Comparatives studies of different drying process of strawberry hot air drying freeze-drying and swell-drying : application on the biological compounds preservation

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Maritza ALONZO MACÍAS

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«Etudes comparatives de différents processus de séchage de fraise par air chaud, lyophilisation et autovaporisation instantanée ; application à la préservation des contenus biologiques »

Directeurs de thèse : Professeur. Karim ALLAF et Dr. José Gerardo MONTEJANO GAITÁN

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Maritza Alonzo Macías

March, 2013

Abstract

The aim of this study was to evaluate the effect of hot air drying (HAD), freeze-drying (FD) and swell drying (SD, which is a coupling of hot air drying to instant controlled pressure drop, DIC) on the strawberry (Fragaria var. Camarosa) to compare and to contrast its quality in terms of drying and rehydration kinetics, bioactive compounds and its antioxidant activity, and texture parameters as crunchy and crispy features. The obtained results shown that SD method helped to reduce the drying time leading to a low-cost processing compared with classical hot air drying and freeze-drying. SD globally preserved the strawberry's nutritional value and bioactive compounds, increasing their availability. Moreover, a strong correlation between antioxidant activity and total anthocyanin content was established in SD strawberries. On the other hand, the swell-dried strawberries showed an interesting macro and micro-structure. They presented a high expansion ratios and significant crispness provoked by the micro-alveolation phenomenon induced as consequence of the instant decompression process in the DIC treatment. Moreover, it was possible to instrumentaly measure the crispy/crunchy features of the final dried samples. By assessing such crispy and healthy contents of fruit "snacking", it was possible to modify, control, and optimize DIC operating parameters. And, it can be designed according to the industrial or consumer needs.

Résumé :

La présente étude concerne l’évaluation de l’impact du séchage par air chaud (HAD), lyophilisation (FD) et « swell drying » (SD), procédé couplant le séchage par air chaud avec le procédé de Détente Instantanée Contrôlée (DIC), sur les fraises (Fragaria var. Camarosa). Il s’agit de comparer et de contraster les performances des procédés et la qualité du produit fini séché en termes des cinétiques de séchage et de réhydratation, de contenus en molécules bioactives et activité antioxydante, et des paramètres caractéristiques de texture comme croquant et croustillant. Les résultats obtenus ont montré que le procédé de SD comparé aux procédés classiques de séchage et de lyophilisation, réduit d’une façon importante le temps de séchage ainsi que les coûts d’opération. D’autre part, SD conserve la qualité nutritionnelle des fraises en gardant leur contenu en composants bioactifs et en augmentant leur disponibilité. De plus, une corrélation importante entre la capacité antioxydante et le contenu total d’anthocyanes a été établie. D’autre part, les fraises séchées par SD ont montré une très intéressante macro et micro-structure. Les produits ont présenté une haute expansion et une croustillance significative dû au phénomène de micro-alvéolation par décompression instantanée par DIC. D’ailleurs, il a été possible de mesurer les caractéristiques instrumentales de croustillance/croquance des échantillons finaux séchés. Grâce à la possibilité de modifier, contrôler et optimiser les paramètres opératoires du procédé DIC, il a été possible d’obtenir un produit du type « snack » croustillant avec une très haute valeur nutritionnelle.

Table of Contents

Table List

Figures List

Nomenclature

HAD	Hot Air Drying
FD	Freeze-Drying
SD	Swell-Drying
db	Dry-basis
m_i	Material weight before (g)
m_d	Material weight after drying (g)
$D_{eff,d}$	Effective diffusivity of dehydration, m2/s
$\delta W_{s,d}$	Starting accessibility of dehydration, db
$td_{3.0\%}$	Drying time at 3.0%, min
$D_{eff,r}$	Effective diffusivity of rehydration, m2/s
$\delta W_{s,r}$	Starting accessibility of rehydration, db
$tr_{300\%}$	Rehydration time at 300%, min
WHC	Water holding capacity, db
TPC	Total phenolic content (mg eq. GA/g db)
FC	Flavonoid content (mg eq. Rutin/g db)
TAC	Total anthocyanins content (mg eq. Pe-3-Gl/g db)
Cy-3-Gl	Cyanidin-3-glucoside (mg/g db)
Pe-3-Gl	Pelargonidin-3-glucoside (mg/g db)
DPPH	Antioxidant activity (%)
F_{max}	Maximum penetration force (N)
X_{max}	Maximum penetration distance (mm)
W_{max}	Total work at Xmax

<F>	Average puncturing force (N)
n	Total number of peaks
N	Spatial frequency of structural micro-ruptures (m-1)
f	Average micro-ruptures force (N)
wrupture	Average work for micro-ruptures
ΔX	Penetration distance for each micro-rupture peak (mm)
ΔF	Individual force drops for each micro-rupture peak (N)
$\varepsilon_{absolute}$	Absolute expansion ratio
$\varepsilon_{relative}$	Relative expansion ratio
$\rho_{intrinsic}$	Density intrinsic (g/cm3)
$\rho_{specific}$	Density specific (g/cm3)
ρ_{sand}	Density of sand (g/cm3)
m_{sample}	mass of sample (g)
m_{sand}	mass of sand (g)
$m_{s,1}$	mass initial of sand (g)
$m_{s,2}$	mass final of sand (g)

Introduction

Strawberry is universally recognized as having a basic chemical composition that accentuates their sweet taste, fruity aroma, and healthy properties that are enjoyed by societies throughout the world. It is a good source of essential vitamins and minerals, and has diverse phytochemical compositions that relate to consumer satisfaction and health (da Silva et al., 2007). The chemical composition strawberry can be highly variable depending on the cultivar, growing location, ripeness stage, and harvest and storage conditions.

Around the world, it is consumed "in natura" or in processed form, such as jams, juices, and jellies by their sweet taste and potential benefits to the health (Giampieri et al., 2012). Mainly, strawberry contains phenolic compounds and anthocyanins, two large and heterogeneous groups of biologically active molecules, they are known by their antioxidant activities (Panico et al., 2009). Phenolic compounds present in strawberries are ellagic and p-coumaric acid; flavonoids as quercetin, kaempferol and myricetin. Anthocyanins are a group of phenolic compounds responsible for the red-blue color of many fruits and vegetables. Pelargonidin 3-glucoside, cyaniding 3-glucoside and pelargonidin 3-rutinoside are the main anthocyanins found in strawberries, which are responsible for their bright red color (Böhm, 1994; Crecente-Campo et al., 2012). Moreover, several researchers have demonstrated that strawberry have a greater antioxidant capacity (2-to 11-fold) than apples, peaches, grapes, … (Wang et al., 1996; Scalzo et al., 2005). And, by its antioxidant activity, they are important in the prevention of certain types of cancers, as well as, anti-inflammatory functions, cardiovascular, obesity and other chronic diseases (Crecente-Campo et al., 2012).

Unfortunately, strawberry postharvest life is relatively short, due to their highly fragile structure and their high rates of respiration (Modise, 2008). At the same time, it is highly susceptible to bruises and fungal attacks (Blanda et al., 2009). This problem affects also its bioactive compounds and antioxidant activity.

Hence, to extent the shelf-life strawberry and preserve its bioactive activity, large range of unit operations have been proposed and used to preserve it. New operations such swell-drying (instant controlled pressure drop, DIC-assisted hot air drying) is proposed. DIC is a high temperature short time (HTST) treatment followed by an abrupt pressure drop towards a vacuum implying an autovaporization of small amount of water from the products.

Therefore, the swell-drying products have a controlled texture expansion to improve the quality product and the physical properties. This texture change results in higher porosity, as well as the increases of the specific surface area and reduces the diffusion resistance of moisture during the final dehydration step (Mounir et al., 2012). Moreover, this structural change provides a versatile function in the dried foods, producing the "snacking". But it could be considered as a highly-functional snack, due to its preservation of vitamins, bioactive compounds, color and flavor. And, it is proposed that crunchiness and crispiness are the textural attributes that better describe the snack quality and even freshness. Both, crunch and crisp features are studied by instrumental methods, as puncture test. This method can provide important information about the functionality of fruit snack and it can be supported by microstructure analysis.

In consequence, this study is structured as follows. In the first section, the literature review is presented. The results section is divided in three chapters, each one presents a paper published, except the last, it is in revision by the journal.

PART I

LITERATURE REVIEW

CHAPTER I.1

STRAWBERRY ASSESSMENT

I.1.1 Strawberry

The popularity and worldwide demand for fresh and processed strawberries have made them one of the most extensively researched berries in the world. The quality of fresh strawberries as a function of their chemical composition and organoleptic attributes is an important area of study (Zhao, 2007). Color, texture, odor and the balance between sweetness and sourness have been identified as important determinants of overall quality of strawberry fruit (Montero et al., 1996). And, numerous studies have indicated that strawberry's quality is the most important factor that influence for consumer acceptance (Montero et al., 1996; Cordenunsi et al., 2003; da Silva et al., 2007; Hancock et al., 2008; Giampieri et al., 2012; Holzwarth et al., 2012).

I.1.1.1 Definition and plant varieties

The strawberry (Fragaria x ananassa Duch.), a member of the rose family, is not really a berry, but an achene or "false" fruit. A strawberry consists of many tiny individual fruits embedded in fleshy scarlet receptacle. The brownish or whitish specks, commonly considered seeds, are the true fruits, known as achenes. Each achene surrounds a tiny seed. These berry components make strawberries relatively high in fiber (Harris, 2007). In Figure 1 a typical fresh strawberry is shown.

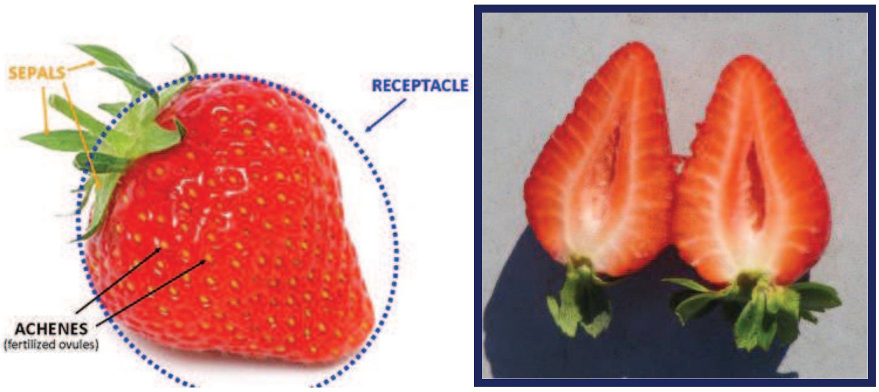


Figure 1. Typical strawberry in fresh form (Camarosa variety).

Nowadays, over 600 different strawberry varieties are in the worldwide (Source: “USDA”). They are stem from five or six original wild species. The strawberry varieties are so different in shape, color and taste. Typically, the larger the berry, the more water it contains, the smaller the berry, the greater the intensity of flavor (Figure 2). Also, all of them are available in the commercial market.

In United States, there are over 100 varieties offered by over 40 different companies. Specifically, the state of California has several strawberry varieties in commercial production, each with its own characteristics, advantages and harvest time. And the University of California developed 55.1% of varieties used for the total state acreage in 2011 (Source: “CSC”).

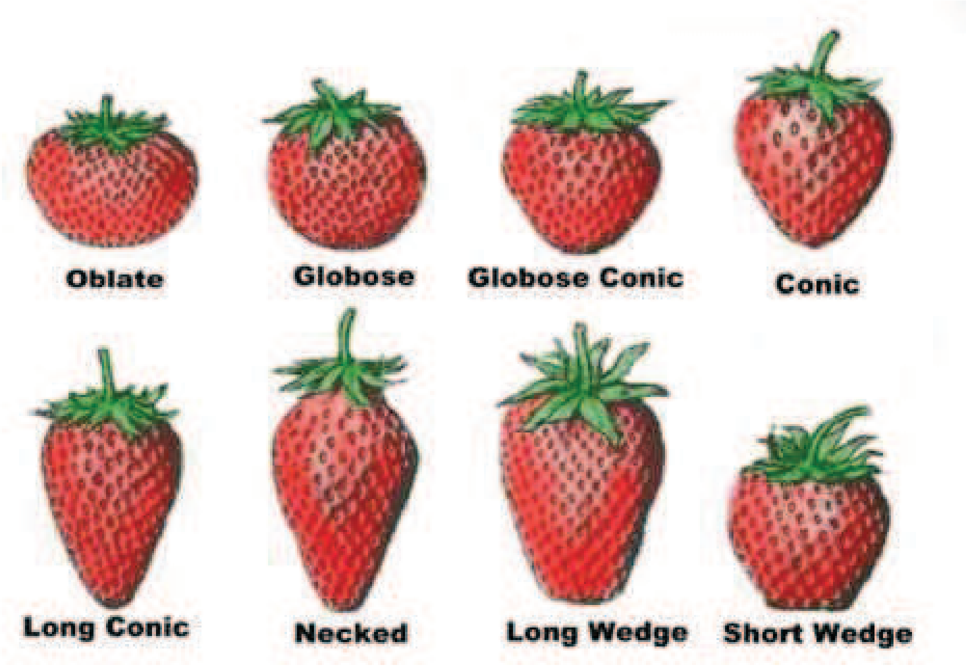


Figure 2. Typical strawberry shapes. Source: “CSC”

Some varieties of strawberry patented by the University of California patented are Aromas, Camarosa, Camino Real, Capitola, Carlsbad, Chandler, Diamante, Fern, Gaviota, Irvine, Oso Grande, Pacific, Seascape, Selva and Ventana. Descriptions of some of them are as follows (Source: “CSC” and “NCCIA”):

- Aromas. It is large and firm fruit. It has a great flavor with good color and a bright sheen.
- Camino Real. It is firm and has a dark red fruit with a long shelf life and good flavor.

- Chandler. Fruit is medium to large, long to flattish wedge, moderately firm, juicy berry with good flavor and freezes well.
- Camarosa. It was released by the University of California in 1992 with the US Plan Patent No.08708. This fruit is larger and firmer than Chandler, very flat conic, productive, has good appearance, is very firm, has good flavor, and is widely adapted producing fruit over an extended period at low latitudes. Can be used for fresh-market and processing. Also, it is the most productive variety in the worldwide.

There are other important varieties in the market, as Festival, Palomar, Sweet Charlie, Florida and Albion (Source: “NCCIA”)

I.1.1.2 Nutritional composition

Strawberry is excellent source of vitamins and minerals, such vitamin C, folate and potassium. And, it is relatively low in calories. The strawberry nutritional label is shown in Table 1. (Harris, 2007). Thanks to its composition, it is consume frequently in fresh condition; however, the fresh product is usually locally available over a very limited time and production far outweighs fresh demand.

Table 1. Nutrition facts for whole strawberries. Source: USDA National Nutrient Database.

Nutrition Facts	Amount Per Serving	% DV*	Amount Per Serving	% DV*
Seving Size 1 cup (144 g)	**Total Fat** 0g	1%	**Total Carbohydrate** 11 g	4%
	Saturated Fat 0 g	0%	Dietary Fiber 3 g	12%
Calories **50**	**Cholesterol** 0 mg	0%	Sugars 7 g	
Fat Calories 4	**Sodium** 1 mg	0%	**Protein** 1 g	
**Percent Daily Values are based on a 2, 000 calorie diet. Your daily values may be higher or lower depending on your calorie needs.*	Vitamin A 0%	Vitamin C 141%	Calcium 2%	Iron 3%

I.1.2 Worldwide production

The strawberry is native to temperate regions around the world. It is grown in annual or perennial production systems in the field or is planted in soilless media in tunnels or greenhouses to target “off-season” markets. Hence, the worldwide production of strawberry estimated in 2011 was 4.6 million tons, Table 2.

Table 2. World strawberry production in tons. Source: "Faostat"

Country	2006	2007	2008	2009	2010	2011
USA	1,090,440	1,109,220	1,148,530	1,270,620	1,292,780	1,312,960
Turkey	211,127	250,316	261,078	291,996	299,940	302,416
Spain	330,485	269,139	281,240	263,700	275,300	514,027
Egypt	128,349	174,414	200,254	242,776	238,432	240,284
Korea, South	205,307	203,227	192,296	203,772	231,803	NA
Mexico	191,843	176,396	207,485	233,041	226,657	228,900
Japan	190,700	191,400	190,700	184,700	177,500	182,091
Poland	193,666	174,578	200,723	198,907	176,748	166,159
Germany	173,230	158,658	150,854	158,563	166,911	154,418
Russia	227,000	230,400	180,000	185,000	165,000	184,000
Italy	143,315	160,558	155,583	163,044	153,875	150,000
Morocco	112,000	120,000	130,000	355,020	140,600	140,733
Total world	3,973,243	4,001,721	4,136,802	4,596,614	4,366,889	4,594,539

NA: No Data Available

The main contributors, descending in order of production, were USA, Turkey, Spain, Egypt, and Mexico (Figure 3, FAO, 2013). In 2011, the Unites States had 56,140 acres harvest and 1.3 million tons, making it the largest producer in North America (FAO, 2013 and USDA, 2013). In United States, 63% and 13% of the total acreage is in California and Florida, respectively, where strawberry is produced using annual production systems and more than 75% is fresh marketed (Figure 4, USDA, 2013). Fresh strawberry is available year-round using traditional annual and perennial production systems (Zhao, 2007). Other states in the United States produce strawberries predominantly using perennial production systems, with the third largest produces, Oregon (6% of acreage), processing more than 95% on their production (Figure 4, USDA, 2013). However, it is difficult for states like Oregon, that produce high-quality processed strawberry, to compete with processed fruit produced at lower cost in Mexico and California.

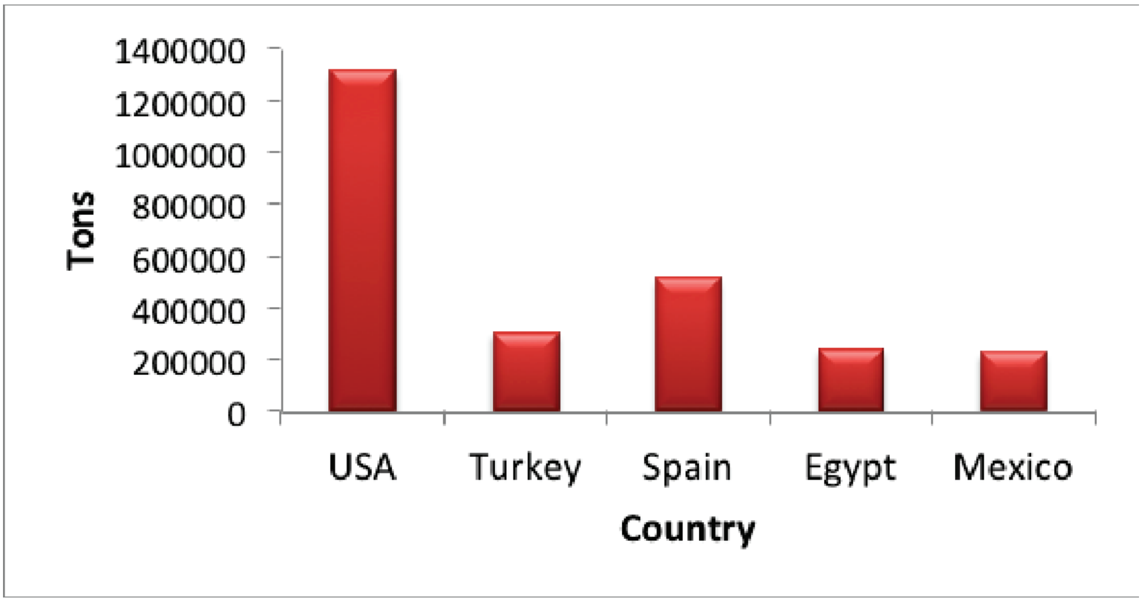


Figure 3. World strawberry production in 2011. Source: "Faostat"

The most common commercial varieties in California are the Camarosa, Diamante, Chandler, and Selva. Proprietary and other varieties, representing about 32% of acreage, are bred and grown for individual shipping companies, and are not available to the public (Harris, 2007).

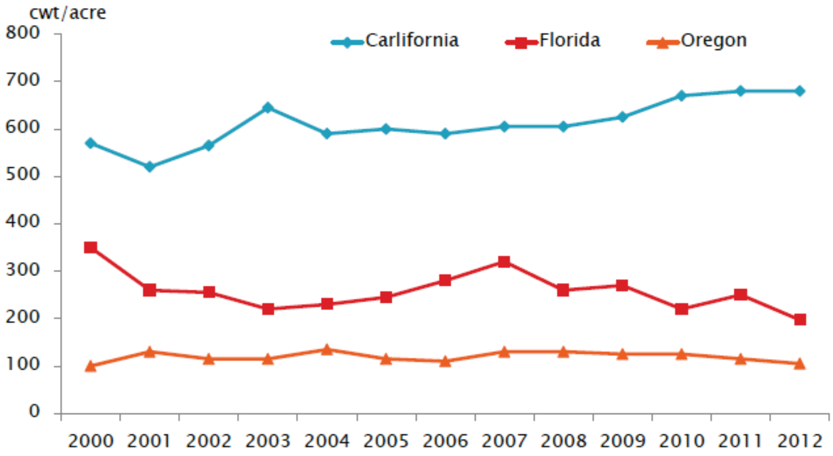


Figure 4. *Mean strawberry production in United States. Source: "USDA"*

According the Food and Agriculture Organizations of the United Nations (FAO, 2013), in 2011 Mexico produced 228,900 tons of strawberries on 17,243 acres using annual production systems (Table 2). Mexico typically exports about 30,000 tons/year, of which 70% is processed and 30% is fresh. Most of the exports are to the United States, but fruit is also shipped to Canada, Japan, and Europe (SIAP, 2013).

The strawberry's production in Turkey has increased considerably over the last 10 years (Table 2). Indeed, Turkey is the mean country of Middle East that produced more than 70% of strawberry (Table 3). The production of this fruit in Turkey is mostly on small family farms. Other strawberry-producing countries in this region were Iran (21%), Israel (3%), Lebanon, Palestine, Cyprus, and Jordan (FAO, 2013).

On the other hand, 84% of the total acreage in Africa was accounted by Egypt and Morocco (Table 3). There was also some strawberry production in South Africa, Tunisia, and Zimbabwe. The Californian cultivars in annual production systems were the mean used in most areas of this region. And, Egypt exported mainly to the United Kingdom.

Concerning to South America, strawberries were planted in Chile (28% of the total acreage), Peru (27%), Columbia (15%), Venezuela, Brazil (9%), Paraguay (6%), and Ecuador (4%). About 50% to 70% of the strawberries were shipped fresh, while 30% to 50% were shipped frozen. There was also some strawberry production in Central America, mainly in Guatemala and Costa Rica (Table 3). And, the Californian cultivars in the annual production systems were common.

In Oceania, Australia was the main country with the production of strawberry. It had 79% of the acreage (Table 3).

Table 3. Worldwide production of strawberry in 2011. Source: "Faostat"

Region	Area (Acres)	Production (Tons)
Africa	24,384	396,090
Asia	78,377	749,625
Central America	18,597	241,998
Europa	391,766	1,686,901
Middle East	34,968	336,984
Oceania	6,037	37,350
South America	19,287	149,005
World total	603,636	4,594,539

In addition, the production of organic strawberry is not easy to obtain. However, Zhao (2007) reported that in the 2006 the 3% of the total acreage in California was for the organic strawberries. But, the producers forecast an increase in coming years.

Otherwise, fresh strawberries are most commonly shipped in clamshell containers. Strawberries are processed as individually quick frozen (IQF), bulk frozen, sliced and sugared, freeze-dried, pureed, or juice/concentrate (Harris, 2007).

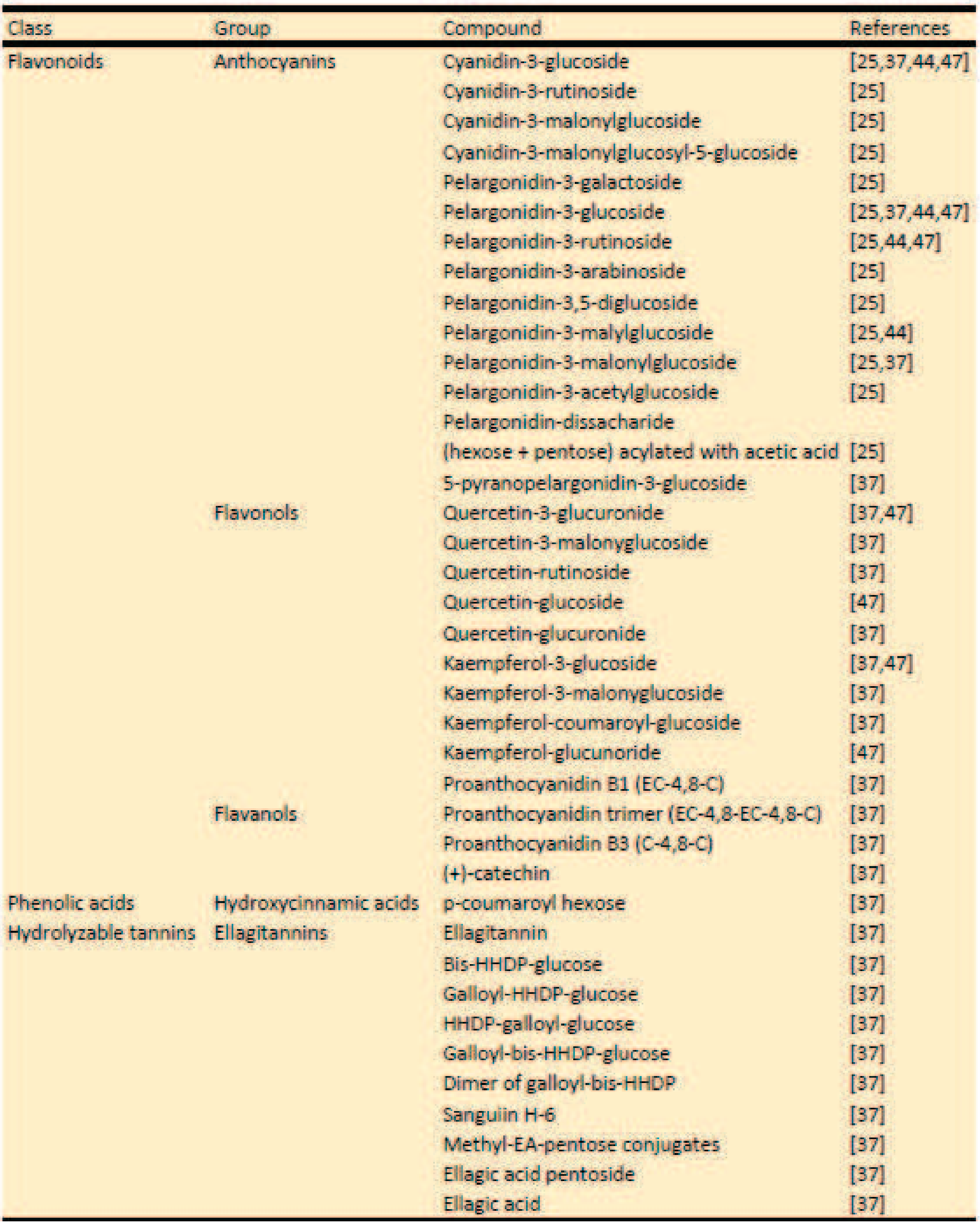
I.1.3 Phytochemicals in strawberry

The "phyto-" of the word phytochemicals is derived from the Greek word phyto, which means plant. Therefore, literally phyto-chemicals are "plant chemicals". And, they are defined as bioactive non-nutrient plant compounds in fruits, vegetables, grains, and other plant foods that have been linked to reducing the risk of major chronic diseases (Liu, 2004). These phytochemicals can be divided into several categories including carotenoids, phenolics, alkaloids, nitrogen-containing compounds, and organosulfur compounds (Figure 5). One of the largest categories of phytochemicals is phenolic compounds. The structure of phenolic compounds contains aromatic ring(s) bearing hydroxyl group(s) and can range from simple molecules to very large oligomers (Seeram et al., 2006). Moreover, phenolic compounds are plant metabolites that are very sensitive and vulnerable to change because they are easily oxidized (Herrera and Luque de Castro, 2005). And, they are found in many fruits and vegetables but are specially abundant in berry fruits (Seeram et al., 2006).

I.1.3.1 Phenolic compounds in strawberry

Phenolic compounds in strawberry are represented by the flavonoids (mainly anthocyanins and flavonols; however, flavanols providing a minor contribution), followed by hydrolyzable tannins (ellagitannins and gallotannins) and phenolic acids (hydroxybenzoic acids and hydroxycinnamic acids), with condensed tannins (proanthocyanidins) being the minor constituents (Giampieri et al., 2012). However, strawberry's phenolic content varies with the cultivar, growing conditions, degree of ripeness, and handling after harvest (Hannum, 2004). Variability in the data is also due to methodological differences, since there is a lack of agreement on what is the appropriate method to analyze these compounds. All of these factors make it difficult to compare the results of different research studies (Zhao, 2007).

Table 4. Polyphenol composition reported in strawberries by Giampieri et al. (2012)



Class	Group	Compound	References
Flavonoids	Anthocyanins	Cyanidin-3-glucoside	[25,37,44,47]
		Cyanidin-3-rutinoside	[25]
		Cyanidin-3-malonylglucoside	[25]
		Cyanidin-3-malonylglucosyl-5-glucoside	[25]
		Pelargonidin-3-galactoside	[25]
		Pelargonidin-3-glucoside	[25,37,44,47]
		Pelargonidin-3-rutinoside	[25,44,47]
		Pelargonidin-3-arabinoside	[25]
		Pelargonidin-3,5-diglucoside	[25]
		Pelargonidin-3-malylglucoside	[25,44]
		Pelargonidin-3-malonylglucoside	[25,37]
		Pelargonidin-3-acetylglucoside	[25]
		Pelargonidin-dissacharide (hexose + pentose) acylated with acetic acid	[25]
		5-pyranopelargonidin-3-glucoside	[37]
	Flavonols	Quercetin-3-glucuronide	[37,47]
		Quercetin-3-malonyglucoside	[37]
		Quercetin-rutinoside	[37]
		Quercetin-glucoside	[47]
		Quercetin-glucuronide	[37]
		Kaempferol-3-glucoside	[37,47]
		Kaempferol-3-malonyglucoside	[37]
		Kaempferol-coumaroyl-glucoside	[37]
		Kaempferol-glucunoride	[47]
	Flavanols	Proanthocyanidin B1 (EC-4,8-C)	[37]
		Proanthocyanidin trimer (EC-4,8-EC-4,8-C)	[37]
		Proanthocyanidin B3 (C-4,8-C)	[37]
		(+)-catechin	[37]
Phenolic acids	Hydroxycinnamic acids	p-coumaroyl hexose	[37]
Hydrolyzable tannins	Ellagitannins	Ellagitannin	[37]
		Bis-HHDP-glucose	[37]
		Galloyl-HHDP-glucose	[37]
		HHDP-galloyl-glucose	[37]
		Galloyl-bis-HHDP-glucose	[37]
		Dimer of galloyl-bis-HHDP	[37]
		Sanguiin H-6	[37]
		Methyl-EA-pentose conjugates	[37]
		Ellagic acid pentoside	[37]
		Ellagic acid	[37]

EA, ellagic acid; HHDP, galloylbis-hexahydroxydiphenoyl.

[25] is da Silva et al. (2007); [37] is Aaby et al. (2007); [44] is Tulipani et al. (2008);and [47] is Wang and Millner (2009)

The Folin Ciocalteu (FC) reagent is the common method for determining the amount of total phenolics in berries, with the total amount of phenolics expressed as gallic acid equivalents. Even though, this method has several limitations, such as differential responses of various groups of phenolics to the FC reagent and interference from nonphenolic compounds with reducing capacity, it is a simple assay to perform and has been widely used (Montero et al., 1996; Kähkönen et al., 1999; Zhao, 2007; de Oliveira et al., 2009).

Giampieri et al. (2012), gathered the main polyphenol composition in strawberries reported by different studies (Table 4).

I.1.3.2 Anthocyanins

The anthocyanins group is responsible for cyanic colors ranging from salmon pink through red and violet to dark blue of most flowers, fruits, and leaves angiosperms (Quideau, 2006). In the case of strawberry and other berries, the anthocyanins give to berries their red and blue hues and also, they act as potent antioxidants (Mazza, 2007). Hence, the anthocyanin composition in strawberry has been the object of various studies, but is still not fully characterized regarding minor pigments (da Silva et al., 2007). However, anthocyanins in strawberries are the best known polyphenolic compounds and quantitatively the most important (Giampieri et al., 2012). More than 25 different anthocyanin pigments have been described in strawberries of different varieties and selections (da Silva et al., 2007). However, pelargonidin-3-glucoside (Pe3Gl) is the major anthocyanin in strawberries independent from genetic and environmental factors, and the presence of cyanidin-3-glucoside (Cy3Gl) seems to be constant in strawberries, although only in smaller proportions, Figure 6 (Hannum, 2004; Tulipani et al., 2008). The concentration of both, Pe3Gl and Cy3Gl are in function of the strawberry cultivar. da Silva et al. (2007) analyzed five different cultivars of strawberry (i.e. Eris, Oso Grande, Carisma, Tudnew and Camarosa) and found that the total anthocyanin content ranged between 200 and 600 mg/kg, with Pe3Gl constituting 77-90% of the anthocyanins in the strawberry extracts followed by Cy3Gl (3-10%) and the Camarosa cultivar presented the highest values.

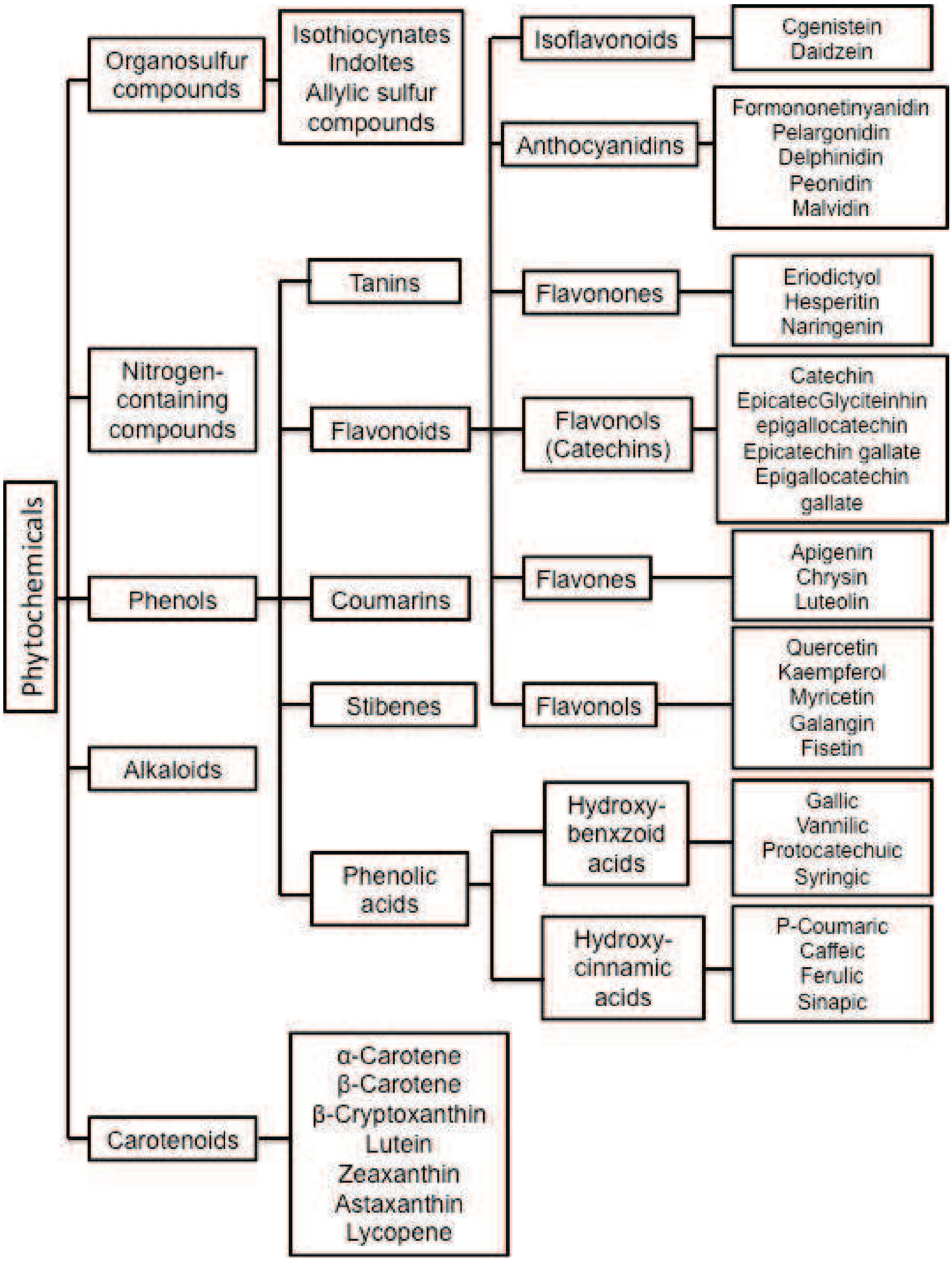


Figure 5. Classification of dietary phytochemicals by Liu (2004).

On the other hand, anthocyanin content increases with ripeness of the fruit, changing from 2 μg/g in small green strawberries to 389 μg/g in fully ripe berries (Hannum, 2004). Kalt et al. (1999) found that the strawberries's anthocyanin content increased during 8 days of storage. And, the magnitude of the change was temperature dependent, the content increased 1.7-fold at 0◦C and 6.8-fold at 30◦C. Wesche-Ebeling and Montgomery (1990) reported a considerable degradation of anthocyanins in processed strawberries due to oxidative enzymes. Hence, anthocyanins' stability depends on their structure as well as on the matrix and composition of the medium. Temperature, pH, light, oxygen and ascorbic acid highly affect the half-life of anthocyanins (Hartmann et al., 2008). Anthocyanins also condense with other phenolic compounds to form oligo- and polymers (Fernandez-Panchon et al., 2008). Moreover, the anthocyanins' changes during processing and storage are visible to the naked eye, especially in the case of strawberry products which are characterized by fast browning (Hartmann et al., 2008).

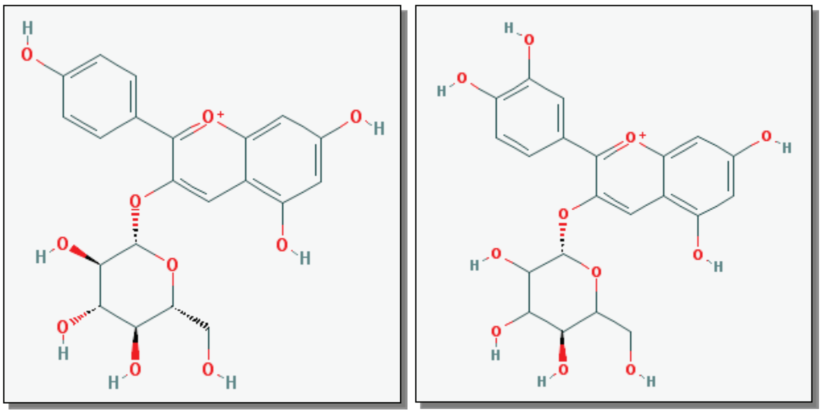


Figure 6. Structure of mean anthocyanins in strawberry. Left) Pelargonidin 3-glucoside, and Right) Cyanidin 3-glucoside

I.1.3.3 Antioxidant activity

The antioxidant power of fruit is closely correlated to the presence of efficient oxygen radical scavengers, such vitamin C and phenolic compounds (Giampieri et al., 2012). Several researchers have demonstrated that strawberry have a greater antioxidant capacity (2-to 11-fold) than apples, peaches, grapes, …. (Wang et al., 1996; Scalzo et al., 2005). In a study by Halvorsen et al. (2006) over 1,000 foods and beverage were analyzed for determine its antioxidant capacity and found that strawberry was ranked third in total antioxidant capacity (TAC) per serving. Only blackberries and walnuts were found to be higher in antioxidant capacity.

Otherwise, TCA is strongly influenced by the individual contribution of different phytochemical compounds in fruit. It means that there is a linear relationship of phenolics and anthocyanins and antioxidant capacity (Zhao, 2007). The study realized by Tulipani et al. (2008), where different strawberries cultivars were analyzed, demonstrated that vitamin C was the responsible for more than 30% of the TAC of strawberry extracts, followed by anthocyanins (25-40%), and the rest was composed mainly by ellagic acid derivatives and flavonols.

On the other hand, there are several methods to analyze the TAC in fruits; however the mainly assays reported and used in strawberry by different researches are as follows:

a. ORAC assay, than can be performed using either phycoerythrin (PE) or fluorescein (FL) as fluorescent probe. It must be taken into account that ORAC-FL renders values four times higher with respect to ORAC-PE (Fernandez-Panchon et al., 2008).
b. ABTS [2,2-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid)]. In this assay, ABTS is converted to its radical cation by addition of sodium persulfate. This radical cation is blue in color and absorbs light at 734 nm. The ABTS radical cation is reactive towards most antioxidants including phenolics, thiols and Vitamin C. During this reaction, the blue ABTS radical cation is converted back to its colorless neutral form. The reaction may be monitored spectrophotometrically. This assay is often referred to as the Trolox equivalent antioxidant capacity (TEAC) assay. The reactivity of the various antioxidants tested is compared to that of Trolox, which is a water-soluble analog of vitamin E (Re et al., 1999).
c. FRAP reagent (ferric reducing antioxidant power). Ferric to ferrous ion reduction at low pH causes a colored ferrous-tripyridyltriazine complex to form. FRAP values are obtained by comparing the absorbance change at 593 nm in test reaction mixtures with those containing ferrous ions in known concentration (Benzie and Strain, 1996).
d. DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging as a free radical. The scavenging capacity of DPPH is evaluated as its percent of discoloration and expressed as antiradical activity (% ARA) (Oomah et al., 2005)

In addition, is important take into account that different values can be obtained for TAC of strawberry due to internal factors as the maturity degree or the genotypic variety, or external factors as the geographical area and the climate where the strawberry was cultivated, inclusive the laboratory where the method was performed (Fernandez-Panchon et al., 2008).

I.1.4 Strawberry and health effects

The hypothesis that dietary antioxidants lower the risk of chronic disease was developed from epidemiological studies. These studies have consistently shown that consumption of whole foods, such as fruits, vegetables, and whole grains, is strongly associated with reduced risk of chronic diseases, especially cancer and cardiovascular disease (Liu, 2004).

In the case of strawberry, in recent years, numerous studies have proven that its wide variety of phytochemicals is bioactive. For example, anthocyanins display a wide range of biological activities, including antioxidant, anti-inflammatory, antimicrobial and anti-carcinogenic activities; improvement of vision; induction of apoptosis; and neuroprotective effects (Mazza, 2007)

Likewise, the individual components of strawberry have demonstrated inhibition of LDL oxidation and lipid peroxidation (Hannum, 2004). And, because of the antioxidant power of the phenolic compounds in strawberries, consumption of this fruit may well have the potential to lower risk of heart disease (Giampieri et al., 2012).

Also, animal studies have indicated that the antioxidant activity of strawberries has the potential to provide benefits to the aging brain (Fernandes et al., 2012).

Now, it is reasonable to believe that strawberry helps contribute to health benefit, based on what we know about their bioactive components.

I.1.5 Preserving processes of strawberry

Like other fruits, strawberries can be consumed ‘’in natura’’, which turns out to be advantageous to consumers since there are no nutritional losses due to processing. On the other side, the preference for fresh fruits is challenging because they have a very short shelf-life, due to their sensitivity to fungal attack and excessive texture softening caused by the natural ripening process (Cordenunsi et al., 2005).

Therefore, the strawberry can be preserved by freezing and drying processes such as freeze, osmotic, microwave, and air drying (Ratti, 2001; Shishehgarha et al., 2002; El-Beltagy et al., 2007; Modise, 2008). Besides, it could consume fresh or in many other forms such as juice, concentrate jam, and jelly and dried rehydrated with yoghurt and bakery products (Harris, 2007).

CHAPTER I.2

DEHYDRATION OF STRAWBERRY

Dehydration is the oldest method to preserve the food. And, the mean objective of drying is to remove water until the water activity is low enough to prevent growth of microorganisms and increase the shelf life of product. However, the drying process not only decreases the water content of the product, but also affects other physical and chemical properties; which will change the shape, crispness, hardness, aroma, flavor and nutritive value of the fresh product.

High-temperature dehydration includes two different unit operations: heat transfer from a heat source to the food material, and mass transfer from the food material to the surrounding media (Fellows, 2000). When high temperature is involved, evaporation of water occurs at normal pressure, while in freeze-drying, temperature and pressure are low and sublimation of water (Hammami and René, 1997; Fellows, 2000).

Strawberry drying must consider the effect of temperature on all factors that determine the nature of the fruit, such as phenol content, soluble fiber content, vitamins, etc. (Ioannou and Ghoul, 2012). The use of high temperatures can produce a harmful effect in the product instead of maintaining the qualities for which these products are especially appreciated (Hung and Duy, 2012).

Even though, drying is not the principal preservation or processing method used in strawberry, it is one of the more suitable alternatives to maintain specific functional components such as dietary fiber, pigment, and low molecular weight carbohydrates (Alvarez et al., 1995). Therefore, drying process should be used with special care in strawberry to avoid chemical changes that may lead to the loss of these important functional components (Ioannou and Ghoul, 2012). And also, it should be carried out at low temperatures to produce a low-rate water removal to prevent hardening and sugar crystallization (Doymaz, 2008).

I.2.1 High temperature dehydration

As mentioned above, the high-temperature dehydration process is very complex. However, it is comprehend and studied as a combination of two unit operations acting simultaneously: heat transfer and water mass transfer. Heat is normally produced by a combustion source; an indirect heat exchanger transferring energy to an air stream that conducts it to water in the product. Water evaporates and the water vapor produced is then removed from the product surface and out of the drier by the air stream (Schierbaum, 1965; Fellows, 2000). The heat transferred to the product and the water transferred from the product to the air stream are affected by the air, water content, relative humidity, and dry bulb and wet bulb temperatures (Krokida et al., 1997; Chua et al., 2003; Doymaz, 2008)

I.2.1.1 Drying phenomena in strawberry

When sliced strawberries are placed in a drier, the process does not follow a lineal behavior. Water is removed in different stages due to it depends on the structure, the presence of seeds, and the nature of the skin and epicuticular waxes of the strawberry. The four physical mechanisms of transfer presented in the strawberry are adapted by Mounir and Allaf (2009), Figure 7.

1) External heat transfer: heat is transported from an air stream flowing over or through the material to the strawberry surface. This process occurs because of the temperature gradient and is controlled by a heat transfer coefficient that depends mainly on air speed and flow.
2) Internal heat transfer: by conduction, the heat is transmitted within the strawberry. And, this mechanism depends on the fruit type, water content, and temperature gradient inside the fruit. Hence, in these two processes, the question is to bring the necessary energy to transform water into vapor.
3) Internal water transfer: it is carried out either in liquid form or in vapor phase, by various process including capillarity; molecular diffusivity; the driving forces are the gradients of respectively the water content and the partially pressure. The nature of vegetables structure should not naturally support these water transfer processes. Indeed, generally "trapped" within the cell, water must

firstly cross the cytoplasmic membrane, get to the cellular wall, diffuse through the structure, and reach the external surface to be, subsequently, able to separate from the product. These processes play a very important role and the resistance of the structure to this transfer often seems to be the principal restrictive factor of the operation kinetics.

4) External water transfer: The water transport is generally in vapor form and it is taken to the surface towards outside in order to maintain the possible greatest gradient of humidity, principal driving force of dehydration. At the starting moment, this transport is instant and depending of the interface surface. Afterward, it is normally limited by the intern diffusion.

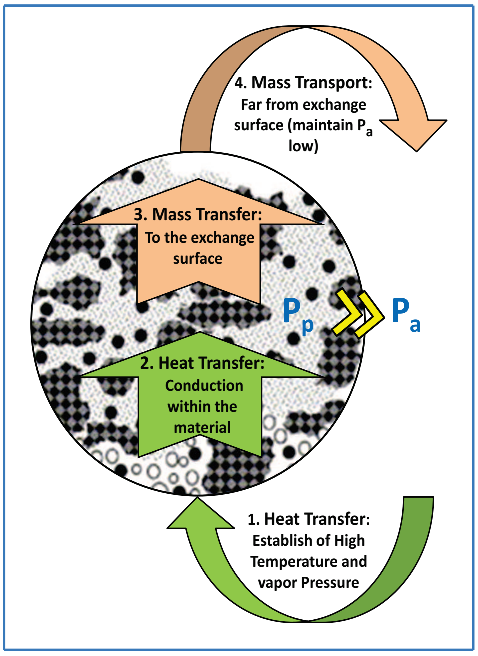


Figure 7. *Four physical transfer phenomena occurred during drying process. 1: External heat transfer by conduction or convection. 2: Internal heat transfer by conduction. 3: Internal mass transfer by diffusion. 4: External mass transport from product surface to surrounding air. Drying process can be intensified by increasing Pp (vapor partial pressure at the exchange surface of the product) being higher than the Pa (vapor partial pressure of external air).*

In addition, the best way to optimize the heat transfer is to control the airflow; the more turbulent the airflow, the higher the heat transfer coefficient, and thus the faster the heat transfer (Chua et al., 2003). Therefore the heat transfer process can be controlled in a well-designed drier by controlling the air temperature, the airflow speed and the nature of the flow, the way the air contacts the product, and the residence time of the product in the drier, since the temperature on the product surface is part of the driving force in the heating process.

And, with the exception of freeze-drying, where the total volume of cells and tissue remains almost constant throughout the drying process, all other drying methods involving heat treatments have a very heterogeneous drying process, where the control of water removal is very important to control shrinkage and other damage produced by the process (Marques et al., 2006; Guiné and Barroca, 2012). Hence, drying conditions and fruit transformation greatly affect product quality (Marques et al., 2009).

Furthermore, for the dehydration of fruits, some pretreatments are used to enhance the drying rate, thus allowing shorter processing times for better product quality, including texture and color, and less damage to valued compounds (vitamins, phenols, etc.). Some of these pretreatments include mechanical or chemical skin perforation and partial water removal with osmotic solutions (Doymaz, 2008; Blanda et al., 2009; Watanabe et al., 2011). All these pre-treatments produce a shorter drying time with a higher drying rate.

I.2.2 Conventional drying methods for strawberries

In this group, sun drying and all mechanical dehydrators that use a heated air stream are included. However, only hot air drying and freeze-drying are described for this section.

I.2.2.1 Hot air drying

Hot air drying is one of most widely used technology for food preservation. This unit operation is applied to reduce the water content of products such as fruits, vegetables, agricultural and herbal products, etc. after harvest (Di Scala et al., 2011; Toontom et al., 2012). A mechanical device is used to carry out this kind of drying. The strawberry may be either static or moving and hot air is conducted in different directions. The variables of this system can be well controlled, including the feeding rate, air velocity, air humidity inside the apparatus, air recirculation conditions, and final moisture content in the product (Arora et al., 2006; Doymaz, 2008).

On the other hand, this operation is characterized by the contact of hot air with humid material, being convection the principal phenomenon. Also, it presents some advantages as inexpensive process, simple method, and control of operating conditions. However, it gives to the product a significant aromatic and nutritional degradation, shrinkage, and loss of rehydration potential (Marques et al., 2006).

Hung and Duy (2012) reported that the beetroot phenolic compounds in hot air dried samples were 13 times lower than freeze-drying samples. Doymaz (2008) demonstrated that the strawberries pre-treated with alkaline ethyl oleate solution and increasing air temperature of hot-air drier helped to increase the drying rate and consequently, to decrease drying time. Also, rehydration of pre-treated samples was much faster than untreated samples. Like this study, sometimes, chemical pre-treatments are necessary to accelerate the hot air drying process. But the problem with the fruit shrinkage is persistent with this method. Maskan (2001) found that the shrinkage of hot air dried kiwifruit was 85%.

I.2.2.2 Freeze-drying

Freeze-drying is considered as the reference process for manufacturing high-quality dehydrated products. This drying process involves a preliminary freezing of the products followed by placing them under reduced pressure (< 300 Pa) with a sufficient heat supply to sublimate ice (2800 J per gram of ice) (Shukla, 2011).

Preliminary freezing of the product stiffens its structure and subsequently prevents solute and liquid motion during freeze-drying. During the formation of ice crystals, they grow and create a uniform network throughout the product that after sublimation yields a dense, spread and homogeneous porous matrix (Hammami and René, 1997). By the sublimation phenomenon (direct change from ice to vapor) freezing water is removed from the strawberry and it helps to explain the capacity of the freeze-dried fruit to rehydrate almost instantaneously (Shukla, 2011).

This operation offers a great fruit nutritional quality, texture, flavor and color, and a product with high porosity. And, it avoids the undesirable shrinkage. Unfortunately, it has a high operating cost, long drying time and high vacuum level (Marques et al., 2006). Also, the poor quality and/or alterations of freeze-dried products that are sometimes encountered are generally linked to the quality of the raw material (nature and degree of ripeness) and to processing conditions (operating pressure, heating temperature, freezing rate, freeze-drying process control).

Compared to classical dehydration techniques, the main advantages of the freeze-drying process are: the preservation of most of the initial raw material properties such as shape, appearance, taste, color, flavor, texture, biological activity, etc. and the high rehydration capacity of the freeze-dried product.

In a study reported by Meda and Ratti (2005) the freeze-dried strawberries had a better nutritional quality and its rehydration capacity was quickly, less than 2 min were necessary to fully rehydrate the slices. In terms of the fruit color that freeze-drying method offers, Guiné and Barroca (2012) found that chroma of dried pumpkin decreased significantly with freeze-drying while the hue angle was maintained constant when is compared with the fresh vegetable. And, Hung and Duy (2012) shown that the total phenolic and flavonoid contents in vegetables as carrot, taro, tomato, red beetroot and eggplant, were significantly higher by freeze-drying method than the conventional heat-drying method.

I.2.3 Innovative drying methods

Major technical innovations in strawberry dehydration include sugar infusion and impregnation under high or low pressure, microwave dehydration under vacuum and pulsed-mode microwave applications (Suthanthangjai et al., 2005; Oey et al., 2008; Patras et al., 2009; Ioannou and Ghoul, 2012). Nowadays is possible to add at this list the technology of instant controlled pressure drop (détente instantanée controlee, DIC), which is distinguish by its ability to handle the widest range of food products, regardless of their sensitivity to heat.

I.2.3.1 Instant controlled pressure drop, DIC

Instant controlled pressure drop was developed, defined and studied by Allaf and Vidal (1988). And since then, many kind of products have been treated and processed, such apple, onions, cranberries, potatoes, mushrooms, tea, tomato, mango, etc. (Mounir et al., 2012). DIC technology was emerged following the theoretical works on "puffing" or expansion process, dating back to the middle 20th century. Utilization of puffing process was limited to the treatment of cereals and it was not adapted to heat-sensitive products such fruits and vegetables (Mounir et al., 2011). But, DIC treatment is based on the fundamental studies concerning the thermodynamics of instantaneity (Allaf, 2012). DIC is a thermo-mechanical processing induced by subjecting the product to an abrupt transition from a high steam pressure to close to a vacuum (Ben Amor and Allaf, 2009). Hence, DIC is perfectly adapted to texture-sensitive products such as strawberries.

I.2.3.1.1 DIC reactor and treatment

Several papers have described the experimental set-up of DIC (Maache-Rezzoug et al., 1998); (Louka and Allaf, 2004); (Haddad and Allaf, 2007); (Ben Amor and Allaf, 2009); (Berka-Zougali et al., 2010) and (Mounir et al., 2012). Briefly, the reactor is composed by three main elements, (Figure 8):

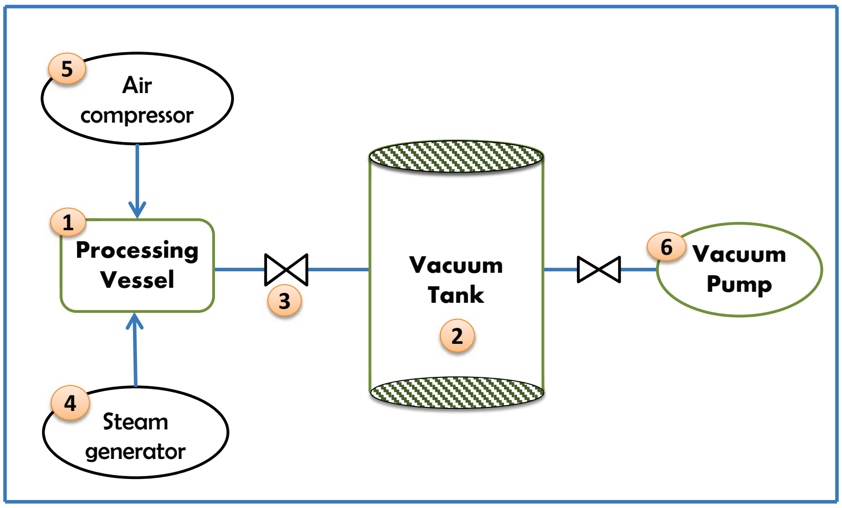


Figure 8. Schematic diagram of the DIC reactor: (1) Processing vessel; (2) Vacuum tank; (3) Quick motion valve; (4) Steam generator; (5) Air compressor (6) Vacuum pump.

A processing vessel; where the samples are placed and treated

A vacuum tank, whose volume is more than 100 times greater than that of the processing vessel;

An instantaneous valve, which ensures a full connection between (1) and (2) in less than 0.1 s

DIC is defined as a high-temperature/short-time (HTST) treatment that consists of subjecting a partially dried material (usually the humidity is close to 30% db) to vapor pressure (P<1.0 MPa) at high temperature (below 180 ºC) for a short time (less than a minute). This high temperature-short-time stage is followed by an abrupt pressure drop to a vacuum (3–5 kPa, Δt~10–60 ms) inducing a mechanical effect such an abrupt pressure drop (ΔP=Δt >2.5 x 105 Pa s-1), provokes simultaneously autoevaporization of a part of water contained in the product and an instanteous cooling of the product which stops their thermal degradation and give a controlled expansion of the product. A DIC pressure drop is characterized by a very high pressure drop rate.

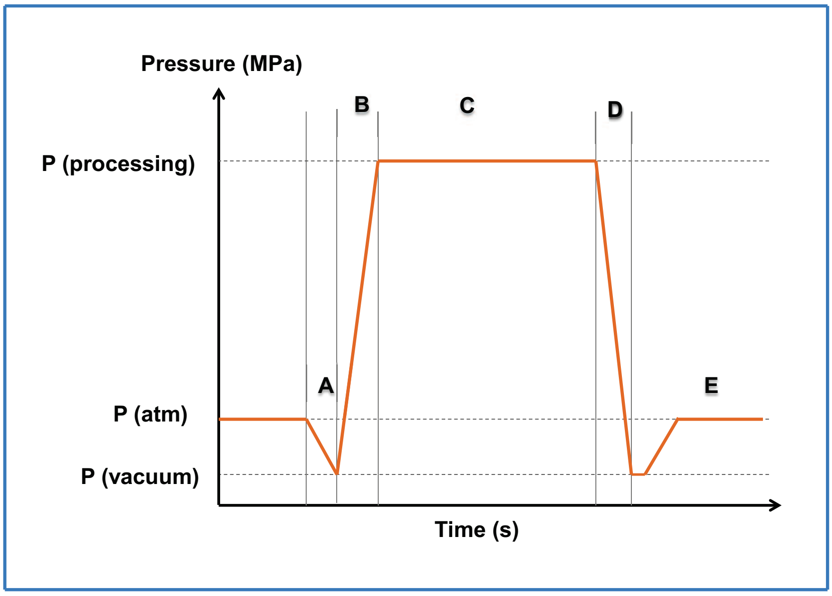


Figure 9. Schematic time-pressure profiles of a DIC process: (A) vacuum establishment; (B) steam injection; (C) pressure and time treatment; (D) instant controlled pressure drop towards vacuum and (E) atmospheric pressure establishment.

Figure 9 shows the different stages of DIC treatment. And they are described as follows:

A. An initial vacuum is established to reduce the air resistance and facilitates the diffusion steam into the product; consequently, a rapid heating is obtained.

B. Saturated steam is injected into the vessel at a pressure level fixed.

C. Pressure and time conditions are given according to the product treatment. An experimental design is used to obtain these conditions.

D. The pressurization is followed by an abrupt decompression towards vacuum.

E. After the vacuum phase, atmospheric air is injected to return to atmospheric pressure for sample recovery.

In addition, it is possible to control the parameters involved in the DIC process to obtain a good end product quality in terms of its expansion ratio, porosity, color, aroma, flavor, etc. (Allaf, 2012).

The process parameters to control are classified in intrinsic and operating process parameters. The first group gathers, shape and size of the raw material, initial water content, specific heat, thermal conductivity, effective diffusivity, and rheological characteristics such as elasticity, viscosity, glass transition, etc. The second group is referred to initial pressure and temperature, total pressure, partial pressure of vapor, initial vacuum pressure, pressure drop rate, thermal processing time, minimal temperature of the product, temperature drop rate, volume ratio of the vacuum tank to the processing vessel, intrinsic density or filling ratio, quantity and apparent volume of the product to be processed, etc. (Mounir et al., 2012).

Therefore, as DIC technology needs products partially dried (water content around 30% db) to the treatment, the solution proposed was assisted it by hot air drying process, forming the swell-drying process (Mounir et al., 2011).

I.2.3.1.2 Swell-drying

As was mentioned, the swell-drying (SD) involves coupling hot air drying to a DIC texturing process. This new process could greatly intensify the conditions given by hot air drying, such air flux, temperature, speed and humidity. And the texturing operations should be proposed as a further intensification to improve both the performance of hot air drying as well as the quality of the final (Mounir et al., 2012). Hence, DIC within SD could help to texturize the strawberry and give it an attractive alternative with the following potential advantages (Albitar et al., 2011; Mounir et al., 2011; Allaf, 2012):

1. DIC expansion remedy the shrinkage problem presented by usual drying, due to the highly porous structure and a greater specific surface area given by DIC process.
2. Preservation of flavor, color and bioactive compounds.
3. It can help in the modernization of the food drying industry, due to it is an operation more effective with less consume of energy, and induces perfect decontamination of the product.
4. Price value of final product will be increased because of its high quality similar even better than freeze-dried.
5. Handling processing cost will be reduced.
6. And, it is considered as a sustainable technology because gives an added value to agro resources.

Some important works reference the effect of swell drying in the fruits and vegetables. A study by Albitar et al. (2011) demonstrated that the onions treated by SD process improved in terms of kinetics and quality of the end product. And, similar results were reported for the apples, their vitamins were preserved and the thermal degradations were so weak with SD (Mounir et al., 2011).

I.2.4 Applications of dried strawberry

Dried strawberry has many applications. It can be used as a food by itself or an ingredient in other food. Some of its uses are classified as follows:

Snack foods. In recent years, use a fruit as snack is an innovation with very good acceptance by consumers. These products contain wild or cultivated strawberry or another berry and are popular due to their health benefits associated with their antioxidant activity, scavenging of free radicals, and high content on soluble dietary fiber (Potter et al., 2013). Also, these snacks may include other ingredients besides dried fruit and cereals, including honey or dried yogurt.

Breakfast cereals. The consume of cereal in the breakfast is very popular. Hence, the addition of strawberry or another berry to breakfast cereals has a double benefit; because of the soluble dietary fiber from berry complement very well the insoluble fiber of cereals. In this case, the moisture dried fruit has to be controlled to prevent the cereal humectation. Also, when low-moisture fruit is used, the fruit texture may not be acceptable at the moment the cereal is mixed with milk or juice. In some cases, berries are laminated after drying so they will have a better texture, but normally they are softened by the addition of water vapor or some type of oil.

Formulated foods. Using the dried strawberry as food ingredient is very popular. It can be an ingredient of ice cream, toppings, fruit pieces in pastries and cookies, yogurt, snacks, and pressed for fruit leathers (Harris, 2007). However, in some of these products, a second heat treatment could damage the dried fruit chemical quality (Ioannou and Ghoul, 2012). So, it is better to use dried fruits that are protected against deterioration of these compounds.

A statistical study reported by Minte (2010) pointed that nine of ten British adults eat snacks between meals, nearly half of them on a daily basis. There are in total an estimated 13 billion at home snacking occasions a year and 6.4 billion occasions on the go. Therefore, as snacking has become part of the day-to-day of our lives, especially for children, it is necessary to work so hard in snacks confection with a positive health benefit.

In this case, swell-drying performance could be a valuable solution for preserving and modifying the structure of strawberry, offering a snack fruit with beneficial effects in human health. In addition, it could have a good acceptance by consumers and food industry.

CHAPTER I.3

QUALITY ASSESSMENTS

Quality is the summary of all characteristics of dried product that are important to the food industry and the consumer needs. In order to determine the quality dried strawberry; several parameters need to be examined. These parameters are dehydration and rehydration kinetics; textural characteristics, expansion ratios, water content, water holding capacity. Only the kinetics and textural analyses are described in this section.

I.3.1 Mathematical Modeling of dehydration and rehydration kinetics

To study the modeling of dehydration and rehydration in strawberry, the modeling proposed by Mounir and Allaf (2009) to expanded biomaterials that involving various exchange surfaces and different internal diffusion processes was adopted.

For this section, the four physical mechanisms of transfer in the drying phenomenon are taken into account. They were explained in the last chapter (Chapter I.2.1.A). It continues as follows:

By assuming that external heat and mass transfers do not limit the whole operation through adequate technical conditions of air flow (i.e. temperature, moisture content and velocity), only internal transfers may intervene as limiting processes (Al Haddad et al., 2008). Also, it is assumed that, within the product the internal mass transfer must be much more accelerated than heat transfer by conduction, due to the values of mass and thermal diffusivities are already known. In such conditions, as drying kinetics are controlled by mass transfer of water within the strawberry, the model proposed by Mounir and Allaf (2009) is adopted. It is traduced by ALLAF (1982) as similar Fick diffusion, equation 1:

$$\frac{\rho_w}{\rho_m}(\overrightarrow{v_w} - \overrightarrow{v_m}) = -D_{eff}\vec{\nabla}\left(\frac{\rho_w}{\rho_m}\right) \qquad \text{Equation 1}$$

Where, ρ_w is the apparent density of water material (kg/m^3); ρ_m is the apparent density of dry material (kg/m^3); v_w is the absolute velocity of water flow within the porous medium (m/s); v_w is the absolute velocity of solid medium (m/s), and D_{eff} is the effective diffusivity of water within the solid medium (m^2/s).

As DIC produces a swelling, the shrinkage phenomena is neglected and it is assumed that ρ_m=constante and v_w=0:

$$\rho_w \overrightarrow{v_w} = -D_{eff} \vec{\nabla} \rho_w \qquad \text{Equation 2}$$

Using the balance mass, the second Fick law is obtained:

$$\frac{\partial \rho_W}{\partial t} = \vec{\nabla} \cdot D_{eff} \vec{\nabla} \rho_w \qquad \text{Equation 3}$$

Where, t is time

However, D_eff considerably varies versus the system temperature and porosity, it is assumed constant, only through the hypothesis of both structural and thermal homogeneities:

$$\frac{\partial \rho_W}{\partial t} = D_{eff} \vec{\nabla} \cdot \vec{\nabla} \rho_w \qquad \text{Equation 4}$$

And by assuming a unidirectional flow:

$$\frac{\partial \rho_W}{\partial t} = D_{eff} \frac{\partial^2 \rho_w}{\partial x^2} \qquad \text{Equation 5}$$

The provided solutions to this diffusion equation closely depend on the initial and boundary conditions. Using Fick's second law, a number of mathematical solutions have been proposed; however, the Crank's solution for a solid matrix was adopted, (Crank, 1975):

$$\frac{W_\infty - W}{W_\infty - W_1} = \sum_{i=1} A_i exp(-q_i^2 \tau) \qquad \text{Equation 6}$$

Where W, W_∞ and W_1 are the amounts of water content (dry basis) in the solid matrix. W is at time t, W_∞ is at equilibrium of water content t → ∞, and W_1 is at the starting of pure diffusion time. W_1 is the value of W at the time t_1 chosen as the beginning of the diffusion model gotten only for long time experiments. The difference between W_o (theoretical value of W gotten by extrapolating the diffusion model) and the experimental one W_i, at t=0, corresponds to the amount of water available on the surface and extracted from it in a very short time. By modifying matrix structure, improving porosity, the values of W_∞ and W_o vary depending on and characterizing DIC treatment:

$$\frac{W_\infty - W}{W_\infty - W_1} = \sum_{1}^{\infty} A_i \, exp(-q_i t)$$

$$= \frac{8}{\pi^2} exp^{-\frac{\pi^2 D_{eff} t}{4{d_p}^2}} + \frac{8}{9\pi^2} exp^{-\frac{9\pi^2 D_{eff} t}{4{d_p}^2}} + \frac{8}{25\pi^2} exp^{-\frac{25\pi^2 D_{eff} t}{4{d_p}^2}} + \frac{8}{49\pi^2} exp^{-\frac{49\pi^2 D_{eff} t}{4{d_p}^2}} + \cdots \qquad \text{Equation 7}$$

A_i and q_i are Crank' coefficients and they are solved according to Fick's number (τ):

$$\tau \colon D_{eff} \frac{t}{{d_p}^2} \qquad \text{Equation 8}$$

Where d_p is the characteristic length (m).

By limiting equation 8 to its first term, it could be expressed as:

$$\frac{W_\infty - W}{W_\infty - W_0} = Aexp(-kt) \qquad \text{Equation 9}$$

Where, k is selected according to the product shape. In this case, an infinite plate is the best adaptable to sliced strawberries

The logarithmic representation of equation 9 as a straight line leads to determine D_{eff} from the slope k:

$$LN(Y) = LN\left(\frac{W_\infty - W}{W_\infty - W_0}\right) = kt \qquad \text{Equation 10}$$

Where k corresponds to:

$$k = \frac{\pi^2 D_{eff}}{4{d_p}^2} \qquad \text{Equation 11}$$

And the effective diffusivity is:

$$D_{eff} = \frac{4{d_p}^2}{\pi^2} k \qquad \text{Equation 12}$$

As the experimental data used for the empirical model exclude the points close to t=0; the extrapolation of the model obtained allowed that the W0 to be determined as, generally, different from the initial humidity content Wi.

The difference δWs between Wi and W0 expresses the humidity quickly removed from the surface, independently from diffusion processes. This quantity has been defined as “starting accessibility of water.

$$\delta W_s = W_i - W_0 \qquad \text{Equation 13}$$

Hence, the values considered to evaluate the drying kinetics of strawberry are effective diffusivity ($\mathrm{D_{eff,d}}$), the starting accessibility ($\delta W_{s,d}$) and the time to get the lowest water content (t_d)

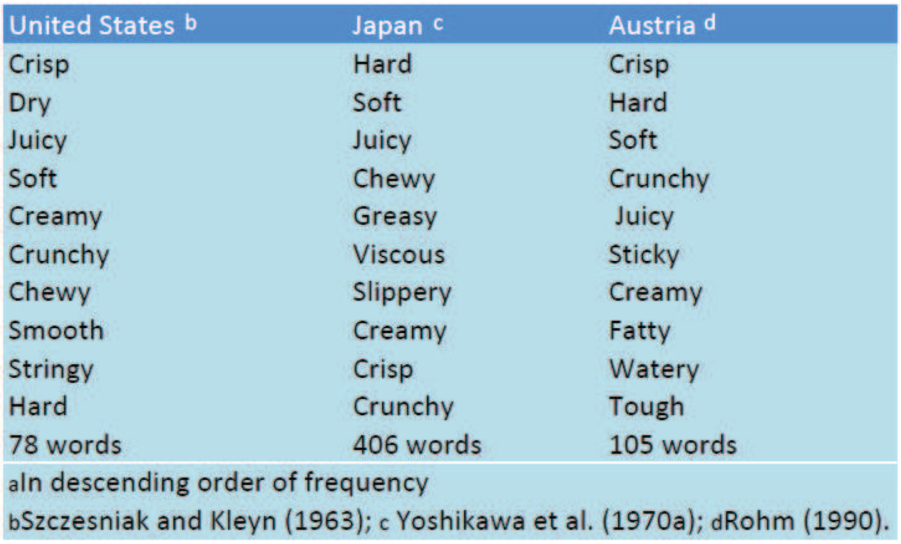
In the case of rehydration kinetics, similar argument is applied. The parameters are rehydration effective diffusivity ($\mathrm{D_{eff,r}}$), rehydration starting accessibility ($\delta W_{s,r}$) and the rehydratation time (t_r).

I.3.2 Texture analysis

The consumers’ appreciation has become one of the main criteria in their food choice, as well as nutrition and flavor (Bourne, 2002a). The contribution of texture to the consumer´s appreciation of a food product has been studied nearly 40 years. Therefore, texture has been defined as the response of the tactile senses to physical stimuli that result from contact between some part of the body and the food. The tactile sense (touch) is the primary method for sensing texture but kinesthetic (sense of movement and position) and sometimes sight (degree of slump, rate of flow), and sound (associated with crisp, crunchy and crackly textures) are also used to evaluate texture (Bourne, 2002a).

The vocabulary used to describe the texture of any kind of food has been really controversial because it depends not only of the foodstuffs characteristics, but also the culture and the language are implicated (Table 5).

Table 5. Most frequently words used to define a food texture (Bourne, 2002a)



United States [b]	Japan [c]	Austria [d]
Crisp	Hard	Crisp
Dry	Soft	Hard
Juicy	Juicy	Soft
Soft	Chewy	Crunchy
Creamy	Greasy	Juicy
Crunchy	Viscous	Sticky
Chewy	Slippery	Creamy
Smooth	Creamy	Fatty
Stringy	Crisp	Watery
Hard	Crunchy	Tough
78 words	406 words	105 words

[a]In descending order of frequency

[b]Szczesniak and Kleyn (1963); [c] Yoshikawa et al. (1970a); [d]Rohm (1990).

In the early studies on the awareness of food texture, the importance of crispness was high-lighted (Roudaut et al., 2002). For instance, word association tests, in which consumers were asked to generate attributes related to a list of specific foods, showed that the term “crisp” was mentioned more often than any other attribute (Szczesniak, 1988; Rohm, 1990). However, this term “crisp”, was confused and sometimes used as a synonym of the term “crunch”.

The sensations ‘‘crisp’’ and ‘‘crunch’’ are difficult to describe especially when different food products are involved. For both wet and dry crisp products the sensations crispness and crunchiness are found to be related to the same type of product properties, i.e. hard, brittle and producing a typical sound at fracturing (Luyten et al., 2004).

In many texture studies, panelists as well as consumers found it very difficult to define crispy and crunchy terms and needed constant probing. However, all insisted that they could perceive a difference between the two, but then struggled to describe this difference, indicating that it was only slight (Fillion and Kilcast, 2002).

In brief, crispy and crunchy are words that are used to describe products that break rather than deform, and the way in which they fracture under the application of a force (Saeleaw and Schleining, 2011). The experimentation of these definitions are shown in Table 6.

Under these definitions and consider that potential changes in the texture of fruit are produced during dehydration process. The fruit texture can become crisp, crunch, brittle, firm, dry, hard, crumbly, etc. All of these changes are based on the nature of the fruit and the drying process applied.

Thus, to understand better these dried product features, particularly the crunchy and crispy behavior, it is necessary to measure them using sensory or instrumental methods.

In sensory methods, consumers are able to describe the differences between crisp and crunch by judging the sound (Roudaut et al., 2002). However, sensory studies are often difficult to compare because of the confusion between concept, the procedures implemented and the difficulties inherent to multi-cultural studies.

For instrumental methods, there has been a great interest in developing instrumental techniques to assess crispness/crunchiness. Instrumental techniques present some advantages, especially in industrial environments where quick and easy-to-use methods are in great demand and economically more profitable (Saeleaw and Schleining, 2011). Moreover, as crispness feature is described as a concept that involves kinesthetic and auditory components; mechanical and acoustic measurements have been developed to interpreter its behavior better (Bourne, 2002b). Additionally, an accurate method for determining texture in dried products is of vital importance to the food scientist and industry.

Hence, within the mechanical methods most commonly used to measure the product crispness, are the puncture tests, due to that they simulate the incisors impact and biting. In this case, a cylindrical or conical probe of small diameter plunges in the specimen at constant and rather low speed. This test has specially been employed for the characterization of foamed products and the probe is expected to fracture separately the different cell walls constituting the product

(Roudaut et al., 2002). The force–deformation pattern is characterized by series of sharp force peaks corresponding to the rupture of individual cell walls (Figure 10).

This force-deformation pattern generally is discussed for biscuits or extruded products. But, in the case of swell-dried fruits, this method helps to describe their texture behavior. However, it is necessary to adjust the method to describe and to distinguish better the crispy and crunchy behavior of swell-dried fruits.

Van Hecke et al. (1998) studied the mechanical and textural behavior of crispy-puffed food extrudes using a puncture test. This method was taken and modified to describe the crispness and crunchiness features in strawberries treated by swell-dried process (proposal is described in the section of results).

This proposal opens the possibility to design healthy snacks according to consumer needs, putting special attention in conserve their crispness. Also, this strawberry snacks can be proposed as ingredient in ready-to-eat foods (e.g. breakfast cereals).

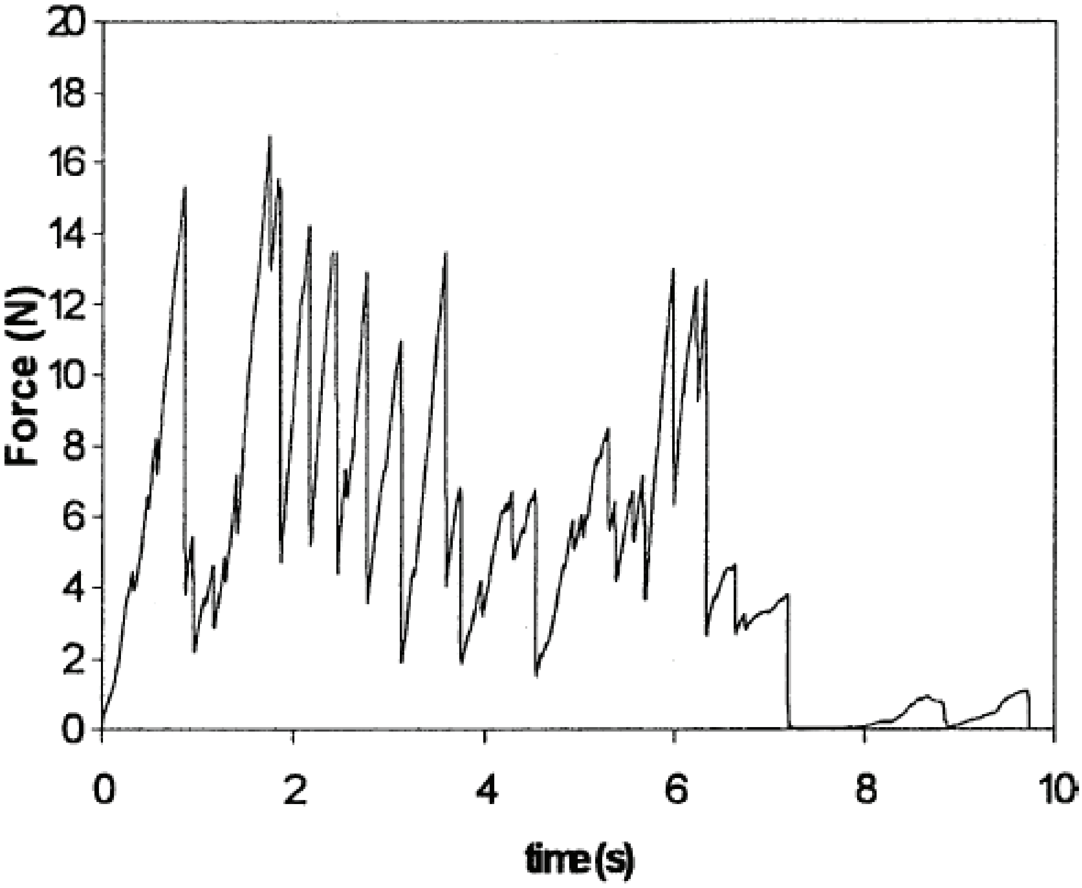
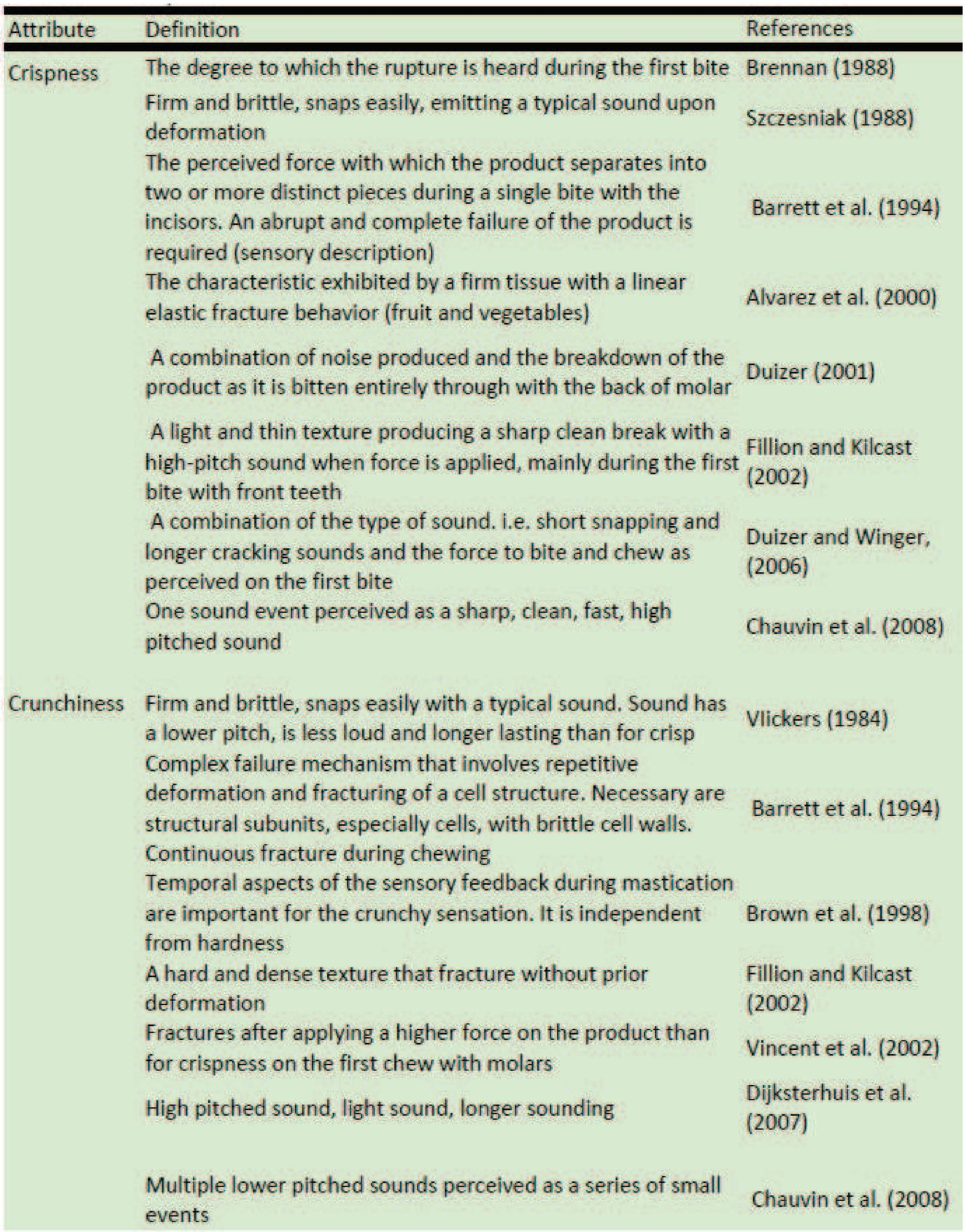


Figure 10. Definition of crispness and crunchiness

Table 6. Definition of crispness and crunchiness (Saeleaw and Schleining, 2011)



Attribute	Definition	References
Crispness	The degree to which the rupture is heard during the first bite	Brennan (1988)
	Firm and brittle, snaps easily, emitting a typical sound upon deformation	Szczesniak (1988)
	The perceived force with which the product separates into two or more distinct pieces during a single bite with the incisors. An abrupt and complete failure of the product is required (sensory description)	Barrett et al. (1994)
	The characteristic exhibited by a firm tissue with a linear elastic fracture behavior (fruit and vegetables)	Alvarez et al. (2000)
	A combination of noise produced and the breakdown of the product as it is bitten entirely through with the back of molar	Duizer (2001)
	A light and thin texture producing a sharp clean break with a high-pitch sound when force is applied, mainly during the first bite with front teeth	Fillion and Kilcast (2002)
	A combination of the type of sound. i.e. short snapping and longer cracking sounds and the force to bite and chew as perceived on the first bite	Duizer and Winger, (2006)
	One sound event perceived as a sharp, clean, fast, high pitched sound	Chauvin et al. (2008)
Crunchiness	Firm and brittle, snaps easily with a typical sound. Sound has a lower pitch, is less loud and longer lasting than for crisp	Vlickers (1984)
	Complex failure mechanism that involves repetitive deformation and fracturing of a cell structure. Necessary are structural subunits, especially cells, with brittle cell walls. Continuous fracture during chewing	Barrett et al. (1994)
	Temporal aspects of the sensory feedback during mastication are important for the crunchy sensation. It is independent from hardness	Brown et al. (1998)
	A hard and dense texture that fracture without prior deformation	Fillion and Kilcast (2002)
	Fractures after applying a higher force on the product than for crispness on the first chew with molars	Vincent et al. (2002)
	High pitched sound, light sound, longer sounding	Dijksterhuis et al. (2007)
	Multiple lower pitched sounds perceived as a series of small events	Chauvin et al. (2008)

CHAPTER I.4

GENERAL OBJECTIVES

The aim of this study was to compare various drying methods; hot air drying (HAD), freeze-drying (FD) and swell drying (SD, instant controlled pressure drop DIC-assisted hot air drying). A comparative study was carried out to evaluate the effect of three drying methods on strawberry (Fragaria var. Camarosa), in terms of

Drying kinetics (drying time, starting accessibility and effective water diffusivity)

Rehydration kinetics (rehydration time, starting accessibility and effective water diffusivity)

Water Holding Capacity (WHC)

Bioactive compounds, including total phenolic content, flavonoid content and total anthocyanin content

The antioxidant activity

Two types of texture (i.e. crunchy and crispy features)

Microstructure impact

PART II

MATERIALS AND METHODS

CHAPTER II.1

MATERIALS

II.1.1 Chemicals and reagents

Gallic acid; Cyaniding-3-glucoside; Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylicacid); Pelargonidin-3-glucoside, which is a hydrophilic analogue of vitamin E; 2,2-Diphenyl-1-picrylhydrazyl (DPPH); and Rutin; were purchased from Sigma Chemical Co., St. Louis, MO, USA. Ethanol and methanol were purchased from J.T. Baker (Deventer, The Netherlands). All other reagents and chemicals of analytical grade were procured from local sources (Queretaro, Mexico and La Rochelle, France) and milli-Q water was used.

Biological material

The variety of strawberry used was Camarosa. The strawberries were purchased from Carrefour (La Rochelle, France). They were transported to the laboratory and stored at 5 ºC for 24 h, washed with tap water and cut in transverse slices with 4-5 mm of thickness. Afterward, for the treatment, the total quantity was divided in three lots for being processed by: hot air drying (HAD), freeze-drying (FD) and swell-drying (SD).

Figure 11. Strawberry raw material.

CHAPTER II.2

METHODS

II.2.1 Treatment Drying Methods

II.2.1.1 Hot air drying, HAD

The slices of strawberries were dried in a hot air drier (Memmert: Universal Oven UNB Model 800) at 50 °C. The initial vapor pressure in the air was 265 Pa and an air flux of 1.2 m/s. Slices were dried until attaining 3.0% of water content dry basis (db), around 24 h. Afterward, the samples were analyzed and recorded as HAD.

II.2.1.2 Freeze-drying, FD

A freeze-drying equipment (model: RP2V, Serail, France) was used for drying the batch of strawberries sliced. The conditions were divided in three steps: external freezing (at -20 °C/2 h), sublimation (-20 °C, 0.66 Pa/12 h) and desorption (25 °C, 0.66 Pa/12 h). Subsequently, the samples were analyzed and recorded as FD.

II.2.1.3 Swell-drying, SD

As swell drying is a DIC-assisted hot air drying. The batch of sliced strawberries was partially hot air dried at the same conditions described in HAD method (50 °C with 265 Pa as the initial vapor pressure in the air, and an air flux of 1.2 m/s) until 18% db. This first step needed about 8 h. Subsequently, the slices were placed in airtight bags and stored in a cold chamber at 5 ºC by 24 h to homogenize their water content (18% db). Afterward, the partially hot air dried strawberries were treated by DIC equipment (ABCAR-DIC Process, La Rochelle, France) according to the experimental design (Table 8). Finally, after DIC treatment, a traditional convective hot air drying at 50 °C was performed for approximately 1 h to get at 3.0% db as final water content. These samples were analyzed and recorded as SD.

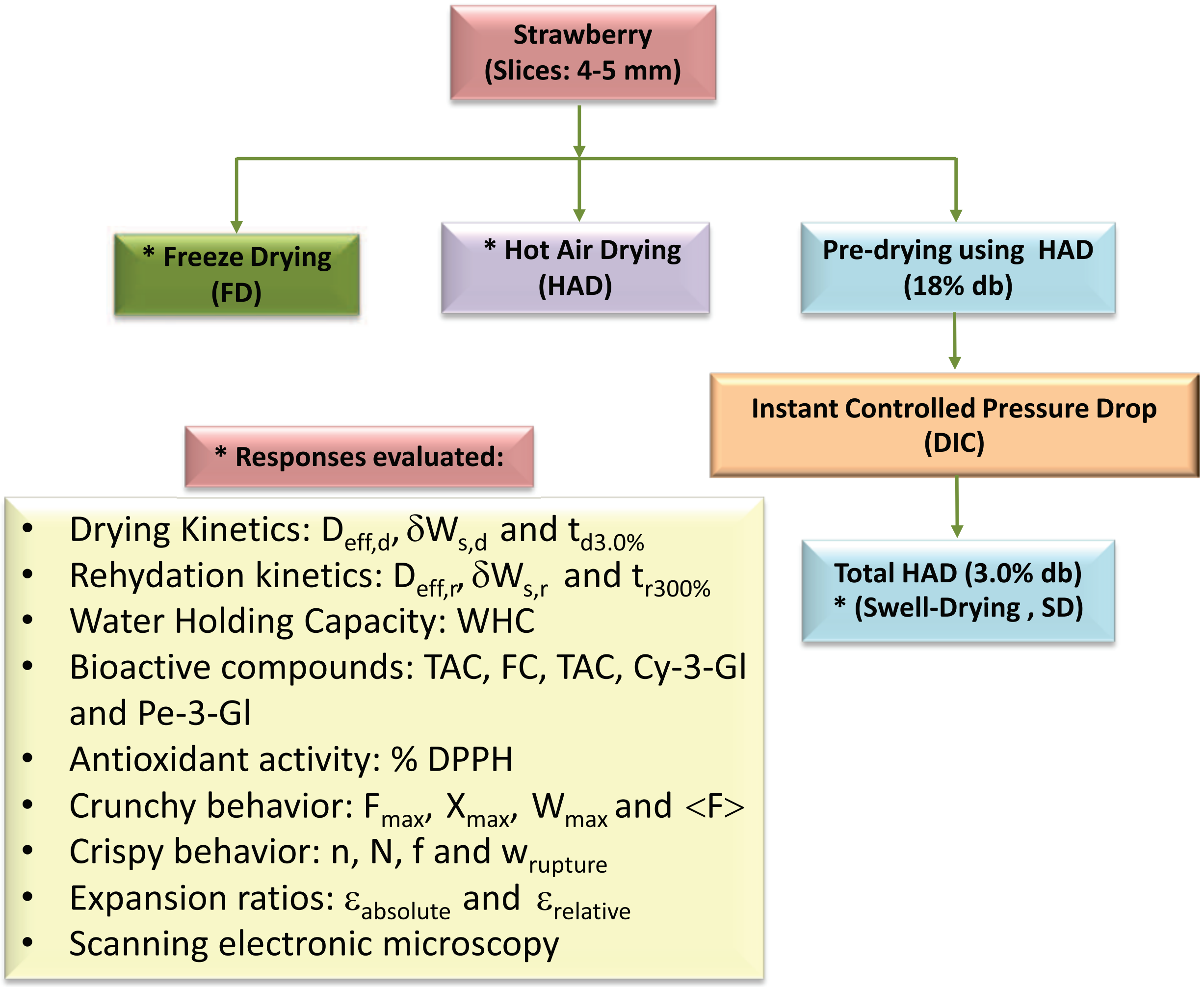


Figure 12. Scheme of treatment and assessment methods adopted for strawberry dried samples.

II.2.2 Assessment Methods

II.2.2.1 Water Moisture Content

Water moisture content was determined following Karathanos method modified (1999). Briefly, the dried strawberries samples were quantified gravimetrically by triplicate. 2.5 ± 0.1 g of samples were drying at 65 °C during 48 h in the oven UFE 400 (Memmert, Germany). The moisture content (W) dry basis (db) was calculated using the following equation:

$$W_{db}\% = \frac{m_i - m_d}{m_d} \qquad \text{Equation 1}$$

Where, m_i and m_d (g) were the material weight before and after drying, respectively.

II.2.2.2 Drying Kinetics

Drying kinetics were performed for HAD and SD samples. Approximately, 3.00 ± 0.05 g of each sample was used. They were placed in the hot air oven (Memmert: Universal Oven UNB Model 800) at 65 ºC and weight loss was recorded using an electronic balance (model EP2102, Ohaus, US). The weight loss was recorded every 5 minutes as interval time during the first 30 minutes, subsequently after 45, 60, 90, 120 minutes, after 120 minutes the weight loss was recorded every hour until equilibrium water content was attained (change on weigh less than 0.01 g).

II.2.2.3 Rehydration Kinetics

The rehydration rate of HAD, FD and SD samples was evaluated. About 0.50 ± 0.02 g of sample was placed in the clip handle tea strainers and submerged in distilled water (at 20 ± 0.05 ºC). At specific time intervals (0, 0.5, 2, 4, 6, 8, 10, 15, 30, 45, 60, 90, 120, 150 and 180 min) samples were taken out of the water, blotted with tissue paper to remove superficial water and reweighted. Weight was recorded using an electronic balance AR2140 (OHAUS, China).

II.2.2.4 Modeling of Drying and Rehydration Kinetics

The model of Mounir and Allaf (2009) was adopted to study the drying kinetics. It consists in three stages: initial surface interaction, diffusion phase and paradoxical phase. The experimental results used for the mass diffusion model exclude the ones close to t=0 as well as the ones implying the paradoxical phase (long time stage). They allow the effective diffusivity (Deff,d) of water within the porous medium to be evaluated. By extrapolating this diffusion model towards t=0, Wo was calculated as the theoretical value of water content db issued from diffusion process. It is usually different from the initial humidity content Wi. The difference between Wi and Wo is defined as the starting accessibility (δWs,d=Wi-Wo). It reflects the water quickly removed from the surface, independently from diffusion process. Adding to this phenomenon, the drying time to get at 3.0% db of water content (td3.0%) was calculated also.

For the rehydration kinetics, a similar model has been applied. Evaluated response parameters were the values of rehydration time to get at water content of 300 % db (tr300%), the starting accessibility (δWs,r) revealing the water immediately held at the surface and the effective diffusivity of rehydration (Deff,r).

II.2.2.5 Water Holding Capacity

The water holding capacity (WHC) for the different dried samples (i.e. HAD, FD and eleven SD samples) was determined using the centrifuge technique. Two grams of the sample in powder were mixed with 20 mL distilled water, placed in 30 mL plastic centrifuge tubes and set at room temperature (20 ± 2°C) by 45 min prior to the test run. The tubes were centrifuged (Centrifuge Model Sigma 3K15) at 3000 rpm for 35 min. After centrifugation, the extra supernatant from the centrifuged sample was drained and the sample was reweighted. The samples were then dried in hot air oven at 65 ºC by 48 h to determine their water content. WHC was calculated as the amount of water (g) absorbed by 100 g of dry basis.

II.2.2.6 Samples extraction

The extraction of HAD, FD and eleven SD strawberry samples were prepared. 0.5 g of each sample were weighted in a 30 mL centrifuge tube, and 10 mL of acidified methanol (1.0 % HCl in methanol, v/v) were added and agitated for 2 h at room temperature in darkness. The sample suspensions were centrifuged at 6000 rpm for 10 min at 4 °C and the supernatants were stored at -20 °C until analysis, the operation was performed in duplicate.

II.2.2.6.1 Total phenolic content

Total phenolic content was estimated by using the Folin-Ciocalteu colorimetric method (Singleton et al., 1999). Briefly, 0.02 mL of the extracts was oxidized with 0.1 mL of 0.5 N Folin-Ciocalteu reagent, and then the reaction was neutralized with 0.3 mL sodium carbonate solution (20%). The absorbance values were obtained by the resulting blue color measured at 760 nm with a Spectrophotometer (UV-Vis Double Beam UVD-3500, Labomed, Inc. USA) after incubation for 2 h at 25 °C. Quantification was achieved on the basis of a standard curve of Gallic acid from 0 to 500 μg/mL. Results were expressed as mg of Gallic acid per g of dry weight (mg eq. GA/g db).

II.2.2.6.2 Flavonoid content

The spectrophotometric assay for the quantitative determination of flavonoid content was determined according to Oomah et al. (2005). Briefly, the method consisted of mixing 50 μL of the methanolic extract with 180 μL of distilled water and 20 μL of a solution of 10 g/L 2-aminoethyldiphenylborate in a 96-well microtitration flat-bottom plate. The absorbance of the solution was monitored at 404 nm with a spectrophotometer (xMark Microplate Spectrophotometer, BioRad, Japan). Extract absorption was compared with a Rutin standard at different concentrations ranging from 0 to 200 μg/mL. Flavonoids content was expressed as mg Rutin per g of dry weight (mg eq. Rutin/g db).

II.2.2.6.3 Total anthocyanin content

0.2 mL of extract was diluted with 1.8 mL acidified methanol (1.0 % HCl in methanol) and absorbance was taken at 250 nm (Spectro UV-Vis Double Beam. UVD-3500 Labomed, Inc. USA). An acid pH was used to take the anthocyanins to the flavylium ion form, which exhibits coloration, thus to be able to quantify them by spectrophotometry. Total anthocyanins concentration (TAC) was calculated as pelargonidin-3-glucoside according to the Equation 2 (Abdel-Aal and Hucl, 1999):

$$\boldsymbol{TAC} = \left(\frac{A}{\varepsilon}\right)\left(\frac{Vol}{1000}\right)(MW)\left(\frac{1}{sample\ weight}\right)10^{6} \qquad \text{Equation 2}$$

Where:

TAC: concentration of total anthocyanin content per sample were expressed as mg pelargonidin-3-glucoside equivalent per g of dry weight (mg eq. Pe-3-Gl/g db)

A: absorbance reading,

ε: molar absorptivity (pelargonidin-3-glucoside = 15,600 L/ (mol cm)),

Vol: total volume of anthocyanin extract, and

MW: molecular weight of pelargonidin-3-glucoside = 433.2 g/mol

II.2.2.6.4 Determination of anthocyanins by HPLC

Strawberry extracts were filtered through a 0.45 µM nylon membrane-filter. HPLC analysis was performed using an Agilent 1200 HPLC system (Agilent Technology 1200 series, Palo Alto, CA), equipped with quaternary pumps, autosampler and a diode array detector. Anthocyanin separation were performed using an Eclipse XDB-C18 column (5 µM, 4.6 mm · 150 mm) at 28 ºC. Mobile phases were constituted of 1.0 % methanol acidified (A) and 5.0 % formic acid (B) at a flow rate of 1 mL/min. The gradient condition started with 20 % A, linearly increased to 85 % A at 10 min, finally it decreased to 20 % A at 15 min. Calibration curves (0-1 mg/mL) were realized to quantify cyanidin-3-glucoside (Cy-3-Gl, mg/g db) and pelargonidin-3-glucoside (Pe-3-Gl, mg/g db).

II.2.2.6.5 Determination of antioxidant capacity by DPPH method

Measurement of antioxidant capacity was carried out using 2,2-Diphenyl-1-picrylhydrazyl (DPPH) as a free radical. Reduction of DPPH by an antioxidant or a free radical produces decreased absorbance at 515 nm. 20 µL of the extract were mixed with 200 µL DPPH (125 µM in 80 % methanol). After 90 min, the plate was read at 520 nm in a spectrophotometer and the antioxidant capacity was calculated as a percentage of DPPH discoloration according to Burda and Oleszek (2001). The analysis was performed in triplicate.

II.2.2.7 Puncture Test

To measure the mechanical properties of the macro-structure of dried strawberry slices (i.e. HAD, FD and SD batches), a puncture test was performed with an INSTRON (Model 5543, USA). The probe used was a stainless steel needle with 1 mm in diameter (Petrotest, VICAT needles ISO 6873-EN26873), moving at a constant speed of 1 mm/s. The analysis consisted in recording the force required to penetrate the dried samples by puncturing the middle of the sliced strawberries. The penetration in the dried fruit was until 2 mm for HAD and 3 mm for FD and SD samples (Figure 13). Five measures were repeated by each batch (i.e. HAD, FD and the eleven SD samples).

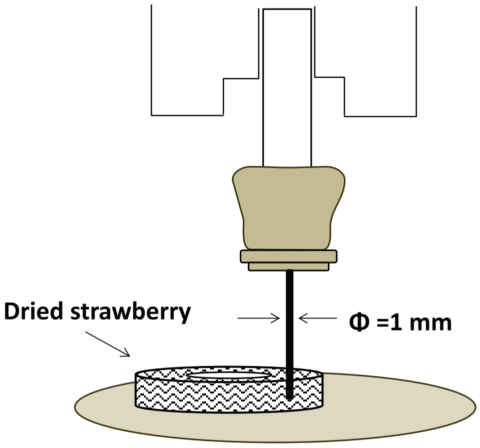


Figure 13. Schematic diagram of puncture test.

II.2.2.8 Fundamental Approach to Analyze the Force-Time Curve

The obtained data by force-displacement curves were analyzed in two parts (Figure 14). The first was for descripting the crunchy behavior parameters (Figure 14, Left) and the second was for the crispy behavior (Figure 14, Right). In this analysis the method reported by Van Hecke et al. (1998) was used also, with slight modifications.

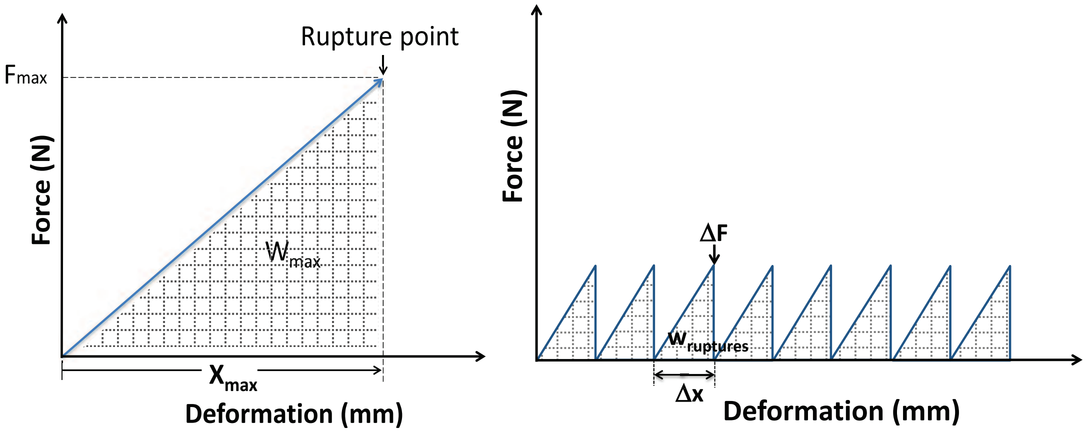


Figure 14. Left) Theoretical force-deformation curves obtained by puncture test: crunchy behavior: maximum penetration force, F_{max} (N); maximum penetration distance, X_{max} (mm) and total work, W_{max}, (J). Right) Theoretical force-deformation curves obtained by puncture test: crispy behavior: the penetration distance for each micro-rupture peak, ΔX (mm); the individual force drops for each micro-rupture peak (ΔF, N) and the average work for micro-ruptures, $w_{rupture}$ (J).

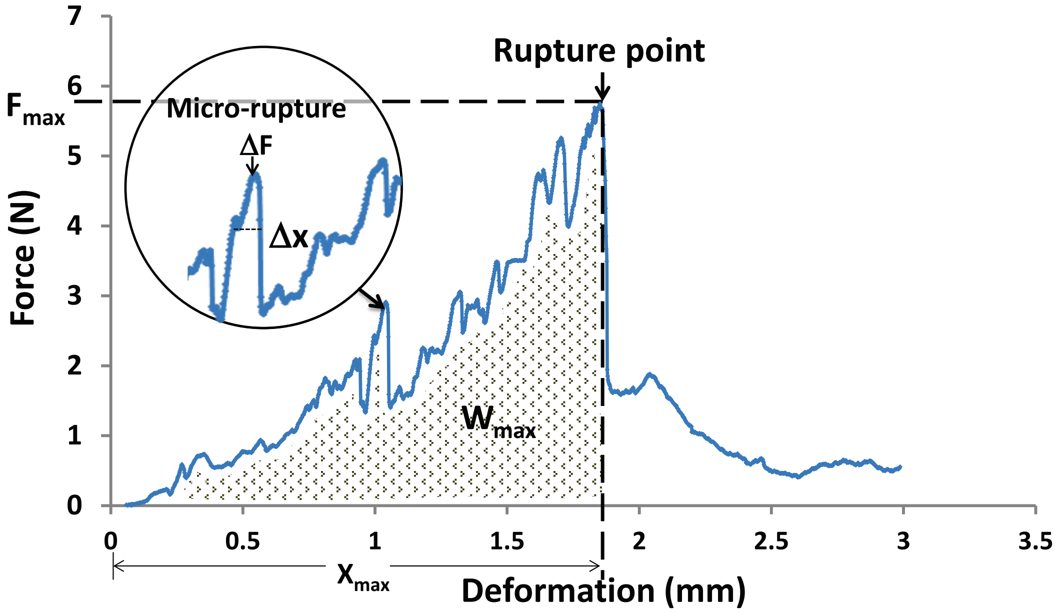


Figure 15. Real force-deformation curve recorded by puncture test: crunchy and crispy behavior.

Various force and work parameters were determined to respectively and separately define the crunchy and crispness properties.

Descripting parameters of Crunchy (Croquant) behavior:

Maximum penetration force (N): F_{max}

Maximum penetration distance (mm): X_{max}

Total work (J):

$$W = \int_0^X F dx$$

Equation 3

Total work at X_{max} (J):

$$W_{max} = \int_0^{X_{max}} F dx$$

Equation 4

Average puncturing force (N):

$$\langle F \rangle = \frac{W_{max}}{X_{max}}$$

Equation 5

Descripting parameters of Crispy (Croustillant) behavior:

Total number of peaks: n

Spatial frequency of structural micro-ruptures (m^{-1}): $$\mathrm{N} = \frac{n}{\mathrm{X}_{max}}$$ Equation 6

Average of micro-rupture force (N): $$\mathrm{f} = \langle \Delta \mathrm{F} \rangle = \frac{\sum \Delta \mathrm{F}}{n}$$ Equation 7

Average work for micro-ruptures (J): $$\mathrm{w}_{rupture} = \langle \frac{\Delta F . \Delta X}{2} \rangle$$

Equation 8

$$= \frac{1}{2} \langle \Delta F \rangle . \langle \Delta X \rangle = \frac{1}{2} f . \frac{X_{max}}{n} = \frac{f}{2N}$$

Where, ΔX is the penetration distance for each micro-rupture peak (mm) and ΔF is the individual force drops for each micro-rupture peak (N). All of these parameters (i.e. X_{max}, W_{max}, <F>, N, f, $w_{rupture}$, ΔX and ΔF) were calculated until F_{max} was reached (Figure 15). The final values were the arithmetic mean of five measurements.

II.2.2.9 Expansion ratios

For the porous materials we studied, two expansion ratios were normally defined: the absolute expansion ratio ε_absolute and the relative expansion ratio ε_relative. The first ε_absolute is the ratio of the apparent volume of the product and the volume of the solid itself. The second ε_relative reflects the increase of volume after processing (FD and SD) compared with the HAD. The absolute and the relative expansion ratios are in function of the product´s densities ρ_intrinsic and ρ_specific (g/m3), which were calculated for each sample as follows:

Absolute expansion ratio: $$\varepsilon_{absolute} = \frac{\rho_{intrinsic}}{\rho_{specific}}$$ Equation 9

Relative expansion ratio: $$\varepsilon_{relative} = \frac{\rho_{specific}\ of\ HAD\ product}{\rho_{specific}\ of\ SD\ or\ FD\ product}$$ Equation 10

Where, the intrinsic density is the density of solid properly said. To measure the intrinsic density (ρintrinsic, g/m3) of each sample (HAD, FD and SD), a gas Pycnometer Micromeritics AccuPyc 1330 (USA) with helium was used.

In the cases of food dried samples, Archimedes method is not possible to be adopted for measuring the specific (apparent) density because of possible interaction between water and the product. Thus, to determine such specific density (ρspecific, g/m3), a tapped method was carried out. Briefly, sand (ρsand = 0.9092 g/cm3 and 71-200 μm diameter) was put into the cylinder (100 mL and 37.018 g of weigh). The cylinder, with the sand, was then tamped 1000 times on an Autotap Quantachrome DA-3 (Florida, USA). After, the weigh was registered and the mass of sand ($m_{s,1}$, g) was calculated. Subsequently, this method is repeated adding a dried sample with a known mass ($m_{sample} \approx 2$ g) into the cylinder with the sand included. And, the weigh was measured and the mass of sand ($m_{s,2}$, g) was calculated. Thus, the specific density of each sample (HAD, FD and SD) was calculated as follows:

Specific density:

$$\rho_{specific} = \frac{(m_{sample})(\rho_{sand})}{m_{s,1} - m_{s,2}}$$

Equation 11

II.2.2.10 Scanning Electronic Microscopy

The micro-structure of dried strawberry samples, HAD, FD and SD (only treatment conditions for DIC 8 and 11), was observed thanks to a scanning electronic microscope (SEM) JEOL 5410LVFEI Quanta 200F (Philips Croissy-sur-Seine, France). Each sample was placed on a covered support using carbon adhesive and the scanning was carried out under partial vacuum (7 Pa) with an accelerating voltage of 20 kV.

II.2.3 DIC Experimental Design

In order to study the effect of DIC operating parameters (saturated steam pressure “MPa” and thermal holding time “s”) on the different response parameters as cited in Figure 12, a 2-parameter, 5-level central composite rotatable design was used with 4 (22) factorial points, 4 (2*2) axial points and a central point triplicated (3) for replications (Table 7). The ranges of operating parameters were defined after preliminary trials. The 11 trials were run in random order to minimize the effects of unexpected variability on observed responses due to external factors (Table 8). The analysis was carried out with the statistical program (Statgraphics, Centurion XV, USA). The mathematical empirical model applied in this study was:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i \chi_i + \sum_{i=1}^{n} \beta_{ii} \chi_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^{n} \beta_{ij} \chi_i \chi_j + \varepsilon \qquad \text{Equation 12}$$

Where:

Y is the response; β_i, β_{ii}, β_{ij} are the regression coefficients; X_i and X_j are the independent variables; ε is the random error; and i and j are the indices of the factors.

To understand better, the results were expressed by:

- The analysis of variance (ANOVA) was used to determine significant differences between independent variables ($p < 0.05$).
- Pareto chart was inserted to identify the impact of variables on various responses. The vertical line in the Pareto chart determines the effects that are statistically significant at the 95 % confidence level. The standardized effect is the estimated effect divided by its standard error. Hence, a low standardized effect can mean either a low effect of the parameter or a large experimental error.
- Surface response methodology plots are used to optimize the various responses.
- General trends to analyze various responses behavior in front of variable changes.
- Empirical model coefficients to determine the regression model for each response and R^2 to accurate fitting models to real data.

Table 7. Coded and real ranges of independent variables used in the 2-variable 5-level rotatable experimental design

Factor/ Coded Level	-α	-1	0	1	+α
Processing pressure (MPa)	0.10	0.19	0.35	0.53	0.60
Processing time (s)	10	13	20	27	30

$\alpha=\sqrt[4]{2^k}$; α is the axial distance and k is the number of experiments of orthogonal design. In this case, k=2 and α=1.4142.

Table 8. Trials in the experimental design for DIC process

	DIC										
Run	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Processing pressure (MPa)	0.60	0.35	0.35	0.53	0.53	0.35	0.17	0.17	0.10	0.35	0.35
Processing time (s)	20	30	20	27	13	20	13	27	20	10	20

PART III

RESULTS

CHAPTER III.1

COMPARATIVE STUDY OF VARIOUS DRYING PROCESSES AT PHYSICAL AND CHEMICAL PROPERTIES OF STRAWBERRIES (FRAGARIA VAR. CAMAROSA)

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Comparative study of various drying processes at physical and chemical properties of strawberries (*Fragaria var. camarosa*)

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Abstract

The objective of this work was to study and compare different drying processes of strawberry. The impact of DIC as texturing process within a swell drying operation was quantified when inserted before the second stage of hot air drying (swell drying SD). The obtained results showed that DIC treatment has a great impact on drying kinetics and performances compared to those of classical hot air drying. The drying of DIC-textured strawberry was accelerated even under low temperature (soft conditions). That can be explained by the direct impact of swelling on diffusivity and starting accessibility. Indeed, the mechanical effect of pressure drop leads to a great expansion of the structure, while the short thermal treatment time can preserve the quality. Thus, the new modified texture makes the trapped water accessible for improving the diffusion especially in the second stage of drying after the shrinkage of product, as well as in the rehydration process; the water holding capacity can be much higher. So the necessary time to reach the optimum final water content for the storage is shorter in case of DIC-swell dried strawberry compared to the classical hot air dried products.

Keywords: Instant Controlled Pressure Drop, capsicum; drying kinetics; rehydration kinetics; water holding capacity

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1. Introduction

Strawberry is one of the most delicate and highly perishable fruits, due to respiration, weight loss and susceptibility to fungal contamination. At the same time, they are sensitive to chemical and microbial deterioration during post-harvest storage and handling, therefore, they have a rather limited shelf life in a fresh form [1]. Hence, large range of unit operations have been proposed and used to preserve it. New operations such as swell-drying and freezing of partially dried products were defined combined to Instant Controlled Pressure Drop (DIC).

DIC is a high temperature short time (HTST) treatment followed by an abrupt pressure drop towards a vacuum implying an autovaporization of small amount of water from the products. It hence induces an instant cooling of treated products preventing their thermal degradation. Such a cooling gotten by abruptly dropping the pressure from high saturated steam level (from 0.1 up to 0.6 MPa to about 5 kPa with a rate of $\Delta P/\Delta t > 0.5$ MPa s^{-1}) [2,3] allows the product to cross the glass transition border. Thus the new swelled/expanded texture obtained after DIC treatment can be maintained. Thus, DIC treatment has two effects: the thermal effect as a result of the short-time/high-temperature induced by saturated steam; and the mechanical effect, which is induced by the difference between the high pressure inside the product and the surrounding vacuum. DIC enhances many unit operations such as drying; freezing and even extraction may not only maintain valuable compounds found in fresh products but can also improve both of their availability and activity. Likewise, DIC process has been used to swell-dry, decontaminate, and texture various fruits and vegetables; it ensures a high quality by improving the kinetics and the capacity of both dehydration and rehydration processes as well as the possibility of preserving and even increasing the organoleptic content and the availability of bioactive compounds such as antioxidant activity [4-6]. Moreover, dried products could be directly consumed as snacking or in many other powder forms to produce high quality puree, jam, ice-cream, baby foods, breakfast cereals, possibly rehydrated with yoghurt and bakery products [7].

The aim of this study was to compare various drying techniques; Hot Air Drying (HAD), Freeze Drying (FD), and Swell drying (SD); coupling the traditional hot air drying to DIC treatment. A comparative study was conducted to evaluate the different drying techniques in terms of drying kinetics (drying time starting accessibility, effective water diffusivity), rehydration kinetics (rehydration time, starting accessibility, effective water diffusivity), and water holding capacity of dried strawberries (Fragaria Var. Camarosa).

2. Materials and Methods

2.1. Materials

The strawberries (Fragaria Var. Camarosa) were purchased from a popular local market of La Rochelle city, France. They were transported to the laboratory and stored at 5ºC for 24 h.

2.2. Methods

2.2.1. Sample Preparation

Strawberries were selected, cleaned and washed with potable water; they were subsequently cut with a hand knife into 4-5 slices. For the treatment, they were divided in three lots for being processed by: hot air HAD, freeze-drying FD and swell drying SD.

2.2.2. Dehydration Methods

2.2.2.1. Hot air drying HAD

Strawberries slices were dried in the hot air dryer (Memmert: Universal Oven UNB Model 800) at 50°C, the initial partial pressure of vapor in the air was 265 Pa with an air flux of 1.2 ms^{-1}. They were dried until attaining 3% d.b (dry basis). These samples were recorded as **HAD**.

2.2.2.2. Freeze Drying FD

A freeze-drying equipment (model: RP2V, Serail, France) was used for drying the strawberry slices. The conditions were divided in three steps: external freezing (at -20°C for 2h), sublimation (-20 °C, 0.66 Pa for 12 h) and desorption (25°C, 0.66 Pa for 12 h). Afterword, the slices were packed in hermetically sealed bags and stored until their characterization. These samples were recorded as FD.

2.2.2.3. Swell Drying SD

The strawberries slices were firstly dried at 50°C in the same conditions for 8 h until attaining 18% d.b of water content. After drying, the slices were packed in zip plastic bags and stored in a cold room at 5°C for 24 h. The partially hot air dried strawberries were treated by the DIC according to experimental design (Table 2); to be completely dried by traditional convective hot air drying at 60 °C to reach about 3% d.b for approximately 1 h. These samples were recorded as **SD**.

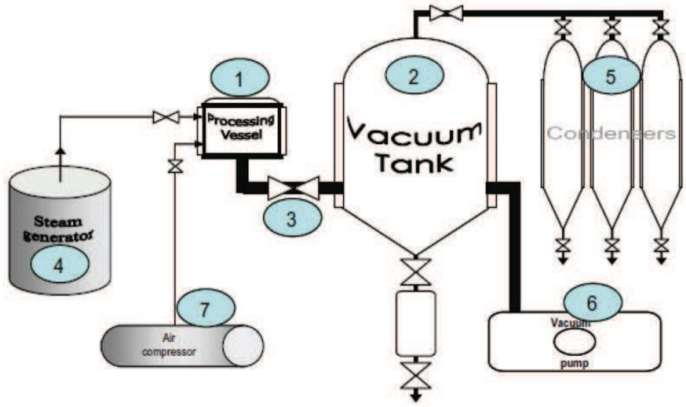

Figure 1. Schematic diagram of the DIC reactor: (1) Processing vessel; (2) Vacuum tank, (3) Quick motion valve; (4) Steam generator; (5) Condensers; (6) Vacuum pump; (7) Air compressor.

The experimental set-up has been largely described by Allaf and Louka (1994); [8]; [2]; [9]; it is composed of three main elements (Figure 1):

1. The processing vessel (1), where the samples are placed and treated.
2. The vacuum system, which consists mainly of a vacuum tank (2) with a volume 130 times greater than the processing vessel, and an adequate vacuum pump. The initial vacuum level was maintained at 5 kPa in all the experiments.
3. A pneumatic valve (3) that ensures the connection/separation between the vacuum tank and the processing vessel. It is capable of producing the abrupt pressure drop within the reactor in less than 0.2 s ($\Delta P/\Delta t > 0.5$ MPa s^{-1}).

2.2.3. Assessment methods

2.2.3.1. Water Content

The water content of different samples (fresh, pre-dried and completely dried strawberries) was determined according to Karathanos's method [10]. Approximately, 2.5± 0.1 g of each sample was dried in the oven UFE 400 (Memmert, Germany) at 65ºC for 48 h. The measurements were triplicated. The water content dry basis (% db) was calculated according to the equation (1):

$$W = \frac{m_i - m_d}{m_d} \quad (1)$$

Where, W is the water content of samples (% db or kg of H_2O/100 kg of dry basis), m_i is the initial weight of the material before drying (kg) and m_d is the final weight of the material after drying (kg).

2.2.3.2. Drying Kinetics

Drying kinetics were performed for HAD and SD samples. Approximately, 3.00 ± 0.05 g of each sample was used. They were placed in the hot air oven (Memmert: Universal Oven UNB Model 800) at 65ºC and weight loss was recorded using an electronic balance (model EP2102, Ohaus, US). The weight loss was recorded every 5 minutes as interval time during the first 30 minutes, subsequently after 45, 60, 90, 120 minutes, after 120 minutes the weight loss was recorded every hour until equilibrium water content (change on weigh less than 0.01 g) was recorded.

2.2.3.3. Rehydration Kinetics

The capacity and rate of rehydration of HAD, SD and FD samples were evaluated as following: strawberry sample (about 0.51± 0.02 g) was placed in the clip handle tea strainers, and submerged in distilled water (at 20 ± 0.05 ºC). At specific time intervals (0, 0.5, 2, 4, 6, 8, 10, 15, 30, 45, 60, 90, 120, 150 and 180 min), samples were taken off from the water, blotted with tissue paper to remove superficial water, and reweighted. Weight was recorded using an electronic balance AR2140 (OHAUS, China).

2.2.3.4. Drying and Rehydration kinetics

As reported by Allaf and Coll., drying kinetic model adopted consists in three stages: initial surface interaction, diffusion phase and paradoxical phase. The experimental results used for the mass diffusion model excluded the ones close to t=0 as well as the ones implying the paradoxical phase (long time stage); they allowed to determine the effective diffusivity ($D_{eff,d}$) of water within the porous medium. By extrapolating this diffusion model towards t=0, W_o was calculated as, usually, different from the initial humidity content W_i. The difference between W_i and W_o defined as the "starting accessibility" $\delta W_{s,d}=W_i-W_o$ reflects the water quickly removed from the surface, independently from diffusion processes. Adding to this phenomenon, the drying time to get water content of 3.0% db was ($t_{d3.0\%}$).

Concerning the rehydration kinetics, a similar model has been applied. Evaluated response parameters were the values of rehydration time to get water content of 300 % db ($t_{r300\%}$), the "starting accessibility" ($\delta W_{s,r}$) revealing the water immediately retained (hold) at the surface and the effective diffusivity of rehydration ($D_{eff,r}$).

2.2.3.5. Water Holding Capacity

The water holding capacity (WHC) for the different dried samples (HAD, SD, FD) was determined using the centrifuge technique. Two grams of the sample in powder were mixed with 20 mL distilled water, placed in 30 mL plastic centrifuge tubes, and allowed to set at room temperature (20 ± 2°C) for about 45 min prior to the test run. The tubes were centrifuged (Centrifuge Model Sigma 3K15) at 3000 rpm for 35 min. After centrifugation, the extra supernatant from the centrifuged sample was drained and the sample was reweighted. The samples were then dried in hot air oven at 65 ºC for 48 h for water content determination. WHC was calculated as the amount of water (g) absorbed by 100 g of dry basis.

2.2.4. Experimental Design

In order to study the effect of DIC operating parameters (saturated steam pressure “MPa” and thermal holding time “s”) on the different response parameters (effective water diffusivity, starting accessibility, the needed time to attain reach a specific water content for both drying and rehydration, and water holding capacity); a 2-parameter, 5-level central composite rotatable design (Table 2) was used with 4 factorial points and 4 axial points while the central point was triplicated. The ranges of operating parameters were defined after preliminary trials (Table 1). The 11 runs were achieved in random to minimize the effects of unexpected variability due to external factors. The analysis was carried out with the statistical program (Statgraphics, Centurion XV, USA). The mathematical empirical model applied in this study is:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i \chi_i + \sum_{i=1}^{n} \beta_{ii} \chi_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^{n} \beta_{ij} \chi_i \chi_j + \varepsilon \quad (2)$$

$$Y = \beta_0 + \beta_1 \chi_1 + \beta_2 \chi_2 + \beta_{11} \chi_1^2 + \beta_{22} \chi_1^2 + \beta_{12} \chi_1 \chi_2 \quad (3)$$

Where Y is the response, β_i, β_{ii}, β_{ij} are the regression coefficients, χ_i are the independent variables, ε is random error, i and j are the indices of the factors.

Results were expressed by:

- Surface response methodology plots to optimize the responses,
- The analysis of variance (ANOVA) to determine significant differences between independent variables ($P \leq 0.05$),
- Pareto charts to identify the impact of variables on responses,
- General trends to analyze responses behavior in front of variable changes,
- Empirical model coefficients to determine the models of each response, and R^2 to accurate fitting models to real data.

Table 1.Coded levels for independent variables used in developing experimental data.

Coded levels	–α	-1	0	1	+α
Saturated steam pressure P (MPa)	0.10	0.17	0.35	0.53	0.60
Processing time t (s)	10	13	20	27	30

α (axial distance)= $\sqrt[2]{N}$; N is the number of experiments of orthogonal design, i.e. of the factorial design. In this case α = 1.4142

Table 2. Experimental design used in DIC treatment for SD.

Run	1	2	3	4	5	6	7	8	9	10	11
Pressure P (MPa)	0.6	0.35	0.35	0.53	0.53	0.35	0.17	0.17	0.10	0.35	0.35
Time t (s)	20	30	20	27	13	20	13	27	20	10	20

3. Results

3.1. Experimental results

3.1.1. Drying Kinetics

The drying kinetics (drying time, starting accessibility, effective water diffusivity) was studied for control (HAD) and DIC treated (SD) strawberries (fig. 2 and 3), the obtained results showed that the SD (DIC treated) samples had a quick drying kinetics compared to control (THD). As shown in the Figure 2, the drying time of all SD samples was shorter than control (HAD). The necessary time to reach 4% dry basis for SD strawberry at 0.60 MPa; 20 s (DIC 1) was about 45 min, while HAD strawberry needed unidentified time to attain the same level of water content dry basis (Figure 3).

Table 3. Results of evaluated drying kinetics parameters: water content at 120 min ($W_{t=120\ min}$), drying time to reach a final water content of 0.05% db ($t_{d3\%}$), starting accessibility ($\delta W_{s,d}$) and effective water diffusivity ($D_{eff,d}$). R^2 is the correlation coefficient between the experimental and predicted data values of the model

Trial no.	Pressure (MPa)	Time (s)	$W_{t=120\ min}$ (% db)	$t_{d3\%}$ (min)	$\delta W_{s,d}$ (% db)	$D_{eff,d}$ (10^{-10} m^2 s^{-1})	R^2 (%)
DIC 1	0.6	20	1.54	49,63	2,68	5,00	98.12
DIC 2	0.35	30	2.58	80,78	1,78	3,13	96.75
DIC 3	0.35	20	1.62	56,50	1,97	5,10	99.59
DIC 4	0.53	27	2.80	88,49	1,64	4,89	95.89
DIC 5	0.53	13	2.28	84,27	1,24	3,16	98.23
DIC 6	0.35	20	2.94	92,52	1,68	3,17	99.25
DIC 7	0.17	13	4.18	125,25	2,19	0,52	99.63
DIC 8	0.17	27	3.99	122,32	1,02	1,62	96.95
DIC 9	0.10	20	6.18	186,85	0,69	0,39	97.35
DIC 10	0.35	10	2.21	83,18	2,57	1,56	97.55
DIC 11	0.35	20	2.36	82,70	2,46	4,50	99.62
Control	-	-	7.45	448,84	0,30	0,11	92.24

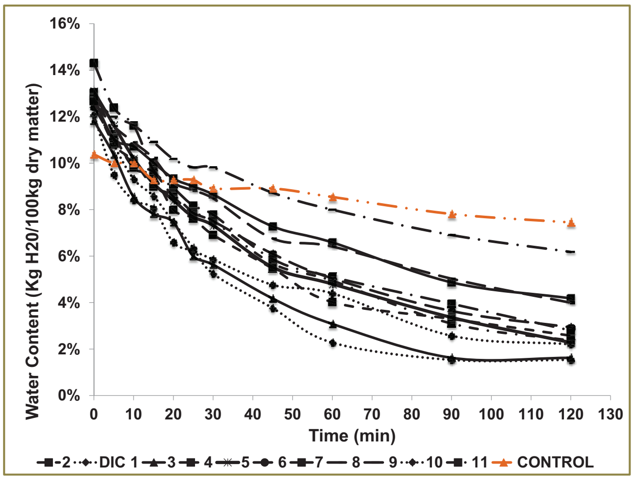

Figure 2. Drying kinetics of dried strawberries: Control (HAD) and SD, the drying was performed (at initial air temperature of 65ºC, initial vapor pressure of 265 Pa, flux velocity of 1.2 m s^{-1}).

The drying kinetics in our study was identified through the starting accessibility $\delta W_{s,d}$ and the effective water diffusivity $D_{eff,d}$; so these characteristics were studied as well. As shown in Table 3, $\delta W_{s,d}$ and $D_{eff,d}$ of SD were increased by about 9 and 46 times respectively compared to control sample (HAD). For SD samples treated by DIC under P=0.60 MPa, t=20 s, they were 2.68 % (db) and 5.00 x 10^{-10} m^2 s^{-1} respectively against 0.30% (d.b) and 0.11x 10^{-10} m^2 s^{-1} for control sample (HAD).

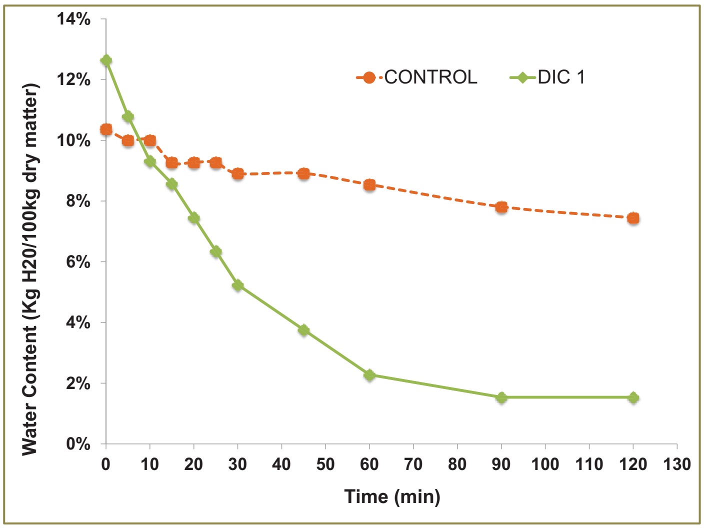

Figure 3. Kinetics of strawberry. Drying performed at 65 ºC. Control (HAD) and SD (DIC treated at P: 0.60 MPa, t: 20 s)

3.1.2. Rehydration Kinetics

The reconstitution of dried material through the rehydration is investigated; the capacity and rate of rehydration were measured (figures 4 and 5). Similar to drying modeling, the rehydration response parameters were studied as well ; water content dry basis at 180 min ($W_{t=180\ min}$), rehydration time to attain a final water content of 300% d.b ($W_{tr300\%}$), starting accessibility ($\delta W_{s,r}$) and effective water diffusivity.

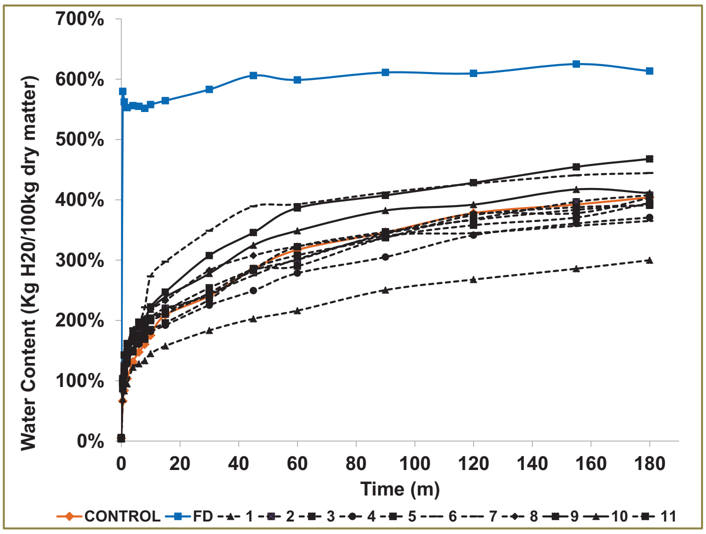

Figure 4. Kinetics of dried strawberry rehydration performed at room temperature (20 ± 0.05ºC): Control (HAD) and SD (DIC treatments 1-11), the rehydration was performed at room temperature

Figure 4 showed the rehydration kinetics (capacity and rate of water absorption) of HAD, FD, and SD samples. The obtained results illustrated an improvement in the capacity and the rate of rehydration for all SD samples compared to control (HAD). The rehydration is an important characteristic of dried food, normally affected by drying technique and drying conditions as well. Our results showed that the behavior of dried product during rehydration is drying technique dependent. The SD samples showed high capacity with rapid rate of water uptake compared to control (HAD), however the FD samples had the highest capacity and rate of water absorption compared to both SD and HAD samples.

During the first five minutes of rehydration time (total time: 180 min), SD samples had a high water uptake (200% d.b) compared to HAD as control (100% db), while the FD samples were found with 550% d.b with rapid rate of water uptake (Figure 5).The DIC1-SD strawberries treated under saturated steam pressure of P: 0.60 MPa for t: 20s were found to get the highest rehydration kinetics.

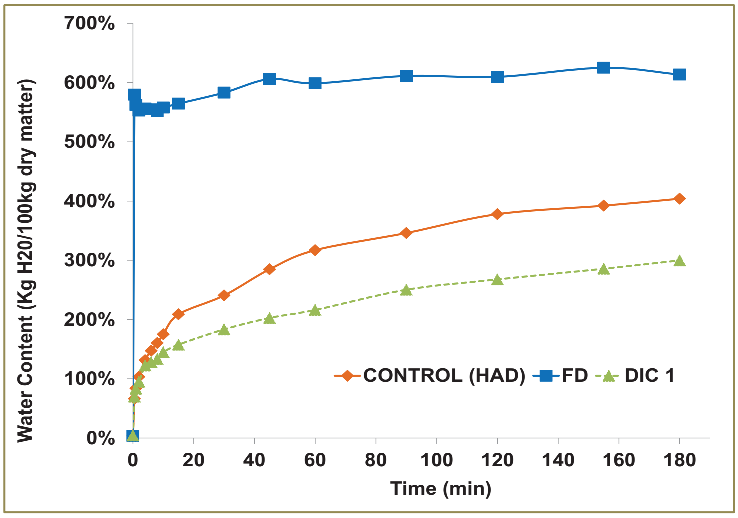

Figure 5. Rehydration kinetics of dried strawberries: Control (HAD) and SD (DIC point 1; P: 0.60 MPa, t: 20 s) the rehydration was performed at room temperature (20 ± 0.05ºC).

Table 4. Water Holding Capacity (WHC) and compute dehydration kinetic parameter: $W_{t=180\ min}$ (water content at 180 min), $t_{r300\%}$ (rehydration time to attain a final water content of 300% db), $\delta W_{s,r}$ (starting accessibility) and ($D_{eff,r}$) effective water diffusivity. R^2 is the correlation coefficient between the experimental and predicted data values of the model.

Trial no.	Pressure (MPa)	Time (s)	WHC (% db)	$W_{t=180}$ min (% db)	$t_{r300\%}$ (min)	$\delta W_{s,r}$ (% db)	$D_{eff,r}$ (10^{-10} m^2 s^{-1})	R^2 (%)
DIC 1	0.6	20	108,16%	299.81	193,57	39,89%	2,77	97.96
DIC 2	0.35	30	228,51%	407.67	66,53	59,95%	2,84	98.37
DIC 3	0.35	20	162,94%	392.06	58,40	41,97%	4,03	98.43
DIC 4	0.53	27	84,55%	370.60	85,66	39,37%	4,74	97.62
DIC 5	0.53	13	230,03%	390.75	65,01	48,60%	3,37	98.23
DIC 6	0.35	20	204,29%	365.00	61,63	74,85%	4,65	99.25
DIC 7	0.17	13	134,78%	444.32	34,41	23,00%	1,19	94.90
DIC 8	0.17	27	133,33%	403.18	60,16	29,50%	2,52	95.89
DIC 9	0.1	20	222,63%	467.73	40,24	45,28%	1,02	98.26
DIC 10	0.35	10	235,97%	411.12	44,89	69,59%	2,13	99.36
DIC 11	0.35	20	157,56%	394.79	65,96	71,67%	4,53	98.95
Control	-	-	288,97	613.5	55,48	10,81%	0,67	98.48
FD	0.6	20	190,44	403.97	37,59	592,94%	2,42	91.19

The starting accessibility $\delta W_{s,r}$ and effective water diffusivity $D_{eff,r}$ revealing the kinectis of rehydration of dried strawberries were increased by 662% and 676% respectively compared to control sample (HAD). SD samples treated by DIC under P=0.35 MPa, t=20 s had $\delta W_{s,r}$ and $D_{eff,r}$ of 71.67%% (d.b) and 4.53 x 10^{-10} m^2 s^{-1} respectively against 10.81%% (d.b) and 0.67 x 10^{-10} m^2 s^{-1} for HAD as control. It worth to mention here that, although the rehydration of freeze dried FD samples were found with $\delta W_{s,r}$ higher than SD samples, one cannot assume FD rehydration as a diffusion phenomenon; it should be only based on a superficial exchange phenomena $D_{eff,r}$ of FD was incomparable in our study.

3.2. Correlation terms

The different response parameters concerning both of drying and rehydration kinetics were:

$\delta W_{s,d}$:	Drying Stating accessibility, % d.b
$D_{eff,d}$:	Effective water diffusivity during drying, m^2 s^{-1}
$t_{d3\%}$:	Dehydration time to attain water content of 3% d.b
$\delta W_{s,r}$:	Rehydration Stating accessibility % d.b
$D_{eff,r}$:	Effective water diffusivity during rehydration, m^2 s^{-1}
$t_{r300\%}$:	Rehydration time to attain a final water content of 300% d.b
WHC:	Water Holding Capacity (% d.b)

Table 5. Correlations between drying and rehydration response parameters, and Water Holding Capacity (WHC).

	$\delta W_{s,d}$	D_{eff}	$t_{d3\%}$	$\delta W_{s,r}$	D_{eff}	$t_{r300\%}$	WHC
$\delta W_{s,d}$	1,00	0,50	-0,74	0,42	0,32	0,42	-0,46
D_{eff}	0,50	1,00	-0,66	0,32	0,84	0,62	-0,54
$t_{d3\%}$	-0,74	-0,66	1,00	-0,60	-0,64	-0,28	0,56
$\delta W_{s,r}$	0,42	0,32	-0,60	1,00	-0,01	-0,22	0,04
D_{eff}	0,32	0,84	-0,64	-0,01	1,00	0,26	-0,43
$t_{r300\%}$	0,42	0,62	-0,28	-0,22	0,26	1,00	-0,46
WHC	-0,46	-0,54	0,56	0,04	-0,43	-0,46	1,00

Normal correlations could be identified; they mainly concerned effective water diffusivity $D_{eff,d}$ and drying time and starting accessibility $\delta W_{s,d}$. Water Holding Capacity WHC was correlated with effective water diffusivity during rehydration $D_{eff,d}$; both revealing deep behavior. However, it was not correlated with starting accessibility $\delta W_{s,r}$, which normally linked to the only exchange surface.

3.3. RSM analysis

3.3.1. Drying operation

3.3.1.1. Drying time

The estimated drying time to attain 3% db as final water content from 10% db for HAD and SD samples was calculated from the Fick's diffusional model. As observed in Table 3, the rapid drying operation was achieved for SD sample (treated by DIC) under P: 0.60 MPa, t: 20s), with time decreasing (compared to control) from 448.84 to 49.63 min.

Erreur ! Source du renvoi introuvable. illustrates the impact of operating parameters (saturated steam pressure, thermal holding time, with constant initial water content) of DIC treatment on the necessary time of drying to obtain final water content of 3% dry basis for SD samples. We observed that the most influencing parameters was the saturated steam pressure, the higher the saturated steam pressure, the shorter the drying time, while the impact of thermal holding time was insignificant and stable as a result of nearby treatment.

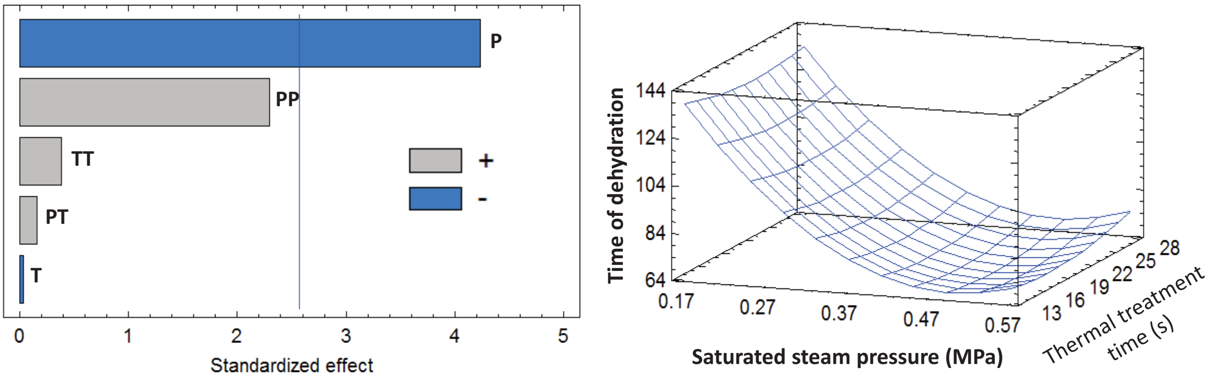

Figure 6. Effects of DIC operating parameters; Pressure (MPa) and time (s) on the drying time ($t_{d0.03\%}$) of SD Strawberries: (left) Pareto Chart and (right) response surface.

3.3.1.2. *Starting accessibility*

Concerning the starting accessibility, there was no significant effect of neither saturated steam pressure nor thermal treatment time (results none shown). However, the mean starting accessibility value for the DIC treated sample was much higher than those of freeze dried samples (1.81% against 0.30% respectively).

3.3.1.3. *Effective water diffusivity*

As the drying is a water removal process, so the diffusion of water and starting accessibility during the drying were studied as well. Figure 7**Erreur ! Source du renvoi introuvable.** illustrated the impact of DIC operating parameters (saturated steam pressure and thermal holding time with constant initial water content) on effective water diffusivity during drying. The obtained results showed that both saturated steam pressure and thermal processing time had significant impacts on effective water diffusivity; the higher the saturated steam pressure, the higher the effective water diffusivity within the product under intensified drying conditions.

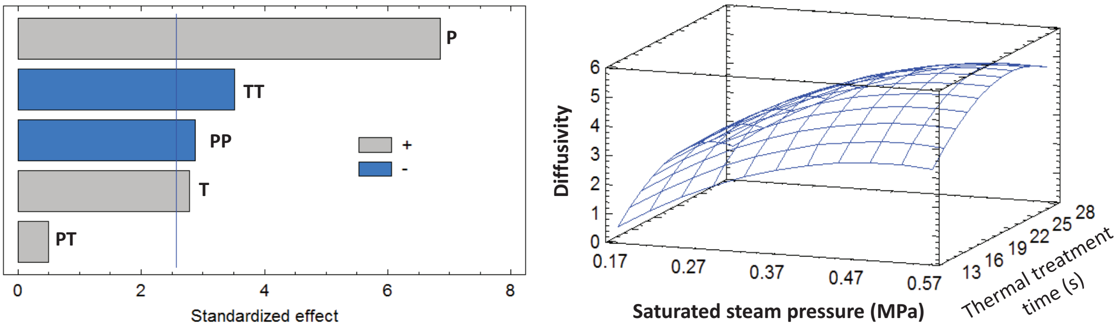

Figure 7. Effects of DIC operating parameters; Pressure (MPa) and time (s) on the starting effective water diffusivity (Deff,d) of SD Strawberries: (left) Pareto Chart and (right) response surface

3.3.2. *Rehydration operation*

3.3.2.1. *Rehydration time*

A comparative study of rehydration kinetics (the capacity and the rate of water uptake during a given time) was performed to compare the behavior of samples dried by different drying techniques (HAD, SD, and, FD), the operating parameters of DIC treatment were evaluated as well but only for SD samples.

Figure 8 showed the influence of the operating parameters (saturated steam pressure and thermal holding time with constant initial water content) of DIC treatment on the rehydration time of SD samples. The saturated steam pressure was the major parameter influencing the rehydration time; the lower the saturated steam pressure, the shorter the rehydration time. The shortest rehydration time was observed for SD samples treated at P: 0.17 MPa, t: 9 s and P: 0.1 MPa, t: 20 s; the rehydration time was then 34.41 min and 40.24 min, respectively in order to attain the 300% db as final water content.

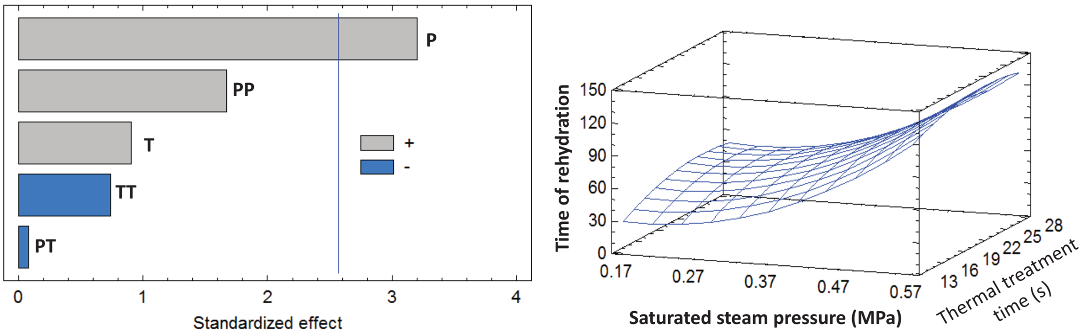

Figure 8. Effects of DIC operating parameters; Pressure (MPa) and time (s) on the rehydration time ($t_{d300\%}$) of SD Strawberries: (left) Pareto Chart and (right) response surface.

3.3.2.2. Starting accessibility

The starting accessibility ($\delta W_{s,r}$) was defined here as the amount of water available or accessible on the product's surface after water up taking, to be subsequently diffused within the product. The effect of DIC operating parameters (saturated steam pressure and thermal holding time with constant initial water content) on the starting accessibility during rehydration was illustrated in Figure 9.

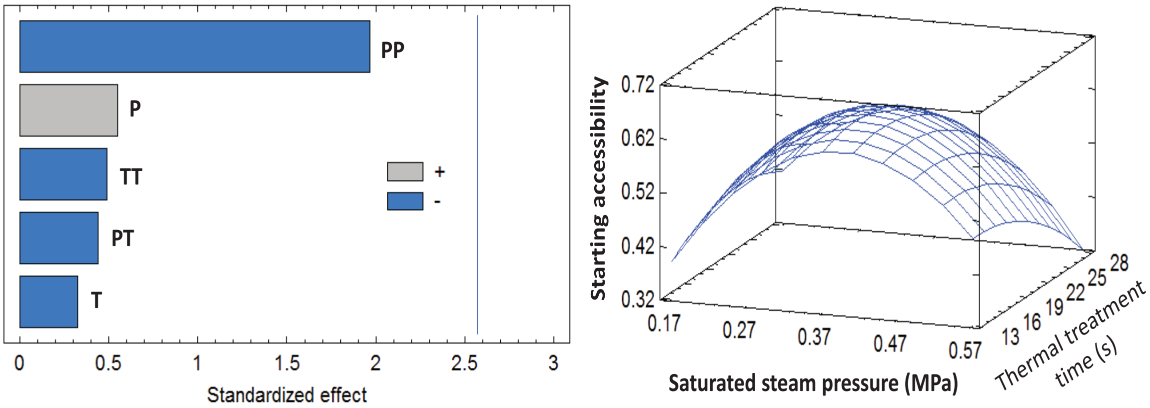

Figure 9. Effects of DIC operating parameters; Pressure (MPa) and time (s) on the starting accessibility (D_{eff_r}) during the rehydration of SD Strawberries: (left) Pareto Chart and (right) response surface.

The results showed that neither P nor t had a significant effect on the $\delta W_{s,r}$. Whereas, the highest starting accessibility (74,85%% db) was obtained under P: 0.35 MPa, t: 20 s compared to control (10,81% db). We observed that the starting accessibility decreased by increasing the saturated steam pressure after 0.35 MPa.

3.3.2.3. Effective water diffusivity

Effective water diffusivity during rehydration of dried products is the transfer phenomenon enables the adsorbed water on the product's surface to be effectively diffused within the product during its rehydration. The impact of DIC operating parameters (saturated steam pressure and thermal holding time with constant initial water content) on the effective water diffusivity was shown in Figure 10. The effective water diffusivity was significantly increased by increasing the saturated steam pressure; the higher saturated steam pressures the higher rate of water diffusivity during the rehydration of SD samples, whereas, the thermal holding time had a slight effect. It is interested to mention here that a similar behavior was observed for the effective water diffusivity during drying where the saturated steam pressure was the major affecting the effective water diffusivity while the effect of thermal holding time was slight reflecting a god definition of time limits and nearby treatment.

The rapid rate of effective water diffusivity $D_{eff,r}$ (4,6510^{-10} m^{2} s^{-1}) was obtained for SD sample (treated at P: 0.35 MPa, t: 20 s) against 0,67x 10^{-10} m^{2} s^{-1} for control sample (HAD) with an increase of 694% (table 4). As mentioned before that the rehydration of freeze dried products is not diffusion phenomenon but it based on superficial exchange phenomenon; thus the effective water diffusivity of FD was incomparable in our study.

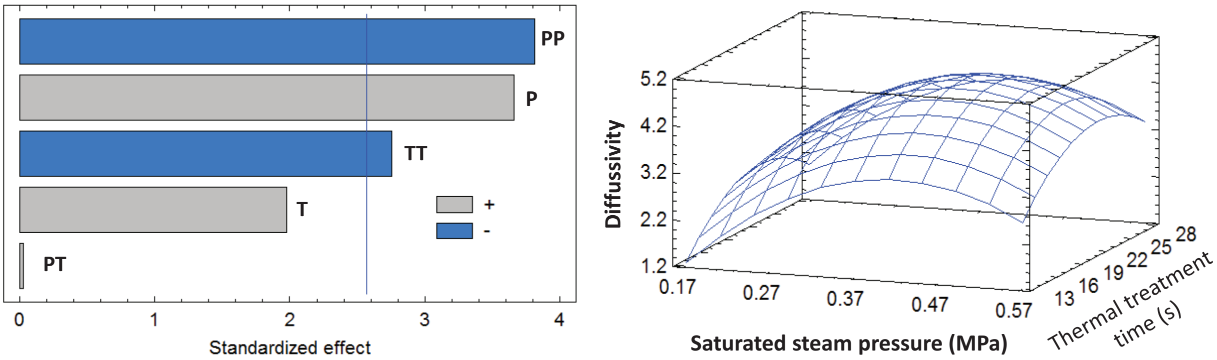

Figure 10. Effects of DIC operating parameters; Pressure (MPa) and time (s) on the effective water diffusivity (D_{eff_r}) during the rehydration of SD Strawberries: (left) Pareto Chart and (right) response surface

3.3.3. *Water holding capacity*

The capacity of water holding of strawberry samples dried by different techniques of drying was studied, was studied (fig. 12), the water holding capacity was significantly decreased with increasing the saturated steam pressure; the higher saturated steam pressure the lower water holding capacity, while the thermal holding time had insignificant effect. The HAD strawberry samples was found with the highest values of water holding capacity compared to FD and SD samples. The high capacity (235.97%) to hold water was found for SD treated at P: 0.35 and t: 10 s (Table 6). The study of DIC operating parameters (saturated steam pressure and thermal holding time at constant initial water content) showed that neither the saturated steam pressure nor thermal holding time had a notable effect on this response parameter.

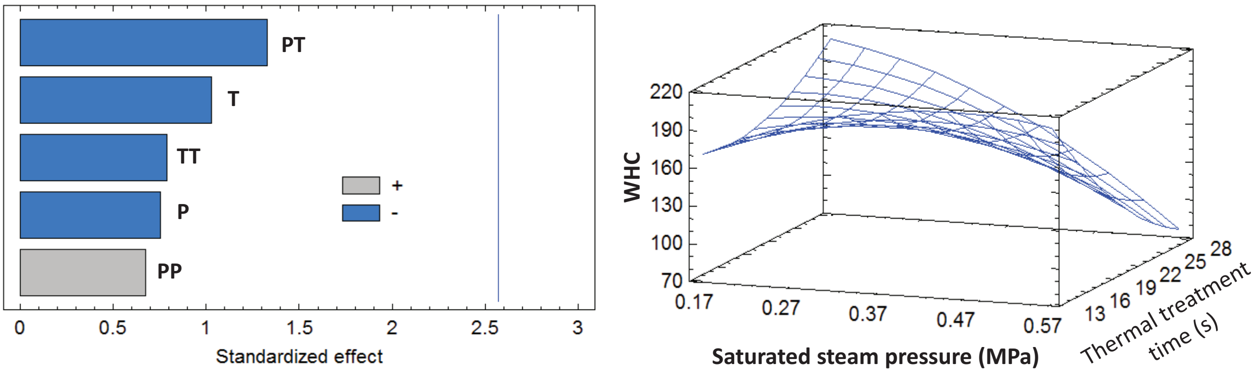

Figure 11. Effects of DIC operating parameters; Pressure (MPa) and time (s) on the water holding capacity (% db) of SD Strawberries: (left) Pareto Chart and (right) response surface

Table 6. Water Holding Capacity (% db) of dried Strawberries: Freeze drying FD, Traditional Hot Air Drying; THD (control), and Swell Drying SD.

	THD	FD	SWELL-DRYING SD samples										
			DIC1	DIC2	DIC3	DIC4	DIC5	DIC6	DIC7	DIC8	DIC9	DIC10	DIC11
WHC (%db)	289	190	163	236	204	135	158	229	108	223	133	230	85

4. Discussion

Drying is one of the most common methods to preserve strawberries [7, 11, 12] and following up its kinetics is the best way to design, predict a model and optimize this process [1, 13, 14]. The traditional food hot air drying commonly includes two periods. The first involves quick water removal (until the critical moisture point) often associated with product's shrinkage which finally dramatically reduces the diffusivity of water within the material with almost great deformation of the product [15-17]. The second has limited water removal as a result of the low diffusivity value, implying long-time period, high heating temperature and hence thermal degradation [18] revealed by a loss of vitamins and bioactive molecules, degradation of pigments and color, and poor nutrition value with a high energy consummation.

So new trends in food processing are focused on the marriage between new and innovative techniques to the Traditional Hot Air Drying (HAD) with the objective of drying resulting in costs reduction (short drying-time with low energy consumption), and product's quality preservation.

In this study, Instant Controlled Pressure Drop DIC was coupled to HAD; defined as Swell Drying SD, in order to intensify the HAD. The operation can be considered as an intensification of HAD. The obtained results showed the shorter time of SD compared to HAD (control) with lower final water content. This can be explained by the structural modifications occurred as a result of texturing by DIC. Some of these modifications were the breakdown of the plant cell walls entrapping water inside. SD is a relevant solution to dried product's shrinkage (texture compactness), product deformation, super heating, and hence thermal degradation (loss of vitamins and bioactive molecules, degradation of pigments and colour, and poor nutrition value).

Texturing by DIC induced an autovaporization of a small amount of product's water resulting in open texture as a result of gas (saturated steam) expansion within the product. The later produced some mechanical constrains on the cell wall leading to its expansion and to get pores specially since pressure dropping towards a vacuum allows crossing the glass transition border.

The internal water transfer (water diffusion) is the driven force in both drying and rehydration, the open and spongy texture improved significantly the starting accessibility and effective water diffusivity during both drying and rehydration operations. The higher the effective water diffusivity, the shorter the drying and/or rehydration times. These results are in agreement of those reported by other authors; Pilatowski et al., (2010) and Cong et al., (2009) reported time decreasing from 205 min to 11.10 min for paddy rice [19] [20]; Mounir et al., (2009) reported a significant decrease in drying time of apple from 6 h to 1 h [21] and Al Haddad et al. showed a significant decrease in drying time, when they studied the DIC swell drying SD coupled to a final drying by microwaves (700W). This study was carried out on apple and mango cubes. They reported needed time was less than 5 min in the case of DIC coupled to the drying by microwaves, followed by 2 hours for the usual SD. While, they found that HAD needed 8 hours to attain a higher water content (5% db as final moisture content) [22].

The low final water content of SD samples was explained by the rapid removal of water as the diffusivity was improved compared to HAD samples. Others studies reported different levels of final moisture content confirming that the drying kinetics and the final water content are drying techniques and conditions dependent.

Water holding capacity revealed the amount of water absorbed during rehydration (capacity and rate), the low capacity of water holding of SD compared to HAD is due to the structural modification, the texture was become open and spongy which makes it difficult to catch and hold the absorbed water, this can explain the low capacity of water holding for FD samples, in addition to the texture collapse of FD products. The low water holding capacity for SD strawberries may be due to some broking cell walls.

The RSM analysis for all response parameters showed that DIC saturated steam pressure was the major affecting on the studied response parameters. This can be explained by the mechanical strains induced as a result of steam expansion within the product implying some chemical and textural modifications.

5. Conclusions

Different drying techniques were studied in terms of drying kinetics, starting accessibility and water effective diffusivity during drying. Some of physical and functional properties of dried strawberries were studied as well, such as rehydration kinetics (capacity and rate), starting accessibility and water effective diffusivity during rehydration and the water holding capacity.

The obtained results shows that the swell drying SD can be used as an alternative technique to dry the foodstuffs with high quality during short time decreasing the costs of the operation. The product quality attributes are drying technique dependent. The SD is a flexible process; the operating parameters (saturated steam pressure and thermal processing time) can be optimized to meet the product's quality and attributes depending on industrial and consumer needs as well.

6. Acknowledgements

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CHAPTER III.2

COMPARATIVE STUDY OF THE EFFECTS OF DRYING METHODS ON ANTIOXIDANT ACTIVITY OF DRIED STRAWBERRY (FRAGARIA VAR. CAMAROSA)

Comparative study of the effects of drying methods on antioxidant activity of dried strawberry (Fragaria var. Camarosa)

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Comparative study of the effects of drying methods on antioxidant activity of dried strawberry (Fragaria var. Camarosa)

1. Abstract

Hot air drying (HAD), freeze-drying (FD), and swell-drying (SD, coupling instant controlled pressure drop, DIC, to standard hot air) were applied to strawberries (Fragaria var. Camarosa). The total phenol, total flavonoid, and total anthocyanin contents were evaluated versus the drying methods. The correlations between the bioactive compounds and antioxidant activity were investigated. The obtained results showed that the differences in phenol levels were no quite comparing the three drying techniques; however, great variations were reported for anthocyanin and flavonoid content.

A strong correlation between the antioxidant activity and anthocyanin content was found in SD strawberries. Also, it was observed that saturated steam pressure (P) of DIC texturing operation, had a significant effect on the studied parameters compared to the thermal holding time (t). The optimum conditions of DIC were P=0.35 MPa for t=10 s to obtain the highest levels of phenols, flavonoids, and anthocyanins, as well as antioxidant activity.

Keywords: antioxidant activity, anthocyanins, phenolic compounds, instant controlled pressure drop, drying, strawberry.

2. Introduction

The health benefits resulting from the use of natural products rich in bioactive substances have promoted a growing interest from pharmaceutical, food and cosmetic industries. Strawberries are really attractive by their red color, excellent taste and as source of bioactive phenolic compounds including hydroxycinnamic acids, ellagic acid, ellagitannins, flavan-3-ols, flavonols and anthocyanins (Giampieri, et al., 2012; Oszmiański, Wojdyło, & Kolniak, 2009). Moreover, strawberries are economically and commercially important and widely consumed fresh or in processed forms, such as jams, juices, and jellies by their sweet taste and potential benefits to the health (Giampieri, et al., 2012). And, by their antioxidant activity, they are important in the prevention of certain types of cancers, as well as, anti-inflammatory functions, cardiovascular, obesity and other chronic diseases (Basu, et al., 2009; Crecente-Campo, Nunes-Damaceno, Romero-Rodríguez, & Vázquez-Odériz, 2012; Giampieri, et al., 2012; Hannum, 2004; Olsson, et al., 2004; Oszmiański, et al., 2009). It is established that oxidation processes are involved in various chronic and degenerative diseases and that the intake of chemical constituents with antioxidant activity, found in plants in high concentrations, has beneficial effects on health. Phenolic compounds and anthocyanins, two large and heterogeneous groups of biologically active molecules, are known to be dietary components in fruits and vegetables with antioxidant activities (Panico, et al., 2009). Phenolic compounds present in strawberries are ellagic and *p*-coumaric acid; flavonoids as quercetin, kaempferol and myricetin. Anthocyanins are a group of phenolic compounds responsible for the red-blue color of many fruits and vegetables. Pelargonidin 3-glucoside, cyaniding 3-glucoside and pelargonidin 3-rutinoside are the main anthocyanins found in strawberries, which are responsible for their bright red color (Böhm, 1994; Crecente-Campo, et al., 2012). These bioactive compounds are of prominent importance; in fact, anthocyanin pigments constitute an integral part of the sensory attributes and contribute directly to the coloration of the strawberries. Anthocyanins were claimed to possess diverse biological properties and therefore, they are considered as the main secondary metabolites with a potential nutritional value. *In vitro* oxidation assays showed that the antioxidant activity of strawberries has been directly correlated with anthocyanin content in the fruit (Andersen, Fossen, Torskangerpoll, Fossen, & Hauge, 2004). However, this content is affected by the cultivar, ripening stage, storage conditions and their post-harvest treatment (Crecente-Campo, et al., 2012; Olsson, et al., 2004)

Unfortunately, strawberries postharvest life is relatively short, due to their highly fragile structure and their high rates of respiration (Modise, 2008). At the same time, they are highly susceptible to bruises and fungal attacks (Blanda, et al., 2009). This problem affects also their bioactive compounds.

To extent their shelf life and preserve their bioactive compounds, technologies as hot air drying and freeze-drying were used. Comparing the two processes, freeze-drying is the best method applied in the industry to preserve high-value foods such as coffee, spices, food ingredients and strawberries; however, as it is costly and time consuming process, its applications or uses are limited to high value foods and pharmaceutics (Ratti, 2001). On the other hand, hot air drying is considered as the most ancient process used to preserve foods; it offers dehydrated products that have an extended life, up to a year but, unfortunately, the quality of a conventionally dried product is usually drastically reduced compared to the original foodstuff.

Thus, new trends in drying process are used to improve the quality of dried foods and preserve their nutraceutical value. New technologies, such as swell-drying “SD”; Instant Controlled Pressure Drop “DIC”-assisted hot air drying; can improve the process performances, and the quality attributes of dried foods such as strawberries. SD is revealed by many authors (Albitar, Mounir, Besombes, & Allaf, 2011; Haddad & Allaf, 2007; Kamal, Sobolik, Kristiawan, Mounir, & Allaf, 2008; Louka & Allaf, 2004; Sabah Mounir, Allaf, Mujumdar, & Allaf, 2012; S. Mounir, Besombes, Al-Bitar, & Allaf, 2011). Their work reviewed the effect of DIC on the quality attributes of dried food products and on drying process performance. Furthermore, the SD is largely used at industrial scale to produce swell-dried products (ABCAR-DIC Process, La Rochelle, France).

DIC is a high temperature–short time (HTST) treatment followed by an abrupt pressure drop towards a vacuum crossing the glass transition boundary: the pressure dropping induces an abrupt cooling of treated product preserving the expanded state of the new obtained structure (Sabah Mounir, et al., 2012).

The aim of this study was to compare three processes of drying; swell-drying (SD), freeze-drying (FD), and classical hot air drying (HAD) in terms of quality attributes, including total phenolic content, flavonoid content, total anthocyanin content and the antioxidant activity of dried strawberries.

3. Materials and Methods

3.1. *Chemicals and reagents*

Cyaniding-3-glucoside; Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylicacid); Gallic acid; Pelargonidin-3-glucoside, which is a hydrophilic analogue of vitamin E; 2,2-Diphenyl-1-picrylhydrazyl (DPPH); and Rutin; were purchased from Sigma Chemical Co., St. Louis, MO, USA. Ethanol and methanol were purchased from J.T. Baker (Deventer, The Netherlands). All other reagents and chemicals of analytical grade were procured from local sources (Queretaro, Mexico) and milli-Q water was used.

3.2. *Biological material*

The strawberries (Fragaria var. Camarosa) were purchased from Carrefour (La Rochelle, France). They were immediately transported to the laboratory and stored at 5 ºC until the next day. Strawberries were sorted, washed with tap water and cut with kitchen knife into slices of 4-5 mm as thickness. After that, the total quantity was divided in three batches; one for each process; hot air drying (HAD), freeze-drying (FD) and swell-drying (SD).

3.3. Water content

Water content was determined according to a slightly modified Karathanos method (1999). Moisture of all dried strawberries were quantified gravimetrically in triplicate by drying 2.5 ± 0.1 g of samples in a laboratory drying oven (UFE 400 Memmert, Schwabach, Germany), at 65 °C during 48 h. The water content (W) in dry basis (% db), of samples was calculated according to the following Equation 1:

$$W_{db} = \frac{\mathrm{m_i} - \mathrm{m_d}}{\mathrm{m_d}}\ \% \tag{1}$$

Where: $\mathrm{m_i}$ and $\mathrm{m_d}$ are strawberry mass (g) before and after complete drying, respectively.

3.4. Dehydration Techniques

3.4.1. Hot air drying (HAD)

Strawberries slices were dried in hot air drier (Memmert: Universal Oven UNB Model 800, Schwabach, Germany) at 50 °C. The initial partial pressure of vapor in the air was 265 Pa with an air flux of 1.2 m/s. Slices were dried until attaining 3.0 % of water content (db). The total time of drying was about 24 hours. These samples were recorded as **(HAD)**.

3.4.2. Freeze-drying (FD)

A freeze-drying equipment (model: RP2V, Serail, France) was used to freeze-dry the strawberry slices. The strawberry samples were frozen outside from the freeze-dryer at -20 °C/2 h, the frozen samples were transferred immediately to the freeze-drying system to carry out their drying; sublimation (-20 °C, 0.66 Pa/12 h) and desorption (25 °C, 0.66 Pa/12 h). The freeze-dried samples were packed in airtight bags and stored until their assessments. These samples were recorded as **(FD)**.

3.4.3. Swell-drying (SD)

As previously mentioned, swell-drying is a DIC-assisted classical hot air drying. Thus, strawberry samples were partially hot air dried at 50 °C (Memmert: Universal Oven UNB Model 800, Schwabach, Germany) until a water content of 18 % db was attained. The initial partial pressure of vapor in the air was 265 Pa with an air flux of 1.2 m/s. This step needed about 8 h (Alonzo-Macías, Mounir, Cardador-Martínez, Montejano-Gaitán, & Allaf, 2012). The samples were stored in a cold room at 5 ºC for 24 h within air tight bags in order to homogenize the sample water content. Subsequently, the partial hot air dried strawberries were treated in a DIC-reactor (Figure 1) according to the experimental design (Table 2). Finally, after DIC treatment, the treated samples were dried under the same conditions of the hot air drying before the DIC treatment, but this step needed only 1 h to attain a suitable level of water content for storage, about 3.0 % db. These samples were recorded as (SD).

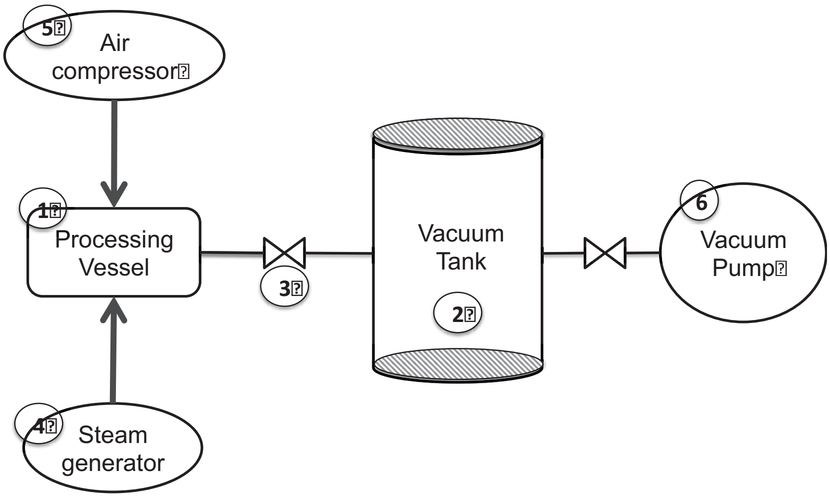

Figure 1. Schematic diagram of the DIC reactor. 1: Processing vessel; 2: Vacuum tank; 3: Abrupt opening valve; 4: Steam generator; 5: Air compressor 6: Vacuum pump. It can be briefly described as followed: ***A)*** The processing vessel, where samples are placed and treated. ***B)*** The vacuum system, which consists mainly of a vacuum tank with a volume 130 times greater than the processing vessel, and an adequate vacuum pump. The initial vacuum level was almost maintained at 5 kPa in all the experiments. ***C)*** A pneumatic valve that ensures the connection/disconnection between the vacuum tank and the processing vessel inducing the abrupt pressure dropping within less than 0.2 s ($\Delta P/\Delta t > 0.5$ MPa/s). DIC reactor has been largely described in many scientific papers (Ben Amor & Allaf, 2009; Haddad & Allaf, 2007; Louka & Allaf, 2004; Sabah Mounir, et al., 2012).

3.5. Samples extraction

The different strawberry samples (0.5 g) were weighted in a 30 mL centrifuge tube, and 10 mL of acidified methanol (1.0 % HCl in methanol, v/v) were added and agitated for 2 h at room temperature in darkness. The sample suspensions were centrifuged at 6000 rpm for 10 min at 4 °C and the supernatants were stored at -20 °C until analysis, the operation was performed in duplicate.

3.5.1. Total phenolic content

Total phenolic content was estimated by using the Folin-Ciocalteu colorimetric method (Singleton, Orthofer, & Lamuela-Raventós, 1999). Briefly, 0.02 mL of the extracts was oxidized with 0.1 mL of 0.5 N Folin-Ciocalteu reagent, and then the reaction was neutralized with 0.3 mL sodium carbonate solution (20 %). The absorbance values were obtained by the resulting blue color measured at 760 nm with a Spectrophotometer (UV-Vis Double Beam UVD-3500, Labomed, Inc. USA) after incubation for 2 h at 25 °C. Quantification was achieved on the basis of a standard curve of Gallic acid from 0 to 500 µg/mL. Results were expressed as mg of Gallic acid per g of dry weight (mg eq. GA/g db).

3.5.2. Flavonoid content

The spectrophotometric assay for the quantitative determination of flavonoid content was determined according to Oomah, Cardador-Martínez, and Loarca-Piña (2005). Briefly, the method consisted of mixing 50 µL of the methanolic extract with 180 µL of distilled water and 20 µL of a solution of 10 g/L 2-aminoethyldiphenylborate in a 96-well microtitration flat-bottom plate. The absorbance of the solution was monitored at 404 nm with a spectrophotometer (xMark Microplate Spectrophotometer, BioRad, Japan). Extract absorption was compared with a Rutin standard at different concentrations ranging from 0 to 200 µg/mL. Flavonoids content was expressed as mg Rutin per g of dry weight (mg eq. Rutin/g db).

3.5.3. Total anthocyanin content

0.2 mL of extract were diluted with 1.8 mL acidified methanol (1.0 % HCl in methanol) and absorbance was taken at 250 nm (Spectro UV-Vis Double Beam. UVD-3500 Labomed, Inc. USA). An acid pH was used to take the anthocyanins to the flavylium ion form, which exhibits coloration, thus to be able to quantify them by spectrophotometry. Total anthocyanins concentration (TAC) was calculated as pelargonidin-3-glucoside according to the Equation 2 (Abdel-Aal & Hucl, 1999):

$$\boldsymbol{TAC} = \left(\frac{A}{\varepsilon}\right)\left(\frac{Vol}{1000}\right)(MW)\left(\frac{1}{sample\ weight}\right)10^{6} \qquad (2)$$

Where:

TAC*:* concentration of total anthocyanin content per sample were expressed as mg pelargonidin-3-glucoside equivalent per g of dry weight (mg eq. Pe-3-Gl/g db)

A: absorbance reading,

ε: molar absorptivity (pelargonidin-3-glucoside = 15,600 L/ (mol cm)), Vol: total volume of anthocyanin extract, and

MW: molecular weight of pelargonidin-3-glucoside = 433.2 g/mol

3.5.4. Determination of anthocyanins by HPLC

Strawberry extracts were filtered through a 0.45 µM nylon membrane-filter. HPLC analysis was performed using an Agilent 1200 HPLC system (Agilent Technology 1200 series, Palo Alto, CA), equipped with quaternary pumps, autosampler and a diode array detector. Anthocyanin separation were performed using an Eclipse XDB-C18 column (5 µM, 4.6 mm · 150 mm) at 28 ºC. Mobile phases were constituted of 1.0 % methanol acidified (A) and 5.0 % formic acid (B) at a flow rate of 1 mL/min. The gradient condition started with 20 % A, linearly increased to 85 % A at 10 min, finally it decreased to 20 % A at 15 min. Calibration curves (0-1 mg/mL) were realized to quantify cyanidin-3-glucoside (Cy-3-Gl, mg/g db) and pelargonidin-3-glucoside (Pe-3-Gl, mg/g db).

3.5.5. Determination of antioxidant capacity by DPPH method

Measurement of antioxidant capacity was carried out using 2,2-Diphenyl-1-picrylhydrazyl (DPPH) as a free radical. Reduction of DPPH by an antioxidant or a free radical produces decreased absorbance at 515 nm. 20 µL of the extract were mixed with 200 µL DPPH (125 µM in 80 % methanol). After 90 min, the plate was read at 520 nm in a spectrophotometer and the antioxidant capacity was calculated as a percentage of DPPH discoloration according to Burda and Oleszek (2001). The analysis was performed in triplicate.

3.6. DIC Experimental Design

The operating parameters of DIC treatment in this study were only the saturated steam pressure (MPa) and the thermal holding time (s), while the initial water content (W) of strawberries was maintained constant at 18 % db. Hence, in order to study these parameters on the various response parameters (total phenolic content, flavonoid content, total anthocyanin content, pelargonidin-3-glucoside, cyanidin-3-glucoside and antioxidant activity), a central composite rotatable design was used (Statgraphics, Centurion XV, USA) (Table 1). For the 2 factors, the design resulted in 11 trials; 4 (2^2) factorial points, 4 axial points to form a central composite design, and 3 center points for replications (Table 2). The ranges and the center point (Table 1) were defined after preliminary trials. The 11 trials were run in random order to minimize the effects of unexpected variability on observed responses due to external factors. The mathematical empirical model applied in this study was:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i \chi_i + \sum_{i=1}^{n} \beta_{ii} \chi_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^{n} \beta_{ij} \chi_i \chi_j + \varepsilon \qquad (3)$$

Where:

Y: the response, β_i, β_{ii}, β_{ij}: the regression coefficients, X_i and X_j: the independent variables, ε: random error, and i and j: the indices of the factors.

For more understanding and interpreting the results,

- The analysis of variance (ANOVA) was used to determine significant differences between independent variables ($p < 0.05$),
- Pareto chart was used to identify the impact of variables on various responses. The vertical line in the Pareto chart determines the effects that are statistically significant at the 95 % confidence level,
- Surface response methodology plots to optimize the various responses,
- General trends to analyze various responses behavior in front of variable changes,
- Empirical model coefficients to determine the regression model for each response and R^2 to accurate fitting models to real data.

Table 1. Coded and real ranges of independent variables used in the 2-variable 5-level rotatable experimental design

Factor (Coded Level)	-α	-1	0	1	+α
Processing pressure (MPa)	0.10	0.19	0.35	0.53	0.60
Processing time (s)	10	13	20	27	30

α (axial distance) $=\sqrt[4]{2^k}$, k is the number of experiments of orthogonal desig. In this case, k=2 and α=1.4142.

Table 2. Trials in the experimental design for DIC process

	DIC										
Run	1	2	3	4	5	6	7	8	9	10	11
Pressure, P (MPa)	0.60	0.35	0.35	0.53	0.53	0.35	0.17	0.17	0.10	0.35	0.35
Time, t (s)	20	30	20	27	13	20	13	27	20	10	20

4. Results and discussion

The present study was carried out to evaluate the antioxidant capacity, total phenolic, total flavonoid, and total anthocyanin contents in strawberries samples dried by different techniques. Hence, the discussion and the interpretation of the results are presented in two parts; a comparison between the different drying techniques (HAD, FD and SD) and, on the other hand, a study of operating parameters of DIC treatment in order to optimize the texturing operation within SD in the light of obtained results.

4.1. Total phenolic content

Table 3 shows the total phenolic content (TPC) in different dried strawberries. The TPC were not quite different in the studied drying methods. The TPC in HAD, FD and SD (DIC 10, 0.35 MPa and 10 s) were 16.18, 18.41, and 14.47 mg eq.GA/g db, respectively. The TPC in FD samples was higher than those in HAD and SD by 12 % and 21 %, respectively, and TPC in SD samples was decreased by 11 % compared to HAD samples. This phenomenon can be explained by the thermal damage of free phenols occurred during the long time of drying in the case of HAD samples and by the thermo-mechanical effects of DIC treatment. Hung and Duy (2012) reported similar behavior in their study, when comparing the effect of drying methods on bioactive compounds in vegetables. They found that the free phenols in freeze-dried vegetables were significantly higher than those in hot air dried vegetables.

Table 3. Bioactive compounds evaluated in SD, HAD and FD strawberries.

Sample	Pressure (MPa)	Time (s)	TPC[a]	FC[b]	TAC[c]	Cy-3-Gl[d]	Pe-3-Gl[e]	% ARA at 250 μM
DIC 1	0.60	20	17.14	4.15	4.96	0.60	0.92	43.20
DIC 2	0.35	30	16.06	3.19	6.17	1.49	1.99	54.36
DIC 3	0.35	20	14.58	2.93	6.26	1.66	2.29	54.27
DIC 4	0.53	27	16.34	3.58	4.71	0.42	0.62	42.35
DIC 5	0.53	13	16.67	3.28	5.71	1.12	1.73	45.85
DIC 6	0.35	20	14.81	2.86	6.59	1.69	2.38	51.90
DIC 7	0.17	13	13.97	2.79	5.98	2.55	3.35	49.87
DIC 8	0.17	27	15.76	3.25	6.59	2.24	2.99	53.42
DIC 9	0.10	20	14.60	2.70	5.76	2.49	3.68	49.68
DIC 10	0.35	10	14.47	3.01	7.00	2.34	3.07	56.82
DIC 11	0.35	20	16.35	3.06	5.96	1.78	2.43	53.61

HAD	16.18	3.08	6.69	1.58	1.64	51.67
FD	18.41	3.99	8.31	2.06	2.60	51.34

[a] Total phenolic content (mg eq. GA/g db)
[b] Flavonoid content (mg eq. Rutin/g db)
[c] Total anthocyanin content (mg eq. Pe-3-Gl/g db)
[d] Cyanidin-3-glucoside (mg/g db)
[e] Pelargonidin-3-glucoside (mg/g db)

In order to compare the operating parameters of DIC treatment, Figure 2 (a, b) shows the effect of saturated steam pressure (MPa) and thermal holding time (s) on the TPC of SD samples. The highest value of TPC (17.14 mg eq.GA/g db) was verified for samples treated at 0.6 MPa as saturated steam pressure for 20 s. According to obtained results of DIC treatment, the saturated steam pressure had a significant and positive effect on the TPC compared to the thermal holding time. Hence, the higher the saturated steam pressure, the higher the TPC. This behavior is maybe due to the mechanical effect induced by the dropping pressure towards a vacuum, resulting in a broken-down the cell walls and thus the formation of some vacuoles and pores within the product thanks to water autovaporization. Such new structures can increase the availability of the bound phenols and facilitate, subsequently, their extraction; while HAD and FD do not affect phenol-cell wall association (Hung & Duy, 2012). Albitar, et al. (2011) proved that, the increase in phenol availability is dependent not only on the DIC operating parameters, such as saturated steam pressure and processing time, but also the initial water content.

This result is not in contradiction with the previously found, when the different drying methods (HAD, FD and SD) were compared because the DIC is a heat treatment (temperature and time couple treatment). Hence, some of these compounds, as free phenols, were destructed under sever conditions of high temperature treatment (high saturated steam pressure and longtime treatment) before broken-down the cell walls.

The obtained regression model of TPC was as follows with $r^2 = 82.7$ %:

$$TPC = 10.9115 + 5.81679P + 0.181985t + 10.526P^2 - 0.420635Pt + 0.000786558t^2 \tag{4}$$

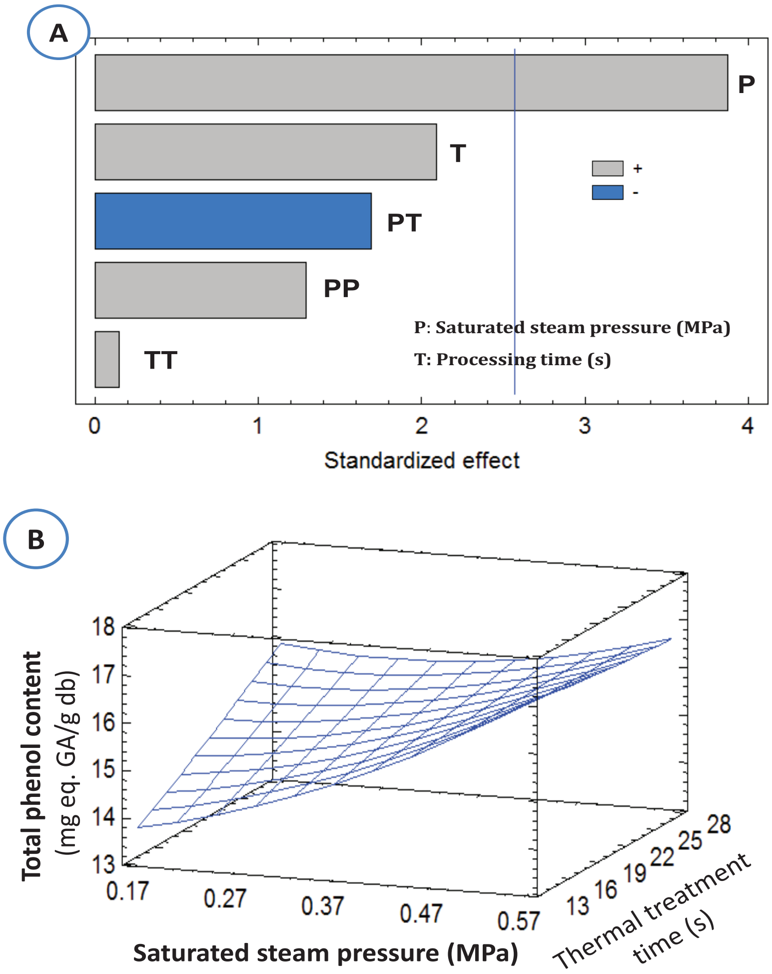

Figure 2. Effects of DIC operating parameters; pressure (MPa) and time (s) on the total phenols content (TPC; mg eq. GA/g db) of SD strawberries: A) Pareto Chart and B) Response Surface.

4.2. *Flavonoid Content*

Total flavonoid content (FC) in hot air drying, freeze-drying and swell-drying is listed in Table 3. It was observed that thermal processes had a large influence in flavonoid availability, which depends on the magnitude and duration of drying processes. Flavonoid contents of HAD, FD and SD (0.35 MPa, 10 s) strawberries were 3.08, 3.99 and 3.01 mg eq. Rutin/g db, respectively. There were not significant differences by these treatments with respect to the flavonoids content. However, the slight difference may be due to the thermal degradation of these compounds. Drying processes lead also to flavonoid degradation. The proportion lost depends on the drying method. Freeze-drying is the less aggressive method followed by hot air drying; while microwave and vacuum drying can have an intermediate degradation. (Dong, Ma, Fu, & Guo, 2011; Viña & Chaves, 2008; Zainol, Abdul-Hamid, Bakar, & Dek, 2009; Zhang, Hettiarachchy, Horax, Chen, & Over, 2009).

The impact of DIC operating parameters (pressure and time) on FC is shown in Figure 3 (a, b). Similar behavior in TPC was observed for FC. The saturated steam pressure had a significant effect on the FC compared to the thermal holding time. Hence, the higher the saturated steam pressure, the higher the flavonoid content. At saturated steam pressure of 0.6 MPa during 20 s, the highest value of FC (4.15 mg eq. Rutin/g db) was recorded for treated samples.

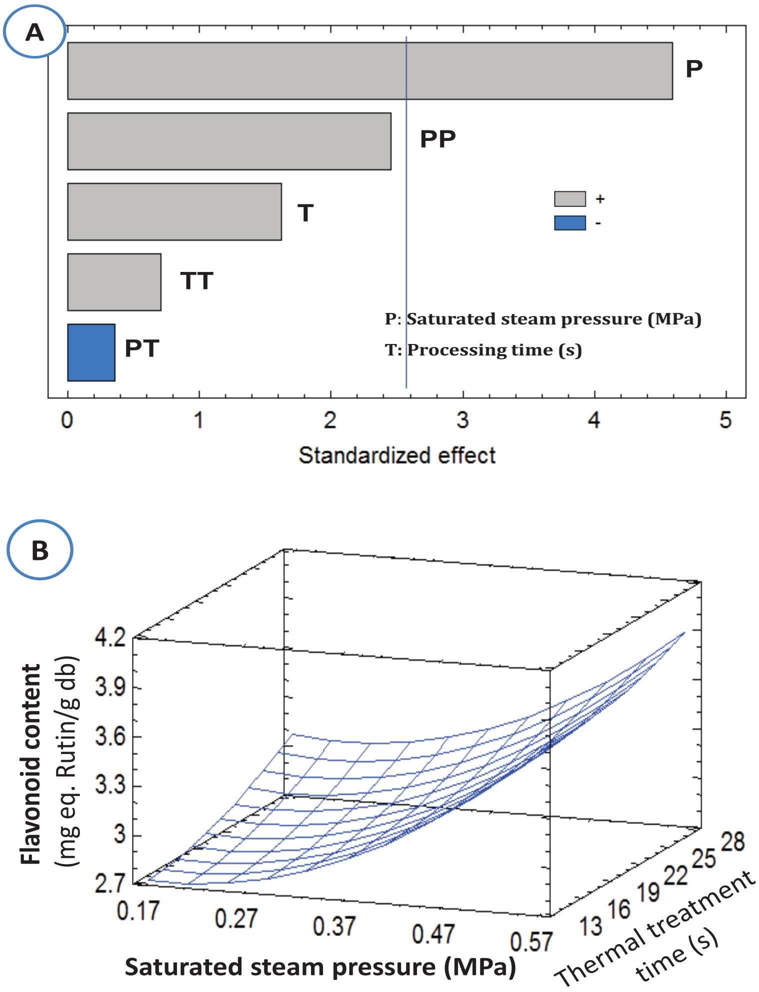

Figure 3. Effects of DIC operating parameters; pressure (MPa) and time (s) on the flavonoid content (FC; mg eq. Rutin/g db) of SD strawberries: A) Pareto Chart and B) Response Surface

The degradation of flavonoids not only depends on temperature and magnitude of heating; it may depend also on other parameters such as pH, phytochemicals, structure and even the presence or absence of oxygen.

The thermal degradation of HAD products correlates with the slowness of the operation, due to the fact that shrinkage leads to a very low diffusivity. DIC texturing can dramatically increase the diffusivity, reducing the drying time, preserving the natural nutritive value, and, by opening the structure and possibly breaking cell walls, releasing the bound flavonoids and dramatically improving the availability of these compounds (S. Mounir, et al., 2011). As an example, Sabah Mounir, et al. (2012) reported that the amount of quercetin in DIC-treated apple compared to untreated fresh samples was increased by up to 700 %. They obtained similar results with other fruits (e.g., cranberry fruits and seeds, sumac) and vegetables. Furthermore, results for onions proved that the instantaneity of the pressure drop toward a vacuum is an important factor influencing the availability of flavonoids (S. Mounir, et al., 2011).

The obtained regression model of FC was as follows with r^2= 85.64 %:

$$FC = 3.06594 - 2.30023P - 0.024343t + 7.0409P^2 - 0.031746Pt + 0.00133928t^2 \quad (5)$$

4.3. Total Anthocyanin Content

The total anthocyanin content (TAC) in dried strawberry was investigated in several drying methods. As reported in Table 3, TAC was higher in the FD samples than HAD and SD samples by 19 % and 16 %, respectively. A slight difference was observed in TAC between HAD and SD, an increase by 4 % in TAC was reported in SD samples compared to HAD samples.

DIC treatment at 0.35 MPa of pressure for 10 s, gave the highest value of TAC, 7.00 Pe-3-Gl/g db. Evaluating the effect of DIC operating parameters on the TAC in SD strawberries, in Figure 4 (a, b) it was observed that the saturated steam pressure had a great influence compared to the thermal holding time. Thus, the higher the saturated steam pressure, the lower the TAC. The negative effect may be due to the thermal degradation of strawberries' anthocyanins. The highest values of TAC were found in SD samples treated at low pressure (under soft conditions). Ben Amor and Allaf (2009) reported that the yield of Total Monomeric Anthocyanin content (TMA) in dried Malaysian Roselle calyces was improved by up to 135 % under soft conditions of 0.18 MPa as saturated steam pressure during 18 s.

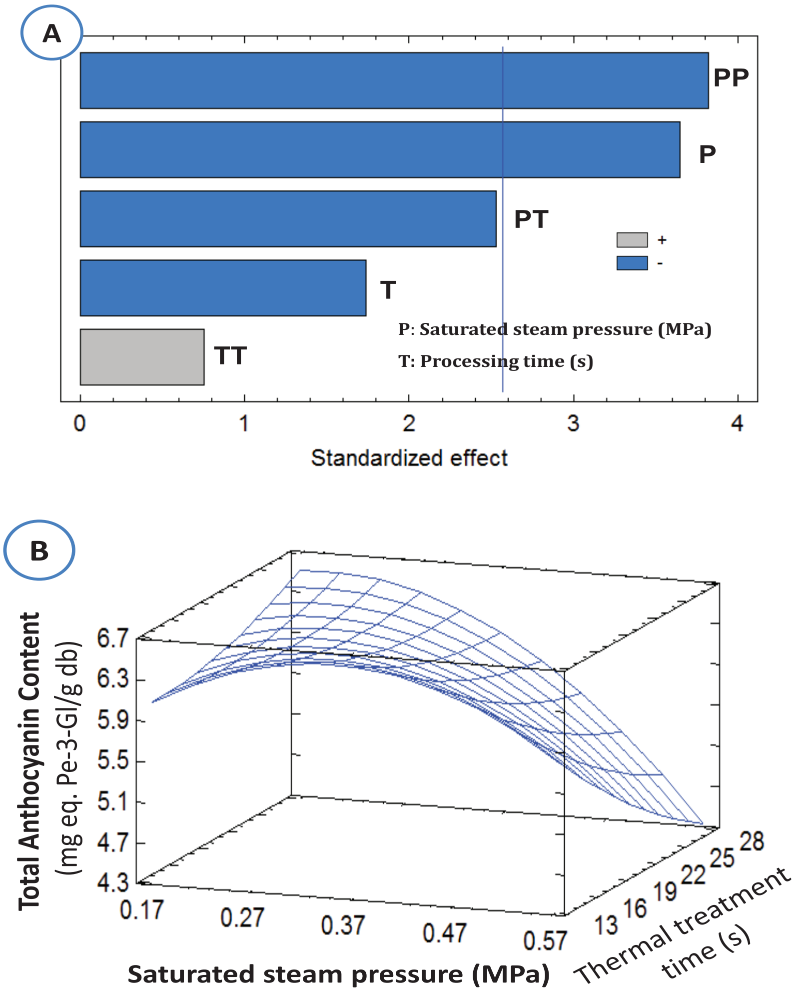

Figure 4. Effects of the saturated steam pressure (MPa) and the thermal treatment time of DIC on the total anthocyanin content (TAC; mg eq. Pe-3-Gl/g db) of SD strawberries. A) Pareto Chart and B) Response Surface.

The obtained regression model for TAC, with $r^2 = 89.17$, was:

$$TAC = 4.28351 + 15.1557P + 0.00122738t - 15.7794P^2 - 0.319444Pt + 0.0020663t^2 \qquad (6)$$

The principal anthocyanins in strawberries are pelargonidin-3-glucoside (Pe-3-Gl) and cyanidin-3-glucoside (Cy-3-Gl) (da Silva, Escribano-Bailón, Pérez Alonso, Rivas-Gonzalo, & Santos-Buelga, 2007; Giampieri, et al., 2012). Pelargonidin-3-glucoside is the major anthocyanin in strawberries independent from genetic and environmental factors and the presence of cyanidin-3-glucoside seems to be constant and in less quantity (Giampieri, et al., 2012; Patras, Brunton, Da Pieve, & Butler, 2009).

Anthocyanins were quantified by HPCL using Cy-3-Gl and Pe-3-Gl standards. The levels of Cy-3-Gl and Pe-3-Gl are listed in Table 3. It was found that SD strawberries samples had the highest levels of Cy-3-Gl and Pe-3-GI compared to HAD and FD. The level of Cy-3-Gl in SD samples was increased by 32 % and 11 % compared to HAD and FD samples, respectively; while Pe-3-GI was increased by 47 % and 15 % compared to HAD and FD samples, respectively. The highest level of these anthocyanin types was obtained at DIC texturing parameters of 0.35 MPa and 0.10 MPa as saturated steam pressure for 10 s and 20 s as thermal holding time, respectively.

Although, the highest levels of Cy-3-Gl and Pe-3-Gl were obtained in SD strawberry samples, the saturated steam pressure had a significant effect on strawberry's content of these compounds compared to the thermal holding time. The higher the saturated steam pressure, the lower the levels of Cy-3-Gl (Figure 5; a, b) and Pe-3-Gl (Figure 6; a, b).This phenomenon can be explained by the thermal destruction of these compounds as a result of increasing the saturated steam pressure during the treatment. Therefore, the highest levels were obtained under soft conditions (low saturated steam pressure and short time treatment) as early mentioned.

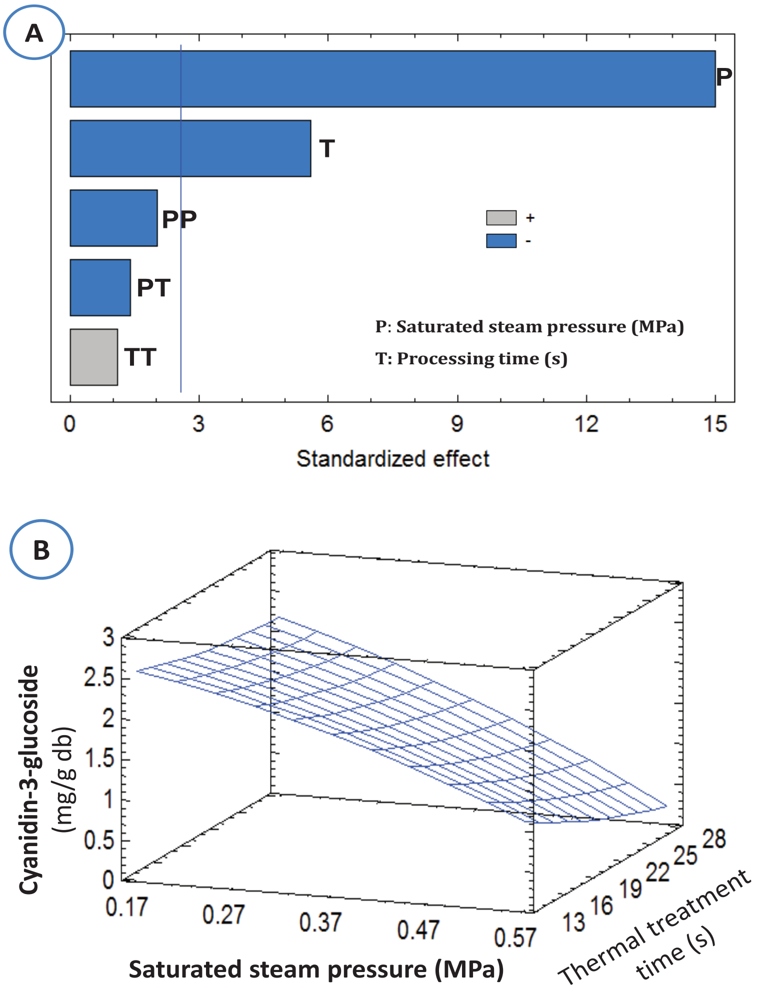

Figure 5. Effects of DIC operating parameters (pressure; MPa and time; s) on the cyanidin-3-glucoside (Cy-3-Gl; mg/g db) of SD strawberries. A) Pareto Chart and B) Response Surface.

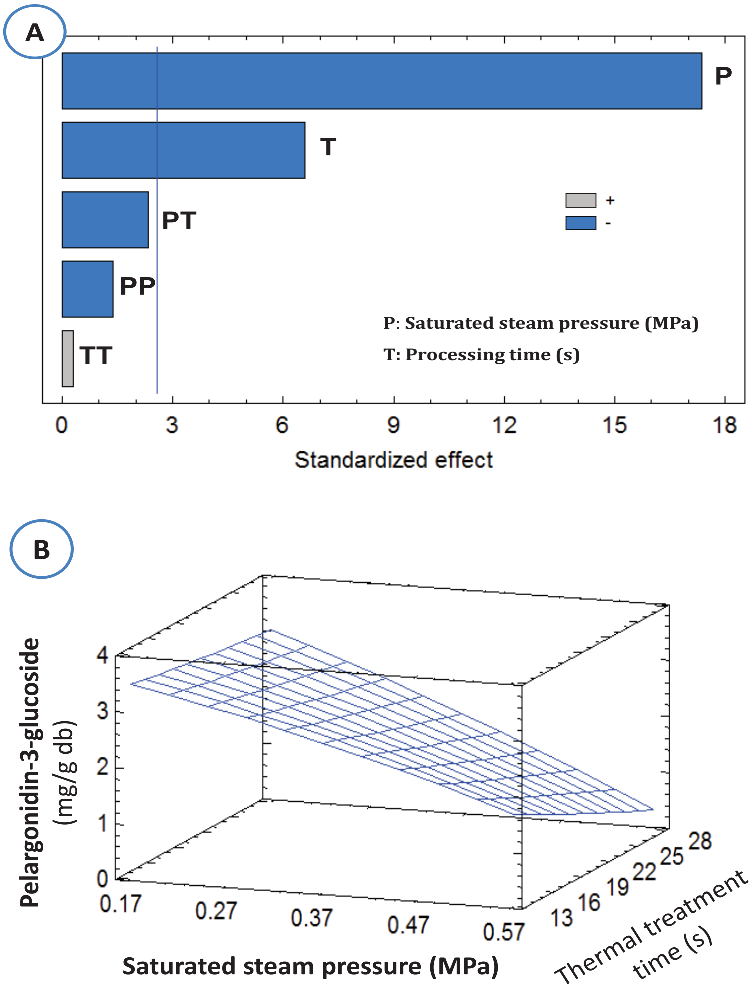

Figure 6. Effects of DIC parameters (saturated steam pressure; MPa and thermal treatment time; s) on the pelargonidin-3-glucoside (Pe-3-Gl; mg/g db) of SD strawberries. A) Pareto Chart and B) Response Surface.

The obtained regression models for Cy-3-Gl and Pe-3-Gl were as follows with r^2= 98.15 and 98.60, respectively:

$$Cy\text{-}3\text{-}Gl = 3.48232 + 0.01362P - 0.0659896t - 3.68443P^2 - 0.07738Pt + 0.0013393t^2 \quad (7)$$

$$Pe\text{-}3\text{-}Gl = 4.1305 - 0.475243P - 0.0186178t - 2.8997P^2 + 0.14881Pt + 0.00042943t^2 \quad (8)$$

4.4. Antioxidant capacity

The antioxidant capacity of fruits is closely correlated to the presence of efficient oxygen radical scavengers, such as vitamin C and phenolic compounds (Giampieri, et al., 2012). Strawberries have a greater antioxidant capacity (2 to 11-fold) than apples, peaches, pears, grapes, tomatoes, oranges, or kiwi fruit (Giampieri, et al., 2012; Scalzo, Politi, Pellegrini, Mezzetti, & Battino, 2005; H. Wang, Cao, & Prior, 1996). In the present study, scavenging capacity was evaluated as percent discoloration of a free radical DPPH solution and expressed as antiradical activity (% ARA). The concentration tested for the different extracts in this essay was 250 μM (μM equivalent of Gallic acid).

As shown in Table 3, there was no significant difference in % ARA of HAD and FD samples. Whereas, it is increased by 9 % and 10 % in SD samples (56.82 %) compared to HAD (51.67 %) and FD (51.34 %) samples respectively.

The effect of saturated steam pressure and thermal holding time on % ARA was illustrated in Figure 7 (a, b). The saturated steam pressure had a negative effect on the % ARA; it means that in SD samples, the higher the saturated steam pressure, the lower the % ARA. However, the highest % ARA was found in SD strawberries samples treated under the softest conditions (lowest saturated steam pressure for shortest time treatment). For example, the highest level of % ARA was found at 56.82 % for SD samples treated at 0.35 MPa for 10 s.

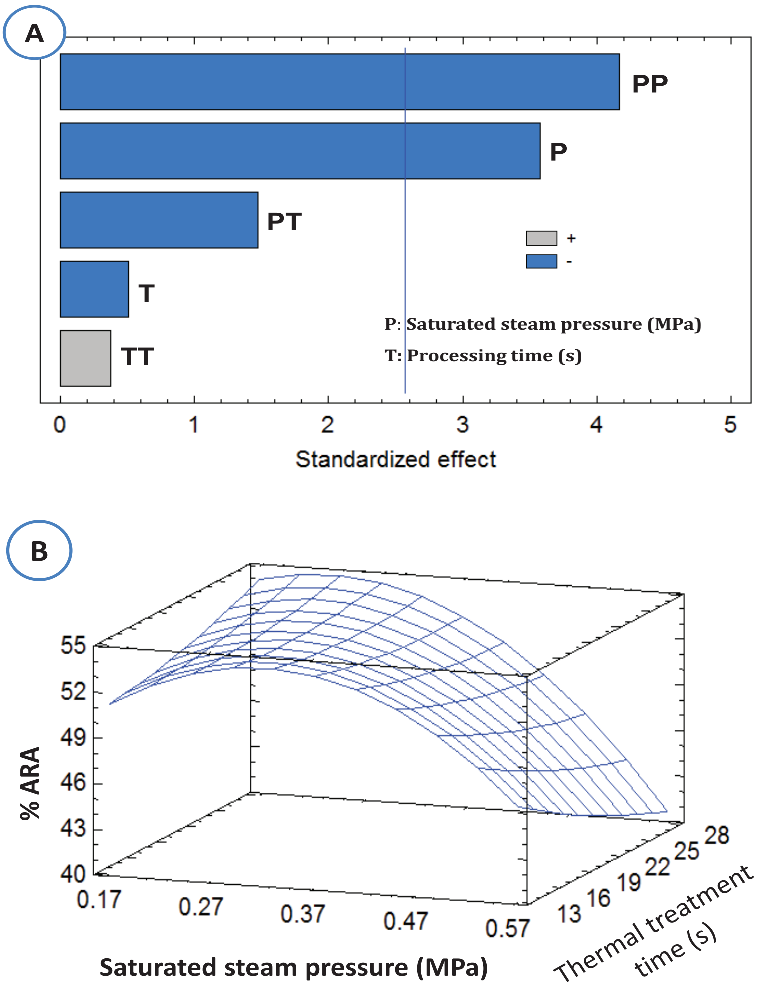

Figure 7. Effects of DIC operating parameters; pressure (MPa) and time (s) on the antioxidant activity (% ARA) of SD strawberries: A) Pareto Chart and B) Response Surface

It is difficult to explain the evolution of the antioxidant activity according to heat process conditions. Too numerous factors are implied in its evolution. A decrease in phenolic content does not lead systematically to a decrease of the antioxidant activity. Indeed, with lower phenolic content, one can also have a higher antioxidant activity (Buchner, Krumbein, Rohn, & Kroh, 2006; Murakami, Yamaguchi, Takamura, & Atoba, 2004). Thus, an increase of antioxidant activity is noticed in many studies using thermal processes (Chandrasekara & Shahidi, 2011; Hartmann, Patz, Andlauer, Dietrich, & Ludwig, 2008; Sharma & Gujral, 2011). However, interactions are important phenomena, which act on the antioxidant activity of molecules. Depending on this environment, synergies between antioxidant compounds and the food matrix can occur (S. Wang, Meckling, Marcone, Kakuda, & Tsao, 2011). In some cases, the antioxidant capacity of flavonoids in a food matrix is enhanced (Freeman, Eggett, &

Parker, 2010); while in others, this antioxidant activity is reduced (Davidov-Pardo, Arozarena, & Marín-Arroyo, 2011; Hidalgo, Sánchez-Moreno, & de Pascual-Teresa, 2010), or it remains constant (Leitao, et al., 2011).

The obtained regression model for the antioxidant capacity was as followed with r^2= 87.61:

$$\%ARA = 37.8219 + 101.779P + 0.118656t - 129.495P^2 - 1.3988Pt + 0.00774239t^2 \quad (9)$$

4.5. Correlation between DPPH radical scavenging and TPC, FC and TAC in swell-dried strawberries

The highest correlation was found between TAC and DPPH scavenging in swell-dried strawberries with r^2 = 0.8337 (Figure 8). While, the correlations between DPPH scavenging and FC and TFC were observed with r^2 = 0.4129 and 0.2956, respectively. These results indicated that antioxidant capacity was strongly correlated to TCA (Figure 8) and not correlated to FC and TFC in SD strawberry samples. Therefore, these results are in agreement with those obtained by Andersen et al. (2004). These authors reported that the antioxidant activity of strawberries was directly correlated with anthocyanin content in the fruit.

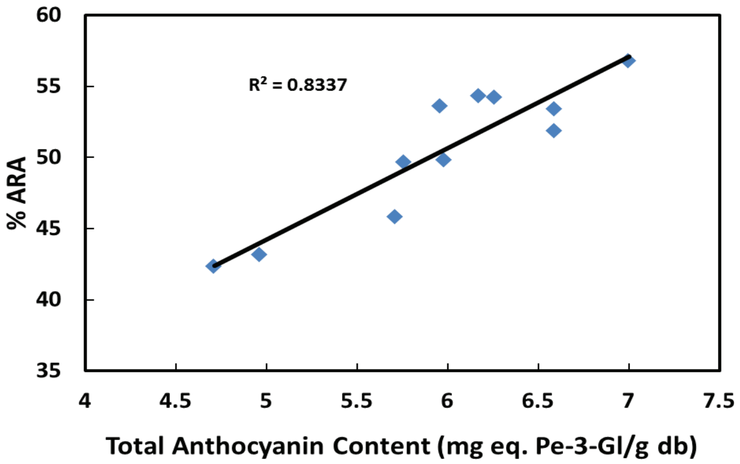

Figure 8. Correlation between DPPH radical scavenging and TAC in swell dried strawberries

5. Conclusions

As a general tendency, these results show that swell-drying technique can be considered as an alternative of drying method for fragile fruits, such as strawberries. Mainly because SD method helps to reduce the time of drying (Alonzo-Macías, et al., 2012) and, subsequently, decreases the consumed energy and drying costs compared to classical hot air drying and freeze-drying. Additionally, SD globally preserves the nutritional value and bioactive molecules and increases the availability of these compounds. It was demonstrated that at optimal DIC conditions (0.35 MPa as saturated steam pressure for 10 s) SD strawberries were richer in anthocyanins, phenolic compounds and flavonoids compared with the other drying methods. A strong correlation between antioxidant activity and total anthocyanin content was established in SD strawberries.

Thus, DIC is a flexible operation that can be optimized to meet the consumer and industry's needs.

6. Acknowledgment

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CHAPTER III.3

TEXTURE AND STRUCTURE ANALYSIS OF DRYING STRAWBERRY (FRAGARIA VAR. CAMAROSA) BY INSTANT CONTROLLED PRESSURE DROP

TEXTURE AND STRUCTURE ANALYSIS OF DRYING STRAWBERRY (*Fragaria* var. Camarosa) BY INSTANT CONTROLLED PRESSURE DROP

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ABSTRACT

The aim of this study was to evaluate the effect of hot air drying (HAD), freeze-drying (FD) and swell drying (SD, is a coupling of hot air drying to instant controlled pressure drop, DIC) on the strawberry (*Fragaria* var. Camarosa) to compare and to contrast its quality in terms of texture parameters as crunchy and crispy features, the expansion ratios and the microstructure's modification. The obtained results showed that SD strawberry had a significant swelled structure and high crispness behavior. Also, its relative expansion ratio increased thrice more than HAD samples. Moreover, it was observed that saturated steam pressure (P) of DIC texturing operation compared to the thermal holding time (t), had a significant effect on the maximum penetration distance (X_{max}) and the average of micro-ruptures force (f) on crunchiness and crispness, respectively. Hence, these structural changes provide a versatile swell-dried strawberry as highly-functional snack that was able to be evaluated instrumentally by puncture test.

Keywords: *crunchy, crispy, texture, instant controlled pressure drop, expansion ratio, strawberry, puncture test*

NOMENCLATURE

HAD	Hot Air Drying
FD	Freeze-Drying
SD	Swell-Drying
db	Dry-basis
m_i	Material weight before (g)
m_d	Material weight after drying (g)
F_{max}	Maximum penetration force (N)
X_{max}	Maximum penetration distance (mm)
W_{max}	Total work at X_{max}
<F>	Average puncturing force (N)
n	Total number of peaks
N	Spatial frequency of structural micro-ruptures (m^{-1})
f	Average micro-ruptures force (N)

$w_{rupture}$	Average work for micro-ruptures
ΔX	Penetration distance for each micro-rupture peak (mm)
ΔF	Individual force drops for each micro-rupture peak (N)
$\varepsilon_{absolute}$	Absolute expansion ratio
$\varepsilon_{relative}$	Relative expansion ratio
$\rho_{intrinsic}$	Density intrinsic (g/cm^3)
$\rho_{specific}$	Density specific (g/cm^3)
ρ_{sand}	Density of sand (g/cm^3)
m_{sample}	mass of sample (g)
m_{sand}	mass of sand (g)
$m_{s,1}$	mass initial of sand (g)
$m_{s,2}$	mass final of sand (g)

INTRODUCTION

From commercial point of view, strawberry is widely consumed fresh or in processed forms. In addition, strawberry consumption is recognized by its potential benefits in the human health, thanks to bioactive phenolic compounds (Oszmiański *et al.*, 2009; Giampieri *et al.*, 2012). Also, it has a very soft and fragile texture, which tends to disintegrate when are incorporated, in fresh form, into food such as yoghurts, ice creams as well as other processed products. Food industry, commonly use strawberry in dried form to preserve it and to handle it easily as an ingredient. Up to now, solar drying, hot air drying, freeze-drying and vacuum drying are the conventional methods used to process fruits and vegetables. However, they present some disadvantage for the quality product, as deterioration of significant bioactive compounds and structural textural damages. Indeed the shrinkage of product is usually produced by very long time exposure of hot air drying. In addition, the difficulties in processing, as grinding and rehydration are barriers to adopt hot air process for a large range of fruit and vegetable (Mounir *et al.*, 2012). Furthermore, freeze-drying has high cost manufacturing, mainly due to high energy consumption coupled with loss of flavor and color, which greatly reduces its utilization (Ratti, 2001).

A new drying operation has been proposed as an alternative to improve: a) the drying process performance, b) the intensification of the texture and the quality attributes of dried foods, and c) to reduce the energy consumption that directly impacts in the manufacturing cost. It also has the ability to handle ranges of food products, regardless of their sensitivity to heat (e.g. strawberry, cranberry, blackberry, guava, mango, onion, carrot, pepper, potato, apple, etc.) (Albitar *et al.*, 2011; Mounir *et al.*, 2011; Alonzo-Macías *et al.*, 2012; Mounir *et al.*, 2012; Téllez-Pérez *et al.*, 2012). This technology is the instant controlled pressure drop, called, the Détente Instantanée Contrôlée (DIC).

It was defined in 1988 (Allaf and Vidal) as a high temperature short time (HTST) treatment followed by an abrupt pressure drop towards a vacuum (pressure drop speed higher than 0.5 MPa/s). DIC-assisted hot air drying is a texturing stage between pre and final hot air drying operation. This coupling is better known as swell-drying (Kamal *et al.*, 2008; Albitar *et al.*, 2011; Mounir *et al.*, 2011; Alonzo-Macías *et al.*, 2012). Therefore, the swell-drying products have a controlled texture expansion to improve the quality product and the physical properties. This texture change results in higher porosity, as well as the increases of the specific surface area and reduces the diffusion resistance of moisture during the final dehydration step (Mounir *et al.*, 2012). Moreover, this structural change provides a versatile function in the dried foods, producing the "snacking". But it could be considered as a highly-functional snack, due to its preservation of vitamins, bioactive compounds, color and flavor.

However, texture is a very important feature of all kinds of foods that impact directly in the consumer acceptability. More specifically, texture has a specific importance in such a snacking. Texture is primarily the response of tactile senses to physical stimuli that results from contact between some part of the body and the food (Bourne, 2002a). The cellular structure of food materials, in both macro (porosity and relative density) and micro (cell wall thickness, cell diameter, and their distributions) scales. It also influences in the mechanical properties (Sozer *et al.*, 2011). The most important characteristics of dry cellular materials, which determine their mechanical behavior are the volume fraction of air, the mechanical properties and the structure of the solid matrix, as well as having closed or open cells (Van Vliet and Primo-Martín, 2011).

In the case of the snack products obtained by drying processes of fruits and vegetables, is proposed that crunchiness and crispiness are the textural attributes that better describe their quality and even freshness (Luyten *et al.*, 2004). These features, as well as hardness, are likely the most important texture attributes of hard solid products (i.e. dry cellular materials). They are related to the fracture properties of food materials. And, they belong to the most frequently used texture descriptors in the United States, Japan, France, Austria… (Bourne, 2002a; Roudaut *et al.*, 2002; Nishinari *et al.*, 2008; Saeleaw and Schleining, 2011; Van Vliet and Primo-Martín, 2011). In general, both crispy and crunchy food products are brittle products, which mean absence of plastic behavior; only elastic behavior till rupture exists. They relatively easily break producing a sharp sound (Al Chakra *et al.*, 1996; Luyten *et al.*, 2004; Saeleaw and Schleining, 2011). The distinction between crispy and crunchy features is not so clear. Indeed, different works suggest that crispy and crunchy refer to different concepts (Table 1).

And the question is still open (Roudaut *et al.*, 2002). The definitions given varied between different studies and likely between countries and products (Roudaut *et al.*, 2002; Luyten *et al.*, 2004; Nishinari *et al.*, 2008). Sometimes, the panelists as well as consumers found it very difficult to distinguish between crispy and crunchy terms and needed constant probing, However, all insisted that they could perceive a difference between the two, although struggling to describe this difference, indicating that it was only slight (Saeleaw and Schleining, 2011).

By this research, crunchiness and crispness were defined according to French language and culture. Crunchiness “croquant” is defined as linear elastic behavior till the complete fracture (brittle; e.g. hot air dried products, almonds, …). On the other hand, crispness “croustillant” is understood as the same but small continuous linear elastic behavior till the successive fractures during chewing (e.g. swell-drying and freeze-drying products, biscuits…). At the same time, to carry out measurements of the physical aspects of texture perception in foods, different methods have been proposed. They involve two main categories: sensory and instrumental analysis. These last measurements include mechanical measurements (e.g. compression, penetration), and acoustical procedures (Roudaut *et al.*, 2002; Van Vliet and

Primo-Martín, 2011). And sometimes, a combination of acoustic analysis with mechanical testing for analyzing the crispness is used. Nonetheless, instrumental measurements are generally preferred to evaluate objective the attributes relate to the mechanical properties (Altamirano-Fortoul *et al.*, 2012).

TABLE 1. A compilation of polyglot list of the terms crunchy and crispy from Drake (1989), Dacremont (1992) and Nishinari *et al.* (2008).

Language:	**Feature**		**Food example**
English	Crunchy	Crispy	***Crunchy:*** raw carrot, apple, pickled ginger
French	Croquant	Croustillant	
Spanish	Crocante / Crujiente	Crujiente / Quebradizo	
Italian	Croccante		
Portuguese	Quebradiço (com ruido)	Quebradiço / Crocante	***Crispy:*** breakfast cereals, biscuit, snack
Japanese	Karikarisuru	Paripari/Baribari	
Chinese	Cui beng	cui	

To describe the texture (i.e. crunchiness and crispness features) in the swollen-food products a puncture test has been widely applied (Van Hecke *et al.*, 1998) for simulate the incisors impact at biting (Roudaut *et al.*, 2002). This test measures the force required to push a punch or probe into a food. It is characterized by (a) a force measuring instrument, (b) penetration of the probe into the food causing irreversible crushing (i.e. to fracture separately the different cell walls constituting the product) or flowing of the food, and (c) the depth of penetration is usually held constant (Bourne, 2002b). Hence, the deformation and fracture behavior of crunchy/crispy food products are often studied as a function of time/displacement at lower rates of deformation in order to be able to study the different fracture events separately (Van Hecke *et al.*, 1998; Saeleaw and Schleining, 2011). It means, that the force-deformation pattern is characterized by series of sharp force peaks corresponding to the rupture of individual cell walls (Van Hecke *et al.*, 1998; Roudaut *et al.*, 2002).

Regarding to the different instruments and settings to puncture test, there is no information or any criteria to select them. The model including diameter and velocity of the probe (i.e. cylindrical or needle) depends on the food product (Altamirano-Fortoul *et al.*, 2012).

Therefore, instrumental methods, as puncture test, and microstructure analysis could be an alternative for providing more information about different snack foods.

The aim of this study was to evaluate the effect of drying by swell drying, which is instant controlled pressure drop DIC-assisted hot air drying, compared with other drying processes such as conventional drying and freeze-drying on the two types of texture (i.e. crunchy and crispy behavior) in the specific case of strawberry (*Fragaria* var. Camarosa).

MATERIALS AND METHODS

Sample Preparation

The strawberries (*Fragaria* var. Camarosa) were purchased from a local market (La Rochelle, France). They were cut in transverse slices with 4-5 mm of thickness. Afterward, the total quantity was divided in three batches. One batch for each process: hot air drying (HAD), freeze-drying (FD) and swell drying (SD).

Treatment Drying Methods:

1. Hot air drying, HAD

The slices of strawberries were dried in a hot air drier (Memmert: Universal Oven UNB Model 800) at 50 °C. The initial vapor pressure in the air was 265 Pa and an air flux of 1.2 m/s. Slices were dried until attaining 3.0% of water content dry basis, around 24 h. Afterward, the samples were analyzed and recorded as **HAD**.

2. Freeze-drying, FD

A freeze-drying equipment (model: RP2V, Serail, France) was used for drying the batch of strawberries sliced. The conditions were divided in three steps: external freezing (at -20 °C/2 h), sublimation (-20 °C, 0.66 Pa /12 h) and desorption (25 °C, 0.66 Pa/12 h). Subsequently, the samples were analyzed and recorded as **FD**.

3. Swell drying, SD

As swell drying is a DIC-assisted hot air drying. The batch of sliced strawberries was partially hot air dried at the same conditions described in HAD method (50 °C with 265 Pa as the initial vapor pressure in the air, and an air flux of 1.2 m/s) until 18% db (dry basis). This first step needed about 8 h. Subsequently, the slices were placed in airtight bags and stored in a cold chamber at 5 ºC by 24 h to homogenize their water content (18% db). Afterward, the partially hot air dried strawberries were treated by DIC equipment (ABCAR-DIC Process, La Rochelle, France) according to the experimental design (Table 2). Finally, after DIC treatment, a traditional convective hot air drying at 50 °C was performed for approximately 1 h to get at 3.0% db as final water content. These samples were recorded as **SD**.

TABLE 2. Trials in the experimental design for DIC process.

					DIC						
Factor	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
P (MPa)	0.60	0.35	0.35	0.53	0.53	0.35	0.17	0.17	0.10	0.35	0.35
t (s)	20	30	20	27	13	20	13	27	20	10	20

P: Saturated steam pressure and t: thermal holding time.

DIC technology was initially developed by Allaf and Vidal (1988). Thus, the experimental set up of DIC equipment (Fig. 1) has been largely described in several papers (Maache-Rezzoug *et al.*, 1998); (Louka and Allaf, 2004); (Haddad and Allaf, 2007); (Ben Amor and Allaf, 2009); (Berka-Zougali *et al.*, 2010) and (Mounir *et al.*, 2012).

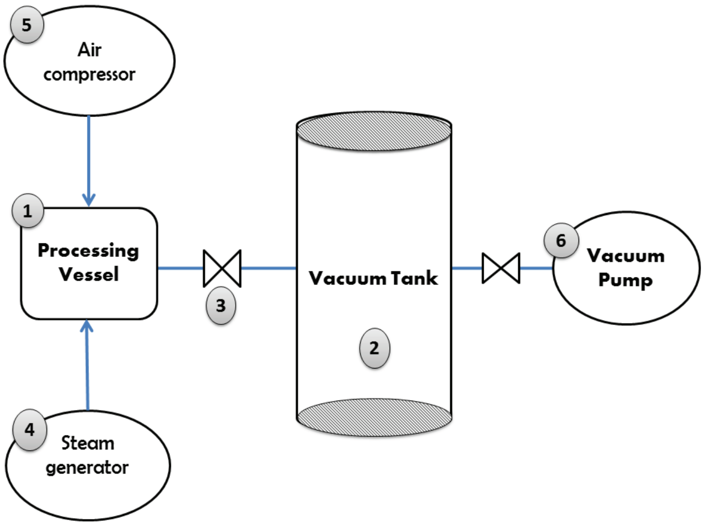

Figure 1. Schematic diagram of the DIC reactor (1) Processing vessel; (2) Vacuum tank; (3) Quick motion valve; (4) Steam generator; (5) Air compressor (6) Vacuum pump. It is composed of three main elements: A) The processing vessel (1), where strawberries samples were placed and treated; B) The vacuum system, which consists mainly of a vacuum tank (2) with a volume 130 times greater than the processing vessel, and an adequate vacuum pump. The initial vacuum level was maintained at 5 kPa in all the experiments; C) A pneumatic valve (3) that ensures the connection/separation between the vacuum tank and the processing vessel. It is capable of producing the abrupt pressure drop within the reactor in less than 0.2 s.

Briefly, DIC process is based on the thermal effects induced by subjecting the strawberries samples for short time (13 to 27 s) to high pressure saturated steam (0.17 to 0.53 MPa). This high temperature-short time stage is followed by an instant pressure drop towards a vacuum (5 kPa) inducing a mechanical effect; such an abrupt pressure drop ($\Delta P/\Delta t > 0.5$ MPa/s), provokes simultaneously autovaporization of a part of water contained in the product and an instantaneous cooling of the products which stops their thermal degradation and give a controlled expansion of the product (Fig. 2).

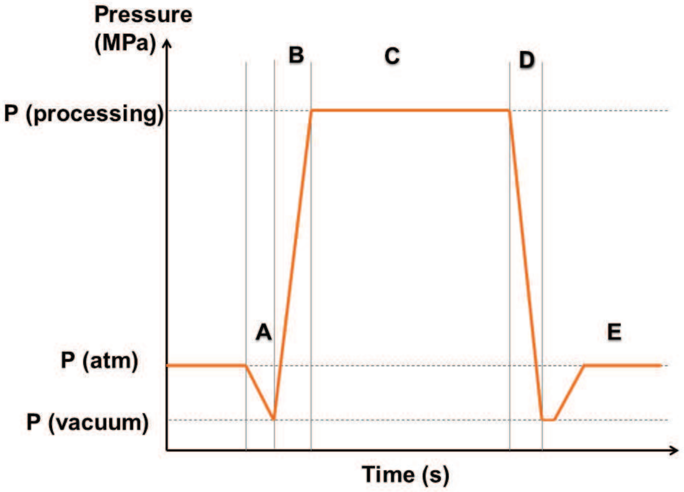

Figure 2. Schematic time-pressure profiles of a DIC process (A) vacuum establishment; (B) steam injection; (C) pressure and time treatment; (D) instant controlled pressure drop towards vacuum and (E) atmospheric pressure establishment.

Assessment Methods

Water Moisture Content

Water moisture content was determined following Karathanos method modified (1999). Briefly, the dried strawberries samples were quantified gravimetrically by triplicate. 2.5 ± 0.1 g of samples were drying at 65 °C during 48 h in the oven UFE 400 (Memmert, Germany). The moisture content (W) dry basis (db) was calculated using the following equation:

$$W_{db}\% = \frac{m_i - m_d}{m_d} \qquad \text{Eq. 1}$$

Where, m_i and m_d (g) were the material weight before and after drying, respectively.

Puncture Test

To measure the mechanical properties of the cellular structure of dried strawberries sliced (i.e. HAD, FD and SD batches), a puncture test was performed with an INSTRON (Model 5543, USA). The probe used was a stainless steel needle with 1 mm in diameter (Petrotest, VICAT needles ISO 6873-EN26873), moving at a constant speed of 1 mm/s. The analysis consisted in recording the force required to penetrate the dried samples by puncturing the middle of the sliced strawberries. The penetration in the dried fruit was until 2 mm for HAD and 3 mm for FD and SD samples (Fig. 3A). And, five measures were done by each batch (i.e. HAD, FD and the eleven SD samples).

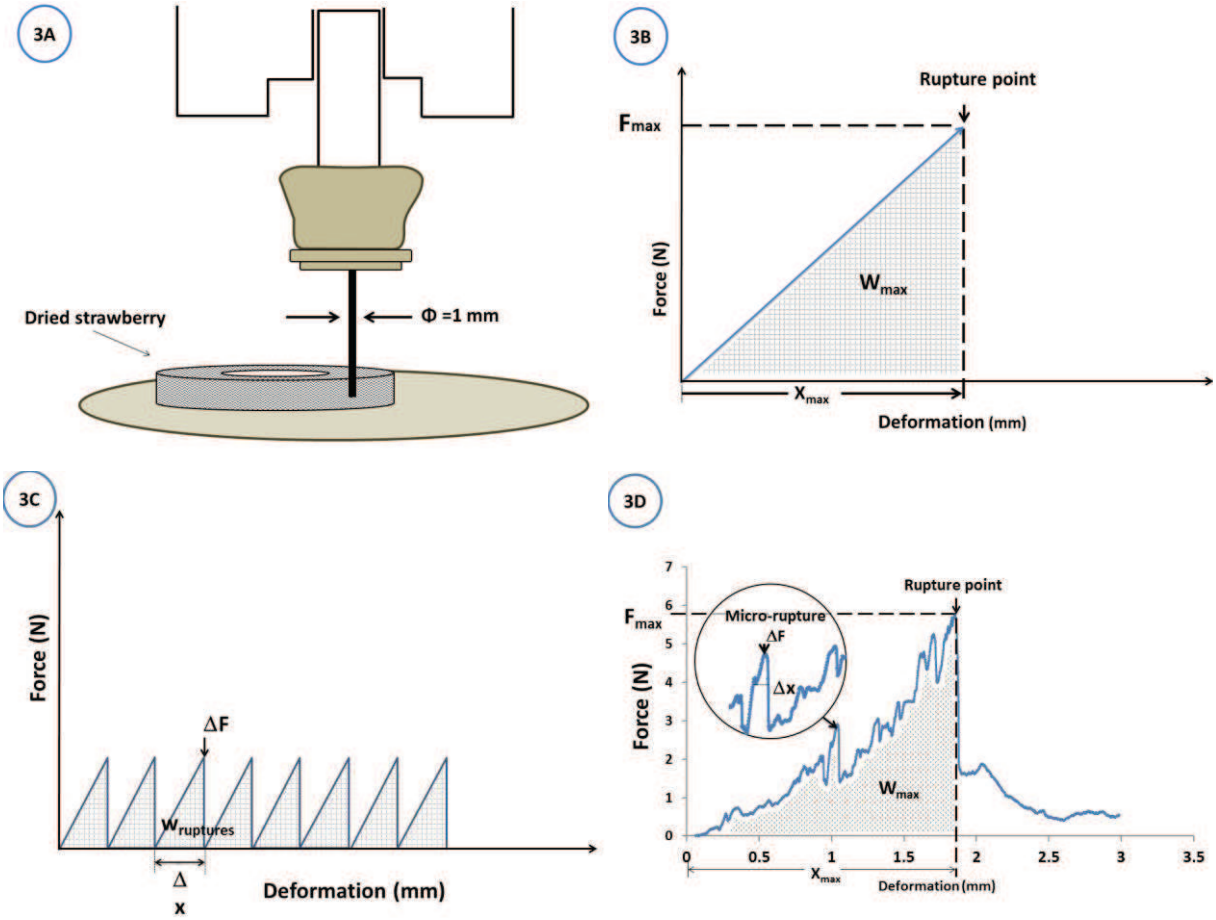

Figure 3. **(A)** Schematic diagram of puncture test. **(B)** Theoretical force-deformation curves obtained by puncture test: *crunchy behavior*: maximum penetration force, F_{max} (N); maximum penetration distance, X_{max} (mm) and total work, W_{max}, (J). **(C)** Theoretical force-deformation curves obtained by puncture test: *crispy behavior*: the penetration distance for each micro-rupture peak, ΔX (mm); the individual force drops for each micro-rupture peak (ΔF, N) and the average work for micro-ruptures, $w_{rupture}$ (J). **(D)** Real force-deformation curve recorded by puncture test: *crunchy and crispy behavior*.

Fundamental Approach to Analyze the Force-Time Curve

The obtained data by force-displacement curves were analyzed in two parts (Fig. 3B-C). The first was for descripting the crunchy behavior parameters (Fig. 3B) and the second was for the crispy behavior (Fig. 3C). In this analysis the method reported by Van Hecke *et al.* (1998) was used also. The following parameters were determined as:

Descripting parameters of Crunchy (Croquant) behavior

Maximum penetration force: F_{max} (N)

Maximum penetration distance: X_{max} (mm)

Total work:

$$\mathrm{W(J)} = \int_0^X F dx \qquad \text{Eq. 2}$$

Total work at X_{max}:

$$\mathrm{W}_{max}\ \mathrm{(J)} = \int_0^{X_{max}} F dx \qquad \text{Eq. 3}$$

Average puncturing force:

$$\langle F \rangle\ \mathrm{(N)} = \frac{\mathrm{W}_{max}}{\mathrm{X}_{max}} \qquad \text{Eq. 4}$$

Descripting parameters of Crispy (Croustillant) behavior

Total number of peaks: n

Spatial frequency of structural micro-ruptures:

$$\mathrm{N}\ (m^{-1}) = \frac{n}{X_{max}} \qquad \text{Eq. 5}$$

Average of micro-rupture force:

$$\mathrm{f\ (N)} = \langle \Delta \mathrm{F} \rangle = \frac{\sum \Delta \mathrm{F}}{n} \qquad \text{Eq. 6}$$

Average work for micro-ruptures:

$$\mathrm{w}_{rupture}\ (\mathrm{N.m} = \mathrm{J}) = \langle \frac{\Delta F . \Delta X}{2} \rangle = \frac{1}{2} \langle \Delta F \rangle . \langle \Delta X \rangle = \frac{1}{2} f . \frac{X_{max}}{n} = \frac{f}{2N} \qquad \text{Eq. 7}$$

Where, ΔX is the penetration distance for each micro-rupture peak (mm) and ΔF is the individual force drops for each micro-rupture peak (N). All of these parameters (i.e. X_{max}, W_{max}, <F>, N, f, $w_{rupture}$, ΔX and ΔF) were calculated until F_{max} was reached (Fig. 3D). And, the final values were the arithmetic mean of five measurements.

Expansion ratios

For porous materials, two expansion ratios are normally defined; the absolute expansion ratio, $\varepsilon_{absolute}$ and the relative expansion ratio, $\varepsilon_{relative}$. The first $\varepsilon_{absolute}$ is the ratio of the apparent volume of the product and the volume of the solid itself. The second $\varepsilon_{relative}$ reflects the increase of volume after processing (FD and SD) compared with the HAD. The absolute and the relative expansion ratio are in function of the product´s density (ρ, g/m^3) and they were calculated to each sample as follows:

Absolute expansion ratio: $$\varepsilon_{absolute} = \frac{\rho_{intrinsic}}{\rho_{specific}}$$ Eq. 8

Relative expansion ratio: $$\varepsilon_{relative} = \frac{\rho_{specific}\ of\ HAD\ product}{\rho_{specific}\ of\ SD\ or\ FD\ product}$$ Eq. 9

Where, the intrinsic density is the density of solid properly said. To measure the *intrinsic density* ($\rho_{intrinsic}$, g/m^3) of each sample (HAD, FD and SD), a gas Pycnometer Micromeritics AccuPyc 1330 (USA) with helium was used.

In the cases of food dried samples, Archimedes method is not possible to be adopted for measuring the specific (apparent) density because of possible interaction between water and the product. Thus, to determine such *specific density* ($\rho_{specific}$, g/m^3), a tapped method was carried out. Briefly, sand (ρ_{sand} = 0.9092 g/cm^3 and 71-200 µm diameter) was put into the cylinder (100 mL and 37.018 g of weigh). The cylinder, with the sand, was then tamped 1000 times on an Autotap Quantachrome DA-3 (Florida, USA). After, the weigh was registered and the mass of sand ($m_{s,1}$, g) was calculated. Subsequently, this method is repeated adding a dried sample with a known mass ($m_{sample} \approx 2$ g) into the cylinder with the sand included. And, the weigh was measured and the mass of sand ($m_{s,2}$, g) was calculated. Thus, the *specific density* of each sample (HAD, FD and SD) was calculated as follows:

Specific density: $$\rho_{specific} = \frac{(m_{sample})(\rho_{sand})}{m_{s,1} - m_{s,2}}$$ Eq. 10

Scanning Electronic Microscopy

The micro-structure of dried strawberry samples, HAD, FD and SD (only treatment conditions for DIC 8 and 11), was observed thanks to a scanning electronic microscope (SEM) JEOL 5410LVFEI Quanta 200F (Philips Croissy-sur-Seine, France). Each sample was placed on a covered support using carbon adhesive and the scanning was carried out under partial vacuum (7 Pa) with an accelerating voltage of 20 kV.

Statistical and Experimental Design

To study the effect of saturated steam pressure (MPa) and thermal holding time (s) of DIC process on the crunchiness and crispness features, and the expansion ratios of dried strawberries, a 2-parameter, 5-level central composite rotatable design was used, Table 2. The experimental design yielded 11 experiments with 4 (2^2) factorial points, 4 axial points to form a central composite design and 3 center points for replications, Table 3. The 11 experiments were run in random in order to minimize the effects of unexpected variability in observed responses due to external factors, Table 2.

TABLE 3. Coded and real levels for independent variables used in 2-variables 5-level rotatable experimental design.

Coded Level	P: Processing pressure (MPa)	t: Processing time (s)
-α	0.10	10
-1	0.19	13
0	0.35	20
1	0.53	27
+α	0.60	30

$\alpha = \sqrt[4]{2^k}$; α is the axial distance and k is the number of experiments of orthogonal design. In this case k=2 and α= 1.4142.

The different responses analyzed for crunchiness were the maximum penetration force (F_{max}, N), the maximum penetration distance (X_{max}, mm), the total work at X_{max} (W_{total}, J) and the average puncturing force (<F>, N). Concerning to the crispness, the responses evaluated were the total number of peaks (n), the spatial frequency of structural micro-ruptures (N, m^{-1}), the average of micro-rupture force (f, N) and the average work for micro-ruptures ($w_{rupture}$, J). The expansion ratios were considered at both aspects of absolute $\varepsilon_{absolute}$and relative $\varepsilon_{relative}$.

The analysis was done with Statgraphics, (Centurion XV, USA) statistical program. The mathematical empirical model applied is:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i \chi_i + \sum_{i=1}^{n} \beta_{ii} \chi_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^{n} \beta_{ij} \chi_i \chi_j + \varepsilon \qquad \text{Eq. 11}$$

Where Y is the response, β_i, β_{ii}, β_{ij} are the regression coefficients, X_i and X_j are the independent variables, ε is random error, i and j are the indices of the factors.

For each response, Pareto Charts was introduced to identify the impact of variables ($p < 0.05$). The Response Surface Methodology (RSM) was used to optimize treatment conditions depending on consumer needs. The general trends allow to analyzing responses behavior in front of variable changes. The empirical model coefficients were defined to determine the models of each response, and R^2 value to accurate fitting models to real data.

RESULTS AND DISCUSSION

The present study was performed to evaluate the effect of various drying processes (HAD, FD and SD) on the strawberry's structure and its instrumental crunchy and crispy features. Therefore, the interpretation and discussion of the obtained results are presented as follows.

Expansion ratios

Strawberry's expansion ratios are parameters that allowed analyzing globally, the effect of drying process (HAD, FD and SD) on the product's structure. The results gathered in Table 4 shown that freeze-drying strawberry had the highest value of both, $\varepsilon_{absolute}$ and $\varepsilon_{relative}$.The product processed by traditional drying showed the opposite behavior for these parameters. On the other hand, SD samples had both expansion ratios higher than HAD but smaller than FD sample. And, under certain conditions of DIC process (DIC 6, P=0.35 MPa and t=20 s) in SD samples, the relative expansion ratio increased thrice more than samples resulting from HAD processes (3.61 compared to 1). In this sense, expansion greatly depend on the DIC operating parameters (saturated steam pressure and thermal treatment time), whereas the intrinsic density remains invariable (results not shown). This behavior of swelling or expansion produced by DIC process was also observed by Louka and Allaf (2004), they found that the vegetables such as onions, carrots and potatoes had a swelling of 200-300% compared to control samples. Additionally, the expansion and density, as a quality parameters, are very important in the characterization, the functional properties and the quality prediction of dried food and they are essential in the design of food processes and processing equipment (Rodríguez-Ramírez *et al.*, 2012). However, both expansion and density have to be complemented with instrumental parameters to develop foodstuffs according to consumer needs.

TABLE 4. Expansion ratios of SD, HAD and FD strawberries.

SD sample	1	2	3	4	5	6	7	8	9	10	11	HAD	FD
$\varepsilon_{absolute}$	4.09	3.77	3.54	3.64	4.52	3.21	2.44	1.91	4.19	2.90	3.05	**1.15**	**18.26**
$\varepsilon_{relative}$	3.48	3.10	2.92	2.97	3.62	2.70	2.07	1.59	3.56	2.49	2.60	**1.00**	**14.13**

P is the saturated steam pressure

t is the time of processing

$\varepsilon_{absolute}$ is the absolute expansion ratio

$\varepsilon_{relative}$ is the relative expansion ratio

Effect of Puncture Test on the Texture of Dried Strawberries

The force-deformation curves recorded by puncture test were analyzed in two main parts. The first was the crunchiness and the second part was the crispy behavior.

Crunchy Behavior

As mentioned above, the crunchy behavior in dried strawberry is defined as a linear elastic behavior till the complete fracture of the structure is reached. Hence, the first parameter defined in the force-deformation curve was F_{max}, which represents the maximum force to punch the dried strawberry. And, the F_{max} is gotten at certain distance that was identified as maximum penetration distance, X_{max}. Table 5 gathers the values calculated for these parameters and for the total work (W_{total}) and the average puncturing force (<F>) obtained to describe the crunchiness behavior of HAD, FD and different treatment conditions of SD samples. Fig. 4 exemplifies the main behavior of the time-deformation curves obtained from HAD, FD and SD (DIC 11, P=0.35 MPa and t=20 s) samples.

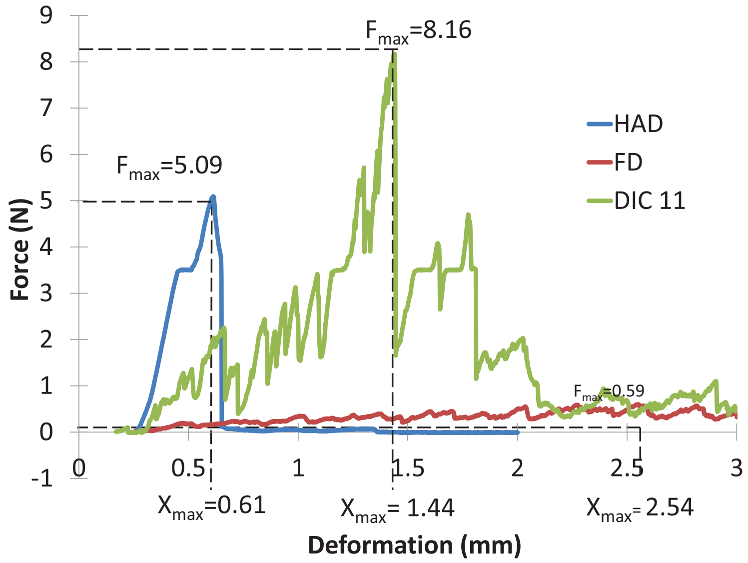

Figure 4. Force-deformation curve from fracture tests on strawberries dried by different methods; HAD, FD and SD.

In general, F_{max} had a significant effect in FD strawberries compared with HAD and SD samples, Table 5. It was too small, as well as the W_{total} used to penetrate the FD sample. Contrary behavior was observed in HAD and SD samples, Table 5. Hot air drying strawberries needed a maximum force and a total work of penetration smaller than swell-drying samples. Concerning to <F>, which is the mechanical resistance given by the product when the force to punch it is applied, in the average of DIC samples was higher than those in HAD and FD by 18% and 88%, respectively (Table 5).

On the other hand, the impact of DIC operating parameters (saturated steam pressure and processing time) on the different responses to measure the crunchiness of strawberry are shown in Table 5). The saturated steam pressure had a significant and positive effect ($p < 0.05$) on X_{max} compared to the thermal holding time (Fig.5A). Hence, the higher the saturated steam pressure, the higher X_{max}. The optimized conditions were calculated for an optimum value of 2.66 mm, with a saturated steam pressure of 0.6 MPa and 30 s of thermal treatment time (Fig.5B).

The obtained regression model for the maximum penetration distance is follows, with R^2=71.69%

$$\text{Xmax} = 1.43273 - 0.438414P - 0.0376025t - 0.52104P^2 + 0.120939Pt + 0.000694876t^2 \qquad \text{Eq. 12}$$

TABLE 5. Texture analysis in SD, HAD and FD strawberries.

Sample	**Crunchy Behavior**				**Crispy Behavior**			
DIC	[a] F_{max}	[b] X_{max}	[c] W_{total}	[d] <F>	[e] n	[f] N	[g] f	[h] $W_{rupture}*e^{-4}$
1	5.73	2.16	3.59	1.65	160.75	86.27	0.1734	10.06
2	7.65	1.79	5.47	2.57	113.60	73.91	0.1911	13.27
3	6.43	1.59	2.33	1.67	129.83	89.35	0.1043	6.69
4	6.60	2.31	5.49	2.46	164.40	80.93	0.1946	13.56
5	4.88	1.16	2.00	1.65	82.60	79.48	0.1489	9.55
6	5.49	1.76	3.93	2.09	129.00	81.22	0.1708	11.07
7	3.77	1.03	1.39	1.36	71.60	76.97	0.0767	5.10
8	3.81	1.57	1.54	0.97	128.00	93.46	0.0484	3.14
9	8.74	1.13	2.51	2.24	77.25	79.16	0.0907	6.58
10	7.28	1.69	3.08	1.93	99.40	78.22	0.1910	13.95
11	5.66	1.41	2.33	1.60	100.50	84.69	0.1239	7.90
Average DIC	**6.00 ± 1.55**	**1.60 ± 0.41**	**3.06 ± 1.43**	**1.84 ± 0.48**	**114.27 ± 31.51**	**82.15 ± 5.76**	**0.1376 ± 0.05**	**9.17 ± 3.62**
Average of central DIC points	**5.86 ± 0.50**	**1.59 ± 0.17**	**2.86 ± 0.93**	**1.79 ± 0.26**	**119.78 ± 16.70**	**85.09 ± 4.08**	**0.13 ± 0.03**	**8.56 ± 2.26**
HAD	**4.33**	**0.75**	**1.10**	**1.50**	**22.40**	**56.70**	**0.2085**	**22.12**
FD	**0.91**	**1.24**	**0.35**	**0.23**	**123**	**110.59**	**0.0168**	**0.82**

[a] Maximum penetration force (N);

[b] Maximum penetration distance (mm);

[c] Total work at X_{max} (J);

[d] Average puncturing force (N);

[e] Total number of peaks;

[f] Spatial frequency of structural micro-ruptures (m^{-1});

[g] Average of micro-rupture force (N);

[h] Average work for micro-ruptures (J)

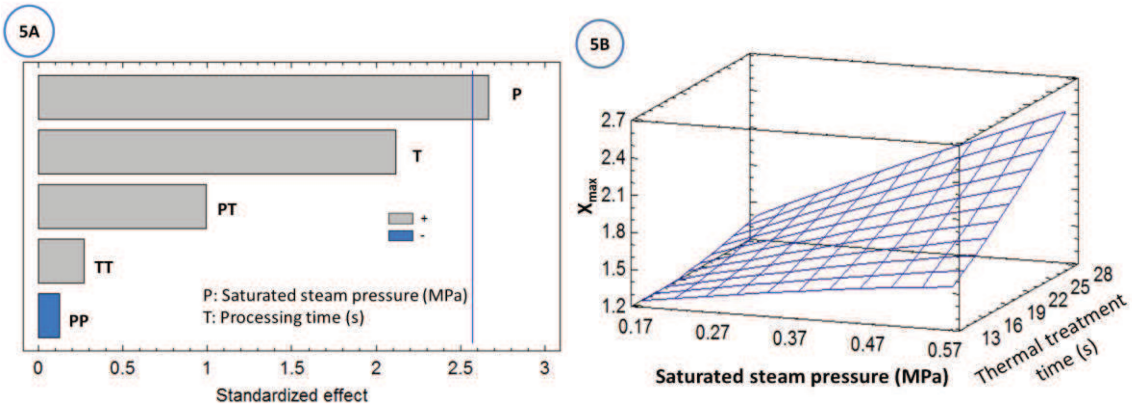

Figure 5. Effect of DIC operating parameters; saturated steam pressure (MPa) and time processing (s) on the *maximum penetration distance* (X_{max}, mm), a parameter of crunchy behavior in the strawberry's texture. **(A)** Pareto Chart and **(B)** Response Surface.

Furthermore, the mean correlations were analyzed between the four parameters (F_{max}, X_{max}, W_{total} and <F>) of crunchiness presented in strawberry dried by HAD, FD and SD processes.

The highest correlation was found between <F> and F_{max} with R^2=0.8083, Fig. 6A. Another important correlation with R^2= 0.7270 was observed between <F> and W_{total}. And, the last one was between X_{max} and W_{total}, with R^2=0.6257.

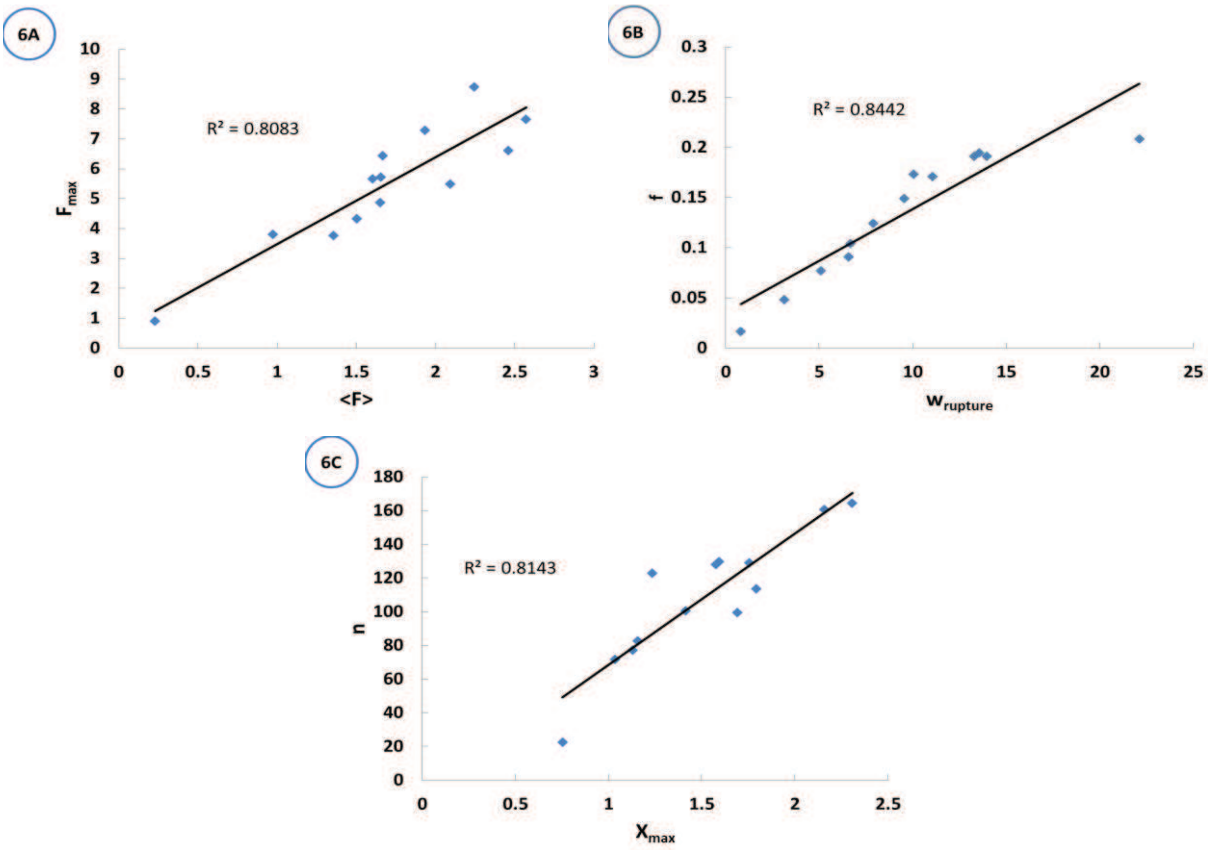

Figure 6. Mean correlations between crunchy and crispy behavior. **(A)** <F> and F_{max} for crunchiness; (B) $w_{rupture}$ and f for crispness; (C) X_{max} and n between both, crunchy and crispy behavior.

Crispy Behavior

In the case of crispy behavior of dried strawberry, the crispness or croustillant feature was used to describe the small continuous linear elastic behavior till the successive fractures during chewing of dried strawberry. Hence, the mean parameters analyzed that described the crispness behavior in the dried strawberry (HAD, FD and SD) are presented in Table 5. Therefore, the small fractures recorded during puncture test were gathered in the total number of peaks (n) and in the spatial frequency of structural micro-ruptures (N); however the last one is dependent on X_{max}. Thus, the n value in HAD product was smaller than FD and SD samples in 82% and 80%, respectively. Similar behavior was observed for the N value; it was small in 49% for FD and 31% for SD samples compared with the values obtained in HAD strawberry. In case of SD samples compared with FD, no significant difference was found for the total number of micro-ruptures, but FD presented a spatial frequency of structural micro-ruptures higher in 26% than SD strawberries. Relating to the average on micro-rupture force (f) and the average work for micro-ruptures ($w_{rupture}$), the least values were for FD samples. And HAD strawberries had a significant difference in f and $w_{rupture}$ with SD samples. These values in HAD were higher than SD fruits.

Nevertheless, as process parameters and macrostructure are difficult to separate, the operating parameters of DIC showed an effect of saturated steam pressure (MPa) and time processing (s) on the average of micro-rupture force (f) (Fig. 7A-B). Similar behavior in X_{max} was observed for f. The saturated steam pressure had a great influence compared to the thermal holding time (Fig. 7A). The higher saturated pressure time, the higher f. Hence, the DIC treatment at 0.6 MPa of saturated steam pressure and 30 s of thermal holding time gave the highest value of f, 0.2447 N (Fig. 7B).

The obtained regression model for the average of micro-rupture force is follows:

$$\mathrm{f} = 0.247114 + 0.207209P - 0.0194438t - 0.37914P^2 + 0.0146887Pt + 0.0003652846t^2 \qquad \text{Eq. 13}$$

With R^2= 72.26%

Respect to correlations, they were studied between the crispness parameters (i.e. n, N, f and $w_{rupture}$) for the three drying process applied at strawberry. A correlation between f and $w_{rupture}$ was the highest, with R^2=0.8442 (Fig. 6B). While, the correlation between N and $w_{rupture}$ and f were observed with R^2=0.7172 and R^2=0.5439, respectively.

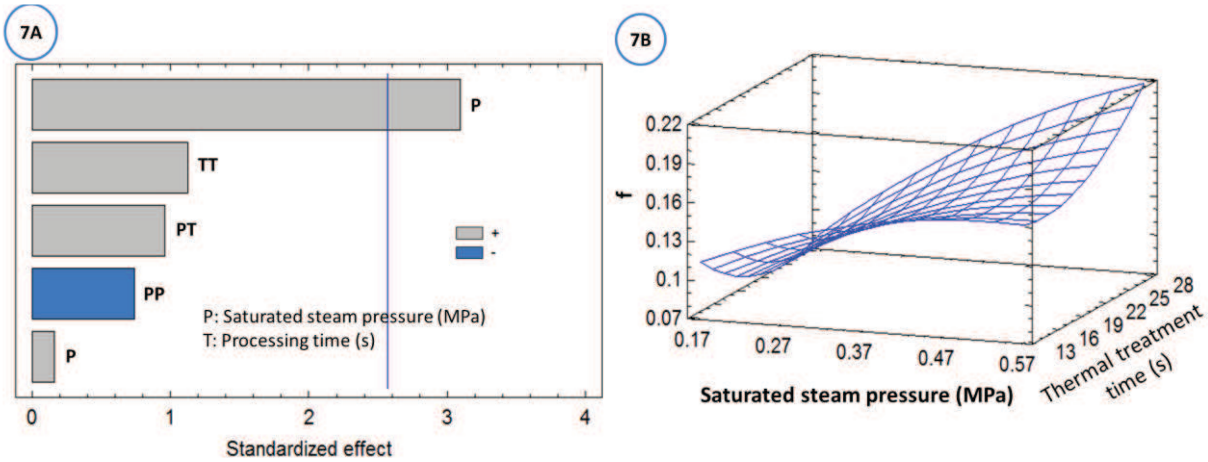

Figure 7. Effect of DIC operating parameters; saturated steam pressure (MPa) and time processing (s) on the *average of micro-rupture force* (f, N), a parameter of crunchy behavior in the strawberry's texture. (**A**) Pareto Chart and **(B)** Response Surface.

Correlations Between Crunchiness, Crispness and Expansion Ratios.

Only two correlations were observed between eight parameters (e.g. X_{max}, n) that described the crunchy and crispy behavior of this study. The highest correlations was observed between X_{max} and n, with R^2=0.8143 (Fig. 6C). And, the second correlation with R^2=0.5311 was obtained between <F> and f. In contrast, there was just one correlation between $\varepsilon_{relative}$ and N, with R^2= 5445. These results indicated that crunchiness and crispness were strongly correlated.

The overall of these results could be explained by the effect of shrinkage phenomena in HAD, the cell walls broken in FD and the swelling or expansion phenomena in SD strawberries. Namely, the arrangement of cells in fruits and vegetables is strongly marked by the processing (Hammami and René, 1997; Wang *et al.*, 2011; Guiné and Barroca, 2012). And it influences directly in the textural behavior and functionality of foodstuffs. Therefore, the cell walls networking are contracted in the strawberry after HAD, producing a hard and brittle structure in the product. In contrast, FD strawberries have a membranes system disrupted that behave more like a sponge characterized by network tortuosity (Voda *et al.*, 2012). And, it provokes a soft texture and many micro-ruptures in the FD fruit. However, the micro-ruptures will have a small force and work. In case of SD products, the cells arrangement is better defined due to the micro-alveolation phenomenon produced as consequence of the decompression process in the DIC treatment. The swelling products will be highly crispy with a significant number of micro-ruptures, and considerable force and work.

At the same time, crispness is an important and desirable sensory attribute and there is a great deal of interest in correlating crispness to instrumental recorded data (Tsukakoshi *et al.*, 2007; Arimi *et al.*, 2010). Hence, this puncture test method helps strongly to elucidate crunchiness and crispness features; such are very important attributes in the swell-dried fruits. And, it means that is possible to concoct a crispy snack produced by swell-drying performance and accordingly with the consumer needs.

Impact of Processes in the Microstructure

Fig. 8 shows the impact of drying processes on strawberry's microstructure. The cross section micrographs of dried strawberries, shown structural differences between HAD, FD and SD processes (Fig. 8). The shrinkage of HAD product is evident in the image; however, the cell structure is relatively organized, Fig. 8A. With respect to FD micrograph, it shows that cell walls of strawberry were broken, Fig. 8B. On the other hand, SD images illustrate a strawberry's microstructure expanded (Fig. 8C-D). It can be identified by the dark regions that represent the cavities of the pores expanded. And, the structure of cell walls was well preserved. However, in SD samples, the structure modification is highly dependent of the operating parameters (saturated steam pressure, MPa and thermal holding time, s) used for the DIC treatment. These observations were consisted with the results of puncture test.

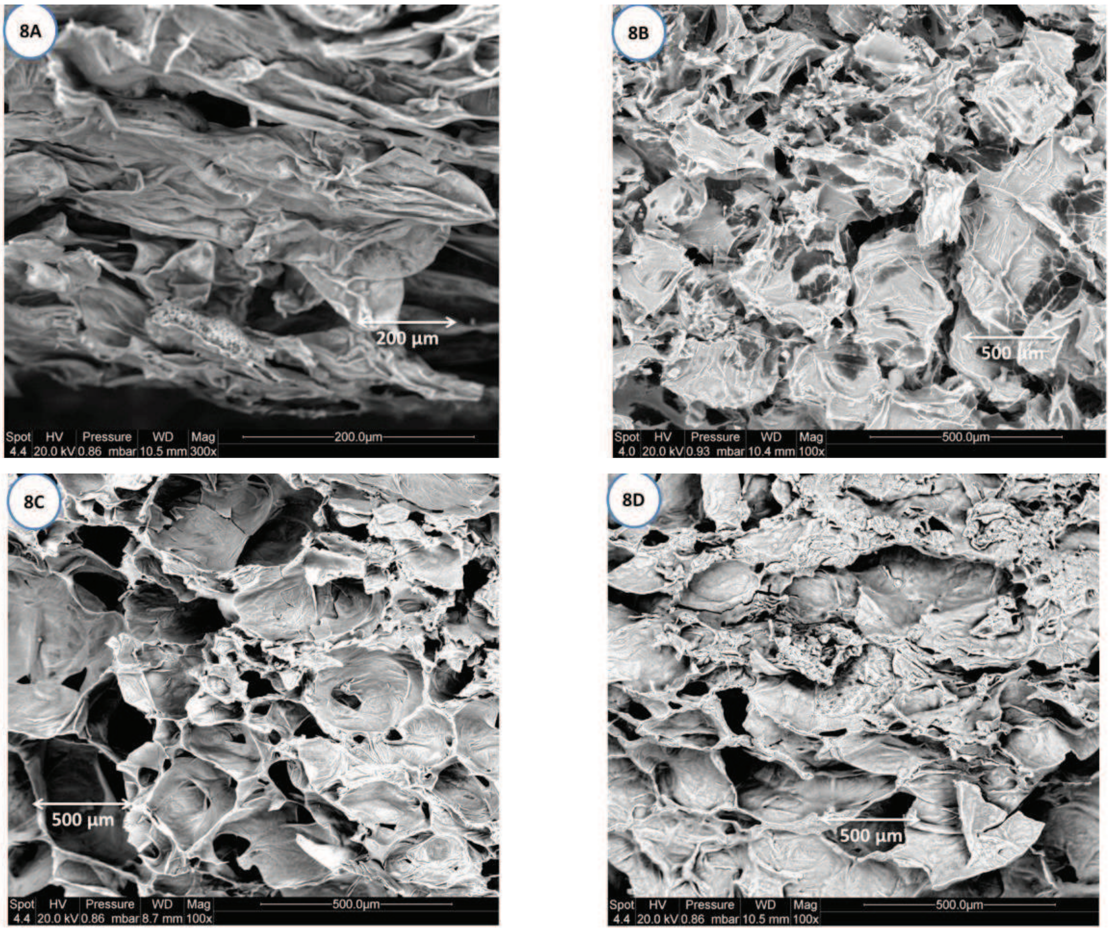

Figure 8. Scanning Electron Micrographs of cross-section of strawberry treated by different drying methods **(A)**; Hot Air Drying **(B)**; Freeze-Drying at **(C)**; Swell-Drying (DIC 8) at P=17 MPa and t=27 s, and **(D)**; Swell-Drying (DIC 11) at P=35 MPa and t=20 s of treatment conditions.

In fruits treated by freeze-drying, is normal the formation of ice crystals that destroy the tissue during the freezing step. Likewise, this damage is limited in function of the rates of freezing (Hammami and René, 1997). Voda *et al.* (2012) analyzed SEM images of carrots processed by freeze-drying and found that during the freezing the growth of an ice crystal ruptures, pushes, and compresses cells and this damage is more pronounced in slowly frozen tissue which yields bigger ice crystals.

In the case of SD samples, this structure modification produced by DIC treatment, can intensify the mass transfer phenomena, improving the effective water diffusivity during both drying and rehydration operations of strawberries reported in a previously work (Alonzo-Macías *et al.*, 2012). This effect is observed not only for strawberries but also other kind of fruits and vegetables treated by DIC (Ben Amor and Allaf, 2009; Albitar *et al.*, 2011; Téllez-Pérez *et al.*, 2012).

CONCLUSIONS

Based on our experimental study, it is possible to obtain a crispy fruit modifying, controlling, and optimizing the DIC operating parameters. Thus, this snack product can be confectioned according to the consumer needs. In case of strawberry was possible to reduce the shrinkage phenomena in swell-drying samples. Consequently, the swell-dried strawberries showed an interesting macro and micro-structure. They had a high expansion ratios and significant crispness provoked by the micro-alveolation phenomenon induced as consequence of the decompression process in the DIC treatment.

On the other hand, the most important correlations were between F_{max} and <F> and between f and $w_{rupture}$ for crunchiness and crispness features, respectively. And, there was just one correlation between $\varepsilon_{relative}$ and N.

Hence, the present study opens the possibility to use the puncture test as an instrumental source to measure the crispness on swell-dried fruits and vegetables. Also, it could be used as a complement of the analysis to describe better the physical attributes of swelled products.

Additionally, DIC technology can compete with freeze drying process and is a better alternative instead of using the hot air drying process to preserver strawberries. This proposal is in terms of the high-quality in the product with a low-cost of processing and the high diversification of the fruit obtained with DIC performance.

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PART IV

CONCLUSIONS AND PERSPECTIVES

CHAPTER IV.1

CONCLUSIONS

The overall results shown that swell-drying technique can be considered as an alternative of drying method for fragile fruits, such as strawberries. Because of SD method helped to reduce the time of drying and is a low-cost processing compared with classical hot air drying and freeze-drying. At the same time, it could face the shrinkage phenomenon that is very common in hot air drying samples.

Additionally, SD globally preserved the strawberry's nutritional value and bioactive compounds, increasing their availability. Also, it was demonstrated that at optimal DIC conditions (0.35 MPa as saturated steam pressure for 10 s) SD strawberries were richer in anthocyanins, phenolic compounds and flavonoids compared with the other dried samples and increased the availability of these compounds. Moreover, a strong correlation between antioxidant activity and total anthocyanin content was established in SD strawberries.

On the other hand, the swell-dried strawberries showed an interesting macro and micro-structure. They had a high expansion ratios and significant crispness provoked by the micro-alveolation phenomenon induced as consequence of the instant decompression process by DIC treatment.

Hence, the present study opens the possibility to use the puncture test as an instrumental way to measure the crispness on swell-dried fruits and vegetables. Since it also can estimate the crunchy content, it will be possible to use it as complement analysis to describe better the physical attributes of swelled products, and to optimize the treatment and texturing conditions.

Thus, it was possible to obtain a crispy high nutritional quality dried strawberry modifying, controlling, and optimizing the operating parameters of DIC. Thus, this snack product can be confectioned according to the industrial and consumer needs.

CHAPTER IV.2

PERSPECTIVES

This thesis has made original contribution to knowledge by providing basic and applied information on drying strawberries, using different treatments as hot air drying, freeze-drying and swell-drying. However, the main points that are yet to be addressed for further studies are explained as follows:

Process:

To improve swell-drying performances two solutions are proposed. It is possible to optimize the parameters used for the hot air drying in the first part of SD process. They are the air flux rate, temperature and humidity. Some improvements depending on the products can also be defined such as intermittency and sun drying… The second possibility in terms of process is to use microwaves or DDS technology instead of hot air drying in the last stage of SD process. Both suggestions are to decrease the time and cost operation and increase the quality of end product.

Product:

It is necessary to extend this study to other fruits and vegetables to technically support the industrial scale of final products for various applications (baby foods, nutraceutics…) to make them commercially available.

Assessments:

Since we could define an instrumental method to quantify the texture of swell-dried snacking, more texture measurements by penetration test are important to perfectly optimize the treatment parameters and to obtain the highest quality products. Our analyses were defined for one diameter and with a pre-determined velocity. It will be very important to study the correlations between the products, thickness and these puncture assessment parameters through the force-time curves obtained. It is also important to define a “standard instrumental method independently of the product”.

Other techniques such as acoustical methods for brittle materials should help to well describe the sound emitted by snacking products, and its correlation with sensorial acoustical content. Thus, a sensorial analysis must be included for further studies. The consumer's acceptance is crucial to get uniform quality of final products at industrial scale. Particularly, when a new product is developed and it presents a health potential benefit. Since the swell-dried strawberry issued from this research is an alternative of snacking products, medical studies should be carried out to identify much better its impact on health and nutritional effect, more specially for children. Hence, measurements of the various phytochemical bioavailabilities (i.e. phenols and anthocyanins) through human feeding studies are necessary to give evidences of its health benefits. Additionally, it is also interesting to identify the metabolites of these compounds and their bioactivity.

In terms of quality product, it is necessary to evaluate the profile of volatile compounds by gas chromatography-mass spectrometry (GC-MS) to compare the effect of drying methods (i.e. SD, HAD and FD).

Finally, it is indispensable to evaluate comparatively the shelf-life of various dried products depending on the processes, specially in terms of nutritional component degradation.

PART V

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