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From Laws of Nature to Dynamic Models of Processes

1.1. General laws

In very general terms, models of processes rely on two types of ingredients:

– *Conservation laws*: these are the backbone of the model and are used to write balances:

- energy balances, based on the first law of thermodynamics;

- mass balances, issued from the law stated by Lavoisier and often summarized as “nothing is lost, nothing is created, everything is transformed”.

– *Kinetic laws*: kinetic laws express the rate at which phenomena unfold (heat transfers, mass transfers, chemical or biological reactions) and introduce time in models.

Depending on the studied domains and scales, conservation laws may be expressed in a wide range of forms, sometimes “hidden” by sophisticated mathematical operators such as the divergence of a vector field. Our proposal is to use an intuitive formulation, which is the point of departure for any process model:

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by Gilles TRYSTRAM and Cristian TRELEA. © ISTE Ltd 2025.

$$\begin{pmatrix}\text{Mass or energy}\\ \text{accumulation}\end{pmatrix} = \begin{pmatrix}\text{Input}\\ +\\ \text{Production}\end{pmatrix} - \begin{pmatrix}\text{Output}\\ +\\ \text{Consumption}\end{pmatrix} \quad [1.1]$$

In this form, equation [1.1] can be applied to both energy and mass balances. The art of modeling consists of choosing the forms of energy (thermal, mechanical, electrical, etc.) and mass (chemical species) that are relevant for a given application, as well as their potential transportation by fluids and their transformations by chemical and biological reactions.

An important specific case is that of the permanent regime, also known as the steady state. This regime is characterized by the fact that all quantities at a given point (temperatures, concentrations, etc.) are constant in time. This means that there is no net accumulation, or in other terms, everything that goes in or is produced (per time unit) must also go out or be consumed:

$$\begin{pmatrix}\text{Mass or energy}\\ \text{accumulation}\end{pmatrix} = 0 \quad \Leftrightarrow \quad \begin{pmatrix}\text{Input}\\ +\\ \text{Production}\end{pmatrix} = \begin{pmatrix}\text{Output}\\ +\\ \text{Consumption}\end{pmatrix} \quad [1.2]$$

The kinetic laws express the rate at which phenomena occur. In general, the rate depends on local conditions: temperature and concentrations of reactants for the reactions, difference in temperature for thermal transfers, differences in concentration or activity for mass transfers, fluid velocity for transportation phenomena, etc. This can be expressed as follows:

$$\begin{matrix}\text{Rate at which}\\ \text{a phenomenon occurs}\end{matrix} = \text{Function (Local conditions)} \quad [1.3]$$

For a more concrete illustration of these notions, let us now consider representative examples of phenomena and approaches encountered in the food industry.

1.2. Physical model: drying

Since ancient times, humans have tried to stabilize perishable products to have them available for consumption beyond the periods of production, harvesting, hunting or fishing. Reducing water availability in the products inhibits many of the physical, chemical and enzymatic phenomena responsible for their degradation. This is achieved by the addition of substances such as salt or sugar to trap water molecules (salted or candied products) or by the elimination of a significant part of the initially present water (dry products) by various drying processes.

Currently, drying operations are still very common in the agri-food industry and are largely responsible for energy consumption in this sector. Indeed, water removal most often requires supplying the required latent vaporization or sublimation heat. Owing to the quantitative description of the drying process, this process can be *in fine*-sized and optimized, taking into account the technical, economic and quality criteria of the product.

1.2.1. *Drying model at the scale of the individual grain or of the "thin layer"*

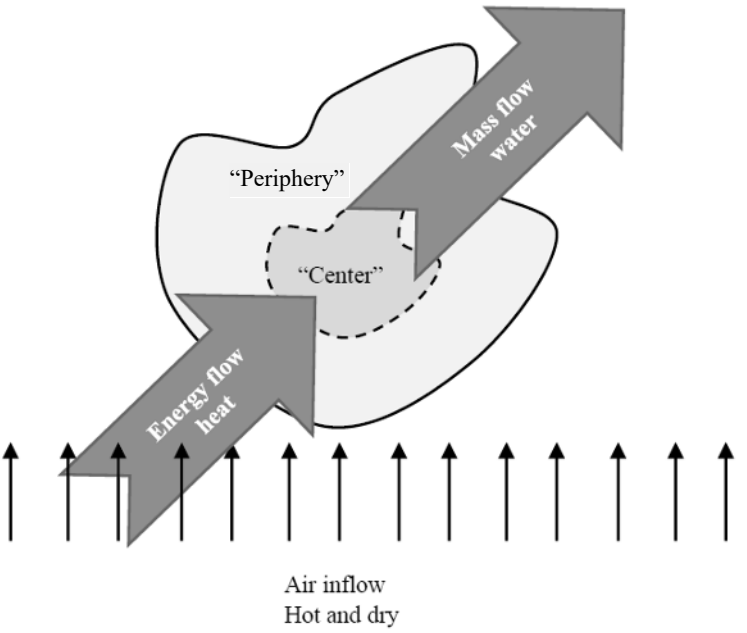


Figure 1.1. *Schematic representation of the hot air drying of a divided product at the scale of a grain or a droplet*

In agriculture and industry, products such as cereals or liquids transformed into powders (milk, juice, etc.) are often dried using hot air under forced convection. The hot air supplies the energy required to change the state of water from liquid into vapor and at the same time carries the resulting water vapor away from the product. This chapter does not cover other drying modes, such as microwave energy supply, lyophilization (drying frozen products by sublimation) or the traditional drying by

natural convection and a solar radiation energy supply. There is a rich literature on these methods.

The situation studied is schematically represented in Figure 1.1. It is applicable to any divided product located in a fluid stream, but to set the context, let us consider a corn grain in a stream of hot air. Drying a drop of milk in an atomization tower may be performed in a similar manner, with additional complications due, for example, to the significant change in the drop size during drying.

The first important phenomenon is the thermal energy supplied by hot air; part of this energy is used for water evaporation, whereas the other part heats the grains from the periphery inward. A second phenomenon is water evaporation at the surface of the grain, which is carried away by the hot air stream. The periphery of the grain is depleted in liquid water, which tends to be replaced by water coming from the center through diffusion in the solid matrix. If we are interested not only in the water content but also in the physicochemical quality indicators that might be affected by heating, the corresponding reactions should be added to this model.

1.2.1.1. *How to choose the level of fineness of our model*

To apply the laws of physics and chemistry and quantitatively describe the abovementioned phenomena, several choices are essential for the complexity of the resulting model.

> QUESTION.– What is the level of detail at which grain geometry should be considered? Should we conduct grain tomography and use the 3D meshing obtained to solve the equations of internal transfer and surrounding air flow? The visual examination of a handful of corn convincingly shows that the shape and size of the grains are highly variable. Should this examination work be conducted on a grain bucket, truck or silo?

It is difficult to find a perfectly rigorous scientific answer to these questions. However, this is the type of question that every modeling practitioner is asking when starting to work, and all of the remaining questions are determined by the answer.

According to the authors' point of view, what proves mainly helpful is the past experience, the physical common sense and the objective of the model. A 3D geometry model of a single grain requires significant work, but this is simply unfeasible for an industrial quantity of grain. The resulting equations would involve thousands and even millions of variables and would take months to be solved by the most powerful computers.

However, why would we need it? What manufacturer would be interested in having a detailed knowledge of the water distribution in every part of each grain of their silo? If the objective is to calculate the average water content of a large batch, common sense indicates that a detailed exploration of the shape of each grain is perfectly useless. It is difficult to rigorously prove this assertion. This would require building an extremely detailed model, averaging the obtained result and then comparing it to a simpler model. If there is an agreement of predictions at a previously specified precision level, then the simple model should be adopted.

In practice, a scientist rarely has the time and means to undertake such a comparison operation, whereas for an engineer in the industry, it is practically impossible. According to our experience, in process engineering, relatively powerful simplifying hypotheses should always be adopted a priori, comparing the predictions of the obtained model to experimental measurements and, if needed, refining the model. Depending on the objective of the study, the available experimental measurements and the personal experience of the modeling scientist, the degree of simplification can be set at various levels.

After having given up a detailed 3D examination of each corn grain, we can now ask questions on the flow of air around the grain.

> QUESTION.– Should we solve the Navier–Stokes equations to find the air flow velocity at each point around a grain? Should we consider a stack of grains, regular or not, and of what size?

Even when one or several grains of regular shape, for example, simply spherical, solving the fluid flow equations is a difficult task, which requires a high level of specific know-how, cutting-edge software and a relatively long calculation time. Before starting, let us ask the following question: what exactly will the model be used for? The heat and water vapor transfers at the surface of the grain depend on the local velocity. In a first approximation, they will be more intense on the side of the grain exposed to the air flow and weaker on the opposite side. The proximity of other grains will reduce the air passage section and, at a constant flow rate, will locally increase the velocity. However, since we have no specific interest in the details of the water distribution of each grain, we do not need to know the air velocity at each point of its surface. For this first model, we consider an average velocity and therefore average transfer coefficients.

> QUESTION.– Should we pay attention to the differences in temperature, water content and possible quality indicators inside a representative average grain, or can we consider the grain as a homogeneous entity?

Intuitively, if the main resistance to heat transfer is at the surface of the grain, then the temperature inside it will essentially be homogeneous. Conversely, if thermal conduction inside the grain is the limiting factor, the differences in temperature between the center and the periphery will be significant, with consequences, for example, for the heterogeneity of quality indicators and therefore for degradation at certain points.

Fortunately, the process engineer's toolkit contains well-tested tools to address these questions, in the form of dimensionless numbers. In the case of interest, the Biot number precisely represents the ratio between the resistance to internal and external heat transfer of a body (Green and Southard 2018):

$$B_i = \frac{\text{Resistance to internal heat transfer}}{\text{Resistance to external heat transfer}} = \frac{\text{External thermal conductance}}{\text{Internal thermal conductance}} = \frac{h\, l_c}{\lambda} \quad [1.4]$$

where h (W m^{-2} K^{-1}) is the global heat transfer coefficient at the surface of the body, l_c (m) is its characteristic dimension and λ (W m^{-1} K^{-1}) is its thermal conductivity.

According to experience and detailed calculations, for high Biot numbers, typically $B_i > 1$, the internal resistance is predominant, and the thermal gradients inside the object are significant (Sacadura 2015). Conversely, for low Biot numbers (e.g. $B_i < 0.1$), the predominant resistance is situated at the surface, and the internal temperature can be considered homogeneous. The modeling practitioner must decide between the two, depending on the expected degree of precision and complexity of the final model.

A brief investigation of the literature may provide us with several estimations for the sought-for values. Importantly, at this stage, we do not need precise values but only orders of magnitude to determine the complexity of the model to be adopted. According to Romdhana et al. (2016), for example, we can estimate the following:

$$B_i = \frac{h\, l_c}{\lambda} \sim \frac{10 \times 10^{-2}}{10^{-1}} = 1 \quad [1.5]$$

We are therefore near the gray zone, where we cannot confidently ignore the thermal gradients, but we cannot expect them to be of crucial importance.

A similar reasoning can be applied to mass transfers. The corresponding dimensionless number is known as the mass transfer Biot number and is written similarly:

$$B_{im} = \frac{\text{Resistance to internal mass transfer}}{\text{Resistance to external mass transfer}} = \frac{\text{External conductance}}{\text{Internal conductance}} = \frac{k\, l_c}{D} \quad [1.6]$$

where k (m s^{-1}) is the global mass transfer coefficient at the surface of the body, l_c (m) is still the characteristic size and D (m^2 s^{-1}) is the diffusion coefficient.

In the case of interest, that of a granular food product, the following estimation can be made:

$$B_{im} = \frac{k\, l_c}{D} \sim \frac{10^{-3} \times 10^{-2}}{10^{-9}} = 10^4 \quad [1.7]$$

Here, the resistance to internal mass transfer, which is linked in particular to water diffusion, is clearly important. To obtain an even remotely realistic model, we must therefore consider a non-homogeneous distribution of water content inside a grain.

One additional question needs to be addressed before starting to write equations.

> QUESTION.– Should the nonhomogeneous structure of the grain be taken into account? The internal structure of a grain is complex: pericarp, vitreous kernel, farinaceous kernel, germ, etc. The properties of these various parts also differ, so is it necessary to know them all for a proper description of grain drying?

At first glance, the answer seems to be clearly affirmative since the necessity of determining the water distribution inside the grain was established above. For example, water diffusivity might significantly vary between these various components. However, its determination is far from being trivial. Should we invest considerable effort in determining the water diffusion coefficient in each component of the grain?

It turns out that it is possible to save much time, money and effort by thoroughly examining our initial question: do we really want to know the water content in the pericarp, vitreous kernel, farinaceous kernel, etc., during drying? After drying, the grains are stored, and water transfer ends when equilibrium between various parts is reached.

Indeed, we need to consider water content gradients only to account for the kinetics of global drying; this is indicated by the high mass transfer Biot number. What part of the grain has exactly what humidity at a given moment is not important for the intended use of the model: choosing the air temperature and drying duration, calculating the energy consumption, etc.

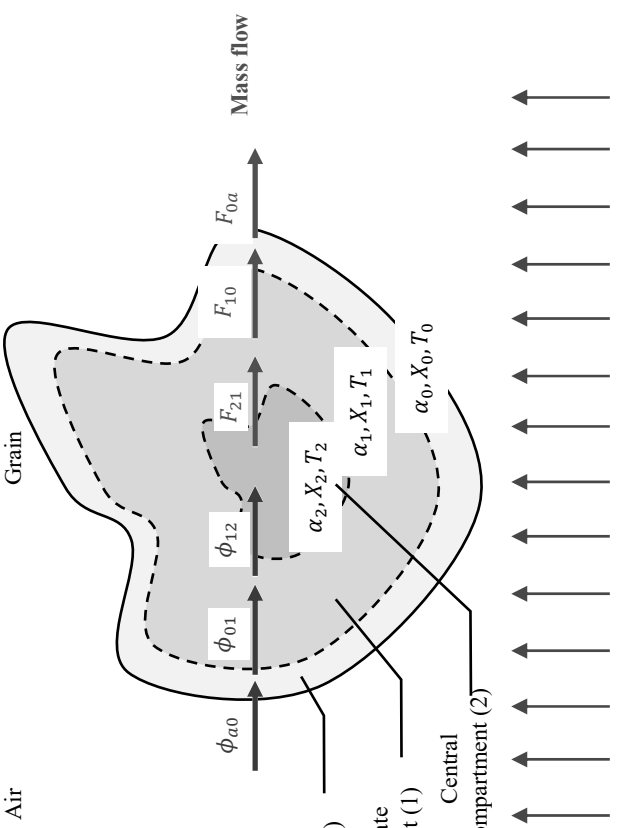


Figure 1.2. *Schematic representation of a compartmental model for the description of heat and mass transfers in a drying grain. For a color version of this figure, see www.iste.co.uk/trystram/bioprocesses.zip*

What practical conclusions can therefore be drawn from all these considerations? We want a relatively simple model, which, without too many details, reflects the distribution of humidity inside the grain and possibly of temperature, as well as exchanges with the surrounding air. A model known as "compartmental" is perfectly adapted to this level of description. A schematic representation is given in Figure 1.2.

As an illustration, we consider three compartments. This choice is, to a large extent, arbitrary and can be reviewed depending on the expected degree of fineness of the description. Inside each compartment, the grain properties (temperature, humidity, density, etc.) are considered homogeneous, and transfers take place between the compartments. The surface compartment, numbered "0", is considered thin and is the location of external transfers, such as water evaporation. The remaining compartments, numbered "1" and "2" from the surface to the center of the grain, contain most of the grain mass and volume in similar proportions. Generally, the humidity and temperature gradients are expected to be greater at the grain surface than at its center, hence the idea of having a finer "meshing" toward the surface, for a better representation of phenomena, at equal numbers of compartments.

Once the geometry is chosen, we can start writing the model equations.

1.2.1.2. *Mass balance equations for water*

Water migration from the center of the product to the air is the main phenomenon we focus on in this drying model. We decompose the grain and the air into two components, water on one side and dry matter on the other, which represents "everything else". For each of these compartments, we can write, inspired by equation [1.1], the following:

$$\frac{dm_{w0}}{dt} = F_{10} - F_{0a} \qquad [1.8]$$

$$\frac{dm_{w1}}{dt} = F_{21} - F_{10} \qquad [1.9]$$

$$\frac{dm_{w2}}{dt} = -F_{21} \qquad [1.10]$$

Here, m_{wi} (kg) is the mass of water contained at a given moment in compartment number "i" (Figure 1.2). For each compartment, the mass variation per unit time is given by the difference between the incoming flow $F_{i+1,i}$ (kg s^{-1}) and

the outgoing flow $F_{i,i-1}$. For the outside (0), the next compartment is the air (a), and for the central compartment (2), there is no ingoing flow.

1.2.1.3. *Heat balance equations*

To write the enthalpy balance for each compartment, several mechanisms must be taken into account: heat conduction, thermal energy transportation by mass flows and, for the external compartment, water phase change from liquid to vapor:

$$\frac{dH_0}{dt} = \phi_{a0} - \phi_{01} + F_{10}c_w(T_1 - T_{ref}) - F_{0a}c_w(T_0 - T_{ref}) - F_{0a}\Delta\widehat{H}_{vap} \quad [1.11]$$

$$\frac{dH_1}{dt} = \phi_{01} - \phi_{12} + F_{21}c_w(T_2 - T_{ref}) - F_{10}c_w(T_1 - T_{ref}) \quad [1.12]$$

$$\frac{dH_2}{dt} = \phi_{12} - F_{21}c_w(T_2 - T_{ref}) \quad [1.13]$$

Here, H_i (J) are the enthalpies of each compartment, $\phi_{i,i+1}$ (W) are the conductive flows, and the terms written as $F_{i,i-1}c_w(T_i - T_{ref})$ represent the enthalpy flows carried by mass flows; in this case, water, with a specific heat capacity c_w (J kg^{-1} K^{-1}). The term $F_{0a}\Delta\widehat{H}_{vap}$ represents the energy flow absorbed for water evaporation in the external compartment. Importantly, the enthalpy is defined up to an arbitrary additive constant. We will follow the use in process engineering by considering the enthalpy zero at $T_{ref} = 0$°C and, in the case of water, in the liquid state. All of the terms in the above equations have dimensions of energy per unit time or power (W), with the specific heat capacity of water (c_w) being in J kg^{-1} K^{-1} and the mass enthalpy of water vaporization in J kg^{-1}.

Once the balance equations being established, the kinetic equations can be written, particularly the expressions of mass and energy flows.

1.2.1.4. *Mass transfer equations for water*

At this stage, we must decide how to quantify the water content of each compartment of grain and air. Several choices are available, for example:

– water mass;

– number of moles;

– concentration, that is, water mass per unit volume;

– chemical activity or potential;

– partial pressure;

– water content in "humid basis" or mass fraction, that is, water mass per total mass (water + dry material);

– water content on a "dry basis", that is, water mass per mass of dry material;

– etc.

To comply with the tradition in the field of drying and to simplify the writing of balance equations, we choose the water content on a dry basis X (kg kg^{-1}) to describe the state of each compartment in terms of water content:

$$X_i = \frac{m_{wi}}{m_{si}}, \quad i \in \{0, 1, 2\} \qquad [1.14]$$

In our model, X_i will be three "state variables" related to mass transfer. As the laws of physics can usually be expressed in terms of other quantities (mass, concentration, partial pressure, etc.), a correspondence with the water content on a dry basis needs to be established each time.

Let us start by defining the "size" of each compartment. Among the various possibilities (sizes, volume, total mass, etc.), we choose the definition that is the easiest to link to transfer equations we are interested in, namely, the dry mass fraction:

$$\alpha_i = \frac{m_{si}}{m_s}, \quad i \in \{0, 1, 2\} \qquad [1.15]$$

where α_i (kg kg^{-1}) is the dry mass fraction contained in the compartment number "i", the mass m_{si} (kg) is the corresponding dry mass and m_s (kg) is the total dry mass of the grain. For these definitions, we chose the dry mass rather than the total mass, as it remains constant during drying.

As the sum of the masses of each compartment forms the total mass, this obviously yields:

$$\sum_{i=0}^{2} \alpha_i = \frac{\sum_{i=0}^{2} m_{si}}{m_s} = 1 \qquad [1.16]$$

With these definitions, we can write the dry water and total masses of each compartment in a useful form as follows:

$$m_{si} = \alpha_i m_s \quad [1.17]$$

$$m_{wi} = m_{si} X_i = \alpha_i m_s X_i \quad [1.18]$$

$$m_i = m_{si} + m_{wi} = \alpha_i m_s (1 + X_i) \quad [1.19]$$

Using equation [1.18], for example, we can write the water mass variation (m_{wi}) in the balance equations (equations [1.8] to [1.10]) in terms of the water content variation (X_i):

$$\frac{dm_{wi}}{dt} = \alpha_i m_s \frac{dX_i}{dt} \quad [1.20]$$

We now have to write the mass flows ($F_{i,i-1}$) as a function of water content (X_i). For this purpose, we assume that the liquid water transferred inside the grain is essentially diffusive and that this phenomenon can be explained by analogy with the first Fickian law. This law stipulates that the mass flux (mass transferred per unit time and unit area) is proportional to the gradient of concentration (variation in concentration per unit distance), with the coefficient of proportionality being precisely the diffusion coefficient. We adapt this formulation to our compartmental model in the following form:

$$\frac{F_{i,i-1}}{A_{i,i-1}} = D_w \frac{W_i - W_{i-1}}{l_{i,i-1}} \quad [1.21]$$

In this formula, $A_{i,i-1}$ (m^2) is the area of the surface that separates compartments i and $i-1$, $l_{i,i-1}$ (m) is the average or "effective" diffusion distance that takes into account the shape of the compartments, D_w ($m^2 s^{-1}$) is the coefficient of water diffusion in the grain and W_i (kg m^{-3}) is the water concentration (mass of water per unit volume).

To obtain a consistent description on the basis of the chosen state variables (water contents), concentrations should be expressed as a function of these variables.

Assuming that the dry mass is uniformly distributed inside the grain, the volume of each compartment V_i (m^3) is proportional to the dry mass fraction (α_i):

$$V_i = \alpha_i V \quad [1.22]$$

where V (m^3) is the total volume of grain. We can now express W_i as follows:

$$W_i = \frac{m_{wi}}{V_i} = \frac{\alpha_i m_s X_i}{\alpha_i V} = \rho_s X_i \quad [1.23]$$

where $\rho_s = \frac{m_s}{V}$ (kg m^{-3}) is the density of dry grain. The combination of the above equations yields:

$$F_{i,i-1} = \frac{A_{i,i-1} D_w \rho_s}{l_{i,i-1}} (X_i - X_{i-1}) \quad [1.24]$$

A specific case remains to be addressed: water vapor transfer from the external compartment to the ambient air (F_{0a}). The gas phase transfers in the vicinity of a solid–gas interface are usually described by means of a transfer coefficient k_{0a} (m s^{-1}) that takes into account the shape of the solid, the flow velocity near the interface, the properties of the gas, etc.:

$$\frac{F_{0a}}{A_{0a}} = k_{0a}(W_{0v} - W_{av}) \quad [1.25]$$

Here, the concentrations refer to water in the gaseous state (vapor). The concentration of water vapor should therefore be linked to the product level (W_{0v}) and to the liquid water content (X_0). The partial pressure of the water vapor in thermodynamic equilibrium with the product p_{ov} (Pa) is given by:

$$p_{ov} = a_w(X_0)\, p_{vsat}(T_0) \quad [1.26]$$

Water activity (a_w) is a dimensionless quantity ranging between 0 and 1 that expresses the "availability" of water related to a product: a value of 1 means totally free water, whose partial pressure is that of the pure body (p_{vsat}), whereas a value of 0 corresponds to total bound water with zero partial pressure.

Among these two extremes, water activity depends on the water content in a complex manner, which depends on the product composition and structure. In practice, it must therefore be experimentally determined for each product and possibly modeled by a more or less empirical formula. We will therefore assume that this relation is known for our corn grain.

Moreover, the saturated vapor pressure (p_{sat}) strongly depends on the local temperature (T_0), which is well known, tabulated and modeled in various physics and chemical engineering books.

If we consider that water vapor is an ideal gas, we readily have the relation between the concentration W_{0v} and the partial pressure p_{ov}:

$$W_{ov} = \frac{m_{ov}}{V_0} = p_{ov}\frac{M_w}{R_g T_0} = a_w(X_0)\, p_{vsat}(T_0)\frac{M_w}{R_g T_0} \quad [1.27]$$

In this equation, M_w (kg mol^{-1}) is the molar mass of water and R_g (J mol^{-1} K^{-1}) is the universal gas constant. Importantly, this relation is rigorously valid at thermodynamic equilibrium, but we intend to use it in a drying context and therefore out of equilibrium. We can assume that p_{ov} is the partial pressure in the immediate vicinity of the humid product, which is therefore in equilibrium with it, and that the resistance to vapor transfer inside the product is "absorbed" in the transfer coefficient k_{0a}, which is, by definition, an apparent or effective quantity. The thickness of the external compartment, in which water evaporation is assumed to occur, must therefore be "weak". In general, this type of semiqualitative reasoning is the price to pay for a relatively simple description of phenomena.

Let us now focus on the case of drying air. To express the water vapor concentration W_{av} as a function of its water content X_a, we will once more use the law of ideal gas for water vapor and dry air:

$$W_{av} = \frac{m_{av}}{V_a} = p_{av}\frac{M_w}{R_g T_a} \quad [1.28]$$

$$X_a = \frac{m_{av}}{m_a} = \frac{p_{av}}{p_a}\cdot\frac{M_w}{M_a} \quad [1.29]$$

where m_a (kg), p_a (Pa) and M_a (kg mol^{-1}) are the mass, the partial pressure and the equivalent molar mass of the dry air contained in a given air volume V_a around the grain, respectively. Considering that the sum of the partial pressures of water vapor and dry air is the atmospheric pressure, after some algebra, we can express the partial pressure of water as follows:

$$p_{av} = \frac{X_a}{\frac{M_w}{M_a} + X_a}\, p_{atm} \quad [1.30]$$

We are now able to combine the various fragments to rewrite the mass transfer model (equations [1.8]–[1.10]) using water contents (X_i) as state variables:

$$\alpha_0 m_s \frac{dX_0}{dt} = \frac{D_w A_{10}}{l_{10}}\rho_s(X_1 - X_0)$$

$$- \frac{k_{0a}A_{0a}M_w}{R_g}\left[a_w(X_0)\,\frac{p_{vsat}(T_0)}{T_0} - \frac{X_a}{\frac{M_w}{M_a}+X_a}\cdot\frac{p_{atm}}{T_a}\right] \quad [1.31]$$

$$\alpha_1 m_s\frac{dX_1}{dt} = \frac{D_w A_{21}}{l_{21}}\rho_s(X_2 - X_1) - \frac{D_w A_{10}}{l_{10}}\rho_s(X_1 - X_0) \quad [1.32]$$

$$\alpha_2 m_s\frac{dX_2}{dt} = -\frac{D_w A_{21}}{l_{21}}\rho_s(X_2 - X_1) \quad [1.33]$$

Our mass transfer model has the form of a system of three differential equations, corresponding to three state variables, which are the water contents of each compartment. Even if the result may seem scary, it is still possible to recognize the terms coming from the mass flows between compartments, as well as between the external compartment and the air. We will then need initial conditions (initial water content of the grain) and many parameters.

A special chapter will be dedicated to obtaining these parameters, as it is generally a problem in itself, but we may anticipate a difficulty related to the arbitrary definition of compartments. After division by m_s, factors of the form $\frac{D_w A_{i,i-1}}{l_{i,i-1}}\frac{\rho_s}{m_s}$ will appear, whose quantities $A_{i,i-1}$, representing the areas of separation between the compartments, and $l_{i,i-1}$, effective diffusion distances, are not well defined. The problem can be slightly simplified, resulting in only one unknown parameter for each factor of this type, for example, as follows:

$$\frac{1}{\tau_{i,i-1}} = \frac{D_w A_{i,i-1}}{l_{i,i-1}}\frac{\rho_s}{m_s} \quad [1.34]$$

This factor has the dimension of the inverse of time, leading to the idea of introducing constants $\tau_{i,i-1}$ (s) that can be interpreted as characteristic times of transfer between compartments. Notably, the initial hypotheses of a uniform diffusion coefficient everywhere and of the distribution of dry mass proportional to the volume of each compartment are not actually necessary: all variability inside the grain was "absorbed" at these apparent characteristic times:

$$\alpha_0\frac{dX_0}{dt} = \frac{1}{\tau_{10}}(X_1 - X_0) - \frac{k_{0a}A_{0a}M_w}{m_s R_g}\left[a_w(X_0)\,\frac{p_{vsat}(T_0)}{T_0} - \frac{X_a}{\frac{M_w}{M_a}+X_a}\cdot\frac{p_{atm}}{T_a}\right] \quad [1.35]$$

$$\alpha_1 \frac{dX_1}{dt} = \frac{1}{\tau_{21}}(X_2 - X_1) - \frac{1}{\tau_{10}}(X_1 - X_0) \quad [1.36]$$

$$\alpha_2 \frac{dX_2}{dt} = -\frac{1}{\tau_{21}}(X_2 - X_1) \quad [1.37]$$

Our model is now more readable, with the most complex part being related to the transfer between grain and air. The good news is that the quantities that appear in this context have a precise physical meaning and can therefore be determined by experiments or found in appropriate databases.

1.2.1.5. *Heat transfer equations*

Similar to mass transfers, we have several possibilities for the state variables of the thermal model, the most common being enthalpies or temperatures. We will choose the latter, which is the most common in the literature.

We must therefore start by expressing the enthalpy of each compartment i that appears in equations [1.11]–[1.13] as a function of its temperature T_i, which is assumed to be homogeneous. Enthalpy is an additive (extensive) quantity, defined with respect to a state of reference (solid for dry material, liquid for water) at a reference temperature:

$$H_i = H_{ref,i} + C_i(T_i - T_{ref}) \quad [1.38]$$

where C_i (J K^{-1}) is the heat capacity of the considered compartment. The enthalpy variation is due not only to the variation in temperature but also to heat capacity:

$$\frac{dH_i}{dt} = C_i \frac{dT_i}{dt} + \frac{dC_i}{dt}(T_i - T_{ref}) \quad [1.39]$$

Let us recall that for the needs of our model, the grain is composed of water and dry material. In our case, the variation in the heat capacity of a compartment is due to water mass variation, and the dry mass is constant according to our initial hypothesis:

$$C_i = m_{si}c_s + m_{wi}c_w \quad [1.40]$$

$$\frac{dC_i}{dt} = c_w \frac{dm_{wi}}{dt} \quad [1.41]$$

For the external compartment, for example, we obtain, by combining equations [1.8], [1.11], [1.39] and [1.41]:

$$c_w(F_{10} - F_{0a})\left(T_0 - T_{ref}\right) + C_0\frac{dT_0}{dt} = \phi_{a0} - \phi_{01} + F_{10}c_w\left(T_1 - T_{ref}\right) - F_{0a}c_w\left(T_0 - T_{ref}\right) - F_{0a}\Delta\widehat{H}_{vap} \quad [1.42]$$

or, after simplification,

$$C_0\frac{dT_0}{dt} = \phi_{a0} - \phi_{01} + F_{10}c_w(T_1 - T_0) - F_{0a}\Delta\widehat{H}_{vap} \quad [1.43]$$

Importantly, the obtained model is independent of the chosen reference temperature (T_{ref}) and reference enthalpy (H_{ref}). Furthermore, the terms in $F_{0a}c_wT_0$ no longer appear, which means that the *outgoing* mass flow at the temperature of the considered compartment does not change this temperature, as intuitively expected. However, it modifies the enthalpy by modifying the quantity of material. On the other hand, the *ingoing* flow modifies the temperature proportionally to the temperature gap with respect to the source compartment of the mass flow (term $F_{10}c_w(T_1 - T_0)$), and the change in state also has a role (term $F_{0a}\Delta\widehat{H}_{vap}$). The presented model is valid as long as mass flows are oriented from the inside to the outside of the grain ($F_{i,i-1} \geq 0$), as presented in Figure 1.2. If these flows are reversed, following humidity condensation at the surface, for example, the form of the heat transfer equations should change, as the "source" compartments for the mass flows would in this case be different.

Let us now formulate the conduction heat flows $\phi_{i,i+1}$. Our approach is similar to Fourier's law, according to which the heat flux (thermal energy transferred by conduction through a unit surface per unit time) is proportional to the temperature gradient, that is, to the temperature variation per unit distance. The coefficient of proportionality is the thermal conductivity of the medium λ (W m^{-1}K^{-1}):

$$\frac{\phi_{i,i+1}}{A_{i,i+1}} = \lambda\frac{T_i - T_{i+1}}{l_{i,i+1}} \quad [1.44]$$

Similar to mass transfer, $A_{i,i+1}$ is the area of the surface between neighboring compartments i and $i+1$, whereas $l_{i,i+1}$ is the average or effective distance that separates them and takes into account their form.

The heat exchange with the ambient air is specific, as it involves convective transfer in the air boundary layer surrounding the grain. This mechanism is usually represented by a transfer coefficient h_{a0} (W m^{-2}K^{-1}):

$$\frac{\phi_{a0}}{A_{a0}} = h_{a0}(T_a - T_0) \quad [1.45]$$

Using a similar approach for all of the compartments and assembling the various fragments, we can now rewrite the heat balance equations (equations [1.11] to [1.13]) as follows:

$$\begin{aligned}(m_{s0}c_s + m_{w0}c_w)\frac{dT_0}{dt} \\ = h_{a0}A_{a0}(T_a - T_0) - \lambda\frac{A_{01}}{l_{01}}(T_0 - T_1) \\ + \quad F_{10}c_w(T_1 - T_0) \quad - \quad F_{0a}\Delta\widehat{H}_{vap}\end{aligned} \quad [1.46]$$

$$\begin{aligned}(m_{s1}c_s + m_{w1}c_w)\frac{dT_1}{dt} \\ = \quad \lambda\frac{A_{01}}{l_{01}}(T_0 - T_1) - \lambda\frac{A_{12}}{l_{12}}(T_1 - T_2) \\ + \quad F_{21}c_w(T_2 - T_1)\end{aligned} \quad [1.47]$$

$$(m_{s2}c_s + m_{w2}c_w)\frac{dT_2}{dt} = \lambda\frac{A_{12}}{l_{12}}(T_1 - T_2) \quad [1.48]$$

These equations can be processed slightly further to highlight the water contents (X_i) chosen as state variables for the mass transfer model rather than the corresponding masses (m_{wi}).

For this, each equation must be divided by the constant quantity $m_s c_s$. This will lead to the appearance of coefficients of the form $\frac{\lambda A_{i,i+1}}{m_s c_s l_{i,i+1}}$ whose dimension is the reciprocal of time.

Following the same reasoning as for mass transfer, we will introduce new coefficients $\tau_{i,i+1}$ that can be seen as characteristic times of heat transfer:

$$\frac{1}{\tau_{i,i+1}} = \frac{\lambda\, A_{i,i+1}}{m_s c_s l_{i,i+1}} \quad [1.49]$$

With these notations, the thermal model becomes:

$$\alpha_0\left(1 + \frac{c_w}{c_s}X_0\right)\frac{dT_0}{dt} \quad [1.50]$$

$$= \frac{h_{a0}A_{a0}}{m_s c_s}(T_a - T_0) - \frac{1}{\tau_{01}}(T_0 - T_1) + \frac{F_{10}}{m_s}\frac{c_w}{c_s}(T_1 - T_0) - \frac{F_{0a}}{m_s}\frac{\Delta\widehat{H}_{vap}}{c_s}$$

$$\alpha_1\left(1 + \frac{c_w}{c_s}X_1\right)\frac{dT_1}{dt} = \frac{1}{\tau_{01}}(T_0 - T_1) - \frac{1}{\tau_{12}}(T_1 - T_2) + \frac{F_{21}}{m_s}\frac{c_w}{c_s}(T_2 - T_1) \quad [1.51]$$

Our efforts are completed. In the end, the complete dynamic model involves six coupled differential equations (equations [1.35]–[1.37] and [1.50]–[1.52]), corresponding to six chosen state variables: three water contents and three temperatures, one for each of the three compartments.

The balance equations were initially written for extensive quantities (water masses and enthalpies) and have finally led to intensive quantities (water contents and temperatures) and units of dry mass. Therefore, they apply to any amount of grain, provided that we know the characteristics of the air (water content, temperature, etc.) in contact with this grain. This situation is sometimes referred to as a "thin layer", as opposed to a "thick layer", where the properties of the air in contact with the following layers are modified by exchanges with the previous layers. A model for a thick layer can be obtained by considering several models of thin layer in series, completed by mass and enthalpy balances on the air that passes successively through them.

1.3. Biological model: example of brewing fermentation

Fermented beverages and food products are important in many cultures. The transformation by "food grade" microorganisms is seen not only as a means of stabilization by lowering the pH and producing inhibitor molecules (acetic acid, lactic acid, ethanol, etc.) for undesirable microorganisms but also as a means to change texture and taste (yogurt, cheese) or produce an effect on the consumer's mood (alcoholic beverages).

In addition to food processing, there are many other examples of biotechnological processes, such as in the pharmaceutical industry (antibiotics, etc.), chemical industry (organic acids, enzymes, etc.) and power industry (ethanol biofuel).

Among the wide variety of food biological transformation processes, we choose one relatively well-known process that is practiced on a large scale: alcoholic fermentation used in brewing.

In the beer manufacturing process, alcoholic fermentation is only one stage. However, it is important, as sugars present in beer wort, mainly maltose, are converted into ethanol and into carbon dioxide.

Ethanol contributes to the organoleptic perception of beer and to its consumption in a festive context, whereas carbon dioxide is partially reintroduced during bottling and is dissolved in the liquid, which consequently becomes sparkling and bubbly. During this stage, many aroma compounds are produced, which largely contribute to organoleptic perception by consumers and beer specificity (Renger et al. 1992; Sablayrolles and Ball 1995).

To structure our presentation, we will schematically decompose our model into a model of alcoholic fermentation and a model of aroma compound production. In reality, the two processes are obviously linked, as they occur simultaneously and are the result of the metabolic activity of the brewing yeast.

1.3.1. *Alcoholic fermentation model*

In practice, brewing fermentation takes place in a closed tank (Figure 1.3), known in this context as a fermenter or bioreactor. The size of the tank, which is made from an inert material, most often stainless steel, can vary widely: from several (or a dozen) liters at a private person or at a microbrewery to the size of a building in a large industrial brewery. The tank is partially filled with liquid fermentation wort while leaving a headspace filled with CO_2 released by fermentation.

Since alcoholic fermentation actively releases CO_2, in general, there is no mechanical stirring system; stirring is produced by CO_2 bubbles that rise to the surface. The process is anaerobic, there is no oxygen supply system and no other element is supplied during fermentation.

All needed ingredients are initially contained or added to the wort, including the initial quantity of yeast. The only mass transfer to the outside is the release of CO_2 in the gaseous form, accompanied by possible volatile compounds that it may drive.

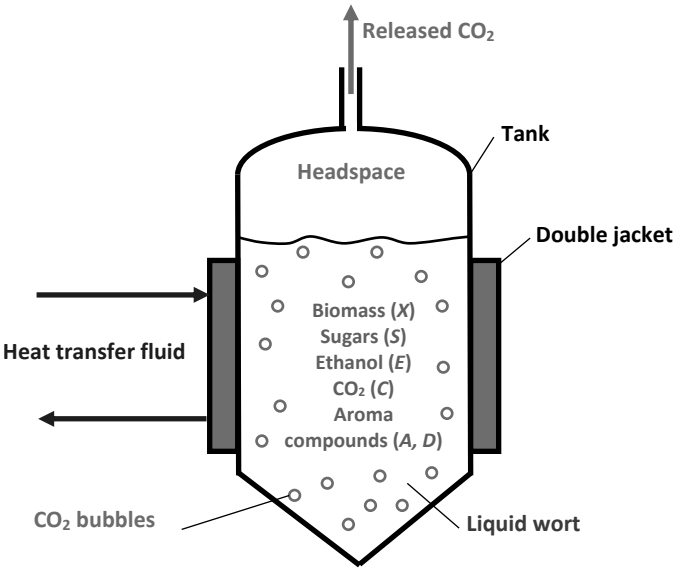


Figure 1.3. *Schematic representation of a brewing fermentation tank*

The most common beers, known as low fermentation or lager beers, are produced at temperatures of approximately 10°C, hence below the ambient temperature. Moreover, the transformation of sugars into ethanol and CO_2 is exothermal, which tends to significantly increase the wort temperature. Brewery fermenters therefore have a cooling system, most often consisting of a heat transfer fluid circulating in a double jacket. On the other hand, there is no heating system.

1.3.1.1. *How to choose the level of detail of the model*

In each modeling project, before starting to write equations, there are some choices to be made, which are essential for the complexity of the resulting model.

> QUESTION.– What level of detail should be considered when mapping the various concentrations inside the fermenter? Is 3D meshing of the tank necessary to solve the equations of reaction and flow of fluid, naturally stirred by gas bubbles that rise and are produced by these reactions? Should we add heat transfers that depend on flows and can contribute to them by natural convection? The biochemical reactions we are interested in are, in turn, strongly dependent on the temperature and local concentrations of various compounds. Moreover, yeasts may flocculate at some stages of fermentation and either fall to the bottom of the fermenter or rise to the surface.

Stated in this manner, the modeling problem is obviously complex, with strong coupling between biochemical reactions, heat transfers and mass flows. Before starting this journey, which appears to be very difficult and full of obstacles, let us take a step back with respect to the information we might realistically have access to and to the intended use of the model.

Concerning the available information, the measurements of the concentrations of the compounds of interest are conducted in the laboratory and their number is limited. In a project of reasonable size, it is generally impossible to conduct enough measurements to reach a temporal and spatial resolution that is sufficient to highlight potential inhomogeneities inside the fermenter and their change in time. Moreover, a very large number of gas bubbles appear and grow in a manner that is difficult to predict; detailed modeling of the flows they generate is an enormous challenge.

However, why would we need such a level of detail? Yeasts flocculate toward the end of fermentation when transformation is largely complete. The wort extracted after fermentation undergoes other operations (storage, filtration, transfer from one tank to another, etc.), during which it has enough time to mix. To provide results that can be used by the manufacturer and the consumer, our model will have to calculate average quantities.

Given all of these considerations, the effort invested in building a spatial model appears execessive for operational use in process engineering. In what follows, we will therefore consider that the content of the fermentation tank is well agitated and concentrations and temperature are uniform at any point. Our model will therefore describe spatially averaged phenomena and will not focus on flows, which is a significant simplification. For an advanced scientific study of mechanisms, the choices might have been different.

> QUESTION.– To what extent should we focus on the effects of CO_2 release? The CO_2 produced during fermentation is first dissolved in the wort before it reaches the saturation level, even a supersaturation, and is released under gaseous form. In this way, it may carry volatile molecules, particularly water, which would reduce the volume of liquid in the fermenter.

Modeling of gas–liquid transfers is common in process engineering. The best known example is the transfer of oxygen, which may be limiting in certain aerobic fermentations, where its consideration is therefore essential. For the case of CO_2 release, which we focus on, an analysis of the literature shows that most of the time the passage to the dissolved phase, then to the gaseous phase, is often ignored in alcoholic fermentation models, whether in the brewing or wine industry (Miller and

Block 2020; Lara et al. 2022); in these models, everything happens as if CO_2 was directly released in the form of gas. Some articles consider this phenomenon in further detail (Trelea et al. 2004) and conclude that, under usual brewing conditions, dissolved CO_2 represents less than 10% of the total CO_2 produced, whereas supersaturation is moderate (less than 5%) and disappears as soon as CO_2 production slows down by the end of fermentation.

CO_2 dissolution cannot be fully ignored, but it is not a major phenomenon. It will be integrated into our model in a simplified manner: our assumption is that CO_2 dissolves up to its level of saturation and is fully released afterward. This will spare us from the tedious determination of the volumetric gas–liquid transfer coefficient, which has a very small contribution to our model and is moreover dependent on agitation; however, agitation is in turn generated by the formed gas bubbles and is therefore dependent on the fermentation rate.

With respect to the possible water losses by evaporation carried by the released CO_2, a quick calculation may be reassuring. At a typical temperature of brewing fermentation of 10°C, the saturated water vapor pressure is approximately 1,230 Pa (Singh and Heldman 2013). According to the ideal gas law, this represents 9.4 g of water per m^3 of gas. Brewing fermentation typically releases approximately 20 m^3 of CO_2 per m^3 of wort, whose density is approximately 1,020 kg m^{-3} (Trelea et al. 2001a). Overall, this information means that even if the released CO_2 was saturated in water, the loss of water would represent less than 200 g for 1,000 kg of wort, which is less than 0.02%. Our model can therefore ignore water losses and consider the fermentation volume to be constant.

> QUESTION.– To what level of detail should heat transfers be described? The temperature in the fermenter is usually controlled by the circulation of a heat transfer fluid in a double jacket. This control must compensate the heat released by fermentation, which is highly variable according to the fermentation progress, as well as heat loss to the ambient air. Transfers are made by conduction in the tank walls and by convection in the heat transfer fluid of the double jacket, in the wort contained in the fermenter and in the air. Heat balances can also contain the powers consumed by the evaporation of the main components in the wort, such as water and ethanol. Without aiming toward 3D modeling of flows and transfers, a detailed model of all of these phenomena can rapidly prove to be relatively complex. However, is it really necessary?

Once again, the answer depends on the intended use of the model. If the objective is to precisely quantify various powers, limiting transfers as well as cooling requirements for temperature control, then the answer is affirmative.

This type of study was conducted for wine fermentation tanks (Colombié et al. 2007). In this book, we assume that the objective of the model is related mainly to the biochemical aspects of fermentation, such as the consumption of sugars and the production of ethanol and aroma compounds. The description of the thermal aspects will therefore be limited to a bare minimum.

As temperature has a very strong influence on these biochemical processes, we will explore fermentations conducted at various fixed temperatures, as well as temperatures variable in time. We will assume that the control system is correctly sized and able to achieve the desired temperature profiles; however, there are two limitations:

– An increase in temperature can be achieved only with the heat released by fermentation. This corresponds to the reality of most industrial brewing fermenters, where the control system can only cool the wort but cannot heat it. The maximal rate of temperature increase will therefore be proportional to the instantaneous fermentation rate.

– The rate of temperature decrease is also limited, either by the heat transfers to the double jacket or by the available cooling power.

We will therefore replace the development of a relatively complex thermal model with *constraints* on the achievable temperature profiles.

1.3.1.2. *Mass balance equations for the wort components of interest*

The wort resulted from the brewing process has an extremely complex composition, with hundreds of different molecules present in highly variable concentrations, from milligrams to hundreds of kilograms per cubic meter. Fermentation microorganisms contain hundreds of enzymes that may transform these compounds and produce new compounds. To obtain a model that is useful in process engineering, it is neither realistic nor necessary to try a complete description of the fermentation process. This approach might facilitate a better comprehension of yeast metabolism, but this is beyond the scope of our book. We will therefore consider only a limited number of compounds and reactions.

The driving force of any microbiological transformation is the living cell, which here is the brewing yeast. From the perspective of a chemical reaction, biomass acts here as a catalyst. More precisely, the enzymes produced by the cells catalyze the reactions, but for a given physiological state of the microorganism, the catalytic activity is generally considered proportional to the quantity of the present biomass (Bastin and Dochain 1990). We will therefore focus on the biomass growth.

From a quantitative perspective, the predominant reaction is the transformation of wort sugars that can be used by yeast (sugars known as "fermentable", mainly maltose) into ethanol and CO_2. Unsurprisingly, this reaction is practically always taken into account in the alcoholic fermentation models:

$$\underset{\text{maltose (S)}}{C_{12}H_{22}O_{11}} + \underset{\text{water}}{H_2O} \rightarrow 4\,\underset{\text{ethanol (E)}}{C_2H_6O} + 4\,\underset{\substack{\text{carbon}\\\text{dioxide (C)}}}{CO_2} \qquad [1.52]$$

Reaction [1.52] being predominant, sugar consumption and ethanol and CO_2 production are expected to be almost proportional to one another. This is not strictly true, as sugars are used in many other minority reactions, but experimental measurements confirm this hypothesis with good precision (Trelea et al. 2001a). Our model will therefore be able to describe, with a single reaction rate and adequate coefficients of proportionality, the consumption of sugars and the production of ethanol and CO_2.

Furthermore, under brewing conditions, the increase in biomass is practically proportional to the production of ethanol and CO_2. This does not result from a well-defined chemical reaction; it is simply an experimental fact. On the other hand, it is not valid under wine-making conditions, for example, where nitrogen limitation leads to a rapid halt in biomass growth, whereas alcohol fermentation [1.52] continues unhindered (Malherbe et al. 2004). However, in the case studied here, the proportionality between the increase and the advancement of alcoholic fermentation is reasonably verified, allowing the simplification of the model by defining a single reaction rate [1.52] and a coefficient of proportionality for biomass growth.

Using the formalism of reactive schemes (Bastin and Dochain 1990), these considerations can be summarized as follows:

$$S \xrightarrow{X} X + E + C \qquad [1.53]$$

where S represents the substrate (fermentable sugars), X represents the biomass (yeast), E represents the ethanol and C represents the CO_2 produced. The fact that a single reaction is considered means that we should specify a single rate, and the variations in all the compounds present in this reaction are proportional. Mentioning the biomass X above the arrow recalls its catalyst role, the rate being proportional to the quantity of biomass present.

The fact that a single substrate is involved, in this case, sugars, means that all of the others, such as the nitrogenous substrate (here, amino acids) or other microelements required for the growth of living cells, are present in excess; in other words, they are non-limiting.

We can now start writing the mass balances for the compounds mentioned in equation [1.53], according to the general formula [1.1]. For this, we must choose one among these compounds (S, X, E and C) that is known as the "reference" compound, whose consumption or production will define the reaction rate. From a mathematical perspective, this choice is perfectly arbitrary; any of them can complete the task. We will choose the CO_2 produced (C) as a reference compound for the reaction [1.53]; its production rate will therefore be, by convention, the rate of alcoholic fermentation. This choice is in fact justified by a practical consideration, the CO_2 produced being the most readily measurable online (Corrieu et al. 2000).

Finally, the balances of type [1.1] must be applied to additive (extensive) quantities, such as the mass (kg) or the amount of substance (mole). Alternatively, its use in the biotechnological field strongly favors the quantities expressed per unit volume of reaction medium. The wort volume being V, balances can be written as follows:

$$\frac{d(CV)}{dt} = r_C V \qquad [1.54]$$

$$\frac{d(XV)}{dt} = Y_{X/C}\, r_C V \qquad [1.55]$$

$$\frac{d(EV)}{dt} = Y_{E/C}\, r_C V \qquad [1.56]$$

$$\frac{d(SV)}{dt} = -Y_{S/C}\, r_C V \qquad [1.57]$$

In these equations, r_C is the reaction rate [1.53] with respect to the chosen reference compound, i.e. the CO_2 produced, expressed in kg of CO_2 per m^3 of wort and per hour. X, E and S are the mass concentrations of biomass, ethanol and fermentable sugars (kg m^{-3}), respectively; these compounds are uniquely present in the wort, and the masses per unit volume represent concentrations. On the other hand, the CO_2 produced is mostly released in the form of gas and only a small part is dissolved in the wort; C represents the mass of CO_2 produced per unit volume of wort and *not* a concentration, even though it is expressed in the same units (kg m^{-3}).

> NOTE ON THE NOTATION.– To keep the text light, we will denote by X, E, S, etc., the mass concentrations of the compounds of interest and sometimes the substances themselves. The exact meaning should be clear depending on the context.

The production of biomass and ethanol being assumed to be proportional to that of CO_2, and their production rate, is also written using r_C and adequate coefficients of proportionality ($Y_{X/C}$ and $Y_{E/C}$, equations [1.55] and [1.56]). In the context of biotechnologies, these coefficients of proportionality (in kg per kg of reference compound) are known as "yields".

> NOTE ON THE TERMINOLOGY.– Depending on the chosen reference compound, this name may be at odds with the usual meaning of yield; for example, such a coefficient may be above 1 if a compound was produced or consumed in a larger quantity than the reference compound. In the case of equation [1.53], we would tend to call the yield, for example, the mass of ethanol obtained from 1 kg of sugar ($Y_{E/S}$). To remain within this more restrictive definition of yield, we should have replaced, for example, $Y_{E/C} = \frac{Y_{E/S}}{Y_{C/S}}$. In what follows, we will continue to call "yield" the coefficients Y according to the use in biotechnologies, while keeping in mind that they are simple coefficients of proportionality between compounds produced or consumed in a reaction and not necessary yields in the economic sense.

Equation [1.57] expresses the consumption of fermentable sugars during alcoholic fermentation, still using the fermentation rate (r_C) and the corresponding coefficient of proportionality ($Y_{S/C}$). The convention we make here is to keep yields Y positive and indicate consumption by the sign "–" in the corresponding balance equation.

Finally, the volume of the fermentation medium (V) is constant; as discussed above, it cancels out in all equations [1.54]–[1.57]. We maintained it in this first writing of equations to highlight that the balances can be made only for extensive quantities (here, masses).

> NOTE ON THE VOLUME VARIATIONS.– If the volume was not constant, its variation would introduce additional terms, for example, $\frac{d(SV)}{dt} = V\frac{dS}{dt} + S\frac{dV}{dt}$. The balance equations written "directly" on concentrations, which can be encountered in many books and articles, are, in fact, shortcuts where the terms due to the volume variation passed to the right of the equality and have various names, for example, of dilution terms in the case of liquid addition in the reactor (Bastin and Dochain 1990).

Considering these notes, the mass balance equations can be slightly simplified and reorganized. The volume (V) cancels out since it is constant. Moreover, the biomass (X), ethanol (E) and residual sugars (S) can all be expressed as a function of

the chosen reference compound (C), as they vary in a proportional manner, and the yields $Y_{X/C}$, $Y_{E/C}$ and $Y_{S/C}$ are constant:

$$\frac{dC}{dt} = r_C \quad [1.58]$$

$$X = X_{ini} + Y_{X/C}\, C \quad [1.59]$$

$$E = Y_{E/C}\, C \quad [1.60]$$

$$S = S_{ini} - Y_{S/C}\, C \quad [1.61]$$

We consider here the zero initial conditions for the CO_2 and ethanol produced ($C_{ini} = 0$, $E_{ini} = 0$). Hence, the alcoholic fermentation model ultimately involves only a single independent state variable (C).

1.3.1.2. *Expression of the fermentation rate*

We will translate the generic formula [1.3] for the case of alcoholic fermentation, taking into account the major phenomena described in the literature: the driving role of the biomass (X), the limitation by the carbonaceous substrate (S), the inhibition by the ethanol produced (E) and the effect of temperature (T), which we intend to vary for the operation and optimization of the process:

$$r_C = r_{mCX}(T)\, \frac{S}{S_L + S}\, \frac{1}{1 + \left(\frac{E}{E_I}\right)^{n_I}}\, X \quad [1.62]$$

In this expression, r_{mCX} represents a specific maximal fermentation rate, in kg of CO_2 produced per kg of biomass present and per hour, in the absence of limitation and of inhibition. It is directly dependent on the physiology of the microorganism used, and for a given microorganism, it is strongly dependent on temperature. Given that living cells are the seat of catalytic reactions, as shown by [1.53], the production rate of CO_2 per unit volume of medium (r_C) is proportional to the concentration of biomass (X).

We prefer writing equation [1.62] in a slightly different form to avoid the "heterogeneous" nature of the specific rate r_{mCX}. Indeed, this method mixes biomass units and CO_2 units; however, in the literature, these two quantities are expressed with a wide range of units, for example, kilograms or cubic meters of gaseous CO_2 at a certain pressure and temperature, kilograms of humid biomass, dry biomass or number of cells, measured using a certain method, etc. This is why it is difficult to find numerical values for the specific rate, and these are highly dependent on the

CO_2 and biomass measurement protocols. Expressing the biomass (X) as a function of CO_2 (C) from equation [1.59], we obtain:

$$r_C = r_{mC}(T)\ \frac{S}{S_L + S}\ \frac{1}{1 + \left(\frac{E}{E_I}\right)^{n_I}}\left(C + \frac{X_{ini}}{Y_{X/C}}\right) \qquad [1.63]$$

The new specific rate (r_{mC}) now contains only time units (h^{-1}). It is independent of CO_2 units that cancel out between the production rate (r_C) and the quantity produced (C), as well as biomass units that are no longer involved. The only link between the quantities of biomass and CO_2 produced is explicitly "located" in the corresponding yield ($Y_{X/C}$).

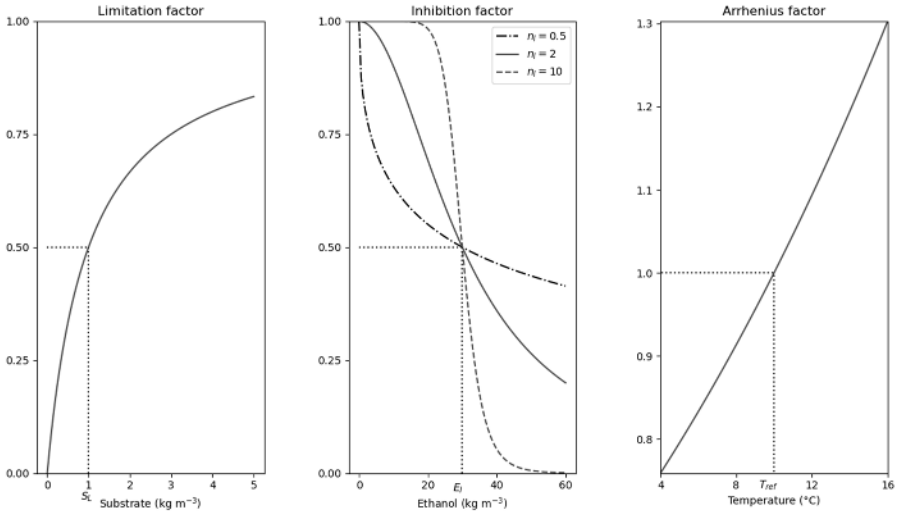
The factor $\frac{S}{S_L+S}$, ranging between 0 and 1 and traditionally referred to as Monod's law or equation, represents the limitation imposed by the substrate (Figure 1.4(A)). The constant S_L, known as the saturation constant or Monod constant, depends on the substrate and the considered microorganism.

For low concentrations in the substrate ($S \ll S_L$), the denominator is practically constant, and the rate is proportional to the concentration in the substrate. For high concentrations ($S \gg S_L$), this factor is practically 1 and the rate is not limited; the metabolic paths are saturated, and the rate no longer depends on the concentration in the substrate. For $S = S_L$, the factor is 1/2; S_L therefore represents the concentration in the substrate for which the reaction rate is half of its maximal value, all being equal.

> NOTE ON MONOD EQUATION.– Although initially empirical (Monod 1942), the Monod equation is almost universally used to describe the substrate limitation of biological reactions. A qualitative justification is that biological reactions are catalyzed by enzymes, and the Michaelis–Menten equation for the rate of enzymatic reactions is formally similar to that of Monod but has a theoretical basis.

The factor $\frac{1}{1+(E/E_I)^{n_I}}$ also ranges between 0 and 1 and represents the effect of the inhibiting product, in this case, ethanol (Figure 1.4(B)). For $E = 0$, this factor is 1 and decreases with increasing inhibitor concentration, tending to 0 for high concentrations ($E \gg E_I$). The form of this decrease depends on the exponent n_I; for low values, it is gradual, whereas for $n_I \gg 1$, the inhibition is abrupt around the threshold concentration E_I (Figure 1.4(B)). For $E = E_I$, the inhibition factor is 1/2; E_I is therefore the concentration of the inhibitor product for which the fermentation rate is half of its maximal value, all being equal.

NOTE ON THE INHIBITION EQUATION.– In contrast to the limitations of substrates, a wide range of inhibition equations exist (Claret et al. 1993). They are more or less empirical, but their shape is generally similar to that in Figure 1.4(B). Some of these equations involve a concentration of the inhibiting compound known as "total", beyond which the reaction rate is zero.



(A) (B) (C)

Figure 1.4. *Effect of various factors on the fermentation rate. (A) Limitation by the substrate for S_L = 1 kg m^{-3}. (B) Inhibition by the product for E_I = 30 kg m^{-3}. (C) Effect of temperature for T_{ref} = 10°C and E_{aC} = 30 kJ mol^{-1}. For a color version of this figure, see www.iste.co.uk/trystram/bioprocesses.zip*

The expression of the rate [1.62] is complete, provided that the temperature effect is specified. Our choice here is a formula inspired by the Arrhenius law:

$$r_{mC}(T) = r_{refC} \exp\left(-\frac{E_{aC}}{R_g}\left(\frac{1}{T+T_{abs}} - \frac{1}{T_{ref}+T_{abs}}\right)\right) \qquad [1.64]$$

With this formulation, the preexponential factor r_{refC} can be readily interpreted: it represents the maximal specific reaction rate at the reference temperature $r_{mC}(T_{ref})$. The reference temperature T_{ref} is arbitrarily fixed in the range of interest, which is here the range of usual brewing fermentation temperatures. E_{aC} is

known as the activation energy and determines the sensitivity of the rate with respect to the temperature (Figure 1.4(C)): the higher this energy is, the greater the variation in the rate with temperature. R_g is the universal gas constant, and T_{abs} = 273.15 K is the constant of conversion of the temperature expressed in degrees Celsius and the absolute temperature.

> NOTE ON THE ARRHENIUS EQUATION.– In the narrow range of temperatures we are interested in, equation [1.64] represents a practically affine dependence, as shown in Figure 1.4(C). A much simpler formula of the type $r_{mC}(T) = r_{refC} + a(T - T_{ref})$ could also have been employed. Although apparently very complex, equation [1.64] is in fact not more suitable for a wider range of temperatures than an affine equation. In reality, the fermentation rate becomes zero at approximately 1°C or 2°C as well as beyond a maximal temperature that the yeast can tolerate, which is approximately 50°C. There is no actual justification for choosing an Arrhenius-type formula in this case. This is rather a common practice in process engineering.

1.3.1.3. *Heat balance equation for wort*

As previously mentioned (section 1.3.1.1), the wort temperature is controlled by the double jacket of the reactor (Figure 1.3). The temperature control system is assumed to be correctly sized but is designed only for cooling the wort, which is the case in industrial fermenters. Indeed, since the reaction [1.52] is exothermal and fermentation takes place at approximately 10°C, it is not usually necessary to heat the reaction medium.

With these considerations, the enthalpy balance for the fermenter can be written as follows:

$$\frac{d(\rho V c T)}{dt} = P_{ferm} - P_{reg} + P_{losses} \qquad [1.65]$$

where ρ (kg m^{-3}) is the density of wort and where c (J kg^{-1} K^{-1}) is its specific heat capacity. For a more intuitive description of the heat balance, we conventionally consider all powers P (W) in equation [1.65] positive and use the sign "–" to indicate the contributions to the temperature decrease.

The first term (P_{ferm}) in the balance equation is related to the enthalpy of the reaction [1.52]. The data that are most widely available in the literature (e.g. Williams 1982), including for more complex sugars, are given in moles of hexose ($C_6H_{12}O_6$). We can then relate the power released by fermentation to the sugar consumption rate [1.57]:

$$P_{ferm} = \frac{d(SV)}{dt} \cdot \frac{\Delta H_{hex}}{M_{hex}} = Y_{S/C}\, r_C V \cdot \frac{-\Delta H_{hex}}{M_{hex}} \quad \geq 0 \qquad [1.66]$$

where $\Delta H_{hex} < 0$ (J mol^{-1}) is the variation in enthalpy associated with the exothermal reaction [1.52] expressed in moles of hexose and where M_{hex} (kg mol^{-1}) is the corresponding molar mass. Attention should be given to time units; the common practice for "slow" fermentation kinetics [1.57] is rather to employ hours or days, whereas for powers in watt [1.65], conversion into seconds should not be forgotten.

Heat losses (P_{losses}) are related to the difference in temperature between the ambient medium (T_a) and the fermentation medium (T):

$$P_{losses} = hA(T_a - T) \quad \geq 0 \qquad [1.67]$$

where A is the surface of contact between the tank and the ambient air and h is the equivalent transfer coefficient. In general, the term P_{losses} is positive, as $T_a \approx 20°C$ and $T \approx 10°C$, even though this might be readily reversed in certain specific cases.

Considering the writing of equation [1.65] and our sign convention, the fact that temperature control cannot cool the fermenter is expressed as follows:

$$P_{reg} \quad \geq 0 \qquad [1.68]$$

We can now estimate the maximal rate of wort temperature increase in the "worst case". The worst case, from the point of view of the increase rate, is when $T \approx T_a$ and losses do not contribute to heating ($P_{losses} \approx 0$); the "best" that the control system can do in this case is not cool ($P_{reg} = 0$). A combination of [1.65] and [1.66] leads to:

$$\frac{dT}{dt} \leq \frac{Y_{S/C}}{\rho c} \cdot \frac{-\Delta H_{hex}}{M_{hex}} \cdot r_C \qquad [1.69]$$

The temperature increase rate (dT/dt) is limited by the instantaneous fermentation rate (r_C) and is independent of the size of the fermenter (V), as might be expected.

In practice, there is also a limit on the maximal rate of temperature decrease. This limit depends in principle not only on the available cooling power but also on losses and hence on the ambient temperature (equation [1.67]) and the current fermentation rate. As describing in detail the thermal model or the control system is

beyond our scope, we propose integrating the cooling rate constraint in a more direct form:

$$-r_T \leq \frac{dT}{dt} \qquad [1.70]$$

We therefore choose a constant limit r_T that can be reached in all of the cases of practical interest by the temperature control system.

1.3.2. *Aroma compounds production model*

We intend to use the developed model, among other purposes, to predict the production of aroma compounds important for the organoleptic perception of beer. This will allow us to control the fermentation process as a function of the targets for the chosen aroma compounds. This requires including the production of these compounds in the model. Once more, the question of the level of detail of the developed model arises.

1.3.2.1. *How to choose the level of detail of the model of aroma compounds*

Beer is a very complex product, with potentially several hundred compounds present in the wort, consumed and/or produced during alcoholic fermentation.

> QUESTION.– How many aroma compounds should we include in our model, and how should we choose them?

An analysis of the literature shows that most authors focus on two large families of chemical compounds that confer a specific flavor to beer: higher alcohols and esters (e.g. Renger et al. 1992). These products in concentrations above their perception threshold in the beer are considered important, thoroughly monitored and sometimes modeled (Gee and Ramirez 1994). Their number is typically on the order of a dozen.

Apart from higher alcohols and esters, which are the desired compounds, brewers also carefully monitor certain vicinal diketones, particularly diacetyl, whose perception threshold is very low and is considered a defect by many consumers who perceive a buttery flavor (Wainwright 1973).

The evolution of diacetyl during fermentation, including a phase of production followed by reduction into a sensory-neutral compound, is quite different from that of higher alcohols and esters.

QUESTION.– Aroma compounds are by definition volatile; should their losses be modeled as being carried by the released CO_2?

The issue of potential losses of volatile molecules is quite difficult. This clearly depends on the volatility of the considered molecule in the brewery wort and at the fermentation temperature. Some studies (e.g. Titica et al. 2000) address this problem by inserting a cold trap that retains the potential molecules driven by the flow of CO_2, but this solution is only applicable in the laboratory; this type of trap does not generally exist at the production site. There is no extensive literature on this subject, but some studies conducted on wine fermentation (e.g. Morakul et al. 2011) indicate losses of up to 70% of the quantity produced for ethyl hexanoate, the most volatile molecule studied, and fermentation conducted at 30°C, the highest temperature considered. For other less volatile molecules and at lower temperatures, losses are significantly lower, for example, less than 10% for ethyl acetate at 20°C.

These considerations show that the matter of volatile molecules must be considered on a case-by-case basis. Overall, brewing fermentation occurs at lower temperatures than in winemaking and the quantity of CO_2 released per unit wort volume is approximately half, which results in lower losses. However, losses may be significant for the most volatile molecules.

As this book is intended for educational purposes, we wish to limit the complexity of the model while maintaining a reasonable representativity of the real process to draw relevant conclusions. Our choice is therefore the following:

– modeling the production of a single desired aroma compound:

- produced in a relatively high quantity, far above the perception threshold in beer,

- was representative for most desired compounds described in the literature by its production dynamics and its sensitivity to temperature,

- was moderately volatile, so that its losses during fermentation can be ignored;

– modeling the production and reduction of an unintended compound in the beer, a defect marker.

For the desired compound, our choice was ethyl acetate. It is produced at relatively high concentrations (several dozen g m^{-3}), which can vary from simple to triple depending on the fermentation temperature (Titica et al. 2000). Moreover, owing to its sufficiently low volatility, even under winemaking conditions (30°C), losses remain below 15% (Morakul et al. 2011). Under brewery conditions (approximately 10°C) and with half of the CO_2 produced, associated losses should

be significantly lower. A more realistic model should include several compounds and model the losses of the most volatile compounds or assume that only the quantity remaining in the wort, that is, the *difference* between production and losses, is modeled.

With respect to the unintended compound, the choice with respect to the literature is relatively simple: it is the so-called "total" diacetyl, that is, including its precursor α-acetolactate (Trelea et al. 2002). In fact, the usual analytic methods do not differentiate between diacetyl and its precursor. Moreover, what matters for the final quality of beer is the absence of α-acetolactate that can transform into diacetyl during storage.

1.3.2.2. *Model for the production of a desired aroma compound*

After studying the literature and serious reflection, we have chosen the ethyl acetate to represent the aroma compounds produced during alcoholic fermentation and which are important for the organoleptic quality of beer. A more complete study would undoubtedly include more compounds, particularly esters and higher alcohols.

The references and the previous discussion have also shown that under usual conditions of brewing fermentation, we can ignore ethyl acetate losses driven by the released CO_2. For more volatile compounds or at higher temperatures, losses should be taken into account. This difficulty can be addressed by considering that the developed model directly represents the difference between the produced and lost compounds.

Most of the existing models (Titica et al. 2000; Mouret et al. 2015) establish a link between the production of aroma compounds and the "main" fermentation kinetics [1.53], represented in our model by the specific rate of production of CO_2 (r_C). Moreover, the formation of an ethyl ester is related to the presence of ethanol (E) as a reactant. These considerations can be schematically summarized in the following form:

$$S + E \xrightarrow{X} A \qquad [1.71]$$

Here, A represents ethyl acetate. The presence of the carbonaceous substrate (S) on the left of the arrow and of the biomass (X) indicates that the reaction is linked to the main yeast metabolism. The balance equation for ethyl acetate can be written as follows:

$$\frac{d(AV)}{dt} = k_A(T)\, E\, r_C V \qquad [1.72]$$

Here, k_A is the production rate, which, according to the literature, is highly dependent on the temperature. We also propose a dependence inspired by the Arrhenius law:

$$k_A(T) = k_{refA} \exp\left(-\frac{E_{aA}}{R_g}\left(\frac{1}{T+T_{abs}} - \frac{1}{T_{ref}+T_{abs}}\right)\right) \quad [1.73]$$

Considering the studied narrow range of temperatures, the dependence expressed by equation [1.73] is practically affine (Figure 1.4(C)), and a similar note to that related to equation [1.64] can be made on the arbitrary character of this formula.

1.3.2.3. *Model for the production of an aroma compound as a defect marker*

As previously discussed, "total" diacetyl (D), including its α-acetolactate precursor, is the main marker of beer flavor defect. It is produced in the early stages of fermentation, and its concentration subsequently decreases because of the reduction of 2,3-butanediol (B), which is neutral from an aroma point of view.

The reaction scheme is as follows:

$$S \xrightarrow{X} D \quad [1.74]$$

$$D \rightarrow B \quad [1.75]$$

We propose the following model to describe the diacetyl concentration:

$$\frac{d(DV)}{dt} = Y_{D/C}(C)\, r_C V - k_D(T)\, DV \quad [1.76]$$

The first term of this equation corresponds to the reaction [1.74] and describes the production of diacetyl, related, as previously described, to the main fermentation kinetics given by the rate of production of CO_2 (r_C), and is considered representative of the general metabolism of the yeast. The production yield ($Y_{D/C}$, in g kg^{-1}) is not constant but decreases with fermentation progress, as observed experimentally. The process of fermentation is represented here by the production of CO_2, which is chosen as a reference compound (C) in the reaction [1.53]. The decrease in production yield is described by the affine formula:

$$Y_{D/C}(C) = \begin{cases} Y_{mD/C}\left(1 - \dfrac{C}{C_D}\right) & \text{if} \quad C < C_D \\ 0 & \text{if} \quad C \geq C_D \end{cases} \quad [1.77]$$

In this formula, $Y_{mD/C}$ is the maximal yield of diacetyl, which is obtained at the beginning of fermentation ($C = 0$). This yield then decreases and becomes zero beyond a certain advancement of alcoholic fermentation ($C \geq C_D$).

The second term of the balance equation [1.76] corresponds to the reaction [1.75] of the reduction of diacetyl to 2,3-butanediol (B). This reaction is assumed to be of first order with respect to the diacetyl concentration, and its rate increases with temperature. This is well known by brewers, who often delay the final cooling of beer at the end of fermentation until a sufficiently low diacetyl concentration is obtained. Another practice that uses the acceleration of reduction with temperature is short and intense heating by means of a heat exchanger. The dependence of the reduction rate on temperature is given by a formula similar to the previous one:

$$k_D(T) = k_{refD} \exp\left(-\frac{E_{aD}}{R_g}\left(\frac{1}{T + T_{abs}} - \frac{1}{T_{ref} + T_{abs}}\right)\right) \quad [1.78]$$

In accordance with reaction [1.75], we could complete the model with a balance equation for 2,3-butanediol (B). However, this compound is not of special interest to us, as its aroma impact is negligible at the concentrations encountered in fermentation during brewing. To avoid unnecessary overload of the model, the description of 2,3-butanediol will be ignored, as well as this balance equation.

1.4. Conclusion on the writing models

There are many books and articles on modeling in which model equations are seemingly emerging from nowhere. Readers might consider themselves lucky if a list of hypotheses is present and the meaning of various terms of equations is described in detail. However, details on how the simplifying hypotheses were formulated and how the equations were written are rarely provided. In front of a blank page, a beginner in the modeling domain might be disoriented, asking themselves: where should I start and where should I stop?

The objective of this chapter is to illustrate, by means of two examples, the type of questions to be considered when writing a model:

– What will the model be used for? This is the key question, which will guide all other choices.

– What aspects should be taken into account?

- Those related to the very objective of the model. For example, if the objective is to study the metabolic network of a cell, it will be essential to consider a

very large number of metabolic paths, reactions and regulations, undoubtedly dozens or even hundreds, despite the complications generated.

- Those that, on the basis of experience or according to the literature, are known to be important phenomena. For example, during winemaking fermentation, the nitrogen metabolism of the yeast is not especially interesting in itself, but nitrogen is limiting and plays an essential role in the production of aroma compounds of interest; therefore, it should be considered.

– What aspects can be a priori ignored?

- Those that are known to have, according to previous studies, minimal effect, in any case with respect to the intended use of the model. For example, beer wort is sufficiently rich in amino acids so that nitrogen is not limiting. Even though its metabolism is essential for the production of certain aroma compounds, it is not necessary to take it explicitly into account.

- Those whose consideration represents an excessive complication with respect to the proposed objective. One typical example is model spatialization; it can be completely ignored, for example, by assuming a homogeneous reactor, or partially ignored, by building a compartmental model by using some symmetries to develop 1D or 2D models before attempting, if needed, the actual 3D.

As noted throughout this chapter, many choices are relatively arbitrary, such as the number of compartments or the exact form of the equation of temperature dependence. On the other hand, other factors are essential, such as the reactant concentration in the expression of the rate of a chemical reaction. Identifying what is essential and what "could also be done in another way" is sometimes difficult and requires a certain experience.

It is therefore not surprising that a wide variety of models can be found in the literature for seemingly similar phenomena and processes. We should not be intimidated by the apparent complexity of certain equations. The terms and factors present in these equations probably have their well-defined role. If the author did not make the effort to specify it or to thoroughly formulate it, it is up to the reader to do so, having in mind the same questions:

– What can this term or factor be used for?

– Do I really need it for *my* model?

– Could the same thing be expressed in a simpler or clearer manner?

In any case, the resulting model reflects the comprehension of phenomena by the modeling practitioner. Collaboration with specialists in the field is therefore

essential (Figure 1.5). The category of specialists should include not only subject-matter expert researchers but also manufacturers, engineers, operators, craftsmen, etc., who have long-term experience and a good intuitive comprehension of the modeled process. These specialists may often find it difficult to express what they know in a way that can be used to build the model. This is referred to as knowledge elicitation, and it is a profession in itself.

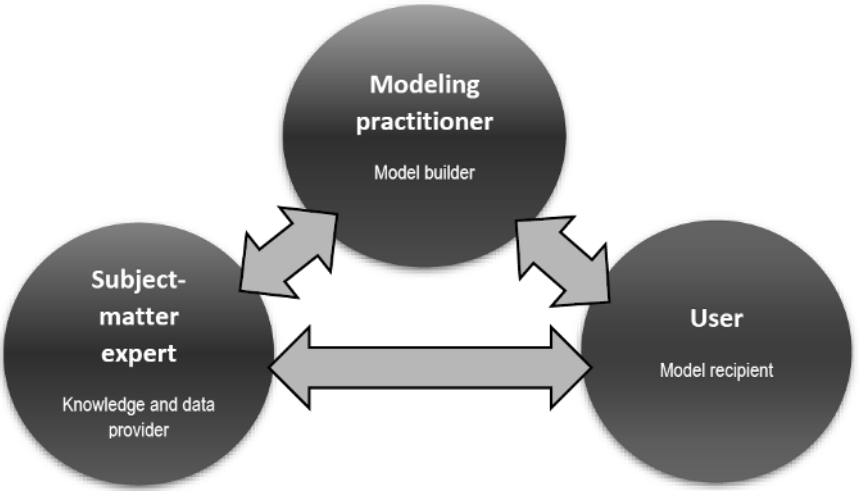


Figure 1.5. *Schematic representation of a modeling process*

The dialog with future users of the model is also important. Indeed, in addition to the obvious purpose for which the model was built, these have a certain number of implicit expectations, and it is important to ensure that they have been taken into account. For example:

– Does the validity range of the model include all of the conditions in which the users intend to operate it? This would avoid consequent disappointments.

– Is the model structured in a sufficiently clear manner, and is the meaning of parameters and variables well defined? This is important for at least two reasons:

- A "client" who thinks that they have a good comprehension of the model, at least in broad terms, would trust the model and tend to use it. This was normally the main objective of the modeling project.

- A model is an object that should be adapted, extended and improved; otherwise, it may become obsolete. Clarity is essential for having easy and robust

future interventions on the model without undermining it. The ease of maintenance is a quality criterion of the model.

– Is model simulation sufficiently easy to make its use sufficiently attractive? This includes an easy-to-access interface and development supported by current software, maintained in the long term and well managed by the model recipient. Conversely, a model developed in an exotic computing environment has more chances to be discarded.

– Is model simulation sufficiently rapid to make its use attractive? If the user wants to conduct several tests, for example, for model-based sizing, but each simulation takes several days (which is quite common for a spatialized model), they may be discouraged and try to find another solution.

The modeling practitioner, as a model builder, is therefore a link in the chain: they understand both the specialist in the process or phenomenon being studied and the model recipient (Figure 1.5). Each role represented in this figure may be assigned to one or more persons and, on the other hand, it is not unusual for one person to play several roles.

Figure 1.5 shows that the modeling process is in fact circular. A model is never completed; it may be reviewed at any time, called into question and adapted for new uses. In other words, it is a living object.

Throughout this chapter, we described how the model equations are written. However, it is too early to perform numerical calculations, as many values are missing. We will now approach this aspect.