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Diffusion of glucose and sodium chloride in green olives during curing as affected by lye treatment

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Abstract

Green olives variety *Arauco* were debittered using lye concentrations of 2.00%, 2.50% and 3.00% of NaOH. Each treatment was then subjected to two rinsing processes with tap water. Next, the olives were cured with brine at 10% sodium chloride concentration. During this curing process, the loss of reducing sugars from, and the diffusion of sodium chloride into the olives was quantified. Effective diffusion coefficients of both solutes in the skin and the flesh were calculated for this period using a diffusion model for a composite hollow sphere. The debittering and rinsing processes, produced greater losses of reducing sugars from the olives with increasing lye concentration. The skin effective diffusion coefficients for both solutes ranged between 1.13×10^{-13} m^2/s and 2.24×10^{-13} m^2/s and were unaffected by lye concentration. The flesh coefficients varied between 2.50×10^{-09} m^2/s and 4.05×10^{-09} m^2/s for sodium chloride and between 1.57×10^{-10} m^2/s and 5.57×10^{-10} m^2/s for reducing sugars and increased with increasing lye concentration. Considering the overall process (debittering/rinsing/curing), the extra time required for debittering with lye at 2.0% is amply compensated during the curing process in terms of release of reducing sugars (needed for the lactic fermentation) into the brine.

Keywords: Diffusion; Sodium chloride; Glucose; Alkali; Debittering; Green olives

1. Introduction

The debittering process is a treatment of the olives with sodium hydroxide solutions with concentrations ranging between 1.5% and 3.0%. The principal objectives of this operation are to eliminate the bitter taste conferred by the glycoside oleuropein (Marsilio & Lanza, 1998) and to increase the permeability of the fruits in order to facilitate the exit of different nutrients to be used by lactic bacteria during the subsequent fermentation process (Papamichael-Balatsouras & Balatsouras, 1988).

The lye treatment gives rise to complex chemical and physical changes in the fruits, and its extent also affects the subsequent diffusion of salt and the progress of the lactic fermentation (Rodriguez de la Borbolla y Alcalá & Rejano, 1979; Sciancalepore, 1984). The skin is a natural barrier to the penetration of NaOH and other solutes to the interior of the olives. Its permeation is a function of the treatment conditions such as lye concentration and temperature, and olive variety and maturity (Barranco, Fernández Escobar, & Ballo, 1997).

Increasing lye concentration and/or temperature accelerates the permeation of the skin (Fernández-Diez, 1985). The effect of lye concentration on the diffusion of NaOH was studied by Maldonado, Zuritz, Gascón, and Rey (2003), while Zuritz, Maldonado, and Gascón (2003) studied the effect of temperature on the same phenomenon.

Drusas, Vagenas, and Saravacos (1988) quantified the diffusion of sodium chloride into green olives placed in brines of various concentrations. They studied untreated olives and olives pretreated with lye at 1.8% for 6 h and calculated salt effective diffusion coefficients assuming a hollow sphere geometry and negligible external resistance to mass transfer. They measured the absorption of salt from changes in brine concentration. Maldonado and Zuritz

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Nomenclature

a	dimensionless internal radius of the hollow sphere	D_F	flesh effective diffusion coefficient (m^2/s)
A	defined in Eq. (4)	D_S	skin effective diffusion coefficient (m^2/s)
$B1$	defined in Eq. (6)	H	$=k_2 - k_1$
$B2$	defined in Eq. (7)	k_1	$=D_F/r_o$
$B3$	defined in Eq. (8)	k_2	$=D_S/(r_s - r_o)$
$B4$	defined in Eq. (9)	r	radial position in the olive flesh (m)
C	dimensionless solute concentration	r_i	internal radius of the olive flesh (m)
$\langle C \rangle$	dimensionless volume average solute concentration	r_o	external radius of the olive flesh and internal radius of the olive skin (m)
c	Solute concentration within the olive flesh (g/kg olive flesh)	r_s	external radius of the olive skin (m)
c_i	initial solute concentration (g/kg olive flesh)	R	dimensionless radius
c_s	Solute concentration at the outer skin surface (g/kg olive flesh)	$R_{(\alpha_1)}$	variable defined in Eq. (5)
		t	time (s)
		α_1	eigenvalues
		θ	dimensionless time

(2003) and Maldonado and Zuritz (2004a) computed effective diffusion coefficients of sodium during the debittering of green olives varieties *Arauco* and *Aloreña*.

Zuritz and Maldonado (2004) quantified the diffusion of sodium through olive skins during and after treatment with NaOH, while Maldonado and Zuritz (2004b) evaluated the diffusion phenomena considering variable diffusion coefficients. In both cases they observed an increase in the skin diffusion coefficient with treatment time.

During the treatment with lye, sugars and other nutrients are lost into the solution. These losses also continue during the rinsing of the olives (Fernández-Diez, 1985) and the subsequent curing in brine. Due to the diffusion process, the brine becomes an appropriate growth media for microorganisms responsible of the lactic fermentation (Bobillo & Marshall, 1991; Marsilio & Lanza, 1998) that will provide the acidity necessary for the stability and preservation of the olives (Marsilio, 1990). The necessary nutrients come from within the olives and their concentration in the brine is determined by the extent of the debittering process.

Chammem et al. (2005), working with olives variety *Meski*, found that the best fermentation process was achieved using a lye concentration of 2% of NaOH and brine with 9% concentration of NaCl. However, other studies indicate that even with brine concentrations between 10% and 13%, spontaneous fermentation can take place (Fernández-Diez, 1985).

Since the debittering process affects the availability of nutrients during the curing stage, and considering that, to date, the diffusion phenomena of reducing sugars has not been quantified from a mass transfer standpoint, the aim of the present work is to evaluate the diffusion of sugar and sodium chloride during the curing process of green olives of the local variety "*Arauco*", as affected by different lye concentrations.

2. Materials and methods

2.1. Sampling

Green olives of the variety "*Arauco*" were used in this study. They were harvested with a Maturity Index 2 (Fernández et al., 1991), corresponding to a green-yellow skin color. A random sample of 50 kg of olives previously graded was selected for the experiments, giving the following average dimensions: weight $= 7.433X10^{-3}$ kg, $\sigma = 0.915 \times 10^{-3}$ kg; equatorial diameter $= 20.50 \times 10^{-3}$ m, $\sigma = 1.59 \times 10^{-3}$ m; length $= 31.38 \times 10^{-3}$ m, $\sigma = 2.20 \times 10^{-3}$ m, skin thickness $= 4.0 \times 10^{-5}$ m.

Lots of 4.5 kg olives each were taken from the previous sample and placed in 10-l plastic containers with lid, to which 3 l of treatment solutions (lye, water and brine) were added at each stage. The temperature was kept constant a 20 °C ± 1, during all the processes. Each treatment was done by triplicate.

The concentrations of NaOH studied were 2.00%, 2.50% and 3.00% (w/v). As customary industry practice, the debittering process was ended when the lye had penetrated 3/4 of the flesh thickness, which was visually determined by colorimetric reaction with phenolphthalein.

After the debittering process, the lye was removed from the containers and the olives were rinsed with tap water for two consecutive periods of 6 h each. At the end of each rinsing process, the water was also totally removed from the containers. Finally, 3 l of brine with 10% of sodium chloride concentration, acidified with 2‰ of each acetic and hydrochloric acid, were added to each container. In order to inhibit microbial activity 1000 UI/ml of nisine (Chrisin™) and 50 ppm of chloranphenicol (Avicloran™) were also added to the brines . The microbial inhibition was checked by periodical microbial analysis (ICMSF).

The containers with the solutions and the olives were maintained in continuous agitation in order to achieve a large surface mass transfer coefficient (large Biot number).

Brine samples were taken periodically during five months. The samples were placed in plastic test tubes, sealed and kept in a freezer at −18 °C until they were analyzed.

2.2. Analytical methods

The concentration of NaCl in the brines was measured by Mohr's method (Pearson, 1976).

Procedure:

1. Add 1 ml sample into an erlenmeyer with 50 ml distilled water.
2. Bring pH between 7 and 9 with alkali or acid.
3. Add 1 ml potassium dichromate 5% as indicator.
4. Titrate with $AgNO_3$ 0.1 N until brownish-red color.

Reducing sugars in brine were determined by Miller's technique (Miller, 1959), employing a Metrolab® UV–visible spectrophotometer.

Reagent preparation:

1. Dissolve 3.5 g of dinitrosalicylic acid in 20 ml of 2 N NaOH. Dissolve as much as possible and break up the lumps. Let stand overnight to complete dissolution.
2. Add 50 ml distilled water. Stir until all is dissolved.
3. Add 30 g K–Na tartrate and bring to 100 ml total volume in a volumetric flask.
4. Store in the dark. Avoid skin contact.

Procedure:

1. Add 1.0 ml sample (sugar 0.2–2.0 g/l) and 1.0 ml reagent to test tubes, including a blank with 1.0 ml distilled water.
2. Immerse in boiling water bath for 10 min, then into ice bath for 10 min.
3. Add 10 ml distilled water to each tube and measure OD at 546 nm.
4. Run also a standard curve with glucose in the range 0.2–2.0 g/l along with the test samples.

The Miller's technique was adapted to determine reducing sugars in olive flesh.

1. Macerate 1 g of olive paste pulp in 50 ml of distilled water at 20 °C ± 1 °C for 30 min.
2. Filter in medium-size pore paper filter.
3. With filtrate proceed as indicated above.

The salt absorbed by the olives was calculated from the changes in brine concentration.

The concentration of reducing sugars in the olives was measured before the debittering process and at the end of the second rinsing. During the curing process, it was calculated from the increase of sugars in the brine.

2.3. Theoretical considerations

In order to calculate the effective diffusion coefficients of both solutes in the skin and the flesh during the curing process, a diffusion model for a composite hollow sphere was adjusted to the experimental data, using the following assumptions (Maldonado & Zuritz, 2004a). See Fig. 1.

1. The flesh and skin of the olives are homogeneous and isotropic with uniform initial concentration (c_i).
2. The olive flesh is a hollow sphere with internal radius r_i and external radius r_o, surrounded by the skin of internal radius r_o and external radius r_s.
3. The thickness of the skin is much less than the internal and external radii, therefore, the difference in surface areas can be neglected.
4. Provided that $(r_s - r_o) \ll (r_o - r_i)$, the accumulation of sodium in the skin can be neglected allowing the assumption of a quasi-steady state diffusion process through the skin.
5. The pit is a concentric solid sphere impervious to the diffusion of solutes.
6. As a simplifying assumption, the model considers constant effective diffusion coefficients in both the skin (D_S) and the flesh (D_F).
7. The system is well-agitated (large mass Biot number) therefore, the skin outer surface ($r = r_s$) reaches the solution average concentration (c_s).

Under the above conditions, the one-dimensional diffusion process with constant effective diffusion coefficients through the flesh (D_F) and the skin (D_S) is expressed in dimensionless form as

$$\frac{\partial^2 C}{\partial R^2} + \frac{2}{R}\frac{\partial C}{\partial R} = \frac{\partial C}{\partial \theta} \tag{1}$$

Eq. (1) is subjected to the following initial and boundary conditions:

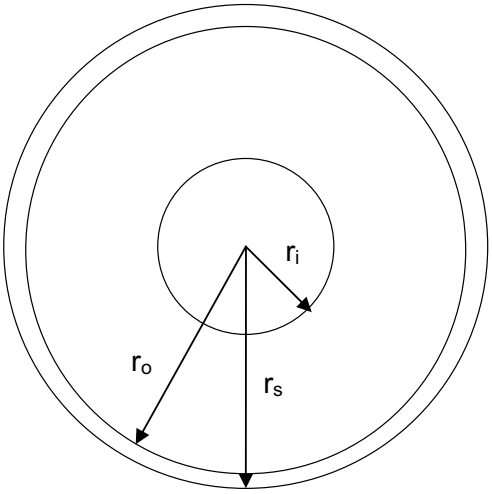

Fig. 1. Schematic of olive cross section showing radial dimensions.

$$\text{IC}: \quad \text{at } \theta = 0 \quad C = 1 \text{ at } a < R < 1 \tag{2a}$$

$$\text{BC1}: \quad \text{at } \theta > 0 \quad \partial C/\partial R = 0 \text{ at } R = a \tag{2b}$$

$$\text{BC2}: \quad \text{at } \theta > 0 \quad \partial C/\partial R = \left[-\frac{D_S/(r_s - r_o)}{D_F/r_o}\right] C \text{ at } R = 1 \tag{2c}$$

where

$$C = (c - c_s)/(c_i - c_s); \quad R = r/r_o; \quad a = r_i/r_o; \quad \theta = D_F t/r_o^2$$

The olive dimensions were adjusted to the radial dimensions of an equivalent sphere of equal volume giving the following: $r_i = 4.29 \times 10^{-3}$ m; $r_o = 11.77 \times 10^{-3}$ m; $r_s = 11.81 \times 10^{-3}$ m and skin thickness $(r_s\text{-}r_o) = 4 \times 10^{-5}$ m.

The average volumetric concentration $\langle C \rangle$ of the solution to Eq. (1) subjected to Eqs. (2a–c) for large processing times was presented by Maldonado and Zuritz (2004a) as

$$\langle C \rangle = \frac{6}{(1 - a^3)} A R_{(\alpha_1)}^2 e^{-D_F \alpha_1^2 t/r_o^2} \tag{3}$$

where

$$A = \frac{(H^2 + k_2^2\alpha_1^2)}{(1-a)(a^2\alpha_1^2 + 1)(k_2^2\alpha_1^2 + H^2) + (Ha + k_2)(H + ak_2\alpha_1^2)} \tag{4}$$

and

$$R_{(\alpha_1)} = (B1 * B2) - (B3 * B1) + a\alpha_1(B1 * B4 + B3 * B2) \tag{5}$$

in which

$$B1 = \frac{\cos(\alpha_1 a)}{\alpha_1} \tag{6}$$

$$B2 = \left[\frac{1}{\alpha_1}(\text{sen}(\alpha_1) - \text{sen}(\alpha_1 a)) + (a\cos(\alpha_1 a) - \cos(\alpha_1))\right] \tag{7}$$

$$B3 = \frac{\text{sen}(\alpha_1 a)}{\alpha_1} \tag{8}$$

$$B4 = \left[\frac{1}{\alpha_1}(\cos(\alpha_1) - \cos(\alpha_1 a)) + (\text{sen}(\alpha_1) - a\,\text{sen}(\alpha_1 a))\right] \tag{9}$$

where α_1 are the eigenvalues that satisfy the following equation:

$$\left[\frac{k_2}{k_1} - (1 + a\alpha_1^2)\right]\text{sen}[(1-a)\alpha_1] + \left[\alpha_1 a\frac{k_2}{k_1} + (\alpha_1 - a\alpha_1)\right] cos[(1-a)\alpha_1] = 0 \tag{10}$$

where

$$H = k_2 - k_1; \quad k_2 = D_S/(r_s - r_o); \quad k_1 = D_F/r_o$$

The flesh and skin effective diffusion coefficients (D_F and D_S) and the eigenvalues (α_1) for each treatment, were estimated using the least squares method, which minimizes the function:

$$S = \sum_{i=1}^{N} (\langle C \rangle_{exp} - \langle C \rangle_{calc})^2 \tag{11}$$

Since the sum of squares of the residuals given as Eq. (11) is a non-linear function of the flesh and skin effective diffusion coefficients (D_F and D_S) and the eigenvalues α_1, the iterative non-linear regression method implemented in the program Microsoft Excel Solver® was used minimizing Eq. (10) simultaneously subjected to the restriction imposed by Eq. (11).

3. Results and discussion

The initial content of reducing sugars in the olives, along with the remaining concentration after the debittering and rinsing processes are shown in Table 1.

The debittering times were 20, 10 and 6 h for lye concentrations of 2.0%, 2.5% and 3.0%, respectively. Even though the olives treated with lye at 2.0% experienced an exposure to the lye between two and three times longer than the olives exposed to the other two lye concentrations, the values show that an increase in lye concentration results in larger loss of reducing sugars, form 63.6% for lye concentration of 2.0% of NaOH to 75.9% for lye concentration of 3.0% of NaOH.

This behavior is consistent with previous reports that increasing lye concentration accelerates the permeation of the skin and the flesh (Fernández-Diez, 1985), decreasing the tortuosity to the diffusion of solutes out of the olives.

Figs. 2 and 3 show respectively the experimental data of the average concentrations of sodium chloride and reducing sugars in the brines of the three treatments.

After the third day, the concentration of NaCl remains almost constant for the rest of the curing process. As Fig. 2 shows, the salt intake was faster for olives treated with larger lye concentration of NaOH.

Meanwhile, during the first two days, the concentration of reducing sugars in the brine is similar for all three treatments (see Fig. 3). From here on, the release of sugars from the olives differs for each treatment. As expected, due to the different sugar content in the olives at the beginning of the curing process, the olives treated with lye at 2.0% of NaOH transferred greater amount of sugar into the brine than the olives treated with the higher lye concentrations.

The maximum amount of reducing sugars transferred to the brine from the olives for each treatment, closely corresponds to one half of the initial sugar concentration in the

Table 1
Initial concentration of reducing sugars in fresh pulp of olives and after debittering and rinsing processes

Sample	Reducing sugars ($\times 10^{-3}$ kg/kg)*	SD ($\times 10^{-3}$ kg/kg)	Losses (%)*
Fresh pulp	74.94[a]	0.60	–
Debittered and rinsed			
2.0% NaOH	27.30[b]	0.39	63.6[b]
2.5% NaOH	22.03[c]	0.43	71.0[c]
3.0% NaOH	18.03[d]	0.44	75.9[d]

* Numbers with different letters in each column denote statistically significant difference ($\alpha = 0.05$).

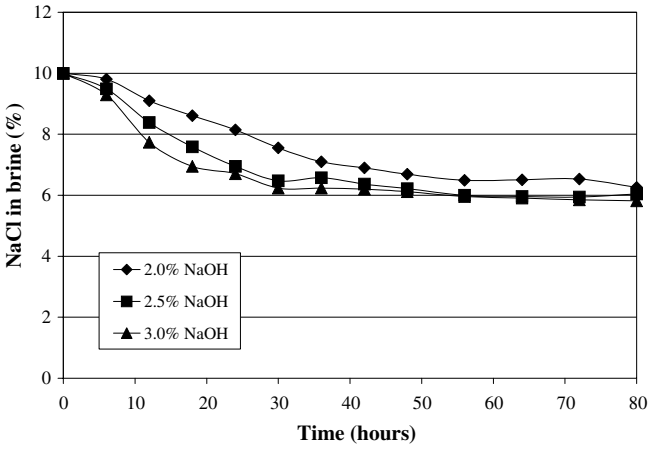

Fig. 2. Concentration of sodium chloride in brine (% w/v) until equilibrium, for debittering treatments with lye at 2.0%, 2.5% and 3.0% of NaOH.

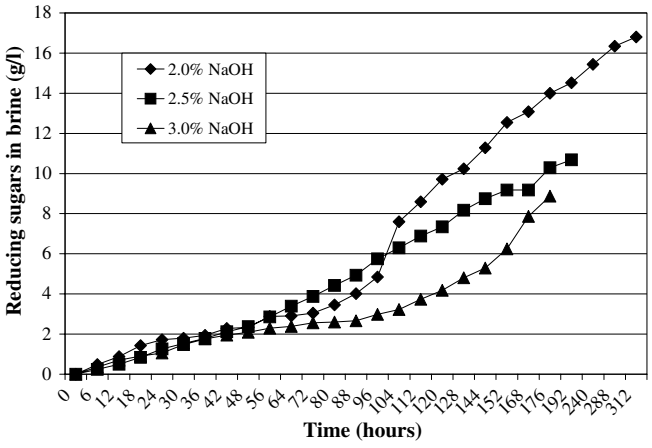

Fig. 3. Concentration of reducing sugars in brine (g/l) until maximum concentration, for debittering treatments with lye at 2.0%, 2.5% and 3.0% of NaOH.

olives at the beginning of the curing process. On the other hand, the time required to release this maximum amount was lesser with olives treated with higher lye concentration. For instance, it took 312 h for the olives treated with lye at 2.0% of NaOH, while it took 192 h for olives treated with lye at 2.5% of NaOH and 176 h for olives treated with lye at 3.0% of NaOH.

Most likely, treatments with higher lye concentration would create a more open structure allowing a faster diffusion of sugars out of the olives. The lye treatment disorganizes the cytoplasmic membranes and causes the rupture of chemical links in hemicellulosic and pectic polysaccharides, as well as the de-esterification of pectins in the middle lamella of the cell walls, increasing dramatically the charge density of the pectic chains due to the free carboxyl groups (Jiménez, Guillén, Sánchez, Fernández-Bolaños, & Heredia, 1995; Jiménez, Guillén, Sánchez, Fernández-Bolaños, & Heredia, 1996; Jiménez, Guillén, Fernández-Bolaños, & Heredia, 1997; Jiménez, Heredia, Guillén, & Fernández-Bolaños, 1997), creating a net negative charge on the molecules causing repulsion between individual pectic chains (Sánchez Romero, Guillén, Heredia, Jiménez, & Fernández-Bolaños, 1998).

The presence of these negative charges could lead to destabilization of the wall structures caused by electrostatic repulsion that would change their conformation and ability to form tridimensional gels leading towards a more "linear" pectic structure. This repulsion could be reinforced by the high pH of the processing liquids that would ensure a total ionization of the carboxyl groups (Jiménez et al., 1995, 1996). This conformational change could probably explain the decrease in tortuosity facilitating the diffusion of sugars out of the olives.

The effective diffusion coefficients of glucose and NaCl calculated for the flesh (D_F) and the skin (D_S) are presented in Table 2. The data indicate that increasing lye concentration gives rise to larger D_F values for both solutes. For instance, for glucose, D_F was 1.57×10^{-10} m^2/s for lye treatment at 2.0% of NaOH, and increased to 3.25×10^{-10} m^2/s and 5.57×10^{-10} m^2/s for lye treatments at 2.5% and 3.0%, respectively. However, this increment was not observed for the skin coefficients (D_S), which were very similar to each other. The order of magnitude of the effective diffusion coefficients listed in Table 2 are consistent with those reported by Maldonado and Zuritz (2003) for diffusion of sodium in olives.

In the flesh, the diffusion coefficients for glucose were one order of magnitude smaller than the coefficients for sodium chloride. For instance, in treatment with 2.5% NaOH, D_F for glucose was 3.25×10^{-10} m^2/s, while for NaCl this value was 3.31×10^{-09} m^2/s. This difference in diffusivity could be due to the difference in molecular size between the glucose and the NaCl. Being the molecule of glucose much larger than the molecule of NaCl, it would be expected that the movement out of the flesh of the former would be slower than the entry of the later into the olive.

Although in the skin the effect is not as noticeable as in the flesh, the skin diffusion coefficients for NaCl are slightly larger than for glucose. For instance, for olives treated with lye at 2.5% of NaOH, the D_S for glucose is 1.36×10^{-13} m^2/s, while for NaCl the value is 2.24×10^{-13} m^2/s.

The skin effective diffusion coefficients were three order of magnitude smaller than the flesh diffusion coefficients for the glucose and four order of magnitude smaller for NaCl. For instance, for olives treated with lye at 2.0% of

Table 2
Effective diffusion coefficients for reducing sugars and sodium chloride in flesh (D_F) and skin (D_S) of olives debittered with different lye concentrations of NaOH

Solute	Treatment	D_F (m^2/s)	D_S (m^2/s)
Reducing sugars	2.0% NaOH	1.57×10^{-10}	1.34×10^{-13}
	2.5% NaOH	3.25×10^{-10}	1.36×10^{-13}
	3.0% NaOH	5.57×10^{-10}	1.13×10^{-13}
Sodium chloride	2.0% NaOH	2.50×10^{-09}	2.04×10^{-13}
	2.5% NaOH	3.31×10^{-09}	2.24×10^{-13}
	3.0% NaOH	4.05×10^{-09}	2.11×10^{-13}

NaOH, for glucose D_S was 1.34×10^{-13} m^2/s and D_F was 1.57×10^{-10} m^2/s, while for NaCl D_S was 2.04×10^{-13} m^2/s and D_F was 2.5×10^{-09} m^2/s.

This difference in diffusivity values is probably due to the different physical structure between the flesh and the skin, which, being the natural barrier of the fruit, has a more impervious structure to the diffusion of different chemical compounds, such as glucose and NaCl.

Drusas et al. (1988) reported values of effective diffusion coefficients for sodium chloride in green olives of the variety *Konservolea* at 20 °C, in the order of 3.2×10^{-11} to 4.3×10^{-11} m^2/s for brine concentrations between 7.3% and 16.4% without pretreatment with alkali, and as high as 1.95×10^{-10} m^2/s for brine concentration of 10.7 % in pretreated olives with lye at 1.8% for 6 h. The difference of the reported values with the ones presented in Table 2 is probably due to the different variety studied and lower lye concentration and debittering time they used. In our experiments the same debittering time took place with lye at 3.0%. The structural difference of the two varieties could also be reflected in the time required to attain constant concentration of NaCl in the brine. They reported 50 days, while in the present case it took only three days. Furthermore, they calculated values of "overall" effective diffusion coefficients (which include the effect of the skin), while the present values differentiate the resistance of the flesh from the resistance of the skin to the diffusion process.

Nonetheless, the D_F values of Table 2 are within the same order of magnitude of those presented by Pflug, Fellers, and Gurevitz (1967), Desai (1977) and Bomben, Durkee, Lowe, and Secor (1974) for the diffusivity of NaCl in pickled cucumbers, as well as for other foodstuffs (Stahl & Loncin, 1979; Wood, 1966; Kormendy & Ganter, 1958). For instance, Pflug et al. (1967) reported diffusivity values from 8.4×10^{-10} to 3.02×10^{-09} m^2/s for pickled cucumbers of different diameters working at temperatures between 21 °C and 71 °C, while Desai (1977) calculated values ranging from 4.0×10^{-10} to 1.2×10^{-09} m^2/s for pickled cucumbers and potato slices at 24 °C and 25 °C. For his part, Bomben et al. (1974) found values on the order of 5.3×10^{-10} to 1.5×10^{-09} m^2/s at temperatures of 25 °C and 49 °C, respectively.

In closing, we can say that since the nutrients, particularly reducing sugars, needed for the growth of the microorganisms responsible of the lactic fermentation, that will provide the acidity necessary for stability and preservation, come from within the olives, a larger initial concentration of sugars at the beginning of the curing process is desirable as it would insure a more complete fermentation which will translate in a medium more acidic in less time.

From the present data we can see that increasing the concentration of NaOH from 2.0% to 2.5%, the loss of reducing sugars increases 19.3%, while the increase is 34% using lye at 3.0%. The debittering times are reduced 50% and 70%, respectively (from 20 to 10 and from 20 to 6 h). Moreover, the time required to reach the maximum concentration of reducing sugars in the brine decreases from 312 h for treatment with lye at 2.0% concentration of NaOH, to 192 and 176 h for treatments with lye concentrations of 2.5% and 3.0%, respectively. This statement would seem to indicate that greater lye concentration will translate in substantial savings in processing time. However, the same maximum concentration of sugars in the brine achieved with lye treatment at 2.5% (10.7 g/l) and with lye treatment at 3.0% (8.9 g/l) is reached in only 132 and 115 h, respectively with olives treated with lye at 2.0%. Looking at the overall process (debittering/rinsing/curing), the extra time required for debittering with lye at 2.0% concentration as compared with the other two processes (10 and 14 h, respectively) is amply compensated during the curing process, needing 60 h less to reach the same concentration of sugar in the brine.

4. Conclusions

The loss of reducing sugars from, and the diffusion of sodium chloride into olives variety *Arauco*, treated with different lye concentrations of NaOH (2.0%, 2.5% and 3.0%) was quantified. Greater losses of reducing sugars from the olives were measured after the debittering and rinsing processes, with higher lye concentrations of NaOH. During the curing process, the time required to attain the maximum concentration of sugar in the brine was inversely proportional to lye concentration used. Effective diffusion coefficients of both solutes in the skin and the flesh were calculated for the curing period by adjusting to the experimental data, a diffusion model for a composite hollow sphere, consisting of a thin skin and a thicker flesh, with constant flesh and skin effective diffusion coefficients (D_F and D_S). The flesh effective diffusion coefficients (D_F) varied between 2.50×10^{-09} m^2/s and 4.05×10^{-09} m^2/s for NaCl and between 1.57×10^{-10} m^2/s and 5.57×10^{-10} m^2/s for reducing sugars. For both solutes the flesh diffusion coefficients increased with increasing lye concentration. The skin effective diffusion coefficients (D_S) for both solutes ranged between 1.13×10^{-13} m^2/s and 2.24×10^{-13} m^2/s and were unaffected by lye concentration. Considering the overall process (debittering/rinsing/curing), the extra time required for debittering with lye at 2.0% is amply compensated during the curing process in terms of release of reducing sugars (needed for the lactic fermentation) into the brine.

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