

## Chapter 4

### Biscuit macroscopic baking model

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#### 4.1 Introduction

The quality of bakery products rely both on formula and processing conditions, and some qualities can be improved by optimizing a formula and processing condition.

The principal process steps of biscuits mainly consist of mixing, sheeting/depositing, baking and cooling. Each of these steps influence different quality attributes and final properties. However, in every case, the baking step is one of the most important key factor, because, during the cooking time, the raw dough piece is transformed in the final biscuit, resulting in a specific texture. For this reason a lot of researchers try to describe the physical process affecting the biscuit inside the oven. Therefore, a mathematical program, able to describe the transport phenomena and the physical changes inside the baking chamber, can reduce the time and the costs involved.

In order to predict temperature, water distribution, height, porosity and other bakery attributions, the knowledge of product properties is very important, these include heat capacity, density and others during baking time, in addition to dependence on water content, temperature, and so on. Moreover, it is very important to know the mechanical properties of dough during the evolution time to characterise and simulate the material's performance during processing and for quality control [Dobraszczyk B. J. et al. 2003]. For the last purpose rheological principles and theory can be used. However, the literature divides into researcher groups that apply the rheological principle and then use rheology to find the link between the recipe, baking condition and the final texture and structure, and other groups that use the classical approach to the transport phenomena and then only write the heat and mass transport equations with appropriate boundary conditions and material properties. Moreover, biscuits, like any other baked system, are inherently heterogeneous systems, but most of the proposed approaches consider the material pseudo-homogeneous, to translate the physical aspects into a mathematical model capable of predicting the final biscuit characteristics. This means that all the phenomena refer to an equivalent homogeneous system, the properties of which are somehow modified to account for the presence of bubbles. Thus effective material properties are properly defined. However, these approaches have an evident undoubtedly mathematical advantage when numerically solving the obtained equations, and may be applicable in a straightforward way to

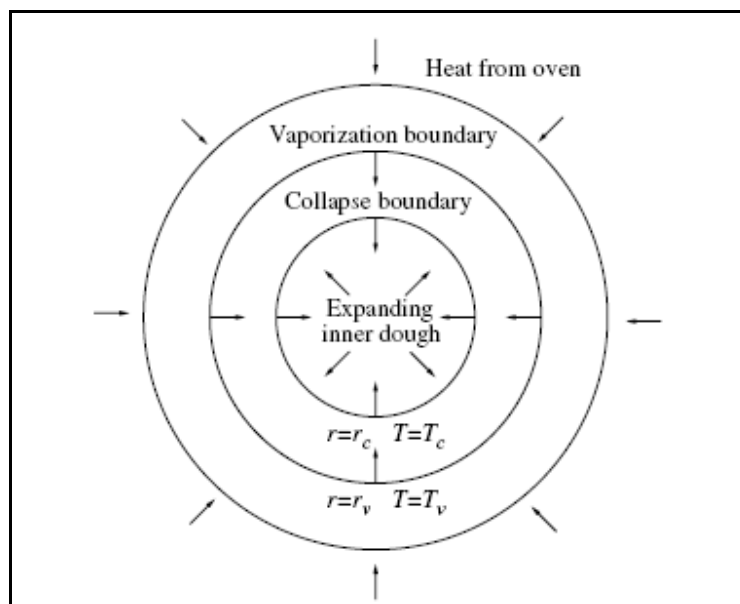
industrial conditions, since they are essentially based on some adjustable parameters introduced by the heat and mass transport models, nevertheless in this way the heterogeneous feature is missed. This implies that properties appearing to be mainly responsible for the product structure and texture, as for instance, the rheological behaviour of the dense cereal paste, its surface tension, and the interface thermodynamic equilibrium, cannot be taken properly into account.

In recent years, there has been growing interest in modelling heat and mass transport. [Broyart B. et al. 2002](#), [K. Thorvaldsson et al. \(1999\)](#), [A. K. Datta 2006](#), [M. Sakin et al. 2006](#) developed models to simulate the baking period. The model of [Broyart B. et al. 2002](#) took into account the heat transfer by radiation, convection, conduction and heat transfer by product-water phase change. In the model, the mass transfer fluxes, exchanged between the baking atmosphere and biscuits during baking, are controlled by the difference between the vapour partial pressure air assumed in equilibrium with the biscuit and the vapour partial pressure of the bulk air stream in the baking oven. All the material parameters are calculated by literature data and the Euler's method was used to solve a set of equations with the initial condition coming from a pilot plant oven. [K. Thorvaldsson et al. \(1999\)](#) wrote a 1-D mathematical model that can describe and simulate the mechanisms of simultaneous heat, water and vapour transport and the numerical method used for the differentiation was an unconditionally stable finite difference method, Implicit Euler. Another 1-D model was written by [M. Sakin et al. 2006](#) that analysed cake batter, considered as an infinite slab, neglecting the thermal gradient effect on moisture transfer. It was assumed that the moisture transfer is one-dimensional diffusion in the upward direction from the bottom of the product toward the top surface, described by Fick's law of diffusion. The simulated curves were compared with the experimental ones. The effective moisture diffusivity of cake batter during baking at different oven temperatures was determined. It was significantly affected by baking temperature and the average moisture content of cake batter. [Shin-Yee Wong et al. 2006](#) developed a two-dimensional model for dough in continuous movement. The dough was considered as solid material with heat parameter only depending on the temperature. It was modelled in unsteady state conditions, writing the equation of momentum, mass and energy conservation, using commercial software and moreover using periodic boundary conditions to simulate the movement in the 4 zones of oven. To simulate the bread baking process with volume change, [A. K. Datta 2006](#) formulated a model for multiphase porous media, describing a number of simultaneous heat and mass transfer processes in foods that involve strong internal evaporation, incorporating the large deformation to have the volume change.

D.R. Jefferson et al. 2005 formulated a model depending on the single bubble, representing the global system. In this model pressure as a driven force was considered in the growth of a single isolated bubble in a dough. Moreover, the model assumes a specific temperature for its bubble rupture criterion. Therefore, when the bubble reaches the fracturing temperature, the bubble is assumed to fracture and the pressure inside the bubble becomes atmospheric.

Bubbles are taken to be spherical and the mathematical model is written down as though the bread dough were a homogeneous material without any small-scale bubbly structure. In this homogenised model, bubble collapse is taken to occur at a temperature characteristic of the setting and fracturing of the dough matrix, which is referred to as the collapse temperature.

The model is solved in a spherically symmetric geometry: the model is formulated as a set of partial differential equations governing heat transfer inside the bread, coupled with a set of ordinary differential equations governing moving boundaries (relating to bubble collapse and to moisture vaporization) and inner dough expansion. It is assumed that bubble diameters are initially distributed log-normally, and that as the inner part of the dough expands, all bubbles in that part expand in proportion to one another.



**Figure 4. 1** - Diagram of spherically symmetric model of a loaf during baking showing moving boundaries and dough movement.

Hadiyanto et al. 2007 developed a generic baking model, which can be divided into three parts: the heat and mass transfer model, the state changes owing to the heat treatment (transformation model) and the

product quality model. The mass balances was written for liquid water, water vapour and CO<sub>2</sub> gas. Water vapour and CO<sub>2</sub> are considered as an ideal gas which is in equilibrium with liquid water content. The energy balance concerns conduction, evaporation-condensation, and the water vapour and CO<sub>2</sub> fluxes. The liquid water and water vapour are correlated by the water activity and partial vapour pressure relationship in the sorption isotherm. The balances for water, water vapour and CO<sub>2</sub> are written using the Fick's law and by CO<sub>2</sub> production. Mass fluxes of CO<sub>2</sub> and water vapour depend on local pressure differences, kinematic viscosity and permeability of product. The changes of height are caused by the increasing pressure inside the gas cells in dough due to the release of water vapour and CO<sub>2</sub> from baking powder or from yeast. Moreover, the dough is considered as a visco-elastic material for which the deformation, caused by expansion, can be expressed by the Maxwell equation and it is driven by pressure difference between total pressure inside the product and ambient pressure. The rate of extension describes then the change of height.

The study of [J. Zhang et al. 2006](#) modelled the transport phenomena inside the bread crumb and then heat transport, liquid water transport and water vapour as well as CO<sub>2</sub> transport. Deformation is driven by internal pressure build up as a result of vapour and CO<sub>2</sub> generation and their transport. The governing equation for deformation is based on the principle of virtual work (PVW). The material was assumed viscoelastic (Maxwell). The mechanical properties of bread change with temperature and the deformation affects transport through changes in characteristic dimension, porosity and effective conductivity, and so on. A fully coupled model was developed for deformation and multiphase heat and mass transfer in bread baking. The model was validated using experimental data on baking. Axisymmetric geometry is used in this study. At the surface of the bread, moisture loss is through convection. Heat transfer is through convection and radiation. The coupled transport and deformation are solved simultaneously using a finite element code developed from the authors.

[M. Lostie et al. 2002](#) proposed a 1-D mathematical model of heat and mass transfer for a sponge cake. The material, considered as a viscous compressible medium, expanded owing to liquid water vaporization, and the local deformation rate being proportional to the local overpressure. To take into account the rheological behaviour of batter, they related the local volume deformation to the local overpressure. The batter was considered able to expand only in one direction, because of a rigid mould that prevents spreading, then radial deformation. The local volume deformation rate was equal to the axial one, which corresponds to the axial velocity gradient:

$$(P - P_{am}) = \eta \frac{\partial v}{\partial x} \tag{4.1}$$

Where  $\eta$  is the bulk viscosity of the batter.

The final model equations set was obtained by inserting the constitutive relation in the equations. The resulting set of partial derivative equations were solved discretising with a finite volume scheme and solving with the time partial derivative with the Crank–Nicholson centred difference scheme. To simulate the first baking period, [Lostie et al.](#) used properties not constant with time, but that change with water content, temperature, pressure and total porosity of material. The drying rate and the oven air temperature were used as boundary conditions in the calculation code. The model is valid for the heating period because the correlations and data used in the model are estimated in the first part of baking, before the crust and crumb zone. To complete the cake baking model [M. Lostie et al.](#) subsequently presented in 2004 [[M. Lostie et al. 2004](#)] only a model concerning the second baking period “crust and crumb”. Experimental data were estimated by trials in a laboratory oven and the batter weight and the oven temperature served as boundary conditions for the simulations, whereas the other curves were used for cake properties estimation. Moreover, the initial conditions, like internal temperature, water content and thickness of the cake, for the differential equations written were evaluated at the end of the first baking period (“heating up” period) obtained from the experimental baking curves [[Lostie, 1998](#); [Lostie et al., 2002a, 2002b](#)]. The cake is considered formed by two structurally distinct layers: a dry crust with constant shape and porosity and a wet deformable crumb; the heat and mass transfer is deemed unidirectional with the gas phase moving through the crust by permeation under a total pressure gradient according to Darcy’s law. The heat is transferred through the crust by conduction, according to Fourier’s law with an equivalent thermal conductivity. The convective heat transport owing to the gas flow within the material is neglected and the heat and mass transfer in the crust are in the steady state, the temperature and the pressure profiles being linear; there is no heat and mass transfer within the crumb, so that the temperature, the water content and the pressure are uniform through it; the crumb, always considered as a viscous compressible medium, expands due to the liquid water vaporization, the local deformation rate being proportional to the local overpressure. The model uses adjustable parameters which depend on the product properties and on the operating conditions and which have to be numerically estimated using some experimental baking curves.

[J. Fan et al. 1999](#) modelled the dynamics of oven rise of dough during baking. They considered the growth of gas cells to be as a result of the thermally-induced release of CO<sub>2</sub> and water vapour from the aqueous dough phase. The model is independent of the number of gas cells present initially in the dough. They modelled a spherical gas cell of initial radius  $R_0$  surrounded by a shell of liquid dough,

considered as viscous fluid, with a constant mass. Dough cells contain only carbon dioxide and water vapour. The gas cells are closed and their number in the dough remains constant during the entire period of baking. The dough behaves rheologically as a power law fluid and dough temperature is uniform with position but is time-dependent. In considering the volume expansion of the dough, they first examined the growth of an isolated gas cell as the temperature changed. Finally, the model ignores bubble coalescence. The equations involved in the model were transformed to a dimensionless form and solved numerically by using the 4th Runge - Kutta method using the above initial conditions.

[Morales M. E. S. et al. 2004](#) studied the modelling of heat and mass transfer during the baking of biscuits. The principal objective of the work was to study a model for heat and mass phenomena during the precooking and freezing of biscuits, and compare the final cooking in a conventional or microwave oven by measuring the quality attributes of the product. Moisture transfer during precooking was considered a diffusion phenomenon for a solid cylinder. The moisture content in a solid cylinder such as a biscuit is a function of both radius and time:

$$\frac{\partial M}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( rD \frac{\partial M}{\partial r} \right) \quad 4.2$$

where M is the biscuit moisture content (%wet basis) at baking time t (s), r is the radial position (m) in R, and D is the moisture diffusivity coefficient (m<sup>2</sup>/s). Biscuits were modelled as a finite cylinder body in which the analytical solution is given by the interaction of two infinite geometries: infinite cylinder and infinite slab, following the method of Heldman and Singh in their work of 1981. In this way they calculated the temperature profile.

Many of the works reported in this brief review consider the dough as solid material, not taking into account the system heterogeneity and then the connected volume expansion. Only a small minority of the papers examined analyze the dough and impute the expansion to the overpressure inside the bubble, but do not consider the eventuality of the mechanical criterion for the coalescence, which cause the break of layer around the bubbles, or an eventual stabilization criterion. Instead, in this work a model capable of taking into account bubble growth, coalescence and collapse to predict final biscuit properties is developed. The main idea is to split biscuit behaviour into two parts called micro- and macro-systems, the first one being heterogeneous, while the latter is pseudo-homogeneous. The information obtained at the micro level are transferred to the macro, which through a proper numerical solution gives the transient values of temperature, humidity, and component concentrations at any point of a spatial grid into which the system is subdivided, from which the height of the biscuit may be

computed at any time. In such a way the pseudo-homogeneous computational advantages are maintained without missing the heterogeneous character.

## **4.2 Baking modelling**

In the present work we seek to analyse the evolution of the baking period for a crunchy biscuit type, which is made by an industrial process and that can be schematized as a series of steps: mixing, standing, forming and baking.

During mixing a certain amount of air bubble nuclei is inserted into a mixture essentially constituted of flour, water and other minor ingredients. After a proper time of standing, during which the raising agents start to react to produce some substances capable of blowing the dough, the biscuit is subjected to a forming, usually on a band belt. Finally, the belt passes through a heating oven where the biscuit baking is carried out for a few minutes, depending on the type and size. The heating is realised by applying either irradiative or convective heat fluxes. Gas bubbles grow due to both the thermal expansion and the thermodynamic equilibrium between the dense phase and the gas, allowing the increase of the total amount of moles of the gas phase. Whilst at the beginning it is possible to admit that the bubbles behave as single closed cells, when increasing their diameter, interactions between them occur and bubble coalescence is generally observed. Thus the biscuit reaches a maximum height with only a small loss of water, thereafter a more or less pronounced mechanical collapse of the structure is observed, evidenced by a sharp decrease of both the total height of the biscuit and its water content. Thus, as a consequence of raising agents and thermal treatment during the entire process, the main phenomena involved in biscuit production are:

1. bubble expansion
2. bubble coalescence
3. biscuit collapse
4. biscuit drying

The overall phenomenon depends on several factors: dough rheological properties, transport properties, void fraction, heat treatment, process features and so on. In addition, during this stage the biscuit shrinks as a consequence of water loss that is ascribed to evaporation from both the external surfaces and the new surfaces made available for evaporation by the air cell opening towards the external ambience. For these reasons transport phenomena of both energy and mass must play a crucial role in determining the final biscuit characteristics.

The proposed model aims to deal only with the baking phase, while mixing and standing are roughly considered as an initial condition for the baking. In addition no spread was considered and therefore forming on the belt was neglected. Thus a 1-D model was assumed to be sufficient to describe the biscuit behaviour during baking according to the steps enumerated before. Every step was modelled according to some specific physical hypotheses as reported in the following, so generating in such a way a series of microsystems, every one characterised by the assumption that they must represent both thermodynamic and mechanical equilibrium conditions. The microsystem is treated essentially as a sink for the macrosystem and represent the link between them. The thermodynamic and mechanical variables computed by the so-called macrosystem, are put in equilibrium condition by applying a single microsystem according to the considered step. Then the equilibrium information obtained at micro level, being essentially bubble radius, and the split of the components between gas and paste phases, are transferred to the macrosystem which deals with the transport phenomena, operating essentially with effective properties. By integrating heat and mass balance equations with reference to a discretised 1-D spatial grid and for any given initial and boundary conditions, the new values of the thermodynamic and mechanical variables are obtained and sent again to the microsystem. This procedure is iterated at any grid point and at any time. By collecting the data coming out of this computing procedure at any instant, the transient height, temperature and water content of a biscuit are obtained.

#### **4.2.1 Bubble opening**

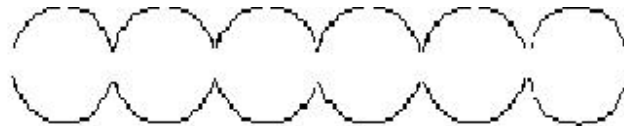
It was stated that the bubbles inserted at the beginning into the dense cereal paste, grow as a consequence of the combined actions due to Raising Agents decomposition, water evaporation, and temperature increase. As mentioned in chapter 2, at the start the bubbles may be considered as submerged in an infinite medium of a viscoelastic paste and the system is subjected to both mechanical and thermodynamic equilibrium. Moreover, the amount of new products or components present at any time in the gas bubble is determined by a thermodynamic flash, while the bubble volume is computed by the mechanical equilibrium. Thus, from a theoretical point of view, the process has been considered to change as a quasi-static transformation, allowing passing through the equilibrium stages.

In chapter 3 the coalescence problem was dealt with. It was stated that the bubbles grow as long as either the reactions proceed or until the temperature increases, but if the reactants are completely consumed or temperature remains constant, the growing stops, but it is well-known that the classic baking time is of a few minutes, and then not sufficient to reach an internal constant temperature



profile. Therefore another mechanism was considered to stop bubble growth. In fact, when bubbles expand, their radius increases and they may start to mutually interact, eventually up to their coalescence. In the previous chapter a simple original model was defined, which treated the bubble property, called “coalescence-ability”, as the capability of a single bubble to coalesce. Of course this model works at the micro level and deals with with a heterogeneous system, taking into account the dimension, the shape and distribution of the bubbles.

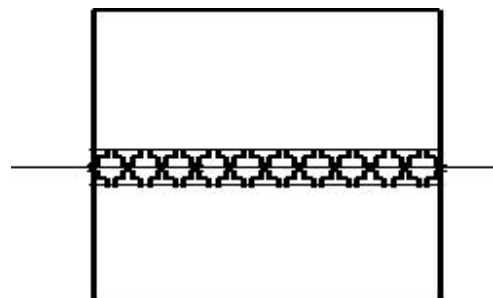
Once a bubble attains coalescence conditions as described above, it would really coalesce if contiguous bubbles are in the same condition (Fig.4.2), otherwise this does not happen. In addition bubbles that are near the biscuit surface might open towards the external ambience, with the consequence that the thermodynamic and mechanical equilibrium is completely changed and a new microsystem is needed.



**Figure 4. 2 - Coalescence between bubble pairs**

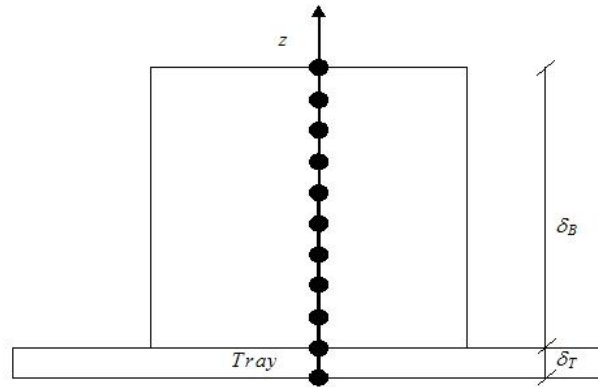
This point is often approached as a crust-crumbs problem, because when modelling the physics of biscuit baking it is necessary to distinguish between the part of the biscuit that is directly exposed to the ambience, i.e. the crust, from the part that is inside biscuit, i.e. the crumb. Generally speaking, the crust becomes quickly rather drier than the crumb, so that it can be considered as a boundary condition for this latter, which in turn contains the majority of developing gas cells and therefore is the most relevant for determining biscuit height.

It was assumed that the biscuit condition of humidity and temperature do not change so significantly, and, moreover, the single microsystem at any given grid point is representative of all the other possible microsystems on the same grid point line.



**Figure 4. 3 - Horizontal coalescence**

It was considered as a 1-D Model and therefore the spatial grid consists of a series of points in the  $z$ -direction (Fig.4.4).



**Figure 4. 4 - The  $z$ -spatial grid**

As a consequence of the one-dimensional assumption, any grid point represents a unique microsystem at the given current conditions.

For this motive, the baking model was built assuming coalescence between horizontal layers (Fig.4.3) and consequently the opening must refer only to horizontally connected bubbles, which means that they must be in the same layer. No other coalescence was considered.

This implies on the one hand that every continuous variable changes only in the  $z$ -direction, and on the other, because coalescence occurs between horizontal layers, that coalescence becomes a property of the grid point. In addition, there is no distinction between crust and crumb and therefore coalescence corresponds inherently even to opening in a 1-D model. Finally, it may be concluded that in the current model coalescence and opening coincide. At the opening the entire considered layer is suddenly connected to the external ambience and therefore an open cell model must be built and applied. It is obvious that in such a way the crust behaviour is to some extent missed, but this may be recovered by putting this information into the boundary conditions.

#### **4.2.2 Biscuit collapse**

When bubbles coalesce, they open towards the ambience, and two different volume reductions are observed: collapse and drying. The first one is assumed to be essentially a mechanical effect, while the latter is ascribed to evaporation consequent on the sudden increase of the biscuit/air surface. Nevertheless, an opening criterion is needed. In fact, what can happen is that a horizontal channel is not completely in coalescence conditions, therefore it can be only partially opened and therefore a rather

difficult condition should be applied with partially opened channels. This inherent difficulty was overcome by reducing the system to a 1-D model and assuming the simultaneous coalescence of all cells contained in each row. It should be reminded that in the 1-D model a row of bubbles corresponds to a single grid point, and therefore coalescence corresponds to opening.

Opening towards the external ambience, imposes that the pressure inside the generated channel-like structure suddenly becomes equal to the ambient pressure. In these conditions an elastic recovery may be expected due to the mechanical action of the unrelaxed stresses.

From a mechanical point of view, the dough structure constituting the channel walls, may be considered as a viscoelastic material, therefore if the relaxation of stresses is not complete at the opening, they will relax completely and consequently a more or less large elastic recovery under constant pressure is shown. The collapse has been interpreted as a mechanical failure of the system, following the coalescence of a series of bubbles that are connected to the external ambience and that therefore pass instantaneously from the relatively high internal pressure to the lower external one.

It should be noticed that under this new condition a decrease of “pearl necklace”, formed by the contiguous bubbles, is expected only if the deformation is still linked to the stress, because it should become the equilibrium value at the external pressure. However, if the stress is fully relaxed the deformation is independent of the pressure and therefore no recovery is shown. With this physical interpretation it is assumed that the more elastic the dough, the greater will prove the collapse.

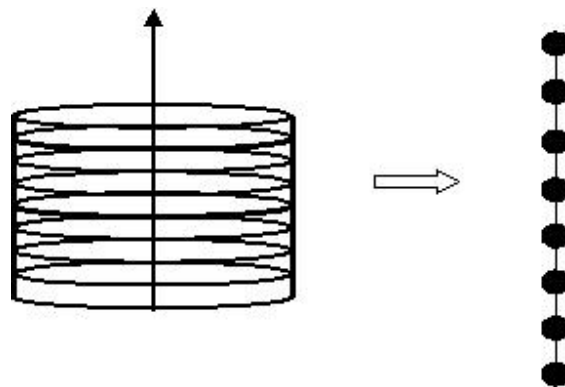
At the opening the thermodynamic equilibrium is missed because the system becomes basically an open thermodynamic system and therefore cannot be at equilibrium and the new surfaces are equivalent to the external transport/evaporating surfaces. To take into account this additional flux and the new surface, available for both mass and heat transfer, a new term must be considered in the mass balance. Generally speaking, the water,  $CO_2$  and  $NH_3$  losses from the channel surface, can be considered as a local generation term in the macrosystem equation, but to make a simpler computation, an open cell microsystem was built. Finally, the volume reduction called shrinkage, is ascribed to the natural continuous water loss at the air/biscuit interface, which is regulated by a simple equilibrium thermodynamics.

### **4.3 Mass transport (Macrosystem)**

The mass transport inside the biscuit must be subdivided into two parts: transport into the dense phase and transport into the gas cells. Owing to the assumption that the variables must be

continuous, a pseudo-homogeneous system is built with effective properties. This is made possible because the transport into the gas is neglected and a pure diffusive transport is considered. This agrees with the assumption that the microsystem is in equilibrium and consequently no transport must be considered. On the contrary, the macrosystem is formed by a continuous matrix that can be seen as a water solution where the presence of the bubbles is hidden in the properties. It should be noticed that the R.A. reaction products are soluble only in water and as a consequence in the macrosystem water can diffuse throughout, whereas the latter, only in water. This has some effect not only on the transport properties but even on the gas-water solution equilibrium of those species. It should also be noted that the concentration of all the species has to be referred to the system where they are effectively contained. The mass transport mechanism of the R.A. products has been assumed to be a pure diffusion into water, and consequently the mass balances refer to this mechanism.

A 1-D macroscopic model was studied assuming that the system may be geometrically transformed from a series of superimposed disks, into single points, corresponding to the grid points (Fig. 4.5).



**Figure 4.5 - D Grid equivalence**

The computing advantage is quite evident, but what is the main gain is also the possibility of writing boundary conditions in a rather simple way. Therefore referring to any disk volume a mass balance is carried out for the main components, which are H<sub>2</sub>O, NH<sub>3</sub> and CO<sub>2</sub>.

### 4.3.2 Water transportation

Owing to the presence of gas bubbles, the water content may be measured referring to two different systems, therefore the following variables are defined:

$$c_w = \frac{\text{moles of water}}{\text{Total volume}} \tag{4.3}$$

$$c_W^* = \frac{\text{moles of water}}{\text{Paste volume}} \quad 4.4$$

By using the definition of void fraction  $\varepsilon$ :

$$\varepsilon = \frac{\text{void volume}}{\text{Total volume}} \quad 4.5$$

the relationship between those variables is found:

$$c_W = c_W^* (1 - \varepsilon) \quad 4.6$$

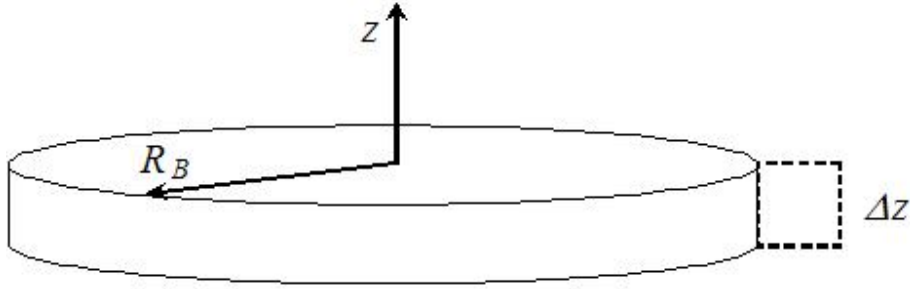


Figure 4. 6 - Control Volume

From a geometrical point of view, the system was considered as a cylinder, with a variation only along the  $z$ -coordinate. The microscopic mass balance of water was written with reference to a control volume obtained as a slice of thickness  $\Delta z$  of the original cylinder (Fig. A10.1). Thus the time rate of change of mass of water in the considered volume element is:

$$Acc^W = \frac{\left[ c_W^* (1 - \varepsilon) \cdot S \Delta z \right]_{t+\Delta t} - \left[ c_W^* (1 - \varepsilon) \cdot S \Delta z \right]_t}{\Delta t} \quad 4.7$$

where  $S$  is the volume surface of the biscuit

$$S = \pi \cdot R_B^2 \quad 4.8$$

The mass balance in the considered control volume is obtained by adding the input and output terms along the  $z$ -direction, and in addition, the generation terms. The latter are water mass  $\mathfrak{R}_W$  generated by the decomposition of R.A reaction per unit of mass of paste, and the mass of water  $S_e^W$  moving to/from the gas bubbles, according to the equilibrium in the microsystem at any time step. Therefore the following expression is found

$$Acc^W = N_W \cdot S \Big|_z - N_W \cdot S \Big|_{z+\Delta z} + \mathfrak{R}_W \cdot (1 - \varepsilon) \cdot S \Delta z \cdot \rho_P - S_e^W \cdot S \Delta z \quad 4.9$$

where  $\rho_P$  is the paste density. The term  $S_e^W$  is measured per unity of volume, and is assumed positive as a sink, which means when water leaves the paste and goes into the gas bubbles. Thus if  $F_W$  is the water molar flux that evaporates/condenses in any bubble and  $n_b^0$  is the number of bubbles per unity of volume, it holds:

$$S_e^W = F_W \cdot 4\pi R^2 \cdot n_b^0 \quad 4.10$$

where  $R$  is the current value of bubble radius. Regarding the input/output terms  $N_W$ , a pure diffusive mechanism is assumed, therefore the  $z$ -component of the water molar flux may be written as:

$$N_W = -D_W \frac{\partial c_W^*}{\partial z} \quad 4.11$$

By substituting Eq.s 4.8, 4.11 and 4.12, after letting the volume element decrease to zero, the continuity equation for water is obtained:

$$\frac{\partial (c_W^* (1-\varepsilon))}{\partial t} = \frac{\partial}{\partial z} \left( D_{eff} \frac{\partial c_W^*}{\partial z} \right) - F_W 4\pi R^2 n_b^0 + \mathfrak{R}_W (1-\varepsilon) \cdot \rho_P \quad 4.12$$

that is the differential form of water balance that may be integrated.

The boundary conditions are the following:

tray/biscuit interface

$$z = \delta_T \quad -D_{eff} \frac{\partial c_W}{\partial z} \Big|_{z=\delta_T} = 0 \quad 4.13$$

biscuit surface

$$z = \delta_T + \delta_B(t) \quad N_W = -D_{eff} \frac{\partial c_W^*}{\partial z} \Big|_{z=\delta_T + \delta_B(t)} = N_W^{ext} = K_y^W (y_{eq}^W - y_\infty^W) \quad 4.14$$

where  $y_\infty^W$  is the water molar concentration in the oven, while  $y_{eq}^W$  is the water molar concentration at the gas/biscuit interface, which must be obtained by imposing the equilibrium condition. This is done by assuming the coincidence of the water activities in the two phases:

$$a_W^B = a_W^{Air} \quad 4.15$$

By assuming Dalton's law ideal for the gas phase, and Raoult's law as reference status for the paste phase, the following expression :

$$y_{eq}^W = \frac{P_W^o \cdot a_W^B}{\pi} = \frac{P_W^o}{\pi} f(c_W^*) \quad 4.16$$

The function  $f$  is found through the absorption isotherm measure, giving the value of the water activity at any value of the concentration into the paste phase.

Finally, the initial condition, at  $t=0$  at every  $z$  point, is:

$$c_W^* = c_W^{*0} \quad 4.17$$

### 4.3.3 Carbon Dioxide and Ammonia transportation

Both the  $\text{CO}_2$  and  $\text{NH}_3$  components are present only in the water because they are completely immiscible in flour, therefore their molar fraction is defined as:

$$x_i = \frac{\text{moles of } i\text{-component}}{\text{Moles of aqueous solution}} \quad 4.18$$

where  $i$ -component stands for the two above-considered substances. As a consequence the transport of those components is due to diffusion in water. Since the solution is diluted with respect to any  $i$ -component, Eq. 4.18 it may be approximated as:

$$x_i = \frac{\text{moles of } i\text{-component}}{\text{Moles of water}} \quad 4.19$$

By using the same control volume as above, the rate of mass change of any  $i$ -component may be expressed as:

$$Acc^i = \frac{\left[ c_W^* (1 - \varepsilon) \cdot S \Delta z \cdot x_i \right]_{t+\Delta t} - \left[ c_W^* (1 - \varepsilon) \cdot S \Delta z \cdot x_i \right]_t}{\Delta t} \quad 4.20$$

Then an expression analogous to Eq. 4.9 referred to the considered components is found:

$$Acc^i = N_i \cdot S \Big|_z - N_i \cdot S \Big|_{z+\Delta z} + \mathfrak{R}_i \cdot (1 - \varepsilon) \cdot S \Delta z \cdot \rho_P + -S_e^i \cdot S \Delta z \quad 4.21$$

where again,  $\mathfrak{R}_i$  is the mass of  $i$ -component generated by R.A. decomposition per unit of paste. The term  $S_e^i$  is the mass per unity of volume of the  $i$ -component moving to/from the bubbles, according to the equilibrium in the microsystem at any time step, assumed positive as a sink for the paste phase:

$$S_e^i = F_i \cdot 4\pi R^2 \cdot n_b^0 \quad 4.22$$

where  $F_i$  is the  $i$ -component molar flux that comes in/out for any bubble.

Regarding the input/output terms, a pure diffusion mechanism in water was assumed, thus Fick's first law of diffusion was used:

$$N_i = -D_{i,W} \frac{\partial \left[ c_W^* (1 - \varepsilon) x_i \right]}{\partial z} + x_i (N_W + N_i) \quad 4.23$$

where  $D_{i,w}$  is the diffusion coefficient of  $i$ -component in water. The molar flux  $N_i$  of the  $i$ -component is negligible if compared to the water molar flux  $N_w$ , therefore:

$$N_i = -D_{i,w} \frac{\partial [c_w^* (1-\varepsilon) x_i]}{\partial z} + x_i \cdot N_w \quad 4.24$$

By substituting Eq.s 4.20 and 4.22-4.23 into Eq. 4.21, after letting the volume element decrease to zero, the continuity equation for any  $i$ -component is obtained:

$$\frac{\partial [c_w^* (1-\varepsilon) x_i]}{\partial t} = \frac{\partial}{\partial z} \left\{ -D_{i,w} \frac{\partial [c_w^* (1-\varepsilon) x_i]}{\partial z} + x_i N_w \right\} - F_i 4\pi R^2 n_b^o + \mathfrak{R}_i (1-\varepsilon) \rho_p \quad 4.25$$

This differential form of the mass balance may be integrated according to suitable boundary and initial conditions. The following boundary conditions were applied:

tray/biscuit interface

$$z = \delta_T \quad N_i \Big|_{z=\delta_T} = -D_{i,w} \frac{\partial [c_w^* (1-\varepsilon) x_i]}{\partial z} \Big|_{z=\delta_T} + x_i \cdot N_w \Big|_{z=\delta_T} = 0 \quad 4.26$$

biscuit surface

$$z = \delta_T + \delta_B(t)$$

$$N_i \Big|_{z=\delta_T+\delta_B(t)} = -D_{i,w} \frac{\partial [c_w^* (1-\varepsilon) x_i]}{\partial z} \Big|_{z=\delta_T+\delta_B(t)} + x_i \cdot N_w \Big|_{z=\delta_T+\delta_B(t)} = x_{wat} \cdot N_i^{ext} \quad 4.27$$

The  $x_{wat}$  term reduces the external flux by taking into account the evidence that the surface available to the  $i$ -component to pass to the gas phase is only the one occupied by water. In fact, the entire surface may be considered as composed of a part that is just water and another that is the dry matter, considered as immiscible for any  $i$ -component. The external flux may be calculated as

$$N_i^{ext} = K_y^i (y_{eq}^i - y_{\infty}^i) \quad 4.28$$

where  $y_{\infty}^i$  is the concentration in the gas phase in the oven, while  $y_{eq}^i$  is the surface value at the gas side. The latter is calculated by imposing the thermodynamic equilibrium at the surface, assuming the coincidence of the water activities in the two phases:

$$a_i^B = a_i^{Air} \quad 4.29$$

By assuming Dalton's law ideal for the gas phase, for the paste phase, when considering substances that at the process temperature are above their critical temperature, Henry's law is a reasonably suitable reference status. Thus for CO<sub>2</sub> it was assumed to hold:



$$y_{eq}^{CO_2} = \frac{H_{CO_2} \cdot x_{CO_2} \cdot a_w^{surf}}{\pi} = \frac{H_{CO_2} \cdot x_{CO_2}}{\pi} f(x_w) \quad 4.30$$

Where the term  $a_w^{surf}$  was put instead of an activity coefficient of  $CO_2$ . This was justified by considering that Henry's constant generally refers to a non-ideal solution with free water, whereas the water solvent in this case is that present in the dough and, therefore, is partially bounded (see Eq. 4.16). The easiest way to take into account this effect is just to multiply for water activity that gives the amount of bounded water equal to 1 just when the water is completely free.

On the contrary, when considering substances that at the process temperature are below their critical temperature, Raoult's law may be reasonably assumed as reference. Thus for  $NH_3$  it was assumed:

$$y_{eq}^{NH_3} = \frac{P_{NH_3}^o \cdot x_{NH_3} \cdot a_w^{surf}}{\pi} = \frac{P_{NH_3}^o \cdot x_{NH_3}}{\pi} f(x_w) \quad 4.31$$

Even in this case, following the same reasons illustrated above, the non-ideality of the water activity dependence on concentration has been taken into account. The initial condition, at  $t=0$  at every  $z$  point, is:

$$x_i = x_i^0 \quad 4.32$$

for any  $i$ -component. The values of the mass transport coefficients were determined through the Chilton Colburn analogy, and referring to the value of  $y_{\infty}^i$  for both  $CO_2$  and  $NH_3$  were assumed equal to 0.

#### 4.4 Energy transport (Macrosystem)

The energy transport model was developed in a way essentially very similar to the above discussed mass transport. It looks simpler than the latter, because the equilibrium conditions do not need any constitutive equation, being expressed just as the continuity of the temperature at interface. This implies that a temperature microsystem is not required, thus  $T$  is a macro-system variable. Inside both the biscuit and on the tray where it lays, the transport mechanism is assumed as a purely conductive one. Regarding the oven, two external heating mechanisms are considered: convective and radiative. In general, the latter is the more relevant, thus in the following a flux  $\Phi_{Oven}$  is given as an input data, while convection is in general assumed as a stagnant flow and consequently a constant value of the transport coefficient may be used.

The energy balances concern both the tray and the biscuit in a series arrangement. In the baking model the 1-D approach was used and therefore the unique spatial variable is  $z$ . The microscopic equation of change is the classic balance equation for a purely conductive transport mechanism, with effective properties to maintain the pseudo-homogeneous frame. To take into account the loss of the radial coordinate and therefore of the lateral heat transport boundary conditions, according to the lumped variable solution method, the latter, which in principle are boundary conditions, have to be considered as sinks for any volume element. Thus the following equation for the tray was used:

$$\frac{\partial}{\partial t}(\rho_{Steel}C_{PSteel}T) = \frac{\partial}{\partial z}K_{Tray}\frac{\partial T}{\partial z} + S_B^L \cdot h_{ext}(T_\infty - T) + S_B^L \cdot (E_{Oven} \cdot \Phi_{Oven} - E_{Tray} \cdot \sigma \cdot T^4) \quad 4.33$$

where the two negative sinks on the right hand are firstly, the heat convection and secondly, the irradiative heating referred to the lateral surface  $S_B^L = \Delta z \cdot 2\pi R_B$ . With this approach the sole boundary condition needed for the tray is

$$z = 0 \quad -K_T \frac{\partial T}{\partial z} \Big|_{z=0} = h_{ext}(T_\infty - T|_{z=0}) + (E_{Oven} \Phi_{Oven} - E_{Tray} \sigma T|_{z=0}^4) \cdot \frac{S_p}{S} \quad 4.34$$

where  $S_p$  is the metallic network surface and  $S = \pi R_B^2$  is total surface.

The same sort of balance applies to the biscuit and the following microscopic change equation is found:

$$\frac{\partial}{\partial t}(\rho_P C_{PDough} T) = \frac{\partial}{\partial z} K_{Dough} \frac{\partial T}{\partial z} - \sum_i \lambda_i S_e^i + S_B^L \cdot h_{ext}(T_\infty - T) + S_B^L \cdot (E_{Oven} \Phi_{Oven} - E_B \sigma T^4) \quad 4.35$$

where a further but positive sink is considered to take into account the evaporation of volatile components, particularly water and ammonia. This term may be rather important when opening occurs because the relative surfaces  $S_e^i$  increase rather significantly. The sole boundary condition required for the biscuit refers to its upper surface:

$$z = \delta_T + \delta_B(t) \\ -K_B \frac{\partial T}{\partial z} \Big|_{z=\delta_T+\delta_B(t)} = h_{ext}(T_\infty - T|_{z=\delta_T+\delta_B(t)}) + (E_{Oven} \Phi_{Oven} - E_B \sigma T|_{z=\delta_T+\delta_B(t)}^4) - \sum_i \lambda_i N_i|_{z=\delta_T+\delta_B(t)} \quad 4.36$$

Since the considered system is a two-phase system, an additional boundary condition is needed at the tray biscuit interface, imposing the continuity of both temperatures and heat fluxes. Therefore the following thermal equilibrium interface conditions apply:

$$T|_{z=\delta_T^-} = T|_{z=\delta_T^+} \quad 4.37$$

$$-K_{Tray} \frac{\partial T}{\partial z} \Big|_{z=\delta_r^-} = -K_B \frac{\partial T}{\partial z} \Big|_{z=\delta_r^+} - \left( E_{Oven} \Phi_{Oven} - E_B \sigma T \Big|_{z=\delta_r^+}^4 \right) \cdot \left( 1 - \frac{S_p}{S} \right) \cdot a \quad 4.38$$

The second term on the right side of Eq.4.38 takes into account the fact that the metallic net allows a reduced radiative flux impinging on the biscuit with a view factor  $a$ . The initial condition for the entire system is:

$$\forall z \quad t=0 \quad T=T_0 \quad 4.39$$

It is worth noticing that the evaporation surfaces must take in account the fact that ammonia is insoluble in the paste phase, but is soluble only in water. This implies that the surface for  $NH_3$  evaporation is reduced just by a factor  $X_W$ .

#### 4.5 Opened cell mechanical equilibrium

When the bubbles open towards the ambience the internal pressure suddenly drops from the actual to the external value. This implies a new mechanical equilibrium with an elastic recovery under constant pressure. Therefore it was proposed to compute the recovery defined as the bubble radius with respect to its value at coalescence, using the relaxation relationship derived from a creep test. In this way the channel still maintains a spherical shape after deformation recovery. In addition, because the properties of dough are time-dependent, it is necessary to know what is the amount of elastic energy stored during the closed cell behaviour, and that can be recovered at opening. This in turn means that a material memory function must be inserted somehow.

The mechanical problem was treated by using the Henky strain  $\varepsilon'$  which measures the deformation starting from a reference radius  $R_c^*$  of the virtual closed cylinder up to the radius at its disclosure towards the ambience:

$$\varepsilon' = -\frac{1}{2} \ln \frac{R_c}{R_c^*} \quad 4.40$$

Starting from this reference configuration, the strain is “stored” and because the viscoelastic solid hypothesis, at collapse it is recovered according to a simple Kelvin Voigt mechanical model:

$$\frac{\varepsilon'}{\varepsilon_0} = w_0 + \sum_i w_i e^{-\frac{t}{\tau_i}} \quad 4.41$$

where  $\sigma_0$  is deformation at collapse,  $w_i$  are the recovery weights and  $\tau_i$  are the retardation times. These parameters are computed from a creep-recovery test by using a 3-element model that proved to be a good fit with the experimental data:

$$\varepsilon'(t) = \varepsilon'_0 \cdot \left( J_0 + J_1 e^{-t/\tau_1} + J_2 e^{-t/\tau_2} + J_3 e^{-t/\tau_3} \right) \quad 4.42$$

For the tested dough it was found that computed parameters are quite independent of the applied stress within a large stress range, because they are simply related to the strain recovery when the stress is instantaneously put to zero. This behaviour is often found for dough. The deformation of a viscoelastic solid is remembered by the structure only during a certain lapse of time according to its material properties. This implies that the deformation  $\sigma_0$  at the maximum height before collapsing, must be computed going backwards for a certain amount of time corresponding to a characteristic material value, which may be assumed practically as a measure of the fading memory of the considered dough. The characteristic reference time  $t^*$  from which the system starts to remember is a measure of the transition in dough behaviour from viscoelasticity to “plasticity”, and it can be determined by a creep test. Creep experimental data were fitted by using a 1-element Kelvin-Voigt model:

$$J = J_0 + J_1 \left( 1 - e^{-\frac{t}{t^*}} \right) + \frac{t}{\eta} \quad 4.43$$

Thus from this equation the value of  $t^*$  is obtained. Below  $t^*$  a viscoelastic behaviour is shown, while above  $t^*$  a plastic behaviour is exhibited. In this sense the defined value represents the fading memory of the considered material. The above-discussed approach is, in principle, a new mechanical microsystem model that has the aim of taking the collapse into account. In fact, the model describes the possibility that the considered channel may collapse and, if this happens, the pearl necklace radius decreases according to the strain recovery mechanism, from which a volume reduction is obtained. In order to take into account the difference of recovery between two different flours, first of all information about the memory function  $t^*$  is needed and may be derived from creep-recovery test of a vacuum dough. These material parameters take into account the evidence that no bubble free surfaces are available to relax the imposed stress and, as a consequence, they give a measure of the “memory time”. Very often if a different flour is used a different void fraction is expected. For instance, if the void fraction  $\varepsilon$  increases, a freer surface would be available to relax the stress and as a consequence a

lower radius recovery would be observed. According to that and matching some available experimental data, the following correlation is proposed:

$$t^* = t_c - (A \cdot t_c + B) \cdot (1 + a \cdot \varepsilon^3)^{1/2} \quad 4.44$$

where A, B and a are fitting parameters.

#### 4.6 Opened cell thermodynamic equilibrium

If coalescence holds, the original closed bubble is suddenly in contact with the external atmosphere and it starts to behave as an open system. In addition, since the bubbles are joined among themselves a sort of equivalent channel has to be accounted for when the heat and mass transfer is modeled, in the gas phase toward the external ambience.

An estimate of the water amount leaving the paste when the cells open towards the external ambience forming a sort of channel, could be obtained by considering the system as an opened paste “pearls necklace”, filled with a gas mixture at the same  $T$  and  $P$  of the external fluid.

The main flux is due to water evaporation from the “pearls necklace surface”, and a mass transport is observed towards the external ambience, where a mass convective mechanism governed by the air velocity  $v_\infty$  is present. Regarding the inner part, the necklace surface should be assumed at thermodynamic equilibrium at a temperature of  $T$  calculated from the macrosystem, then a diffusive transport may be assumed throughout the channel. This problem is quite difficult to solve analytically also because a radial variable should be included, therefore it was preferred to continue following the main general idea of micro- and macro-systems. This means it was preferred to avoid the heterogeneous approach at macro level and to maintain a 1-D model. For this reasons, an equivalent system at micro level was considered.

The interface is calculated as equivalent to the side surface of the pearl necklace and, if the material properties are assumed to be constant at any time (constant  $T$  and  $U$  from macrosystem calculation), a constant water flux computed at the evaporating surface is given by:

$$N_w \Big|_{z=0} = \frac{-D_{w/A}}{D_{Bisc}} (y_{eq} - y_\infty) * EvaporationSurf \quad 4.45$$

The equivalent evaporating surface (*EvaporationSurf*) should be derived from the overall surface of the coalesced bubbles, also accounting for the time-dependent shrinkage due to water loss. In principle this geometric equivalence includes the evaporating surface of all the bubbles ( $n_b$ ) joined as a necklace

$$S^* = n_b \cdot [4\pi R_c(t)]^2 \quad 4.46$$

This value overestimates the effective available surface because in the adjoining zone the dough is missed and no evaporation is possible. In addition, the connection zone proceeds to enlarge as the channel shape moves from a necklace to a proper channel. This means that the ratio between the no-paste zone and the total bubble surface has to increase and the evaporating surface decreases as a consequence. Therefore a reducing factor has to be introduced as a function of time and the physically more reliable way was to link the reducing factor to the time-dependent bubble radius diminution with respect to the initial radius (at the collapse time):

$$S = \left( \frac{Rc}{R_{collapse}} \right)^3 \cdot S^* = \left( \frac{Rc}{R_{collapse}} \right)^3 \cdot \{ n_b \cdot [4\pi R_c(t)]^2 \} \quad 4.47$$

Where  $n_b$  is the number of bubbles for volume and  $R_{collapse}$  the bubble radius at the collapse time.

This term computed in such a way can be send to the macrosystem mass transfer equation as a sink for the paste phase to take into account the effect of the transport phenomena. Of course, the same considerations made for water apply for any component present in the gas bubbles, even if their importance is notably less. As a result even the flux expression is changed because the component profiles reduce to a single point. At any time, according to the collapse model, the exchange surface must be updated to evaluate the new cylinder radius following the recovery, and, according to  $T$  and  $U$  profiles computed by the macrosystem, the equilibrium conditions are updated too. Since the actual surface is important for evaporation, the computation of the shrinkage must take into account this reduction.

#### 4.7 Shrinkage Computation

The drying process that is coupled with biscuit baking implies the onset of shrinkage, which represents the volumetric dimensional reduction mainly due to water loss. It should be noticed that this phenomenon is always present due to the oven conditions that are far from water equilibrium, but the experimental evidence shows that during bubble growing, water tends to go preferably towards the gas bubble also owing to the smallness of the evaporating surfaces. At the opening the evaporating surface

increases considerably and therefore a rather more consistent drying is exhibited, therefore this effect was neglected during rising.

The shrinkage phenomenon was amply studied in the past by Minshkin, Saguy & Karel (1984) and Lang, Sokhansanj and Rohani (1984), reporting the dimensional variation of dough with the water loss thanks to a linear equation like the following:

$$V_{bisc}(t) = V_{bisc\_p} (1 + K_{shr} (U - U_0)) \quad 4.48$$

Where  $V_{bisc}(t)$  is the biscuit volume with time,  $V_{bisc\_p}$  is the biscuit volume at the maximum height,  $K_{shr}=1.18$  was suggested by experimental data and the value of the initial humidity ( $U_0$ ) was assumed constant and equal to 17%. Therefore the biscuit volume diminishes linearly according to the water loss during the baking period.

#### 4.8 Calculation Method

The equations system was solved applying the “Lumped Heat Capacity Method” [Holman, J.P, 1972; Mills, A. F., 1999], which is normally applied especially for heat transport, but which can be used by analogy for mass transport. The method requires the spatial definition of domain for the integration. Since it was supposed that the variability of temperature and concentrations are only in z-direction, the domain is an integration grid having the points equispaced at distance  $\Delta z$  (fig.4.8).

The “Lumped Heat Capacity Method” returns the temperature of a single  $\Delta V$  as a function of time. The method requires the absence of a spatial temperature distribution in  $r$  direction (in this specific case), then for the single  $\Delta V_i$  it is possible write as follows:

$$\rho_i C_{pi} \Delta V_i \frac{\Delta T}{\Delta t} = q_i \quad 4.49$$

where  $q_i$  is the heat given to the point  $i$  for radiation, convection, etc. [Holman, J.P, 1972].

Then, because each volume element,  $\Delta V_i$ , behaves like a small “lumped capacity” and the interaction of all the elements determines the behaviour of the object during a transient process, if we define the thermal capacity as:

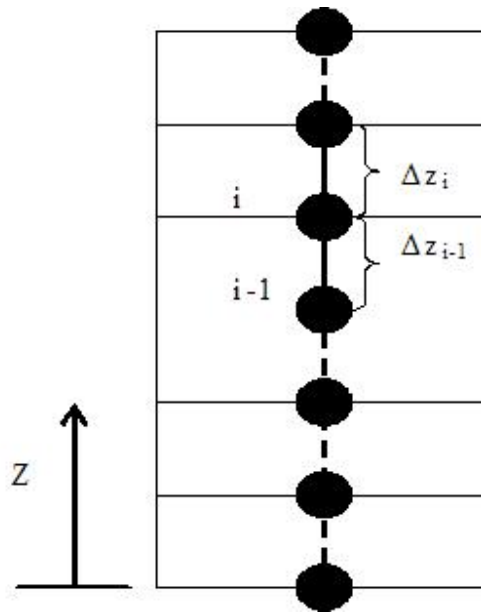


Figure 4.7 – Calculation Domain

$$C_i = \rho_i C_{pi} \Delta V_i \quad 4.50$$

Thus, the general resistance-capacity formulation for the energy balance can be written for the individual node in this way :

$$q_i + \sum \frac{T_j^p - T_i^p}{R_{ij}} = C_i \frac{T_i^{p+1} - T_i^p}{\Delta t} \quad 4.51$$

Where  $R_{ij}$  is the resistance (convective, conductive....) between one grid point and another.

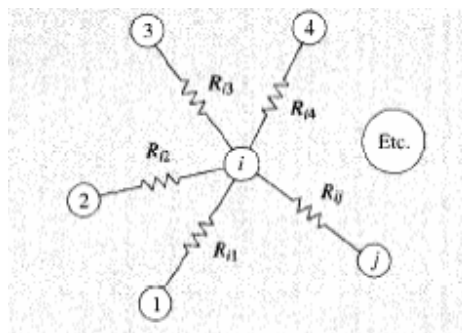


Figure 4.8 – General scheme of grid points

The lumped approach is well-suited and has advantages when it comes to flexibility in time- and temperature-varying boundary conditions, calculation speed and effort, simplicity in implementation and analysis technique. This method allows the introduction in simple way of the  $q_i$  terms that can be seen as sinks for the system.



The system of equations in paragraphs 4.3 and 4.4 are coupled, the material parameters are dependent on temperature and concentration or the molar fraction of the component present in the system. For this reason, it was assumed that, at every time step, the physical properties do not change very much and, then we can calculate the parameters with the value of T and concentration/molar fraction calculated at the previous step. This hypothesis is more valid because a small time step was chosen. Another problem is the initial expansion of the system and the successive shrinkage after collapse, because this phenomenon implies a different dimensional increase/reduction of different  $\Delta z_i$ , because of bubble expansion and humidity gradients. The problem was overcome by calculating the new  $\Delta z$  as the arithmetic mean of the real dimension of the interval at every instant of time. The numerical approximation of  $\Delta z$  calculation can be improved, but in every case the results are comfortable in terms of stability and velocity calculation and for this motive the program was considered acceptable for the pre-established purpose.

#### 4.9 Thermodynamic and transport properties

The following paragraph reports all the material parameters necessary for the simulation of the baking of a crunchy biscuit, relative to material and energy transport. Many of these were obtained from the literature data, while for the density value, surface tension, void fraction, number of bubbles and water activity laboratory tests were performed .

##### 4.6.1 Equilibrium Constants

The equilibrium constants were found in Perry R. H. and Green D. (1984):

$$\begin{aligned}
 & \text{H}_2\text{O Vapour Pressure [Pa]} \\
 P_{H_2O}^0 &= \frac{10^{\left(8.07131 - \frac{1730.63}{T - 273.15 + 233.426}\right)}}{760} \cdot 101325 \quad 4.52
 \end{aligned}$$

$$\begin{aligned}
 & \text{NH}_3 \text{ Vapour Pressure [Pa]} \\
 P_{NH_3}^0 &= 10^{\left(9.858926852 - \frac{1106.875614}{T - 11.4970708}\right)} \quad 4.53
 \end{aligned}$$

$$\begin{aligned}
 & \text{CO}_2 \text{ Henry's Function [Pa]} \\
 H_{CO_2} &= 4534293.75 \cdot T - 1176741506.25 \quad 4.54
 \end{aligned}$$

The water activity was measured in the United Biscuits (UK) laboratory in accordance with their standard procedures:

Water Activity:

$X_W > 0.006$  moles/total moles

$$a_w = (26.672 \cdot X_W^3 - 26.338 \cdot X_W^2 + 8.5353 \cdot X_W - 0.0471) \cdot \text{Shift } T \quad 4.55$$

$$T < 100^\circ\text{C} \quad \text{Shift } T = \exp\left(292.96 \cdot \left(\frac{1}{298} - \frac{1}{T}\right)\right) \quad 4.56$$

$$T > 100^\circ\text{C} \quad \text{Shift } T = \exp\left(292.96 \cdot \left(\frac{1}{298} - \frac{1}{373}\right)\right) \quad 4.57$$

$X_W < 0.006$

$$a_w = 0 \quad 4.58$$

#### 4.6.2 Heat Conductivity and Emissivity

Thermal conductivity, since it appears in the macrosystem, must take into account the pseudo-homogeneity assumed for the considered system. Therefore, when the gas cells are closed, the current literature indicates the following so-called *EUKEN* equation giving the effective heat conductivity,  $K_{eff}$ , for a composite material constituted by a continuous phase ( $K_{CONT}$ ) and a dispersed one ( $K_{DISP}$ ) of spherical shape, as a function of the volumetric fraction of the dispersed phase  $\phi$ :

$$K_{eff} = K_{CONT} \frac{K_{DISP} + 2K_{CONT} - 2\phi(K_{CONT} - K_{DISP})}{K_{DISP} + 2K_{CONT} + \phi(K_{CONT} - K_{DISP})} \quad 4.59$$

The validity of this equation was proved [Sakiyama et al., 1990] for spheres organized in several spatial distributions, e.g. simple, body-centred and face-centred cubic lattices, and for both uni and bi-modal dimension distributions, in the specific case of  $K_{DISP} / K_{CONT} = 0.01$ . When considering dough, air gas spherical cells are embedded in a dense cereal paste, therefore eq.4.52 seemed to well-approximate the considered physical condition. According to the rather low value of the air conductivity, the equation may be approximated as

$$K_{eff} = K_{CONT} 2 \frac{1-\phi}{2+\phi} \quad 4.60$$

To determine  $K_{CONT}$ , data were taken from vacuum paste sheet, but it should be noticed that all the same a certain amount of gas remains entrapped in the samples during mixing even if the

bubbles are rather small according to the vacuum degree imposed. An approximate computation was made by assuming that the number of bubbles remains the same, but the volume is much less because of the vacuum level. therefore it is possible to determine the volumetric fraction and the value of  $K_{CONT}$  from the following:

$$K_{CONT} = \frac{1}{2} K_{MEAS} \frac{2 + \phi}{1 - \phi} \quad 4.61$$

The value obtained by this procedure at 30°C gives a value that is rather close to that measured, therefore it was chosen to approximate  $K_{CONT}$  to  $K_{MEAS}$ . Experimental measurements were made as a function of  $T$  and water content  $X_W$  and the following results were obtained by data fitting:

$$K_{MEAS} = f(T) f(X_W) \quad 4.55$$

Thus in principle the resulting equation should read:

$$K_{eff} = f(\Phi) f(T) f(X_W) \quad 4.56$$

It should be noticed that, if a 1D model is assumed, the equation represents a too strong functionality and therefore must be reduced. In fact, it should apply only in a 3D model.

This approach holds for coalescence, thereafter the value of the heat conductivity is  $K_{CONT}$ . It should be noted that because up to coalescence the water content almost remains constant, the humidity dependence does not play an important role.

The value of continuous phase (Dough heat conductivity), furnished by UB literature data, is the following:

$$K_{Dough} = (0.00101429 \cdot T + 0.04872584) \cdot (4.6628 \cdot X_W + 0.0726) \quad 4.57$$

For the tray the heat conductivity is:

$$K_{Tray} = (0.0153 \cdot T + 8.2774) \cdot (1 - \epsilon_{Tray}) \quad 4.58$$

and for the Air is:

$$K_{Air} = 0.00007252 \cdot T + 0.003674 \quad 4.59$$

all the conductivity values are measured in W/(m·K). Moreover the emissivity value of the tray, oven and biscuit are the following:

$$\text{Tray [W/(m·K)]: } E_{Tray}=1 \quad 4.60$$

$$\text{Oven [W/(m·K)]: } E_{Oven}=1 \quad 4.61$$

$$\text{Biscuit [W/(m·K)]: } E_B=0.95 \quad 4.62$$

### 4.6.3 Mass Diffusivity

The Diffusivity of Water in the dense paste [m<sup>2</sup>/s], also furnished by UB, takes into account the dependence of diffusivity on the void fraction of material thanks to a function  $f(\varepsilon)$ :

$$D_{WD} = \left( 0.00000012 + \frac{\varepsilon \cdot 0.00008}{101325} \right) \cdot \frac{\exp(-6 \cdot \exp(-20 \cdot X_W) + 22600)}{8.31439 \cdot T} \cdot f(\varepsilon) \quad 4.63$$

The function  $f(\varepsilon)$  before coalescence is the following:

$$f(\varepsilon) = \frac{(1-\varepsilon)^{\frac{2}{3}}}{(1-\varepsilon)^{\frac{2}{3}} + \varepsilon} \quad 4.64$$

while after coalescence the function is:

$$f(\varepsilon) = (1-\varepsilon) \quad 4.65$$

for the diffusivity of Ammonia in water, Carbon Dioxide in water we have respectively:

$$D_{NH_3/W} = (0.00000012 \cdot X_W) \cdot \frac{T}{298} \quad 4.66$$

$$D_{CO_2/W} = (0.00000000177 \cdot X_W) \cdot \frac{T}{298} \quad 4.67$$

and for the diffusivity of water vapour in the water, ammonia in air, carbon dioxide in air we have respectively:

$$D_{W/A} = 0.001 \cdot T^{1.75} \cdot \frac{\left( \frac{(MW_{Air} + MW_{Wat})}{MW_{Air} \cdot MW_{Wat}} \right)^{0.5}}{\frac{P_{atm}}{101325} \cdot (N_{iair}^{1/3} + N_{iwat}^{1/3})^2} \cdot \frac{1}{10000}} \quad 4.68$$

where:  $N_{iair} = 20.1$  air atomic diffusion volume,  $N_{iwat} = 12.7$  water atomic diffusion volume,  $MW_{Air}$  molecular weight of air,  $MW_{Wat}$  molecular weight of water.

$$D_{NH_3/A} = 0.001 \cdot T^{1.75} \cdot \frac{\left( \frac{(MW_{Air} + MW_{NH_3})}{MW_{Air} \cdot MW_{NH_3}} \right)^{0.5}}{\frac{P_{atm}}{101325} \cdot (N_{iair}^{1/3} + N_{iNH_3}^{1/3})^2} \cdot \frac{1}{10000}} \quad 4.69$$

Where  $N_{iair} = 20.1$  air atomic diffusion volume,  $N_{iNH_3} = 14.9$  ammonia atomic diffusion volume,  $MW_{NH_3}$  molecular weight of ammonia.

$$D_{CO_2/A} = 0.001 \cdot T^{1.75} \cdot \frac{\left( \frac{(MW_{Air} + MW_{CO_2})}{MW_{Air} \cdot MW_{CO_2}} \right)^{0.5}}{\frac{Patm}{101325} \cdot (N_{iAir}^{1/3} + N_{iCO_2}^{1/3})^2} \cdot \frac{1}{10000} \quad 4.70$$

where  $N_{iAir} = 20.1$  air atomic diffusion volume,  $N_{iCO_2} = 26.9$  carbon dioxide atomic diffusion volume. All the diffusivity value are measured in [m<sup>2</sup>/s].

#### 4.6.4 Specific Heat

The specific heat of the biscuit can be calculated as the weighted mean of the principal component of the dough biscuit [Andrieu et al. 1989] :

$$C_{PDough} = \sum_i C_i \cdot x_i \quad 4.71$$

The dough is principally constituted of fat, protein carbohydrate and water, then the eq. 4.66 becomes the following:

$$C_{PDough} = C_{PFat} \cdot X_{Fat} + C_{PProt} \cdot X_{Prot} + C_{PCarb} \cdot X_{Carb} + C_{PWat} \cdot X_W \quad 4.72$$

where  $X_{OFat} = 0.12$ ,  $X_{OCarb} = 0.63$ ,  $X_{OProt} = 0.05$ . Then the heat capacities are the following:

$$C_{PFat} = (1.984 + 0.001473 \cdot T - 0.0000048 \cdot T^2) \cdot 1000 \quad 4.73$$

$$C_{PProt} = (2.008 + 0.001208 \cdot T - 0.000001312 \cdot T^2) \cdot 1000 \quad 4.74$$

$$C_{PCarb} = (1.548 + 0.001962 \cdot T - 0.000005939 \cdot T^2) \cdot 1000 \quad 4.75$$

$$C_{PWat} = (4.176 - 0.0009086 \cdot T + 0.000005473 \cdot T^2) \cdot 1000 \quad 4.76$$

The specific heat is measured in [J/(kg·K)].

For the Air the heat capacity is equal to 1046 J/(kg·K) and for Steel the relation is the following:

$$C_{PSteel} = (0.1774 \cdot T + 431.09) \cdot (1 - \varepsilon_{Tray}) \quad 4.77$$

#### 4.6.5 Latent Heat

Water [J/mole]:

$$\lambda_w = 40550 \quad 4.78$$

Ammonia [J/mole]:

$$\lambda_{NH_3} = 232620 \quad 4.79$$

Since the water is partially bounded, the value of the energy needed to pass from the liquid to the vapour phase must be increased. By recalling that the link between activity and vaporization heat is logarithmic, the following equation was used:

$$\lambda = \lambda_o (1 - \ln a_w) \quad 4.80$$

#### 4.6.6 Density

Steel Density [kg/m<sup>3</sup>]:

$$\rho_{Steel} = (-0.4338 \cdot T + 7899.2) \cdot (1 - \varepsilon_{Tray}) \quad 4.81$$

Paste Density [kg/m<sup>3</sup>]:

$$\rho_p = 1300 \quad 4.82$$

#### 4.6.7 Surface Tension

Dough/Gas interface [Pa·m] (internal data of UB):

$T < 55^\circ C$

$$\gamma = \frac{(0.0005 \cdot T^2 - 0.1219 \cdot T + 30.022)}{1000} \quad 4.83$$

$T > 55^\circ C$

$$\gamma = \frac{22.37}{1000} \quad 4.84$$

#### 4.10 Initial Conditions

The initial condition for the simulation program are reported in the following:

- **Void fraction**

It was measured and considered constant, depending on the starting flour considered:

Heygates  $\varepsilon = 5\%$

Carr's  $\varepsilon = 3.7\%$

- **Number of bubbles**

The number of bubbles remains constant and is computed as follows:

$$n_b^o = \frac{\text{Volume voids}}{\text{Volume single bubble}} = \frac{V_{tot} \cdot \varepsilon}{V_b} = \frac{I}{V_b} \cdot \frac{W_{Bisc}}{\rho_P} \cdot \frac{\varepsilon}{1 - \varepsilon} \quad 4.85$$

- **Initial temperature:**  $T = 308 \text{ K}$

#### 4.11 Block Diagram of the main programme and conclusions.

The baking model is essentially constituted of two interacting operations: the microsystem and the macrosystem. Simply speaking, the microsystem works in heterogeneous conditions and is based on equilibrium, therefore different computing blocks are considered according to the different equilibrium conditions. This allows managing the whole model in a rather easy way, because it is possible to change single micromodels as needed, without changing the main computing programme. On the other hand there is the macrosystem that represents the connection tool for those single blocks that are in turn essentially subroutines of the computing programme. It was chosen to have a core loop that is the baking process, while all the other process steps are considered before start the loop.

Thus, the first step of the computation consists into giving the data input which are:

**Initial Conditions:** Temperature, Diameter, Height, Void Fraction, R.A. concentration, Water Content

**Operational Conditions:** Heat Flux Top & Bottom, Dew Point,  $T_{\text{oven}}$

**Numerical Conditions:** Grid for Tray and Biscuit, Time step.

Some of these may be changed and stored in suitable files. The second step is the evaluation of the mixing and standing processes occurring before the biscuit comes into the oven.

The mixing of the components is the process step during which the structural network is mainly generated, and this is carried out with specially designed mixers. However, during stirring, depending on the movement of the blades, a certain amount of air is entrapped into the formed dough, which represent the initial nuclei for gas bubble development. Of course, the amount and dimensions depend on the specific characteristics of the ingredients used, and above all on the flour adopted. After mixing, the obtained loaf is left to rest for a while in a closed ambience, and this process step is called standing. The number of air moles resulting from these two processing steps, was obtained by means of an iterative method based on the knowledge of the final bubble diameter ( $15 \mu\text{m}$ ) as obtained from experimental evidence. The computation starts from the assumption that the bubble pressure is the sum of the atmospheric pressure and the surface tension, thus from the thermodynamic equilibrium the current air moles are computed. The mixing is carried out for 541 s and, however, the R.A. decomposition reactions already occur, but owing to the process conditions, it was admitted that at the end the product concentration is set to 0. Thus this is equivalent to a decrease of the initial R.A. concentrations. Then the dough is put in a closed ambience and the so-called standing step is carried

out. The temperature is between  $30^{\circ}\text{C}$  and  $40^{\circ}\text{C}$ , therefore an average of  $35^{\circ}\text{C}$  was assumed. The total mole amount contained inside the gas bubble, the internal pressure and the volume of any single bubble may be calculated and will represent the initial condition for the baking model computation. From the initial diameter it is possible to compute the pressure as the atmospheric pressure plus twice the interfacial tension divided by the bubble radius. The amount of air moles entrapped must satisfy thermodynamic equilibrium, therefore a flash computation is run assuming a first tentative value of the air moles and iterating calculation till the pressure matches the imposed value and the known diameter. The computation details are the same as the flash used in the microsystem referred to closed cells.



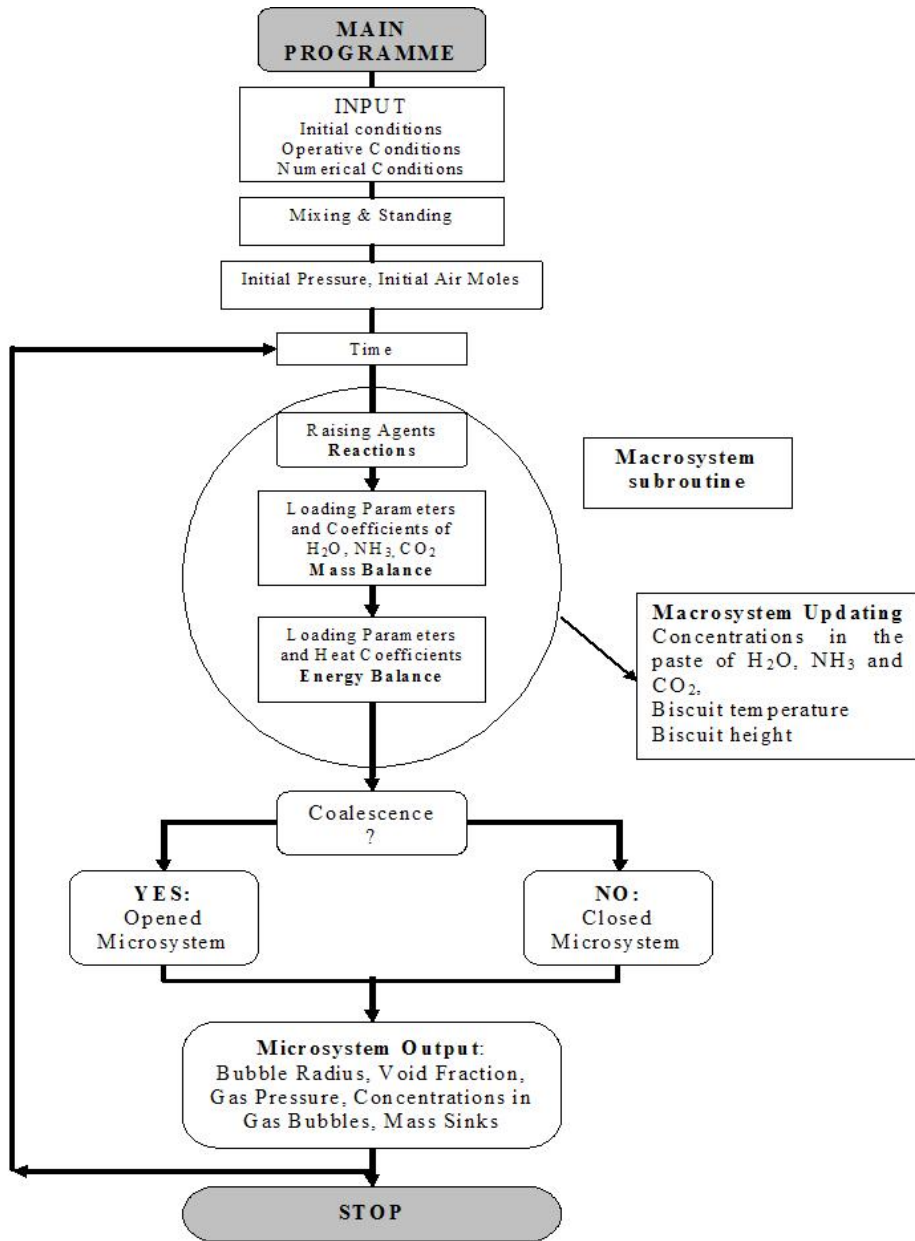


Figure 4. 9 – Block diagram of programm

After the mixing and standing step, the baking computation programme may start. The whole computation is based on a quasi-static transformation, implying an alternation between equilibrium and physical transport. Thus at any time the values of the current variables are determined at equilibrium and after, according to the Raising Agent kinetics and to the time-dependent boundary conditions, they are updated by applying the considered transport mechanisms. Of course, the new computed values influence the effective values of all the properties used in the computation because the macrosystem is

a pseudo-homogeneous system. There are several subroutines to be effected that are separate from the main computation direction and they are carried out again when needed to update the material properties. Once the updating is done, the new data have to go to the proper equilibrium stage. This means that a preliminary control is carried out on which microsystem must be used. The main difference in this 1-D version is the coalescence, therefore at the end of the macro computations a decision is made on the flow diagram, whether to use open or closed cells for any grid point. The thermodynamic and mechanical equilibrium laws according to the given microsystem, establish the amount of mass that goes into the gas phase, the new bubble radius and pressure, and finally, the mass sink with respect to the paste.

#### **4.12 References**

- Broyart, B., G. Trystram, Modelling heat and mass transfer during the continuous baking of biscuits, *J Food Eng.ing* 51: 47-57, 2002.
- Dobraszczyk, B. J., M. P. Morgenstern, Rheology and breadmaking process, *Journal of cereal science* 38, 229-245, 2003.
- Nantawan Therdthai and Weibiao Zhou, Recent Advances in the Studies of Bread Baking Process and Their Impacts on the, *Bread Baking Technology, Food Sci. Technol. Res.*, 9 (3), 219–226, 2003.
- Thorvadsson, K., H. Janestad, A model for simultaneous heat, water and vapour diffusion, *J Food Eng.ing* 55: 167-172, (1999).