

**Integrated Master in Bioengineering  
Specialization in Biological Engineering**

***Effects of storage conditions on the stability of  
raspberry foams***

**Master thesis**

of

**Sara Isabel Freitas Morais**

**Developed within the discipline of Dissertation**

Conducted at

**Chair of Food and Bioprocess Engineering of the Technical University of  
Munich (TUM)**



Technische Universität München

Supervisor (FEUP): **Dr. Lúcia Santos**

Supervisor (TUM): **M. Sc. Mine Özcelik**

**Department of Chemical Engineering**



**FEUP** FACULDADE DE ENGENHARIA  
UNIVERSIDADE DO PORTO

**September, 2018**



## Acknowledgements

I would like to formally acknowledge my gratitude to the following identities.

First of all, I would like to express my profound gratitude to my beloved parents, for supporting my education and always believing in my capacities.

I would also like to thank my supervisor Dr. Lúcia Santos for her help, encouragement and insightful comments. I am grateful, as well, to my supervisor M. Sc. Mine Özcelik for her availability, expert direction, enjoyable cooperation and for all the support she offered me. In particular, I would like to express my gratitude to Prof. Dr.-Ing. Kulozik for the opportunity to do my master thesis at the chair for food and bioprocess engineering and to the Erasmus+ programme for the financial support.

I am thankful to all the people from the Chair of food and bioprocess engineering of the technical university of Munich for the warm welcome, good work environment and for allowing me to use all the required facilities and resources.

To my dear friends from the class of biological engineering, I would like to thank you for the friendship and mutual support in this journey.

Finally, I take this opportunity to express gratitude to my sister, companion and friends for their unconditional support.

---

Professor Lúcia Santos, supervisor of this dissertation is an integrated member of LEPABE – Laboratory for Process Engineering, Environment, Biotechnology and Energy, financially supported by: project POCI-01-0145-FEDER-006939 (Laboratory for Process Engineering, Environment, Biotechnology and Energy – UID/EQU/00511/2013), funded by European Regional Development Fund (ERDF) through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (PIDDAC) through FCT – Fundação para a Ciência e a Tecnologia/MCTES; project “LEPABE-2-ECO-INNOVATION” – NORTE-01-0145-FEDER-000005, funded by Norte Portugal Regional Operational Programme (NORTE 2020), under PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).



## Abstract

Nowadays, the consumption of healthy snacks made from dehydrated berries has been increasing because of the consumer concern about healthy eating habits. Raspberry foams consist in fruit puree added with maltodextrin (MD), potato protease inhibitors (PPI) and pectin (P) which is mixed with the addition of air and dried afterwards. It can be consumed as a snack or converted to powder and applied in cereals, yogurts or other snacks.

The aim of this work was to study the storage stability of raspberry foams, dehydrated by microwave freeze-drying (MWFD), during a period of 12 weeks. The foams were analysed regarding residual moisture content (RMC), water activity ( $a_w$ ), color, texture, ascorbic acid and anthocyanins. The influence of MD (as a foam stabilizer) during storage was studied using a varying concentration of 5, 15 or 30% (w/w) maltodextrin. Additionally, three types of sample concerning different processing stages were also dried with microwave freeze-drying and analysed during storage, more specifically: raspberry splits; puree (without additives) and non-foamed solutions. Conventional freeze-drying (FD) technique was also applied to all samples and compared to MWFD. Storage conditions were 37, 20 and 4 °C (under vacuum) and in chambers (no vacuum applied) with different controlled relative humidity environments ( $a_w$  of 0.11, 0.22, 0.33).

Samples produced by microwave freeze-drying and freeze drying achieved the same quality after drying and over storage. The addition of MD, PPI and P improved the stability of all the quality parameters. After the end of storage at 37 °C, 15% MD foam presented a retention of 69% of ascorbic acid, 86% of anthocyanins, and color was maintained. Although, raspberry splits suffered the highest increase in residual moisture content and water activity during the storage, having reached  $5.96 \pm 0.47\%$  and  $0.403 \pm 0.03$ , respectively, all the samples were still considered microbiologically safe.

The 5% MD foam presented the highest stability of RMC (3.9% was maintained) and  $a_w$  (increased from 0.23 to 0.25). On the other hand, the 15% and 30% MD foams presented similarly higher stability of color (total color difference only visible with a trained eye) and retention of anthocyanins (87%) and ascorbic acid (70%). Different amounts of maltodextrin did not have an influence in the texture stability of raspberry foams. High temperature, relative humidity and presence of oxygen caused a negative impact in the studied quality parameters. The 15% MD foam stored under vacuum at 20 °C and 4 °C were presented the highest retention of anthocyanins and total ascorbic acid.

**Keywords:** raspberry foams, stability, microwave freeze-drying, freeze-drying, maltodextrin



## Resumo

O consumo de *snacks* saudáveis de frutas desidratadas tem aumentado com a crescente preocupação do consumidor em ter uma alimentação saudável. As espumas de framboesa consistem em puré de fruta com adição de maltodextrina (MD), inibidores de protease de batata (PPI) e pectina (P), ao qual é adicionado ar e realizada posterior desidratação. Podem ser utilizadas como snack ou em pó, sendo aplicadas em cereais, iogurte ou outros *snacks*.

O objetivo deste trabalho foi estudar a estabilidade de armazenamento das espumas de framboesa, desidratadas pela técnica de liofilização por micro-ondas (MWFD), durante 12 semanas. As espumas foram analisadas tendo em conta o conteúdo de humidade residual (RMC), a atividade de água ( $a_w$ ), a cor, a textura, o ácido ascórbico (AA) e as antocianinas (ACN). A influência da maltodextrina como estabilizador das espumas, durante o armazenamento, foi estudada, tendo em conta uma concentração variável de 5, 15 e 30% (m/m) de MD. Adicionalmente, foram também testados três tipos de amostras, nomeadamente: pedaços de framboesa; puré (sem aditivos) e soluções (sem adição de ar), considerando assim os diferentes estados de processamento. A técnica de liofilização convencional (FD) foi também aplicada a todas as amostras e comparada com a técnica de MWFD. As condições de armazenamento foram 37, 20 e 4 °C (sob vácuo) ou em câmaras (sem vácuo aplicado) com diferentes ambientes de humidade relativa ( $a_w$  de 0,11, 0,22, 0,33).

As amostras produzidas por FD e por MWFD atingiram a mesma qualidade após a secagem e durante o armazenamento. A adição de MD, PPI e P melhorou a estabilidade em todos os parâmetros estudados. Após armazenamento a 37 °C, a espuma com 15% MD apresentou retenção de 69% de ácido ascórbico, 86% de antocianinas e a cor foi mantida. Embora os pedaços de fruta desidratada tenham sofrido o maior aumento de RMC e  $a_w$ , após armazenamento, atingindo valores de  $5,96 \pm 0,47\%$  e  $0,403 \pm 0,03$ , respetivamente, todas as amostras foram consideradas microbiologicamente seguras.

A espuma com 5% MD apresentou maior estabilidade em RMC (mantendo 3,9%) e  $a_w$  (aumentou de 0,23 para 0,25). Enquanto espumas com 15 e 30% MD apresentaram, similarmente, maior estabilidade na cor (diferença total de cor apenas visível com olhos treinados) e retenção de ACN (87%) e AA (70%). A variação da concentração de MD não influenciou a estabilidade da textura das espumas durante o armazenamento. Alta temperatura, humidade relativa e presença de oxigênio tiveram um impacto negativo na estabilidade das espumas. A espuma de 15% MD armazenada sob vácuo a 4 e 20 °C obteve a maior estabilidade de antocianinas e ácido ascórbico.

**Palavras-chave:** espumas de framboesa, estabilidade, liofilização por micro-ondas, liofilização convencional, maltodextrina





## Statement declaration

I, Sara Isabel Freitas Morais, hereby declare, on my word of honour, that this work is original and that all non-original contributions were properly referenced with source identification.

Funchal, 17<sup>th</sup> September of 2018



---

(Sara Isabel Freitas Morais)



# Index

<b>Acknowledgements</b> .....	<b>i</b>
<b>Abstract</b> .....	<b>iii</b>
<b>Resumo</b> .....	<b>v</b>
<b>Statement declaration</b> .....	<b>vii</b>
<b>Index</b> .....	<b>ix</b>
<b>Figure list</b> .....	<b>xi</b>
<b>Table list</b> .....	<b>xiii</b>
<b>Glossary</b> .....	<b>xv</b>
<b>1 Background motivation</b> .....	<b>1</b>
<b>1.1 Background motivation</b> .....	<b>1</b>
<b>1.2 Thesis objectives</b> .....	<b>2</b>
<b>2 Introduction</b> .....	<b>3</b>
<b>2.1 Chemical composition of raspberry</b> .....	<b>3</b>
2.1.1 Anthocyanins .....	3
2.1.2 Ascorbic acid .....	5
<b>2.2 Raspberry foams</b> .....	<b>6</b>
<b>2.3 Food drying techniques</b> .....	<b>8</b>
2.3.1 Freeze-drying .....	9
2.3.2 Microwave freeze-drying .....	10
<b>2.4 Importance of storage on the quality of dehydrated products</b> .....	<b>12</b>
<b>3 State of art</b> .....	<b>17</b>
<b>4 Materials and methods</b> .....	<b>25</b>
<b>4.1 Materials</b> .....	<b>25</b>
4.1.1 Reagents .....	25
4.1.2 Equipment .....	25
4.1.3 Software .....	26
<b>4.2 Methods</b> .....	<b>26</b>
4.2.1 Experimental plan .....	26

4.2.2	Sample Preparation .....	26
4.2.3	Drying process .....	27
4.2.4	Packaging and storage .....	28
4.2.5	Sample analysis .....	29
<b>5</b>	<b>Results and discussion .....</b>	<b>33</b>
<b>5.1</b>	<b>Influence of drying method.....</b>	<b>33</b>
<b>5.2</b>	<b>Influence of structure .....</b>	<b>36</b>
<b>5.3</b>	<b>Influence of maltodextrin concentration .....</b>	<b>42</b>
<b>5.4</b>	<b>Influence of storage temperature .....</b>	<b>46</b>
<b>5.5</b>	<b>Influence of storage relative humidity.....</b>	<b>48</b>
<b>5.6</b>	<b>Overview .....</b>	<b>49</b>
<b>6</b>	<b>Conclusion .....</b>	<b>51</b>
<b>7</b>	<b>Future work and limitations .....</b>	<b>52</b>
<b>8</b>	<b>References .....</b>	<b>53</b>
	<b>Appendix .....</b>	<b>A</b>

## Figure list

Figure 1 - Possible mechanism of thermal degradation of cyanidin-3-glucoside. Adapted from (Patras et al., 2010).	4
Figure 2 - Oxidation reaction of ascorbic acid to dehydroascorbic acid (Harvey, 2016).	5
Figure 3 - Phase diagram for water (Kessler, 2002).	9
Figure 4 - Representation of dielectric dipoles rotation and ion displacement in an alternating field (Püschner and Hoon, 2007).	11
Figure 5 - RMC of 15% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.	33
Figure 6 - Water activity of 15% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.	33
Figure 7 - Hardness of 15% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.	34
Figure 8 - Color parameters of 15% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.	34
Figure 9 - Total ACN retention of 30% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.	35
Figure 10 - Total AA retention of 30% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.	35
Figure 11 - Representation of the different dried structures analysed. A – Raspberry splits; B – Raspberry puree; C – Raspberry solution with 15% MD; D – Raspberry foam with 15% MD.	36
Figure 12 - Influence of structure on water activity. Solution and foam with 5% PPI, 15% MD and 2.5% P. Samples stored under 37 °C, vacuum packed.	38
Figure 13 - Influence of structure on RMC. Solution and foam with 5% PPI, 15% MD and 2.5% P. Samples stored under 37 °C, vacuum packed.	38
Figure 14 - Influence of structure in the color. On the right, overall view of color parameter L,a,b. On the left, zoomed in graph, focusing in the redness (+a*) and yellowness (+b*). Solution and foam with 5% PPI, 15% MD and 2.5% P. Samples stored under 37 °C, vacuum packed.	38
Figure 15 - Influence of structure on the retention of ACN during storage at 37 °C. Vacuum-packed samples.	41
Figure 16 - Influence of structure on the retention of AA during storage at 37 °C. Vacuum-packed samples.	41
Figure 17 - Influence of MD concentration in the water activity during storage at 37 °C. Vacuum-packed samples.	43
Figure 18 - Influence of MD concentration in the RMC during storage at 37 °C. Vacuum-packed samples.	43
Figure 19 - Influence of MD concentration on the hardness of foams, during storage at 37 °C. Vacuum-packed samples.	43
Figure 20 - Influence of MD concentration in the color. On the left, overall view of color parameter L,a,b. On the right, graph focusing on the brightness (L*) and redness (+a*). Vacuum-packed samples, stored under 37 °C.	44
Figure 21 - Influence of MD concentration on the retention of AA during storage at 37 °C. Vacuum-packed samples.	45

Figure 22 - Influence of MD concentration on the retention of ACN during storage at 37 °C. Vacuum-packed samples. ....45

Figure 23 - Influence of storage temperature in the  $a_w$  of 15% MD MWFD foam. Vacuum-packed samples. ....46

Figure 24 - Influence of storage temperature in the RMC of 15% MD MWFD foam. Vacuum-packed samples. ....46

Figure 25 - Influence of storage temperature in the color of 15% MD foam. Vacuum-packed samples. ....47

Figure 27 - Influence of storage temperature on the total AA retention of the 15% MD foam. Vacuum-packed samples. ....48

Figure 26 - Influence of storage temperature on the ACN retention of the 15% MD foam. Vacuum-packed samples. ....48

## Table list

Table 1 - Anthocyanin compounds of fresh raspberry ( <i>Rubus idaeus</i> ) (Kassim et al., 2009; Torre and Barritt, 1977).....	4
Table 2 - Ascorbic acid present in different fresh red raspberry ( <i>Rubus idaeus</i> ) cultivars. ....	5
Table 3 - Dielectric properties of liquid water (25 °C) and ice (-2 °C) at 2.45 GHz frequency. Adapted from (Abbasi and Azari, 2009). ....	11
Table 4 - Studies concerning the stability of fresh berries regarding the analysis of ACN and vitamin C content and color. ....	20
Table 5 - Studies concerning the storage stability of dehydrated fruits, regarding the analysis of ACN and vitamin C content, color and moisture content. ....	21
Table 6 - Studies concerning the storage stability of dehydrated fruit powders, regarding the analysis of ACN and vitamin C content, color, moisture content and water activity. ....	22
Table 7 - Different meanings of $\Delta E$ (Lübbe, 2013).....	31
Table 8 - Operating conditions of the of the shear test with the 5 blade Kramer shear cell.	31
Table 9 - Influence of structure in the total color difference ( $\Delta E$ ) after 12 weeks of storage at 37 °C. Reference to week 0. Vacuum-packed samples (Consult Table 7 for $\Delta E$ meaning). ....	39
Table 10 - Influence of MD concentration in the total color difference ( $\Delta E$ ) after 12 weeks of storage at 37 °C. Reference to week 0. Vacuum-packed samples (Consult Table 7 for $\Delta E$ meaning).....	44
Table 11 - Influence of T °C in the total color difference ( $\Delta E$ ) after 12 weeks of storage. 15 % MD foam, vacuum-packed samples (Consult Table 7 for $\Delta E$ meaning). Reference to week 0.....	47
Table 12 - Results of the quality parameters (RMC, $a_w$ , ACN and AA content) of raspberry and foam after MWFD (week 0) and after 12 weeks of storage under different values of relative humidity ( $a_w = 0.11; 0.22; 0.33$ ). ....	49
Table 13 - Retention of total anthocyanins and ascorbic acid of 15% MD foam, after 12 weeks of storage under different conditions.....	50





## Glossary

+a*	Redness
+b*	Yellowness
AA	Ascorbic acid
ACN	Anthocyanins
AD	Air-drying
$a_w$	Water activity
DHA	Dehydroascorbic acid
DSC	Differential scanning calorimetry
ERH	Equilibrium relative humidity
FD	Freeze-drying
HPLC	High-performance liquid chromatography
L*	Brightness
LPDE	Low density polyethylene
MD	Maltodextrin
MPA	Metaphosphoric acid
MWFD	Microwave freeze-drying
P	Pectin
$P$	Vapor pressure of water
$P_0$	Saturated vapor pressure of pure water
PET	Polyethylene terephthalate
PPI	Potato protease inhibitors
PPO	Polyphenol oxidase
RH	Relative humidity
RMC	Residual moisture content
$\tan \delta$	Loss tangent
TCEP	Tris(2-carboxyethyl)phosphine
$T_g$	Temperature of glass transition
VD	Vacuum-drying
w.b	Wet basis



# 1 Background motivation

## 1.1 Background motivation

Nowadays, consumers are more concerned about their health and tend to adopt a healthy life style. A healthy diet based on products which contain bioactive or functional ingredients has an increased nutritional value (Fu et al., 2001).

Among healthy natural products, fruit plays an important role to improve our health and well-being as it provides an optimal combination of phytochemicals and other bioactive compounds such as fiber and vitamins (De Ancos et al., 2000). A diet which includes fruit and vegetables has been correlated with a decrease of chronic diseases, such as coronary heart disease and cancer (Talcott, 2007). Previous research showed that the recommended intake of products rich in fiber such as fruits is around 30–45 g/day (Colin-Henrion et al., 2009; Mosquera et al., 2012).

Berry fruits are widely recognized by their sweet taste and healthy properties. Berries provide an important source of carbohydrates, vitamins, minerals, dietary fibers, polyphenolics and have low levels of calories (Talcott, 2007). More specifically, they contain bioactive compounds such as anthocyanins, catechins and phenolic acids which have antioxidant, antimicrobial, anti-inflammatory and anticancer properties (Četojević-Simin et al., 2015).

Raspberry (*Rubus idaeus*) is one of the most commonly used berries in the food industry and belongs to the plant family of Rosaceae (Ochoa et al., 1999). The seasonal production and the short shelf-life of raspberries limit their fresh consumption. The shelf life can be extended by using processing techniques such as freezing and/or dehydration methods or producing puree, juice or jam (Mosquera et al., 2012). However, some fruit properties such as color, texture, flavor or nutritional value can be altered depending on the processing method (Bruijn et al., 2015). Thus, there is a requirement to create innovative processing alternatives for obtaining storage stability while minimizing changes in fruit quality properties (Sette et al., 2017).

New food technologies, such as foam-mat drying, are being studied to develop innovative products. This technology consists of drying a fruit puree mixed with foaming agents. The resulting structure of dried foams offers the desired porous texture for a typical snack product. Additionally, it can also be converted into powder and applied in cereals, yogurts, juices or other snacks. During consumption, this structure offers a pleasant aroma release between its open pores, which creates a value-added product (Kandasamy et al., 2014). Moreover, foam-mat drying is a simple, economical and efficient technique since the

drying can be accelerated by the higher surface exposure, which leads to a lower mass transfer resistance (Hardy and Jideani, 2015).

Among dehydration techniques, freeze-drying (FD), also known as lyophilization, has been commonly studied. It is considered as the reference process for producing high-quality dehydrated products due to low temperature and high vacuum level (Hammami and Floris, 1997). Although FD is an efficient method to maintain the fruit properties, it is associated with high production costs due to its long process time (Duan et al., 2010; Ratti, 2001; Zhang et al., 2006).

On the other hand, microwave freeze-drying (MWFD) is an innovative method that applies volumetric heating by microwaves. It has been developed to overcome the time and energy limitations of conventional conduction heating methods (Duan et al., 2010; Figiel, 2009).

However, in the food industry, it is important to produce not only healthy new products for the consumer but also long-lasting products.

Therefore, a raspberry snack product that combines microwave freeze-drying and foaming as well as the study of its changes during storage, could be a significant innovation for the snack food processing industry.

## **1.2 Thesis objectives**

The aim of the project was to evaluate the stability of dried raspberry foams for the quality parameters: moisture content, water activity, color, texture, vitamin C and anthocyanins content, during storage under different conditions. Foams containing three concentrations (5, 15, and 30%) of maltodextrin (foam stabilizer) were studied at constant concentrations of potato protease inhibitors (5%) and pectin (2.5%). Raspberry splits, puree and non-foamed solutions were also produced and stored to verify whether the structure has an influence on the shelf-life stability or not. In addition, microwave freeze-drying and conventional freeze-drying (as a reference method) were performed to all tested samples. Samples were stored at 37, 20 and 4 °C (under vacuum) to analyse the influence of storage temperature. In order to understand the influence of relative humidity, samples were stored in chambers with different controlled relative humidity environments ( $a_w = 0.11; 0.22; 0.33$ ).

## 2 Introduction

### 2.1 Chemical composition of raspberry

The exploitation of raspberry in diverse areas of food and health products has been increasing due to their nutritional benefits and pleasant colors, flavors, and tastes (Talcott, 2007).

Chemical composition of raspberries depends on the growing area, variety, plant age, seasonal variations and time of harvest (de Ancos et al., 1999; Sadowska et al., 2017). The main chemical components of this fruit are carbohydrates (sugars and dietary fibers), proteins, lipids (97.8% unsaturated fatty acids), minerals (ash) and vitamins (Table A1 in Appendix) (Rao and Snyder, 2010; Talcott, 2007).

Raspberry flavor is associated to consumer satisfaction and is expressed by the concentration of soluble sugars (sucrose, glucose, and fructose) counterbalanced by the presence of organic acids and aroma volatiles. Organic acids present in raspberries, such as malic and citric acid, can also contribute for fruit preservation (fresh or processed), by maintaining a low pH and stabilizing anthocyanins (Section 2.1.1.) and ascorbic acid (Section 2.1.2.). Other factor that contributes for the consumer acceptance is the appealing color derived from anthocyanins (de Ancos et al., 1999; Talcott, 2007).

Red raspberry (*Rubus idaeus*) is also composed by a wide variety of polyphenolic phytochemicals including phenolic acids, flavonoids, lignans and ellagitannins (Mazur et al., 2014; Rao and Snyder, 2010). The bioactive compounds present in raspberry demonstrated to have health benefits such as anti-inflammatory, antineurodegenerative, anti-proliferative (in human cancer cells), antioxidant, antiviral and antibacterial activities (Bobinaitė et al., 2012; Četojević-Simin et al., 2015; Pantelidis et al., 2007; Zhang et al., 2010).

#### 2.1.1 Anthocyanins

Anthocyanins (ACN) are a common phytochemical present in fruit and vegetables and are responsible for the red color of raspberries (Ochoa et al., 1999). These water-soluble pigments are synthesized by plants and are classified as flavonoids due to their chemical structure. They are formed by an aglycone (anthocyanidin), sugar units (attached at the 3-hydroxyl position of the anthocyanidin) and in many cases acyl groups (Talcott, 2007; Wallace and Giusti, 2013).

The variations in chemical structure of anthocyanins (Figure B1 in Appendix) is mainly caused due to differences in the number of the hydroxyl groups in the molecule, degree of methylation of these OH groups and number of aromatic acids attached to it (Mazza and Miniati, 1993; McGhie and Walton, 2007; Patras et al., 2010).

Among all ACN compounds in red raspberry (Table 1), previous research showed that cyanidin-3-sophoroside is correlated to the red pigment present in this fruit and cyanidin-3-glucoside is the least stable pigment (Figure B1 in Appendix) (de Ancos et al., 1999; Rommel et al., 1990).

Table 1 - Anthocyanin compounds of fresh raspberry (*Rubus idaeus*) (Kassim et al., 2009; Torre and Barritt, 1977).

Compound	Amount (mg/100 g)	
	Latham cultivar	Willamette cultivar
Cyanidin-3-sophoroside	25.4	35.6
Cyanidin-3-glucosylrutinoside	7.2	n.s.
Cyanidin-3-glucoside	3.9	16.8
Cyanidin-3-rutinoside	2.3	n.s.
Pelargonidin-3-sophoroside	0.06	4.3
Pelargonidin-3-glucosylrutinoside	0.1	n.s.
Pelargonidin-3-glucoside	0.12	n.s.
Pelargonidin-3-rutinoside	0.005	n.s.

n.s.: not specified

Degradation of anthocyanins can be related to high temperatures of processing or storage, conditions causing oxidation, cleavage of covalent bonds or enhanced oxidation reactions (Palamidis and Markakis, 1975; Patras et al., 2010). Figure 1 shows an example of cyanidin-3-glucoside degradation and formation of intermediate compounds.

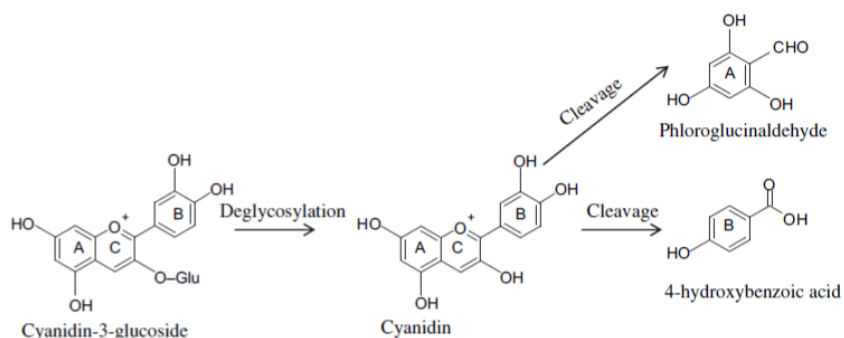


Figure 1 - Possible mechanism of thermal degradation of cyanidin-3-glucoside. Adapted from (Patras et al., 2010).

The mechanism of anthocyanin degradation is still unclear, though some authors suggest different theories. As showed in Figure 1, anthocyanin compounds consist in two aromatic rings (A and B) that are bound together by three carbon atoms that form an oxygenated heterocycle (ring C) (Welch et al., 2008). In a strawberry pigment degradation research, Markaris et al. (1957) proposed the opening of the heterocycle and formation of a chalcone as the first step of the anthocyanins degradation. Later, Adams (1973) suggested that when heat is applied to anthocyanins, these compounds first suffer hydrolysis of the glycosidic bond (position 3), followed by conversion of the aglycon to a chalcone and further transformation into a coumarin glucoside derivative with a loss of the B-ring. Further degradation can lead to brown products, especially in the presence of molecular oxygen (Markakis, 1982). Anthocyanin degradation at high temperatures is also related with the

Maillard reaction (non-enzymatic browning), which occurs in the presence of reducing sugars and proteins during food processing or long-time storage. This reaction is intensified by the presence of oxygen and its products (furfural and hydroxymethylfurfural) can condense with the anthocyanins to form compounds with a brown coloration (Ferrari et al., 2013; Tonon et al., 2010).

On the other hand, the presence of oxygen can accelerate the degradation of anthocyanins through action of oxidising enzymes such as polyphenol oxidase (PPO) (Jackman et al., 1987a). The reaction between PPO and catechins can lead to the formation of quinones which react with the anthocyanins to form brown products (Kader et al., 1999).

### 2.1.2 Ascorbic acid

Ascorbic acid (AA) or vitamin C is present in many berries and has relatively high concentrations in raspberry (Table 2) (Ochoa et al., 1999). Moreover, AA contributes for the health benefits of raspberry, being responsible for around 20% of the total antioxidant capacity, enhancing the immunity system, synthesizing collagen and hormones and having antiscorbutic activity (Bobinaitė et al., 2012; Talcott, 2007).

Table 2 - Ascorbic acid present in different fresh red raspberry (*Rubus idaeus*) cultivars.

Red raspberry cultivar	Amount (mg/100 g)	Reference
Willamette	40.9	(Milivojević et al., 2013)
Meeker	44.3	(Milivojević et al., 2013)
Polana	16.8	(Bobinaitė et al., 2012)
Polka	17.2	(Bobinaitė et al., 2012)
Glen Moy	24.4	(Bobinaitė et al., 2012)

The content of the ascorbic acid is used as an indicator of the overall nutritional quality of fruits and vegetables due to its labile nature compared to other nutrients. If ascorbic acid is retained, other nutrients normally will be preserved as well (Lin et al., 1998; Wang et al., 2010). Moreover, Ochoa et al. (1999) showed that the rate of ascorbic acid oxidation had an influence on anthocyanins loss in strawberry products.

The stability of vitamin C can be influenced by temperature, light exposure, ascorbic acid oxidase, atmosphere and food processing (Talcott, 2007). Total vitamin C comprises ascorbic acid and dehydroascorbic acid (DHA). DHA is formed when AA is oxidized by oxygen in a reversible reaction (Figure 2). Both have similar vitamin C activity, but only ascorbic acid has reducing properties, being important for inhibiting browning reactions (Mitcham, 2007).

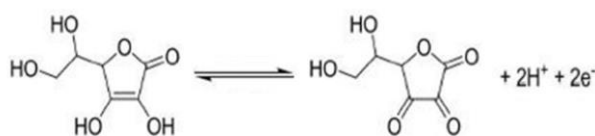


Figure 2 - Oxidation reaction of ascorbic acid to dehydroascorbic acid (Harvey, 2016).

## 2.2 Raspberry foams

In the food industry, raspberries can be used in different ways such as: beverages (e.g. smoothies, milk shakes, juices); jams; jellies; dried fruits; dairy products (e. g. ice cream, yogurt, puddings) and bakery goods (e. g. cakes, muffins) (Tumbas-Šaponjac et al., 2015; Zhao, 2007).

For the industry of dehydrated products, a technique called foam mat drying was developed to establish higher drying rates and product quality (Lobo et al., 2017). The foaming process consists in adding gas (usually air) and foaming agents to a liquid concentrate (e.g. fruit puree). This process creates a porous structure (foam) which is spread out in a layer and subsequently subjected to a drying process (Brygidyr et al., 1977; Kandasamy et al., 2014; Rajkumar et al., 2007) . The final product can be used as a crispy snack or powder for application in yogurts, cereals, juices, among other applications (Thuwapanichayanan et al., 2012). Research in the topic suggests that the porous structure of foams and their large surface area, increases the mass transfer rates when compared to the original solid food. Consequently, this leads to shorter times of dehydration (Kandasamy et al., 2014; Lobo et al., 2017).

Foams are systems with two phases, the dispersed and continuous phase, which are separated by a thin layer called lamellar phase (thin wall of bubble) (Eisner et al., 2007; Hardy and Jideani, 2015). Foam characteristics such as density, stability and form depend on the chemical nature of the fruit, pulp characteristics, soluble solids and type and concentration of foaming agents and stabilizers (Hart et al., 1963; Karim and Wai, 1999). The air-liquid interface of bubbles present in foams is unstable due to the surface tension that goes against the forces needed for its maintenance, leading to foam collapse (Hardy and Jideani, 2015). Hence, the choice of an appropriate foaming agent is an important factor for improving foam stability (Thuwapanichayanan et al., 2012).

Proteins are foaming agents commonly used due to their amphiphilic character (Rodríguez Patino et al., 2008). They adsorb at the air-liquid-interface and interact with the lamella by means of hydrophobic or electrostatic forces, hydrogen bonds or covalent linkages (Hardy and Jideani, 2015). This results in the formation of a viscoelastic film network around the air bubbles which reduces the surface tension instability and retain the entrapped air (Franco et al., 2015; Karim and Wai, 1999).

In the food industry, proteins with animal origin (e.g. whey protein, casein, egg albumin) are often more used as a foaming agent (Franco et al., 2015; Zayas, 1997). Since the market of vegetarian and vegan products is increasing, there is an interest in exploring the utilization of proteins from plant origin (Brett, 2010). These proteins are generally considered less efficient, as foaming agents, than proteins with animal origin due to structure damaging



during the extraction process (van Koningsveld et al., 2002). However, new methods to extract potato protein that can preserve its functional properties have been developed (Løkra and Strætkevorn, 2009; Schmidt et al., 2018; van Koningsveld et al., 2002). Despite having inferior foaming properties than whey protein (Jackman and Yada, 2006), potato protein obtained by gentle methods (e.g. ultrafiltration or anion-exchange chromatography), proved to be at least comparable to casein and egg albumin (Ralet and Guéguen, 2001; van Koningsveld et al., 2002).

In addition, stabilizing agents contribute to avoid foam collapse during dehydration (Ratti and Kudra, 2006). Polysaccharides with high molecular weight, such as maltodextrin (MD), are frequently used as stabilizing agents. As they are hydrophilic, do not tend to adsorb at the air–water interface. Therefore, they can strongly contribute for the stability of foams by acting as thickening or gelling agents and forming a polysaccharide-protein complex by non-covalent interactions (Dickinson and Galazka, 1991; Herceg et al., 2007; Ratti and Kudra, 2006).

Sugars present in fruit purees, such as fructose, glucose or sucrose, have low molecular weight and are very hygroscopic in their amorphous state (Fazaeli et al., 2012; Sablani et al., 2008). Consequently, they cause stickiness after foam drying by reducing the value of glass transition temperature ( $T_g$ ) (Jaya and Das, 2004). Since the  $T_g$  value can be increased with the presence of high molecular weight compounds like maltodextrin, with low dextrose equivalent (DE), this substances are used as drying aids, decreasing stickiness and improving product stability (Farahnaky et al., 2016; Jaya and Das, 2004; Seerangurayar et al., 2017; Silva et al., 2006). Hence, maltodextrin is tasteless, not having influence in the flavor of the product and can protect sensitive substances and maintain the initial color of the product before drying (Buera et al., 2005; Green and Angell, 1989; Lee and Timasheff, 1981). Pectin can also be added to foams for stabilization as a gelling agent (Thakur et al., 1997).

There are a few factors that have influence on the quality of dried foams such as drying conditions, composition, air, temperature, foaming velocity, relative humidity and thickness (Franco et al., 2015).

Foam-mat drying demonstrated a good product quality in fruits like starfruit (Karim and Wai, 1999), mango (Jaya and Das, 2004), apple juice (Raharitsifa et al., 2006), banana (Thuwapanichayanan et al., 2008), mandarin (Kadam Rai et al., 2011) or papaya (Kandasamy et al., 2014). Furthermore, Darniadi et al. (2018) observed that foam mat freeze-drying of blueberry juice was suitable for retaining most of the characteristics of the original juice.

This method is simple, economical, energetic efficient and promotes high speed drying (Hardy and Jideani, 2015). Hence, due to the low drying times, the nutrients can be preserved, and the browning rates are lower (Lobo et al., 2017). One of its disadvantages is the poor heat

transfer through the air bubbles. However, the utilization of microwave drying overcome this problem in drying of blackcurrant and tomato pulp (Qadri and Srivastava, 2014; Qadri and Srivastava, 2017; Zheng et al., 2011).

## 2.3 Food drying techniques

Throughout the history, food has been preserved by drying. Water is a dominant component in food, especially in fruit related products (85.8% of raspberry composition is water). Therefore, products containing water are more susceptible to microbial spoilage and deteriorative chemical reactions (Četojević-Simin et al., 2015; Ratti, 2001).

In order to remove water and increase the shelf-life stability of perishable products like fruits several drying methods are applied such as for e.g.: air drying, freeze-drying, spray drying, vacuum drying and microwave freeze-drying (Figuerola, 2007).

Air-drying (AD) is a common drying process due to its low operating cost and simple operation procedure. On the other hand, as it involves hot-air it is related with long drying times and high temperatures which contributes for the degradation of nutritional compounds, aroma, color and product structure (Fellows, 2009c; Gaukel et al., 2017; Ratti, 2001).

Among these methods, FD is the reference technique for producing high-quality dehydrated products since it can preserve most of the initial product properties (Ratti, 2001; Tumbas-Šaponjac et al., 2015). However, freeze-drying has high energy consumption and capital costs due the freezing step and long drying time needed which limits its utilization (Wang et al., 2010). For e.g. Heldman and Hartel (1997) concluded that freeze drying costed as nearly five times the spray drying.

For application on fruits, spray drying consists in the atomization of fruit juice into small drops which are exposed to a hot air current forming fruit dried powder. Some advantages of this technique are the fast and simple process as well as its application at large scale. However, some of its limitations are the fact that it can only be used to produce powder, the high temperatures used, the volatile losses and high energy costs (Fellows, 2009c; Figuerola, 2007).

Vacuum-drying (VD) is a drying method that uses reduced pressures and heating by conduction. This provides the evaporation of water at low temperatures. Consequently, vacuum-drying preserves most of the chemical, sensorial, and nutritional properties. Nevertheless, VD drying time is one of the longest of all drying processes which leads to high energy consumption and costs (Gaukel et al., 2017).

A viable dehydration method for industrial use should preserve the quality of the initial product, exhibit high efficiency and low costs. Therefore, applying a microwave field to the freeze-drying process can speed up the process (Huang et al., 2011). This method is called

microwave freeze-drying (MWFD). Moreover, the final product can have the same properties as freeze-drying and be obtained in a shorter time and consequently with lower costs (Willert-Porada, 2007).

### 2.3.1 Freeze-drying

Freeze-drying (FD) is a method of dehydration of frozen products based on sublimation under vacuum. The product heating is made by conduction from a direct contact source as for e.g. a heating plate. The first step is to freeze (crystallize) the water originally present in the product. Freezing must be fast to create small ice crystals and consequently not damage the cells while sublimation takes place (Fellows, 2009c). As this step is done at low temperatures, enzymes are inactivated and consequently bioactive compounds are protected from enzymatic degradation (Tumbas-Šaponjac et al., 2015).

Therefore, during the drying, the frozen water is directly converted from the solid state to the vapor phase (Haseley and Oetjen, 2017). For that, operating conditions need to be set lower than the triple point of water (0.095 °C, 6.11 mbar) as showed in Figure 3. In the primary phase of drying (sublimation), the material is heated at low temperatures. The water vapor is conducted by diffusion and convective flow through the porous structure of the product and posteriorly is removed by a condenser. When all frozen water had been removed, the secondary drying phase (desorption) takes place. Therefore, at above zero temperatures, most of the unfrozen water adsorbed on the solid matrix is removed (Berk, 2013; Hua et al., 2010).

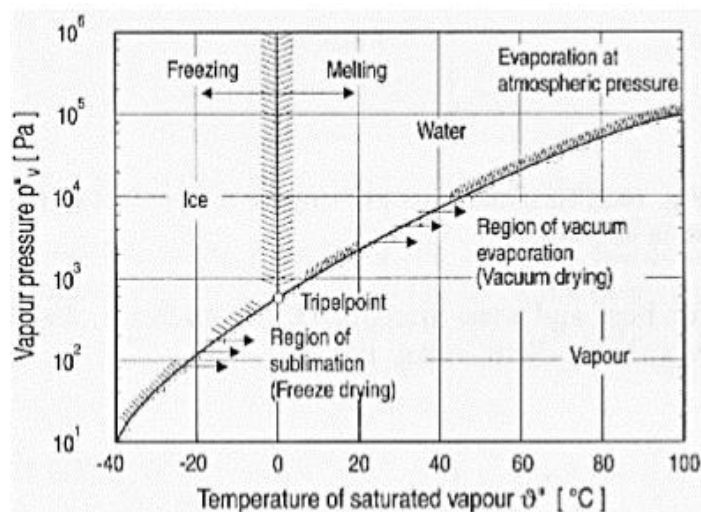


Figure 3 - Phase diagram for water (Kessler, 2002).

FD final products have a porous structure, good rehydration properties and maintain color properties, nutritional compounds and biological activity. As the water is directly converted from solid to gaseous phase, the water-soluble substances (responsible for aroma)

are maintained as well due to the fact that they cannot diffuse in liquid water (Berk, 2013; Ratti, 2001; Wang et al., 2010).

In freeze-drying, the product is heated by conduction from the surface to the center. As the drying occurs in layers, the heat and mass transfers are non-uniform (Gunasekaran, 1999). Besides, as water is not present in the liquid state, cannot be transported to the surface by capillary forces but only by diffusion (Gaukel et al., 2017). Consequently, the low transfer rate results in an increased drying time and a high energy consuming process (Duan et al., 2010; Zhang et al., 2006). Hence, this technique is only used to dry high value products which have delicate aromas or textures as for e.g. coffee, herbs, spices, berry fruits, etc. In addition, it can also be utilized in the preparation of active enzymes (e.g. for producing cheese) and microbial cultures for long-term storage (Fellows, 2009c).

### **2.3.2 Microwave freeze-drying**

Nowadays, microwave energy is a common heat source due to its fast and internal heating by dipole rotation and ionic conductance in the products (Duan et al., 2010; Wang and Xi, 2005). Like FD, this drying method is also composed by three steps (freezing, sublimation under vacuum and desorption of unfrozen bound water) (Duan et al., 2010; Jiang et al., 2010). The difference between them is that the microwave field heats the product volumetrically and proporcionates a faster and consequently more economic process (Duan et al., 2010; Wang et al., 2004; Willert-Porada, 2007).

In microwave heating process there is an interaction between dielectric materials and the electromagnetic waves. Therefore, microwaves penetration into the food leads to dipolar interactions (Meda et al., 2017; Salazar-González et al., 2012). The molecule of water is constituted by a negatively charged oxygen atom and two positively charged hydrogen atoms, which results in an electric dipole. Once microwave energy is applied, the dipoles present in the water and other polar components start to rotate and align to the electric field (polarize) (Fellows, 2009b). This phenomenon is called orientation polarization (Figure 4) (Püschner and Hoon, 2007; Schiffmann, 1995). The polarity rapidly changes from positive to negative and the opposite (several million times per second) (Fellows, 2009b). Therefore, the dipoles rotation to align with the changing polarity causes molecular kinetic energy (Meda et al., 2017; Rynnänen, 1995) The heat created by the molecular friction increases the temperature of water molecules and is transferred to the surrounding molecules (Fellows, 2009b; Jiang et al., 2010; Püschner and Hoon, 2007). Moreover, also other factors influence heating such as the electrically charged ions present in dissolved salts of the water (which move and produce an electric current after an electric field is applied) (Figure 4) and the specific heat of the product (Fellows, 2009b; Meda et al., 2017).

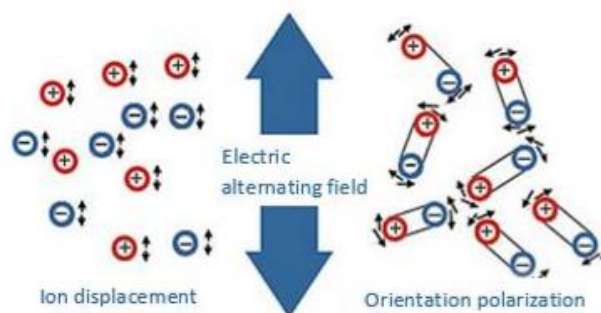


Figure 4 - Representation of dielectric dipoles rotation and ion displacement in an alternating field (Püschner and Hoon, 2007).

The quantity of energy absorbed from electromagnetic waves by food is related to the dielectric loss factor ( $\epsilon''$ ), that describes the ability of the material to dissipate electrical energy. This factor is a dimensionless number and depends on the temperature, moisture content, presence of salts and structure of the food (Fellows, 2009b). Additionally, other related food electric properties are the dielectric constant ( $\epsilon'$ ), which represents the rate at which energy penetrates in the material and the loss tangent ( $\tan \delta$ ), that reveals the facility which a food can be penetrated by electromagnetic waves and convert this electrical energy to heat (Fellows, 2009b). Equation 1 shows the relation between this properties.

$$\epsilon'' = \epsilon' \tan \delta \quad (1)$$

Table 3 shows that the low dielectric constant and loss factor of ice results in a high penetration depth of the microwaves and consequently sublimation within the whole sample occurs which leads to a high energy conversion in the beginning of drying. Moreover, due to the low dielectric losses when the food is frozen, energy is mainly absorbed by the organic molecules of the product (Abbasi and Azari, 2009; Ozcelik and Püschner, 2017; Wang et al., 2011).

Table 3 - Dielectric properties of liquid water (25 °C) and ice (-2 °C) at 2.45 GHz frequency. Adapted from (Abbasi and Azari, 2009).

	<b>Water</b>	<b>Ice</b>
Dielectric constant	78.1	3
Dielectric loss factor	10.4	0.003
Penetration depth (cm)	1.65	1121

MWFD represents a technology capable of retaining volatile and nutrient compounds as well as other quality properties, such as color and texture (Ozcelik and Püschner, 2017).

There are only a few reported MWFD studies. Yet this technique has been proving its efficiency for drying food materials such as for e.g. sea cucumber (Duan et al., 2010), potato slices (Wang et al., 2010), cabbage (Duan et al., 2007) and beef (Wang and Shi, 1999).

Although MWFD overcomes the problem of long drying times, there are drawbacks associated with this technology. One of them is the uneven temperature distribution due to the nonuniform distribution of microwaves. Other problem is the plasma formation at the low

pressures, which can lead to localized melting of the ice and quality deterioration of the product (Wray and Ramaswamy, 2015). As mentioned before, Table 3 shows the difference in loss factors of water and ice. Due to this difference, water produced by ice melting heats faster and leads to widespread melting contributing for structure collapse of the product (Duan et al., 2010; Fellows, 2009b; Gaukel et al., 2017).

## 2.4 Importance of storage on the quality of dehydrated products

Processing methods such as drying are important to extend the shelf-life of perishable fruits. Shelf-life has been defined as the time during which a product retain critical quality properties (Bruijn et al., 2015). Depending on how processing and storage are conducted, fruit products can face changes in desirable quality factors for the consumer such as nutritional compounds, color, flavor, texture and moisture content (Bruijn et al., 2015). Besides the physical changes, other mechanisms related with food spoilage include the effects of chemical or enzymic reactions and the activities of microorganisms (Fellows, 2009a). In this context, it is essential to determine the effect of storage on the quality properties of a food industry product.

Deterioration of foods by microorganisms can take place rapidly, whereas enzymic and chemical reactions take place more slowly during storage (Fellows, 2009a). In either case both moisture content and water activity are two of the most important factors that affect the rate of food deterioration reactions (Bruijn et al., 2015). The moisture content is not enough to predict the stability of foods, since some foods are unstable at a low moisture content, whereas other foods are stable at relatively high moisture contents (Fellows, 2009a). It is the water activity ( $a_w$ ), that determines the available free water for microbial growth, enzymatic activity, and chemical reactions (Figuerola, 2007).

Water in food exerts a vapor pressure, and this depends on the amount of water present, the temperature and the concentration of dissolved solutes (for e.g. sugars) in the water. In this context, water activity is calculated by the ratio between the vapor pressure of water in the food ( $P$ ) and the saturated vapor pressure of pure water at the same temperature ( $P_0$ ) as presented in the Equation 2 (Fellows, 2009a).

$$a_w = \frac{P}{P_0} \quad (2)$$

When an equilibrium between the product and the atmosphere is reached, the  $a_w$ -value can also be expressed as the equilibrium relative humidity (ERH) divided by 100, expressed as a fraction (Figuerola, 2007; Roudaut and Debeaufort, 2010). This relation is important to control the storage kinetics for low-moisture products.

When water activity is controlled, it is possible to avoid potential sources of spoilage. In this context,  $a_w$  values  $< 0.6$  inhibit all microbial activities ( $< 0.9$  most bacteria,  $< 0.8$  most yeast and  $< 0.7$  all fungi) (Ekpong et al., 2016; Figuerola, 2007). Besides, non-enzymatic browning and enzymatic activities are related with  $a_w$  values of 0.70. Therefore, in order to have a safe berry product during storage, it is critical to reduce water activity to a level of less than 0.60 (Bruijn et al., 2015).

During drying, the water removal is related to the creation of an amorphous matrix, in which soluble and insoluble substances, compatible with water, are molecularly disordered (Mosquera et al., 2012; Wang et al., 2012). Amorphous materials can be present in the glassy or rubbery state. The change from one state to the other happens at a specific temperature for each material. This temperature is called the glass transition temperature ( $T_g$ ) (Mosquera et al., 2012). The physical change in the amorphous material, is induced by the addition of heat and the uptake of low molecular weight substances. With the increase in temperature through and above the  $T_g$ , a material in the glassy state becomes soft or rubbery, showing lower viscosity and increased mobility (Bell and Hageman, 1994).

The knowledge of these states is important to understand the product changes during storage since the glassy state (present at temperatures below the  $T_g$ ) is considered more rigid and stable. Therefore, in order to minimize the reaction rates of undesired physical and chemical changes it is recommended to store the food in the glassy state, even though, molecular motion and degradation reactions may still occur but at much slower rates than in the rubbery state (Bell, 1995; Gradinaru et al., 2003; Syamaladevi et al., 2011). The glass transition occurs at a critical value of water content and water activity ( $a_w$ ) of the sample and depends on the storage temperature. Hence,  $T_g$ ,  $a_w$  and water content are used as a reference parameter to characterize the quality, stability and safety of food systems (Roos, 1995; Syamaladevi et al., 2011).

Fruit powder, rich in low molecular weight sugars, is more susceptible to changes in mechanical properties (e.g. development of stickiness), in the rubbery state (Telis and Martínez-Navarrete, 2009). Moreover, the rate of non-enzymatic or enzymatic browning and oxidation of compounds increases at temperatures higher than  $T_g$  (Mosquera et al., 2012; Roos, 1995). Therefore, the glass transition temperature can be increased with the addition of high molecular weight substances, such as maltodextrin, reducing the stickiness and producing free flowing powders with extended shelf-life (Jaya and Das, 2004; Mosquera et al., 2012; Silva et al., 2006; Telis and Martínez-Navarrete, 2009).

In this context, storage conditions such as temperature, humidity, oxygen and light exposer, as well as, the characteristics of the food such as moisture content, color, water

activity, nutritional compounds and pH, represent the factors which control the deterioration of food (Betts and Walker, 2004; Fellows, 2009a).

Temperature is an important factor which has direct influence on microbial growth rates, oxidation of lipids or pigments, browning reactions and vitamin losses (Fellows, 2009a; Taoukis and Giannakourou, 2004). Cortés et al. (2009) demonstrated that a temperature of storage higher than 20 °C had a faster degradation of vitamin E in freeze-dried apple slices. In addition, bael powder stored at low temperature (7 °C) had better retention of color, flavor, texture and ascorbic acid when compared to the samples stored in a range of 18-35 °C (Sagar and Kumar, 2014). On the other hand, Bruijn et al. (2015) showed that even after long-term storage at ambient temperature, but without exposure to atmospheric oxygen and light, microwave-treated strawberries had a 94% retention of their antioxidant properties.

Consumers expect no changes in the product through the storage time. Therefore, the color analysis of food is an important sensorial quality factor and its changes can limit the shelf life of many processed foods (Huxsoll et al., 1989). Fruit products are highly susceptible to browning reactions of both non-enzymatic and enzymatic nature during storage. This reaction not only affect the color but can also contribute for the loss of vital nutrients such as ascorbic acid and anthocyanins. One of the reasons for the high rate of browning in fruit products is related with the abundance of sugars, especially, reducing sugars (Raju and Bawa, 2007).

During storage, enzymatic activity of hydrolase and oxidase enzymes can affect the flavour, colour and texture of berries (Fellows, 2009a; Talcott, 2007). Polyphenol oxidase and peroxidase are the enzymes which are most responsible for destruction of phytochemicals and quality characteristics in berries (Miesle et al., 1991; Talcott, 2007; Wesche-Ebeling and Montgomery, 1990). Factors such as storage temperature and fruit ripeness have influence in their activity. However, as previously mentioned, water activity is important in the preservation of dried products. So, as diffusion of chemical compounds or substrates and enzymes do not take place under low conditions of moisture and water activity, dehydrated products have lower reaction rates, being more stable under storage (Figuerola, 2007).

Packaging also plays an important role in the storage stability of dried products since they are susceptible to changes of the environment, such as absorption of atmospheric moisture. To satisfy the needs of the consumers, dehydrated products should have an extended shelf-life but still maintaining the characteristics of the products after processing. Therefore, packaging materials should provide a barrier between the product and the environment, protecting it from microorganisms, physical, chemical and sensory changes. In addition, containers should be hermetically sealed to avoid oxygen, water vapor, and volatiles transfer. In many cases, oxygen is also removed from packages due to its contribution in



deteriorative reactions (Figuerola, 2007). The stability of an oxygen sensitive product, when packed, depends on package oxygen permeability, oxygen concentration in the package headspace, temperature and relative humidity (Giacin and Hernandez, 1997).

Materials which have also ultraviolet light protection can control deterioration caused by light (Figuerola, 2007). Additionally, aluminium bags which are a typical three-layer pouch structure that has an outer layer of polyethylene terephthalate (PET), a middle layer of aluminium foil and an inner layer of low density polyethylene (LDPE) can also be employed. PET is the most used polyester and has good mechanical properties and low permeability to gases, being utilized for strength and toughness of the three-layer pouch. Aluminium, offers protection against moisture, light and gas and is commonly used when the product is subjected to vacuum packaging. Finally, LDPE is relatively inert chemically, has good heat ability to seal, strength and compatibility with all foods. Moreover, it is easily coated onto aluminium (Johansson, 1993; Robertson, 1998).

Subsequently, the study of quality parameters such as residual moisture content, water activity, color,  $T_g$ , and nutritional content, during the storage of new products in the food industry, contributes to the development and improvement of the product. Additionally, different storage conditions must be studied.



### 3 State of art

Nowadays, the consumer seeks for food products which have long shelf-life and, at the same time, maintain the majority of their initial qualities. Furthermore, after storage, these products must also be appealing to the consumer regarding biological safety, color, texture and nutritive value. Therefore, storage stability studies represent great interest for the food industry. Although there are a wide number of studies regarding the storage stability of fresh and dehydrated food, no literature was found regarding the study of freeze-dried or microwave freeze-dried raspberry foams or powder.

The following Tables 4, 5 and 6 depicts the information about relevant publications, studying the storage stability regarding the color, texture, moisture content, water activity, anthocyanins and vitamin C content of fruits/vegetables. Table 4 comprises studies found about storage, under different conditions, of fresh berries, with particular emphasis on raspberries. Table 5 comprises the studies found about the storage of microwave vacuum-dried or freeze-dried fruits. Finally, Table 6 comprises the information found in publications about the storage stability of fruit/vegetable powders. In the majority of the presented studies, these powders were produced by mixing the puree or juice of fruit with food additives and afterwards drying it with different drying methods, depending on the study. Different additives were analyzed to verify their contribution for the storage stability of food powders.

In Table 4, the perishable character of fresh berries during storage can be observed, since, depending on the raspberry cultivar, even frozen raspberries lost 33-55% and 27-48% of anthocyanins and vitamin C, respectively, after a storage period of 12 months (de Ancos et al., 2000a; de Ancos et al., 2000b). Also, some studies demonstrated that when increasing storage temperature, the storage stability of color, vitamin C and anthocyanins decreased. As an exception, Kalt et al. (1999) observed an increase of anthocyanins after 8 days of storage at 20 °C. In the literature, it was found that titratable acidity of raspberry may decrease during storage and, consequently, organic acids, through interconversion with carbohydrates, can provide carbon skeletons for the synthesis of ACN (Kalt et al., 1999; Mazza and Miniati, 1993).

As it can be observed in Table 5, the dehydration process had a positive impact in the storage stability of berries, since Bruijn et al. (2015) demonstrated that vacuum microwave-dried strawberries stored at 20 °C for 6 months, without the presence of oxygen presented less anthocyanins degradation than fresh strawberries which were maintained at lower temperature and shorter storage time (Hartmann et al., 2008). Through the analyses of data present in Table 5, it can be concluded that storage stability of dehydrated fruits is dependent on the relative humidity values, as increased RH in the storage environment caused more

changes in color, moisture content and vitamin C (Acevedo et al., 2006; Bruijn et al., 2015; Uddin et al., 2002). Moreover, higher temperatures resulted in a negative impact on color and texture of freeze-dried apples (Acevedo et al., 2006; Cortés et al., 2009). In contrast of what was expected, Cortés et al. (2009) noticed that freeze-dried apple packed under vacuum showed stronger changes in the color parameters  $L^*$  (brightness) and  $+a^*$  (redness) than in samples packed without vacuum. These results were explained by the mechanical effects of vacuum, which could have contributed for volumetric contractions of the samples.

On the other hand, Table 6 contains the information found in the literature, about the storage stability of fruit or vegetables powders, which were dehydrated. These powders are commonly used in the food industry to produce instant juices or soups, to add in yogurts and snacks, among other applications.

Since the addition of high molecular weight compounds is known to decrease stickiness and improve product stability (Farahnaky et al., 2016; Jaya and Das, 2004; Seerangurayar et al., 2017; Silva et al., 2006), in most of the studies present in Table 6, food stabilizers were added to the processing of powders with the purpose of studying their capacity to improve the storage stability of samples. The food additive most used in the present studies was maltodextrin.

In the studies performed by Telis and Martínez-Navarrete (2009), freeze-dried grapefruit powder improved color stability in samples with maltodextrin or Arabic gum comparing with samples without additives. The author also concluded that maltodextrin with low dextrin values had a better effect than maltodextrin with high dextrin values. Moreover, Mosquera et al. (2012) demonstrated that adding these compounds to the strawberry pulp decreased the hygroscopicity of the powder and increased the  $T_g$ . In addition, Gabas et al. (2007) proved that at the same RH, samples with both food stabilizers showed lower equilibrium moisture contents and were less affected by increasing temperature.

The anthocyanins retention during storage was also improved by the addition of MD in spray-dried bayberry powder (Fang and Bhandari, 2011). The author demonstrated that depending on the RH of the storage environment, the decrease of ACN was about 7-27%, at 5 °C, 9-37% at 25 °C and 9-94% at 40 °C, during 6 months of storage. Also Moser et al. (2017) observed that greater amount of MD combined with soy protein in Spray-dried grape juice powder, stored at 5 °C, contributed for the highest anthocyanin retention.

In general, the studies of Table 6 demonstrated that at higher storage temperatures and relative humidity values, the changes in the quality parameters increased. However, foam-mat dried tomato powder, demonstrated better color stability when stored at 20 °C than at 2 °C and -10 °C (Lovrić et al., 1970).

Another important parameter was the type of material used for packaging. For example, Sagar and Kumar (2014) investigated the vitamin C, color and moisture content stability of air-dried bael powder with maltodextrin and tricalcium phosphate (anti caking agent), stored for 6 months in different packaging materials and at different temperatures. The author verified that the stability of samples was significantly affected by packaging materials. In addition, some studies showed the negative impact of oxygen for the storage.

Table 4 - Studies concerning the stability of fresh berries regarding the analysis of ACN and vitamin C content and color.

Sample	Experimental Conditions	Studied Parameter	Results	Ref.
Strawberry puree	Storage at 8 °C for 11 weeks	ACN	Losses of an average of 41%.	(Hartmann et al., 2008)
		Vitamin C	Losses around 92%.	
Raspberry pulp	Storage at 4, 20, and 37°C; Canning in glass flasks; For 90 days;	ACN	Degradation increased with temperature. After 50 days of storage no sample presented ACN content.	(Ochoa et al., 1999)
		Vitamin C	Degradation increased with temperature.	
		Color	Most stable color and best visual appearance at 4 °C. Color variation during storage was correlated with the thermal degradation of anthocyanin as cyanidin-3-glucoside;	
Raspberry	Stored at 0, 10, 20, and 30 °C; For 8 days;	ACN	Anthocyanins increased by about 2.5 times, after 8 days of storage at 20 °C. Changes in these components were less after 10 and 30 °C storage and least at 0 °C;	(Kalt et al., 1999)
		Vitamin C	During the same period at 20 °C, ascorbate content decreased by 22%. At 30 °C, 46% of the ascorbate was lost by the end of the storage period;	
Raspberry (Autumn Bliss, Heritage, Rubi and Zeva cultivars)	Frozen samples at -20 C for 12 months	ACN	Cyanidin 3-glucoside suffered the most significant degradation in Autumn Bliss cultivar. This cyanidin was not degraded in the Heritage cultivar; In Autumn Bliss cultivar, the total anthocyanin diminished in a range of 12-48% compared with the raw fruit value; Significantly decrease of ~15-27% in both, Rubi and Zeva cultivars. Cyanidin 3-glucoside decreased 21-34% in Rubi and 15-40% in Zeva cultivars, compared with raw product concentration;	(de Ancos et al., 2000a; de Ancos et al., 2000b)
		Vitamin C	There were significant decreases in vitamin C, from 33 to 55%, depending on the cultivar	
		Vitamin C	Little loss of vitamin C at 1 and 10°C. Wrapping reduced AA loss by 5 times at 1 and 10°C and by 2 times at 20°C	
Strawberries	Stored for 8 days at 1 or 10°C, or 4 days at 20°C, either unwrapped or wrapped in polyvinyl chloride (PVC)	Vitamin C		(Nunes et al., 1998)

Table 5 - Studies concerning the storage stability of dehydrated fruits, regarding the analysis of ACN and vitamin C content, color and moisture content.

Sample	Experimental Conditions	Studied Parameter	Results	Ref.
Vacuum microwave-dried strawberry	Stored at 20 °C without O <sub>2</sub> and light exposure for 6 months; Initial aw of sample: 0.64; Stored in plastic bags, made of 70- $\mu$ m-thick film of polyethylene with an outer layer of polyamide and vacuum sealed;	ACN	Degradation of 32 %.	(Bruijn et al., 2015)
Freeze-dried apple slices	Samples stored at 50 °C in hermetic chambers with RH values between 0.057 and 0.958;  Samples exposed to different RH.	Moisture content  Color	Slow increase of the equilibrium moisture content at low $a_w$ range and a sharp increase at higher $a_w$ values (>0.80).  Negligible color changes at low $a_w$ and maximum browning at $a_w = 0.50$ .	(Acevedo et al., 2006)
Freeze-dried apple slices	Stored at temperature: 4, 20 and 30 °C for 180 days; Packed: with and without vacuum in plastic bags of Polyamide/Polyetilen.	Color	At 4 °C, the color was acceptable after storage. No significant differences in +a* and +b* values between samples packed with and without vacuum; At 20 °C, in both samples packed with and without vacuum, the +a* and +b* values increased; At 30 °C, the +b* parameter increased in both vacuumed and no vacuumed samples until 90 days. After that, +b* values tended to stay stable; L* and +a* values suffered a higher decrease with increasing temperature in samples stored under vacuum;	(Contés et al., 2009)
Freeze-dried guava	Stored in different RH environments: $a_w = 0.43$ ; 0.75; 0.84; 0.97.	Vitamin C	Loss of the crunchy characteristics, caused by progressive moisture gain (related to permeability of packaging material); Texture was negatively affected by the vacuum packing due water permeability of the package. Low temperatures (4°C) helped to preserve the textural properties;	(Uddin et al., 2002)

Table 6 - Studies concerning the storage stability of dehydrated fruit powders, regarding the analysis of ACN and vitamin C content, color, moisture content and water activity.

Sample	Experimental Conditions	Studied Parameter	Results	Ref.
Spray dried grape juice powder	Samples with different concentrations of soy protein (S) or whey protein (W) and maltodextrin (MD); Stored at 5, 25 and 35 °C for 150 days;	ACN	Greater amount of MD combined with S, stored at 5 °C, presented the highest anthocyanin retention; At 35 °C, samples presented the highest degradation rate;	(Moser et al., 2017)
Foam-mat air dried mandarin pulp powder	Foaming agents: carboxy methyl cellulose, milk or egg white; Packed and sealed in low density polyethylene followed by aluminium laminated foil bags, for 6 months.	Color	The storage time and temperature did not influence the color ( $\Delta E^*$ < 1.5 at the end of storage), except for the samples containing W and MD stored at 35 °C;	(Kadam et al., 2011)
Vacuum dehydrated ripe mango powders	Stored at ambient temperature (27–32 °C) for 6 months; Packed in two types of pouches: - Polyester poly (PP) (40.2 mm thickness); -Metalized polyester (12 mm thickness) with polyethylene (40.2mm thickness) (MPP); No additives.	Vitamin C	Retention of 25-30% and 17-18% in MPP and PP packaged powders, respectively.  Increased in samples of both packaging materials in the 1st month and again from the 4th month onwards. Both packaging materials were not completely impermeable to the water vapor transmission. However, the moisture gain was within the permissible limits for microbiologic safety.	(Hymavathi and Khader, 2005)
Freeze-dried grapefruit juice powder	Additives: maltodextrin with low dextrin values (LDE); maltodextrin with high dextrin values (HDE), or gum Arabic. Samples stored at 23 °C in a RH environment between zero and 0.84.	Color	Maltodextrin LDE and Arabic gum improved stability against collapse and color. In samples with additives, color was stable until $a_w = 0.22$ , while without these compounds presented changes at $a_w = 0.12$ ; Above $a_w = 0.22$ , $L^*$ showed a continuous decrease, more accentuated in maltodextrin HDE and Arabic gum; $+a^*$ and $+b^*$ values increased at the intermediate $a_w$ values (except for the $+a^*$ of samples with MD LDE) and then suffered a steady decrease at higher $a_w$ ; $\Delta E^*$ was higher in $0.2 \leq a_w \leq 0.5$ , and varied as a function of the type of additive;	(Telis and Martínez-Navarrete, 2009)



Table 6 - Studies concerning the storage stability of dehydrated fruits or fruit powders, regarding the analysis of ACN and vitamin C content, color, moisture content and water activity (Cont.).

Sample	Experimental Conditions	Studied Paramete	Results	Ref.
Freeze-dried strawberry powder	Additives: Maltodextrin or Arabic gum; Samples placed at 20 °C in hermetic chambers with RH ranging between 11% and 75%;	Moisture content	Adding maltodextrin and Arabic gum to the strawberry pulp improved the stability of samples, decreasing the hygroscopicity of the powder and increasing the Tg; Slow increase in the equilibrium moisture content in the low aw range, and a higher increase at intermediate aw values (0.600); Arabic gum was slightly more effective than maltodextrin in maintaining stability of the powders;	(Mosquera et al., 2012)
Spray-dried bayberry powders	Additive: maltodextrin; Samples stored in hermetically sealed desiccators with different RH (aw = 0.1; 0.22; 0.33; 0.44); Maintained at 5 °C, 25 °C or 40 °C for 6 months;	ACN	Under an $a_w$ of 0.11-0.44, the ACN decreased by about 7-27%, after 6 months storage at 5 °C; At 25 °C the decreases were between 9-37%; At 40 °C the decreases were in the range 9-94%; At the same temperature, the higher the aw, the higher losses of ACN;	(Fang and Bhandari, 2011)
Foam-mat dried tomato powder	Initial RMC of sample = 3%; Samples were stored at -10 °C, 2 °C, 20 °C, and 37 °C in air and nitrogen atmospheres for 1 year;	Color	Storage at 20 °C was better for color retention than storage at 2 °C, or -10 °C; Storage in an inert atmosphere improved color retention; At 37 °C non-enzymic browning, and an increase in water content caused fast darkening;	(Lovrić et al., 1970)
Vacuum-dried coconut milk powder	Additives: acacia gum and maltodextrin; Samples packed and sealed in aluminium foil laminated polyethylene pouches (thickness: 50 µm); At 38±2 °C in a RH of 90±1%; After every 7 days, for approximately 50 days, the samples were analysed;	Moisture content Water activity	Increased from 0.05 to 0.112 kg water kg dry solid <sup>-1</sup> during storage; The shelf life was 30 days and moisture gain was found to be the limiting reaction for the safe storage; Increased from 0.375 to 0.728 during storage.	(Jena and Das, 2012)
Spray-Dried Blackberry Powder	Additives: MD, Arabic gum, or a blend of both carrier; Stored at 25 or 35 °C and at RH of 32.8% for 5 months;	ACN	Temperature negatively influenced the stability of anthocyanins. MD provided greater stability.	(Ferrari et al., 2013)

Table 6 - Studies concerning the storage stability of dehydrated fruits or fruit powders, regarding the analysis of ACN and vitamin C content, color, moisture content and water activity (Cont.).

Sample	Experimental Conditions	Studied Paramete	Results	Ref.
Spray-dried black carrot powder	Samples were stored at 4 °C and 25 °C with light illumination.	ACN Color	Anthocyanins content decreased 33% at 25 °C, and 11% at 4 °C after 64 days of storage. After 8 weeks of storage, the pink color of the samples was not changed at 4 °C where it was turned to brown at 25 °C.	(Ersus and Yurdagel, 2007)
Vacuum-dried pineapple pulp powder	Powders with and without additives (18% MD or 18% Arabic gum) were analyzed at 20, 30, 40 and 50 °C in a water activity range of 0.06-0.90.	Moisture content	At the same water activity, samples with both additives showed lower equilibrium moisture contents and were less affected by increasing temperature than the ones without them;	(Gabas et al., 2007)
Air dried bael powder	Additives: maltodextrin (drying aid) and tricalcium phosphate, TCP (anti caking agent); Samples were packed in polypropylene (PP), low density polyethylene (LDPE) and high-density polyethylene (HDPE) pouches; At 7 °C (85 % RH) and ambient condition (18-35 °C) (50-60 % RH) for 6 months;	Vitamin C Color Moisture content	Higher retention of color and vitamin C in samples stored in HPDE and at 7 °C. There was continuous increase of moisture in all the samples and it was significantly affected by packaging materials; The increase was higher at ambient temperature;	(Sagar and Kumar, 2014)

## 4 Materials and methods

### 4.1 Materials

#### 4.1.1 Reagents

Frozen raspberry (summer harvest from Bulgaria, sort Willamette Brix: 10 % pH (25 °C): 3) and raspberry puree (No. 300100300795) was obtained from Mainfrucht GmbH & Co. KG (Gochsheim, Germany). Potato-protease inhibitors (Solanic® 300, model substance) were acquired from Avebe (Ceendam, Netherlands). Maltodextrin (DE6, model substance) was obtained from Nutricia GmbH (Erlangen, Germany). Pectin (Instant CJ 204, model substance) was obtained from Herbstreith & Fox (Neuenbürg, Germany). Meta-phosphoric-acid (CAS: 37267-86-0, 33.5%) and Tris(2-carboxyethyl)phosphine (CAS: 51805-45-9, ≥ 98 %) were obtained from Sigma-Aldrich chemistry GmbH (Taufkirchen, Germany).

Hydrochlorid acid (CAS: 7647-01-0, 37 %, fuming) was acquired from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). Lithium chloride (CAS: 7447-41-8, ≥ 98 % purified) and potassium acetate (CAS: 127-08-2, purified) were obtained from VWR Prolabo (Leuven, Belgium). Magnesium chloride hexahydrate (CAS: 7791-18-6) was acquired from Sigma-Aldrich chemistry GmbH (Taufkirchen, Germany).

#### 4.1.2 Equipment

Weight measurements were performed with an analytical scale RC 250 S (Sartorius AGk, Göttingen, Germany) and a precision scale MC1 LC4800P (Sartorius AGk, Göttingen, Germany). Solution preparation was accomplished using Hei-Torque 100 laboratory stirrer (Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) and foam was produced by an aerating system Mondomix A-05 (Mondomix Holland b. v, Almere, Netherlands). Samples were dried using a microwave freeze-dryer  $\mu$ WaveVac0150fd (Püschner GmbH & Co. KG, Schwanewede, Germany) and a freeze-dryer Gamma 1-20 (Christ freeze dryer GmbH, Osterode am Harz, Germany). Dried samples were packed in aluminium bags A200300 with 12  $\mu$  PET/12  $\mu$  aluminium /75  $\mu$  LDPE (Long Life for Art, Eichstetten, Germany) and vacuum was accomplished using a Multivac vacuumizer (MULTIVAC Sepp Haggenmüller SE & Co. KG, Wolfertschwenden, Germany). Storage bags were sealed by a table top sealer Wusing 300 H (Long Life for Art, Eichstetten, Germany) and stored in an incubator Nüve EN 120 (Buchner Labortechnik, Pfaffenhofen, Germany). Quantification analysis of anthocyanins and ascorbic acid were accomplished using a high-performance liquid chromatography, HPLC 1100 Series (Agilent Technologies, Santa Clara, CA, USA) with a column Luna 3  $\mu$ m C18 (2) 100 Å 250 x 4,60 mm (Phenomenex Ltd., Aschaffenburg, Germany) and a centrifuge Multifuge 1 S-R (Heraeus Holding GmbH, Hanau, Germany).

An ultra-turrax homogenizer Polytron (Kinematica, Luzern, Switzerland) was used to homogenized the sample of raspberry splits. Moisture measurements were achieved by using a Karl-Fischer-Titrator V20S (Mettler-Toledo GmbH, Greifensee, Switzerland) and a Moisture-analyzer Smart Turbo (CEM Corporation, Matthews, USA). Water activity was assed by a water activity analyser HygroLab C1 (Rotronic, Bassersdorf, Switzerland). Color was evaluated with a color analyser SP68 (X-Rite Europe GmbH, Regensdorf, Germany). Texture measurements were accomplished using a texture analyser TA.XT.plus with a Kramer shear cell with 8.2x6.3 cm, h = 9 cm and section area = 51.66 cm<sup>2</sup> (Stable Micro Systems Ltd, Godalming, UK).

### 4.1.3 Software

The control of the microwave freze-dring system was accomplished using WaveCAT 2007 4.1.2.4 (Ralf Graute & Püschner GmbH & Co KG, Schwane wede, Germany). Texture analysis were accomplished using Exponent Software SMS Version 6.1.6.0 (Stable Micro Systems Ltd, Godalming, UK). Anthocyanins and ascorbic acid quantification were performed with ChemStation B.04.03 (Agilent Technologies, Santa Clara, USA). Graphs construction was performed using Origin Pro 9.0G 64 Bit (OriginLab Corporation, Northampton, MA, USA).

## 4.2 Methods

### 4.2.1 Experimental plan

The first stage of the experiment consisted in the production of fresh samples to posteriorly dry with MWFD and FD. Therefore, raspberry, puree, solution and three different foam samples were produced (Consult section 4.2.2). After drying (Consult section 4.2.3), the samples were packed and stored in different conditions (Consult Section 4.2.4). During 12 weeks of storage, quality analyses were performed every 4 weeks. These analyses consisted in study the residual moisture content (RMC), water activity ( $a_w$ ), color, texture and vitamin C and anthocyanins content of samples (Consult section 4.2.5). Experiments were done in duplicate, to prove that no other declaration was given. Detailed information on each step of the process is described in this chapter. Figure C1 in Appendix shows the different parameters investigated in the experience throughout storage.

### 4.2.2 Sample Preparation

In order to produce the three different raspberry foams, it was necessary to produce the respective solutions as a first step. In this work, the term solution means the solution of raspberry puree with PPI, MD and P, without being foamed (added in the *Mondomix*). For this purpose, the raspberry puree was frozen under -20 °C and moved to a -4 °C room to unfreeze, some days before the production of solution. For the preparation of solutions, the necessary puree amount was weighed, as well as all powder components (maltodextrin, potato protease inhibitors,

pectin) according to the three established formulations in which maltodextrin content varied (5, 15, 30%) at constant potato-protease inhibitors (5%) and pectin (2.5%) concentrations.

These formulations were chosen according to the results of preliminary studies about the influence of different concentrations of maltodextrin, protein and pectin (Heigl, 2017).

The powder components were first mixed in a beaker and slowly added to the puree container, to make an homogeneous solution, under an agitation of 350 rpm provided by the laboratory stirrer Hei-Torque 100 with a paddle mixer with six paddles. Afterwards, the solutions were transferred to a -4 °C room and stirred for about 24 h so that the potato-protease inhibitors had time to hydrate.

Before foaming, the solutions were taken from the -4 °C room and maintained at room temperature under 350 rpm for at least 1 h. For producing the foams, each solution was added in the *Mondomix*, a foaming equipment that consists in a continuous aerating system. Parameters such as pressure and aeration were controlled for each formulation according to Table D1 in Appendix.

After obtaining the desired conditions for each foam, 300 g of foam were spread homogeneously into a big petri dish with a diameter of 230 mm for the microwave freeze-dryer and 100 g were spread into smaller petri dishes (190 mm) for the freeze-dryer. The height of the foam was marked with a pen on the outside of the dish.

The samples were directly frozen in a -80 °C freezer (to not destroy the foam structure) for a minimum of 24 h to prepare them for the drying process. To observe the influence of the product structure, samples of raspberry, puree and solution (with the formulation of 5% PPI; 15% MD; 2.5% pectin) were also transferred to the petri dishes mentioned above and the same procedure was done.

### **4.2.3 Drying process**

#### **4.2.3.1 Microwave freeze drying**

The equipment used for the microwave freeze-drying (MWFD) of the samples was  $\mu$ Vac0150fd (Püschner GmbH & Co. KG, Schwanewede, Germany). The equipment had to be warmed up before introducing the sample to guarantee a good processing. Afterwards, the samples were taken from the -80 °C freezer and brought inside a styrofoam box and finally placed in the centre of the turntable. A value of 30 °C was set for the drying, as well as, a pressure of 0.1 mbar.

During drying, at 0.75 w/g, some aspects were often verified to guarantee the quality of it, such as the presence of plasma, foam collapse, reflection of energy, product weight and water loss, as well as, the stability of the established parameters. As the maximum product temperature was set at 30 °C, when this value was exceeded, the software automatically regulated the product

temperature with a pulsed input of microwave power to generate an indirect product cooling. The drying was stopped after 10 minutes without weight loss ( $< 0.2$  g/min).

#### **4.2.3.2 Freeze-drying**

All samples were freeze-dried in parallel with the MWFD to obtain a comparison of the product through the two drying methods. Therefore, the set values of temperatures and pressure were the same. The equipment used was the freeze-dryer Gamma 1-20 (Christ freeze dryer GmbH, Osterode am Harz, Germany), which was warmed-up for 10 minutes.

Posteriorly, as well as, in the MWFD, the samples were taken from the  $-80$  °C freezer and were placed in four shelves, where the lowest one was connected to the system. After adding the samples in each shelf, the shelf system was put into the condenser and the system was closed in order to start the drying with the previously mentioned parameters. During drying all shelves were heated by bars connected to the freeze-dryer. The drying time was selected according to previous work (Heigl, 2017).

#### **4.2.4 Packaging and storage**

##### **4.2.4.1 Samples packed under vacuum**

After the drying, the samples were added in brown glass bottles. For each analysis, four bottles were filled so that the samples were separated by each week of analysis (week 0, 4, 8 and 12). The bottles were separately placed in aluminum bags with  $12\ \mu$  PET/ $12\ \mu$  aluminium / $75\ \mu$  LDPE and vacuum was accomplished using a multivac vacuumizer. Storage bags were then sealed by a table top sealer and stored in an incubator at  $37$  °C for an accelerate storage test. As a comparison element, also a sample of foam with 5% PPI, 15%MD and 2.5% pectin was stored at  $20$  °C and  $4$  °C.

##### **4.2.4.2 Samples stored in different relative humidity environments**

Saturated salt solutions of lithium chloride (LiCl), potassium acetate (KCH<sub>3</sub>COO) and magnesium chloride (MgCl<sub>2</sub>) were prepared to create different relative humidity environments. These solutions were prepared to adjust the *a<sub>w</sub>* values to 0.11, 0.22 and 0.33, respectively (Greenspan, 1977). To prepare the LiCl solution, 680 g of salt were transferred to 850 mL of distilled water. For the KCH<sub>3</sub>COO solution, 1800 g of salt were added in 650 mL of distilled water. 2000 g of MgCl<sub>2</sub> were transferred to 850 mL of distilled water. All solutions were prepared under stirring.

Solutions were stirred overnight in glass bottles and then 80 mL of each solution were transferred into closed glass jars containers, with a rubber seal ring. A layer of solid salts was added to the glass jars to confirm that the solution would always remain saturated. The jars were at  $20$  °C. After 24 hours, 9 g of each dried sample were weighed in three glass petri dishes (3 g in each petri dish). Metallic supports were added to the glass jars and the petri dishes with the

sample were placed in the supports. Each glass jar only contained one petri dish with sample. The jars were quickly sealed to prevent gas leakage (Wrolstad et al., 2005).

For each sample 9 jar glasses were prepared (3 different environments each one with 3 jars containing 3 g each). This way, the glasses were just opened in the respective week of analysis (week 4, 8 and 12).

## **4.2.5 Sample analysis**

### **4.2.5.1 Product moisture**

The initial moisture of the fresh samples (before drying) of raspberry, puree and solutions, was measured by means of convectively heating and microwaves in the Smart Turbo (CEM Corporation) by adding 2 g of each sample in quartz glass fiber pads.

After drying, samples were converted in a homogeneous powder by grinding with a porcelain mortar to facilitate the moisture content and water activity measurements.

For the measurement of the water activity ( $a_w$ ), appropriated plastic cuvettes were homogeneously filled with the powder and inserted in the water activity analyser.

The residual moisture (RMC) content measurement of dried samples was performed using the Karl-Fischer-method (KF), which is supported by the Bunsen-reaction (Mettler -Toledo, 2012). The measurement was performed in a volumetric KF-compact-titrator. Therefore, the solvent (methanol solution) was continuously stirred by a magnetic stirrer while the KF-reagent was added and titrated until there was no water anymore (pre-titration). Then, an amount of 0.001 - 0.1 g of the dried powder sample was added in the chamber, as fast as possible, to minimize the exposure of the chamber to the humid surrounding air. Afterwards, the sample was mixed for 600 s to dissolve the powder in the solution before the titration started. Finally, after the titration, the percental moisture content was given by the system according to the amount of sample and the amount of iodine needed to remove all the water from the chamber.

### **4.2.5.2 Ascorbic acid and anthocyanin content**

Ascorbic acid and anthocyanins content was measured with the high-performance liquid chromatography (HPLC) 1100 Series (Agilent Technologies, Santa Clara, CA, USA).

As a first step, a solution of 3% metaphosphoric acid (MPA) and 1% Hydrochlorid acid (HCl) were separately prepared to protect the AA and anthocyanins content of the samples. The first solution was prepared to protect AA from oxidation to DHA. Therefore, 30 g of crystalline 33.5% MPA were weighed and diluted in 1000 g of distilled water in a glass beaker with a magnetic stirrer. The MPA solution was kept in the fridge at 8 °C.

The structure of anthocyanins is highly pH dependent, specifically more stable at pH < 3, when the flavylium cation is formed (Khoo et al., 2017). For this reason, the 1% HCl solution

was produced to adjust the pH value. Thus, to prepare this solution, 54 mL of 33.7% fuming HCl were pipetted in 2000 mL of distilled water.

For measuring the AA and anthocyanins content of dried samples, 0.5 g of powder was weighed in a 50 mL falcon tube and filled up to 30 g of each respective solution. In the case of fresh samples (not dried samples), 2 g were weighed, and the falcon tubes were filled up to 20 g of each solution. Additionally, only for the raspberry samples an ultra-turrax homogenizer was used to smash the raspberry seeds in the solution.

The falcon tubes were kept at -20 °C until the measurement was performed. Before adding the samples in the HPLC, they were thawed at 20 °C in the water bath for 1 hour and the tubes were shaken for 30 minutes in the case of the AA samples and 180 minutes in the case of anthocyanins. Then, they were centrifuged at 6000 g for 10 minutes. The supernatant was filtrated with a 0.45 µm cellulose acetate (CA)-filter into a 2 mL Eppendorf tubes for the elimination of molecules that could destroy the HPLC-column.

Afterwards, 500 µL of the filtrate were transferred into brown vials, for the determination of free AA and anthocyanins. For the measurement of the total AA, 250 µL of the filtrate plus 250 µL of Tris(2-carboxyethyl)phosphine (TCEP) > 98 % were pipetted into the vials. TCEP solution was added to react with the sample and reduce DHA back to AA. To obtain this solution 35.84 mg of TCEP were weighed with a precision scale and diluted in 25 mL of distilled water.

After this procedure, the vials were put in the HPLC 1100 Series (Agilent Technologies). An AA standard > 99.9% was used for the detection of AA and three anthocyanins were selected for the detection with a mixed standard: Cyanidin-3-glucoside, Cyanidin-3-sophoroside and Cyanidin-3-rutinoside. The operation conditions for the HPLC-column are presented in the Table E1 in Appendix.

The obtained chromatograms were analysed with the software ChemStation B.04.03 (Agilent Technologies, Santa Clara, USA). The amount of AA and anthocyanins was calculated according to the areas of the peaks of the relevant components (identified by the retention time of the standards). The final results were calculated according to the injection volume and the dilution factor of the samples, obtaining ascorbic acid results in mg/g sample and anthocyanin contents in µg/g sample.

#### 4.2.5.3 Color analysis

The color of the samples was evaluated according to the color space CIELAB ( $L^*a^*b^*$ , CIE = Commission Internationale de l'Eclairage) (Nielsen, 2014). The device used was a spectral photometer color analyser SP68 (X-Rite Europe GmbH, Regensburg, Germany). For this purpose, the parameter middle day light (D65) was selected. The results were given in terms of three color parameters. The  $L^*$  - value describes the brightness and varies between  $L^* = 0$  (black for absorption) and  $L^* = 100$  (ideal white). The  $a^*$  - value describes redness ( $+a^*$ ) and



greenness ( $-a^*$ ) and  $b^*$  - values reflects yellowness ( $+b^*$ ) and blueness ( $-b^*$ ). In order to compare the color changes during storage, the total color difference ( $\Delta E$ ) was calculated according to formula 3 (Saengrayap et al., 2015):

$$\Delta E = \sqrt{(L^*_0 - L^*_n)^2 + (a^*_0 - a^*_n)^2 + (b^*_0 - b^*_n)^2} \quad (3)$$

The meaning of  $\Delta E$  as visible quality is explained in Table 7.

Table 7 - Different meanings of  $\Delta E$  (Lübbe, 2013).

$\Delta E$	Meaning
0-1	Invisible difference
1-2	Only obvious to a trained eye
2-3.5	Obvious to an untrained eye
3.5-6	An obvious difference
>6	A very obvious difference

#### 4.2.5.4 Texture analysis

Texture analysis were performed only for the foam samples using a TA-XT plus Texture Analyzer (Stable Micro Systems Ltd, Godalming, UK). This device applies a combination of shearing, compression, and extrusion loads to the product. Hardness is expressed as peak force in the first compression of product. The measurement of force/time was obtained with a 5 blade Kramer shear cell.

The calibration of the height was done before the measurement and the distance for all measurements was set to 8.5 cm. Afterwards, 10 g of sample were added in the cell and the test was run according to the operating conditions presented in Table 8.

Table 8 - Operating conditions of the of the shear test with the 5 blade Kramer shear cell.

Parameters	Operating Conditions
Load cell	50 kg
Crosshead speed	2 mm/s

The software Exponent (Stable Micro Systems Ltd.) showed the results of the measurements in a graph of force (N) versus time (seconds) and automatically calculated the maximum force, number of peaks and the linear distance according to the obtained curves.

#### 4.2.5.5 Statistical analysis

One-way and two-way ANOVA tests, from the Analysis ToolPak of Excel tool, were used for determination of differences between the different conditions of the experiment. A probability level of ( $p \leq 0.05$ ) was considered to be significant for all statistical procedures.



## 5 Results and discussion

In this chapter the results regarding the stability of raspberry foams during storage will be presented. The stability of all samples was evaluated according to the quality parameters: moisture content, water activity, color, texture, anthocyanins and ascorbic acid. The influence of the drying method, product structure, maltodextrin concentration, storage temperature and relative humidity on these quality parameters was analysed.

### 5.1 Influence of drying method

All samples were dried with the microwave freeze-drying and the freeze-drying methods in order to observe if there was any significant difference between the quality of samples after drying and during storage. Although there is a variety of literature about the quality comparison of food dried with MWFD and FD, more research should be conducted regarding the comparison of the product quality during storage.

Both dehydration methods proved to achieve the same conditions of residual moisture content and water activity for all samples. Figures 5 and 6 show the example of 15% (w/w) MD foam. Before drying, foam presented 75% (w.b) moisture content. After drying, the values of RMC and  $a_w$  were similar between both methods. Foam dried with MWFD presented a RMC of  $2.95 \pm 0.51\%$  and  $a_w$  of  $0.15 \pm 0.04$ , while foam dried with FD presented  $2.97 \pm 0.02\%$  and  $0.14 \pm 0.03$ , respectively. In addition, during storage under  $37^\circ\text{C}$ , the vacuum-packed foams demonstrated a similar water activity behaviour for both MWFD and FD.

During all storage period, the difference of RMC between the drying methods was not significant ( $p > 0.05$ ). However, the high standard deviation of the MWFD result of week 12 ( $\pm 0.74\%$ ) could explain a possible occurrence of operating errors due to the sample exposure to the atmosphere and its rapid absorption of water after the opening of the aluminium bags and during sample conversion to powder.

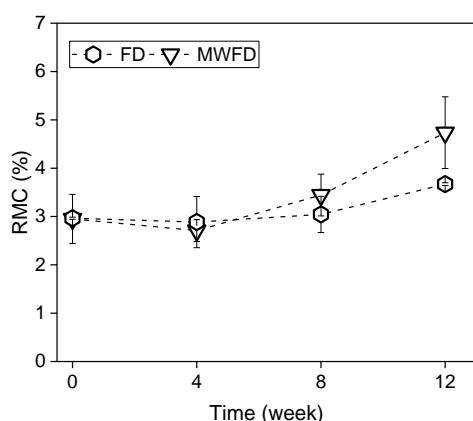


Figure 5 - RMC of 15% MD foam dried with FD and MWFD and stored at  $37^\circ\text{C}$ , vacuum packed.

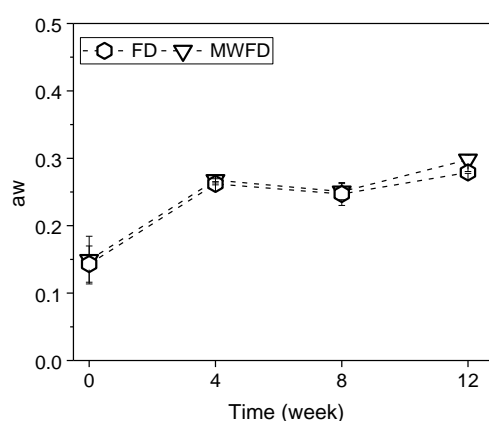


Figure 6 - Water activity of 15% MD foam dried with FD and MWFD and stored at  $37^\circ\text{C}$ , vacuum packed.

Results obtained for foam hardness (Figure 7) show that FD samples presented slightly higher initial hardness than the ones dried with MWFD. Nevertheless, the difference of this values during all the experiment was not significant ( $p > 0.05$ ) since hardness of both samples converged to a similar value after 4 and 12 weeks of storage.

The color parameters, brightness ( $L^*$ ) and yellowness ( $+b^*$ ) were found to be similar for both methods after drying and during storage ( $p > 0.05$ ) (Figure 8). On the other hand, the redness ( $+a^*$ ) of MWFD after 12 weeks of storage at 37 °C was higher ( $p < 0.05$ ).

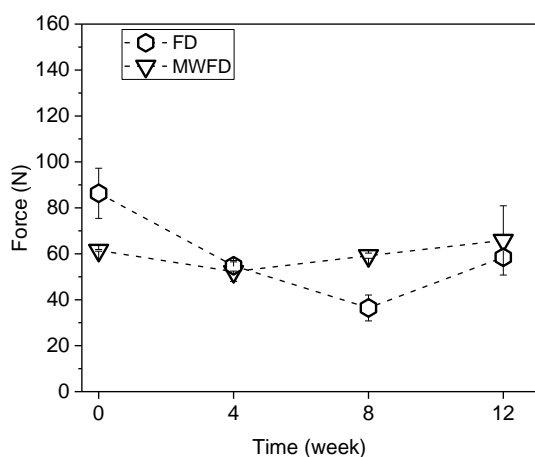


Figure 7 - Hardness of 15% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.

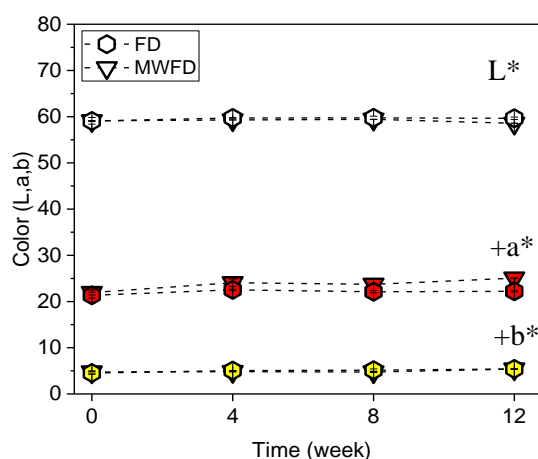


Figure 8 - Color parameters of 15% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.

The comparison of anthocyanin and ascorbic acid content of foams dried with MWFD and FD is presented in Figures 9 and 10. It was found that after drying, the total anthocyanin content was  $0.686 \pm 0.023$  and  $0.695 \pm 0.004$  (mg/g of sample) for MWFD and FD, respectively. On the other hand, the total ascorbic acid content in week 0 was  $0.352 \pm 0.009$  (mg/g of sample) for the microwave freeze-dried foam and  $0.334 \pm 0.001$  (mg/g of sample) for the freeze-dried sample. Between both methods, the initial proportion of cyanidin-3-glucoside, cyanidin-3-rutinoside and cyanidin-3-sophoroside had a similar value, around 19, 11 and 70%, respectively. The same was observed to the free (non-oxidised) and dehydroascorbic acid, which had a similar value between the two methods of around 88% and 11%, respectively. These results corroborate with the ones obtained in experiments with potato slices, which showed that the retention of vitamin C and all color parameters in samples dried with FD and MWFD did not have significant differences (Wang et al., 2010). Moreover, experiences carried out in blueberries, showed that despite the fact that MWFD retained slightly higher amount of anthocyanins, the difference between both methods was not significant and both retained most of the initial anthocyanin content of the fresh fruit (Ozcelik and Püschner, 2017).

For both anthocyanin and AA content, samples dried with MWFD showed to have significant more retention ( $p < 0.05$ ) of these compounds during storage under vacuum, at 37 °C.

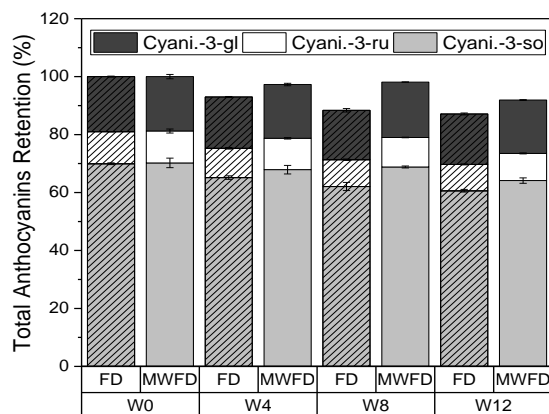


Figure 9 - Total ACN retention of 30% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.

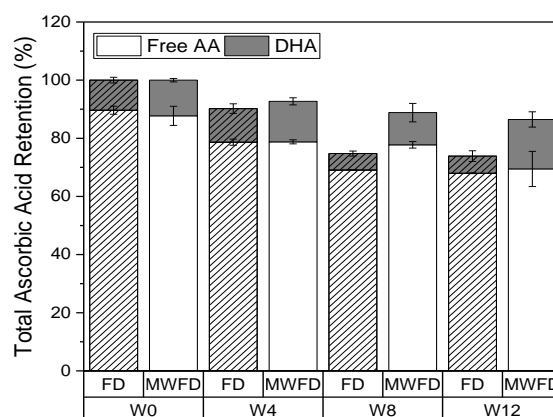


Figure 10 - Total AA retention of 30% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.

To summarise, MWFD demonstrated to achieve at least the same foam quality than FD after drying and over storage. The comparison of these two methods for the drying of raspberry splits can be consulted in Appendix F, where the results corroborate with the ones presented. The use of MWFD demonstrated to be a good option to replace conventional FD due to similar product quality and shorter drying times which result in lower energy consumption. The only disadvantage of microwave freeze-drying observed was the instability of the drying when compared to FD, resulting sometimes in hot spots (sample collapsing) (Consult Appendix G). In experiences with microwave freeze-dried raspberry foams, Ozcelik et al. (2019) observed the occurrence of hot spots with increasing MW power. Therefore, high levels of microwave power can cause a local non-uniformity of the temperature distribution, resulted from fast overheating and intensified by local melting of ice crystals. Due to the difference in loss factors of water and ice, the water produced by ice melting heats faster and leads to widespread melting contributing for structure collapse of the product (Duan et al., 2010; Fellows, 2009b; Gaukel et al., 2017). To control the stability of the drying process, Duan et al. (2010) suggested to apply higher microwave power in the sublimation phase and lower power in the desorption phase.

## 5.2 Influence of structure

Structure is an important determinant of food quality and storage behaviour (Venir et al., 2007). Considerable research has already been done on the freeze-drying of raspberry. (Michalczyk et al., 2009; Syamaladevi et al., 2011; Tumbas-Šaponjac et al., 2015). However, in order to study whether raspberry foams could have an improved shelf life stability, the influence of structure was studied. To compare the results, raspberry splits, puree and non-foamed solutions were also produced and stored in the same conditions. Figure 11 presents the four structures analysed.



Figure 11 - Representation of the different dried structures analysed. A – Raspberry splits; B – Raspberry puree; C – Raspberry solution with 15% MD; D – Raspberry foam with 15% MD.

The moisture content of raspberry splits, puree and solution with 5% (w/w) PPI, 15% (w/w) MD and 2.5% (w/w) P, before drying, was 87%, 91% and 75% (w.b), respectively. Foam had the same initial moisture content than solution since it was produced from it.

After the drying, all structures presented similar values of RMC and  $a_w$ , approximately 3% and 0.13, respectively. During 12 weeks storage at 37 °C, the highest increase both in moisture content and water activity was observed in raspberry samples, reaching a value of  $5.96 \pm 0.47\%$  and  $0.403 \pm 0.03$ , respectively (Figures 12 and 13).

On the other hand, values of RMC obtained from foam samples suggested that this was the most stable structure during the 12 weeks of storage at 37 °C. The same behaviour was observed with solution (unfoamed) samples until the eighth week of storage ( $p > 0.05$ ). However, the moisture content of solution, analysed after 12 weeks, showed an increase. This last result was unexpected since the addition of the carbohydrates increases the average molecular weight of the solids fraction of both foam and solution samples, which should have contributed for the storage stability of the solution as it happened with foam (Jaya and Das, 2004; Mosquera et al., 2012; Telis and Martínez-Navarrete, 2009). This result could be explained by a possible fissure in the aluminium bag, which was not noticed and could contribute for the increase in moisture content due to contact with the RH of the outside.

One of the reasons to explain the moisture uptake of samples during storage could be related with the water vapour permeability of the packaging film (Kumar and Mishra, 2004). The information about the permeability characteristics of most of the commercially available

packaging materials generally specifies only the permeability in a particular temperature and relative humidity (RH) (Samaniego-Esguerra and Robertson, 1991). According to the specifications of the three layer pouches used to storage the samples in this experimental work, the water vapour permeability is  $< 0.01 \text{ g/m}^2\cdot\text{d}$  at  $23 \text{ }^\circ\text{C}$  and  $85\% \text{ RH}$ . Since the water vapour permeability of a film can change with the temperature and RH (Samaniego-Esguerra and Robertson, 1991), the fact that this samples were stored at  $37 \text{ }^\circ\text{C}$  could indicate that the packaging material was not completely impermeable to the water vapour transmission. Moreover, (Samaniego-Esguerra and Robertson, 1991) demonstrated that the water vapour transmission rate of a package material containing LDPE and PET increased with the temperature increasing, at a constant RH.

The glass transition temperature can be used to predict the storage stability of dehydrated food (Bell, 1995; Gradinaru et al., 2003; Syamaladevi et al., 2011). After drying, the determination of  $T_g$  of all samples by differential scanning calorimetry (DSC) was performed by *Mondelēz International, Inc.* All the samples presented a  $T_g > 60 \text{ }^\circ\text{C}$  which predicted a stable storage under this temperature due to the glassy state of the samples. These results were obtained while the samples had the initial moisture content (3%) and water activity (0.13), in the week 0. However, the glass transition temperatures of berries decrease as water content increases, due to the plasticization effect of water on the amorphous compounds of the matrix (Syamaladevi et al., 2009). This could had resulted in a lower  $T_g$  during the storage, especially for raspberry splits. In case this value was lower than  $37 \text{ }^\circ\text{C}$ , samples could had turn into the rubbery state and therefore become less stable. Therefore, the measurement of the  $T_g$  of the samples after a long period of storage should be performed in to take further conclusions.

On the other hand, although raspberry suffered the highest increase in RMC and  $a_w$ , all the samples, including puree, solution and foam samples, could still be considered safe in terms of microbiological spoilage after the storage period, due to an water activity below 0.6 (Bruijn et al., 2015; Figuerola, 2007).

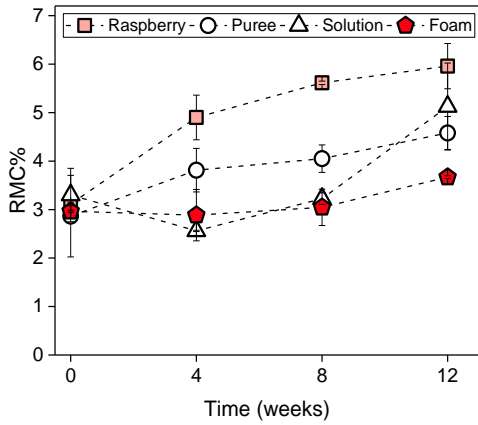


Figure 12 - Influence of structure on RMC. Solution and foam with 5% PPI, 15% MD and 2.5% P. Samples stored under 37 °C, vacuum packed.

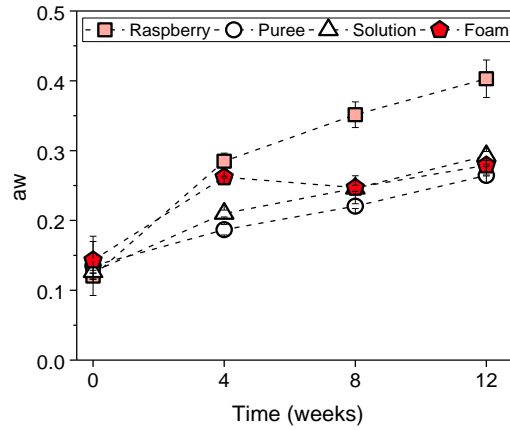


Figure 13 - Influence of structure on water activity. Solution and foam with 5% PPI, 15% MD and 2.5% P. Samples stored under 37 °C, vacuum packed.

Regarding the color of the different structures after drying, solution and foam samples were lighter and presented less redness and yellowness than the raspberry splits and puree, as a result of the added additives, specially the maltodextrin (Figure 14). In addition, these compounds contributed for the color maintenance during the 12 weeks of storage at 37 °C resulting in no significant difference ( $p > 0.05$ ) in solution and foam results for brightness, redness and yellowness. Moreover, Table 9 shows the total color difference after the period of storage, with reference to the week 0. The difference in color was invisible ( $\Delta E < 1$ ) in the case of solution and only obvious to a trained eye ( $\Delta E = [1-2]$ ) in foam (Lübbe, 2013).

On the other hand, raspberry and puree samples suffered an evident browning, having a decrease in redness and increase in yellowness during storage. These results can be confirmed in Table 9, which shows that, after 12 weeks, a very obvious difference ( $\Delta E > 6$ ) could be observed in both raspberry and puree.

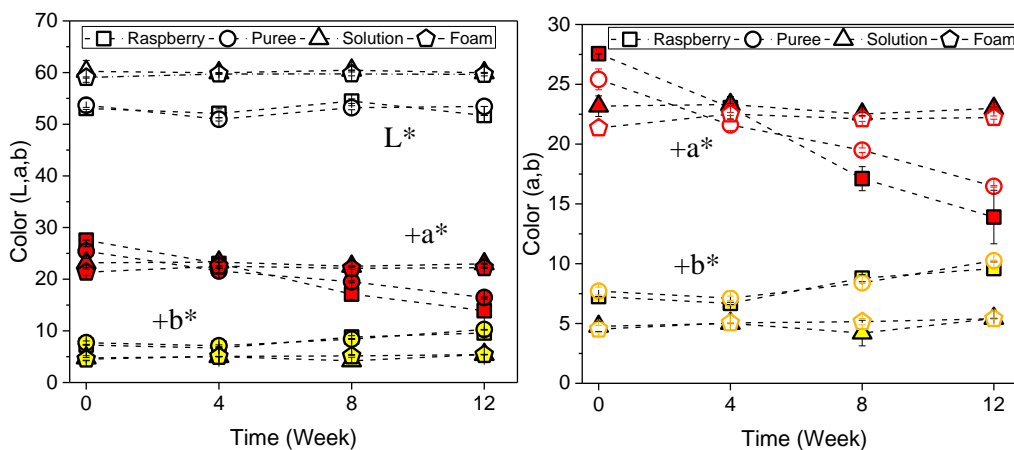


Figure 14 - Influence of structure in the color. On the right, overall view of color parameter L,a,b. On the left, zoomed in graph, focusing in the redness (+a\*) and yellowness (+b\*). Solution and foam with 5% PPI, 15% MD and 2.5% P. Samples stored under 37 °C, vacuum packed.

In experiments with freeze-dried apple tissue, Venir et al. (2007) observed browning at high water activity and moisture content. This conditions facilitates molecular diffusion and



therefore contributes for enzymatic oxidation and polymerisation of oxidized phenols, which causes browning (Venir et al., 2007). These results corroborate with the results obtained for the raspberry, as RMC and  $a_w$  were higher in these samples and browning occurred.

In addition, Telis and Martínez-Navarrete (2009) studied the color changes in grapefruit juice powder (with and without additives of different carbohydrate polymers) and observed that for all samples the color coordinates changed with increasing water content. However, while the samples with additives started to present color changes above an  $a_w$  of 0.22, the color of samples without additives started changing at an  $a_w$  of 0.12. In solution and foam samples, the same was observed, since the addition of the MD, PPI and P contribute for the color stability during 12 weeks storage, at 37 °C.

Table 9 - Influence of structure in the total color difference ( $\Delta E$ ) after 12 weeks of storage at 37 °C. Reference to week 0. Vacuum-packed samples (Consult Table 7 for  $\Delta E$  meaning).

Sample	$\Delta E$		
	Week 4	Week 8	Week 12
Raspberry	4.67±1.07	10.66±0.88	13.92±2.29
Puree	4.72±0.58	5.99±0.16	9.30±0.05
15% MD solution	0.39±0.08	1.13±0.45	0.75±0.05
15% MD foam	1.44±0.08	1.25±0.05	1.380±0.003

In the literature was also found that the color of raspberries is related to their anthocyanin composition, as well as, other factors such as pH, vitamin C and organic acids content (Brouillard, 2012; de Ancos et al., 1999). In fact, cyanidin-3-sophoroside has been reported as the red pigment that is responsible for the color of red raspberry fruit (de Ancos et al., 1999; Rommel et al., 1990) which corroborates with the anthocyanins results obtained for raspberry and puree during storage. As a consequence of the significant decrease in cyanidin-3-sophoroside on these samples (Figure 15), the decrease of redness can be explained.

In overall, the losses of total anthocyanins were 92% and 76% for the raspberry and puree, respectively (Figure 15). In the case of solution and foam there was only a slight decrease of the total anthocyanins content which resulted in a retention of 89% and 86%, respectively. Clearly, the addition of MD, P and PPI contributed for the protection of samples against anthocyanins degradation, when compared to the samples without additives.

The high degradation of anthocyanins in raspberry splits and puree can be related to the high temperature of storage. Since the samples were stored at 37 °C, this could had contributed for the hydrolysis of the glycosidic bond (Figure 1 in Section 2.1.1) and further ACN degradation which could lead to brown products, especially in the presence of molecular oxygen (Markakis, 1982). Anthocyanins degradation can also be related with the Maillard reaction (non-enzymatic browning), in long-time storages at high temperatures (Ferrari et al., 2013; Tonon et al., 2010). Other explanation could be the presence of oxygen which can accelerate

the degradation of these compounds through action of oxidising enzymes such as PPO (Jackman et al., 1987a). Since the samples were packed under vacuum, one of the reasons that could explain the higher loss of anthocyanins in raspberry samples than in puree could be due to traces of oxygen entrapped in the cavity of the berries (Daravingas and Cain, 1965). On the other hand, even if the permeability to oxygen of the storage bags could had change with the temperature of storage, maltodextrin could still had contributed for the formation of a denser and more oxygen impermeable system, providing a better storage stability of the samples with this additive (Cai and Corke, 2000; Ferrari et al., 2013).

Furthermore, the higher water content of raspberry and puree, when compared to the foam and solution (unfoamed) samples, could also be responsible for the higher degradation rate due to the increase of the molecular mobility (Ferrari et al., 2013; Venir et al., 2007).

In Figure 16, it can be observed the same tendency for the retention of the total AA, where the raspberry and puree samples suffered an accentuated decrease, having a retention of only 7% after 12 weeks. For solution and foam the retention of the total AA was 68% and 69%, respectively, after the storage period. The decrease of AA was higher than the decrease of anthocyanins for these samples, being more accentuated in the first 4 weeks of storage and less in the rest of the storage period.

As the samples were stored at 37 °C, the combination of the high temperature and the increasing moisture content and  $a_w$  could had contributed for the degradation of AA, especially in raspberry and puree samples (Cui et al., 2008). Hence, Kirk et al. (1977) observed that the loss of vitamin C in dehydrated food was depending on storage temperature, water activity and moisture content when samples were stored in containers with no headspace (to avoid the presence of oxygen). However, in the presence of oxygen the degradation of AA is intensified (Dennison and Kirk, 1978).

Other explanation could be the non-enzymatic browning that can also contribute for AA loss, which gets oxidized to dehydroascorbic acid. DHA can then react with amino groups to form brown pigments (Löschner et al., 1990).

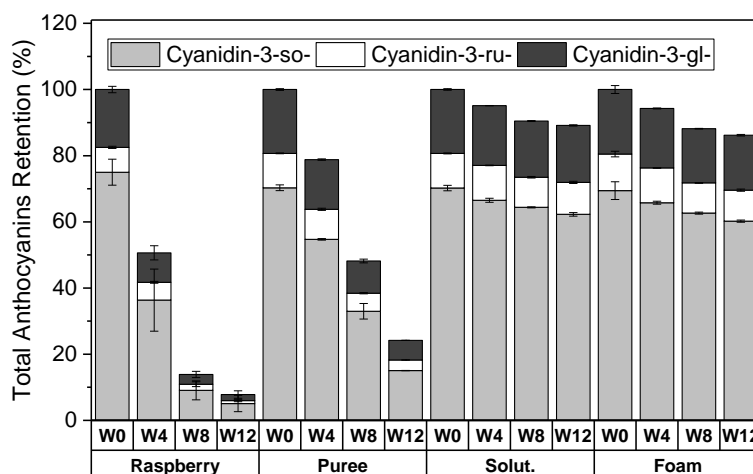


Figure 13 - Influence of structure on the retention of ACN during storage at 37 °C. Vacuum-packed samples.

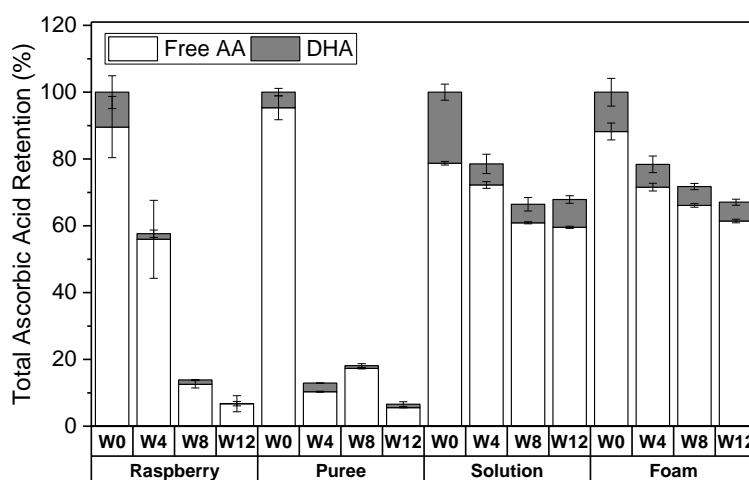


Figure 14 - Influence of structure on the retention of AA during storage at 37 °C. Vacuum-packed samples.

As an overview, raspberry samples were the most unstable during storage at 37 °C, having significant losses in the vitamin C and anthocyanins content, suffering more browning and having a higher increase in RMC and water activity. Although with better results than raspberry, puree samples during storage were, as well, considered unstable, except for water activity that increased slightly (in the same level of solution and foam). The foaming procedure (addition of air) does not have an influence on the storage stability. In fact, solution (non-foamed) and foam demonstrated similar high retention ( $p > 0.05$ ) in most of the quality parameters during storage which can be explained by the addition of maltodextrin, potato protease inhibitors and pectin and their effects on the increasing  $T_g$ , and creation of a surface barrier (Telis and Martínez-Navarrete, 2009). In fact, the presence of proteins may have contributed for the formation of a viscoelastic film network (Franco et al., 2015; Karim and Wai, 1999). Also, the interaction between proteins and polysaccharides (MD) could create a polysaccharide-protein complex by non-covalent interactions. Therefore, the interactions between the added additives may be the reason for the protection against the quality loss of samples.

Despite the fact that foams and solution (non-foamed) presented similar results, for the application as a snack product, the foaming process creates a highly porous structure, promoting a new and intense sensory perception during chewing because the aroma is released instantaneously (Carvalho et al., 2017; Ozcelik et al., 2019).

### 5.3 Influence of maltodextrin concentration

The storage stability of dehydrated products with low molecular weight sugars can be improved by increasing the temperature of glass transition (Syamaladevi et al., 2011). Maltodextrin is commonly used for this purpose in foam-mat drying researches, due to its high molecular weight (Farahnaky et al., 2016; Jaya and Das, 2004; Seerangurayar et al., 2017; Silva et al., 2006). In experiences with mango powder, Jaya and Das (2004) showed that the effect of maltodextrin on the stability of the powders was higher than the effect of other additives such as tricalcium phosphate and glycerol monostearate.

Raspberry foams with three different concentrations of MD were studied, in order to understand its influence in the stability of raspberry foams, during storage.

Before drying, the 5%, 15% and 30% MD foams had a moisture content of  $80.5 \pm 0.3\%$ ,  $74.7 \pm 1.6\%$  and  $66.8 \pm 0.1\%$  (w.b), respectively. As expected, the highest concentration of MD contributed to the lowest moisture content, and therefore the shortest drying time, as similarly obtained by (Ozcelik et al., 2019).

After drying, the lowest residual moisture content was observed in the 30% MD foam and the highest in the 5% MD foam (Figure 17). These results were expected since addition of a higher amount of MD, increased the total solid content and therefore reduced the moisture content of samples (Quek et al., 2007). However, during storage, the RMC and  $a_w$  values of the 15% and 30% MD samples increased, until reaching similar values as the 5% MD foam. This last foam (5% MD) showed constant values during all storage period (Figures 17 and 18). At a constant temperature, the RMC of food can change until it comes into an equilibrium with the relative humidity of the storage atmosphere (Fellows, 2009a). This could be a reason for the increase in the RMC and  $a_w$  of the 15% and 30% MD foams.

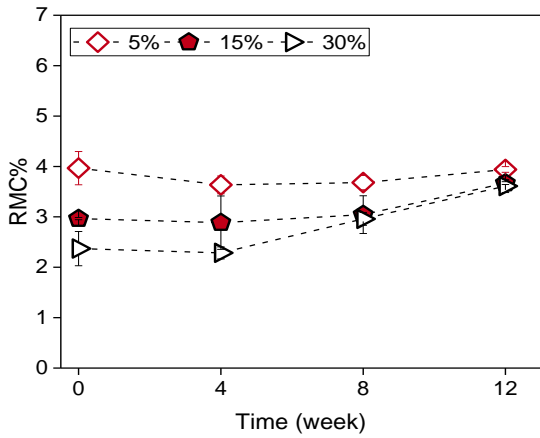


Figure 17 - Influence of MD concentration in the RMC during storage at 37 °C. Vacuum-packed samples.

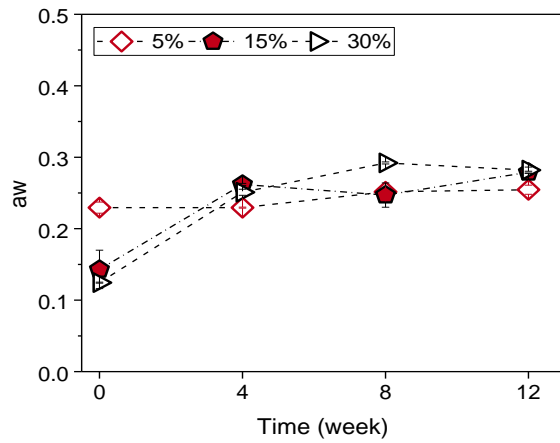


Figure 18 - Influence of MD concentration in the water activity during storage at 37 °C. Vacuum-packed samples.

The hardness of foams depending on the MD concentration is presented in Figure 19. As expected, the hardness increased with the increasing maltodextrin, since the foams with higher amount of this compound presented less moisture content. Although there was a slight increase in the moisture content of the 15 and 30% MD foams, the hardness of all samples did not present significant changes during storage ( $p > 0.05$ ).

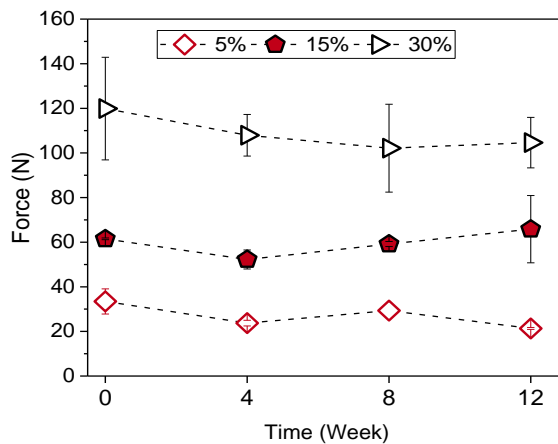


Figure 15 - Influence of MD concentration on the hardness of foams, during storage at 37 °C. Vacuum-packed samples.

The influence of MD concentration on the color parameters of the foams is present in Figure 20. All samples presented the same value of yellowness after drying and during storage. It was observed that the 15% and 30% MD foams maintained their color after 12 weeks of storage, presenting a total color difference only visible with a trained eye (Table 10).

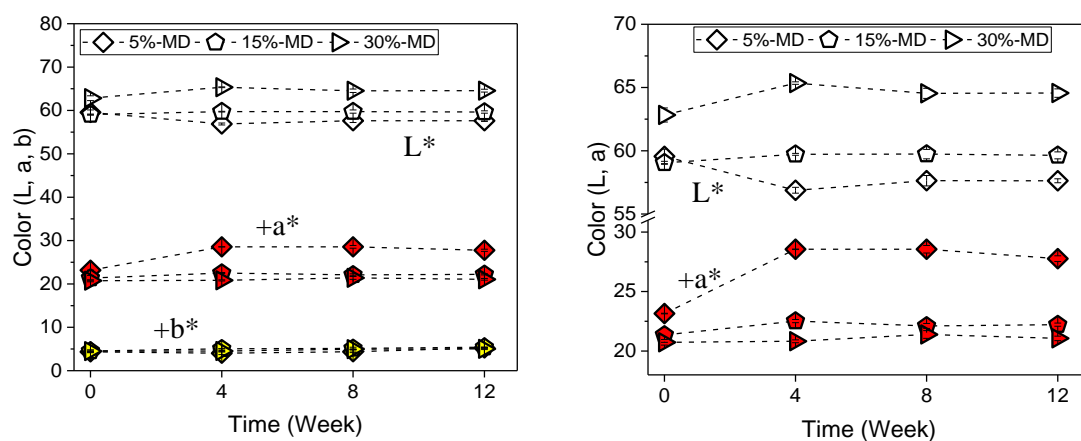


Figure 16 - Influence of MD concentration in the color. On the left, overall view of color parameter L,a,b. On the right, graph focusing on the brightness (L\*) and redness (+a\*). Vacuum-packed samples, stored under 37 °C.

On the other hand, the increase of redness from the 5% MD foam resulted in an obvious difference of color after 12 weeks of storage (Table 10). This could be related to the fact that these samples presented more amount of raspberry puree and less percentage of additives. As the puree is the component responsible for the red coloration of samples, it was expected that the 5% MD foam was more vulnerable for changes in redness than the other foams.

Table 10 - Influence of MD concentration in the total color difference ( $\Delta E$ ) after 12 weeks of storage at 37 °C. Reference to week 0. Vacuum-packed samples (Consult Table 7 for  $\Delta E$  meaning).

Sample	$\Delta E$		
	Week 4	Week 8	Week 12
<b>5% MD</b> , 5% PPI, 2.5% P	6.04±0.10	5.74±0.44	5.08±0.30
<b>15% MD</b> , 5% PPI, 2.5% P	1.44±0.08	1.25±0.05	1.380±0.003
<b>30% MD</b> , 5% PPI, 2.5% P	2.53±0.08	1.92±0.23	1.86±0.23

The influence of maltodextrin concentration on the anthocyanins and vitamin C retention can be consulted in Figure 21 and 22, respectively.

After drying, the total anthocyanins amount of the 5, 15 and 30% MD foams, was 3430.4±50.2, 1048.1±49.3 and 694.75±3.7 µg/g sample, respectively. As expected, the total anthocyanins value was higher in the samples with less addition of powder per sample. Contrary to what was expected, the samples with the lowest MD concentrations were not the ones containing higher initial AA values. The initial AA amounts for the 5, 15 and 30% MD foams, respectively, were 0.43±0.02, 0.56±0.01 and 0.334±0.001 mg/g sample.

During storage, it can be observed that the stability of anthocyanins and total ascorbic acid retention increased with the increasing MD. Moreover, Moser et al. (2017) also reported that a higher amount of MD in grape juice powder could prevent the transformation of the ACN to other less stable forms, due to the complexing of the dextrans with the flavylium cation form of the anthocyanins.

Although the 30% MD foam presented the highest stability, the difference between the ACN retention of this foam and the 15% MD one was not significant ( $p > 0.05$ ). The fact that the 5% MD foam presented the lowest ACN and AA retention during storage also correlates with the increasing of redness previously mentioned. According to Mishra et al. (2017), the increase in  $a^*$  could be explained due to oxidation. Hence, Hayashi et al. (1985) observed the formation of a red pigment when studied mixtures of ascorbic acid with proteins at low moisture content and high temperatures.

After 12 weeks, the total ACN retention of the 5, 15 and 30% MD foams were  $70.6 \pm 3.2\%$ ,  $86.5 \pm 0.4\%$  and  $87.1 \pm 0.9\%$ , respectively. Even with higher retention, the 30% MD foam presented less anthocyanin concentration ( $605.2 \pm 6.6 \mu\text{g/g}$  sample) than the 5% MD foam ( $2420.5 \pm 108.7 \mu\text{g/g}$  sample), after the storage period, due to the higher initial ACN concentration of the 5% MD foam. However, it was observed that the decrease in the ACN retention in the 5% MD foam was more accentuated than the others. Therefore, it is assumed that when subjected to a longer storage period, this foam would end up expressing a lower concentration of anthocyanins than the others.

After storage, the total vitamin C retention was  $50.4 \pm 0.2\%$ ,  $68.7 \pm 0.8\%$  and  $73.9 \pm 2.0\%$  for the 5, 15 and 30% MD foams, respectively. In this case, the highest AA concentration, after 12 weeks, was found in the 15% MD foam ( $0.387 \pm 0.004 \text{ mg/g}$  sample), which was expected, as this foam presented the highest initial AA concentration.

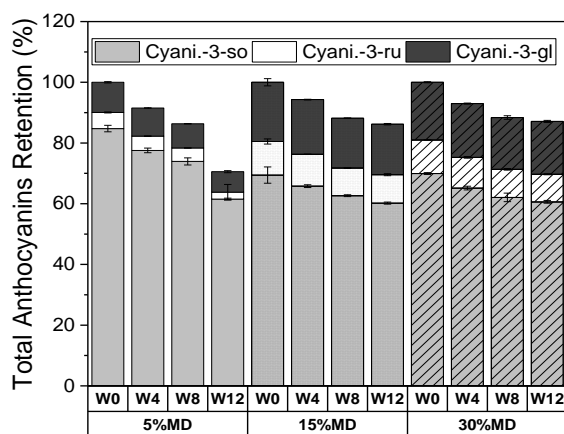


Figure 21 - Influence of MD concentration on the retention of ACN during storage at 37 °C. Vacuum-packed samples.

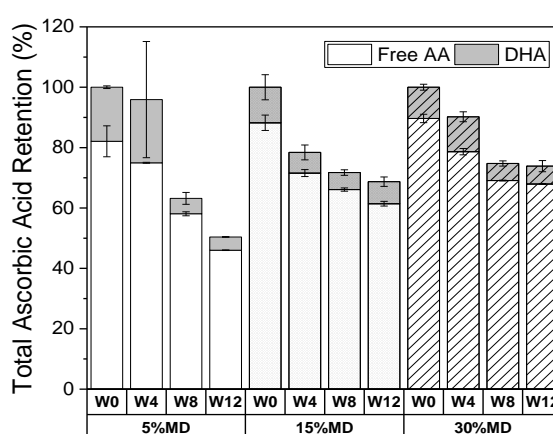


Figure 22 - Influence of MD concentration on the retention of AA during storage at 37 °C. Vacuum-packed samples.

As a summary, the relation between the MD concentration and the stability of foams, during storage, varied for the different studied parameters.

While the 5% MD foam presented higher stability for the moisture content and water activity parameters, the 15 and 30% presented similarly higher stability in the color and retention of ACN and AA. However, further studies should be performed to confirm if, after a longer storage time, the addition of 30% MD could result in higher anthocyanin concentration

than the 5% MD due to the higher retention obtained with higher maltodextrin concentration. Considering the vitamin C content, the 15% MD foam presented the best relation between quantity of ascorbic acid per gram of sample and retention during storage.

Moreover, the varying maltodextrin concentration did not have an influence in the hardness stability of raspberry foams.

## 5.4 Influence of storage temperature

Temperature is an important factor to consider during storage of food due to its influence in degradation reactions and loss of nutritive compounds (Fellows, 2009a; Taoukis and Giannakourou, 2004).

In the previous sections, the results were shown for a storage under 37 °C, which is considered a reference temperature for accelerated shelf-life studies (Labuza and Schmidl, 1985). In order to study the effect of temperature in the storage stability of the foams, the 15% MD foam was also stored at 20 °C.

Figures 23 and 24 show the results obtained for the residual moisture content and water activity, respectively, during storage. The RMC of the foam stored at 20 °C, after 12 weeks of storage, was  $3.8 \pm 0.6\%$ . It can be observed that this value was similar to the initial one (week 0), which was  $3.8 \pm 0.6\%$ . It was expected a stable RMC value during all the storage period. However, the high moisture content obtained after 8 weeks of storage could be explained due to a possible absorption of water vapour from the atmosphere while opening the aluminium bags or during sample conversion to powder.

On the other hand, the increase in moisture content of the foam stored at 37 °C was obtained during all the storage period.

The  $a_w$  values were similar in both foams, except during the last 4 weeks of storage, where a slight increase of water activity in the 37 °C foam was noticed ( $p < 0.05$ ).

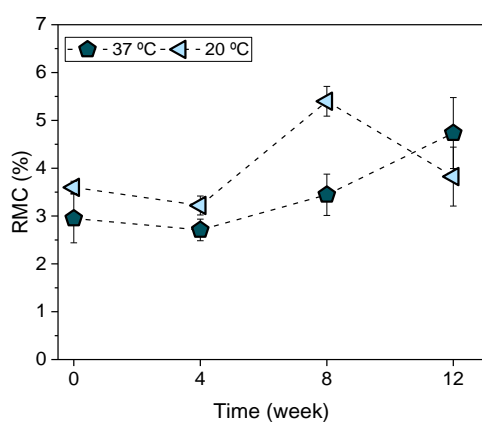


Figure 17 - Influence of storage temperature in the RMC of 15% MD MWFD foam. Vacuum-packed samples.

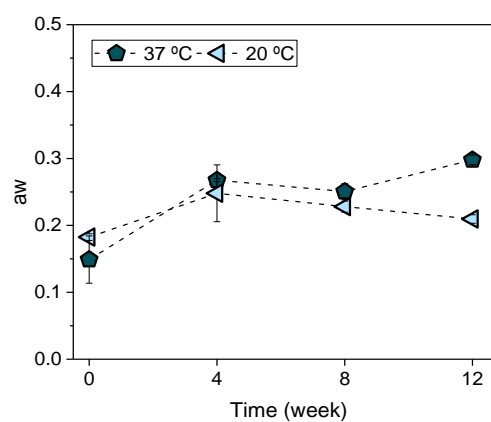


Figure 18 - Influence of storage temperature in the  $a_w$  of 15% MD MWFD foam. Vacuum-packed samples.



Regarding the influence of temperature on the color stability of foams, it can be observed that when stored at 37 °C, the foam was more stable during storage (Figure 25). Under 20 °C, the decrease in brightness ( $L^*$ ) was not significant ( $p > 0.05$ ). However, the foam suffered a significant increase ( $p < 0.05$ ) in redness ( $+a^*$ ). This result was not expected since in the literature was found that storage at lower temperatures were better for color retention than higher temperatures, which causes non-enzymic browning (Ersus and Yurdagel, 2007; Lovrić et al., 1970; Ochoa et al., 1999).

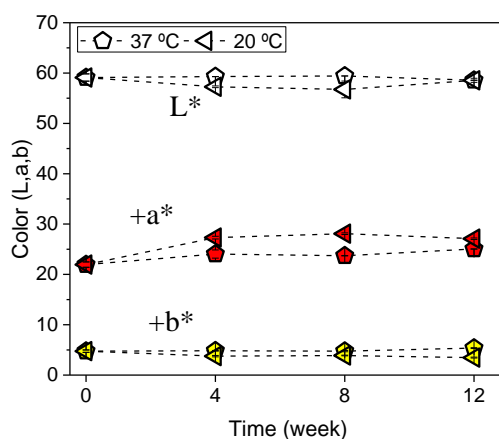


Figure 19 - Influence of storage temperature in the color of 15% MD foam. Vacuum-packed samples.

After 12 weeks, the total color difference (Table 11) was obvious to an untrained eye ( $\Delta E = [2-3.5]$ ) for the foam stored at 37 °C and obvious for the foam stored at 20 °C ( $\Delta E = [3.5-6]$ ) (Lübbe, 2013).

Table 11 - Influence of T °C in the total color difference ( $\Delta E$ ) after 12 weeks of storage. 15 % MD foam, vacuum-packed samples (Consult Table 7 for  $\Delta E$  meaning). Reference to week 0.

Sample	$\Delta E$		
	Week 4	Week 8	Week 12
37 °C	2.12±0.801	1.80±0.02	3.21±0.02
20 °C	5.75±0.170	6.71±0.73	5.34±0.21

The values obtained for the color do not corroborate with the ones obtained for the anthocyanins retention (Figure 26). The graph shows that the foam stored at 20 °C had no losses in the total anthocyanin content, while at 37 °C the retention of ACN was  $86.2 \pm 0.4\%$ . In fact, temperature is the most significant factor for anthocyanins stability during storage since they are highly thermal sensitive (Cemeroglu et al., 1994).

For the vitamin C retention (Figure 27), it can also be concluded that a storage temperature of 20 °C was more favourable to maintain this compound. After 12 weeks of storage, while the foam maintained at 37 °C had a retention of  $65.1 \pm 0.2\%$ , the foam stored at 20 °C had a total retention of the compound ( $110.2 \pm 12.9\%$ ). However, it can be observed that after 4 and 8 weeks

of storage, a decrease in the DHA was observed. Although the same dried sample is divided in four for the four moments of analysis, it is possible that due to the occurrence of hotspots during MWFD, the samples analysed in the 4 and 8 weeks had different initial composition of AA.

Moreover, although all samples were produced under the same conditions, the foam utilized for the storage at 20 °C presented, at week 0, different values of the three cyanidins, DHA and free ascorbic acid. This could be one of the reasons for the differences in the storage stability between foams. To have a better understanding about the influence of temperature in the storage stability, further studies should be performed, where the initial nutritional composition of foams is the same.

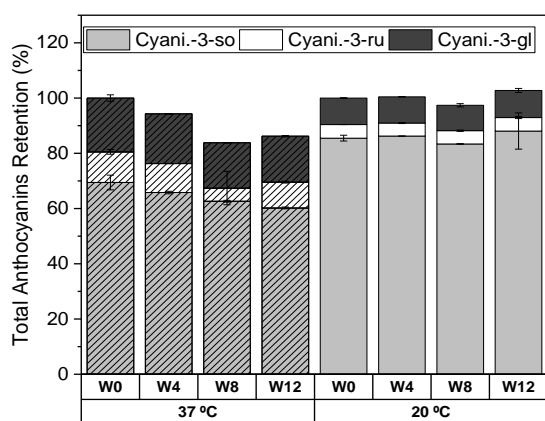


Figure 26 - Influence of storage temperature on the ACN retention of the 15% MD foam. Vacuum-packed samples.

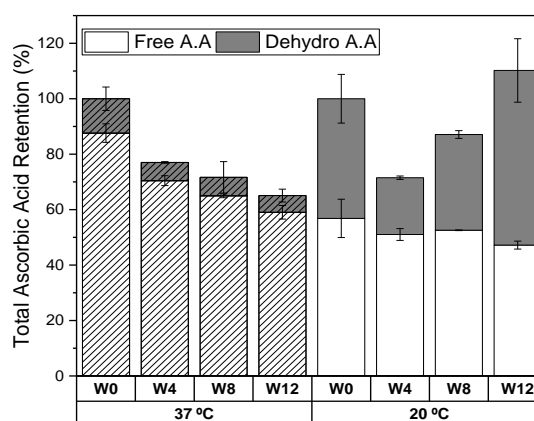


Figure 27 - Influence of storage temperature on the total AA retention of the 15% MD foam. Vacuum-packed samples.

To sum up, as found in the literature, the storage temperature had an impact in the stability of foams. In general, the foam expressed more stability when stored at 20 °C. In experiences with storage of bayberry powders, Fang and Bhandari (2011) demonstrated a decreased in ACN of maximum 37% at 25 °C, while at 40 °C, the declines in this compound were 94%.

## 5.5 Influence of storage relative humidity

Relative humidity is an important factor that has influence on storage, since the RH of food tend to reach an equilibrium with the relative humidity of the storage atmosphere (Fellows, 2009a), which can change the moisture content values.

Therefore, the 5%, 15% and 30% MD foams were stored under relative humidity values of 11%, 22% and 33%, at room temperature. The raspberry splits were also stored under the same conditions as a comparison sample. The results of samples after drying and after 12 weeks of storage under these conditions are present in Table 12.

Although the water activity of samples reached higher levels than the water activity of the environment salt solutions inside the chambers, it can be observed that, in general, the moisture content and water activity of samples increased with the increasing relative humidity. One

possible explanation for the fact that water activity of samples, after 12 weeks of storage, had not reached the same values of each environment salt solution could be that the chambers were not completely sealed which caused a difference in the relative humidity inside the chambers.

Table 12 - Results of the quality parameters (RMC,  $a_w$ , ACN and AA content) of raspberry and foam after MWFD (week 0) and after 12 weeks of storage under different values of relative humidity ( $a_w = 0.11$ ; 0.22; 0.33).

		Week 0	$a_w = 0.11$	$a_w = 0.22$	$a_w = 0.33$	
RMC (%)	<b>Raspberry splits</b>	3.79 ± 0.33	5.43 ± 0.04	6.36 ± 0.85	7.54 ± 0.06	
	<b>Foam</b>	<b>5% MD</b>	3.17 ± 0.11	2.93 ± 0.28	4.66 ± 0.21	5.61 ± 0.42
		<b>15% MD</b>	3.30 ± 0.14	2.60 ± 0.10	4.26 ± 0.22	4.74 ± 0.01
		<b>30% MD</b>	1.55 ± 0.30	2.81 ± 0.29	3.60 ± 0.30	4.90 ± 0.25
Water activity	<b>Raspberry splits</b>	0.217 ± 0.044	0.253 ± 0.002	0.319 ± 0.003	0.308 ± 0.006	
	<b>Foam</b>	<b>5% MD</b>	0.176 ± 0.009	0.216 ± 0.009	0.281 ± 0.006	0.349 ± 0.006
		<b>15% MD</b>	0.149 ± 0.035	0.242 ± 0.007	0.339 ± 0.004	0.382 ± 0.001
		<b>30% MD</b>	0.056 ± 0.001	0.224 ± 0.001	0.336 ± 0.006	0.396 ± 0.001
Total Anthocyanins Retention (%)	<b>Raspberry splits</b>	100	81.2 ± 7.5	74.3 ± 2.9	71.4 ± 5.7	
	<b>Foam</b>	<b>5% MD</b>	100	95.5 ± 1.2	93.4 ± 0.4	89.5 ± 0.5
		<b>15% MD</b>	100	55.5 ± 0.2	65.4 ± 1.3	51.7 ± 0.3
		<b>30% MD</b>	100	95.0 ± 0.4	92.5 ± 0.1	89.9 ± 0.4
Total Ascorbic Acid Retention (%)	<b>Raspberry splits</b>	100	72.3 ± 6.9	67.4 ± 1.9	70.4 ± 0.1	
	<b>Foam</b>	<b>5% MD</b>	100	98.9 ± 0.2	88.4 ± 2.0	71.4 ± 0.3
		<b>15% MD</b>	100	76.9 ± 0.4	68.6 ± 4.7	70.2 ± 1.5
		<b>30% MD</b>	100	82.1 ± 0.5	76.4 ± 5.3	73.9 ± 0.1

Regarding the anthocyanins and vitamin C retention during storage, it can as well be verified, in Table 12, that in the majority of samples, the retention of these compounds decreased with the increasing relative humidity, as expected. In the literature was found that in studies with bayberry powders, Fang and Bhandari (2011) showed that the higher the  $a_w$  of the storage environment, the higher the ACN losses. Moreover, Uddin et al. (2002) also concluded that in freeze drying guava, the degradation of vitamin C increased with the increasing water activity of the environment.

## 5.6 Overview

As a final step of the experiment, a 15% MD foam stored at 4 °C under vacuum and the same foam stored only in brown flasks (no vacuum) at the same temperature were analysed (Table 12) in order to clarify the influence of the storage temperature and vacuum on foams. The remaining values present in the Table 13 were previously showed in this Section 5. The

values present in the column of 20 °C *non-vacuumed* are the results obtained for the storage under a RH of 33%, mentioned in Section 5.5.

Table 13 - Retention of total anthocyanins and ascorbic acid of 15% MD foam, after 12 weeks of storage under different conditions.

	<b>4 °C non- vacuumed</b>	<b>4 °C vacuumed</b>	<b>20 °C non- vacuumed</b>	<b>20 °C vacuumed</b>	<b>37 °C vacuumed</b>
<b>ACN retention (%)</b>	89.4±1.6	99.9±1.2	51.7±0.3	102.8±7.7	86.2±0.4
<b>AA retention (%)</b>	81.73±0.01	94.9±1.8	70.2±1.5	110.2±12.9	65.1± 0.2

As an overview, it can be concluded that the storage condition which enable a higher retention of anthocyanins and vitamin C were at 4 °C and 20 °C, when the foam was stored under vacuum. However, for application in the snack industry, storage at 4 °C is not commonly used.

It was possible to conclude that temperature and presence of oxygen were important factors to have in mind for foam storage since at 37 °C and in samples stored with the presence of oxygen, the degradation of ACN and total ascorbic acid was more accentuated. In fact, Jackman et al. (1987b) expressed that oxygen is the most deteriorative agent for anthocyanins and its absence contributes to the decrease of the negative effect of temperature on anthocyanins.

## 6 Conclusion

In this work, the stability of raspberry foams was evaluated regarding the moisture content, water activity, color, texture and anthocyanins and vitamin C, during storage under different temperature (4, 20 and 37 °C) and relative humidity (11, 22 and 33%). Foam samples were produced using 5, 15, and 30% (w/w) of maltodextrin and raspberry splits, puree and non-foamed solutions were also produced and stored to compare the results. All samples were dried using microwave freeze-drying and freeze-drying.

MWFD demonstrated to achieve at least the same foam quality than FD after drying and over storage regarding the studied quality parameters, constituting a good option to replace conventional FD due to lower drying times.

The addition of MD, PPI and P proved to improve the stability of foamed and non-foamed solutions during storage when compared to raspberry splits and puree, which were produced without additives. Hence, after 12 weeks of storage at 37 °C, solution and foam retained, respectively, 61% and 62% more vitamin C and 81% and 78% more anthocyanins than raspberry. The additives also contributed for a better color maintenance over storage. Although, raspberry splits suffered the highest increase in RMC and  $a_w$ , all the samples could still be considered microbiologically safe.

Both solution and foam demonstrated similar results in most of the studied quality parameters which indicates that the foaming process was not a relevant parameter in storage stability. However, for use as a snack, foams present a better sensory acceptance.

Regarding the MD concentration of foams, while the 5% MD foam presented higher stability for RMC and  $a_w$  parameters, the 15% and 30% presented similarly higher stability in the color and in retention of ACN (around 87%) and total AA (around 70%). On the other hand, the varying maltodextrin concentration did not have an influence in the hardness stability of raspberry foams.

Furthermore, high values of storage temperature, RH and the presence of oxygen had a negative impact in the studied quality parameters. Foam stored under vacuum at 20 °C presented the most satisfactory results for retention of ACN and total AA, around 100% retention.

To conclude, raspberry foams demonstrated improved storage stability when compared to the dehydrated fruit itself and the fruit puree, which makes these foams a strong potential snack for the food industry, in the future.

## 7 Future work and limitations

The main limitations endured in the present work included equipment availability, such as the Karl Fischer-compact-titrator and the microwave freeze-drier. The difficulties in scaling-up the process of producing foams in the beginning of the experience. Finally, the short time available was as well a limitation for the obtained results, since a great number of samples had to be produced in a short time, to still be stored during the next 12 weeks. Otherwise, it would be possible to repeat the experiment and obtain more statistically reliable results.

For future work, it would be interesting to extend the storage time to clarify some of the trends obtained in this work such as whether the addition of 30% MD in foams could result in higher anthocyanin concentration in long term storage than the 5% MD foam.

Additionally, as in some samples the water content increased, measurements of the differential scanning calorimetry (DSC) to determine the  $T_g$  of samples after the storage period are required in order to evaluate if the  $T_g$  decreased over storage.

Moreover, the scaling-up of foam production should be optimized and an energy consumption balance should be performed.

Although results are not presented in this work, during the experiment, raspberry splits, puree, solution and foam samples were produced and sent to several food industry companies in order to obtain sensory analysis results. The results showed a good acceptance of the product, as a snack, from the consumer. Therefore, the production of foams from different fruits could be relevant for the food industry. At the end of the experiment, a preliminary development of mango, banana and melon foams was performed. These foams are presented in Figure H1 in Appendix.

Other interesting options for the next steps are the study of different types of packaging materials and the analysis of the total antioxidant capacity of raspberry foams, which represents a great interest for the food industry.

## 8 References

- Abbasi, S., Azari, S., (2009). Novel microwave–freeze drying of onion slices. *International journal of food science & technology*, 44(5), 974-979.
- Acevedo, N., Schebor, C., Buera, M.d.P., (2006). Water–solids interactions, matrix structural properties and the rate of non-enzymatic browning. *Journal of Food Engineering*, 77(4), 1108-1115.
- Adams, J., (1973). Thermal degradation of anthocyanins with particular reference to the 3-glycosides of cyanidin in acidified aqueous solution at 100 °C. *Journal of the science of food and agriculture*, 24(7), 747-762.
- Mettler-Toledo AG, (2012). Introduction to the Karl Fischer Titration Global. *MarCom Switzerland*. Accessed in 10/05/2018, from <https://www.mt.com/dam/MT-NA/KF/KarlFischer-Guide4.pdf>.
- Bell, L.N., (1995). Kinetics of non-enzymatic browning in amorphous solid systems: distinguishing the effects of water activity and the glass transition. *Food Research International*, 28(6), 591-597.
- Bell, L.N., Hageman, M.J., (1994). Differentiating between the Effects of Water Activity and Glass Transition Dependent Mobility on a Solid State Chemical Reaction: Aspartame Degradation. *Journal of agricultural and food chemistry*, 42(11), 2398-2401.
- Berk, Z., (2013). Chapter 23 - Freeze Drying (Lyophilization) and Freeze Concentration. *Food Process Engineering and Technology (Second Edition)*. Academic Press, San Diego, 567-581.
- Betts, G.D., Walker, S.J., (2004). Chapter 10 - Verification and validation of food spoilage models. *Understanding and Measuring the Shelf-life of Food*. Woodhead Publishing, 184-217.
- Bobinaitė, R., Viškelis, P., Venskutonis, P.R., (2012). Variation of total phenolics, anthocyanins, ellagic acid and radical scavenging capacity in various raspberry (*Rubus spp.*) cultivars. *Food Chemistry*, 132(3), 1495-1501.
- Brett, J.A., (2010). The Political-Economics of Developing Markets versus Satisfying Food Needs. *Food and Foodways* 18(1-2), 28-42.
- Brouillard, R., (2012). Chapter 1 - Chemical structure of anthocyanins, *Anthocyanins as Food Colors*. Elsevier Science, 1-38.
- Bruijn, J., Rivas, F., Rodriguez, Y., Loyola, C., Flores, A., Melin, P., Borquez, R., (2015). Effect of Vacuum Microwave Drying on the Quality and Storage Stability of Strawberries. *Journal of Food Processing and Preservation*, 40(5), 1104-1115.
- Brygidyr, A.M., Rzepecka, M.A., McConnell, M.B., (1977). Characterization and Drying of Tomato Paste Foam by Hot Air and Microwave Energy. *Canadian Institute of Food Science and Technology Journal*, 10(4), 313-319.
- Buera, P., Schebor, C., Elizalde, B., (2005). Effects of carbohydrate crystallization on stability of dehydrated foods and ingredient formulations. *Journal of Food Engineering*, 67(1), 157-165.
- Cai, Y., Corke, H., (2000). Production and properties of spray-dried amaranthus betacyanin pigments. *Journal of food science*, 65(7), 1248-1252.
- Carvalho, L.M.T., Nogueira, T.Y.K., Mauro, M.A., Gomez-Alonso, S., Gomes, E., Da-Silva, R., Hermosin-Gutierrez, I., Lago-Vanzela, E.S., (2017). Dehydration of jambolan [*Syzygium cumini* (L.)] juice during foam mat drying: Quantitative and qualitative changes of the phenolic compounds. *Food research international* (Ottawa, Ont.), 102, 32-42.
- Cemeroglu, B., Velioglu, S., Isik, S., (1994). Degradation kinetics of anthocyanins in sour cherry juice and concentrate. *Journal of food science*, 59(6), 1216-1218.
- Četojević-Simin, D.D., Velićanski, A.S., Cvetković, D.D., Markov, S.L., Četković, G.S., Tumbas Šaponjac, V.T., Vulić, J.J., Čanadanović-Brunet, J.M., Djilas, S.M., (2015). Bioactivity of Meeker and Willamette raspberry (*Rubus idaeus* L.) pomace extracts. *Food Chemistry*, 166, 407-413.
- Colin-Henrion, M., Mehinagic, E., Renard, C., Richomme, P., Jourjon, F., (2009). From apple to applesauce: Processing effects on dietary fibres and cell wall polysaccharides. *Food Chemistry*, 117(2), 254-260.

- Cortés, M., Chiralt, A., Suarez, H., (2009). Influence of storage conditions on freeze-dried apple fortified with vitamin E. *Vitae*, 16(1), 31-41.
- Cui, Z.-W., Li, C.-Y., Song, C.-F., Song, Y., (2008). Combined Microwave-Vacuum and Freeze Drying of Carrot and Apple Chips. *Drying Technology*, 26(12), 1517-1523.
- Daravingas, G., Cain, R., (1965). Changes in the anthocyanin pigments of raspberries during processing and storage. *Journal of food science*, 30(3), 400-405.
- Darniadi, S., Ho, P., Murray, B.S., (2018). Comparison of blueberry powder produced via foam-mat freeze-drying versus spray-drying: evaluation of foam and powder properties. *Journal of the science of food and agriculture*, 98(5), 2002-2010.
- de Ancos, B., Gonzalez, E., Cano, M.P., (1999). Differentiation of raspberry varieties according to anthocyanin composition. *Zeitschrift für Lebensmitteluntersuchung und-Forschung A*, 208(1), 33-38.
- de Ancos, B., Gonzalez, E.M., Cano, M.P., (2000a). Ellagic acid, vitamin C, and total phenolic contents and radical scavenging capacity affected by freezing and frozen storage in raspberry fruit. *Journal of agricultural and food chemistry*, 48(10), 4565-4570.
- de Ancos, B., Ibañez, E., Reglero, G., Cano, M.P., (2000b). Frozen Storage Effects on Anthocyanins and Volatile Compounds of Raspberry Fruit. *Journal of agricultural and food chemistry*, 48(3), 873-879.
- Dennison, D., Kirk, J., (1978). Oxygen effect on the degradation of ascorbic acid in a dehydrated food system. *Journal of food science*, 43(2), 609-618.
- Dickinson, E., Galazka, V.B., (1991). Emulsion stabilization by ionic and covalent complexes of  $\beta$ -lactoglobulin with polysaccharides. *Food Hydrocolloids*, 5(3), 281-296.
- Duan, X., Zhang, M., Mujumdar, A.S., (2007). Studies on the Microwave Freeze Drying Technique and Sterilization Characteristics of Cabbage. *Drying Technology*, 25(10), 1725-1731.
- Duan, X., Zhang, M., Mujumdar, A.S., Wang, S., (2010). Microwave freeze drying of sea cucumber (*Stichopus japonicus*). *Journal of Food Engineering*, 96(4), 491-497.
- Eisner, M.D., Jeelani, S.A.K., Bernhard, L., Windhab, E.J., (2007). Stability of foams containing proteins, fat particles and nonionic surfactants. *Chemical Engineering Science*, 62(7), 1974-1987.
- Ekpong, A., Phomkong, W., Onsaard, E., (2016). The effects of maltodextrin as a drying aid and drying temperature on production of tamarind powder. *International Food Research Journal*, 23(1), 300-308.
- Ersus, S., Yurdagel, U., (2007). Microencapsulation of anthocyanin pigments of black carrot (*Daucus carota L.*) by spray drier. *Journal of Food Engineering*, 80(3), 805-812.
- Fang, Z., Bhandari, B., (2011). Effect of spray drying and storage on the stability of bayberry polyphenols. *Food Chemistry*, 129(3), 1139-1147.
- Farahnaky, A., Mansoori, N., Majzoobi, M., Badii, F., (2016). Physicochemical and sorption isotherm properties of date syrup powder: Antiplasticizing effect of maltodextrin. *Food and Bioproducts Processing*, 98, 133-141.
- Fazaeli, M., Emam-Djomeh, Z., Kalbasi Ashtari, A., Omid, M., (2012). Effect of spray drying conditions and feed composition on the physical properties of black mulberry juice powder. *Food and Bioproducts Processing*, 90(4), 667-675.
- Fellows, P.J., (2009a). Chapter 1 - Properties of food processing. *Food Processing Technology (Third Edition)*. Woodhead Publishing, 11-95.
- Fellows, P.J., (2009b). Chapter 20 - Dielectric, ohmic and infrared heating. *Food Processing Technology (Third edition)*. Woodhead Publishing, 581-609.
- Fellows, P.J., (2009c). Chapter 23 - Freeze drying and freeze concentration. *Food Processing Technology (Third Edition)*. Woodhead Publishing, 687-699.
- Ferrari, C.C., Marconi Germer, S.P., Alvim, I.D., de Aguirre, J.M., (2013). Storage stability of spray-dried blackberry powder produced with maltodextrin or gum arabic. *Drying Technology*, 31(4), 470-478.



- Figiel, A., (2009). Drying kinetics and quality of vacuum-microwave dehydrated garlic cloves and slices. *Journal of Food Engineering*, 94(1), 98-104.
- Figuerola, F.E., (2007). Chapter 11 - Dehydration of berries. *Berry Fruit: Value-Added Products for Health Promotion*. CRC Press, 313-334.
- Franco, T.S., Perussello, C.A., Ellendersen, L.d.S.N., Masson, M.L., (2015). Foam mat drying of yacon juice: Experimental analysis and computer simulation. *Journal of Food Engineering*, 158, 48-57.
- Fu, L., Xu, B.-T., Xu, X.-R., Gan, R.-Y., Zhang, Y., Xia, E.-Q., Li, H.-B., (2011). Antioxidant capacities and total phenolic contents of 62 fruits. *Food Chemistry*, 129(2), 345-350.
- Gabas, A.L., Telis, V.R.N., Sobral, P.J.A., Telis-Romero, J., (2007). Effect of maltodextrin and arabic gum in water vapor sorption thermodynamic properties of vacuum dried pineapple pulp powder. *Journal of Food Engineering*, 82(2), 246-252.
- Gaukel, V., Siebert, T., Erle, U., (2017). Chapter 8 - Microwave-assisted drying, *The Microwave Processing of Foods (Second Edition)*. Woodhead Publishing, 152-178.
- Giacin, J., Hernandez, R., (1997). Factors affecting permeation, sorption, and migration processes in package-product systems. *Food storage stability*. CRC Press, 274-334.
- Gradinaru, G., Biliaderis, C.G., Kallithraka, S., Kefalas, P., Garcia-Viguera, C., (2003). Thermal stability of *Hibiscus sabdariffa L.* anthocyanins in solution and in solid state: effects of copigmentation and glass transition. *Food Chemistry*, 83(3), 423-436.
- Green, J.L., Angell, C.A., (1989). Phase relations and vitrification in saccharide-water solutions and the trehalose anomaly. *The Journal of Physical Chemistry*, 93(8), 2880-2882.
- Greenspan, L., (1977). Humidity fixed points of binary saturated aqueous solutions. *Journal of research of the national bureau of standards*, 81(1), 89-96.
- Gunasekaran, S., (1999). Pulsed microwave-vacuum drying of food materials. *Drying Technology*, 17(3), 395-412.
- Hammami, C., Floris, R., (1997). Determination of Freeze-drying Process Variables for Strawberries. *Journal of food engineering*, 32(2), 133-154.
- Hardy, Z., Jideani, V.A., (2015). Foam-mat drying technology: A review. *Critical Reviews in Food Science and Nutrition*, 57(12), 2560-2572.
- Hart, M.R., Graham, R.P., Ginnette, L.F., Morgan, A.I., (1963). Foams for foam-mat drying. *Food Technology*, 17(5), 1302-1304.
- Hartmann, A., Patz, C.-D., Andlauer, W., Dietrich, H., Ludwig, M., (2008). Influence of processing on quality parameters of strawberries. *Journal of agricultural and food chemistry*, 56(20), 9484-9489.
- Harvey, D., (2016). 9.4: Redox Titrations. *LibreTexts*. Accessed in 03/07/2018, from [https://chem.libretexts.org/LibreTexts/Northeastern/09%3A\\_Titrimetric\\_Methods/9.4%3A\\_Redox\\_Titrations](https://chem.libretexts.org/LibreTexts/Northeastern/09%3A_Titrimetric_Methods/9.4%3A_Redox_Titrations)
- Haseley, P., Oetjen, G.W., 2017. Chapter 1 - Foundations and Process Engineering. *Freeze-Drying*. Wiley, 1-165.
- Hayashi, T., Terao, A., Ueda, S., Namiki, M., (1985). Red Pigment Formation by the Reaction of Oxidized Ascorbic Acid and Protein in a Food Model System of Low Moisture Content. *Agricultural and Biological Chemistry*, 49(11), 3139-3144.
- Heigl, A., (2017). Influence of foam composition and microwave power on drying behavior and product quality of microwave freeze-dried raspberry foams (master thesis). *Wissenschaftszentrum Weihenstephan Für Ernährung, Landnutzung und Umwelt*. Technische Universität München (Freising).
- Heldman, D.R., Hartel, R.W., (1997). Chapter 8 - Dehydration. *Principles of Food Processing*. Springer US, 177-218.

- Herceg, Z., Režek, A., Lelas, V., Krešić, G., Franetović, M., (2007). Effect of carbohydrates on the emulsifying, foaming and freezing properties of whey protein suspensions. *Journal of Food Engineering*, 79(1), 279-286.
- Hua, T.C., Liu, B.L., Zhang, H., (2010). Chapter 2 - Fundamentals of Freeze-drying. *Freeze-Drying of Pharmaceutical and Food Products*. Elsevier Science, 18-54.
- Huang, L.-l., Zhang, M., Mujumdar, A.S., Lim, R.-x., (2011). Comparison of four drying methods for re-structured mixed potato with apple chips. *Journal of Food Engineering*, 103(3), 279-284.
- Huxsoll, C.C., Bolin, H.R., King, A.D., (1989). Physicochemical Changes and Treatments for Lightly Processed Fruits and Vegetables. *Quality Factors of Fruits and Vegetables*. American Chemical Society, 203-215.
- Hymavathi, T.V., Khader, V., (2005). Carotene, ascorbic acid and sugar content of vacuum dehydrated ripe mango powders stored in flexible packaging material. *Journal of Food Composition and Analysis*, 18(2), 181-192.
- Jackman, R., Yada, R., (2006). Functional Properties of Whey-Potato Protein Composite Blends in a Model System. *Journal of Food Science*, 53(5), 1427-1432.
- Jackman, R.L., Yada, R.Y., Tung, M.A., (1987a). A review: separation and chemical properties of anthocyanins used for their qualitative and quantitative analysis. *Journal of Food Biochemistry*, 11(4), 279-308.
- Jackman, R.L., Yada, R.Y., Tung, M.A., Speers, R.A., (1987b). Anthocyanins as food colorants - a review. *Journal of food biochemistry*, 11(3), 201-247.
- Jaya, S., Das, H., (2004). Effect of maltodextrin, glycerol monostearate and tricalcium phosphate on vacuum dried mango powder properties. *Journal of Food Engineering*, 63(2), 125-134.
- Jena, S., Das, H., (2012). Shelf life prediction of aluminum foil laminated polyethylene packed vacuum dried coconut milk powder. *Journal of Food Engineering*, 108(1), 135-142.
- Jiang, H., Zhang, M., Mujumdar, A.S., (2010). Physico-chemical changes during different stages of MFD/FD banana chips. *Journal of Food Engineering*, 101(2), 140-145.
- Johansson, F., (1993). Chapter 2 - Plastic packaging materials for foods. *Polymer packages for food-materials, concepts and interactions: a literature review*. SIK Institutet för livsmedelsforskning, Göteborg, Sverige, 5-16.
- Kadam, D.M., Rai, D.R., Patil, R., Wilson, R.A., Kaur, S., Kumar, R., (2011). Quality of fresh and stored foam mat dried Mandarin powder. *International journal of food science & technology*, 46(4), 793-799.
- Kader, F., Irmouli, M., Zitouni, N., Nicolas, J.-P., Metche, M., (1999). Degradation of cyanidin 3-glucoside by caffeic acid o-quinone - Determination of the stoichiometry and characterization of the degradation products. *Journal of agricultural and food chemistry*, 47(11), 4625-4630.
- Kalt, W., Forney, C.F., Martin, A., Prior, R.L., (1999). Antioxidant capacity, vitamin C, phenolics, and anthocyanins after fresh storage of small fruits. *Journal of agricultural and food chemistry*, 47(11), 4638-4644.
- Kandasamy, P., Varadharaju, N., Kalemullah, S., Maladhi, D., (2014). Optimization of process parameters for foam-mat drying of papaya pulp. *Journal of food science and technology*, 51(10), 2526-2534.
- Karim, A.A., Wai, C.C., (1999). Foam-mat drying of starfruit (*Averrhoa carambola* L.) purée - Stability and air drying characteristics. *Food Chemistry*, 64(3), 337-343.
- Kassim, A., Poette, J., Paterson, A., Zait, D., McCallum, S., Woodhead, M., Smith, K., Hackett, C., Graham, J., (2009). Environmental and seasonal influences on red raspberry anthocyanin antioxidant contents and identification of quantitative traits loci (QTL). *Molecular nutrition & food research*, 53(5), 625-634.
- Kessler, H.G., (2002). Food and bio process engineering: dairy technology. *Verlag A. Kessler*, (Munich, Germany). Accessed at 21/06/2018, from [http://verlag-kessler.de/joomla/images/pdf/inh\\_food.pdf](http://verlag-kessler.de/joomla/images/pdf/inh_food.pdf).

- Khoo, H.E., Azlan, A., Tang, S.T., Lim, S.M., (2017). Anthocyanidins and anthocyanins: colored pigments as food, pharmaceutical ingredients, and the potential health benefits. *Food & Nutrition Research*, 61(1), 1361779.
- Kirk, J., Dennison, D., Kokoczka, P., Heldman, D., (1977). Degradation of ascorbic acid in a dehydrated food system. *Journal of food science*, 42(5), 1274-1279.
- Kumar, P., Mishra, H.N., (2004). Storage stability of mango soy fortified yoghurt powder in two different packaging materials: HDPP and ALP. *Journal of Food Engineering*, 65(4), 569-576.
- Labuza, T.P., Schmidl, M.K., (1985). Accelerated shelf-life testing of foods. *Food technology (USA)*, 9(2), 57-62.
- Lee, J.C., Timasheff, S.N., (1981). The stabilization of proteins by sucrose. *The Journal of biological chemistry*, 256(14), 7193-7201.
- Lin, T.M., D. Durance, T., Scaman, C.H., (1998). Characterization of vacuum microwave, air and freeze dried carrot slices. *Food Research International*, 31(2), 111-117.
- Lobo, F.A., Nascimento, M.A., Domingues, J.R., Falcão, D.Q., Hernanz, D., Heredia, F.J., de Lima Araujo, K.G., (2017). Foam mat drying of Tommy Atkins mango: Effects of air temperature and concentrations of soy lecithin and carboxymethylcellulose on phenolic composition, mangiferin, and antioxidant capacity. *Food Chemistry*, 221, 258-266.
- Løkra, S., Strætkvern, K.O., (2009). Industrial proteins from potato juice. A review. *Food*, 3(1), 88-95.
- Löschner, J., Kroh, L., Vogel, J., (1990). Chapter 1 - Ascorbic acid - A carbonyl component of non-enzymatic browning reactions. *Zeitschrift für Lebensmittel-Untersuchung und Forschung*, 191(4-5), 302-305.
- Lovrić, T., Sablek, Z., Bošković, M., (1970). Cis-trans isomerisation of lycopene and colour stability of foam-mat dried tomato powder during storage. *Journal of the science of food and agriculture*, 21(12), 641-647.
- Lübbe, E., (2013). Visuelle Abmusterung und Farbmessung. *Farbempfindung, Farbbeschreibung und Farbmessung*. Springer, 123-158.
- Markakis, P., (1982). Chapter 6 - Stability of Anthocyanins in Foods. *Anthocyanins As Food Colors*. Academic Press, 163-180.
- Markaris, P., Livingston, G.E., Fellers, C.R., (1957). Quantitative aspects of strawberry pigment degradation. *Journal of food science*, 22(2), 117-130.
- Mazur, S.P., Nes, A., Wold, A.-B., Remberg, S.F., Aaby, K., (2014). Quality and chemical composition of ten red raspberry (*Rubus idaeus L.*) genotypes during three harvest seasons. *Food Chemistry*, 160, 233-240.
- Mazza, G., Miniati, E., (1993). Anthocyanins in fruits, vegetables, and grains. *CRC Press (Boca Raton, Florida)*, 105.
- McGhie, T.K., Walton, M.C., (2007). The bioavailability and absorption of anthocyanins: towards a better understanding. *Molecular nutrition & food research*, 51(6), 702-713.
- Meda, V., Orsat, V., Raghavan, V., (2017). Chapter 2 - Microwave heating and the dielectric properties of foods. *The Microwave Processing of Foods (Second Edition)*. Woodhead Publishing, 23-43.
- Michalczyk, M., Macura, R., Matuszak, I., (2009). The effect of air-drying, freeze-drying and storage on the quality and antioxidant activity of some selected berries. *Journal of Food Processing and Preservation*, 33(1), 11-21.
- Miesle, T., Proctor, A., Lagrimini, L., (1991). Peroxidase activity, isoenzymes, and tissue localization in developing highbush blueberry fruit. *Journal of the American Society for Horticultural Science*, 116(5), 827-830.
- Milivojević, J., Rakonjac, V., Pristov, J.B., Maksimović, V., (2013). Classification and fingerprinting of different berries based on biochemical profiling and antioxidant capacity. *Pesquisa Agropecuária Brasileira*, 48(9), 1285-1294.

- Mishra, P., Brahma, A., Seth, D., (2017). Physicochemical, functionality and storage stability of hog plum (*Spondia pinnata*) juice powder produced by spray drying. *Journal of food and science technology*, 54(5), 1052-1061.
- Mitcham, E., (2007). Chapter 7 - Quality of berries associated with preharvest and postharvest conditions. *Berry Fruit: Value-Added Products for Health Promotion*. CRC Press, 207-228.
- Moser, P., Telis, V.R.N., de Andrade Neves, N., García-Romero, E., Gómez-Alonso, S., Hermosín-Gutiérrez, I., (2017). Storage stability of phenolic compounds in powdered BRS Violeta grape juice microencapsulated with protein and maltodextrin blends. *Food Chemistry*, 214, 308-318.
- Mosquera, L.H., Moraga, G., Martínez-Navarrete, N., (2012). Critical water activity and critical water content of freeze-dried strawberry powder as affected by maltodextrin and arabic gum. *Food Research International*, 47(2), 201-206.
- Nielsen, S., 2014. Chapter 32 - Color Analysis. *Food Analysis*. Springer US, 573-586.
- Nunes, M., Brecht, J., Morais, A., Sargent, S., (1998). Controlling temperature and water loss to maintain ascorbic acid levels in strawberries during postharvest handling. *Journal of food science*, 63(6), 1033-1036.
- Ochoa, M.R., Kessler, A.G., Vullioud, M.B., Lozano, J.E., (1999). Physical and Chemical Characteristics of Raspberry Pulp: Storage Effect on Composition and Color. *LWT - Food Science and Technology*, 32(3), 149-153.
- Ozcelik, M., Ambros, S., Heigl, A., Dachmann, E., Kulozik, U., 2019. Impact of hydrocolloid addition and microwave processing condition on drying behavior of foamed raspberry puree. *Journal of Food Engineering* 240, 83-98.
- Ozcelik, M., Püschner, P.A., (2017). Chapter 16 - Microwave plant requirements and process control for advanced applications. *The Microwave Processing of Foods (Second Edition)*. Woodhead Publishing, 350-380.
- Palamidis, N., Markakis, P., (1975). Stability of grape anthocyanin in a carbonated beverage. *Journal of food science*, 40(5), 1047-1049.
- Pantelidis, G.E., Vasilakakis, M., Manganaris, G.A., Diamantidis, G., (2007). Antioxidant capacity, phenol, anthocyanin and ascorbic acid contents in raspberries, blackberries, red currants, gooseberries and Cornelian cherries. *Food Chemistry*, 102(3), 777-783.
- Patras, A., Brunton, N.P., O'Donnell, C., Tiwari, B.K., (2010). Effect of thermal processing on anthocyanin stability in foods; mechanisms and kinetics of degradation. *Trends in Food Science & Technology*, 21(1), 3-11.
- PubChem, (2004). National Center for Biotechnology Information. Accessed at 10/05/2018 from <https://pubchem.ncbi.nlm.nih.gov/compound/14034151>.
- Püschner, P., Hoon, L.L.S., (2007). Microwave vacuum drying of fruits & vegetables. *PÜSCHNER GMBH + CO KG (Schwanewede, Germany)*. Accessed at 15/05/2018, from [http://www.pueschner.com/downloads/publications/2007\\_article\\_mw-vacuum-drying\\_hk2007-short\\_pap.pdf](http://www.pueschner.com/downloads/publications/2007_article_mw-vacuum-drying_hk2007-short_pap.pdf).
- Qadri, O.S., Srivastava, A.K., (2014). Effect of microwave power on foam-mat drying of tomato pulp. *Agricultural Engineering International: CIGR Journal*, 16(3), 238-244.
- Qadri, O.S., Srivastava, A.K., (2017). Microwave-Assisted Foam Mat Drying of Guava Pulp: Drying Kinetics and Effect on Quality Attributes. *Journal of food process engineering*, 40(1), e12295.
- Quek, S.Y., Chok, N.K., Swedlund, P., (2007). The physicochemical properties of spray-dried watermelon powders. *Chemical Engineering and Processing: Process Intensification*, 46(5), 386-392.
- Raharitsifa, N., Genovese, D., Ratti, C., (2006). Characterization of Apple Juice Foams for Foam-mat Drying Prepared with Egg White Protein and Methylcellulose. *Journal of Food Science*, 71(3), E142-E151.

- Rajkumar, P., Kailappan, R., Viswanathan, R., Raghavan, G.S.V., (2007). Drying characteristics of foamed alphonso mango pulp in a continuous type foam mat dryer. *Journal of Food Engineering*, 79(4), 1452-1459.
- Raju, P.S., Bawa, A.S., (2007). Food Additives in Fruit Processing. *Handbook of Fruits and Fruit Processing*, 145.
- Ralet, M.-C., Guéguen, J., (2001). Foaming Properties of Potato Raw Proteins and Isolated Fractions. *LWT - Food Science and Technology*, 34(4), 266-269.
- Rao, A.V., Snyder, D.M., (2010). Raspberries and human health: a review. *Journal of agricultural and food chemistry*, 58(7), 3871-3883.
- Ratti, C., (2001). Hot air and freeze-drying of high-value foods: a review. *Journal of Food Engineering*, 49(4), 311-319.
- Ratti, C., Kudra, T., (2006). Drying of Foamed Biological Materials: Opportunities and Challenges. *Drying Technology*, 24(9), 1101-1108.
- Robertson, G.L., (1998). Chapter 7- Metal packaging materials. *Food Packaging: Principles and Practice*. Taylor & Francis, 121-156.
- Rodríguez Patino, J.M., Carrera Sánchez, C., Rodríguez Niño, M.R., (2008). Implications of interfacial characteristics of food foaming agents in foam formulations. *Advances in Colloid and Interface Science*, 140(2), 95-113.
- Rommel, A., Heatherbell, D., Wrolstad, R., (1990). Red raspberry juice and wine: effect of processing and storage on anthocyanin pigment composition, color and appearance. *Journal of food science*, 55(4), 1011-1017.
- Roos, Y.H., (1995). Chapter 10 - Food Processing and Storage. *Phase Transitions in Foods*. Academic Press (San Diego), 313-347.
- Roudaut, G., Debeaufort, F., (2010). Chapter 6 - Moisture loss, gain and migration in foods and its impact on food quality. *Chemical Deterioration and Physical Instability of Food and Beverages*. Woodhead Publishing, 143-185.
- Ryynänen, S., (1995). The electromagnetic properties of food materials: A review of the basic principles. *Journal of Food Engineering*, 26(4), 409-429.
- Sablani, S.S., Shrestha, A.K., Bhandari, B.R., (2008). A new method of producing date powder granules: physicochemical characteristics of powder. *Journal of Food Engineering*, 87(3), 416-421.
- Sadowska, K., Andrzejewska, J., Klóska, Ł., (2017). Influence of freezing, lyophilisation and air-drying on the total monomeric anthocyanins, vitamin C and antioxidant capacity of selected berries. *International Journal of Food Science & Technology*, 52(5), 1246-1251.
- Saengrayap, R., Tansakul, A., Mittal, G.S., (2015). Effect of far-infrared radiation assisted microwave-vacuum drying on drying characteristics and quality of red chilli. *Journal of food science and technology*, 52(5), 2610-2621.
- Sagar, V.R., Kumar, R., (2014). Effect of drying treatments and storage stability on quality characteristics of bael powder. *Journal of food science and technology*, 51(9), 2162-2168.
- Salazar-González, C., San Martín-González, M.F., López-Malo, A., Sosa-Morales, M.E., (2012). Recent Studies Related to Microwave Processing of Fluid Foods. *Food and Bioprocess Technology*, 5(1), 31-46.
- Samaniego-Esquerro, C.M., Robertson, G.L., (1991). Development of a mathematical model for the effect of temperature and relative humidity on the water vapour permeability of plastic films. *Packaging Technology and Science*, 4(2), 61-68.
- Schiffmann, R., (1995). Chapter 11 - Microwave and Dielectric Drying. *Handbook of Industrial Drying*. CRC Press, 9780824789961.
- Schmidt, J.M., Damgaard, H., Greve-Poulsen, M., Larsen, L.B., Hammershøj, M., (2018). Foam and emulsion properties of potato protein isolate and purified fractions. *Food Hydrocolloids*, 74, 367-378.

- Seerangurayar, T., Manickavasagan, A., Al-Ismaili, A.M., Al-Mulla, Y.A., (2017). Effect of carrier agents on flowability and microstructural properties of foam-mat freeze dried date powder. *Journal of Food Engineering*, 215, 33-43.
- Sette, P., Franceschinis, L., Schebor, C., Salvatori, D., (2017). Fruit snacks from raspberries: influence of drying parameters on colour degradation and bioactive potential. *International Journal of Food Science & Technology*, 52(2), 313-328.
- Silva, M.A., Sobral, P.J.A., Kieckbusch, T.G., (2006). State diagrams of freeze-dried camu-camu (*Myrciaria dubia* (HBK) Mc Vaugh) pulp with and without maltodextrin addition. *Journal of Food Engineering*, 77(3), 426-432.
- Syamaladevi, R.M., Sablani, S.S., Tang, J., Powers, J., Swanson, B.G., (2009). State diagram and water adsorption isotherm of raspberry (*Rubus idaeus*). *Journal of Food Engineering*, 91(3), 460-467.
- Syamaladevi, R.M., Sablani, S.S., Tang, J., Powers, J., Swanson, B.G., (2011). Stability of anthocyanins in frozen and freeze-dried raspberries during long-term storage: in relation to glass transition. *Journal of food science*, 76(6), 414-421.
- Talcott, S.T., (2007). Chapter 2 - Chemical components of berry fruits. *Berry Fruit: Value-Added Products for Health Promotion*. CRC Press, 51-72.
- Taoukis, P.S., Giannakourou, M.C., (2004). Chapter 3 - Temperature and food stability: analysis and control. *Understanding and Measuring the Shelf-Life of Food*. Woodhead Publishing, 42-68 .
- Telis, V.R.N., Martínez-Navarrete, N., (2009). Collapse and Color Changes in Grapefruit Juice Powder as Affected by Water Activity, Glass Transition, and Addition of Carbohydrate Polymers. *Food Biophysics*, 4(2), 83-93.
- Thakur, B.R., Singh, R.K., Handa, A.K., Rao, M., (1997). Chemistry and uses of pectin—a review. *Critical Reviews in Food Science & Nutrition*, 37(1), 47-73.
- Thuwapanichayanan, R., Prachayawarakorn, S., Soponronnarit, S., (2008). Drying characteristics and quality of banana foam mat. *Journal of Food Engineering*, 86(4), 573-583.
- Thuwapanichayanan, R., Prachayawarakorn, S., Soponronnarit, S., (2012). Effects of foaming agents and foam density on drying characteristics and textural property of banana foams. *LWT - Food Science and Technology*, 47(2), 348-357.
- Tonon, R.V., Brabet, C., Hubinger, M.D., (2010). Anthocyanin stability and antioxidant activity of spray-dried açai (*Euterpe oleracea* Mart.) juice produced with different carrier agents. *Food Research International*, 43(3), 907-914.
- Torre, L.C., Barritt, B.H., (1977). Quantitative evaluation of Rubus fruit anthocyanin pigments. *Journal of food science*, 42(2), 488-490.
- Tumbas-Šaponjac, V.T., Četković, G.S., Stajčić, S.M., Vulić, J.J., Čanadanović-Brunet, J.M., Đilas, S.M., (2015). Optimization of the bioactive compounds content in raspberry during freeze-drying using response surface method. *Chemical Industry and Chemical Engineering Quarterly*, 21(1-1), 53-61.
- Uddin, M.S., Hawlader, M.N.A., Ding, L., Mujumdar, A.S., (2002). Degradation of ascorbic acid in dried guava during storage. *Journal of Food Engineering*, 51(1), 21-26.
- van Koningsveld, G.A., Walstra, P., Gruppen, H., Wijngaards, G., van Boekel, M.A.J.S., Voragen, A.G.J., (2002). Formation and Stability of Foam Made with Various Potato Protein Preparations. *Journal of agricultural and food chemistry*, 50(26), 7651-7659.
- Venir, E., Munari, M., Tonizzo, A., Maltini, E., (2007). Structure related changes during moistening of freeze dried apple tissue. *Journal of Food Engineering*, 81(1), 27-32.
- Wallace, T.C., Giusti, M.M., (2013). Chapter 2 - Basic Anthocyanin Chemistry and Dietary Sources. *Anthocyanins in Health and Disease*. CRC Press, 13-91.
- Wang, J., Xi, Y.S., (2005). Drying characteristics and drying quality of carrot using a two-stage microwave process. *Journal of food Engineering*, 68(4), 505-511.

- Wang, J., Xiong, Y.-S., Yu, Y., (2004). Microwave drying characteristics of potato and the effect of different microwave powers on the dried quality of potato. *European Food Research and Technology*, 219(5), 500-506.
- Wang, R., Zhang, M., Mujumdar, A.S., (2010). Effects of vacuum and microwave freeze drying on microstructure and quality of potato slices. *Journal of Food Engineering*, 101(2), 131-139.
- Wang, R., Zhang, M., Mujumdar, A.S., Jiang, H., (2011). Effect of salt and sucrose content on dielectric properties and microwave freeze drying behavior of re-structured potato slices. *Journal of Food Engineering*, 106(4), 290-297.
- Wang, Y., Zhang, M., Mujumdar, A.S., Mothibe, K.J., Roknul Azam, S.M., (2012). Effect of blanching on microwave freeze drying of stem lettuce cubes in a circular conduit drying chamber. *Journal of Food Engineering*, 113(2), 177-185.
- Wang, Z.H., Shi, M.H., (1999). Microwave freeze drying characteristics of beef. *Drying Technology* 17(3), 434-447.
- Welch, C.R., Wu, Q., Simon, J.E., (2008). Recent Advances in Anthocyanin Analysis and Characterization. *Current analytical chemistry*, 4(2), 75-101.
- Wesche-Ebeling, P., Montgomery, M.W., (1990). Strawberry polyphenoloxidase: purification and characterization. *Journal of food science*, 55(5), 1315-1319.
- Willert-Porada, M., (2007). Microwave vacuum drying in the food processing industry. *Advances in Microwave and Radio Frequency Processing: Report from the 8th International Conference on Microwave and High-Frequency Heating held in Bayreuth (Germany)*. Springer Berlin Heidelberg, 426-435.
- Wray, D., Ramaswamy, H.S., (2015). Novel Concepts in Microwave Drying of Foods. *Drying Technology*, 33(7), 769-783.
- Wrolstad, R.E., Acree, T.E., Decker, E.A., Penner, M.H., Reid, D.S., Schwartz, S.J., Shoemaker, C.F., Smith, D.M., Sporns, P., (2005). Chapter A -Water. *Handbook of Food Analytical Chemistry, Volume 1: Water, Proteins, Enzymes, Lipids, and Carbohydrates*. Wiley, 1-70.
- Zayas, J.F., (1997). Foaming properties of proteins, Functionality of proteins in food. *Springer*, 260-309.
- Zhang, L., Li, J., Hogan, S., Chung, H., Welbaum, G.E., Zhou, K., (2010). Inhibitory effect of raspberries on starch digestive enzyme and their antioxidant properties and phenolic composition. *Food Chemistry*, 119(2), 592-599.
- Zhang, M., Tang, J., Mujumdar, A.S., Wang, S., (2006). Trends in microwave-related drying of fruits and vegetables. *Trends in Food Science & Technology*, 17(10), 524-534.
- Zhao, Y., (2007). Chapter 10 - Freezing process of berries. *Berry Fruit: Value-Added Products for Health Promotion*. CRC Press, 292-310.
- Zheng, X.-Z., Liu, C.-H., Zhou, H., (2011). Optimization of Parameters for Microwave-Assisted Foam Mat Drying of Blackcurrant Pulp. *Drying Technology*, 29(2), 230-238.

---

# Appendix

## A. Nutrient composition of raspberries

Table A 1 - Nutrient composition of raspberries according to the U.S department of agriculture nutrient database.  
Adapted from (Talcott, 2007).

---

<b>Raspberry nutrient composition</b>	<b>Quantity per 100 g</b>
<b>Water (g)</b>	85.8
<b>Protein (g)</b>	1.2
<b>Total lipids (g)</b>	0.65
<b>Ash (g)</b>	0.46
<b>Carbohydrates (g)</b>	11.9
Total Fiber (g)	6.5
Total sugars (g)	4.42
Sucrose (g)	0.2
Glucose (g)	1.86
Maltose (g)	2.35
<b>Vitamins (mg)</b>	30.7
Total ascorbic acid (mg)	26.2
$\alpha$ -Tocopherol (mg)	0.87
$\gamma$ -Tocopherol (mg)	1.42
$\Delta$ -Tocopherol (mg)	1.04
Others	1.17

---



## B. Chemical structure of some anthocyanins compounds

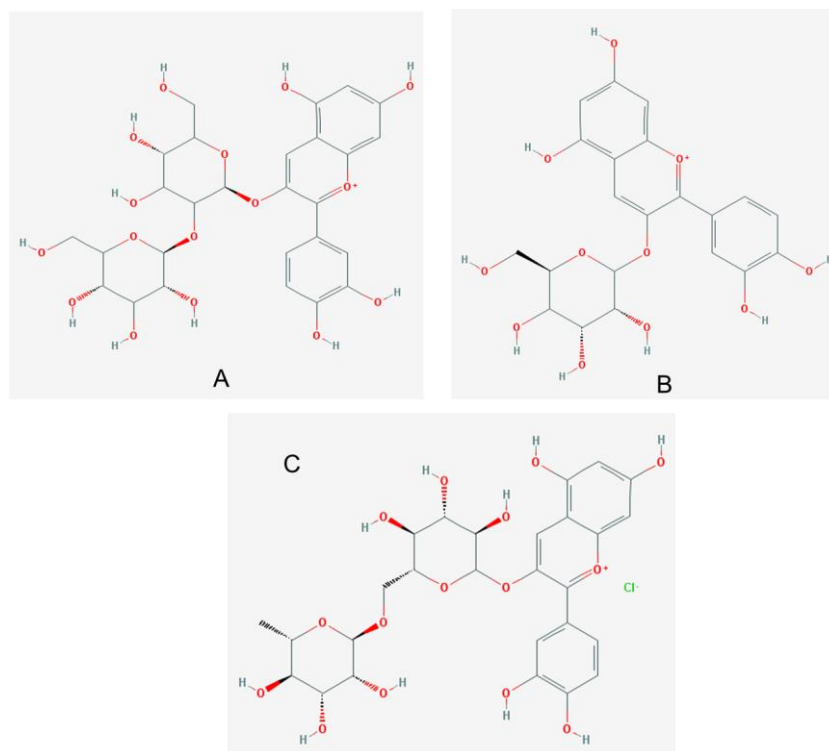


Figure B 1 - Chemical structure of some anthocyanins compounds. A - Cyanidin 3-sophoroside; B - Cyanidin-3-glucoside; C - Cyanidin-3-rutinoside. Adapted from (PubChem Compound Database, 2004).

## C. Main parameters studied during storage

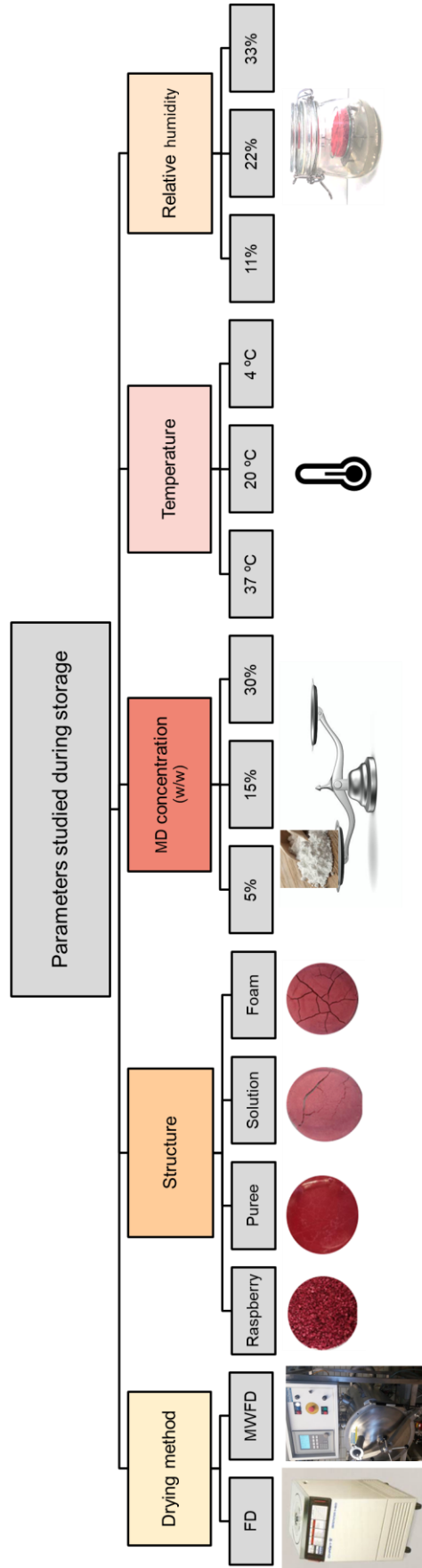


Figure C.1 - Schematic representation of the main parameters studied over the storage period.

## D. Operation parameters for production of foams

Table D 1 - *Mondomix* parameters used in the production of the different foams.

Parameter	5% PPI + 2.5% P		
	5 %MD	15% MD	30% MD
Head Rotation	600 rpm	500 rpm	500 rpm
Air	90 mm	55 mm	100 mm
Input Pressure	5 bar	4 bar	4 bar
Pressure in the mixing head	0.5 bar	0.5 bar	1 bar
Regulator of pressure in the mixing head	0.5 bar	0.5 bar	0.9 bar

## E. Parameters used in the HPLC-column

Table E 1 - Parameters used in the HPLC-column for the ascorbic acid and anthocyanins determination.

Parameter	Ascorbic acid/ Anthocyanin Specification:
Method name:	Anthocyane1D/Ascorbinsäure_Zorbax
Column:	Phenomenex Luna 3 $\mu$ 250 x 4,6mm/Zorbax 300 SB-C18; Rapid Resolution; 4,6*150mm; 3,5 $\mu$ m
Standard injection volume:	20 $\mu$ l/10 $\mu$ l
Detector:	VW 520nm/ VWD 243nm
Temperature:	20/22 °C
Flow:	0.5 mL/min/0.8 mL/min
Pump:	binary pump
Eluent A:	100% dist. water +0,2% TFA
Eluent B:	100% ACN +0,2% TFA

## F. Influence of drying method on the storage stability of raspberry splits

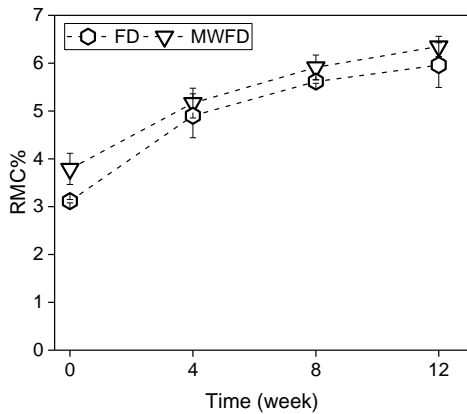


Figure F 1 - RMC of raspberry splits dried with FD and MWFD and stored at 37 °C, vacuum packed.

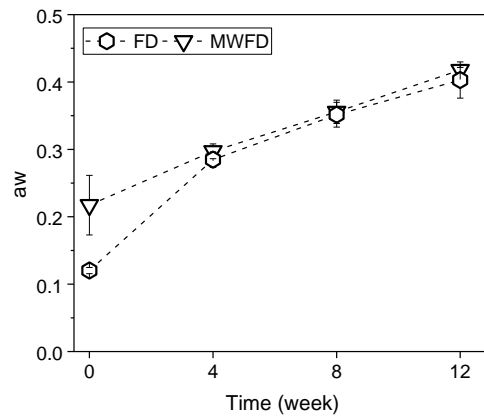


Figure F 2 - Water activity of raspberry splits dried with FD and MWFD and stored at 37 °C, vacuum packed.

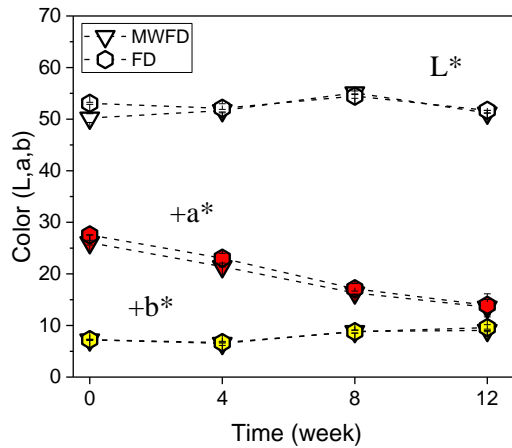


Figure F 5 - Color parameters (L,a,b) of raspberry splits dried with FD and MWFD and stored at 37 °C, vacuum packed.

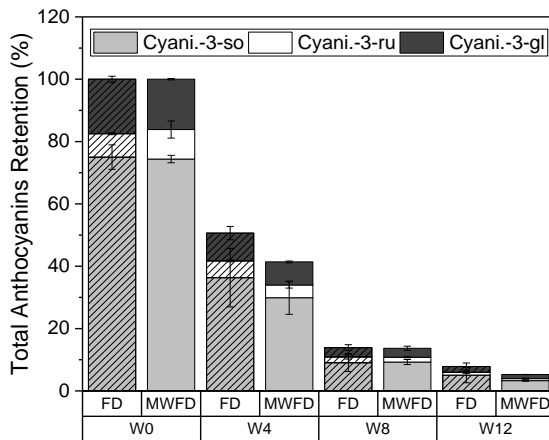


Figure F 3 - ACN retention of raspberry splits, dried with FD and MWFD and stored at 37 °C, vacuum packed.

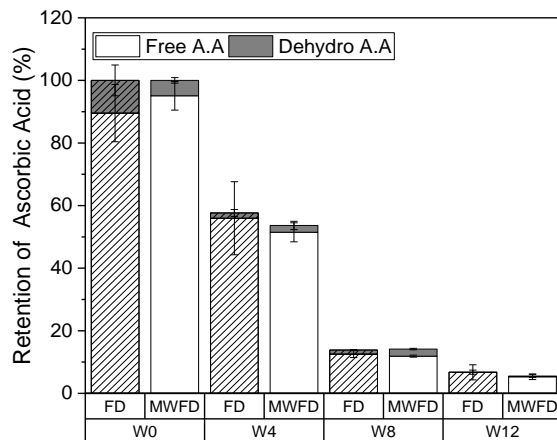


Figure F 4 - ACN retention of 30% MD foam dried with FD and MWFD and stored at 37 °C, vacuum packed.

## G. Example of foam collapsing (hot spots)



Figure G 1 - Foam collapsing (hot spots) caused by microwave freeze-drying.

## H. Product development experiment

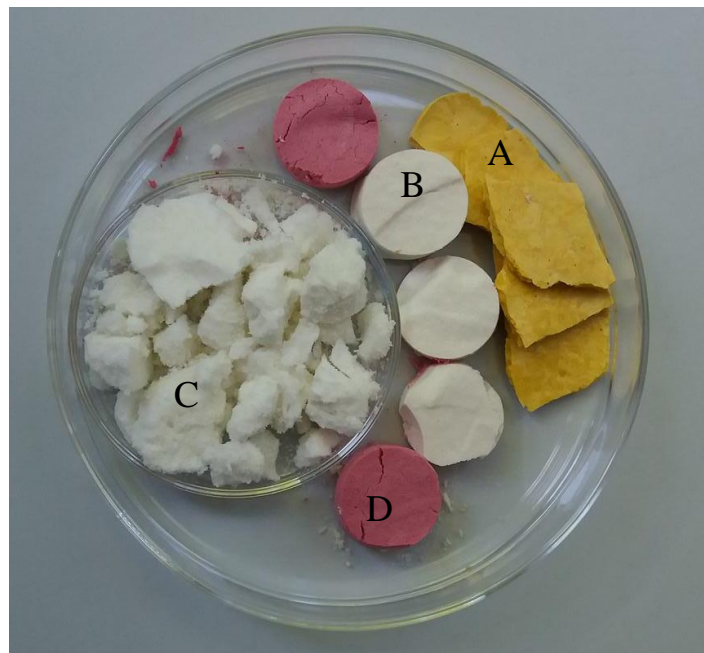


Figure H 1 - Preliminary development of mango (A), banana (B) and melon foams (C). D - Raspberry foam.