



Research note

Mass transfer of CO₂ in MAP systems: Advances for non-respiring foodsR. Simpson^{a,*}, C. Acevedo^b, S. Almonacid^a^a Universidad Técnica Federico Santa María, Departamento de Procesos Químicos Biotecnológicos y Ambientales, Av. España 1680, Valparaíso, Chile^b Universidad de Santiago de Chile (USACH), Departamento de Ciencia y Tecnología de Alimentos, Facultad Tecnológica, Avenida Ecuador 3769, Santiago, Chile

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ABSTRACT

The use of technologies that modify food environment for preservation purposes has been extensively studied in the past two decades. Even though technological advances have been made, most of the modified atmosphere packaging (MAP) development has been empirical.

In this short communication, a revision of general equations of mass transfer and criteria to design MAP systems was carried out. Mathematical relationships and models to evaluate the flux of CO₂ for the packaging of non-respiring foods are discussed. Data to predict CO₂ uptake for the food, such as solubility and diffusion in refrigerated MAP systems are given.

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1. Introduction

The concept behind the packaging of food in modified atmospheres (MAP) is replacing the air surrounding the food, with a mixture of gases in a different proportion to the air (Parry, 1995). Mixtures of CO₂/O₂/N₂ are generally used, but other non-toxic gases can also be used.

Carbon dioxide (CO₂) is the most important gas in MAP systems, since it is non-toxic and has a bacteriostatic effect (not bactericide, neither for anaerobics nor for aerobics). The higher the CO₂ concentration is the lower is microorganism's respiration and growth rate. Although the bacteriostatic mechanism of this gas on microorganisms is not entirely clarified, there is a widely accepted theory. The decrease in respiratory rate of microorganisms is caused by the dissolution of CO₂, modifying the pH of food, and distancing them from their optimum growth rate (Farber, 1991). In addition, the lower the temperature, the greater the inhibitory effect of carbon dioxide, probably due to increased CO₂ solubility at low temperatures (Ogrydziak and Brown, 1982).

Unlike controlled atmosphere, the concentration and quantity of CO₂ that is in contact with the food varies over time (Simpson et al., 2001a). There are several mechanisms involved in the change in CO₂ concentration, among which the permeability of the packaging material and CO₂ absorption by the food are the most important. The literature on the use of MAP systems for non-respiring foods is plentiful (Jakobsen and Bertelsen 2002; Sivertsvik et al., 2002), but research in which engineering design criteria are used

is relatively scarce. At this respect, mathematical models based on mass transfer phenomena are quantitative tools that when applied to non-respiring foods allow for design and process optimization, permitting the generation of high quality products, and diminishing the time and cost of laboratory tests (Simpson and Carevic, 2004).

In this article, we would like to present and discuss the mathematical relationships and models involved in mass transfer to predict the behavior of CO₂ in MAP systems for non-respiring foods.

2. Mass balance of CO₂ in the package headspace

When a modified atmosphere is applied in the package headspace, the initial gas concentration will change during storage. The headspace atmosphere composition is dynamic and changes occur mainly due to food metabolism, microbial respiration, gas solubility and permeability of the packaging material. Food and microbial metabolism are responsible for consumption of oxygen and CO₂ production. For non-respiring foods, the oxygen uptake is not considered; nevertheless, it is known that muscle tissue can respire in the first few days after slaughter, thereafter decreasing with time (Jakobsen and Bertelsen, 2002). The microbial activity can affect the composition of CO₂, because they consume oxygen and produce CO₂; however, this is only significant when it has reached the end of shelf life and deterioration is evident (Pfeiffer and Menner, 1999), so it is not considered a factor in the design of a MAP system (Simpson et al., 2001a).

Several studies have attempted to model the kinetics of CO₂ concentration in the headspace of the package. These models are based on a simple mass balance, which is applicable to non-respiring

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Nomenclature

A	package area	t	time
B_i	Biot number	V	volume of headspace
C	concentration	v	partial volume
D	diffusivity	W	mass of food
D_{EFF}	effective diffusivity	X	biomass concentration
d	diameter	x	distance in the X-axis
Gr	Grashof number	$Y_{CO_2/X}$	yield of carbon dioxide and biomass
Gr_m	mass Grashof number	φ	package permeability
H	Henry's constant	Ψ	package transmission
J	flux	μ	specific growth rate
k_C	convective coefficient (concentration gradient)		
k_P	convective coefficient (pressure gradient)		
L	thickness of packaging material	Suffixes	
n	number of moles	AIR	air
Nu	Nusselt number	CO ₂	carbon dioxide
P	pressure	EQ	equilibrium
p	partial pressure	FOOD	food
Pr	Prandtl number	H ₂ O	water
R	ideal gas constant	HS	headspace
S	solubility	O	initially condition (at time zero)
Sc	Schmidt number	O ₂	oxygen
Sh	Sherwood number	Pack	package
T	temperature (absolute temperature in Eqs. (2), (3), (19), (20), (21), and (22))		

foods and also to vegetables (Lee et al., 1991; Morales-Castro et al., 1994; Fishman et al., 1995; Talasila and Cameron 1997; Lakakul et al., 1999; Simpson et al., 2001a,b, 2003, 2007; Rotabakk et al., 2007)

$$\left. \frac{\delta n_{CO_2}}{\delta t} \right|_{HS} = \left. \frac{\delta n_{CO_2}}{\delta t} \right|_{PACK} = \left. \frac{\delta n_{CO_2}}{\delta t} \right|_{FOOD} \quad (1)$$

where n is the moles of gas and t is the time.

The first complication arises when trying to model the term for the headspace (left term), because the packaging used for MAP systems are semi-rigid, then extreme cases like constant volume or constant pressure cannot be considered. At pressures and temperatures used in MAP systems, the CO₂ comes close to an ideal gas, for which there are two possible solutions

$$\left. \frac{\delta n_{CO_2}}{\delta t} \right|_{HS} = \frac{V_0}{RT} \frac{\delta p_{CO_2}}{\delta t} \quad \text{Rigid package (constant volume)} \quad (2)$$

$$\left. \frac{\delta n_{CO_2}}{\delta t} \right|_{HS} = \frac{P_0}{RT} \frac{\delta v_{CO_2}}{\delta t} \quad \text{Flexible package (constant pressure)} \quad (3)$$

Where V is the volume of headspace (and v is partial volume), P is the pressure of headspace (and p is the partial pressure), T is the absolute temperature of headspace and R is the ideal gas constant.

In a mathematical analysis reported by Simpson et al. (2001b) for fish stored in a semi flexible tray of PP/EVOH/PP and a film of PET/(PP/EVOH/PP), it was concluded that the difference between the two types of solutions was lower than 2% of the equilibrium concentration; however, the perfectly flexible container was more representative of the MAP system.

Although the partial pressure of CO₂ in headspace is the variable to be considered for mass transfer, MAP systems are normally labeled based on the percentage composition of the gas (%CO₂). Then, information is needed about the other gases (usually N₂ and O₂) in order to calculate the pressure and volume of the system, and thus estimate the percentage composition

$$P = \sum_{i=1}^n p_i \quad \text{Rigid package} (\%CO_2 = 100p_{CO_2}/P) \quad (4)$$

$$V = \sum_{i=1}^n v_i \quad \text{Flexible package} (\%CO_2 = 100v_{CO_2}/V) \quad (5)$$

If the packaging material has a high barrier capacity and oxidation is negligible, then, it can be assumed that the amount of O₂ is roughly constant (Simpson et al., 2001a), mainly because the solubility of this gas in foods is relatively low (Quast and Karel, 1971). The same goes for N₂, because this is an inert gas that does not react with food and its solubility is extremely low. The referred statements were experimentally validated for red meat (Seideman et al., 1979; Zhao and Wells, 1995). Solubilities of CO₂:O₂:N₂ (taken as a substance based on water temperature refrigeration) are in the proportions of 70:2:1, respectively.

3. Package permeability

Transient state permeation in a polymeric film is described by Fick's second law. This law expresses local changes of concentration (C) as a function of time (t) and diffusion coefficient (D), according to

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (6)$$

The application of this law, for the description of the gas transfer through a polymer membrane, has been described by Crank (1975). However, what happens inside the polymer is not relevant to the MAP system design, thus the concept of permeability that is obtained by combining the Fick's first law with Henry's law ($\varphi = SD$) is currently used to predict the flux of the gas (J)

$$J = \frac{\varphi}{L} \Delta p \quad (7)$$

The rate between permeability (φ) and thickness of the film (L) is known as transmission ($\Psi = \varphi/L$). Usually the properties reported by the manufacturers are in regard to this property and not permeability. Then, for the design purposes, the following equation is used

$$\left. \frac{\delta n_{\text{CO}_2}}{\delta t} \right|_{\text{PACK}} = \Psi_{\text{CO}_2} A (p_{\text{CO}_2} - p_{\text{CO}_2/\text{AIR}}) \quad (8)$$

It is important to point out that in respiring foods the permeability of the package is extremely relevant, because foods consume O_2 to produce CO_2 , which must be released to the environment to produce an equilibrium condition (Talasila and Cameron, 1997).

Several advances to optimize permeability of the package material have been developed; one among them, which highlights, is micro perforation (Techavises and Hikida, 2008; González et al., 2008; Fonseca et al., 2000; Chung et al., 2003; Emond et al., 1991; Paul and Clarke, 2002; Renault et al., 1994). However, in non-respiring foods this does not happen, and the barrier properties of the packaging, which are predicted as a resistance should be increased (Greengrass, 1995)

$$\frac{1}{\Psi} = \sum_{i=1}^n \frac{1}{\Psi_i} \quad (9)$$

As a criterion to consider that the loss of gas due to the permeability of the package is marginal (<1%), Eq. (10) is used. The referred equation was deduced from a mass balance for a package with a cubic geometry and with 100% CO_2

$$\Psi [m_{\text{STP}}/m^2 \text{ atm} 24h] \leq 16 \sqrt[3]{\frac{\text{Package Volume in cm}^3}{\text{Days of Storage}}} \quad (10)$$

4. Convection

It is generally accepted that the concentration of CO_2 in the headspace is homogeneous, which is practical but not necessarily real. If a gas permeates through the packaging material and then spreads through the food, a convective flux is created which will carry the molecules from the film to the surface of the food. There is not much information regarding the phenomenon of natural convection which occurs in the headspace of the MAP systems. The reason for this is obvious, it being negligible compared to the phenomenon of molecular diffusion of food (Bertola et al., 1990). This is reflected notoriously when calculating the Biot number (B_i) between the convective resistance of the headspace (k_c) and the diffusion in the food (D). For example, an estimate can be obtained by considering a small water drop of diameter d in a MAP container. The Biot number can easily be calculated assuming a Sherwood number equal to two ($dk_c/D_{\text{CO}_2-\text{AIR}} = 2$)

$$B_i = \frac{\frac{(d/6)}{D_{\text{CO}_2-\text{H}_2\text{O}}} = \frac{(d/6)}{D_{\text{CO}_2-\text{H}_2\text{O}}}}{\frac{1}{k_c}} = \frac{(d/6)}{D_{\text{CO}_2-\text{AIR}}} = \left(\frac{1}{3}\right) \left(\frac{D_{\text{CO}_2-\text{AIR}}}{D_{\text{CO}_2-\text{H}_2\text{O}}}\right) \approx \left(\frac{1}{3}\right) \left(\frac{1.5 \times 10^{-5} \text{ m}^2/\text{s}}{1.5 \times 10^{-9} \text{ m}^2/\text{s}}\right) = 3333 \quad (11)$$

Nevertheless, the effect of natural convection in the headspace of MAP systems has been studied with the analogy of heat and mass transfer of Chilton–Colburn (Simpson et al., 2003), using the dimensionless number of Nusselt (Nu), Grashof (Gr), Prandtl (Pr), Sherwood (Sh) and Schmidt (Sc)

$$Nu = a(GrPr)^{1/4} \Rightarrow Sh = a(Gr_m Sc)^{1/4} \quad (12)$$

where the parameter a takes a value between 1 and 2. For example, when gas is being absorbed by the food, value of a equal to 1.77 is obtained and for the desorption of the gas the value is 1.46. Similar values ($a = 1.5 + 0.2$) have been reported for headspaces in other packaging (Acevedo et al., 2007), so that a general equation could be considered though of little use to predict the phenomenon completely. Nevertheless, the convection equation may have relevance

when modeling the boundary conditions of food covered with a shell because this can be considered as a resistance to CO_2 absorption by the food (Bertola et al., 1990; Mannapperuma et al., 1991)

$$-D \left. \frac{\delta C}{\delta x} \right|_{x=0} = k_p (p_{\text{HS}} - p) \quad (13)$$

5. Diffusion in foods

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions (Crank, 1975). Although there is not much information regarding the mechanisms of mass transfer inside the food, Fick's second law has been the equation most used to represent the dynamic changes of CO_2 in non-respiring foods (Simpson et al., 2001b; Sivertsvik et al., 2004a; Sivertsvik et al., 2004b; Sivertsvik and Jensen, 2005)

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (14)$$

The diffusion in a solid matrix is more complex than the diffusion in a liquid or a gas, because, although CO_2 may seem to diffuse inside the solid matrix, it can actually be spreading through the liquid contents inside the matrix or through the gas phase in a porous solid. Sivertsvik et al. (2004b) discussed that CO_2 should diffuse in the aqueous fraction of the food, so that the diffusion coefficient should be less than that of pure water, which is not always true. In tissues, the CO_2 transfer could also be facilitated by the presence of an intrinsic mechanism such as the enzymatic activity of carbonic anhydrase (Nomenclature of Enzyme Classification: EC 4.2.1.1.), present in cows (Poulsen et al., 2005), pigs (Wang et al., 2006), chickens (Yoshihara et al., 1984), fish (Tohse et al., 2006) and others non-processed fresh foods



Thus, the phenomenon of kinetic mass transfer is described by the effective diffusion, although not being the true value of diffusion, allows for a good estimate of the average CO_2 absorbed by the food in time

$$\left. \frac{\delta n}{\delta t} \right|_{\text{FOOD}} = W \frac{\partial \bar{C}}{\partial t} \quad \text{and} \quad \frac{\partial C}{\partial t} = D_{\text{EFF}} \frac{\partial^2 C}{\partial x^2} \quad (16)$$

Values of effective diffusion are shown in Table 1. There is not much difference between the values of diffusion of CO_2 reported for non-processed fresh meat and fish. The range is small and is between $1.2(+0.7) \times 10^{-9} \text{ m}^2/\text{s}$. Apparently, there is no direct link between the composition of the food and its effective diffusivity, but the values are not off that reported for chilled water (5°C) $\approx 1 \times 10^{-9} \text{ m}^2/\text{s}$ (Jähne et al., 1987).

6. Solubility in foods

Henry's law is widely accepted to describe the process of CO_2 solubility in water at low pressures (Carroll et al., 1991); and by analogy is therefore generally used to describe the sorption of CO_2 in food

$$p = HC \quad (17)$$

This relationship suggests that for food stored in modified atmospheres, the CO_2 concentration in the food (C) is proportional to the solubility (or inverse of the Henry's constant, $S = H^{-1}$) and the equilibrium partial pressure (p)

$$C = Sp \quad (18)$$

Table 1
Diffusion and solubility of CO₂ for non-respiring foods at 0 °C.

	Water (%)	Protein (%)	Fat (%)	pH	Diffusion D × 10 ¹⁰ (m ² /s)	Solubility (mmol/kg atm)	Source
Water	100.0	0.0	0.0		7.8*	77	Carroll et al. (1991)
Anglerfish	82.6	15.8	0.1		16.3	51	Sivertsvik et al. (2004b)
Beef fat						31	Gill (1988)
Beef meat				5.4		43	Gill (1988)
Cod	82.2	16.6	0.3	6.9	16.7	55	Sivertsvik et al. (2004b)
Hake	80.0	17.8	0.3	7.4	5.2	78	Simpson et al. (2001b)
Ham	72.3	17.3	5.7	6.1	37.0	39	Sivertsvik and Jensen (2005)
Gelatin gel	97.0	3.0	0.0			75	Simpson et al. (2001a)
Lamb fat						38	Gill (1988)
Lamb meat				6.2		54	Gill (1988)
Pork fat						27	Gill (1988)
Pork meat				5.8		47	Gill (1988)
Pork meat			24.0	5.7		38	Jakobsen and Bertelsen (2004)
Salmon	69.8	19.2	9.9	6.3	16.2	47	Sivertsvik et al. (2004b)
Salmon	63.8	18.5	15.6		18.4	52	Sivertsvik et al. (2004b)
Salmon	57.9	19.6	21.1		18.2	52	Sivertsvik et al. (2004b)
Sausage	53.3	10.0	30.4	5.9	110	31	Sivertsvik and Jensen (2005)
Sausage	52.9	10.0	31.1	6.5	103	30	Sivertsvik and Jensen (2005)
Tuna	74.0	25.1	0.2		17.4	50	Sivertsvik et al. (2004b)
Wolf-fish	77.6	18.6	2.5		15.7	47	Sivertsvik et al. (2004b)

* Estimated using the correlation proposed by Wilke and Chang (1955). At 5 °C the experimental values reported is $10.5 \times 10^{-10} \text{ m}^2/\text{s}$ (Jähne et al., 1987).

If the permeability of the package is negligible compared to the absorption of food, the partial pressure of equilibrium can be calculated easily from a mass balance in terms of the volume of headspace, the amount of food and its solubility

$$p_{\text{CO}_2}/\text{EQ} \left(WS + \frac{V_{\text{EQ}}}{RT} \right) = \frac{p_{\text{CO}_2,0} V_0}{RT} \quad (19)$$

If the container is rigid, the volume of headspace remains unchanged ($V_{\text{EQ}} = V_0$). However, if the container is flexible, the volume is reduced, but it can be calculate from an overall mass balance, assuming that the absorption of O₂ and N₂ are negligible

$$V_{\text{EQ}} = V_0 - p_{\text{CO}_2}/\text{EQ} \frac{SWRT}{P_0} \quad (20)$$

On the other hand, as CO₂ dissolves in the food, the initial concentration decreases, resulting in a decrease in the total gas pressure and, in the case of a flexible packaging material, it will shrink or collapse around the product. To prevent package collapse,

the initial volume of headspace must be higher than the mass of food ($V_0/W > 1 \text{ l/kg}$) (Simpson et al., 2007). A simple 2 × 2 equations system (Eqs. (19) and (20)) can be used to predict the equilibrium in soluble gas stabilization (SGS), and prevent the collapse of the package. Then, the equilibrium of the headspace produced for SGS of the CO₂ can be easily predicted using Eqs. (21) and (22)

$$V_{\text{EQ}} = \frac{V_0}{2} \left[\left(1 - \frac{SRT}{(V_0/W)} \right) + \sqrt{\left(1 - \frac{SRT}{(V_0/W)} \right)^2 + \left(4 - \frac{(\% \text{CO}_2)_0}{25} \right) \left(\frac{SRT}{(V_0/W)} \right)} \right] \quad (21)$$

$$(\% \text{CO}_2)_{\text{EQ}} = 100$$

$$\frac{200 - 2(\% \text{CO}_2)_0}{\left(1 - \frac{SRT}{(V_0/W)} \right) + \sqrt{\left(1 - \frac{SRT}{(V_0/W)} \right)^2 + \left(4 - \frac{(\% \text{CO}_2)_0}{25} \right) \left(\frac{SRT}{(V_0/W)} \right)}} \quad (22)$$

The solution of the Eqs. (21) and (22) are shown in Fig. 1 using the solubility of CO₂ in water at 0 °C ($S = 77 \text{ mmol/kg atm}$). Because many foods have solubility close to water, Fig. 1 can be used as a preliminary tool to design MAP systems. However, Eqs. (21) and

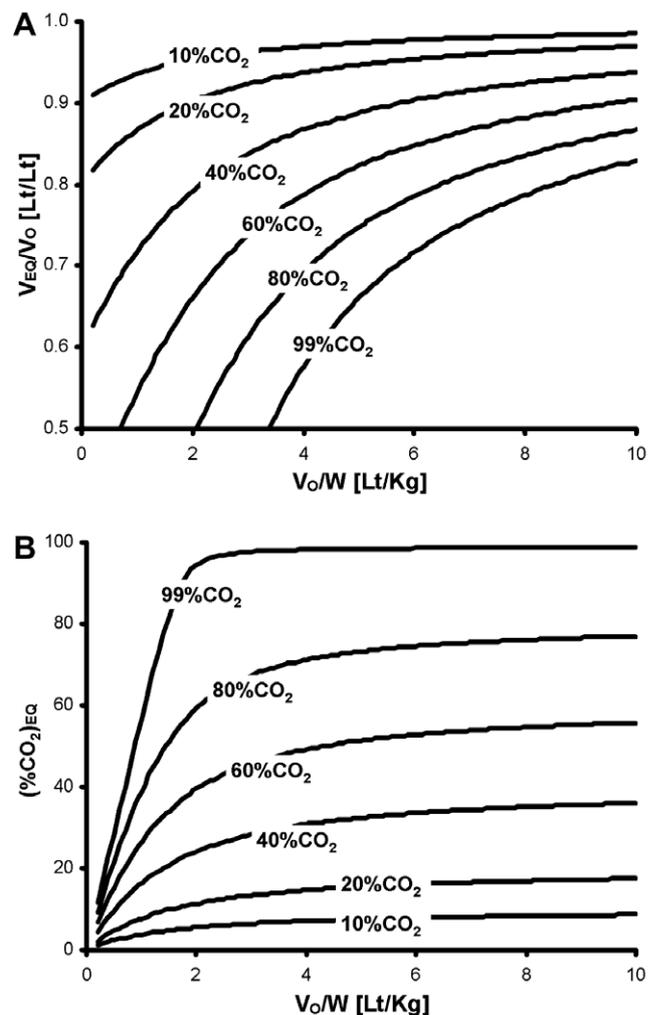


Fig. 1. Equilibrium conditions of the headspace at different headspace/food load (V_0/W) and initial CO₂ concentration considering solubility of water at 0 °C. A. Volume (see Eq. (21)) and B. Concentration of CO₂ (see Eq. (22)).

(22) are only valid when CO₂ is more soluble than the other gases (e.g., mixtures of CO₂/N₂ or CO₂/O₂/N₂ without oxidation). In other cases, it is recommended to use the methodology described by Rotabakk et al. (2008).

Several authors have corroborated that the CO₂ concentration in the food increases proportionally to the amount of CO₂ at the equilibrium condition on headspace (Ledward, 1970; Piergiovanni and Fava, 1992; Zhao et al., 1995; Devlieghere et al., 1998; Jakobsen and Bertelsen, 2004). However, what happens in the transient phase has not yet been studied, although the theory should indicate that Henry's Law is applicable to the surface of the food. The mathematical models for predicting CO₂ in the headspace utilizing this assumption, have no trouble predicting the transient phase and equilibrium, and therefore no evidence exists to show otherwise.

The factors affecting the solubility are numerous, but those most studied have been the amount of water, amount of fat and initial pH (Sivertsvik et al., 2004b). Special emphasis must be placed on the latter, because the pH of food changes as the CO₂ is absorbed by the food, and an acid taste can be perceived if the food is consumed immediately upon removal from the MAP systems (Seiler, 1996).

CO₂ molecule has a greater solubility in water than any other gas used in MAP systems. At 0 °C, its solubility in water is the highest and reaches 77 [mmol/kg atm]. The solubility of CO₂ in aqueous systems decreases when the temperature increases (Carroll et al., 1991); in addition, solubility of CO₂ in water decreases with the increase of NaCl concentration. Over 99% of CO₂ exists as a dissolved gas and less than 1% exists as carbonic acid, which partially dissociates in H⁺, HCO₃⁻ and CO₃²⁻ according to Eqs. (23–25) (Ogrydziak and Brown, 1982)



In meat (pH 5.5 and 0 °C), the solubility of CO₂ is approximately 43 (mmol/kg atm), decreases 0.85 [mmol/kg atm] for the increases of each degree Celsius, and increases in 16 [mmol/kg atm] for each pH unit. The CO₂ molecule is highly soluble in water and oil. In fat at refrigerator temperatures (0–10 °C), the solubility of CO₂ increases with the increase in temperature (Gill, 1988).

7. Temperature

The modified atmosphere packaging helps to increase the shelf life of the product only when used in combination with low temperatures. If the food in modified atmosphere packaging is subjected to temperature abuse, it may come to have a negative impact, making air packaging more effective than MAP (Sivertsvik et al., 2002). Among the most dangerous pathogens is *Clostridium botulinum* type E, which can produce a highly toxic compound at refrigerator temperatures (>3.3 °C). The main problem is that the food will become highly toxic before organoleptic deterioration, since the microorganism growth is not necessarily accompanied by proteolysis (Skinner and Larkin, 1998). A conservative prediction of botulinum toxin production as a function of the temperature (degree Celsius) can be obtained by Eq. (26) (Skinner and Larkin, 1998)

$$\begin{aligned} \text{Log}_{10}(\text{Days of Toxin Formation}) \\ = 0.65 - 0.0525(^{\circ}\text{Celsius}) + \frac{2.74}{(^{\circ}\text{Celsius})} \end{aligned} \quad (26)$$

The bacteriostatic and fungistatic effect of CO₂ is favored at low temperatures. The most accepted theory points to the fact that

the solubility of CO₂ in water decreases with increasing temperature (Ogrydziak and Brown, 1982), however, this is questionable because the solubility in fat increases with temperature, in the range of cooling (Gill, 1988).

The microbial activity is also favored with the increase in temperature, and can affect the composition of the gaseous environment (Simpson et al., 2001a)

$$\left. \frac{\partial n}{\partial t} \right|_{\text{MO}} = \mu Y_{\text{CO}_2/X} X \quad (27)$$

Increasing the temperature increases microbial growth rate (μ), ergo increasing the amount of CO₂ produced by the metabolism of the microorganisms. The use of such equations in a MAP system is extremely complex, because the composition and microbial load are very diverse, the food varies over time (pH, a_w, potential redox and others parameters), and in addition, there is microbial competition. This translates into the fact that the parameters vary from one food to another. Moreover, that they are not constant over time and depend on other factors that are hard to manage and/or quantify. It is worth emphasizing that in a food there are aerobic and anaerobic microorganisms, as well as microorganisms that are inhibited with CO₂, and others which are stimulated with high concentrations of CO₂ (yeast, *C. botulinum* and others), making it extremely difficult to describe microbial growth, and define the parameters that limit the generation of CO₂ and demand for O₂. However, this is only significant when it has reached the end of its shelf life and the deterioration is evident (Pfeiffer and Menner, 1999), which is why it is not considered as a factor when designing a MAP system (Simpson et al., 2001a).

A change in the gaseous environment is intimately linked to changes in temperature, since this has a significant impact on physical properties. The most important property is solubility, because this varies significantly when changing temperature, and may affect the equilibrium condition (Gill, 1988; Sivertsvik et al., 2004b; Sivertsvik and Jensen, 2005). In pure water (0–40 °C), the solubility decreases ~25% per 10 °C increase, and can be represented by an Arrhenius model (Carroll et al., 1991). In meat and fish this change is less noticeable because these foods contain fat (Gill, 1988; Sivertsvik et al., 2004b; Jakobsen and Bertelsen, 2004).

The diffusion coefficient is not affected significantly within the range of refrigeration (Sivertsvik et al., 2004b; Sivertsvik and Jensen, 2005), for which the transient period can be expected not to be affected significantly because of a change in temperature. If the change in the diffusion coefficient of CO₂ in water is calculated with the correlation of Wilke and Chang (1955), an increase of 3% per 10 °C increase is obtained. Simpson et al. (2003) solved the transient problem of simultaneous heat and mass transfer, reporting a marginal change of CO₂ in headspace when changing the temperature from 0 °C to 15 °C.

8. Conclusions and future trends

In the field of MAP system design, it is important to choose the optimum CO₂ concentration for performing the package. Then, it is necessary to estimate the behavior of this gas and predict its transient condition within headspace. The classical approach is based on mass transfer phenomena using Flick's law and coupled with Henry's law. There is not clear evidence about the validity of both laws when applied to foods, but empirical results show consistently good agreement in order to predict the behavior of CO₂ in headspace. Foods are far from ideal systems, and then future studies could be oriented to understand and model the gas motion into food materials.

The use of global parameters such as effective diffusivity and average-solubility are good and necessary tools to design MAP

systems, but not clarifies the scientific aspect of gas–tissue interaction or the real penetration of CO₂ into the food material. It is known that CO₂ decrease microbial activity, but generally, inside the food it is unknown the CO₂ concentration and the only variable available is CO₂ concentration at headspace. In addition, the convective forces in headspace have not been sufficiently investigated.

The activities of specific enzymes that could catalyze the production or uptake of CO₂ and O₂ have been only considered as possible parameters to explain the variation in effective diffusivity, but the fresh food is a metabolically active system, where the different layers of the tissue could have different responses, e.g., it is known that the diffusivity and solubility of CO₂ in fat is completely different to diffusivity in meat tissue.

Just a few values of diffusivity and solubility are reported in literature. This information is very important for the design of an appropriate MAP system. In order to compare if the diffusivity was a good estimator, usually water value is used as a reference, showing that there is not other food rigorously characterized.

As a final conclusion, it is possible considered that the actual mathematical development allows to predict the CO₂ concentration in head space is appropriate and correlate free CO₂ in the headspace with food spoilage. Nevertheless, other important mass transfer aspects, e.g., the real CO₂ gradient inside the food have not been considered as a possible variable to design MAP systems.

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