MODELLING OF HEAT TRANSFER, MASS TRANSFER AND FLAVOUR DEVELOPMENT IN CHOCOLATE CRUMB

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Chocolate crumb is a vacuum dried, crystalline mixture of sugar, milk and cocoa solids and it is manufactured as a base ingredient for the production of milk chocolate. The final drying stages of the manufacturing process confer to the crumb its unique caramelization flavours and structural quality. The caramelization flavours are a product of the Maillard reaction, which is dependent on the time, temperature and moisture content of the material. The aim of this research is to generate a model for the moisture and temperature distribution within the product to achieve a scientific understanding of flavour development.

Heat and mass transfer within a packed bed of crumb is modelled using a multiphysics software (Femlab). Experimental data for mass and heat transfer coefficients were obtained from laboratory experiments and packed bed literature. Kinetic data for the Maillard reaction was obtained by measuring the amount of flavour produced by crumb cooked under specific temperatures, moisture contents and cooking times. This data was then overlaid onto the solutions for the heat and mass transfer profile to gain an understanding of how operating conditions within the drying process can affect the flavour generation.

Keywords: chocolate; crumb; Maillard; drying; finite element; heat transfer.

INTRODUCTION

The aim of the food industry is to produce safe, convenient, good quality foods in sufficient volume to feed the population. In the past food processes have been designed using practical experience alone; empirical understanding of product quality (such as flavour and moisture content) has been used to select the most appropriate commercially available equipment. Food engineering aims to understand the process behaviour of food materials on the macro-scale by applying expertise from chemical and mechanical engineering. Furthermore, foods are complex materials whose breakdown in the mouth (which generates sensations of taste and texture) is poorly understood. Therefore an engineering understanding of food manufacture and its behaviour in the mouth generates a commercial advantage.

In the last 20 years the food market has evolved considerably. Food companies can no longer rely on producing a small number of strong brands to remain successful. Consumers demand a large variety of high quality products; food companies must constantly innovate and launch new products to maintain profits and market share. The microstructure of a material has an influence over the key attributes of a product as evaluated by consumers such as flavour and texture. Many of these properties are poorly understood. For example, chocolate is a complex mixture of polymorphic confectionary fats, sugars and cocoa solids. The process history of the material controls the final crystal form (Pinschower and Fryer, 2000): correct tempering is necessary to obtain crystals with the correct melting temperature and mouthfeel. The polymorphism of chocolate makes it difficult to process, although it is possible (Tewkesbury and Fryer, 2000) to model cooling behaviour over a range of cooling rates.

Advances in the last decade in microscopy techniques and computing capabilities have made it possible to understand a food's structure, its relation to physical properties (so called structure-property relationships) and how to engineer and control these properties (Aguilera and Simpson, 2004). Food microstructure can strongly affect its physiochemical, functional, technological and even nutritional properties. The design of a food product must account for all these relationships whilst maintaining the high standards the consumer expects. Therefore, from an engineering perspective, the microstructure of any food is paramount.

Many of the processes of food manufacture involve mass and heat transfer, and thus the fundamental science involves control and understanding of transport phenomena. In addition, flavour reactions occur. The problem is essentially one of reaction engineering, in which heat and mass transfer are coupled with flavour reactions.

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Aguilera and Stanley (1999) and Saravacos and Maroulis (2000) give a comprehensive review of transport properties in foods.

In this paper, the manufacture of chocolate crumb is considered. A wide variety of milk chocolate types exist today each with distinct flavours and textures attributed to manufacturing techniques. The dairy ingredients are important to the development of flavour, texture and appearance of all milk chocolate (Beckett, 1999). The main distinction between manufacturing processes is whether the dairy ingredients are processed as milk powder or crumb. Crumb is a vacuum dried, crystalline mixture of sugar, milk and cocoa butter. Traditionally production of chocolate using fresh milk was problematic due to its poor shelf life and seasonal variation. The manufacture of crumb solved this as it has superior keeping qualities due to low moisture content (approximately 1% water) and antioxidant properties (Beckett, 1999). The caramelization flavours produced during the manufacturing of crumb are functionally critical in determining the chocolate flavour.

Crumb manufacturing processes are largely proprietary, but most follow the approach shown in Figure 1. Pasteurized milk is concentrated in a multi-effect evaporator to approximately 40% solids. Sugar is then added to the milk and the mixture is condensed in a vacuum cooker to 90% solids at which point the mixture is commonly

known as sweetened condensed milk (SCM). Cocoa liquor is added to the SCM using an inline paddle mixer known as a kneader to produce a paste, which then undergoes rapid dehydration in a vacuum oven to 95% solids. The crumb exits the ovens as a wet solid of variable particle size which is dried further to approximately 1%.

The drying of crumb is carried out at temperatures above 60°C; moisture transport both within crumb particles and in the vapour phase is significant. As the material dries, flavour generation reactions increase in importance. Muresan *et al.* (1999) investigated the aroma profile development during the manufacture of block-milk (white crumb). This study revealed that the final drying stages of crumb manufacture are most important for flavour development i.e. from a liquid–solid phase change to final crumb. The main flavour reaction in foods is called the Maillard reaction, a term used to characterize a group of chemical reactions initiated by the reaction between a reducing sugar and an amino compound, which leads to non-enzymatic browning and flavour development in foodstuffs. The reaction is time, temperature and moisture dependent. Conditions that favour the reaction are generally accepted as low moisture ($<10\%$) and high temperature ($>60°C$) although little in depth analysis has been carried out so far.

The majority of studies have focused on model systems and the identification of the chemical classes formed at defined stages of the Maillard reaction (Labuza *et al.*, 1993; O'Brien *et al.*, 1998). Martins *et al.* (2001) give a comprehensive review of the role of kinetically modelling the Maillard reaction in foods. Kinetic studies of elements of the reaction have been conducted by Wedzicha and colleagues (Wedzicha *et al.*, 1994; Wedzicha and Leong, 1998a, b; Wedzicha, 1999; Davies *et al.*, 1997; Vilchez and Wedzicha, 1997; Gögüs *et al.*, 1998; Leong and Wedzicha, 2000); individual reaction regimes such as sulphite inhibited reactions and the Maillard reaction between glucose and glycine have been studied and rate constants for individual steps in the reaction determined. These studies have revealed temperature to be the most important parameter for the Maillard reaction.

The combination of heating and drying in the crumb making process promotes Maillard reactions that contribute to the antioxidant properties and caramel flavours found in chocolate. The main Maillard reaction in crumb is between lactose (a disaccharide and the main reducing sugar) and the epsilon amino group of lysine present in milk protein. This process is time, temperature and moisture dependent (Minifie, 1989). The final convective drying stage of the process is essential to the flavour and structural quality of the product. The aim of this research is to generate a validated model for the moisture and temperature distribution within the material which can be combined with kinetic models for the Maillard reaction so that a scientific understanding of flavour development may be achieved.

Pasteurised milk

Evaporator I

40 % solids

Sugar →

Batching

70 % solids

Evaporator II

90 % solids

Cocoa butter →

Kneader/mixer

Vacuum Oven

95 % solids

Dryer

99 % solids

Figure 1. Key processing stages for the manufacture of crumb (Beckett, 1999).

EXPERIMENTAL

Drying of Chocolate Crumb

To understand drying on a molecular scale and predict the drying kinetics under various conditions, it is necessary to measure the drying kinetics of the material under well-defined conditions in a laboratory. Edmondson *et al.*
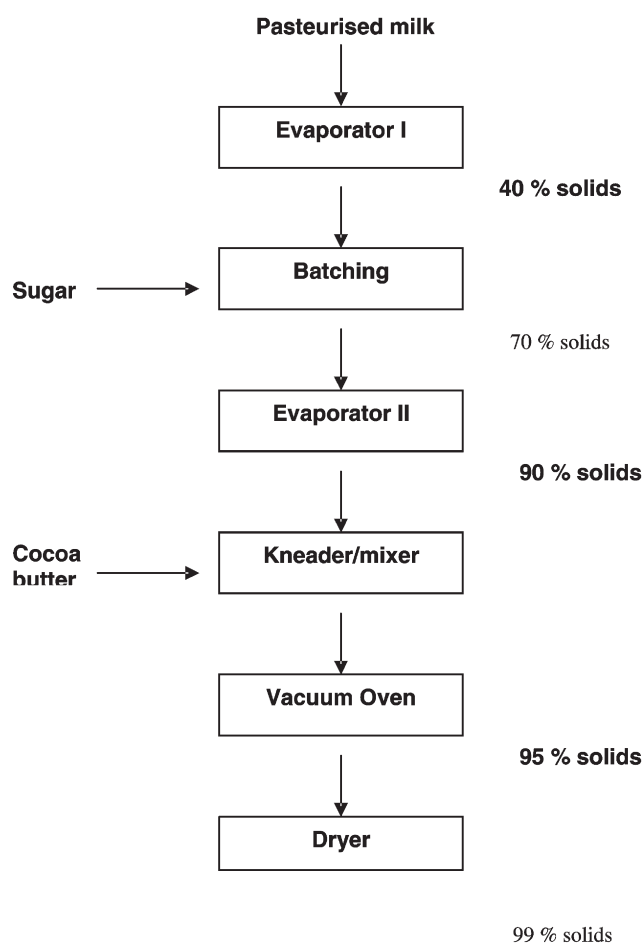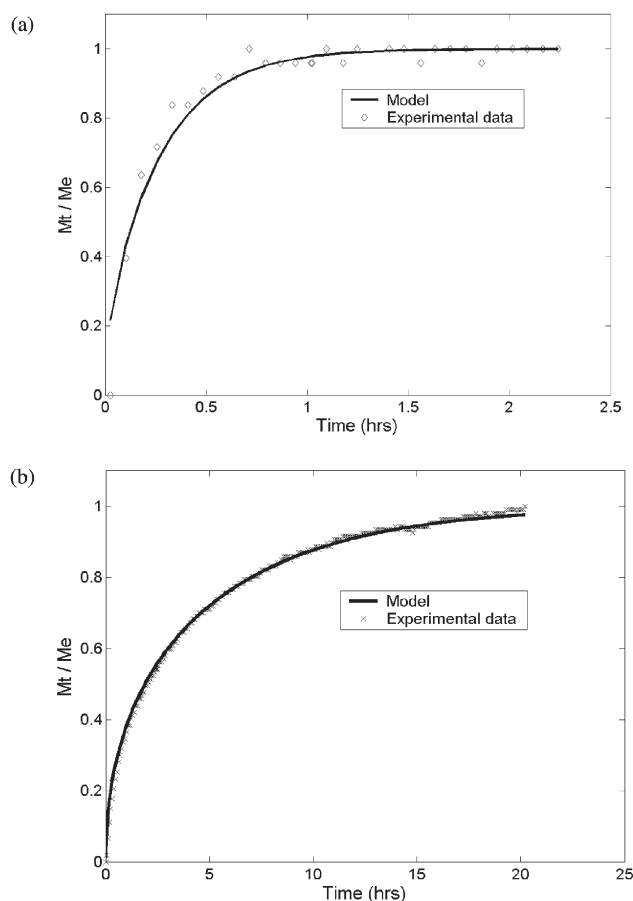
(a)

(b)

Figure 2. Diffusion models fitted to experimental data (Edmondson *et al.*, 2004, 2005): (a) thin layer, (b) sphere, using dry air at 100°C. M_t = moisture content of the sample, M_e = equilibrium moisture content.

(2005) carried out experiments to investigate the drying behaviour of crumb in a thin layer (1 mm particles) and a sphere (30 mm particles), in dry and humid air (initially saturated at 40°C) at 200 L min^{-1} and at 60°C, 80°C and 100°C. The results showed that, as expected, internal diffusion was the controlling moisture mechanism. The diffusion coefficients were estimated by fitting experimental data to Fick's second law using a numerical method of least squares. Figure 2 shows the fit between experiment and theory, and Table 1 lists typical diffusion coefficient values.

It is clear from the results that the diffusion coefficient is very structure dependent; dust has a diffusion coefficient more than 20 times that of a compacted sphere. The

diffusivity of water into humid air is higher than for dry air, suggesting that the surface of the material may become crusted in dry air, restricting moisture loss. The effect of temperature thus appears less important than that of microstructure.

Flavour Development

The flavour reaction kinetics were measured by transferring real conditions found in the convective drying stage onto a laboratory scale. Laboratory work focused on determining the effect of cooking time, temperature and moisture content on the rate of the reaction.

A set of crumb samples was made with a range of moisture contents (1–5%). Multiple samples for each moisture content were created by placing 75 g of crumb into individual aluminium foil bags that were then sealed using a laboratory heat sealer. These samples were then cooked at a range of temperatures (45–110°C) and cooking times (0.5–6 h) in a conventional convective laboratory oven. The amount of flavour in each cooked sample was quantified using a range of analytical techniques. These included using a series 200 Perkin-Elmer HPLC to identify the quantity of key flavour markers [Di-hydro-hydroxy-maltol (DHHM), Maltol, Furaneol and Hydroxyl-methy-furfural (HMF)], a lambda 20 Perkin-Elmer (uv-785A) spectrometer to measure the amount of brown pigment and an air quality sensor to quantify the amount of oxidisable organics in the headspace of a sample (RS components).

The Maillard reaction, like any other chemical reaction, is thermally activated. The temperature dependence of the reaction is represented by an Arrhenius relationship. Table 2 shows activation energies calculated for four flavour markers; the data show activation energies in the order of 100 kJ mol^{-1}.

A simple expression has been used to estimate the level of flavour expected from a cooking temperature and time. Moisture content has not been taken into account because below about 5% moisture, it affects flavour far less than temperature and time. The equation used was

$$f = f_0 + b \cdot \exp[-E/RT] \cdot t \tag{1}$$

where, f is the measure of flavour after cooking and f_0 before cooking, b is the reaction rate (mol m^{-3} s^{-1}), E is the activation energy (kJ mol^{-1}), T is the temperature (K), R is the gas constant (J mol^{-1} K^{-1}) and t is the time (s). The parameters f_0 and E were put into equation (1) using b as a fitting

Table 1. Estimated values for diffusion coefficient for a thin layer and sphere of crumb (Edmondson *et al.*, 2004, 2005).

Thin layer			30 mm sphere		
Air condition	Temperature (°C)	Diffusion coefficient (m^2 s^{-1} * 10^{-10})	Air condition	Temperature (°C)	Diffusion coefficient (m^2 s^{-1} * 10^{-10})
Dry	40	40			
Dry	60	60	Dry	60	4
Dry	80	100	Dry	80	4.45
Dry	100	100	Dry	100	4.5
Dry	120	120			
Humid	60	48	Humid	60	17.1
Humid	80	125	Humid	80	12.5
Humid	100	190			

Table 2. Calculated activation energies (KJ mol^{-1}) for different flavour markers at different moisture contents using Arrhenius equation.

Moisture %	dhhm	Maltol	hmf	Furaneol
1.2	97.8	96	164.2	58.9
1.8	123.3	141.4	146.8	96.7
3.1	148.9	114.8	134.7	104.1
4.1	173.1	72.9	86.6	134.7
5	180.9	185.5	232.2	36.3

parameter. The R^2 values for each analytical technique were: flavour markers = 0.6–0.8; colour = 0.96 and odour = 0.91. The correlation for colour is shown in Figure 3. The fit to such a simple equation for the flavour markers is less good than for colour: markers are both formed and removed, because they are intermediates in the Maillard reaction pathway. Good correlation for colour was also noted by Robbins and Fryer (2003) in the roasting of grains. Equation (1) was used to predict the extent of flavour produced in crumb (1–5% moisture content) under conditions found in the convective drying stage of the process.

MODELLING

Moisture Transfer Mechanisms

The removal of moisture from food systems is a complex physical process with heat and mass transfer taking place simultaneously. The microstructure determines the rate of heat and mass transfer and thus flavours development within the system. Many of the theoretical approaches to understanding drying are based around interpreting the information from drying-rate curves obtained from laboratory experiments. Keey (1978) classifies drying history into three distinct regimes; (1) the induction period, in which the heat and mass transfer processes between the material and the gas stream approach a dynamic equilibrium; (2) 'constant rate period' where the exposed surface of the material is supplied with sufficient moisture to keep it
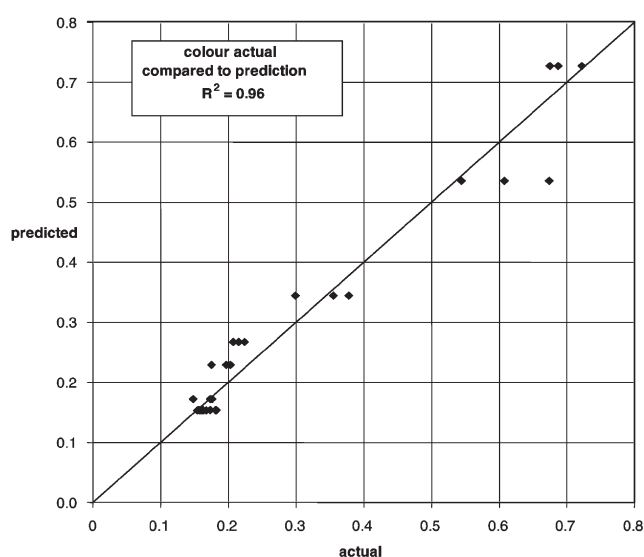

Figure 3. Accuracy of equation (1) in predicting colour from cooking temperature and time.

saturated for drying to be boundary layer controlled, followed by (3) 'falling rate period', in which the drying is by internal moisture diffusion.

During convective drying, energy is supplied from the surrounding environment and moisture transferred from within the solid. To achieve a fully theoretical analysis of the drying process heat and mass transfer must be modelled simultaneously. Reviews of the modelling of heat and mass transfer in foods can be found in Fortes and Okos (1980) and Bruin and Luyben (1980). Most modelling approaches are based around either the theory of irreversible thermodynamics (Luikov, 1975) or a classic (mechanistic) approach (Whitaker, 1977). Luikov derived a set of heat and mass transfer governing equations based on a phenomenological theory. This approach has been adopted by several authors to model the drying of foodstuffs (such as Chen and Johnson, 1969; Husain *et al.*, 1973; Rossen and Hayakawa, 1976; Lobo *et al.*, 1995; Ribeiro *et al.*, 1993). However Luikov's method has several disadvantages, the most significant being the physical relevance of the derived transport coefficients. Whitaker developed a mechanistic model by defining a set of conservation equations for each phase and then volume averaging for all phases. Many authors have developed a similar approach to Whitaker's for porous media (such as Wei *et al.*, 1985; Stanish *et al.*, 1986; Nasrallah and Pere, 1988; Chen and Pei, 1989). This method considers the transition from an individual phase at a microscopic level to the representation of average volume at a macroscopic level. This approach will form the physical basis for modelling in this study. An understanding of moisture movement mechanisms within the porous system is therefore critical.

Mass transfer can be due to a combination of mechanisms: liquid movement due to concentration differences, vapour diffusion due to partial vapour-pressure gradients (caused by temperature gradients), liquid movement due to capillary forces, liquid or vapour flow due to differences in total pressure, effusion (Knudsen) flow, liquid movement due to gravity and surface diffusion (Fortes and Okos, 1980). The microstructure, process conditions, moisture content and period of drying will all have an influence over which transport mechanism dominates within the particle. The internal microstructure of crumb is complex: it is a hygroscopic capillary porous solid having interconnecting voids, as shown in Figure 4 (Edmondson *et al.*, 2004). Either capillary flow, evaporation-condensation or vapour flow may control the moisture transport. Liquid diffusion can only take place if there is moisture continuity within the body. Thus this cannot be used to model the mass transport in low moisture porous systems. Henry (1939) investigated the uptake of moisture by cotton bales and recognized that in low moisture systems the moisture migrates entirely in the vapour phase. Harmathy (1969) later refined Henry's model to develop a set of simultaneous heat and mass transfer during the pendular state of porous systems. It seems likely that a vaporization-condensation mechanism is controlling the moisture movement within the porous media hence this was used here.

Model Description

The convective dryer is the final dehydration stage of the process and is 4 m long. The dryer operates continuously;
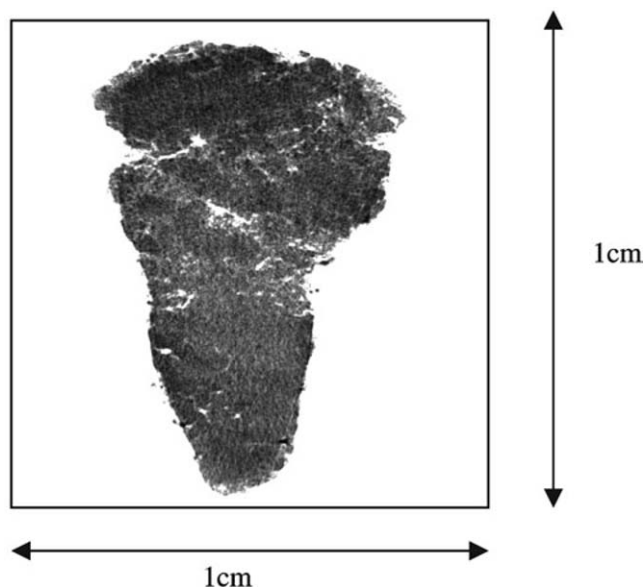
Figure 4. X-ray micrograph of a typical crumb particle, showing voids and cracks in the structure (Edmondson *et al.*, 2004, 2005).

crumb particles enter the dryer at low moisture (4% dry weight) and have a residence time of 6 h. Dry hot air flows counter-currently to the crumb conveyed by gravity down the dryer. Figure 5 shows the flows of each phase along the dryer.

The model considers exchange of heat and moisture between the crumb particles. The model describes the
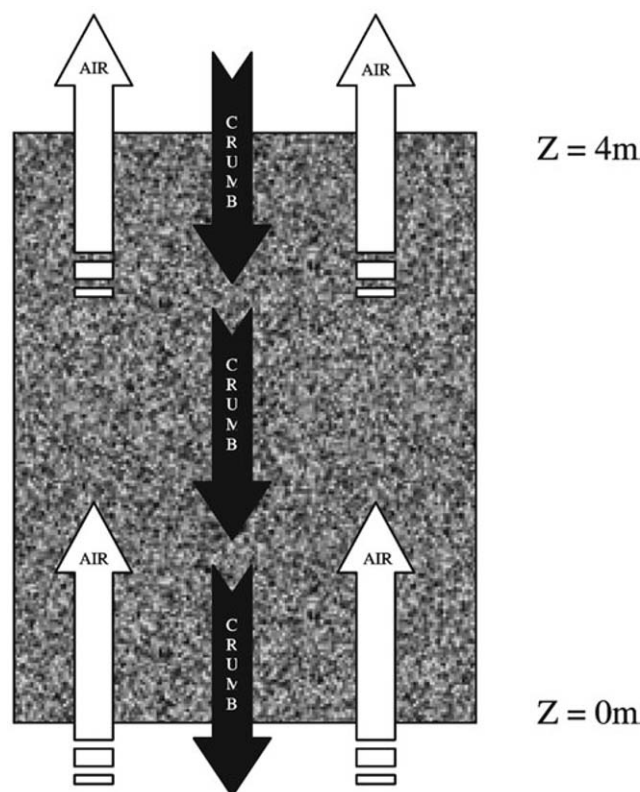

Figure 5. Diagram showing air and crumb flows in the final dehydration stage.

transport mechanisms of moisture and heat at the scale of the particle (micro porous) and the scale of the dryer (macro porous). The two systems are coupled via source terms in the heat and mass transfer processes.

The drying bed is described by one-dimensional geometry of axial coordinate z. The particles are modelled as axisymmetric geometries of spherical coordinate r. The juxtaposition of many such 'particle geometries' defines a 2D geometry representative of the spatial and temporal properties of the drying bed (Femlab Chemical Engineering Module, 2001).

A comprehensive set of fundamental heat and mass transfer conservation equations has been set up, coupled with thermodynamic equilibrium expressions that are dependent on the moisture content of the material. These are solved using a partial differential equation (PDE) solver by employing finite element analysis (Femlab).

Model Assumptions

Crumb particles are modelled as isotropic spheres and move down the bed at constant velocity. The particles are considered solid porous structures containing an immobile liquid phase that evaporates. Water vapour within the crumb diffuses through the porous structure because of vapour pressure gradients and is convected away from the surface of the crumb by the hot air stream. There is no exchange of mass and energy between the different crumb particles packed in the bed. Moist air obeys the ideal gas law. Humidity in the drying air stream is convected in a counter flow manner through the tower. The air stream exchanges heat and mass with the particles. The diffusive outward flux of vapour from the crumb is heated by the hot air and contributes to the mass balance of humidity in the air.

Conservation of Moisture for Crumb Particles and Drying Air Stream

Liquid moisture evaporates within the porous structure as it is convected through the dryer at the falling velocity of the crumb. Conservation of liquid moisture, w, at any point is described by,

$$\frac{\partial w}{\partial t} + \bar{\nabla} \cdot (w\bar{v}) = R_{\mathrm{w}} \qquad (2)$$

where R_{w} = Evaporation (kg water/kg dry solid·s) and $\bar{v}$ (m s^{-1}) is the velocity of the particles. The initial moisture content, w_0, is, 0.04 kg water/kg solid at all radii.

Water vapour diffuses through the porous matrix of the crumb down vapour pressure gradients.

The conservation of moisture in the vapour phase, c (mol m^{-3}), is described by,

$$\frac{\partial c}{\partial t} + \bar{\nabla} \cdot (-D_{\mathrm{va}}\bar{\nabla}c) = R_{\mathrm{c}} \qquad (3)$$

where R_{c} is the evaporation (mol m^{-3} s^{-1}) R_{w} in different units and D_{va} is the diffusivity of water vapour. The initial vapour pressure is the equilibrium vapour pressure at the initial water content and initial temperature of the crumb.

Humidity in the drying air stream is convected with the bulk flow down the dryer. Diffusion of water vapour is

also modelled. Moisture is exchanged between the crumb and the air stream and is defined as a diffusive flux.

The conservation of moisture at any point within the drying air stream, c_2 (mol m^{-3}), is described by,

$$\frac{\partial c_2}{\partial t} + \frac{\partial}{\partial z} \cdot \left(-D_{va} \frac{\partial c_2}{\partial z} + c_2 \bar{u} \right) = R_{c2} \qquad (4)$$

where $\bar{u}$ (m s^{-1}) is the vapour phase velocity and $R_{c2} =$ Diffusive flux $= k_{ext} \ a \ (c_2 - c)$ (mol m^{-3} s^{-1}) between gas and particle surface where k_{ext} (m s^{-1}) is the external mass transfer coefficient and a (m^2 m^{-3}) is the specific area of the particles.

Conservation of Energy for Crumb and the Drying Air Stream

The crumb is assumed to be quasi-homogenous with an effective thermal conductivity k (W m^{-1} K^{-1}). Energy is exchanged between the crumb and the air stream. The heat energy of the air raises the temperature of the diffusive flux to the temperature of the air stream. The conservation of energy in the crumb is described by,

$$\rho_f c_{pf} \frac{\partial T}{\partial t} + \bar{\nabla} \cdot (-k_f \bar{\nabla} T) = R_T \qquad (5)$$

where $R_T = \lambda \cdot R_c$ (J m^{-3} s^{-1}), c_{pf} (J kg^{-1} K^{-1}) is the crumb specific heat ρ_f (kg m^{-3}) is the crumb density and k_f (W m^{-1} K^{-1}) is the effective thermal conductivity.

Heat energy in the drying air stream is conducted and convected. The conservation of energy in the drying air is described by,

$$\rho_a c_{pha} \frac{\partial T_a}{\partial t} + \frac{\partial}{\partial z} \cdot \left(-k_a \frac{\partial}{\partial z} T_a + \rho_a c_{pha} T_a \bar{u} \right) = R_a \qquad (6)$$

where c_{pha} (J mol^{-1} K^{-1}) is the humid heat of the air, ρ_a (kg m^{-3}) is the vapour density, T_a (K) is the air temperature, k_a (W m^{-1} K^{-1}) is the effective thermal conductivity of the vapour, $R_a = c_{pva} \ R_{c2} \ (T_a - T) - h_a \cdot a \cdot (T_a - T)$ (J m^{-3} s^{-1}) is the diffusive flux from the surface where c_{pva} (J mol^{-1} K^{-1}) is the specific heat of water vapour, h_a (W m^2 K^{-1}) is the heat transfer coefficient from the surface of crumb to the bulk vapour and a (m^2 m^{-3}) is the specific surface area.

Kinetic and Thermodynamic Approximations

The evaporation of liquid moisture within the crumb is defined by,

$$\text{evaporation} = k_{evap} a (c_{sat} - c) \qquad (7)$$

where k_{evap} is the evaporation rate constant (m s^{-1}) and c_{sat} (mol m^{-3}) is the saturated vapour concentration defined below.

It is therefore important to relate the vapour pressure with the temperature and moisture content of the solid using an isotherm. Equation (8) is an empirical isotherm

for crumb based on the model derived by Nellist (1976),

$$W_e = 2.22 - 0.48 \log_e (1 - \varphi/100)$$
$$- 1.53 \log_e (T_a) \qquad (8)$$

where W_e is the equilibrium moisture content, φ is the air relative humidity and T_a is the air temperature which gives the following in terms of the water content, w:

$$\varphi = \frac{P_v}{P_{sat}} = 1 - \exp[(w \times 100) + 0.48$$
$$\times \log (T - 273) - 2.22)/-1.53] \qquad (9)$$

$$c_{sat} = \frac{P_{sat}}{RT} (1 - \exp[(w \times 100) + 0.48$$
$$\times \log (T - 273)) - 2.22)/-1.53] \qquad (10)$$

$$P_v = c_{sat} RT \qquad (11)$$

The Clausius–Clapeyron equation is used to model the vapour pressure above free liquid surfaces:

$$P_{sat} = 611 \left(\exp \frac{53.49 - 6808}{T - 5.09 \times \log (T)} \right) \qquad (12)$$

The evaporation rate constant, k_{evap}, is estimated using the data obtained from the laboratory drying experiments (Edmondson *et al.*, 2004). The external mass and heat transfer coefficients, k_{ext} and h_a, are estimated using packed bed literature (Ranz, 1952) by employing the Froessling (1938) equation:

$$N = 2.0 + 0.60 \xi^{1/3} N_{Re}^{1/2}$$

where, $N_{Re} = d\rho v/\mu$, for heat transfer $N = N_{Nu} = h_a d/k$ and $\xi = N_{Pr} = c_{pa}\mu/k$ where d (m) is the particle diameter, k (W m^{-1} K^{-1}) is the thermal conductivity of air, c_{pa} (J Kg^{-1}K^{-1}) is the specific heat of air μ (kg m^{-1} s^{-1}) is the viscosity and for mass transfer $N = N'_{Nu} = k_{ext} d/D_{va}$ and $\xi = N_{Sc} = \mu/\rho D_{va}$ where D_{va} (m^2 s^{-1}) is the water vapour diffusivity and ρ (kg m^{-3}) is the air density.

RESULTS AND DISCUSSION

The distribution of temperature and moisture has been computed for both the crumb and the air stream. The program models the exchange of mass and energy: the drying stage performs continuously and thus the transport processes will reach a steady state at each axial and radial position within the drier. The governing equations set up in this problem are non-linear as the coefficients of the derivatives in the general form are a function of the dependent variables. The solution is numerically difficult as a result, but converges rapidly using the appropriate 'highly non-linear' algorithm within Femlab. The temperature and moisture content used in the rest of the paper show the range of effects that are seen; real conditions have not been used for commercial confidentiality, but results are representative of real conditions.

Heat Transfer

Figure 6(a) and (b) plot the temperatures down the dryer for monosized crumb of two particle diameters, 10 mm and 100 mm. Point zero is the air entry at the bottom of the drier and 4 m is the crumb entry at the top. There is slight instability (less than 2°C) in the temperature profile due to the numerical complexity of the solution, but the trends are clear. The figures show: (1) the temperature profile in the particle centre, (2) at the particle surface, and (3) in the air stream. In the simulation, crumb enters the dryer at 340 K; initially it cools rapidly to the temperature of the air it encounters, and then heats up as it moves down the dryer, encountering progressively hotter air. Air enters the dryer at 378 K and cools progressively along the dryer as it both provides energy for evaporation and warms the crumb particles. Both the air and the crumb approach a thermal equilibrium in the central and upper regions of the dryer ($2.0 < z < 3.5$ m). The temperature of the air is controlled by the amount of evaporation from the material.

The temperature profiles show that the smaller particles have a higher temperature than the larger particles, which reflects the differences in the mass transfer rates seen in the other figures; the drier the particles, the hotter they become. Heat and mass transfer are coupled. As expected, for both particle sizes the centre of the particle heats up slower than the surface but the effect is more apparent for the larger particles as the resistance to heat transfer is
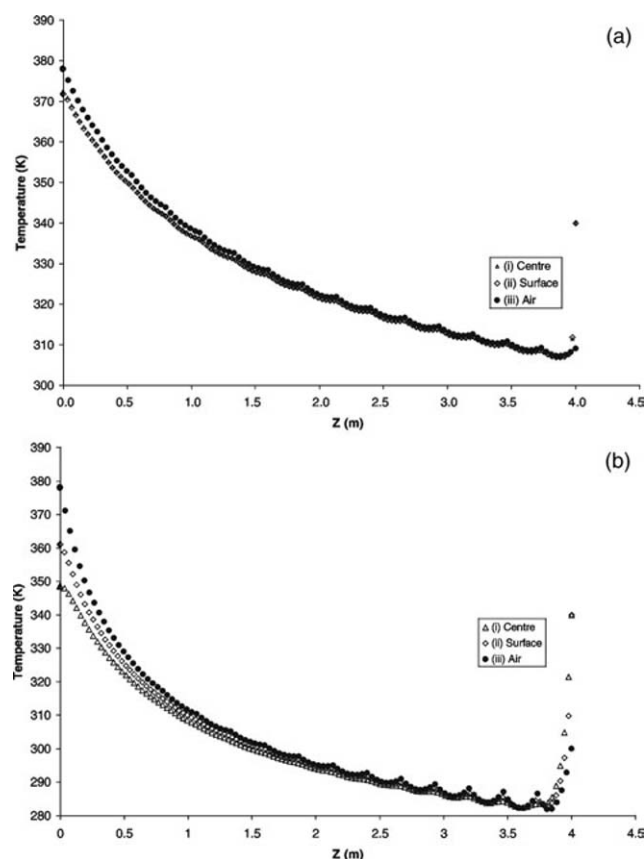

Figure 6. Heat transfer results. (a) Temperature profile a along the dryer for 10 mm particles: (i) the air stream, (ii) the particle surface, and (iii) the particle centre. (b) Temperature profile along the dryer for 100 mm particles: (i) the particle centre, (ii) the particle surface, and (iii) the air stream.

higher. This shows the dependence of the process on the particles size and structure.

Mass Transfer

The water vapour concentration profiles down the dryer are shown in Figure 7(a) and (b) for the two particle diameters. Again small instabilities are seen in the concentration profile but the trends are still clearly visible. The figures show: (1) the water vapour concentration at the centre of the particle, (2) at the surface of the particle, and (3) in the drying air stream plotted on the secondary axis. The inlet water vapour concentration within the particles is at equilibrium with the inlet temperature. This decreases slightly as the particles cool and then increases towards the exit of the dryer reflecting the higher temperature and rate of evaporation. As expected the surface of the particles have a lower concentration as the water vapour will be more rapidly transferred into the drying air than that of the centre whilst the water vapour at the centre of the particle will have to be transported to the surface before leaving the particle. The larger particles have a higher water vapour concentration at the centre, reflecting the limitations to mass transfer of the larger size—the larger particles are much wetter than the smaller particles, as shown in Figure 7(b), and have a correspondingly high vapour pressure. However, the diffusional limitation of the large particles, and the smaller surface area per unit mass, mean that the net evaporation is less. The difference in profiles within the particles for both sizes again reflects the dependence on structure. The air stream enters the dryer virtually dry with a correspondingly low water vapour concentration. This then increases in the opposite direction to the particles as the air travels up through the crumb.

The drying effect of the combination of temperature and vapour pressure is best seen in Figure 7(c) and (d), which shows the solid average moisture content profile and the evaporation rate at the surface for 10 mm and 100 mm particles. Both particles enter the dryer at 4% moisture (dry basis) and dry out as they are conveyed down the dryer. However, the larger particles dry by only a small amount (0.382 at the exit) whilst the smaller particles dry significantly (0.201 at the exit). The evaporation rate for both particles increase towards the exit of the dryer as a consequence of the higher temperatures and resulting mass transfer driving forces.

The above data has been developed for the (unrealistic) condition of a uniform size of particle in the dryer; the difference between the two sizes is due both to internal diffusional resistance and to the change in surface area per unit mass which makes mass transfer from the larger particles much slower. In practice, there will be a size distribution of particles within the dryer, and different sizes of particle will dry to different extents. The temperature and moisture content of the air will result from a combination of all of the evaporation from the particles. The data shown does demonstrate the complexity of the problem and its non-linearity. Very small particles would be expected to dry effectively completely, and be at higher temperatures than the 10 mm particles shown, whilst larger particles will be both colder and wetter. The combination of temperature and moisture content will have significant implications for the development of flavour, as discussed below.
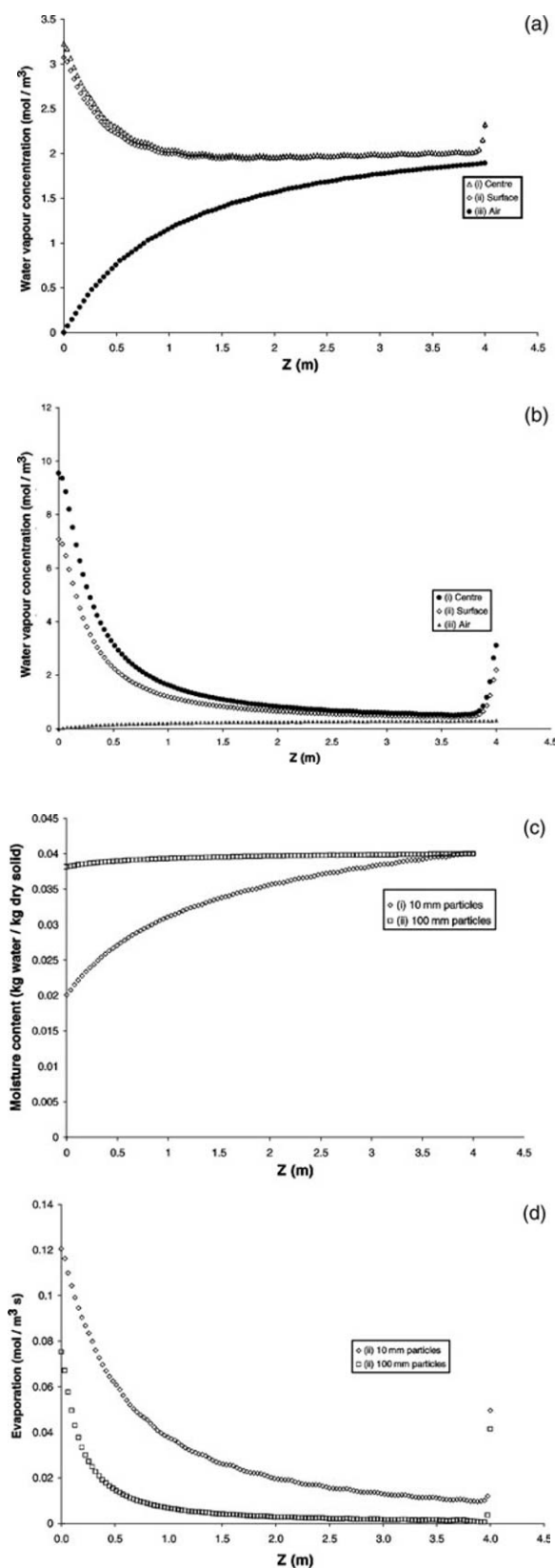
Figure 7. Mass transfer results. (a) Moisture vapour concentration profile for 10 mm particles: (i) the particle centre, (ii) the particle surface, and (iii) the air stream. (b) Moisture vapour concentration profile for 100 mm particles: (i) the particle centre, (ii) the particle surface, and (iii) the air stream. (c) Moisture content profile for particles along the dryer: (i) 10 mm particles and (ii) 100 mm particles. (d) Rate of evaporation (mol m^3 s^{-1}) from surface: (i) 10 mm particles and (ii) 100 mm particles.
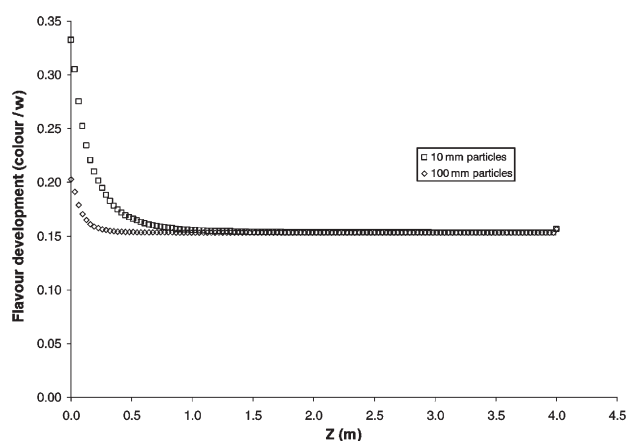

Figure 8. Rate of flavour development in crumb along dryer.

Flavour Development

The temperature–time profiles of the system shown in the figures above can then be used as an input for the flavour model, equation (1). The results of this, in terms of the rate of flavour generation, for the data of Figures 5–6 have been plotted in terms of the colour of the product, in absorbance units (at 310 nm) in Figure 8. The data shows the rate of the process at the surface of the particle. It is clear that flavour development in the model occurs in the air entrance region of the dryer; for the particles shown here, most of the particles are too cold to generate significant flavour. This of course would be different for different particle sizes.

The real system has a wide range of crumb particle size and shape: it will be useful to examine the sensitivity of the flavour reactions to changes in these parameters. Smaller particles develop more flavour as they are rapidly heated, larger particles show little flavour development.

CONCLUSIONS

The problem of linking deterministic engineering models and models for flavour are considerable. A mathematical model has been developed in this paper to define the temperature and moisture profiles in the final dehydration stage of the chocolate crumb process. The model uses a mixture of experimentally-derived data for diffusional behaviour and for flavour development, together with theoretical expressions for moisture and heat transfer. Preliminary results, using approximations to the real conditions, demonstrate the range of temperature and mass transport effects that are seen. As a consequence a better understanding of the way in which flavour is developed in the dryer has been achieved; flavour development in the air-entrance regions of the tower can be identified. Work is underway to complete this characterization and develop an effective model for the real situation that may provide an engineering advantage.

This model could be adapted further to consider alternative drying processes and foods so long as structure–property relationships (Aguilera and Simpson, 2004) are pre-defined. For example liquid diffusion or capillary

flow (Fortes and Okos, 1980) could be taken into account for high moisture food systems. This type of model, combining engineering and food science understanding, is rare in the literature; we hope that, as the need to understand flavour chemistry in foods increases that this type of model will become more widespread.

Future work is being undertaken to verify the model experimentally by accurately measuring local moisture contents and flavour within laboratory scale drying equipment.

NOMENCLATURE

a	specific area of particle, $m^2\,m^{-3}$
b	reaction rate, $mol\,m^{-3}\,s^{-1}$
c	Concentration of moisture in air within particles, $mol\,m^{-3}$
c_2	Concentration of moisture in bed air-stream, $mol\,m^{-3}$
c_{sat}	saturated vapour concentration, $mol\,m^{-3}$
C_p	specific heat, $J\,mol^{-1}\,K^{-1}$
D	the diffusion coefficient, $m^2\,s^{-1}$
d	diameter of the particle, m
E	Activation energy, $kJ\,mol^{-1}$
f	measure of flavour marker, colour or odour after cooking
f_0	measure of flavour marker, colour or odour after before cooking
h	heat transfer coefficient, $W\,m^2\,K^{-1}$
k	thermal conductivity, $W\,m^{-1}\,K^{-1}$
k_{ext}	external mass transfer coefficient, $m\,s^{-1}$
k_{evap}	evaporation rate constant, $m\,s^{-1}$
M_t	moisture content dry basis, $kg\,water\,kg\,dry\,solid^{-1}$
M_e	equilibrium moisture contentkg, $kg\,water\,kg\,dry\,solid^{-1}$
N_{Nu}	Nusselt number
N_{pr}	Prandlt number
N'_{Nu}	Modified Nusselt number
N_{Sc}	Schmidt number
N_{Re}	Reynolds number
P_v	vapour pressureatm, a.t.m.
P_v	saturated vapour pressure, a.t.m.
R	gas constant, $J\,mol^{-1}\,K^{-1}$
r	radius of the particle, m
R_w	evaporation, $kg\,water\,kg\,dry\,solid\,s^{-1}$
R_c	evaporation, $mol\,m^{-3}\,s^{-1}$
R_{c2}	diffusive mass flux from surface of crumb, $mol\,m^{-3}\,s^{-1}$
R_T	heat of evaporation, $J\,m^{-3}\,s^{-1}$
R_a	diffusive energy flux from surface of crumb, $J\,m^{-3}\,s^{-1}$
t	time, s
T	temperature, K
$\bar{u}$	velocity of the bed air-stream in z direction, $m\,s^{-1}$
$\bar{v}$	velocity of the crumb particles in z direction $m\,s^{-1}$
w	moisture content of the solid, $kg\,water\,kg\,dry\,solid^{-1}$
W_e	equilibrium moisture content, $kg\,water\,kg\,dry\,solid^{-1}$
z	length coordinate of the bed, m

Greek symbols

μ	Viscosity of the air, $kg\,m^{-1}\,s^{-1}$
λ	latent heat, $kJ\,kg^{-1}$
ρ	density, $kg\,m^{-3}$
φ	relative humidity, %

Subscripts

f	food material
a	air
va	vapour

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