \rho_s \frac{4}{3}\pi R(t)^3 \tag{17}$$

Therefore, Eqs. (16) and (17) lead to

$$\frac{c(t)}{c_0} = \left(\frac{R(t)}{R_0}\right)^3 \tag{18}$$

Differentiation of Eq. (18) leads to

$$\frac{dc}{dt} = \frac{3c_0R^2}{R_0^3}\frac{dR}{dt} \tag{19}$$

Equations (3), (15) and (19) lead to the final expression of the heat sink term

$$Q = -\frac{3c_0kL}{R_0^2\rho_s}\left(\left(1+\frac{R}{\Delta R}\right)(T-T_m)\right)\sqrt[3]{\frac{c}{c_0}} \tag{20}$$

Acknowledgments

This research was conducted as part of a project funded by Belcolade manufacture (Belgium). The authors wish to thank Pierre Descamps (Belcolade, Belgium) for useful discussions. F.D. and B.H. acknowledge financial support from the Fonds National de la Recherche Scientifique, Belgium. The authors also wish to acknowledge the ARCHIMEDES project for its financial support.

Conflict of interest statement

The authors have declared no conflict of interest.

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