Analysis by non-linear irreversible thermodynamics of compositional and structural changes occurred during air drying of vacuum impregnated apple (*cv. Granny smith*): calcium and trehalose effects.

E. Betoret[a*], N. Betoret[b], J.M. Castagnini[b], P. Rocculi[a], M. Dalla Rosa[a], P. Fito[b].

[a]Dipartimento di Scienze e Tecnologie Agro-Alimentari, Alma Mater Studiorum Universitá di Bologna, Piazza Goidanich 60, 47023 Cesena, Italy.

[b]Institute of Food Engineering for Development, Department of Food Technology, Universitat Politècnica de València, Camino de Vera s/n, 46022 Valencia, Spain.

* Corresponding author: Dipartimento di Scienze e Tecnologie Agro-Alimentari, Alma Mater Studiorum Universitá di Bologna, Piazza Goidanich 60, 47023 Cesena, Italy. Tel: +39 0547 338120 Fax: +39 0547 382348. e-mail address: maria.betoretvalls@unibo.it (E. Betoret)

Abstract

Apple discs were impregnated with isotonic solutions of sucrose and trehalose with and without calcium addition and after air dried. In the vacuum impregnation experiments, the calcium and the replacement of sucrose by trehalose did not have significant effect on the final volumetric deformation of the samples. During air drying two stages of changes were considered. The first one lasted until the saturation of the intracellular liquid phase, and the second one from the saturation of the intracellular liquid phase until the end of the drying process. Mass transfer has been analysed applying nonlinear irreversible thermodynamics. Water flux, water chemical potential and tissue shrinkage have been taken into account in order to accurately describe the mass

transfer phenomena during air drying. A precise definition of chemical potential allowed estimating the partial molar energy needed for breakages and the reversible and irreversible deformations of tissue structure coupled with mass transfer during air drying of apple.

Keywords: apple, drying modelling, vacuum impregnation, calcium, trehalose

NOMENCLATURE

Suc	sucrose	
Tre	trehalose	
Ca	calcium	
s.d.	standard deviation	
a	activity	
w	water	
VI	vacuum impregnation	
w.b.	wet basis	
d.b.	dry basis	
X	volumetric fraction of exchanged liquid	$m^3_{exchanged\ liquid}/m^3_{total}$
x	mass fraction	$kg_{component}/kg_{total}$
V	volume	m^3
V´	partial molar volume	m^3/mol
m	weight	kg
S	area of the interface solid-air	m^2
J	flux	$mol/m^2 \cdot s$
L	phenomenological coefficient	$mol^2/J \cdot m^2$
Mr	molecular weight	kg/mol
t	time	s
T	temperature	K
R	ideal gases constant	J/mol·K
P	pressure	N/m^2
Greek symbols		
μ	chemical potential	J/mol
φ	relative humidity of the air in contact with the fruit	

ρ	density	kg/m^3
ε	porosity	$m^3_{internal\ gas}/m^3_{sample}$
γ	volumetric deformation	$m^3_{volume\ variation}/m^3_{total}$

Subscripts

pi	impregnated product
ml	liquid medium
pf	fresh product
1	at the end of the vacuum stage
e	effective
Ca	calcium
w	water
int	internal
ext	external
O	initial
S	saturation
DE	deformation
R	breakage

Superscripts

cal	calculated

1. INTRODUCTION

In the most part of the studies about food dehydration by hot air, it is accepted that diffusion is the only mechanism implicated in water flux and the operation is modelled using Fick´s equations deduced for ideal gas systems (Bolin & Stafford, 1974; El Halouat & Labuza, 1987; Senhaji *et al.*, 1991; Sabarez & Price, 1999; Yang *et al.*, 2001). In other research papers the transport phenomena are described with coefficients estimated from semi-empirical correlations and referred to samples having a constant and specific dimension. When food shape is not regular (i.e. shrinkage is significant) this approach might significantly limits the model accuracy, providing unreliable predictions of

the system behaviour (Bernstein & Noreña, 2013). Nowadays, there are complex models that analyse the dehydration process by microscopy studies, accounting for heat and mass transfer in the different food phases. In most cases, for their application, these models need parameters that are impossible to obtain experimentally (Ratti, 2001). A lot of efforts have been made trying to model convective drying of food products considering the samples shrinkage (Kowalski, 1996; Hernández *et al*., 2000; Márquez & De Michelis, 2011; Aversa *et al*., 2012; Curcio & Aversa, 2014). Shrinkage affects the predictions of both moisture and temperature profiles (Mayor & Sereno, 2004) and it has necessarily to be taken into account when a mathematical model aimed at describing drying process is being formulated (Márquez & De Michelis, 2011).
The SAFES methodology (Systematic Approach to Food Engineering Systems) is an advanced method to analyse food products and processes (Fito *et al*., 2007). With this method, it is possible to describe products taking into account thermodynamics, physicochemical and structural characteristics and to analyse the changes (i.e. transport phenomena, phase transitions, structural changes…) produced in food by basic operation or transformation phenomena in a systematic way (Fito *et al*., 2007; Barrera *et al*., 2007; Betoret *et al*., 2007).
In polyphasic, multicomponent and structured dried foods, the structure and the structural modifications, suffered by the product during the process, induce fluxes promoted by non diffusional mechanisms from driving forces different to the concentration gradients (Barat *et al*., 2001). Different studies have shown that water transport coupled with deformation-relaxation phenomena have big influence on this aspect (Barat *et al*., 1998; Fito *et al*., 1996). Actually, the incorporation into the product of any components that can affect mechanical

properties of the structure could have influence on the dehydration process kinetics. The irreversible deformation caused to the dried samples strongly damages the cellular tissue, resulting in low quality dehydrated products. Some studies confirm the interaction and the effect of the calcium and the trehalose on the structural characteristics of different fruits (Gras *et al*., 2003; Barrera *et al*., 2004; Barrera *et al*., 2009; Jain *et al*., 2009; Paik *et al*., 2005). These compounds could help to control the deformation, increasing the quality of the final product.

The aim of this work is to determine the calcium and the trehalose effects on the volumetric deformation of apple disc samples and on the tissue shrinkage during drying, when these elements are incorporated into the tissue by vacuum impregnation. The investigation has been also performed analysing the mass transfer kinetics and the deformation-relaxation phenomena by non linear irreversible thermodynamics.

2. MATERIALS AND METHODS

Experiments were carried out using apples (var. *Granny Smith*) purchased from local market. Fruits were cut into disc-shaped samples 5 mm thick, following their vertical axis. The apple skin and seeds were removed with two cylinders. The internal diameter of the samples was 20.7 mm and the external one 64.4 mm. From each fruit five discs were obtained: four were vacuum impregnated with sucrose, sucrose-calcium, trehalose and trehalose-calcium solutions and the fifth was used to determine humidity content and refraction index. Impregnated discs were cut in half: one part was dried using hot air at 40 ºC and the other one was used to determine humidity content, refraction index and water activity.

To impregnate apple samples, four aqueous solutions with sucrose, trehalose, sucrose and calcium and trehalose and calcium were used. The composition of the solutions was calculated in order to be isotonic with the apple tissue.

2.1. Humidity content, water activity and refraction index.

The humidity content was determined following the official method 20.013 (AOAC, 1980) for dried fruits with high sugar content.

The water activity was determined with a dew point hygrometer mod. Aqualab CX-2 (Decagon Devices Inc., Pullman, WA) calibrated previously with saturated reference solutions.

The refraction index was determined with a thermostated refractometer mod. Pal-1 (ABBE ATAGO Co., Tokyo, Japan).

2.2. Vacuum impregnation.

VI operation was carried out with a pilot plant equipment developed in the Department of Food Technology at Polytechnic University of Valencia (Fito *et al*., 1996).

In the vacuum experiments, the sample was immersed in the impregnation solution. A vacuum pressure of 50 mbar was applied for 10 min, and then atmospheric pressure was restored leaving samples immersed in the liquid for an additional period of 10 min.

To determine the impregnation properties of the apple tissue, the experimental methodology developed by Salvatori *et al*. (1998) was followed. Salvatori et al., in (1998) established a general procedure to evaluate the feasibility of VI by determining deformation and impregnation level in the product. In this procedure the samples and the impregnation liquid are weighted at different moments during an experimental vacuum impregnation operation.

2.3. Hot air drying.

Hot air drying operation was carried out with a pilot plant equipment developed in the Department of Food Technology at Polytechnic University of Valencia (Martín, 2002).

Four samples from the same apple, impregnated with sucrose, sucrose-calcium, trehalose and trehalose-calcium solutions, were air dried simultaneously during 900 min. Temperature (40 ± 0.03) ºC and relative humidity of the air (56 ± 2.01) were monitored by a computer during all period. In all the experiments, the flow rate was maintained at 3.7 kg wet air/m^2·s.

The initial humidity of the samples was determined then the samples were weighed (mod. PB303-S, Mettler Toledo Inc., Barcelona, Spain), thickness measured and their images area acquired (mod. D400, Nikon, Barcelona, Spain), all parameters were determined during all the drying process, every 5 min during the first 15 min, at 15 min intervals until one hour of drying, at 30 min intervals until two hours of drying and 1 hour interval until the end of the drying process. Using digitalized images the area of the interface solid-air was estimated by image analysis using the software Photoshop v.7.0 (Adobe Systems Incorporated, USA).

2.4. Statistical analysis.

All the values provided are the average of at least three replicates and to determine the significant differences of the results the analysis of variance test was carried out (One-way ANOVA or Multifactor ANOVA) with confidence level of 95 % ($p < 0.5$) using the program STATGRAPHICS PLUS v.5.1.

3. RESULTS AND DISCUSSION

3.1. Vacuum impregnation: Effect of the different solutes on volumetric deformation of the samples at the end of the vacuum impregnation process.

According to the hydrodynamic mechanism model described by Salvatori *et al*., (1998) and using the weight of the sample registered during the vacuum impregnation experiment, it was possible to determine the impregnation parameters at the end of the vacuum period (X_1, γ_1, ε_1) and also at the end of the vacuum impregnated process (X, γ, ε) (Fito *et al*., 1996; Salvatori *et al*., 1998). In table 2, the average values and standard deviations of these parameters are shown for the apple samples impregnated with the different solutions.

The impregnation volumetric value of the samples (X) can be used in mass balance equation (eq. 1) (Fito *et al.*, 2000) to determine the mass fraction of sugar and calcium that are incorporated into the samples for each case.

$$x_{pi}=\frac{x_{ml}X\frac{\rho_{ml}}{\rho_{pf}}+x_{pf}}{1+X\frac{\rho_{ml}}{\rho_{pf}}} \quad (1)$$

In previous studies it has been proved that impregnation and deformation phenomena are coupled (Fito *et al*., 1996; Salvatori *et al*., 1998). For similar values of effective porosity (ε_e), a decreasing of X value is followed by an increasing in the volumetric deformation of the sample. In the same previous studies, negative values of X_1 have been related with an exit of the native liquid from intercellular spaces of the fresh tissue.

Protective aspects of trehalose in cellular structures (Miller *et al.*, 1997) and membranes (Crowe & Crowe, 1992) might produce an effect in the fruit tissue affecting the impregnation parameters. In the same way, different studies with vegetal tissue impregnated with calcium in different concentration level (Gras *et al.*, 2001; Salvatori *et al*., 2011) have shown that when the calcium content exceed a concentration level of 10 g/L produces a modification in the elastic properties of the structure, and a bigger volumetric deformation of the samples (Betoret *et al.*, 2003). The coupling of the hydrodynamic mechanism with deformation-relaxation phenomena in the solid matrix of the food explains a modification in the elastic properties of the structure at different impregnation levels. Nevertheless, a multiple analysis of variance showed, with a confidence level of 95 % that the presence of calcium and the replacement of sucrose by trehalose did not have a significant effect on the impregnation and volumetric deformation of the samples at the end of the process. In our case it seems that the samples have not reached the calcium or trehalose content needed to affect food structures during VI operation.

3.2. Dehydration operation: determination of the critical point and modelling.

After the VI with the different solutions, apple discs were air dried. Mass and volume variation of the samples were determined during the whole drying process. In figure 1 the values of the variables: humidity (w.b) (x_w) ($kg_w/kg_{product}$), humidity (d.b) referred to the initial value (x_w/x_{wo}), volume referred to the initial value (V/Vo), water flux (J_w) ($mol/m^2 \cdot s$) and chemical potential ($RTlna_w/\varphi$) (J/mol) versus treatment time for each impregnation solution are reported.

Around 200 min of drying, a critical point was identified. At this moment, the liquid phase of the samples becomes saturated (t_s). The determination of the saturation time was established considering the saturation point of an aqueous liquid phase with sucrose and trehalose at 40 ºC. Taking into account the solutes concentration of intra and extracellular liquid phases and the water content of the sample, it was possible to establish the specific drying time in which the liquid phase becomes saturated (Table 3).

At this point, the sample has lost the 70 % of the initial volume (about 82 % at the end of the process). Furthermore, until this moment, the volume loss has been proportional to the humidity loss (d.b) and to the volume loss of the liquid phase. From this point, there was a short period of time (until 300 min) where the product continues losing humidity faster than volume (Figure 2). Finally, from 350 - 400 min the volume did not change and the rest of the variables decreased very slowly.

During the first drying stage, the sample, previously impregnated with the different solutions, is in contact with hot air that has a lower water activity than the fruit tissue. The loss of water from the surface of the fruit produces water chemical potential gradients. The liquid water migrates towards surface by different mechanisms (i.e. apoplastic, symplastic, transmembrane (active and osmotic), diffusive on the liquid phase of the intercellular space…). In all cases, water spontaneous transport towards surfaces consumes free energy. The driving forces that promote this spontaneous transport are based in gradients of intensive state variables (pressure, temperature or concentration, in this last case using chemical potential function). Free energy consumed for water transport, at constant pressure and temperature, can be calculated from the difference between the chemical potential inside and outside the fruit tissue (2):

$$\Delta\mu_w = RT\ln\frac{\Delta\mu_{wint}}{\Delta\mu_{wext}} = RT\ln\frac{a_w}{\varphi} \qquad (2)$$

When different pressures inside and outside the fruit tissue exist (for example, in the case of turgor existence) the equation 2 is transformed into:

$$\Delta\mu_w = RT\ln\frac{a_w}{\varphi} + V'_w(P_{int} - P_{ext}) \qquad (3)$$

When the pressure term is positive (for example in the case of turgor existence) the equation 3 indicates the existence of “free additional energy” available for water transport (Fito *et al.*, 2007).

The chemical potential described as above keeps the physical meaning: the partial molar free energy available for the spontaneous water transport between two points of the system.

Sometimes, this water transport can be conditioned to the necessary modification/generation of the structures with the “additional consumption” of the available free energy for the transport (Fito *et al.*, 2007). In this case, equation 3 is transformed into:

$$\Delta\mu_w = RT\ln\frac{a_w}{\varphi} + V'_w(P_{int} - P_{ext}) - V'_w(\Delta P_{DE} - \Delta P_R) \qquad (4)$$

The equation 4 indicates that the molar free energy available for the mass transport has been reduced by the third term of the equation. The third term of the right side of equation evaluates the molar energy used in the elastic and reversible deformation of the structures ($V'_w \cdot \Delta P_{DE}$) and the dissipated energy in breakages and/or irreversible deformations ($V'_w \cdot \Delta P_R$). The physical meaning of the terms ΔP_{DE} and ΔP_R is: the pressure increments needed to produce elastic deformation and breakages or irreversible deformations respectively or the internal mechanic effort that it is used to modify/generate structures. The energy consumption decreases the water flux that could be possible with the same gradient of chemical potential calculated with equation 2.

The coupling between the different phenomena and the mechanisms of mass and energy transport are common during the cellular systems drying (Barat *et al*., 2001). The water losses necessarily involve the decrease of the protoplast volume and consequently the membrane and the wall are deformed or completely separated (microscopic level) (Seguí *et al*., 2006). The structural changes produced at microscopic level result at macroscopic level with the change of the general aspect of the sample or shrinking and with important modifications in the physicochemical properties during the stage.

Taking into account the above considerations and the non linear irreversible thermodynamics, the water flux from inside the product towards drying air can be calculated by the equation 5 and also quantified by phenomenological equation (Seguí *et al*., 2006):

$$J_w=\frac{1}{S\cdot Mr_w}\frac{\Delta(m\cdot x_w)}{\Delta t} \tag{5}$$

$$L_w=\frac{J_w}{\Delta\mu_w} \tag{6}$$

Taking into account equation 4:

$$L_w=\frac{J_w}{RT\ln\frac{a_w}{\varphi}+V'_w(P_{int}-P_{ext})-V'_w(\Delta P_{DE}-\Delta P_R)} \tag{7}$$

Experimental data obtained in this work allowed calculating the first term of the right side of equation 4. The value of the phenomenological calculated coefficient results:

$$L_w^{cal}=\frac{J_w}{RT\ln\frac{a_w}{\varphi}} \tag{8}$$

The physical meaning of phenomenological coefficient is: a measure of how the driving force gradient can contribute to the water transport. It is possible to predict the second term of right side of equation 4 that can be only a positive value (increasing the driving force) during the first minutes of drying. A small loss of water implicates, in all cases, a turgor loss and therefore the term becomes zero.

When deformation-relaxation phenomena exist the third term of the right side of equation 4 will be negative (depending on the volume increase of the sample in each moment) (Fito *et al.*, 2007). If there is not turgor or related to water transport:

$$L_w^{cal} = L_w \tag{9}$$

When the turgor or deformation-relaxation phenomena exist:

Fruit with turgor: $$L_w^{cal} \geq L_w \tag{10}$$

Deformations: $$L_w^{cal} \leq L_w \tag{11}$$

In the figures 3 and 4 the values of the water flux and phenomenological coefficient, calculated without consider turgor and deformation effects, are represented.

At initial drying stages there is a substantial flux of water from the sample to the drying air. However the chemical potential remains constant. The loss of free water present in the intercellular spaces or pores of the tissue in a product with high moisture content scarcely affects water activity and thereof the chemical potential considered. Then, the water flux is accompanied by a proportional decrease in the chemical potential. During this period the liquid intracellular water is eliminated reducing the water activity of the product. Finally the water strongly linked to the tissue is eliminated. In this period the deformation-relaxation phenomena are very important. Small water fluxes are followed by significant variations in the water activity of the tissue and consequently in the chemical potential considered.

After 10 minutes of drying (when deformation is not excessive) it can be supposed that L_w calculated is close to the real. Assuming this real value, the difference between real and calculated L_w allow us to calculate structural deformation efforts.

$$V'_w(\Delta P_{DE}+\Delta P_R)=\left(\frac{1}{L_w}-\frac{1}{L_w^{cal}}\right)J_w \tag{12}$$

Evolution of the free energy to generate structural deformation/breakages efforts versus time is represented in the figure 5.

The elastic response of plant tissues has been attributed to cellulose, the main component of the cell wall, which provides individual cells with rigidity and resistance to rupture (John & Dey, 1986; Pitt, 1992); to the occluded air in the porous matrix and; to the turgor pressure which leads to the rigidity of plant cells and tissues, and, together with the cell wall, provides the mechanical support for maintaining cell and tissue shape (Bourne, 1976; Alzamora *et al*., 2000). The presence of calcium in the wall matrix can help to maintain middle lamella integrity, since it promotes cross-linking of pectin polymers, and in addition can make pectin macromolecules of the cell wall less soluble through the formation of bridges between them (Salvatori *et al*., 2011). This fact has been related with increasing the stiffness and fragility of the cellular network (Gras *et al*., 2003). In our case, the free energy used for breakages and irreversible deformations is not affected in a general way by calcium. In the samples Tre and Tre+Ca the curves obtained are overlapped; however in the samples Sac and Sac+Ca it is possible to see, at the end of the drying process, a tendency to increase the deformations efforts in the samples impregnated with calcium.

Regarding to sugar treatment, previous work has shown that non-reducing disaccharides such as sucrose and trehalose can protect biological systems from the adverse effects of freezing and drying (European Patent Application, 1999; Aktas *et al*., 2007). Trehalose has been claimed to be a desiccation protectant (Miller *et al*., 1997; Ferrando & Spiess, 2001), suggesting that the use of this sugar could result in an improved preservation of plant cellular structure. Atarés *et al*., (2008) found that apple cylinders osmotically dehydrated with trehalose showed a better solute retention during rehydration, an indicator of the cellular disruption suffered by the material. The ability to form glasses and direct interaction between the sugar and polar groups in proteins and phospholipids would be responsible for stabilization. In our case, it is possible to see clearly the differences between trehalose and sucrose on the evolution of the free energy to generate structural deformations/breakages. After the critical point (200 min drying), when the liquid phase becomes saturated, there is a tendency change between both sugars. The free energy in Sac and Sac+Ca samples decreases abruptly which means the progressive failure of the cellular structure. However the free energy in Tre and Tre+ca samples is maintained until the end of drying, showing a bigger deformation capacity of the samples thus preventing the cellular disruption and breakages. As tissues are dried, hydrogen bonding between trehalose and the polar lipids of biomembranes has been demonstrated to replace the water of hydration at the membrane-fluid interface, preventing the phase transition from lamella to gel phase and the consequent leakage (Nieto *et al*., 2013).

4. CONCLUSIONS

According to obtained results the calcium had not effect on volumetric deformation of samples after vacuum impregnation neither hot air drying. Air drying operation analysis by non linear irreversible thermodynamics allowed calculating the free energy to generate structural deformation/breakages efforts during the drying time for all the samples. The replacement of sucrose by trehalose had significant effect during drying.

The calculations obtained showed bigger free energy related with structural efforts in the samples impregnated with trehalose, an indicator of cellular structure maintenance.

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Table 1. Composition of the VI solutions.

	Sucrose (g/L)	**Trehalose dihydrated (g/L)**	**Calcium (g/L)**
Suc	249.14	-	-
Suc+Ca	124.86	-	49.17
Tre	-	275.35	-
Tre+Ca	-	117.53	41.88

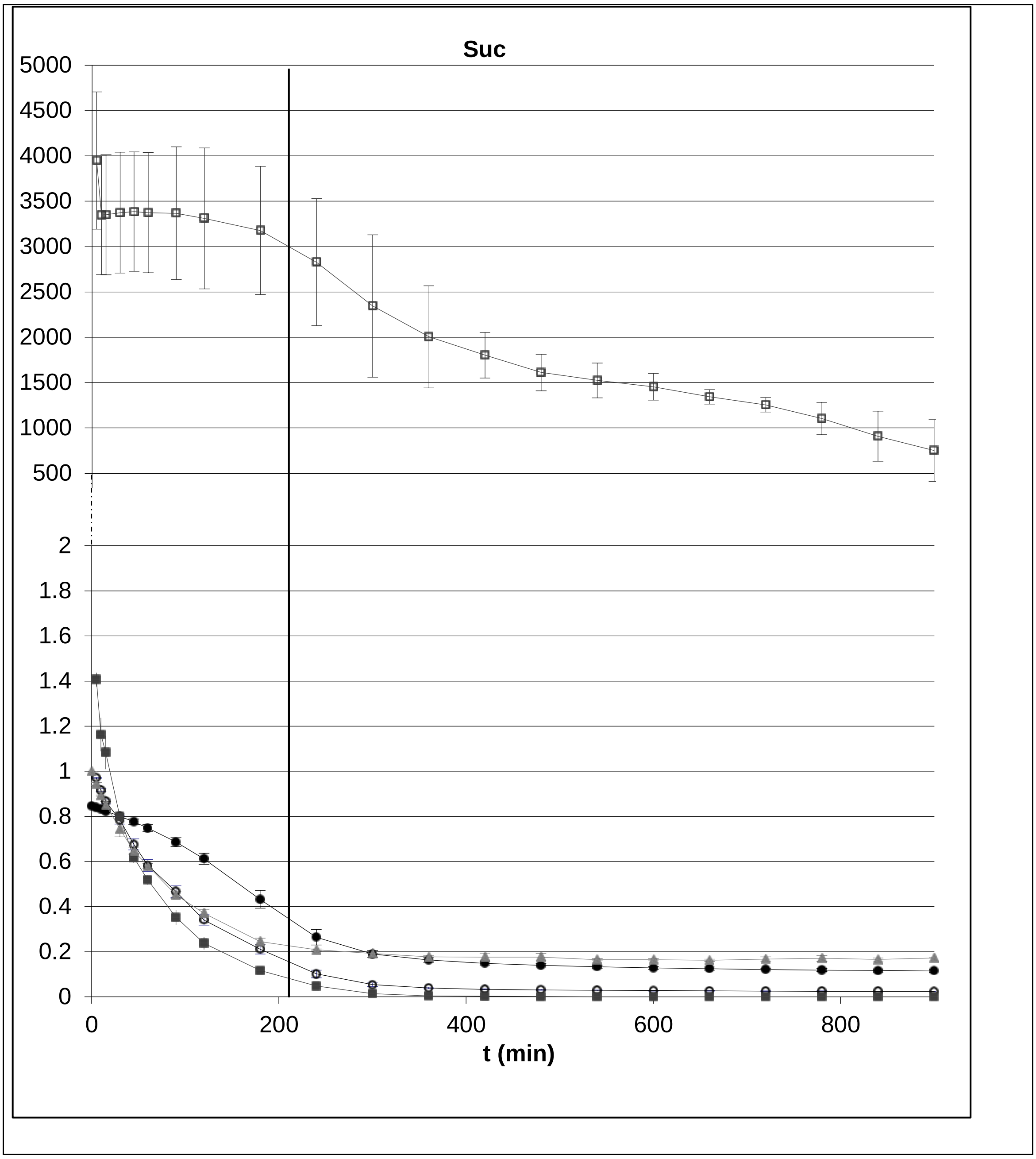
Table 2. Impregnation parameters values and final sugar and calcium concentrations achieved in vacuum impregnated samples (mean (standard deviation)).

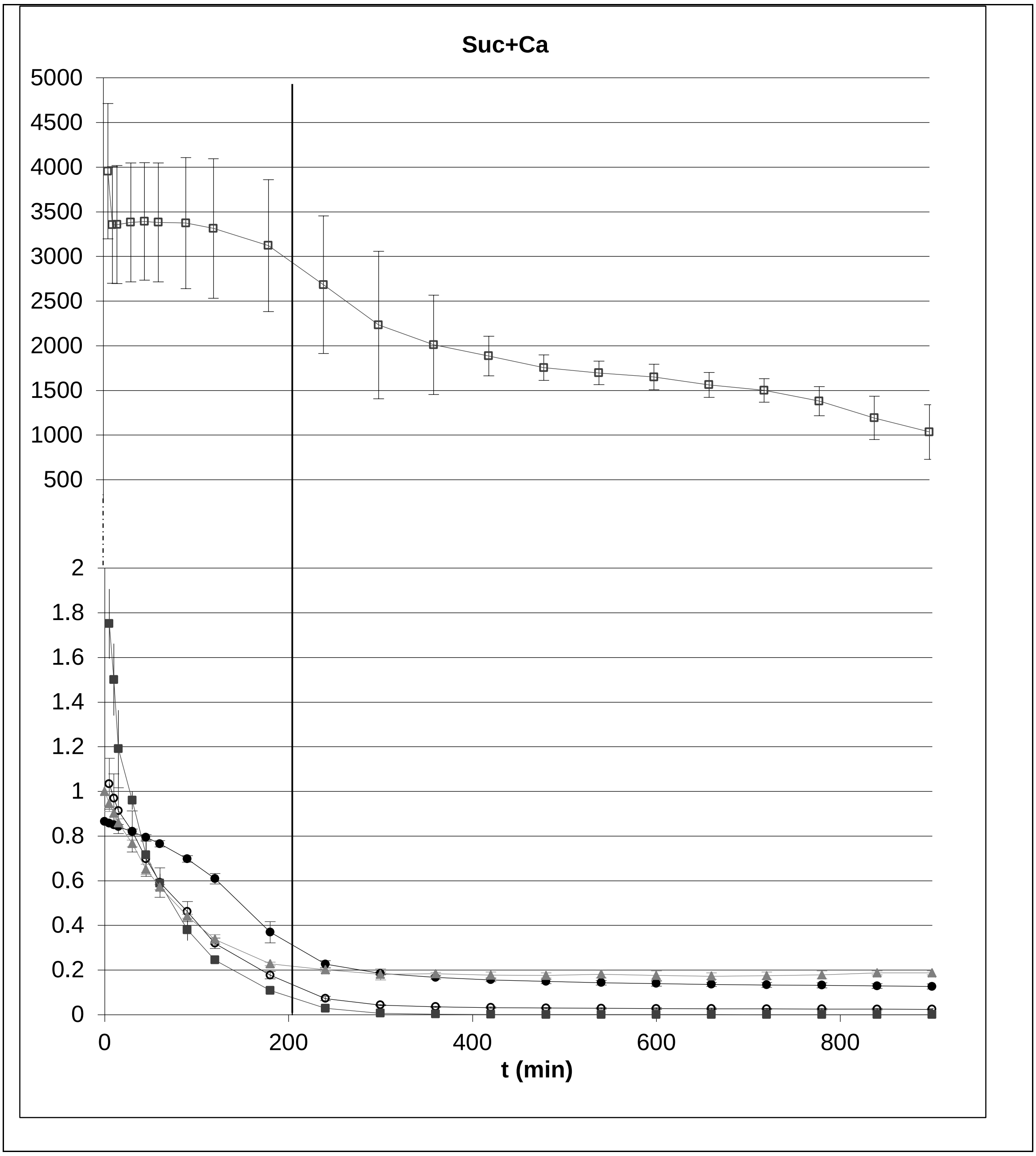
	X_1	X	γ_1	γ	ε_e	x_{sugar}	x_{Ca}
Suc	-0.0221 (0.0015)^{a}	0.19 (0.03)^{a}	0.008 (0.009)^{a}	0.02 (0.02)^{a}	0.205 (0.010)^{a}	0.149 (0.019)	-
Suc+Ca	-0.027 (0.007)^{a}	0.192 (0.019)^{a}	-0.003 (0.003)^{a}	0.0159 (0.010)^{a}	0.213 (0.012)^{a}	0.075 (0.006)	0.029 (0.002)
Tre	-0.042 (0.012)^{a}	0.17 (0.04)^{a}	0^{a}	0.01 (0.02)^{a}	0.208 (0.013)^{a}	0.15 (0.03)	-
Tre+Ca	-0.04 (0.02)^{a}	0.17 (0.05)^{a}	0.020 (0.017)^{a}	0.04 (0.04)^{a}	0.19 (0.02)^{a}	0.065 (0.015)	0.023 (0.005)

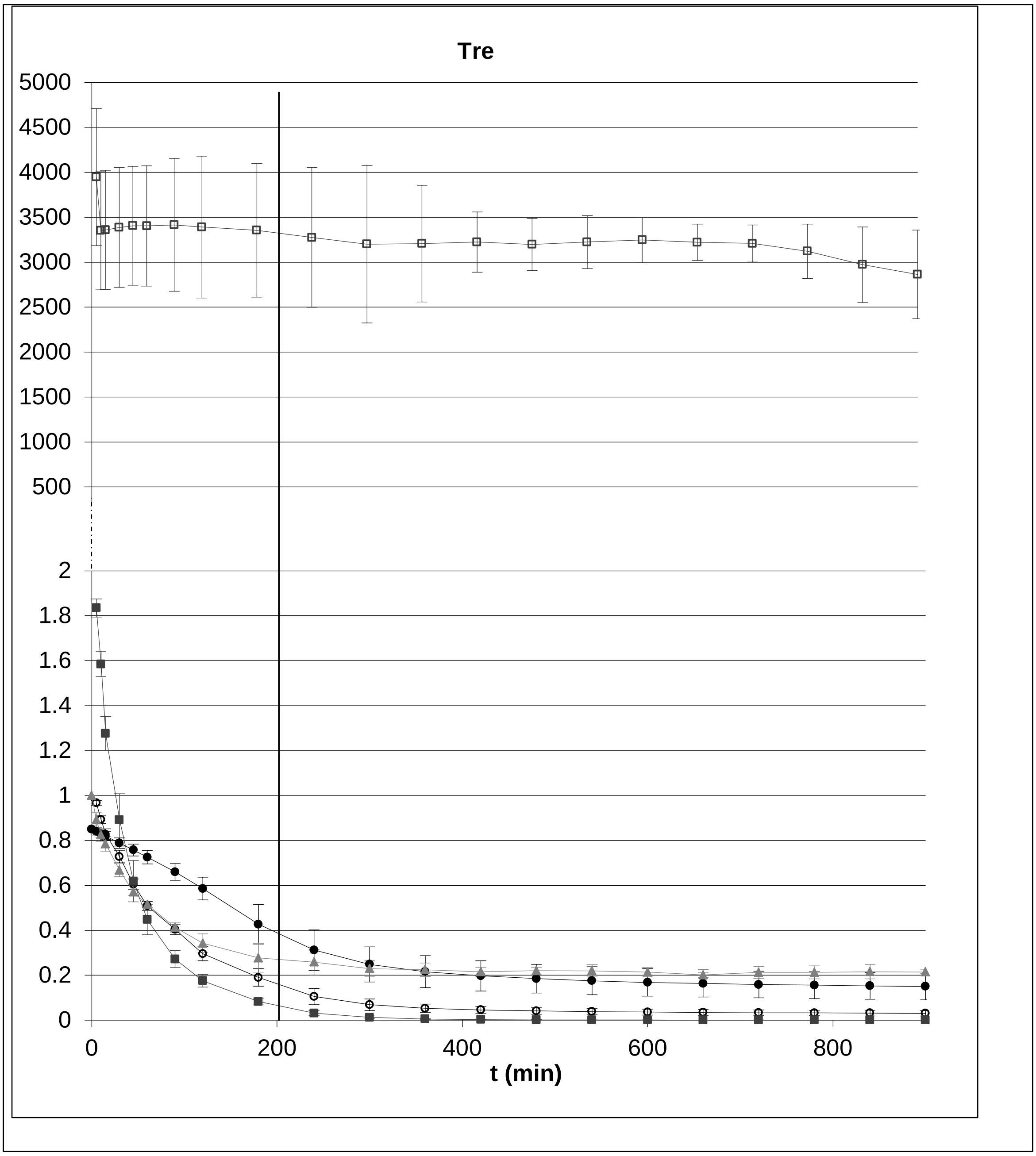
* Values with different superscript letters are significantly different ($p \leq 0.05$).

Table 3. Saturation times and correspondent humidities of the samples.

Treatment	x_w **(w.b)**	t_s **(min.)**
Suc	0.3028	211
Suc+Ca	0.3063	204
Tre	0.3431	202
Tre+Ca	0.3365	180


Suc
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
t (min)


Suc+Ca
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
t (min)



Tre
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
t (min)

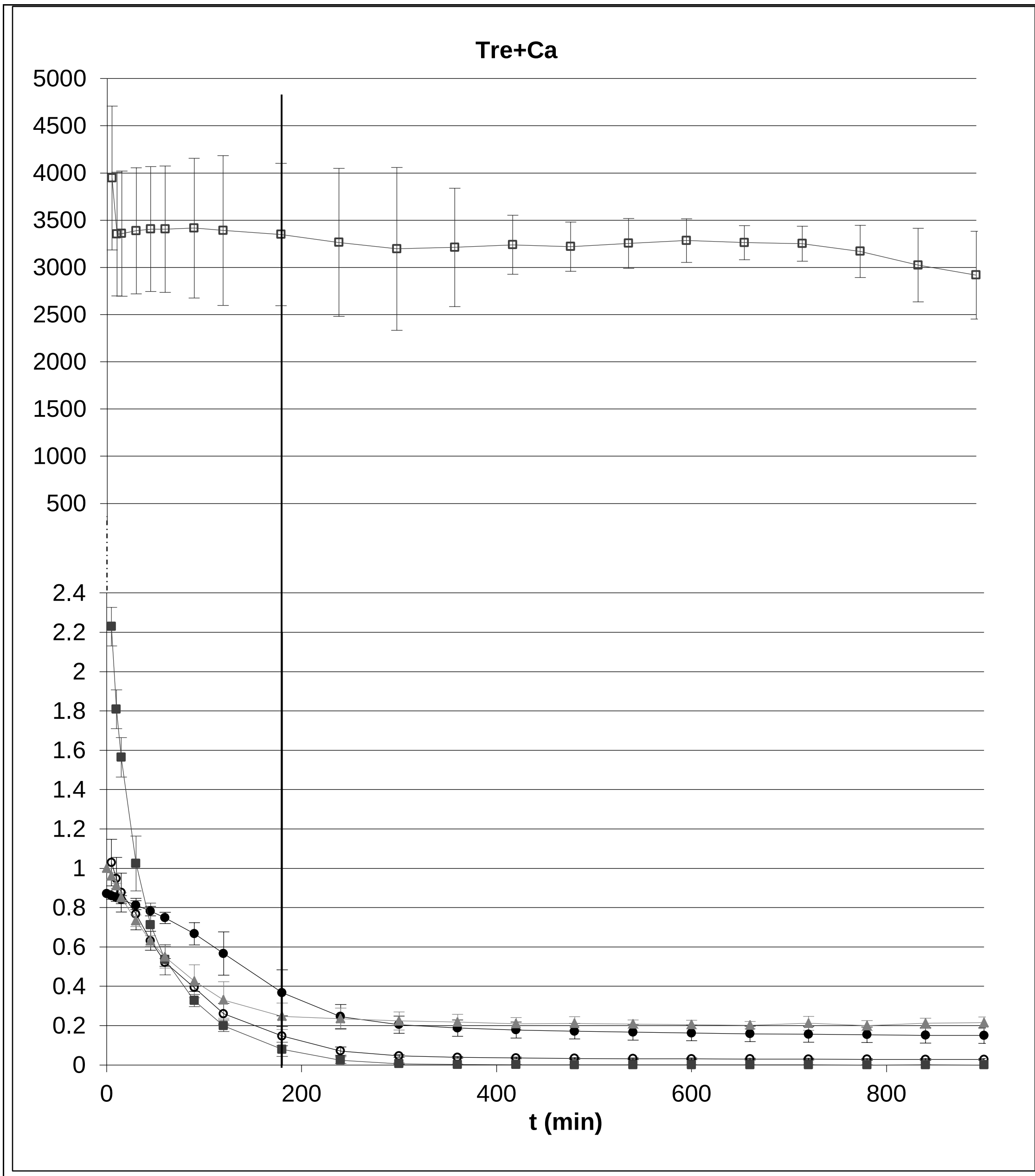


Figure 1. Representation of the humidity (w.b) ● (x_w), humidity (d.b) referred to the initial value ○ (x_w/x_{wo}), volume referred to the initial value ▲ (V/Vo), water flux ■ (J_w) ($mol/m^2 \cdot s$) and chemical potential □ ($RTLna_w/\varphi$) (J/mol) of the samples dried at 40 ºC versus time. Vertical line refers to the saturation time (t_s) (min).

493

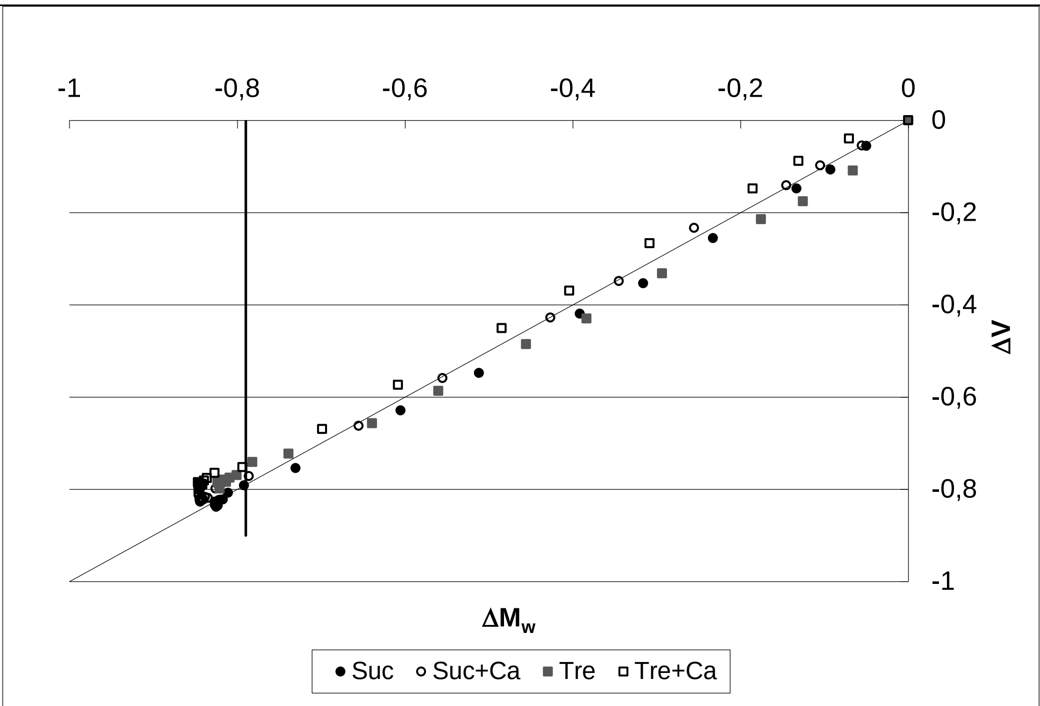


Figure 2. Variation of the total water versus total volume of the sample at 40 ºC. Vertical line refers to the saturation time (t_s) (min).

494

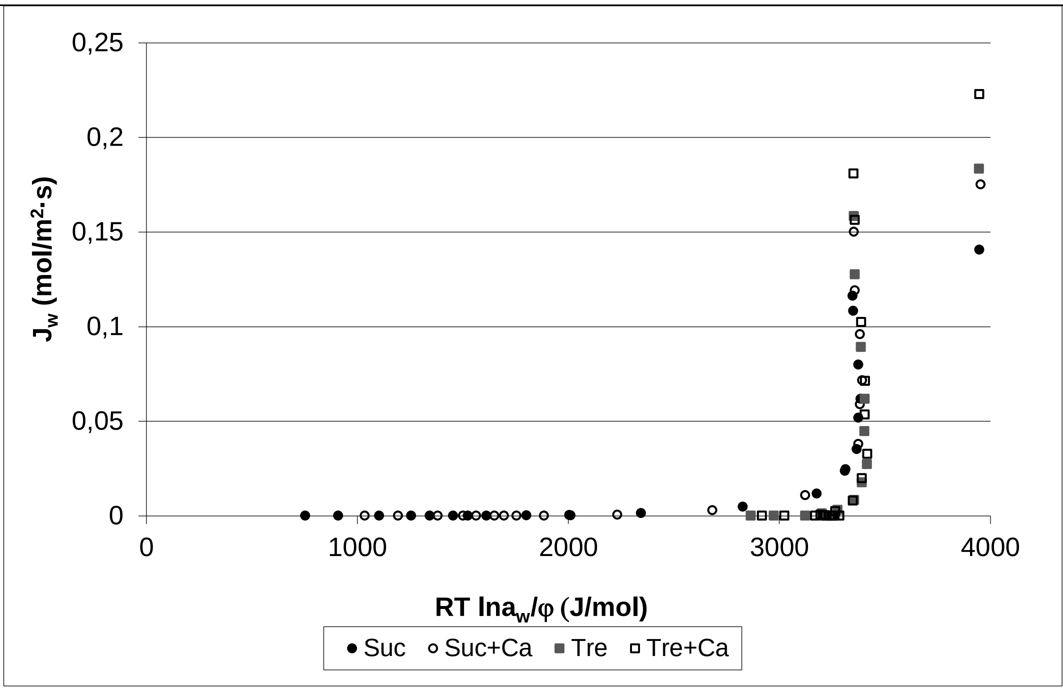


Figure 3. Variation of the water flux J_w ($mol/m^2 \cdot s$) versus driving force (J/mol).

495

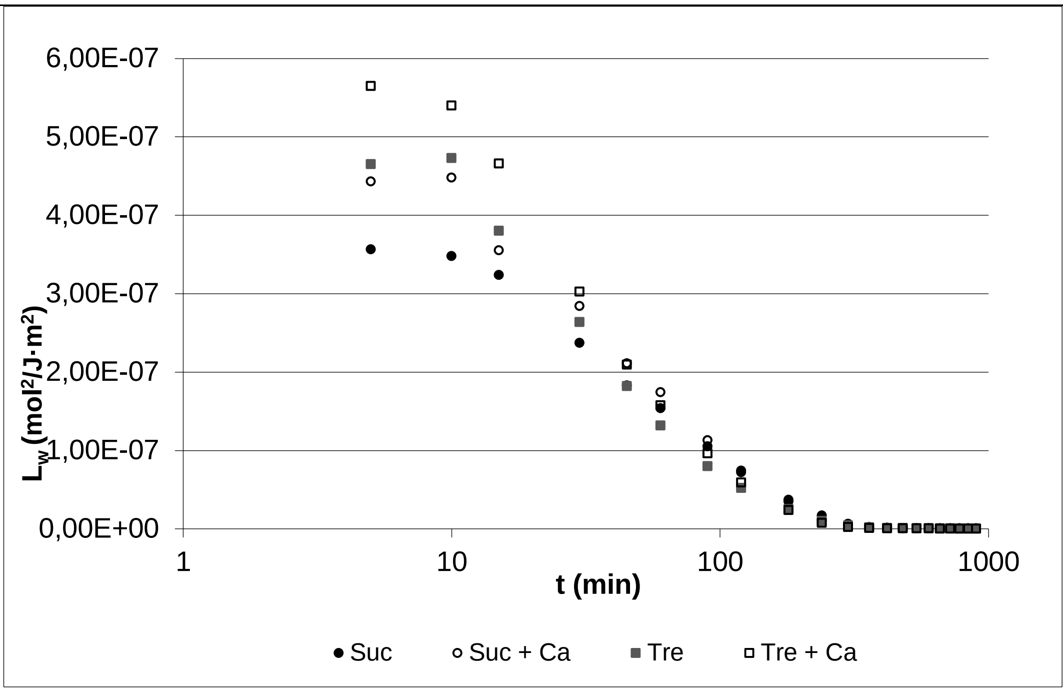


Figure 4. Variation of the phenomenological coefficient L_w ($mol^2/J \cdot m^2$) versus time t (min).

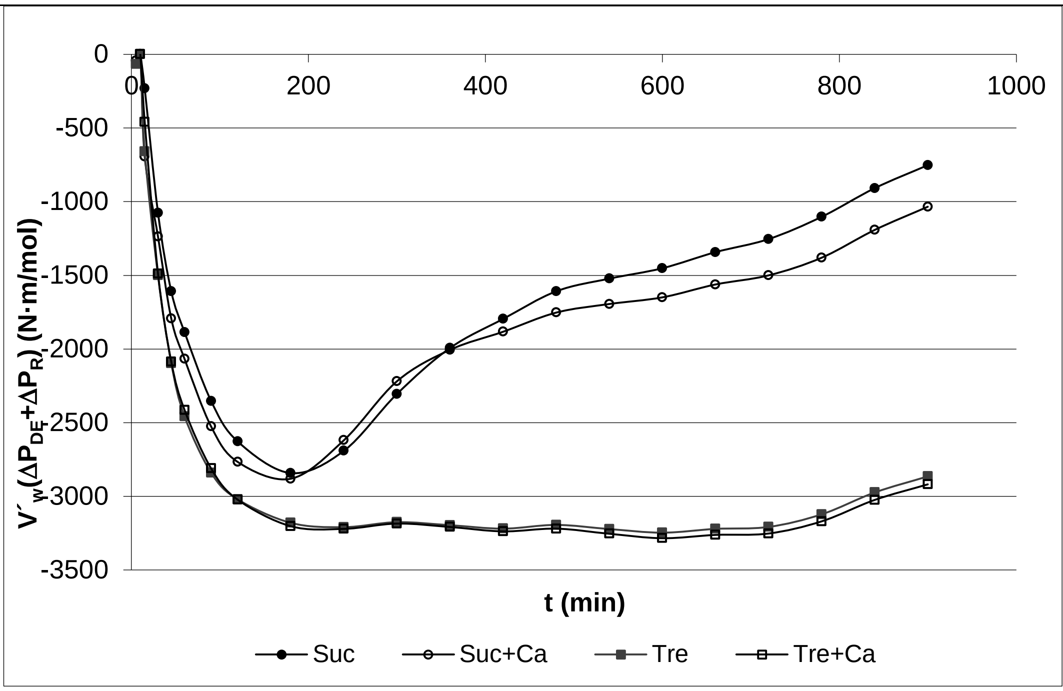


Figure 5. Evolution of the free energy to generate structural deformation/breakages efforts $V'_w(\Delta P_{DE}+\Delta P_R)$ (N·m/mol) versus time t (min).