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Microwave-assisted freeze drying of foamed fruit pulps

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Abbreviations

A	Area	m ²
a	Redness	
AA	Ascorbic acid	
ACY	Anthocyanins	
ANOVA	Analysis of variance	
ASF	Specific surface area	
a _w	Water activity	
b	Yellowness	
c	Concentration	kg m ⁻³
c	Solubility of a dissolved gas	mol L ⁻¹
c	Speed of light	m s ⁻¹
C _p	Heat capacity	J K ⁻¹
CD	Convective drying	
Cyn-3-so	Cyanidin-3-sophorosid	
Cyn-3-gl	Cyanidin-3-glucoside	
Cyn-3-ru	Cyanidin-3-rutinoside	
D	Penetration depth	cm
dm	Dry matter	
d _{50.2}	Median bubble diameter	m
D _[3,2]	Surface-based mean diameter	
D _[4,3]	Volume-based mean diameter	
DE	Dextrose equivalent	
DE°	Degree of methylation	
DSC	Differential scanning calorimetry	
DR	Drying rate	min ⁻¹
DHA	Dehydro ascorbic acid	
DVS	Dynamic vapor sorption	
E	Electric field	V m ⁻¹
ΔE	Total color difference	
evp.	Evaporated	
f	Frequency	s ⁻¹

		Abbreviations
F	Force	N
FF	Foam firmness	
FS	Foam stability	%
FA	Foaming ability	%
FD	Freeze drying	
FE-SEM	Field emission scanning electron microscope	
Free AA	Free ascorbic acid	
g	Gravity	m s^{-2}
G	Gibb's free energy	J
GAB	Guggenheim-Anderson-de Boer	
H	Enthalpi	J
H	Magnetic field	amp m^{-1}
HCl	Hydrochloric acid	
IQR	Interquartile range	
k_H	Henry's Law constant	L atm mol^{-1}
KSC	Kramer shear cell	
L	Brightness	
LM	Light microscopy	
M	Equilibrium moisture content	$\text{kg kg}^{-1}\text{solid dm}$
M_0	Monomolecular layer moisture content	$\text{g H}_2\text{O/g solid dm}$
MD	Maltodextrin	
MR(t)	Moisture ratio at a certain time point of drying	
MPA	Meta phosphoric acid	
MW	Microwave	
MWFD	Microwave-assisted freeze drying	
OV	Overrun	%
P	Pectin	
p	Pressure	Pa
Δp	Laplace pressure	Pa
pH	Potential of hydrogen	
PSD	Particle size distribution	
PPI/PP	Potato protease inhibitors, a fraction of potato protein	
PP	Polypropylene	

PTFE	Polytetrafluoroethylene	
PET	Polyethylene terephthalate	
LDPE	Low-density poly ethylene	
R	Universal gas constant	8.314 J mol ⁻¹ K ⁻¹
r	Radius	m
RH	Relative humidity	%
rpm	Revolutions per minute	min ⁻¹
RP-HPLC	Reversed phase high performance liquid chromatography	
RMC	Residual moisture content	%
S	Entropy	J K ⁻¹
SEM	Scanning electron microscopy	
t	Time	s
T	Temperature	K
T _g	Glass transition temperature	K
TCEP	Tris(2-carboxyethyl)phosphine	
v/v	Volume per volume	
w/w	Weight by weight	
WPI	Whey protein isolate	
Q ₂ (x)	Area based cumulative distributions	

Greek letters

λ	Wavelength	m
ε	Complex permittivity	
ε'	Dielectric constant	
ε''	Dielectric loss factor	
$\tan \delta$	Loss tangent	
ρ	Density	kg m ⁻³
σ	Surface tension	N m ⁻¹
ϕ	Gas volume fraction	



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1 General introduction

1.1 Foam-mat drying with conventional techniques

A well-characterized stable fruit foam uses a snack product by employing a further drying process. The indisputable advantages of foam structure are the heat and mass transfers are faster due to the great inner surface and decreased resistance by the capillary effect of lamellae. Thus, drying can be achieved at low temperatures in a short time than with non-foam material (Brygidyr et al., 1977). So, called foam-mat drying has long been recognized as a simple and relatively economical method to utilize heat-labile, highly viscous, sticky, hard-to-dry materials such as fruits, particularly those with high sugar content (Qadri and Srivastava, 2015). A general definition of foam-mat drying is a liquid or semi-liquid fluid material whipped to a stable foam with the help of a concentration of appropriate foaming agent and foam stabilizer, and thereafter the foam is spread out as a thin layer and subsequently dried by convection using hot air (Karim and Wai, 1999).

The mechanisms leading to instabilities of the foam are important and have to be considered in the design of a successful drying process. To preserve the non-collapsed porous texture after drying, the foam should remain stable with open pores to facilitate water removal during drying. Moreover, collapses in the matrix cause longer drying time and deterioration in the product quality. Therefore, efficient foam drying can only be assured with mechanically and thermally stable foam (Sangamithra et al., 2015b).

The drying process is a rhythm of heat and mass transfer occurring at the same time. The main difference in foam drying is low thermal conductivity of air compared with nonfoamed matrix, as the heat transfer is the driving force. This means that heat transfer occurs at a lower rate in materials with a low thermal conductivity, indicating that the drying rates will not necessarily be accelerated (Ratti and Kudra, 2006).

When mass transfer is the driving force, multiple mechanisms could be involved in the drying. The small and uniform bubbles formed with a cohesive viscoelastic film with low permeability develop new pores as finer pores are opened through moisture movement under the drying stress, thus the internal structure become more porous (Sankat and Castaigne, 2004). The drying is still fast in the foam structure despite heat transfer

being hindered by a large volume of air because the bursting of the sequence of the bubbles promotes the mass and heat transfer due to the new surfaces (Hardy and Jideani, 2017). However depending on its characteristics, foam has some individual features such as density, viscosity, stability, bubble size and size distribution and thickness (Ratti and Kudra, 2006).

Foam-mat drying has been applied to various fruits, such as apple juice (Raharitsifa et al., 2006), banana (Thuwapanichayanan et al., 2008), cowpea (Falade et al., 2003), mandarin (Kadam et al., 2011), star fruit (Karim and Wai, 1999), papaya (Kandasamy et al., 2014), mangos (Jaya and Das, 2004; Lobo et al., 2017), and tomato juice (Kadam et al., 2011), with the help of several foaming agents and foam stabilizers. In contrast to non-foam samples, high product quality comparable to fresh fruit can be achieved in terms of color, flavor, and vitamins, due to minimal heat damage (Kudra et al., 2006; Kadam Rai et al., 2011).

Beyond convective hot air drying, foam-mat can also be dried via conduction (i.e., freeze drying) or electromagnetic radiation (i.e., microwaves). The freeze drying (FD) method is based on water removal by sublimation of foodstuff; thus the structure is preserved which makes it an excellent process for obtaining highly nutritional and unique quality products (Fan et al., 2017). Therefore, some conditions of FD process need to be operated below the triple point of water (0.095°C, 6.11 mbar) (Fig. 1-1) and in an oxygen free environment to achieve gentle processing. The frozen product is heated via conduction through the shelves. Conductive heating directs the temperature gradient from the bottom to the product surface; therefore, heat transfer and mass transfer are limited. The major drawback of the FD method, which limits its use, is its expensive cost due to high energy consumption resulting from the long drying times (Wang et al., 2010). Raharitsifa et al. (2006) combined the advantages of foaming with the FD drying process to overcome the low drying rates in FD. They concluded in their study that FD of foamed materials was limited by heat transfer while nonfoamed was limited by mass transfer.

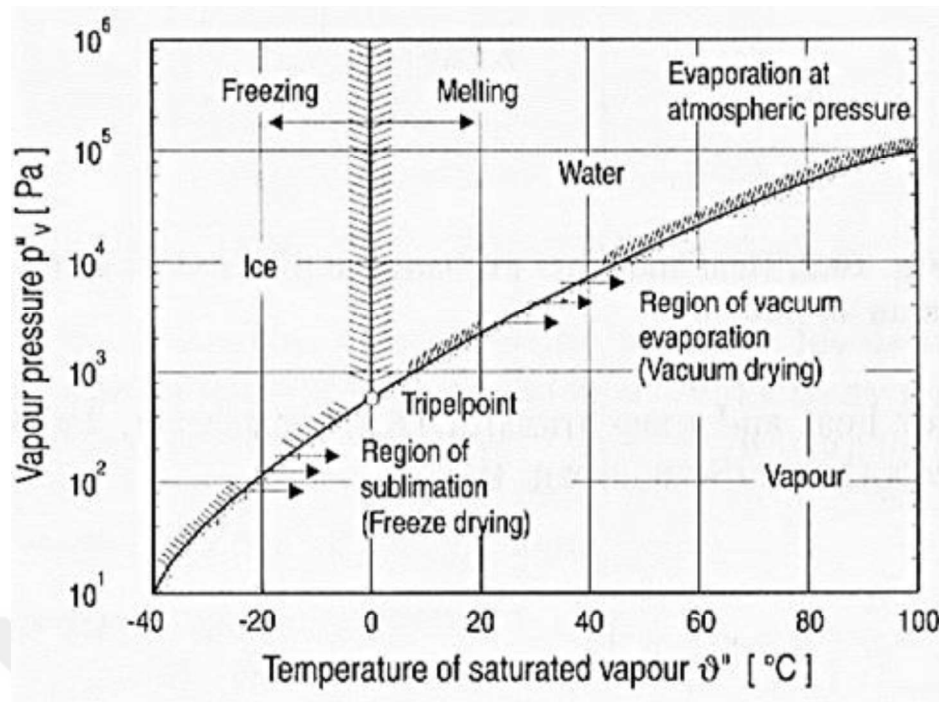


Fig. 1-1. Phase diagram of water, ice and vapor with dependence on saturation vapor pressure and temperature of saturated vapor (Kessler, 2002).

One major drawback of foam-mat drying is poor heat transfer through the entrapped air (Qadri and Srivastava, 2015), another is the limited throughput because the foams are dried in a thin layer (Ratti and Kudra, 2006). Therefore, microwaving can eliminate the heat transfer limitations by volumetric and selective heating (Ozcelik and Püschner, 2017). Applying a microwave field to the freeze drying process, microwave-assisted freeze drying (MWFD), can eliminate the limitations of FD by penetrating directly into the foam while presenting the same gentle drying environment (oxygen free), which in turn results in higher drying rates as a consequence of the efficient drying process (Huang et al., 2011; Zheng et al., 2011). One can expect to have at least the same end-product quality as FD with shorter drying, and consequently with lower processing costs. No research has been conducted so far on drying of raspberry foam via MWFD.

1.2 Characteristics of foams

Bubbles in food are a part of our daily life. No one ever thinks about it, but they are present on our table every day in the form of breads, cakes, croissants, breakfast cereals, beer, butter, cheese, whipped cream, ice-cream, cappuccino, milk shakes, foam sweets, marshmallow, fruit fools, and sorbet (Campbell and Mougeot, 1999). The aer-

ated food market is growing quickly because of the increasing demand of the consumers for the innovative food concept. Foams are getting increasing attention because they have practical advantages because of their appealing texture and enhanced flavor by fast and direct contact with saliva. In the scientific world, foams have a very long history. They received recognition because of Joseph Plateau who is the founder of this field in 1873 (Vignes-Adler and Weaire, 2008).

Foam can be simply defined as a dispersion of gas bubbles in a liquid containing two apparent phases. A liquid continuous phase surrounds a dispersed phase of bubbles of air. Indeed, foam is formed by various bubbles surrounded by fluid films. The thermodynamic definition of foam is based on the principle of minimum energy and the free volume of the system, according to Gibbs law deduced from thermodynamic laws. The minimum energy principle restates the 2nd law of thermodynamics as every system seeks to achieve a minimum of free energy. The change in Gibbs free energy ΔG is a function of enthalpy H , temperature T (Kelvin), and entropy S , which is defined for a general equilibrium process by the following equation:

$$\Delta G = -RT \cdot \ln K = \Delta H - T \cdot \Delta S \quad (1-1)$$

Entropy of a system always increases (2nd law of thermodynamics), and if there is available energy to do work, this energy tends to be used. The interactions between gas in bubbles and the surrounding liquid determine the dynamic stability of foams (Hollinger, 1991). The relation between internal and external pressure for a single bubble at one interface at a given surface tension is defined according to Laplace's law. In accordance with Laplace equation, Δp is a function of the surface tension of the continuous phase σ and the bubble radius r (Damodaran, 2005) (Eq. 1-2):

$$\Delta p = p_b - p_0 = 2 \times \left(\frac{2\sigma}{r} \right) = \frac{4\sigma}{r} \quad (1-2)$$

Internal pressure of bubble p_b and p_0 external pressure of surrounding fluid, the bubble radius r and the surface tension σ . The Δp is two times the Laplace pressure since there is a bubble instead of semi bubble on a layer of interface. The solubility of gas at constant temperature in a given type and volume of liquid is directly proportional to the

partial pressure of gas stated by Henry's law (Bergeron and Walstra, 2005). Henry's law given by following equation introduced the Henry's constant k_H where the larger k_H denotes to a less soluble gas:

$$p = k_H \cdot c \quad (1-3)$$

where p is the partial pressure of the solute, and c is the concentration of solute.

The volume fraction and the diameter of the bubble are fundamental parameters that provide comprehensive knowledge on foam behavior (Khan and Armstrong, 1989). Generally, the gas volume fraction ϕ varies between 0.5 and 0.97. If ϕ is above 0.75, the bubbles are forced to deform (Walstra, 1989). Therefore, the role of the dynamic air-fluid surface behavior is critically important in determining the efficiency of foam formation and stability (Garrett, 2013). Fig. 1-2 depicts the microscope image of the foam structure of raspberry.

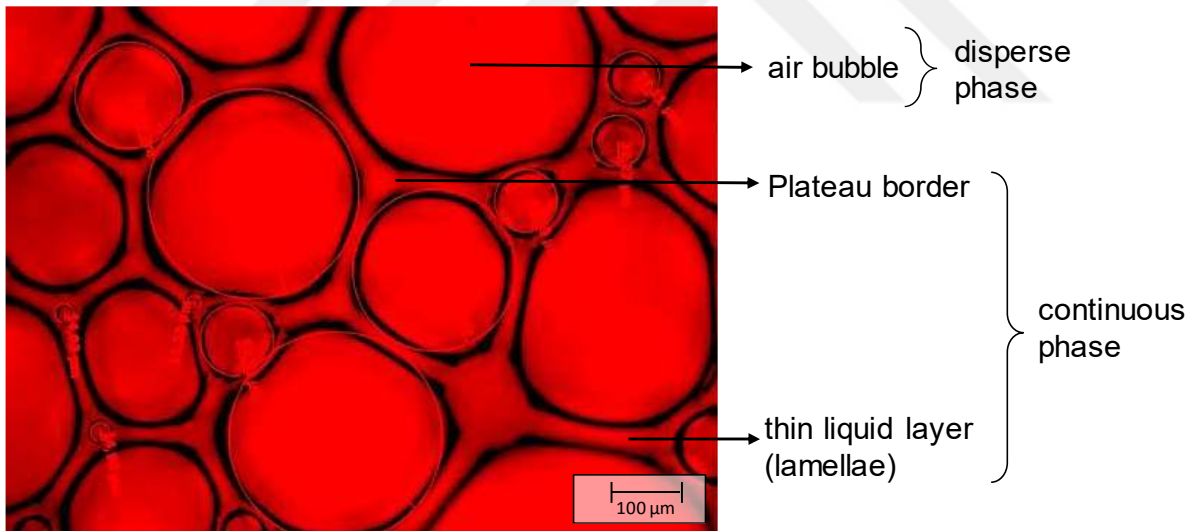


Fig. 1-2. Microscopy of raspberry foam structure.

Bubbles are dissorted into polyhedral with partly plane faces: the thin layers of continuous phase fluid separating the faces of two adjacent bubble are known as "lamellae", while the thicker channels where three lamellae meet are known as "plateau bordes" contributing foam stability (Hailing and Walstra, 1981). Despite the difficulties of mak-

ing a stable foam, there are several ways to produce stable foams. Whipping or shaking, mixing of highly viscous fluids, entrapment, gas injection, extrusion, and puffing are some commonly used method. Among these methods, whipping by means of a rotor-stator entity probably is the most widespread foam formation method used in food industry. Hence the capacity of foam formation is greatly influenced by the foaming conditions (Wilson, 2013). In particular rotational speed and whipping time whereas the distribution of air depends on the applied shear forces by mechanical energy (Schmidt et al., 2018a). To build a foam, high amount of mechanical energy must be applied to the system to increase the interfacial area. This free energy is proportional to the surface tension (Aksenenko et al., 2006). Surface tension has a unit of Joules per square meter or Newton per meter and is simply referred to as the required work to increase the size of the surface; in other words, it is defined as a measure of how much energy is required to make a unit area of interface between two phases (Berry et al., 2015; Dickinson, 1992). Foams are inherently thermodynamically unstable and they are tend to deform one another (Wilson, 2013). Therefore, the addition of biopolymers such as proteins and carbohydrates, and other surfactants, known as surface active compounds, into the air-fluid system helps stabilize the interface during the formation of foams (Dickinson and Izgi, 1996). From the thermodynamic viewpoint, these surface active materials decrease the surface tension and thus the free energy of the system by forming a viscoelastic adsorbed layer and provide the intended kinetic stability (Rodríguez Patino et al., 2008; Wilde et al., 2004).

1.2.1 Destabilization mechanisms of foams

The definition of “foam stability” can only gain meaning if “foam instability” is defined. Therefore, the common destability mechanisms of foam will be explained first to gain better understanding of why and how important it is to form and stabilize foams. Major instabilities that occur as soon as the bubble is formed are drainage, coalescence and Oswald ripening (disproportionation). A schematic representation of the common instabilities of foam structure is depicted in Fig. 1-3.

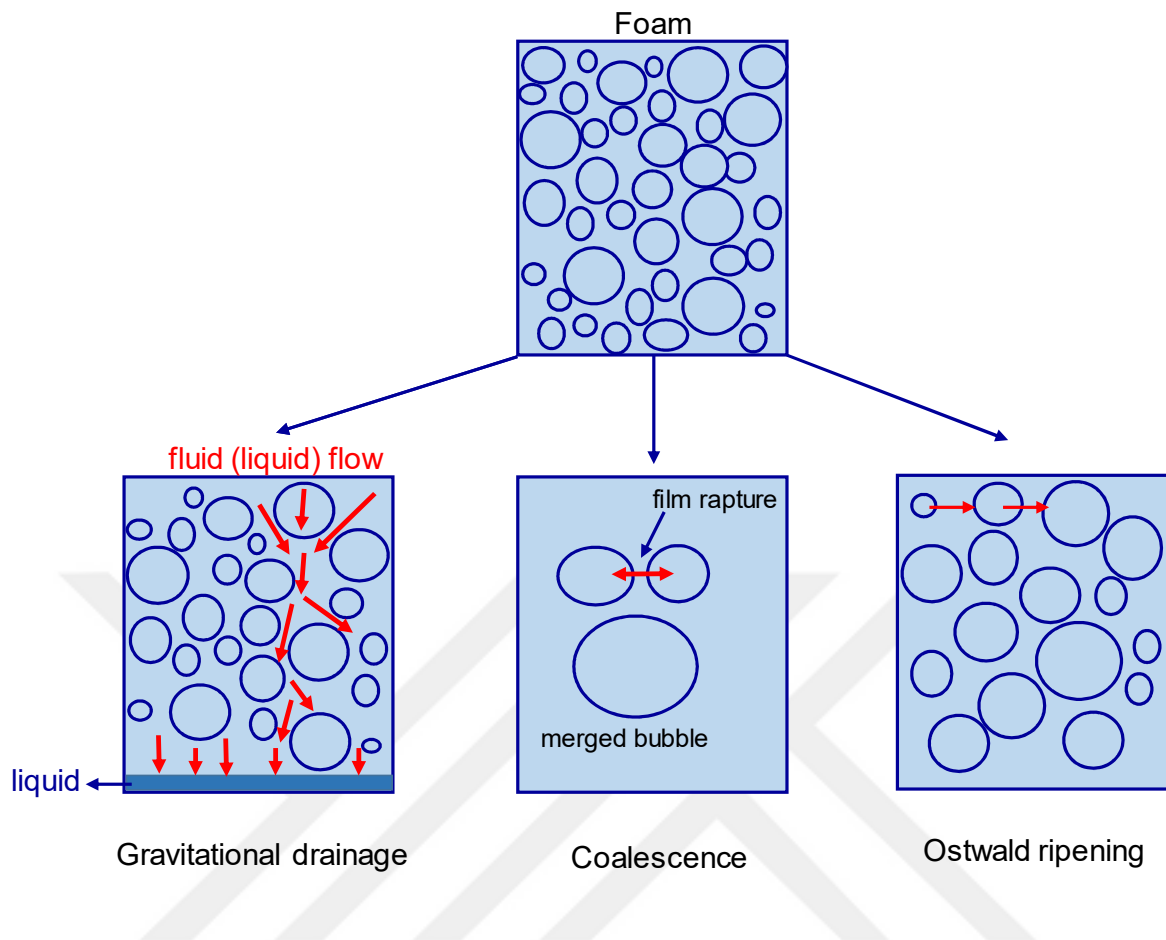


Fig. 1-3. Common destabilising mechanisms of foams (highly schematic).

Ostwald ripening is a thermodynamic phenomenon that is driven by interfacial energy (Markworth, 1985). It takes place when the gas (air) in the bubble has a pressure higher than the corresponding saturation (see Fig. 1-1), leading to gas dissolving in the liquid and diffusing through the matrix and also into the gas phase. Ostwald ripening includes degradation mechanisms of the bubbles regarding the solubility of the dispersed phase based on the radius of the bubble according to Henry's Law. As mentioned earlier, solubility increases with decreasing radius (Taylor, 1998). The difference in pressure is caused by the difference in radius of the bubbles. The pressure in the dispersed phase is always higher than that in continuous phase where the pressure difference is referred to as Laplace pressure Δp . In accordance with Laplace pressure by the given equation 1-2.

In other words, Ostwald ripening is a transport of smaller particles to larger ones. This occurs during the growth of larger bubbles at the expense of smaller bubbles as a

result of Laplace pressure, also referred to as disproportionation (Dickinson et al., 2002). A schematic representation of Ostwald ripening is depicted in Fig. 1-4.

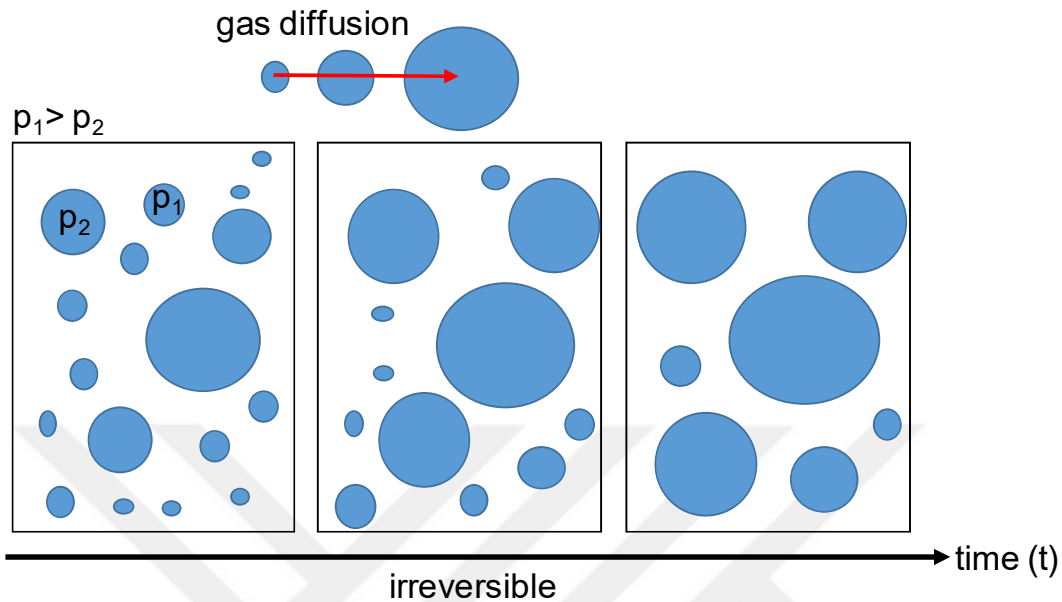


Fig. 1-4. Schematic illustration of Ostwald ripening.

The gas in the vicinity of small bubbles is more soluble than that in the aqueous phase around larger bubbles because the solubility of gas in the continuous phase is affected by pressure. In the continuous phase, the smaller as foam bubbles diffuses toward large bubbles or if the distance is far between small and large bubbles than the small bubble shrinks as time elapses (Kloek et al., 2001). Ostwald ripening can be avoided by changing the surface tension and building an insoluble layer with a protein (Wilson, 2013). Generally, drainage occurs as a consequence of two simultaneous processes. Fluid drains from the lamellae into the plateau borders because of the difference in Laplace pressure. In parallel, the liquid drains through the plateau borders under the effect of gravity (Halling and Walstra, 1981). Because of the gravitational forces causing a discrepancy of hydrostatic pressure between the bottom level and the external surface of the foam, the liquid layer flows toward plateau borders (Kruglyakov et al., 2008). Drainage can be very fast, especially when the bubbles are large. Moreover, the shear flow can cause bubble merging (coalescence) or break-up. Bubble merging

is mainly driven by capillary pressure leading to drainage and impairs the bubbles because of which bubbles collapse. In brief, foam drainage is controlled by laminar flow driven by capillary and gravitational forces where the plateau borders resist drainage. Foam drainage can be retarded by increasing the surface viscosity and elasticity (Koehler et al., 2000; Kruglyakov et al., 2008, 2008; Prud'homme and Khan, 1996). Downward draining liquid eventually leads to coalescence because of the viscosity and non-uniformity of the films leading non-uniform film-drainage rate. Smaller films drain faster and start rupturing earlier, thus causing the coalescence. Coalescence is an irreversible mechanism of fusion of two or more bubbles to a single and bigger bubble involving rupture of the lamellae of the continuous phase (Bhakta and Ruckenstein, 1997; Damodaran, 2005). No matter which one of these mechanisms controls the system, the result is the same at the equilibrium which is no foam. Therefore, bubbles have to form foams and get stabilized. To provide a clear understanding of foam formation and stability, the parameters for assessment of foam are introduced next.

1.2.2 Assessing the properties of foam

Foams are characterized by foaming ability (foamability) refers to air holding capacity that can be measured by means of the gas volume incorporated into the sample solutions; this so called overrun (OV) can be calculated in terms of volume increase (Kreuß et al., 2009). Foamability potential depends on the molecular characteristics of the protein such as the capacity for rapid adsorption and unfolding at the interface (Wilson, 2013). Foam stability (FS) is the ability of a foam to hold air for a given period of time and by the liquid in continuous phase (Ratti and Kudra, 2006). Another important parameter is bubble size and size distribution of bubbles relating to its geometry. As mentioned earlier, bubble size is one of the main factors contributing to the destabilization events because coarsening is directly related to bubble size distribution. Furthermore, bubble size and size distribution determine the uniformity, while characterizing texture and mouth-feel, of the foam. There are various imaging techniques for monitoring foams used to characterize the foam structure including light microscopy (LM) and scanning electron microscopy (SEM) with higher magnification (Campbell, 2008). Bubble size (diameter) can be measured by capturing bubbles via LM imaging, and size distribution can be characterized according to the median bubble diameter related to the bubble volume (Bals and Kulozik, 2003). Mechanically generated bubbles via a

dynamic mixer (rotor-stator) are greatly influenced by the rotational speed of the mixer. It was reported that increasing the rotation speed yielded a decreased mean bubble diameter. Besides, the shorter residence time in mixing increased the mean bubble diameter. (Kroezen and Wassink, 1986). Bubble size and size distribution depend on the viscosity (Dickinson et al., 2002). Furthermore, it is important to note that the bubble size and size distribution are important for the subsequent drying process. Considering the heat and mass transfer, the diffusion pathways and thicknesses of lamella between bubbles directly affect the drying efficiency. No matter the shape of the bubbles, they typically form a disordered structure. Important to consider that too heterogeneous bubble size distribution in foam structure can lead to instability due to the unbalanced forces at the fluid-gas interface (Ratti and Kudra, 2006).

1.2.3 Forming and stabilizing the foams

Considering the aforementioned degradation in foam structures, it is of vital importance to form and stabilize the bubbles. Especially, for “wet” foams, the continuous phase is a low-viscosity fluid; therefore, it is hard to keep them in shape as bubbles deform very fast (Dickinson et al., 2002). Bubbles can be formed and stabilized by allocating so-called foaming agents and stabilizers at the continuous phase. The characteristics of the thin layer separating the bubbles dominate the stability of the foam (Rodríguez Patino et al., 2008). Therefore, the applied formulation has a crucial importance in the characterized structure. In food systems, proteins and polysaccharides perform a techno/functional role as both are surface active components. In particular proteins have an important role in the formation of foam (Schmidt et al., 2018a). The question that arises here is why? In principle, proteins are strongly adsorbed to the gas-liquid interface because of accessible hydrophobic amino acid residues (Murray, 2007). They form viscoelastic adsorbing layers resembling three dimensional gel networks (Murray and Ettelaie, 2004). Consequently, they reduce the surface tension at the interface and thus the free energy of the system. On the other hand, highly adsorbed proteins possess multiple adsorption sites per molecule because of the presence of hydrophobic regions and the conditions such as temperature (Murray, 2007). As a consequence, the desired foam formation and enhanced stability can be achieved by enhancing surface rheology (McClements, 2005). However, their chemical structures are different which changes their stabilizing mechanisms. Proteins of animal origin are widely used

in the food industry such as whey proteins (Lim et al., 2008), milk proteins (López-Fandiño, 2006), and egg albumen (Mleko et al., 2007). Nowadays, both the industry and researchers are searching for new protein sources (Aiking, 2011). However, the trend is more oriented toward plant origin proteins such as soy protein (Wang et al., 2019), amaranth protein (Bolontrade et al., 2013), and chickpea protein (Lafarga et al., 2019) as they have various health benefits (Amagliani and Schmitt, 2017; Rodríguez Patino et al., 2008). In the context of this thesis potato protease inhibitor (PPI/PP) a protein rich fraction (up to 50% of the total protein) of potato protein was used as a foaming agent due to its functionality (Amagliani and Schmitt, 2017; Glusac et al., 2018; Lomolino et al., 2015; Schmitt et al., 1998; Waglay et al., 2014).

1.2.4 Polysaccharide-protein interaction

As already mentioned, the main role of proteins in the food system is film formation by adsorption at the air-liquid-interface (McClements, 2005) and at the same time stabilization by decreasing the interface tension (Rodríguez Patino et al., 2008). Notably, the solubility of the protein for a given liquid is particularly important in the continuous phase and contributes to adsorption during film formation at the interface. On the other hand, the development of intermolecular conjunctions at the interface leads to alteration because of the rheological properties of the surface (Rodríguez Patino et al., 1995). In contrast, insufficiently adsorbed particles at the interfaces cannot close all the air bubbles tightly, thus enabling gas molecules to pass through (Murray and Eteilaie, 2004). From this perspective, additional polysaccharides enhance the adsorption of protein at the interface if the protein concentration is enough to become saturated by itself (Rodríguez Patino et al., 2008). Protein molecules build an intermolecular viscoelastic film-like-network with their cleared hydrophobic side chains via covalent disulfide bridges and non-covalent interactions (Damodaran and Song, 1988; Germain and Aguilera, 2014). This viscoelastic network enhances the strength of the structure against further destabilizing stresses (Hardy and Jideani, 2017). The higher shear viscosity of protein foams can explain the better stability than that of surfactants. Besides, protein adsorbed films with a potential cross-linked network can provide high foam stability against the abovementioned destabilizing events (Rodríguez Patino et al., 2008).

Several researchers state that a combination of protein-polysaccharide (hydrocolloids) builds better functional properties than that of proteins and polysaccharides alone (Schmitt et al., 1998). The two structural benefits of those two key elements enhance solubility, viscosity, gelation, foaming, and surface stability while forming a new complex. However, mixing two or more biopolymers in solution requires special attention due to the interactions between biopolymers. When the solution is dilute enough, the mixing entropy of the system dominates the phase equilibrium as biopolymers are co-soluble. Possible consequences of mixing proteins and polysaccharides are depicted in Fig. 1-5. The entropic contribution is often greater than the enthalpic one; therefore, phase separation is generally the rule (Kruif and Tuinier, 2001). The type of separation depends on the affinity of biopolymers in the solution. It can be either thermodynamic incompatibility (segregation) or associative phase separation (complexation) (Doublier et al., 2000).

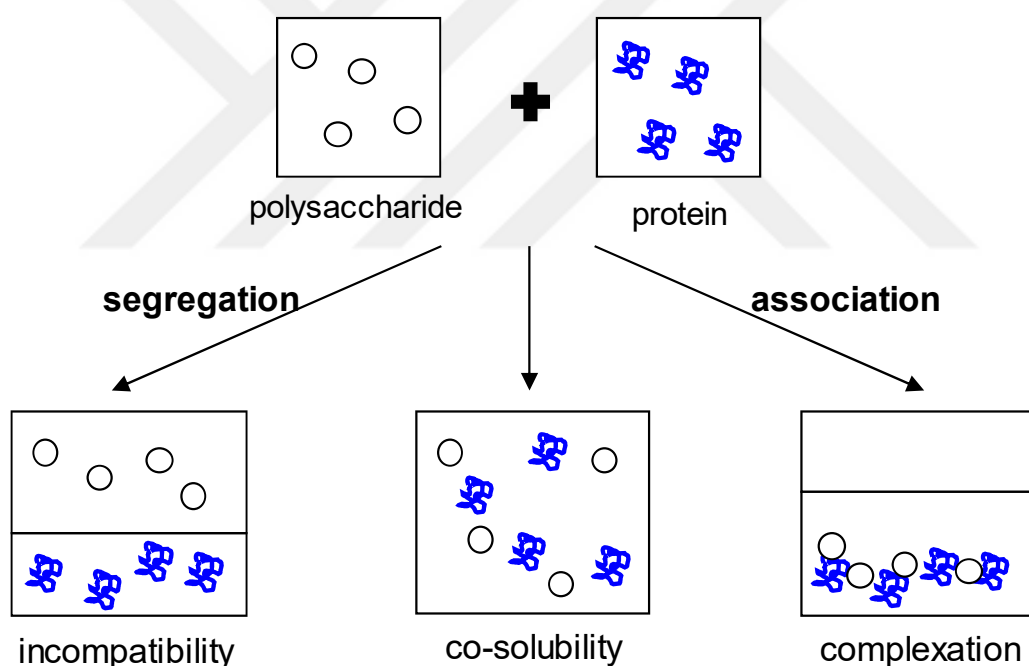


Fig. 1-5. Behavior of protein-polysaccharide mixtures in solution. Modified according to Kruif and Tuinier (2001).

Proteins and polysaccharides have a difference in hydrophilicity because of their chemical structure, according to Flory-Huggins solution theory. So the $\Delta\chi$ -effect is of great importance in thermodynamic phase equilibrium (Grinberg and Tolstoguzov, 1997). At this point, the concentrations of biopolymers are very critical because of the self-association of protein and/or polysaccharides that can cause an increase in $\Delta\chi$ ($\Delta\chi$

>0) resulting in enhanced incompatibility, or interactions between biopolymers are favored ($\Delta\chi < 0$) resulting in associative phase separation. The most common associative phase is called coacervation which consists of a rich solvent phase with very small amounts of biopolymers and a rich biopolymers phase (Doublier et al., 2000). The interactions between biopolymers lower the Gibbs free energy (based on Eq. 1-1); thus, either the energy is lowered, or entropy is raised or both occur at a given pressure and temperature (Kruif and Tuinier, 2001).

Formation of protein-polysaccharide complexes is mainly driven by the interactions between charged macromolecules and interactions between oppositely charged side groups (Tolstoguzov, 1991). Non-electrostatic interactions between bio polymers are hydrogen bonds, hydrophobic interactions, and covalent bonds depending on the composition of the biopolymer. The increasing degree of esterification of pectin and the decrease in temperature have a positive effect on the formation of bubbles when the hydrogen bonds are involved. Hydrophobic interactions are ought to apply for the thermal stabilization of the protein-polysaccharide complex. Amino-groups of the protein and carboxylic groups of the polysaccharides with additional cross-linking agents form covalent bonds. The heat stability can be achieved by linking the protein with polysaccharide (Schmitt et al., 1998).

Potato protein: The properties of plant proteins are equivalent to those of animal proteins in terms of their foaming properties (Rodríguez Patino et al., 2008; Waglay et al., 2014). According to van Koningsveld et al. (2002), potato protein is highly soluble and has a relatively high nutritional quality; hence, it is a good candidate for foam formation and high foam stability, especially in acidic media (Lomolino et al., 2015; Ralet and Guéguen, 2000). Yada (2017) reported that the foamability of potato protein is less effective than that of whey protein but is comparable to that of egg albumin. As the pH of raspberry is relatively low, it is important to evaluate the foam forming ability of proteins at this pH range. van Koningsveld et al. (2002) investigated the foaming characteristics of potato protease inhibitors (PPI) one of the essential fractions of the soluble potato protein, and revealed that PPI has a high foaming capacity and stability. Therefore, PPI is used in this thesis as a foaming agent.

Maltodextrin: Maltodextrin (MD) is a polysaccharide that is commonly used as stabilizer, thickener, and drying or encapsulating agent in the food industry. It can strongly

contribute to the stability of foams by acting as a thickening agent and forming a polysaccharide-protein complex by non-covalent interactions (Dickinson and Galazka, 1991). This is advantageous because of the protective role of MD as a wall material for sensitive substances (ascorbic acid, anthocyanins, aroma-active compounds, etc.) during drying and storage (Lim and Roos, 2017). MD is a long-chain sugar consisting of 2-20 α (1-4) linked D-glucose monomers produced by acid or enzymatic hydrolyses from different starch sources such as potato, corn etc. and the subsequent drying (Ahmed et al., 2009). MDs are classified by DE (dextrose equivalent). The higher the DE value, the shorter the glucose chains with higher solubility. Moreover, the glass transition temperature (T_g) value can be increased with the presence of a high molecular weight with low dextrose equivalent (DE) MD, consequently improving product stability (Jaya and Das, 2004). Maltodextrin DE 6 was used in this study.

Pectin: Pectin (P) is a natural substance in the primary cell wall and is the main middle lamella that forms a supportive layer between cell formation in fruits (Thakur et al., 1997). The gelling type of hydrocolloid pectin is an anionic polysaccharide consisting of linear chains of galacturonic acid obtained from apple, citrus, and grapefruit (Saha and Bhattacharya, 2010). A gel is a viscoelastic system that involves physical association of polymer chains through hydrogen bonding, hydrophobic association, and cation mediated cross-linking leading to a three dimensional network (Phillips and Williams, 2009). Pectins are divided into different groups related to their gelling behavior on the basis of esterification degree (DE° , degree of methylation). The degree of esterification is correlated to the gel setting rates, which means high esterified pectins form gels quicker. Highly esterified citrus pectin with a DE° of 68%-76% was used in this research.

Innovative product concepts can be created by using textural and structural benefits of foams in combination with fruit purees and in turn new structures can be achieved. Important to note that fruit foam can only be created if the foam is stabilized prior to the next processing step (i.e., drying). Additionally, foam structures with the aid of biopolymers can help in the protection and stabilization of active molecules such as flavor, biopolymers, and vitamins present in the fruits. Moreover, the foam structure can enhance aroma release in comparison to whole fruit or unfoamed purees or liquid products.

1.3 Raspberry fruit

Among healthy natural products, fruit plays an important role to support our health and well-being as it provides an optimal combination of phytochemicals and other bioactive compounds such as fiber and vitamins (Ancos et al., 2000). Furthermore, fruits have always been popular among consumers because of their bright color, flavor, texture, and high nutritious value and are a significant part of the diet in many countries (Beekwilder et al., 2005). A diet that includes fruit and vegetables has been correlated with a decrease of chronic and degenerative diseases because the capability of antioxidants to react with free radicals plays a preventive role against various diseases such as coronary heart disease, diabetes, and cancer (Hertog et al., 1993; Hertog et al., 1994; Talcott, 2007). There was even a link found between the total consumption of fruits and vegetables and the reduction of the risk of mortality from major age-related diseases including cardiovascular diseases, diabetes, and cancer (Figiel and Michalska, 2016).

Berries are highly appreciated fruit corps, provide an important source of carbohydrates, essential vitamins, minerals, dietary fibers, and polyphenolics, and have low levels of calories (Beattie et al., 2005; Bobinaitė et al., 2012). More specifically, they contain bioactive compounds such as anthocyanins, catechins, and phenolic acids that have strong antioxidant, antimicrobial, anti-inflammatory, and anticancer properties (Cetojević-Simin et al., 2015; Ponder and Hallmann, 2019)

Raspberries (*Rubus idaeus* L.) are one of the most commonly used berries in the food industry and belong to the plant family of Rosaceae (Ochoa et al., 1999). Based on the fruiting habit, there are two main types of raspberries—summer bearers (i.e., Tullameen, Meeker, Glen Ample) and primocane fruiting types (i.e., Heritage, Autumn Bliss, Polka). Raspberries are the fourth most produced crop berry in the world with 503,393 tons of production. Europe is the third biggest producer following Africa and Asia. Serbia and Montenegro (40% of the total acreage) and Poland (34% of the acreage) are the largest producers in Europe because of favorable climatic conditions (Strik et al., 2007). The chemical composition of raspberries mainly depends on the growing area, variety, plant age, seasonal variations, and time of harvest (Ancos et al., 1999; Sadowska et al., 2017). The most cultivated raspberry (up to 90%–95%) in Serbia is North American Willamette cultivar which has a dark red color, is firm, and is nearly

round with an excellent taste (Cetojević-Simin et al., 2015). The most outstanding cultivars in the industrial market are Willamette and Meeker, while Tulameen and Heritage are a standard in the fresh market (Finn et al., 2008). In this study, “Willamette” cultivar from Serbia was used. Raspberry flavor is generally expressed by the concentration of soluble sugars (sucrose, glucose, and fructose) counterbalanced with the presence of organic acids and aroma volatiles (Aprea et al., 2015). Organic acids present in raspberries, such as malic and citric acid, also contribute to the preservation of the fruit by maintaining a low pH and stabilizing anthocyanins and ascorbic acid (Beekwilder et al., 2005; Zhao, 2007).

Red raspberry (*Rubus idaeus*) comprises various polyphenolic phytochemicals including phenolic acids, flavonoids, lignans, and ellagitannins (Mazur et al., 2014; Rao and Snyder, 2010). The bioactive compounds present in raspberry have numerous health promoting benefits such as anti-inflammatory, anti-neurodegenerative, anti-proliferative (in human cancer cells), antioxidant, antiviral, and antibacterial activities (Bobinaite et al., 2012; Cetojević-Simin et al., 2015, 2015; Pantelidis et al., 2007; Zhang et al., 2010).

Anthocyanins (ACY) are a common phytochemical present in raspberry fruit and is responsible for the red color of raspberries (Ochoa et al., 1999; Teng et al., 2017). These water-soluble pigments are synthesized by plants and are classified as flavonoids because of 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 (Giusti, 2017; Talcott, 2007). The variations in chemical structure of anthocyanins are mainly caused by differences in the number of hydroxyl groups in the molecule, degree of methylation of these OH groups, and the number of aromatic acids attached to it (Fig. 1-6) (Mazza and Miniati, 1993; McGhie and Walton, 2007; Patras et al., 2010). Anthocyanins are bound on the cell walls of the berry to a large extent (Weber and Larsen, 2017). The most abundant anthocyanins in the Willamette cultivar are cyanidin-3-sophoroside (35.6 mg/100 g fresh raspberry) and cyanidin-3-glucoside (16.8 mg/100 g fresh raspberry) where the total amount of anthocyanins are 59.1 mg/100 in fresh raspberry (Torre and Barritt, 1977). According to previous studies, cyanidin-3-sophoroside is well correlated to the red color pigment and

cyanidin-3-glucoside is found to be the least stable pigment compared with other anthocyanins (Ancos et al., 1999; Rommel et al., 1990).

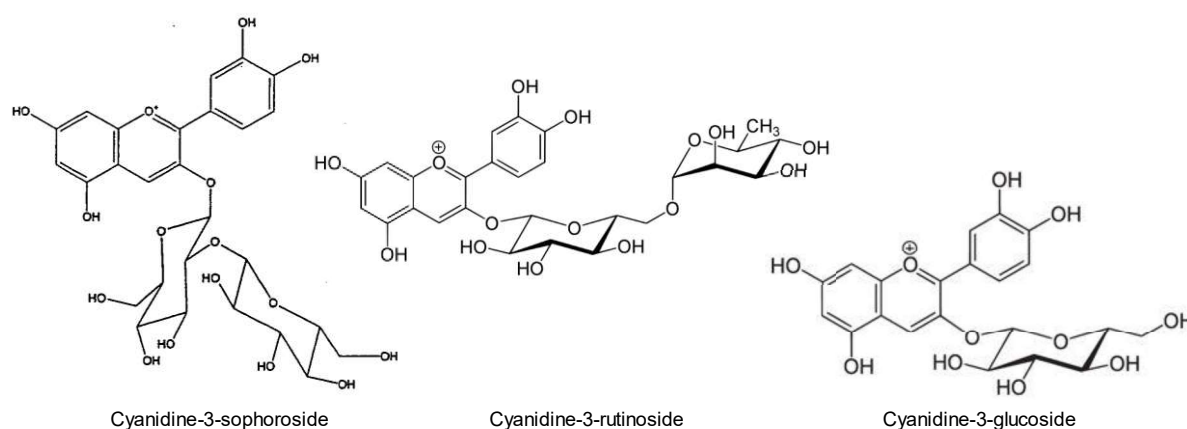


Fig. 1-6. Chemical structure of major anthocyanin compounds present in the raspberry fruit.

Degradation of anthocyanins is mainly related to the processing or storage conditions. The temperature and presence of oxygen is the main factor for the degradation by cleavage of covalent bonds or enhanced oxidation reactions (Palamidis and Markakis, 1975; Patras et al., 2010). Fig. 1-7 presents the possible degradation mechanism of cyanidin-3-glucoside and formation of intermediate compounds.

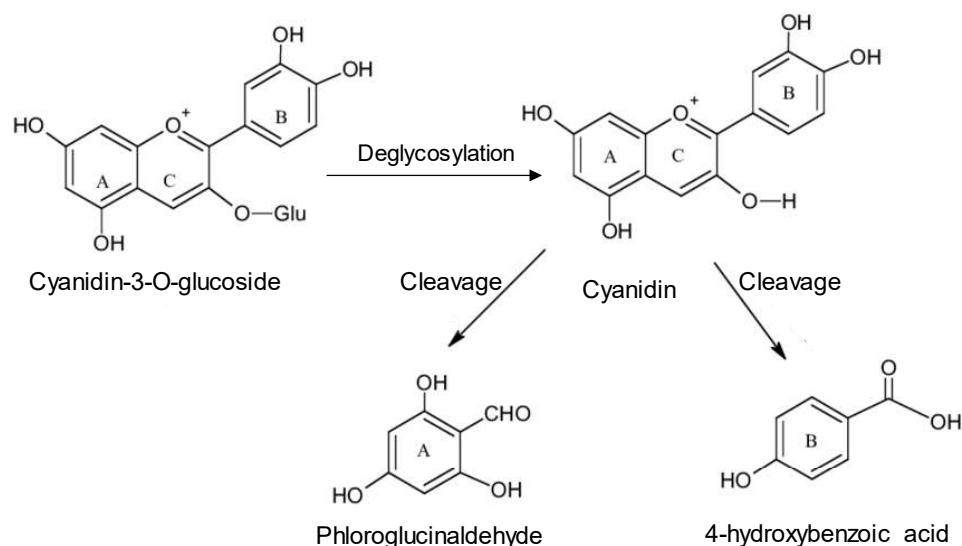


Fig. 1-7. Possible mechanism of thermal degradation of cyaniding-3-glucoside. (according to Patras et al., 2010).

The degradation mechanism of anthocyanin still remains unclear, although some authors have suggested different theories. As presented in Fig. 1-7, anthocyanin compounds consist of 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). Markaris et al. (1957) proposed the opening of the heterocycle and formation of a chalcone as the first step of anthocyanin degradation. Adams (1973) suggested that when heat is applied to anthocyanins, these compounds first suffer from 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 the loss of the B-ring. Further degradation can lead to brown products, especially in the presence of molecular oxygen (Markakis, 1982). Besides these structural influences, the surrounding matrix of anthocyanins also affects its stability (Weber and Larsen, 2017). Anthocyanin degradation at relatively 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 storage. This reaction is intensified by the presence of oxygen and its products (furfural and hydroxymethylfurfural) can condense with anthocyanins to form compounds with a brown coloration (Ferrari et al., 2013; Tonon et al., 2010). In contrast, the presence of oxygen can accelerate the degradation of anthocyanins through the action of oxidizing enzymes such as polyphenol oxidase (PPO) (Jackman et al., 1987). 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).

Ascorbic acid (AA), widely known as vitamin C, in the natural form of L-AA is present in raspberry at relatively high concentrations compared with other types of berries (Zhao, 2007). AA content of varying raspberry cultivars listed in Tab. 1-1.

Tab. 1-1. Ascorbic acid content of various raspberry cultivars.

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

Moreover, AA is responsible for up to 20% of the total antioxidant capacity, enhancing the immune system, and synthesizing collagen and hormones (Bobinaitė et al., 2012; Talcott, 2007). AA is a highly unstable molecule, and several factors have been reported to degrade AA including chemical and enzymatic oxidation. The stability of AA is strongly influenced by temperature, oxygen, and light exposure (Talcott, 2007). Total AA comprises AA and dehydroascorbic acid (DHA). DHA is an oxidized form of AA which is formed under oxidative stress by losing two protons in a reversible reaction (Chebrolu et al., 2012).

As raspberries are prominent types of berries with their healthy and attractive characteristics fulfilling the expectations of consumers, they are widely used in various industrially processed foods such as jams/jellies, frozen, dehydrated, snack foods, confectionery, cereals, powder, food colorant, and dairy. Because of its heat-labile composition, it requires gentle processing as well as storing conditions for maintaining its characteristics as they are very perishable.

1.4 Microwave-freeze-foam drying

1.4.1 Fundamentals of microwave technology

Microwaves are electromagnetic waves at a frequency band of 300 MHz to 300 GHz. Microwaves occupy part of the spectrum between the radio frequency range and infrared and visible light range. The frequency range corresponds to the quantum energies, and is small as compared to the ionization potentials of the elements. That is why microwaves are a part of non-ionizing radiation. Hence, microwaves cannot interact with atoms by transition between principal energy levels, denoting that they cannot break chemical bonds (Durance and Yaghmaee; Kaatze, 1995). The electromagnetic spectrum depicted in Fig. 1-8 shows the most common used frequency bands (915 and 2450 MHz). The frequency f is linked with the speed of light c at a corresponding wavelength λ according to equation 1-5:

$$c = \lambda \cdot f \quad (1-5)$$

Indeed, the name microwave refers to the wavelength within matter, which can be in the micrometer range. Thus, the speed of light in vacuum is given by $c_0 \approx 3 \times 10^8 \text{ m/s}$, where the corresponding wavelength is the range of 1 m-1 mm (Regier et al., 2017).

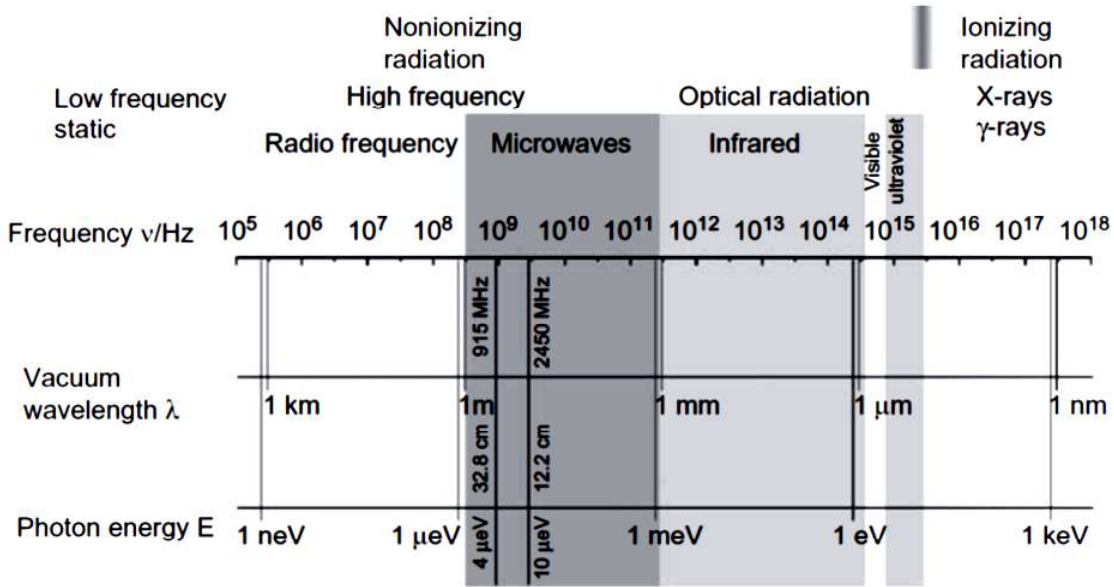


Fig. 1-8. Electromagnetic spectrum (Schubert and Regier, 2005).

Microwaves travel at the speed of light through space and can be either transmitted, reflected, or absorbed by matter depending on their dielectric properties. Electric and electromagnetic phenomena at the macroscopic level can be described according to Maxwell's electromagnetic theory (Schubert and Regier, 2005). The relation between electric field and magnetic field is given by Maxwell's equation (Eq. 1-6 to 1-8):

$$\nabla \times H = \sigma E + \frac{\partial D}{\partial t} \quad (1-6)$$

which showed how the magnetic field H is related to the electric flux density D while

$$\nabla \times E = -\frac{\partial B}{\partial t} \quad (1-7)$$

shows how the electric field E is related to the magnetic flux density B . However, we can choose the mode of microwaves such that the magnetic component is eliminated. Then, for a dielectric material, the equation becomes Eq. 1-8:

$$\nabla^2 E = -\mu \varepsilon \frac{\partial^2 E}{\partial t^2} \quad (1-8)$$

where μ is the permeability representing the interaction between the magnetic fields, and ε is the dielectric constant representing the interection of nonconducting materials

with the electric field. Electromagnetic waves are a blend of an electric component E and magnetic component H . E and H are perpendicular to each other and to the direction of travel, making this a plane wave. Furthermore, they are linearly polarized because E and H are both in one direction. A plane monochromatic electromagnetic wave is depicted in Fig. 1-9.

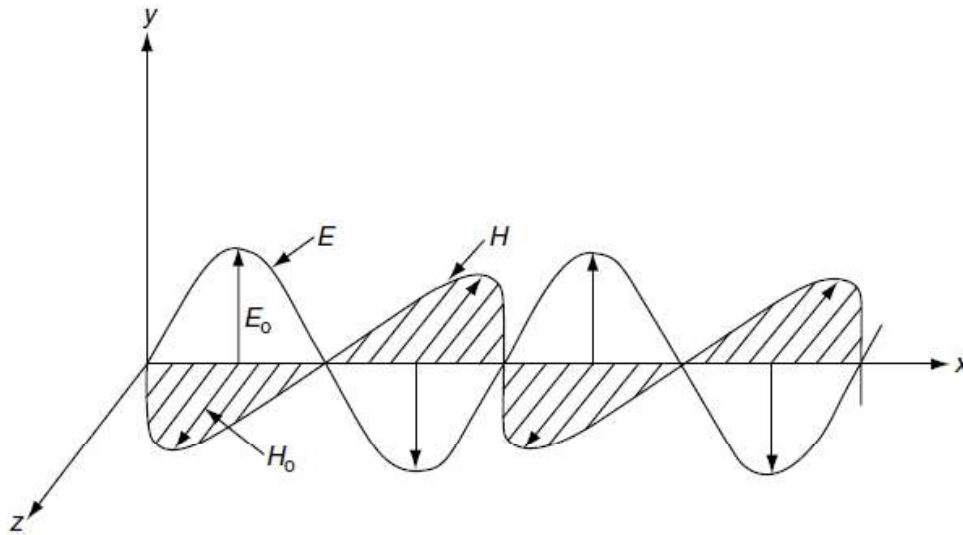


Fig. 1-9. A plane electromagnetic wave. E and H represent the electrical and magnetic components of the wave; E_0 and H_0 are their respective amplitudes (Willert-Porada, 2006).

Notably, when the electromagnetic wave passes through a material, its frequency remains the same; therefore, its wavelength changes which affects the penetration depth (Mujumdar, 1995).

1.4.2 Microwave heating and dielectric properties

A crucial fact is that microwaves and dielectrics are not forms of heat but rather they are forms of energy and are manifested as heat via their interaction with the material (Mujumdar, 1995). As mentioned earlier, microwave heating is a consequence of interactions among dielectric materials and electromagnetic waves. There are several mechanisms for energy conversion. There are two basic mechanisms triggering microwave heating at the molecular level—ionic conduction and dipolar rotation.

Ionic conduction: Ions are charged molecules which are accelerated by the electric field. Many liquids such as water can dissolve salts, acids, and bases which then be-

come dissociated into charged ions. Under an electric field, they move in opposite directions as per their own polarity. This movement occurs many millions of times per second and the energy is converted into kinetic energy and thus to heat (Drouzas and Schubert, 1996). This type of heating does not depend on either temperature or frequency. The developed power per unit volume (P_v) through ionic conduction can be calculated according to Eq. 1-9:

$$P_v = E^2 q n \mu \quad (1-9)$$

where q is the amount of electrical charge on each of the ions, n is the number of ions per unit volume (density of ions), and μ is the mobility level of ions (Willert-Porada, 2006).

Dipolar rotation: Many molecules such as water are dipolar in nature. When an electromagnetic field is applied, polar molecules with an asymmetric electrical charge distribution start to rotate, and maintain an alliance with the alternating field. Although dipoles are normally randomly oriented, the electric field attempts to pull them into alignment. This phenomenon is called orientation polarization (Ryynänen, 1995). Frictional heat is generated through kinetic energy caused by collisional movement of the molecules. Also, the oscillatory migration of ions in the material submitted into a high frequency oscillating electromagnetic field might lead to heating of the food material (Chandrasekaran et al., 2013; Sakiyan et al., 2007). Through these processes, heat is instantly generated within the product domain which leads to a propagation of heat in all directions which is called 3D volumetric heating, making microwaves a unique tool for heating applications (Klinbun and Rattanadecho, 2016). The power dissipated per unit volume is manifested as heat generation rate $\dot{Q}$ (Meda et al., 2017). Hence, the heat generated in microwaves can be calculated according to Eq. 1-10:

$$\dot{Q} = \sigma_e |E|^2 / 2 \quad (1-10)$$

The molecules that efficiently convert microwave energy to heat are called lossy molecules, such as water or other polar molecules, which can absorb energy resulting in heat production. Therefore, the heating effect occurs from the microwave field by energy dissipation (Durance and Yaghmaee).

From an engineering viewpoint, the dielectric behavior of material is important for understanding microwave heating characteristics. Dielectric properties of a product provide information on how the material interacts with electromagnetic energy (Jha et al., 2011; Sosa-Morales et al., 2010). The dielectric constant (ϵ') describes how much of the applied electromagnetic energy can be stored within the material, whereas the loss factor ϵ'' is a how much of this energy can be converted to heat (Tang, 2005). This means that higher dielectric loss factor is better because more energy can be absorbed and converted to heat. The permittivity (ϵ) is a complex quantity used to describe the dielectric properties that influence reflection of electromagnetic waves, or attenuation of the wave energy within material can be calculated according to Eq. 1-11 (Sosa-Morales et al., 2010):

$$\epsilon = \epsilon' - j\epsilon'' \quad (1-11)$$

where j is an imaginary proportion ($\sqrt{-1}$). The dielectric properties of a material depend on several factors such as chemical composition of material, temperature, moisture content, salt content, density, solute content, and the phase of the material such as liquid, solid, or gas (Durance and Yaghmaee; Sosa-Morales et al., 2010). Water is the major absorber of microwave energy in food products. When water is bound, the dielectric loss factor is 0.003 (at 25°C), where as for free water is 12 (Komarov and Tang, 2004; Tang, 2005). As depicted in Fig. 1-10, when the water is solid, the dielectric loss factor is 0.003 (at -20°C) means that water is almost transparent to microwaves and dielectric heating is mainly driven by the organic product itself (Ozcelik and Püschner, 2017).

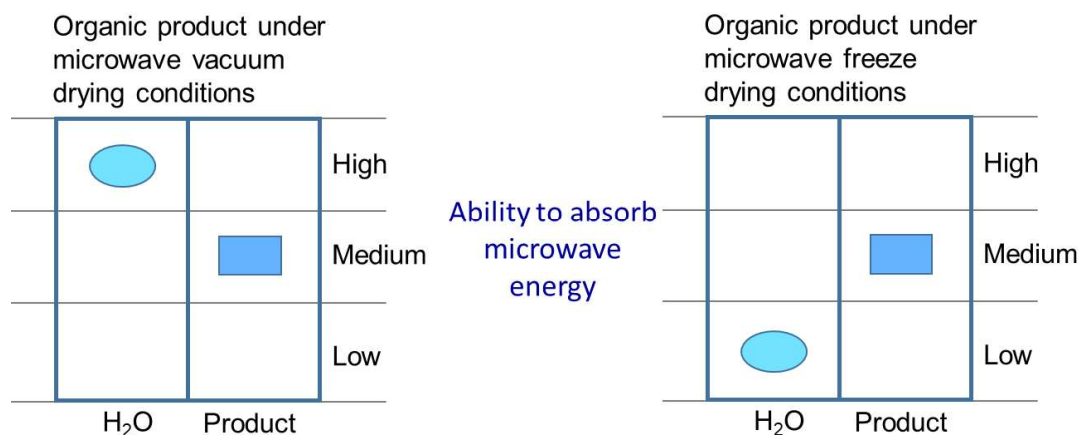


Fig. 1-10. Ability to absorb microwave energy from liquid (at 20°C) and solid water (−20°C) (Ozcelik and Püschner, 2017).

To show the difference between liquid and solid water in terms of their behavior under microwaves, Ozcelik and Püschner (2017) presented an ice cube filled with liquid water. As depicted in Fig 1-11, when the ice cube is exposed to microwave radiation, after a while, water starts to boil while the ice remains cold. This is due to the difference in their dielectric properties.



Fig. 1-11. Frozen ice cube filled with boiling water subjected to microwaves (Ozcelik and Püschner, 2017).

The ratio between the dielectric constant and loss factor is called loss tangent ($\tan \delta = \epsilon' / \epsilon''$) and is defined as the ability of a medium to convert electromagnetic energy to heat at a given frequency and temperature (Metaxas and Meredith, 1983). Although the penetration depth is important, it is not a property of a material but rather is a result of the abovementioned properties. Because electromagnetic heating is bulk heating, it

is important to know how deep the energy can penetrate into the material. The penetration depth is defined as the depth where the dissipated power is reduced to $1/e$ (Euler's number $e \approx 2.718$) of the power entering the surface (Tang, 2005). The penetration depth (D) is the relation between the wavelength (λ) and dielectric properties (ϵ' and ϵ'') of the material which can be calculated according to the simplified Eq. 1-12 (Metaxas and Meredith, 1983):

$$D = \frac{\lambda \sqrt{\epsilon'}}{2\pi \epsilon''} \quad (1-12)$$

The penetration depth of water at 2450 MHz is 1.4 cm (at 45°C) and 1.7 cm (at 90°C) and that of ice is 1100 cm (at -12°C) (Priecel and Lopez-Sanchez, 2018). Therefore, the penetration depth is considerably large under freeze-drying conditions. The penetration depth is highly dependent on the frequency. The industrially used frequency is 915 MHz where the penetration depth is almost 3-fold higher than 2450 MHz.

1.4.3 Drying with microwaves

Two main goals of using microwaves in drying are to accelerate the process and increase the product quality. In the past decade, the utilization of microwave heating in food processing has gained special attention because of its ability to achieve high drying rates with short drying times and high end-product quality including nutritional and sensorial quality and easy operation (Chandrasekaran et al., 2013). Conventional drying methods have disadvantages such as conventional hot air drying leads to quality losses due to relatively high temperatures and long drying times and freeze drying because of poor sublimation heat conductivity inserted through a heated plate leads to a long drying time and thus high operational costs (Fan et al., 2019). A common bottleneck for both methods is a low drying rate because of the heat transfer limitations (Duan et al., 2010a; Lombraña et al., 2001).

Microwaves can overcome this limitations by eliminating the thermal stress that can also overcome the relatively low heat conductivity problem for a wide range of heat-labile food materials (Chizoba Ekezie et al., 2017). Microwaves manifest selective heating in volume/3D of the material and simultaneous mass and heat transfer limitations do not occur. In the 3D volumetric heating mechanism due to the microwaves,

they can penetrate directly into the product, causing rapid internal heating and in particular focusing on the water molecules through dipole rotation and ionic conduction in the matrix materials. As depicted in Fig. 1-12, as the temperature gradient is directed toward the surface, the surface area does not dry out completely and stays permeable (Ozcelik and Püschner, 2017). In contrast, in conventional methods, water evaporation and water vapor transport occurs layer by layer, and water leaves the dry product through its surface via either conduction or convection (Erle, 2005).

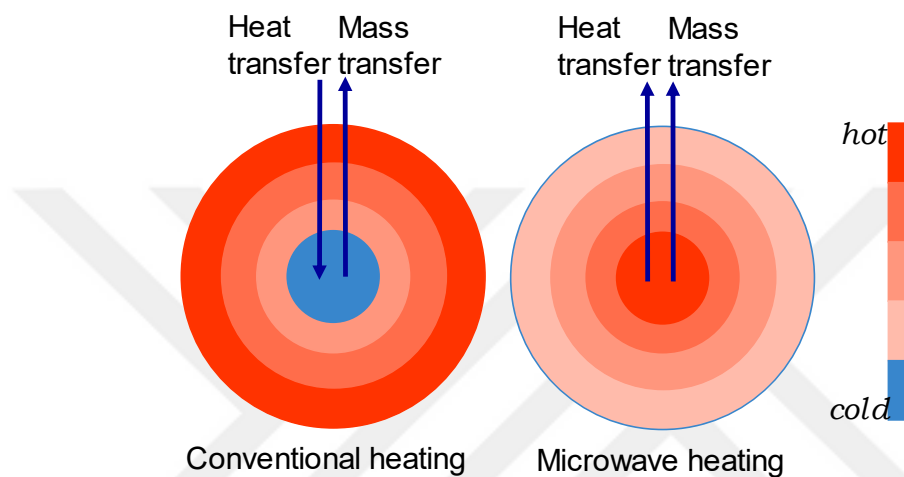


Fig. 1-12. Simplified depiction of drying mechanisms (heat/mass transfer) of conventional versus microwave methods (highly schematic representation, the actual heating and drying profiles are strongly dependent on other factors i.e., size, shape). Modified according to Ozcelik and Püschner (2017).

Besides its several advantages, even though microwave heating is in principle volumetric and hence it is more uniform compared to other techniques, non-uniform heating is the most challenging drawback which needs a special attention (Chandrasekaran et al., 2013). Therefore, combinations that take advantage of conventional methods and microwave heating lead to better processes than microwave alone such as microwave assisted vacuum or microwave assisted freeze drying (Jin et al., 2018; Wang et al., 2018; Zhang et al., 2006).

1.4.4 Microwave-freeze drying

Freeze drying (FD), also known as lyophilization, is considered as the most gentle dehydration process, which occurs by sublimation in the absence of liquid water at a low temperature and oxygen-free environment, which is often taken as a reference method restricted for the food industry to make high added-value products such as

aromatic herbs, ready-to-eat products (fruit, vegetables, fish and meat), and coffee (Marin, 2003). The secondary drying phase of FD, where the bound water is removed, requires more intense energy and proceeds relatively slower. Therefore, this process is a long and recognized as the most expensive (Ratti, 2001). For this reason, the process has to be accelerated while the conditions should be kept the same for obtaining high quality heat-labile products. Simply, FD coupled with microwave heating is called microwave-assisted FD (MWFD) (Fan et al., 2019). The main advantage of MWFD is that the applied microwave energy is volumetrically absorbed by the organic molecules as water has a very low dielectric loss factor at the solid phase. Therefore, poor internal heat transfer is a limitation because the heated shelf plate will then be offset while the entire process takes places at low pressure and low temperature. Thus, higher drying rates can be achieved, which in turn can produce even better quality products than FD because of the short exposure time in the drying process.

There are some critical points for the MWFD process. The processing conditions and limitations should be clearly defined for an individual material. There are some technical problems that still limit the industrial applications of MWFD such as arcing, corona discharges, melting, non-uniform heating, and overheating (hot/cold spots). (Ratti, 2001). When electrical potential across a material exceeds the dielectric strength of the material, dielectric breakdown occurs resulting in ionization of the gas which sharply reduces the electrical insulation of the gas causing sparks or arc. This wastes energy. If electrical discharge continues, referred to as plasma, purple light appears (Durance and Yaghmaee). Corona or plasma discharge occurs because of the ionization of residual gases presented in the vacuum chamber when the electric field intensity is above the threshold value (Lombraña et al., 2001). As depicted in Fig. 1-13, electric field is a function of chamber pressure. It has the minimum value in the pressure range (100-200 Pa) of freeze drying. At a pressure range of 50-100 Pa, the possibility of plasma occurrence is reported to be very low (Duan et al., 2010a; Fan et al., 2019). Moreover, plasma discharge possibility increases when the moisture content decreases. The electric field strength is proportional to the power applied; therefore, plasma discharge can be avoided by controlling the pressure and applied power. On-off cycled MW power strategy with simultaneous control of chamber pressure was found to be a useful method for avoiding this phenomenon (Duan et al., 2010a; Lombraña et al., 2001; Zhang et al., 2006). It can cause localized melting of ice resulting in

thermal-runaway, resulting in uneven heating, hot spots, or burning. Therefore, a proper process control of the design system allowing control of temperature, pressure, and power intensity is required.

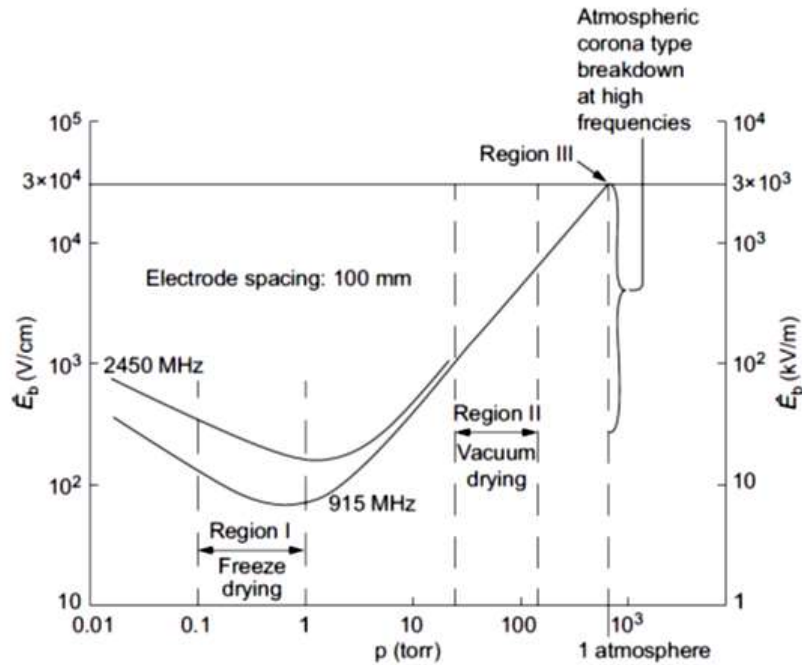


Fig. 1-13. Variation of the electric field threshold value as a function of pressure (Püschner, 2005).

An experimental pilot-scale MWFD system where the drying experiments in this thesis were conducted is shown in Fig 1-14. This dryer has a programmable software where the MW power is controlled with the product temperature and pressure power capability of online monitoring of process parameters including the product weight. A cylindrical microwave cavity (stainless steel, 500 mm diameter, 1 m length, and approximately 200 L) coupled with a maximum power output of 1000 W/2450 magnetron with a water-cooling system was installed on a waveguide launcher where the microwave energy was generated. The unit consists of a circulator and a tuner which enable the magnetron to generate its nominal set microwave power. The vacuum system comprises a vane rotary vacuum pump (Pfeiffer, Asslar, Germany, $76 \text{ m}^3 \text{ h}^{-1}$) and ice condenser with chiller.

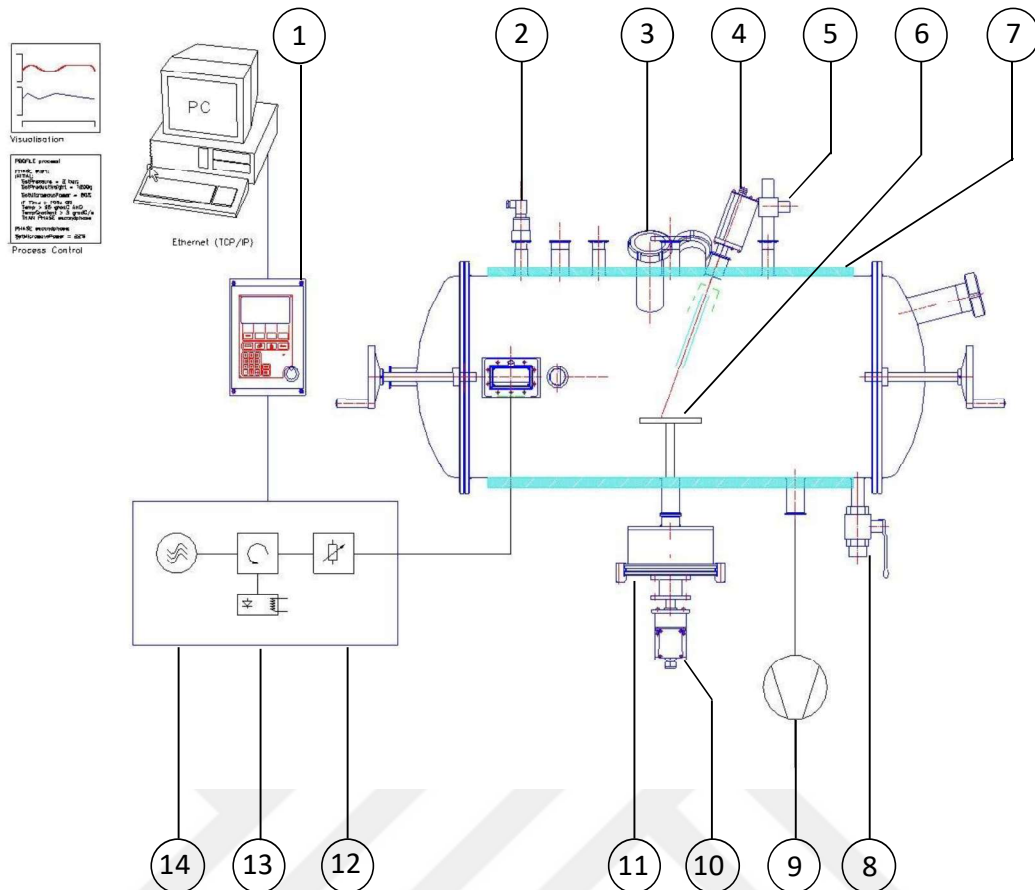


Fig. 1-14. Process flow diagram of microwave freeze dryer (Püschner Microwaves, Schwanewede, Germany).

- 1 Microwave process controller with connection to computer
- 2 Double pressure transducer
- 3 Sight glass
- 4 Infrared temperature sensor, -50 to 250°C
- 5 Automatic valve for breaking vacuum
- 6 Applicator with turntable
- 7 Wall heating
- 8 Manual valve for breaking vacuum
- 9 Port for vacuum gage
- 10 Turntable motor
- 11 Online load cell
- 12 Tuner
- 13 Circulator with device for reflection measurement
- 14 Magnetron

1.4.5 Microwave-freeze-foam drying

Nowadays, the application of microwaves to foam drying has attracted increasing attention. Microwave-foam drying was successfully applied to blackcurrant pulp (Zheng et al., 2011), guava pulp (Qadri and Srivastava, 2015), tomato pulp (Qadri and Srivastava, 2014), corn soaking water (Chai et al., 2016; Qiang et al., 2013) and foamed milk (Ben Souda et al., 2016; Sochanski et al., 1990). However, no work has been reported in the literature on microwave-freeze-foam drying of fruit pulps.

As explained earlier, foam-mat drying has received attention due to its simplicity and enables drying of hard to sticky materials with a high sugar content which are heat sensitive such as fruits. The main advantages of foam-mat drying are lower temperatures and shorter drying times in comparison with non-foamed materials at the same drying technique (Ratti and Kudra, 2006). Nevertheless, the lower thermal conductivity of air bubbles than that of unfoamed liquid is the key aspect limiting heat transfer within the foam material. Microwaves can solve this limitation by generating heat volumetrically in the product domain. Combining the advantages of the three processes, namely foam-mat drying and freeze drying, microwave drying was used. Microwave-freeze-foam drying would be an ideal way to make an efficient high-quality drying method. The underlying drying mechanism is schematically depicted in Fig 1-15.

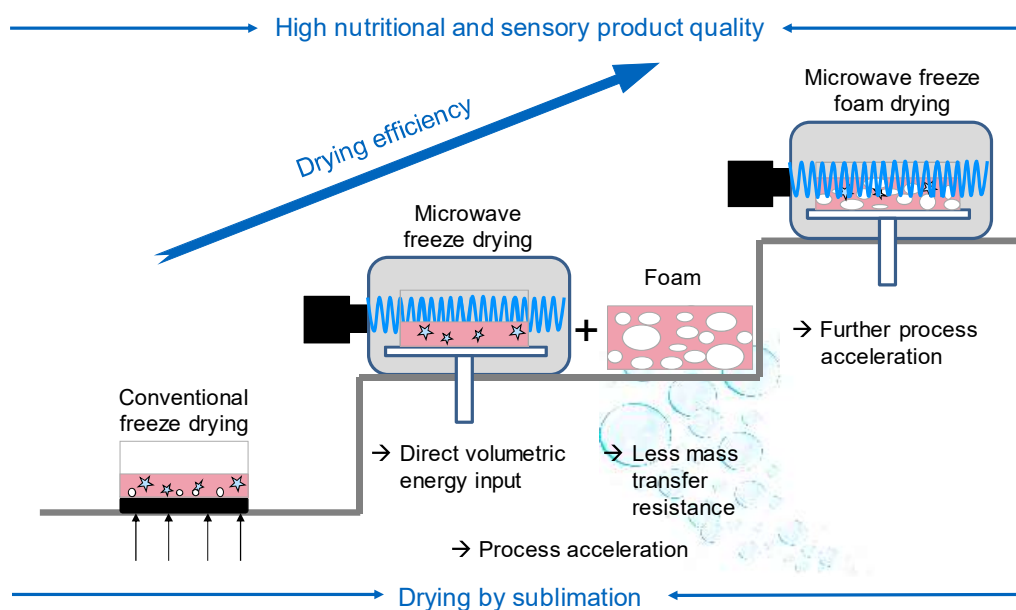


Fig. 1-15. An efficient drying concept for heat sensitive materials: Microwave-freeze-foam drying.

1.5 Basics of analytical techniques for the assessment of product characteristics

1.5.1 Determination methods for dielectric properties

As already explained in Section 1.4.2, volumetric heating involves converting microwave energy to heat based on the dielectric properties of the material. Therefore, dielectric properties of the material are major factors affecting microwave heating (Chandrasekaran et al., 2013). Dielectric properties of a product provide information on how the material interacts with electromagnetic energy. If electromagnetic waves penetrate non-conducting dielectric materials, the wave changes its velocity of propagation depending on the dielectric losses of the material. Thus, inhomogeneities in the food matrix can cause cold and/or hotspot phenomenon, resulting in nonuniform drying. Reflection, absorption, transmission, and refraction are typical modes of interaction between a material and electromagnetic waves. The measurement of these conditions allows the calculation of the dielectric losses of the material within the electromagnetic wave. The formation of ice is of great concern in MWFD, with the dielectric behavior of a material affecting its heating characteristics. While solid water (ice) has a low dielectric loss factor and is almost transparent to microwaves, the dielectric loss factor of liquid water is very high (See Fig 1-10, 11). Dielectric properties of the materials mainly depend on the frequency of the electromagnetic field, temperature, and chemical composition of the material (Meda et al., 2017).

Although a number of techniques are available for measuring the dielectric properties depending on the physical and electrical characteristics of the material and the frequency range, the three most commonly used methods are open-ended coaxial probe, transmission line, and resonant cavity methods (Ohlsson, 1980). These methods are schematically presented in Fig 1-16.

The open-ended coaxial probe method is currently one of the most popular techniques for measuring the dielectric properties of liquid and semi-solid materials including biological food materials, fresh fruits, and vegetables (Venkatesh and Raghavan, 2005). The method is basically a modification of the transmission line method based on a coaxial line which has a tip that senses the signal reflected from the material being tested (Fig. 1-16a). The tip is brought into contact with the material by touching the

probe to a flat face of a solid or by immersing it in a liquid. This method offers broad-band measurements while minimizing sample disturbance. The measured reflection coefficient is related to sample permittivity (Sheen and Woodhead, 1999; Venkatesh and Raghavan, 2005; Wang et al., 2003).

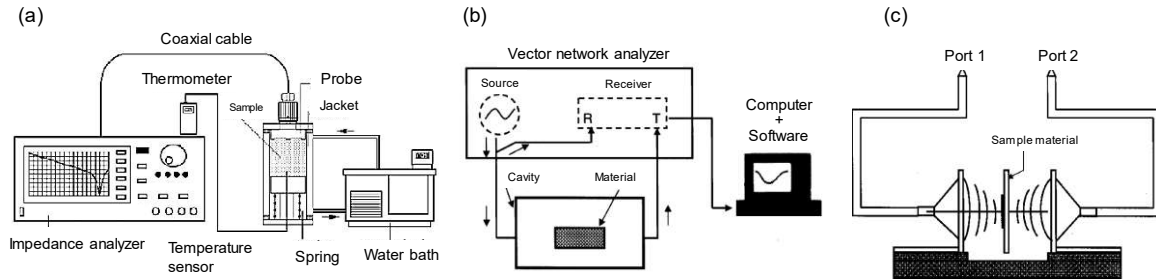


Fig. 1-16. Schematic illustration of methods for determining dielectric properties: (a) open-ended coaxial probe, (b) transmission line-waveguide, and (c) resonant cavity, where the ports are connected to a network analyzer (Venkatesh and Raghavan, 2005; Wang et al., 2003).

The probe method is the easiest to use because it does not require a particular sample shape and requires minimal sample preparation. It is possible to measure the dielectric properties over a wide range of frequencies (500 MHz–110 GHz) (Venkatesh and Raghavan, 2005). Thus, the obtained data can be used for further calculations to understand the response of the material to the electromagnetic field at a certain required frequency and temperature. A major disadvantage of this method is that it is not suitable for measuring materials with a small dielectric coefficient such as oils and plastics (Komarov and Tang, 2004). In this thesis, the open-ended coaxial probe method with a dielectric measurement kit (Model *μWaveAnalyser* Püschner Micro-waves, Schwanewede, Germany) was utilized for determining the dielectric properties of samples.

The transmission line method involves placing a sample inside an enclosed transmission line. The cross-section of the transmission line must be filled with the sample (Fig 1-16b). The method is applicable for both solids and liquids. Despite the higher accuracy and sensitivity of this method, it is difficult to implement and is time consuming (Sosa-Morales et al., 2010).

The resonance cavity method is applicable to solids, involves easy sample preparation, and is adaptable for a wide range of temperatures. This method uses a single-mode cavity (Fig. 1-16c). Once a sample of known geometry is placed in the cavity, the changes in the reflected power of the cavity and the frequency of resonance are

used to compute the dielectric properties of the sample. The cavity method can be accurate and is especially suitable for samples with a very low dielectric loss factor. However, this method provides dielectric properties at only one fixed frequency (Tang, 2005; Wang et al., 2003).

There are several factors that affect the dielectric properties of a material. The chemical composition (e.g., salt content, moisture content, and status of the moisture (frozen, free, or bound water)) of the material, physical structure (density), temperature, and the frequency are major factors that have to be considered (Zhu and Guo, 2017).

1.5.2 Glass transition

Phase is a region in which all the physical properties of a material are essentially uniform. The phase diagram of water with dependence on pressure and temperature was depicted earlier in Fig 1-1. Phase transitions are changes in the physical state of a material. Basically, changes in physical states as a result of changes in temperature, pressure, and water or solid content is referred to as “transition.” Phase transition in food materials occurs during processing or often during storage. The stability of food systems can be defined with its equilibrium phase (Roos and Drusch, 2015). Foods are considered as stable when they are in their solid “glassy” state characterized by high viscosity (10^{12} Pa s) (Roos, 1993). Therefore, a phase diagram is a map associated with equilibrium conditions that provides information of what phase to expect under the applied processing conditions (Rahman, 2006). Accordingly, the process and storage conditions can be determined to obtain a stable product (Hartel et al., 2011). Particularly in the drying process, drying temperature plays an important role that causes detrimental changes within the structure of a matrix. On drying above the critical temperature, referred to as “glass transition temperature (T_g),” glassy solids begin to change into a liquid-like rubbery state (or vice versa) (Bhandari and Howes, 1999). T_g is a property specifically associated with amorphous materials. As a consequence of phase transition, the textural, sensorial, and nutritional quality of a product decreases and usually the shelf life is negatively affected (Hartel et al., 2011). T_g is reversible and it occurs over a temperature range (Roos, 2010). Changes in the physical structure of a material are schematically depicted according to Bhandari and Howes (1999) in Fig 1-17.

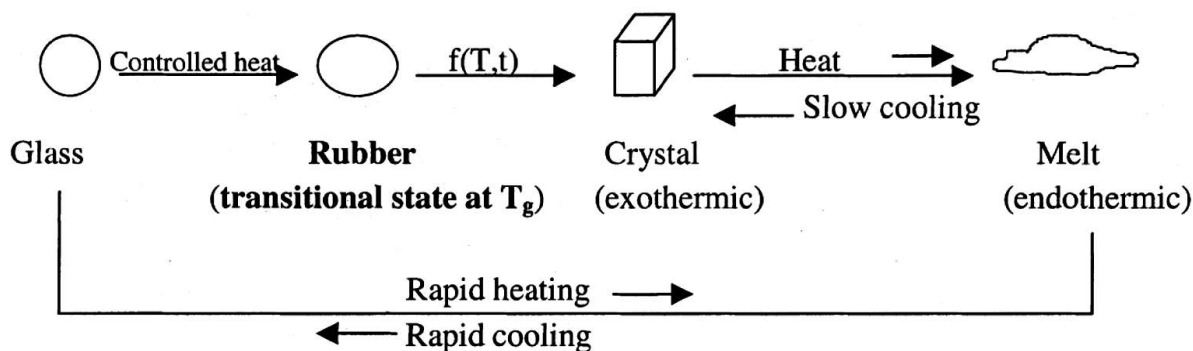


Fig. 1-17. Phase transition of an amorphous glass through rubbery to crystalline state. T: temperature, t: time (Bhandari and Howes, 1999).

From the thermodynamic viewpoint, when the temperature increases above T_g , the physical properties of a material change with an increase in the free molecular volume, an increase in heat capacity (C_p), increases in the thermal expansion coefficient (α) and dielectric coefficient (ϵ), and changes in viscoelastic properties. The free-volume theory refers to the volume unoccupied by the solid matter of the molecules and refers to the volume available for their free movement (Bhandari and Howes, 1999).

Most dried foods exhibit a glassy amorphous form mainly due to insufficient time for the occurrence of crystallization depending on the drying rates. Food solids are mainly lipids and water-soluble components (i.e., carbohydrates, proteins, minerals, and other minor constituents). The physical state of lipids is often related to crystallization. Carbohydrates and proteins are in a nanocrystalline amorphous state, in a crystalline state, or in solution. As they are water soluble, phase transition is significantly affected by the water content; increasing water content increases molecular mobility (Roos and Drusch, 2015). Based on the equilibrium concept, bound water is defined as solute associated water, which is different from bulk water, and poses reduced solubility for other compounds that limits the diffusion. Therefore, better stability can be achieved with bound water with no free water (Syamaladevi et al., 2010).

Raspberries comprise a large group of high sugars like most fruits. Dominant sugars in raspberry are fructose, glucose, and sucrose (Rao and Snyder, 2010). Therefore, the T_g of dried raspberry is associated with the T_g of these sugars dominating the storage stability (Syamaladevi et al., 2009). The state diagram of sucrose as a function of temperature and weight fraction is depicted in Fig 1-18. Carbohydrates with low mo-

lecular weight generally have low T_g and T_g increases with high molecular weight polysaccharides such as maltodextrin (Claude and Ubbink, 2006). Additional advantages of using high molecular weight carbohydrates under controlled conditions in the glassy state are their abilities of film forming, encapsulation, and protective effects with very high barrier properties for sensitive substances (ascorbic acid and anthocyanins) and aroma compounds (Schoonman et al., 2002).

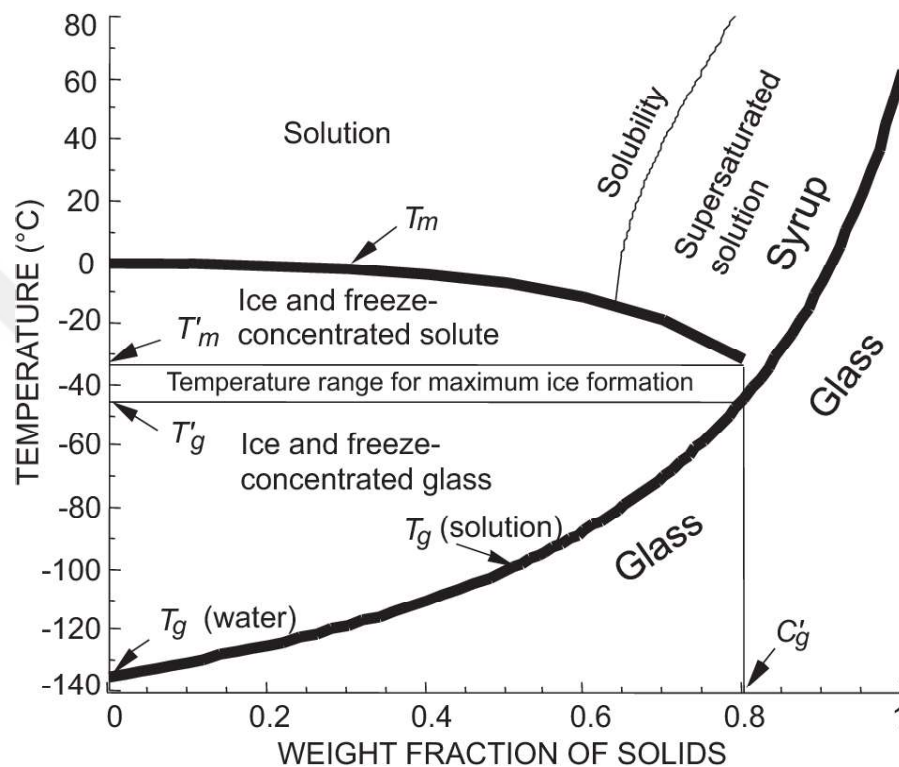


Fig. 1-18. Phase diagram of sucrose. The dependence of glass transition T_g on water content, solubility, and ice formation. The T_m curve represents the equilibrium melting temperature for ice, and T_g' and T_m' refer to the onset glass transition and onset for ice-melting temperatures in a maximally frozen concentrated solution, respectively, (Roos, 2010; Roos and Karel, 1991).

Differential scanning calorimetry (DSC) is one of the most commonly applied methods for determining T_g (Roos and Karel, 1990). The method comprises relative heat flow to a sample pan as temperature is changed at a constant rate. It appears as an endothermal step change in heat flow to a sample resulting from the increase in heat capacity when a material is heated above its glass transition. The T_g values are often reported as the temperature of the inflection point of the change; however, the onset or midpoint and/or endset temperatures of the change in heat capacity may also be considered to specify the range (Hartel et al., 2011; Roos, 2010). Especially for complex mix-

tures, T_g generally occurs over a range of temperatures rather than at a single temperature. The T_g values of dried raspberry powder and maltodextrin (DE6) were reported to be 40.2°C and 197°C, respectively, (Jakubczyk et al., 2010; Syamaladevi et al., 2009)



2 Objective and outline

Based on the abovementioned aspects, functional food concepts combined with fruits are becoming more important in the snack food market owing to the health awareness of consumers. Foams fabricated from fruit pulps can subsequently be dried and consumed as snacks. Such dried foams can disintegrate very quickly upon contact with the saliva in the mouth, leading to a spontaneous flavor release. This "Aroma-Flash" is perceived as a positive sensory experience. The processing, storage, and transportation adversely affect the physical, structural, nutritional, and sensorial quality of food. In particular, with respect to a high-value food with a heat labile nature, the selection of the technique and conditions for preservation are fundamentals for successful processing. Conventional freeze-drying is regarded as the state-of-the-art preservation method because of the absence of oxygen and liquid water and because of the low temperatures, leading to an excellent product quality, especially heat- and oxygen-labile products. It requires long processing times; thus, the high energy consumption leads to an expensive process and expensive end products. In contrast, hot air drying is the most commonly used method; however, it leads to degraded product quality because of the relatively high drying temperatures and the long drying times. Thus, there is a need to search for a new technology that is fast and efficient and can provide high-quality dry fruits that are heat- and oxygen-sensitive.

Therefore, the aim of this thesis is to comprehensively study the application of microwave to freeze drying to promote energy efficiency with increased drying rates, shorter drying times, and therefore, better product quality with a smaller footprint. Further enhancement of the mass and heat transfer would occur by reducing the diffusion limitations with the creation of a foamed structure. For this purpose, raspberry is used as a model fruit with the aid of hydrocolloids. Considering the potential health benefits as well as the positive environmental impact of plant-based proteins, potato protein was applied as a foaming agent with respect to its functionalities. Thus, characterization of raspberry foams was adopted. The subsequent microwave-assisted freeze drying was investigated under varying microwave power input at a defined maximum product temperature and pressure. The respective product characteristics in terms of color, texture, ascorbic acid, and anthocyanins were evaluated. The raspberry pulp was further examined in terms of the plant bioactives and ascorbic acid because of cell destruction

under oxidative stress. Moreover, it was hypothesized that the composition and structure of different raspberry products could affect storage stability. The open porous structure of the foamed raspberry pulp with a larger surface area could induce greater degradation because of the easy accessibility of oxygen. Therefore, dried foamed and un-foamed raspberry pulp with hydrocolloids and the dried raspberry pulp were considered to be a baseline and were examined during storage. Along with the experimental concept, conventional freeze drying was performed as a reference for comparison with microwave assisted freeze drying.

The following chapters are combined with published and unpublished data for a better interpretation of the overall perspective.



3 Results

The following chapters are combined with published and unpublished data. Subsections 3.1, 3.3 and 3.5 are unpublished data and Subsections 3.2, 3.4, 3.6 and 3.7 are published data.

3.1 Characterization of fruit foams

The main objective of this study was to create a new structure by means of foams and subsequent drying for a faster drying process. The open porous structure that enables easier water removal accelerated the drying process. In addition, a foam structure caused a new sensory perception by the open porous structure. The release of flavor from foams is usually more intense as the microstructure can be easily destroyed. Such dried foams can disintegrate very quickly upon contact with the saliva in the mouth, leading to spontaneous flavor release. This "Aroma-Flash" is perceived as a positive sensory experience.

Building on this, to obtain stable foam before and during drying as well as during storage, it is important to achieve a suitable type and concentration of protein and hydrocolloids in the matrix to avoid no foam formation or foam collapse.

3.1.1 Characterization of potato protein isolate

The foaming properties of PPI were compared with those of its competitor, egg white and whey protein isolate, which are widely used animal-derived proteins. Three different types of proteins were applied at varying concentrations (0.5, 1, 2.5, 5, 7.5, and 10%, w/w) to produce foam. Fig. 3-1 presents the data of overrun and foam stability ($t = 30$ min) as a function of protein concentrations. As the protein concentration increased, the viscosity of the continuous phase increased, thus reducing drainage and accordingly increasing foam stability.

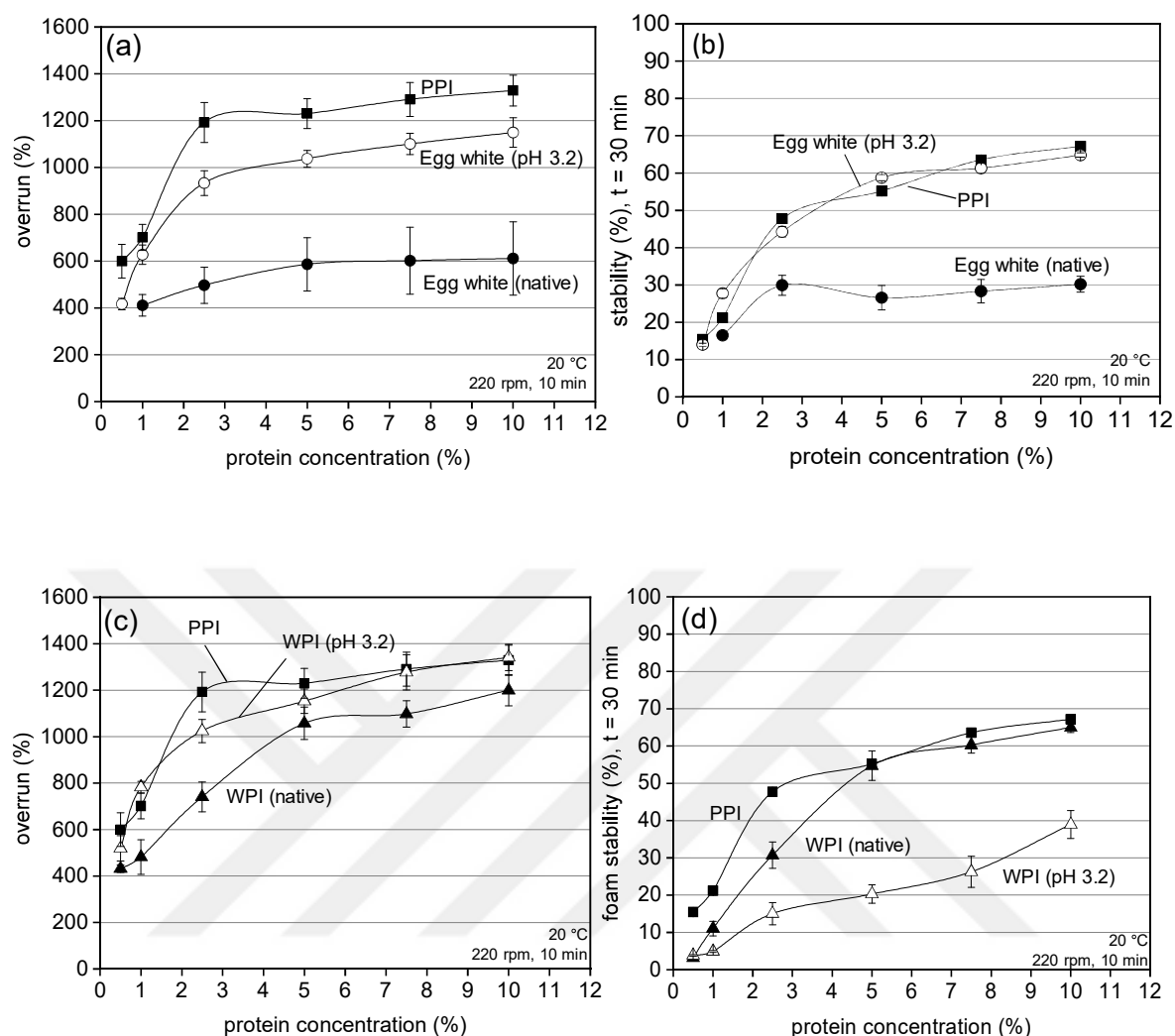


Fig. 3-1. Foam characteristics of different protein types and concentrations (0.5, 1, 2.5, 5, 7.5, and 10%, w/w) in a foam matrix. **(a)** Overrun of egg white (native), egg white (pH 3.2), and potato protein isolate (PPI). **(b)** Foam stability of egg white (native), egg white (pH 3.2), and PPI. **(c)** Overrun of whey protein isolate (native), whey protein isolate (pH 3.2), and PPI. **(d)** Foam stability of whey protein isolate (native), whey protein isolate (pH 3.2), and potato protein isolate.

The PPI showed higher foam stability than egg white and whey protein isolate. High solubility of potato protein was obtained in acidic pH. According to the results presented in Fig. 3-1, at a protein concentration of 10% w/w, the maximum foam stability was obtained, and no significant changes were observed above 10%. Therefore, PPI with a maximum concentration of 10% (w/w) was chosen as the foaming agent in this study.

3.1.2 Influence of whipping time on foam formation

To define the whipping time for raspberry foams, overrun, foam stability, and the changes in foam structure were evaluated at different whipping times. According to Dickinson (1988), the optimum degree of whipping for maximum stability is right before the maximum foam volume is reached. The respective results are displayed in Fig. 3-2 and 3-3.

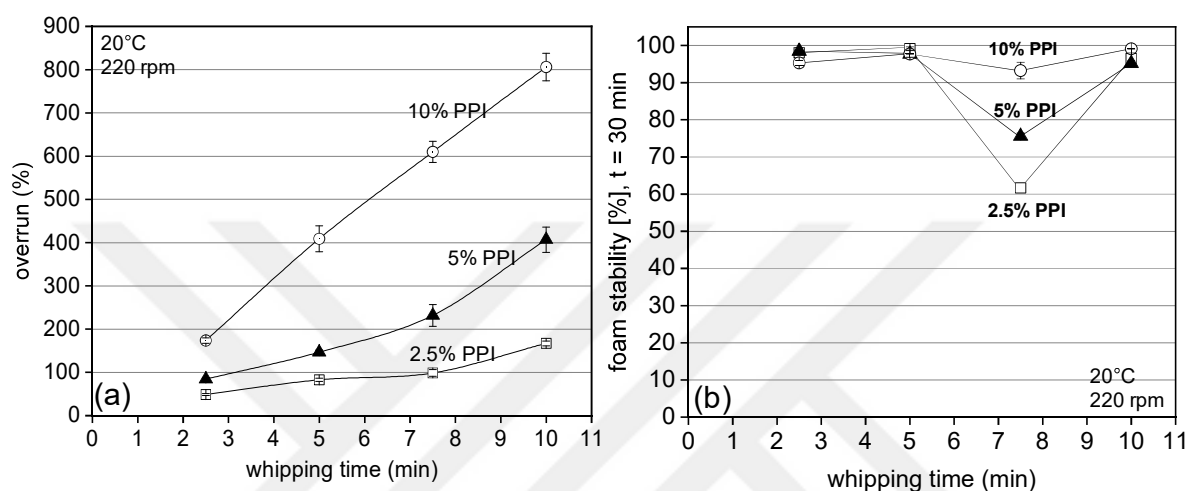


Fig. 3-2. Impact of whipping time on foam properties of the protein matrix at varying protein concentrations (2.5, 7.5, and 10.0%, w/w); **(a)** overrun; and **(b)** foam stability ($t = 30$ min).

During whipping, the beaters cause velocity fluctuations that not only promote bubble break-up where large bubbles are subsequently broken up into smaller bubbles but also cause pressure fluctuations according to Bernoulli's law (van Koningsveld et al., 2002). Increasing whipping time increases the volume of gas incorporated into the foam matrix and consequently the overrun because more and smaller bubbles can be formed. Longer than 10 min whipping time resulted in a decrease in foam volume. This might be because of the continuous surface expansion and protein desorption due to bubble breakage which may have caused extensive protein unfolding leading to a decrease in the effective molar protein concentration (van Koningsveld et al., 2002).

A 100% foam stability was obtained for all tested concentrations. However, with a whipping time of 7.5 min, a drop in foam stability was observed for all concentrations. The respective results on foam structural attributes are given in Fig. 3-3, referring to the 5% (w/w) PPI.

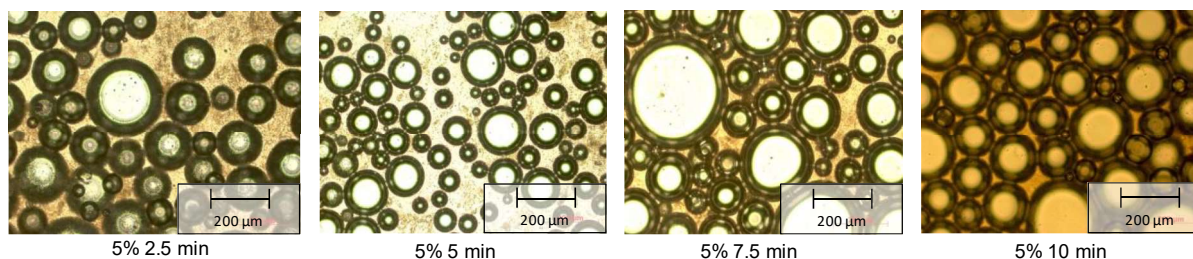


Fig. 3-3. Changes in foam structures as a function of whipping time. The raspberry foam matrix consists of 5% (w/w) potato protein isolate.

At a whipping time of 2.5 min, air bubbles started to become entrapped into the liquid and foam formation begun. At a whipping time of 5 min, more and smaller bubbles were formed, following which bigger ones grew by gas diffusion in the continuous phase. A further increase in whipping time partially disrupted bubbles, and drainage of unfolded protein not yet adsorbed at the interface occurred. The drained liquid was re-whipped for more time; the protein concentration in the fluid formed new bubbles in the continuous phase.

According to the aforementioned results, a whipping time of 10 min at a maximum mixing speed of 220 rpm using a planetary mixer was chosen for producing raspberry foams in this study.

3.1.3 Characterization of foam matrix composition

Foam instability is the most important challenge faced by the foam matrix. The stability of foam decay has to be ensured before, during, and after the drying process. The foaming properties of vegetable proteins are such that foam formation and stabilization may require further improvements of interfacial properties (Rodríguez Patino et al., 2008). This improvement could be achieved with the formulation of a protein-polysaccharide complex that can help further stabilization (Schmitt et al., 1998). In this manner, the protein concentration plays an important role in the continuous-phase composition at the air–water interface. Because of the high water binding capacity and thickening properties of MD and pectin, they can be added to a protein foam to increase the viscosity and thereby enhance stability of a foam. In this context, foam characteristics of the protein-carbohydrate matrix at varying concentrations were investigated. The key factor is the protein to carbohydrate ratio. A proper concentration of protein and polysaccharides can enhance functional properties such as solubility, foam formation, and

stabilization. A higher amount of protein can be adsorbed and can form a multilayer network in the presence of polysaccharide (Rodríguez Patino et al., 2008).

Fig. 3-4 shows the impact of MD concentration on the foam characteristics of 5% (w/w) protein foam. Increasing MD concentration led to a significant decrease in overrun and an increase in foam stability. MD and pectin can form a thickening network in the continuous phase through intermolecular interactions, resulting in an increase in the viscosity which decreases the drainage of the liquid, thus stabilizing the structure. Corresponding data are presented in Fig. 3-4 and 3-5.

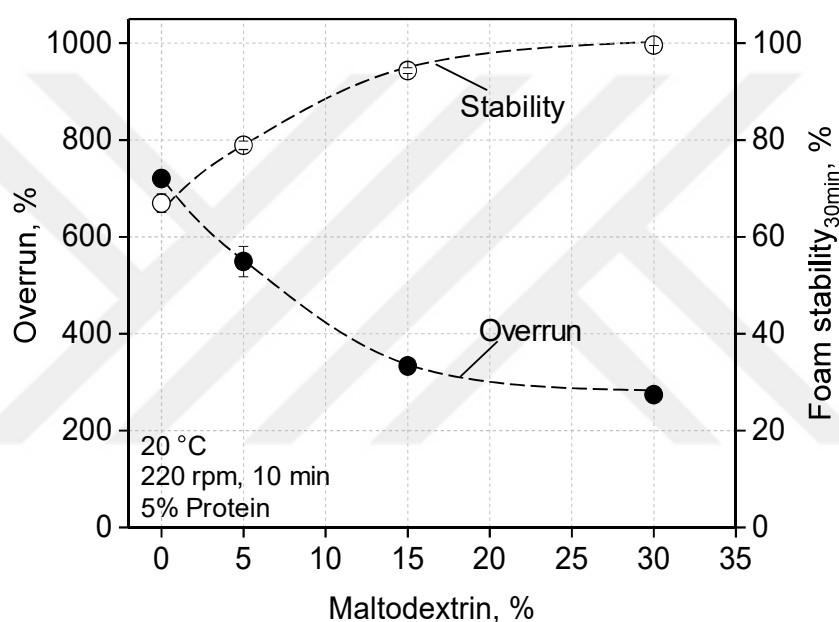


Fig. 3-4. Impact of MD concentration on protein foam characteristics. The foam matrix consists of 5% (w/w) potato protein isolate.

Increasing pectin concentration increased the foam stability while decreasing the overrun as a result of increased viscosity, as presented in Fig. 3-5.

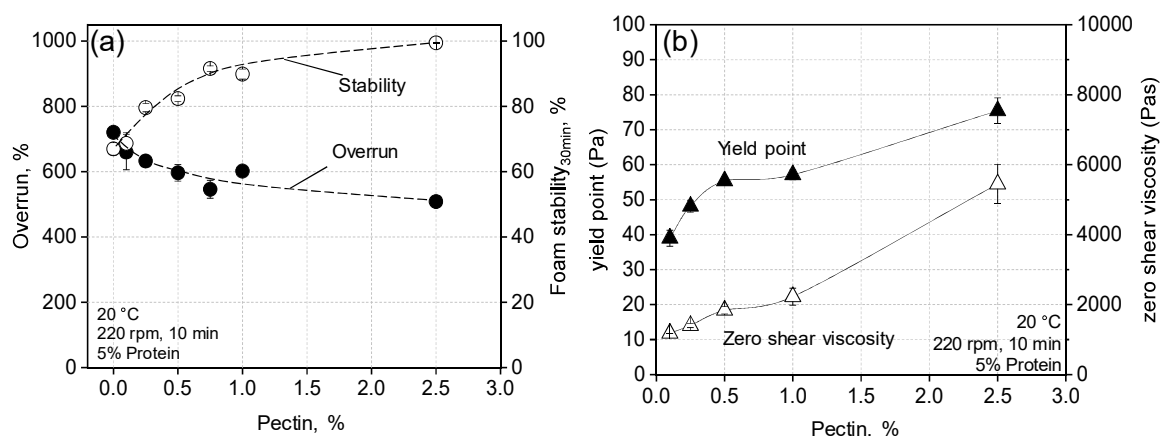


Fig. 3-5 Impact of pectin concentration on protein foam characteristics. The foam matrix consists of 5% (w/w) potato protein isolate. **(a)** Overrun; and **(b)** yield point and zero shear viscosity.

Fig. 3-6 shows foams prepared with raspberry puree at a constant concentration (2.5%, w/w) of PPI with varying MD and pectin concentrations. Higher concentrations of pectin help increase the surface elasticity of the walls of the bubbles.

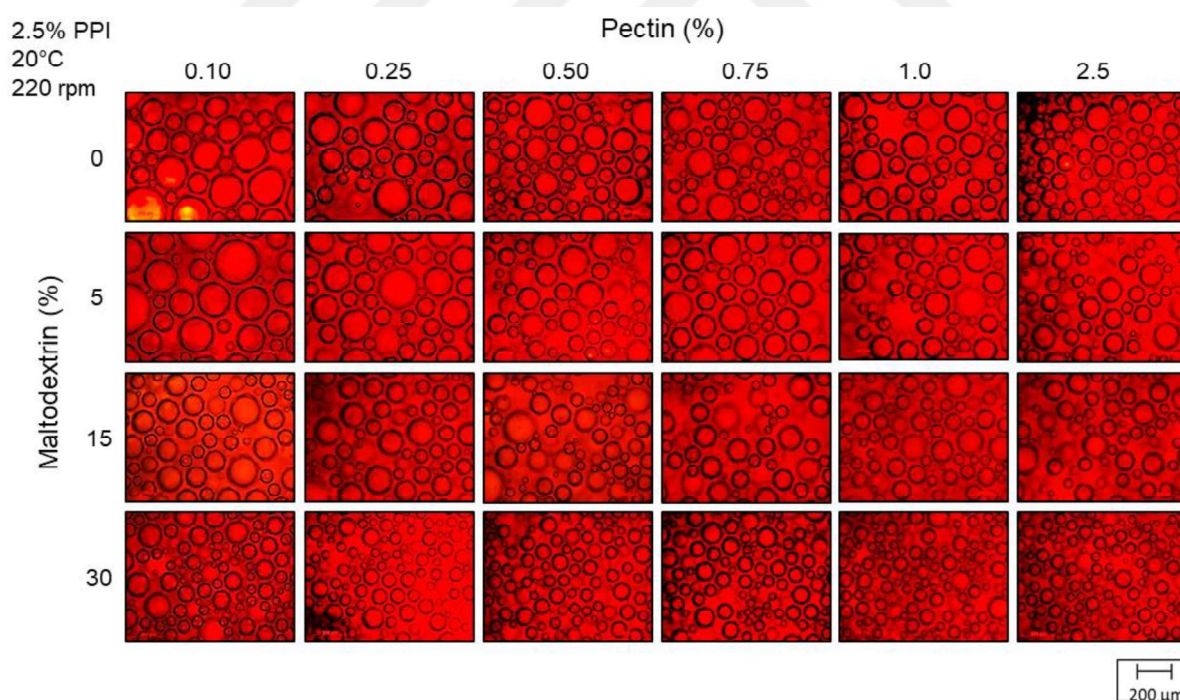


Fig. 3-6. Foam of raspberry puree with 2.5% potato protein isolate with varying pectin and MD concentrations.

Round and more uniform bubbles were obtained at 2.5% (w/w) pectin concentration. The bubble size and size distribution reduced with increasing MD concentration, which has a positive impact on drying stability (Section 3.4). Among both the carbohydrates, MD has a significant impact on the formation of smaller bubbles when the pectin concentration was 2.5% (w/w). Therefore, the concentration of pectin was kept constant at 2.5% (w/w) in this study.

Sensorial quality is another aspect besides foaming properties that needs to be considered while composing a fruit foam. Therefore, the maximum concentration of MD was maintained at 30% (w/w) to avoid losing the raspberry taste in this study. The evaluation of varying protein and MD concentrations is explained more in detail in Section 3.2.

Among the aforementioned results, the formulation of foams that meet the requirements for a gentle drying process were selected according to their foam characteristics, as given in Tab. 3-1. These formulations were used in this study.

Tab. 3-1. Selected foam formulations with respect to foam characteristics.

Selection criterion		Foam formulations		
Parameter	Relevance	Protein % (w/w)	Pectin % (w/w)	Maltodextrin % (w/w)
Foam stability	%100	5.0	2.5	5
Bubble size and size distribution	Small bubbles and narrow size distribution	5.0	2.5	15
		5.0	2.5	30
		2.5	2.5	15
Foam density	Low	7.5	2.5	15
Foam overrun	>450%	10.0	2.5	15

3.2 Impact of hydrocolloids and homogenization treatment on the foaming properties of raspberry fruit puree

Summary and contribution of the doctoral candidate

Stable foam structure was characterized by the aid of hydrocolloids for the production of dried fruit foams as a snack product. Raspberry was chosen as the model fruit. The impact of hydrocolloid addition and homogenization treatment on the foaming characteristics of raspberry fruit puree was investigated.

Stable foam is the key element for the entire process of obtaining aerated fruit snacks. Because of its good foaming properties, potato protein isolate (PPI) is a suitable alternative to proteins of animal origin. Considering the ability of PPI to increase viscosity, to further stabilize the foam, maltodextrin (MD), which is one of the most commonly used drying agents and can help stabilize foam and pectin, one of the most widely used gelling agents among the hydrocolloids, has been used. With this regard, the impact of hydrocolloids on the foaming characteristics was achieved by varying the concentrations of maltodextrin (5, 15, and 30% w/w) and pectin (0.1, 0.25, 0.5, 0.75, 1.0, and 2.5% w/w). Various concentrations of protein were also used (2.5, 5, and 10% w/w). Furthermore, the impact of homogenization treatment of fruit puree on the foam characteristics and puree properties was investigated. Foam was characterized by means of overrun, foam stability, bubble size and size distribution, rheology (yield point), and viscosity.

Foaming was achieved by PPI. MD and pectin enhanced the foam stability with a decrease in overrun and yielded narrower bubble sizes and size distribution. The stabilizing effect of MD involved an increase in the viscosity and thus a retardation of gravitational drainage. Conversely, stabilizing effects of pectin were explained by the formation of protein-pectin complexes, which in turn also enhanced the bulk viscosity and thus retarded gravitational drainage. Homogenization treatment of the fruit puree as an alternative to hydrocolloid addition led to reduced particle sizes and lower viscosity, which in turn was reflected in a modification of foaming properties.

The doctoral candidate, as co-author of this manuscript, partially developed the concept of the experiments and the methods prior to the drying process. She substantially reviewed the existing literature and conducted data analysis and data interpretation.

The contribution of the doctoral candidate on this manuscript was considerable, specifically for the development of the methods and formulations, ensuring a successful foam drying process.



Adapted original manuscript¹

Impact of hydrocolloids and homogenization treatment on the foaming properties of raspberry fruit puree²

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Abstract

The production of healthy, ready-to-eat fruit snacks by means of foam-mat drying has to face the challenge of ensuring high foam stability throughout the entire process. Foaming properties of raspberry puree whipped for 10 min with varying concentrations of potato protein isolate (2.5, 5, 10% w/w) as foaming agent were studied. Furthermore, the impact of hydrocolloids as foam stabilizers, i.e., maltodextrin (5, 15, 30% w/w) and pectin (0.1, 0.25, 0.5, 0.75, 1.0, 2.5% w/w), in combination with the variation of protein concentration as well as the impact of a homogenization treatment of fruit puree on the foam characteristics and puree properties were investigated. Foam stability was enhanced by the increase of protein and hydrocolloid concentration. Maltodextrin and pectin showed similar behavior even though pectin was used at considerably smaller concentrations. Compared to single hydrocolloid systems, the addition of pectin and maltodextrin in combination led to a further enhancement of foam stability, which offered the opportunity to simultaneously decrease the concentration of both hydrocolloids. The destruction of fruit tissue by homogenization treatment resulted in a reduction of mean particle diameters and a decrease of viscosity. Despite the increase in the specific surface area (ASF) and thus, expected enhanced oxidative processes, no changes were observed for ascorbic acid and anthocyanin contents. However, the

¹ Adaptions refer to formatting aspects: e.g., numbering of sections, figures, tables and equations, abbreviations, manufacturer specifications, axis labeling, figure captions and style of citation.

² Originally published in: Food and Bioprocess Technology (2018), Vol. 11, Issue 12, pp. 2253-2264. Permission for reuse of this article was granted by Springer.

structural changes induced by the homogenization treatment significantly affected foaming properties.



3.2.1 Introduction

The consumer demand for healthy, ready-to-eat snacks is showing consistent growth due to the convenient nature of snack products and also their appeal for texture and sensory properties (Brennan et al., 2013). However, the production of such snack products has to face several challenges. Gentle process conditions are required to meet the expectations of high nutritional quality. Moreover, an attractive appearance and texture for a pleasant mouth perception as well as high storage stability have to be ensured. Simultaneously, a natural and intense taste shall be provided. The process of foam-mat drying (Karim and Wai, 1999), i.e., the whipping of a liquid or semi-liquid to a stable foam, and subsequent dehydration by thermal means, offers the possibility to produce aerated snack products exhibiting an intense sensory perception during chewing. The often reported most difficult problem in this process is the instability of the foam before and during drying. If foam stability is unsatisfactory, collapse of the porous structure occurs, resulting in a serious impairment of the drying process and a deteriorated product quality (Hardy and Jideani, 2017; Karim and Wai, 1999; Thuwapanichayanan et al., 2012). As bubble growth and expansion may occur during vacuum drying processes, resulting in possible foam collapse (Kraus et al., 2014), it is of interest to produce foams with reduced gas volume and small bubble sizes.

Due to their high levels of ascorbic acid, anthocyanins and phenolic acids, and hence, associated health benefits (Choi et al., 2012; Stapleton et al., 2008; Stoner et al., 2008; Tsuda, 2016), berries, particularly raspberries, display an ideal basis material for foamed fruit snacks. Foaming conditions of various other fruits such as banana, starfruit, mango and bael were reported earlier (Bag et al., 2011; Karim and Wai, 1999; Rajkumar et al., 2007; Sankat and Castaigne, 2004; Thuwapanichayanan et al., 2012).

Fruit foams as such tend to be unstable, as mentioned above. Besides the raw material, the stability of the foamed product can be improved by the addition of foaming agents and foam stabilizers as well as interactions between them. To achieve this goal, the selection of appropriate foaming agents is therefore required. As reported in literature, various foaming agents such as whey protein concentrate, soy protein isolate or egg white were examined to obtain stable fruit foams (Sankat and Castaigne, 2004; Thuwapanichayanan et al., 2012). In recent years, economic, environmental and health-related issues became the driving forces to use alternative plant sources as

food ingredients. Due to their high surface activity one of the potato protein fractions, denominated as potato protease inhibitor, displays an ideal foaming agent (Schmidt et al., 2018a).

In order to achieve a high foam stability, foam decay needs to be retarded. One possibility is to increase the viscosity of the continuous aqueous phase. The addition of hydrocolloids such as pectin and maltodextrin, which are generally used as gelling and thickening agents in foods, leads to an increase in bulk viscosity and thus, a reduction of gravitational drainage. Several studies have shown that the formation of electrostatic complexes between pectin and egg white protein (Sadahira et al., 2014), whey protein isolate (Narchi et al., 2009) and napin (Schmidt et al., 2010) enhanced foam stability by slowing down liquid drainage. The retardation of liquid drainage was explained by an increased continuous phase viscosity. Wang et al. (2007) have reported on the formation of a highly interconnected gel-like network structure by protein-pectin coacervates when increasing the pectin concentration in protein-polysaccharide mixtures. Several studies have shown that besides the decrease of the DE (dextrose equivalent) value of maltodextrin (Pycia et al., 2016), the increase of maltodextrin concentration leads to more stable foams due to the resulting more viscous serum and hence, a retardation of drainage (Kinsella, 1981; Lau and Dickinson, 2007). Besides the fact that foam stability is enhanced by increasing the viscosity of lamella serum, foam stability can be influenced by effects of sugar on the preferential hydration of protein in the solution (Lee and Timasheff, 1981).

Despite the apparently strong influence of foaming agents and stabilizers on the foam stability and product properties, the impact of fruit puree pre-treatments, such as homogenization, should not be neglected, also from the perspective of aroma release and taste/smell intensity upon chewing, but also in view of oxidative reactions. Fruit purees, i.e., fruit-tissue-based suspensions, are composed of plant-tissue-based particles (fruit tissue cells and their fragments, cell walls, insoluble polymer clusters and chains) dispersed in an aqueous serum phase comprising soluble polysaccharides, sugars, salts and organic acids. Several studies have reported on an effect of high pressure homogenization or other mechanical destruction treatments on both the serum phase and the particles. In particular, a decrease of viscosity for samples such as tomato puree (Tan and Kerr, 2015), apple puree (Espinosa et al., 2011) and tart cherry

puree (Lukhmana et al., 2018) was shown. Moreover, mechanical disruption and fragmentation of fruit tissue can change the properties of the serum phase, in particular process-induced pectin changes like the mechanical solubilization of pectin in the serum phase (Moelants et al., 2014). However, the final rheological behaviour of a puree after mechanical processing is influenced by changes in both the particles of the dispersed phase and the properties of the serum (Augusto et al., 2012; Tanglertpaibul and Rao, 1987).

It was hypothesized that the tissue and cell disruption during homogenization would lead to structural alterations, which would affect the foaming properties of the puree. Moreover, it was assumed that oxidative processes would increase during homogenization and thus, changes in the contents of valuable ingredients would occur.

Therefore, the objectives of this study were, on the one hand, to investigate the foamability of raspberry fruit puree and evaluating the effect of added hydrocolloids such as maltodextrin and pectin on the foamability and foam stability. On the other hand, the impact of a homogenization treatment on the foaming properties as well as ascorbic acid and anthocyanin content was investigated.

3.2.2 Materials and methods

3.2.2.1 Raw materials

Frozen raspberries (Willamette) were provided by Mainfrucht GmbH & Co. KG (Gochsheim, Germany) and stored as whole fruits at -20°C until further processing. As foaming agent, Solanic®300 potato protein isolate (PPI; Avebe, Veendam, Netherlands) consisting of the low molecular fraction, the potato protease inhibitors, was used. Two hydrocolloids, i.e., maltodextrin (MD) and pectin (P), were evaluated for their foam stabilizing ability: maltodextrin with a DE (dextrose equivalent) of 6 was obtained from Nutricia GmbH (Erlangen, Germany). In addition, highly esterified citrus pectin (degree of esterification 68-76%) was kindly provided by Herbstreith & Fox KG (Neuenbürg/Württ, Germany).

3.2.2.2 Raspberry pre-processing and fruit puree preparation

A batch of 50 kg frozen raspberries was crushed using a metal stamp and homogeneously mixed at -20°C . This batch size was chosen to eliminate or equilibrate individual fruits' different composition and consistency. Until further processing, raspberry bits

were stored at -20°C . For pulp preparation, raspberry bits were first thawed at room temperature. Subsequently, a seedless fruit puree was produced using a food mill (GEFU GmbH, Eslohe, Germany) with perforated disks with mesh sizes of 3, 2 and 1 mm.

3.2.2.3 Homogenization

Seedless raspberry puree was treated with the colloid mill IKA LABOR-PILOT 2000/4 (IKA-Werke GmbH & CO. KG, Staufen, Germany). Homogenization was carried out with a gap width of 1 mm and revolution speeds of 3,000, 8,000 or 13,000 rpm. Different speeds were investigated to determine the impact of the respective extent of tissue or cell disruption on physical properties of the fruit puree, such as viscosity or particle size, which in turn was assumed to affect its foaming properties. Non-homogenized puree was used as reference.

3.2.2.4 Sample preparation

Sample solutions for experiments with single hydrocolloids as well as hydrocolloid mixtures were prepared by adding PPI (2.5, 5.0, 10.0% w/w) and maltodextrin (5, 15, 30% w/w) and/or pectin (0.1, 0.25, 0.5, 0.75, 1.0, 2.5% w/w) to the seedless fruit puree (see subsection 3.2.2.2). Full hydration of the powders within the fruit puree was ensured by means of gentle stirring for 30 min at room temperature. For this, the overhead stirrer Hei-TORQUE 100 (Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) equipped with a paddle stirrer with diagonally arranged blades was used at 200 rpm. Trials evaluating the effect of homogenization treatment on foaming properties were carried out with 5% (w/w) PPI without the addition of pectin or maltodextrin.

3.2.2.5 Fruit puree characterization

Solution viscosity after homogenization treatment was determined by shear rheological measurements using the Modular Compact Rheometer MCR 302 (Anton Paar GmbH, Graz, Austria) equipped with a concentric cylinder (CC27, Anton Paar GmbH, Graz, Austria) with an annular gap of 1.13 mm. The applied measuring procedure included a shear rate ramp starting with a linear increase in shear rate from 0 s^{-1} to 100 s^{-1} within 120 s followed by a holding period at 100 s^{-1} for 60 s and a linear decrease of shear rate from 100 s^{-1} to 0 s^{-1} within 120 s. All measurements were performed at a constant temperature of 20°C . Data analysis was carried out using the software RheoPlus V3.61

(Anton Paar GmbH, Graz, Austria). Since all fruit puree samples exhibited shear thinning behaviour, the average apparent viscosity at the holding phase (shear rate of 100 s⁻¹) was taken as a measure of viscosity. Steffe (1996) reported typical shear rates of 101 – 103 s⁻¹ for mixing and stirring in food processing. Therefore, rheological experiments were carried out within this reported shear rate range.

To determine the particle size distribution (PSD) of fruit puree homogenized at varying revolution speeds, a Mastersizer 2000 system (Malvern Instruments Ltd, Worcestershire, UK), which is based on the principle of laser diffraction and equipped with a Hydro 2000S sample dispersion unit (Malvern Instruments Ltd, Worcestershire, UK) was used. Samples were added undiluted to the dispersant (softened water) and measured twice in triplicate. Particle sizes were calculated using the Fraunhofer approximation. In addition to the PSD, the volume-based mean diameter ($D_{[4,3]}$), the surface-based mean diameter ($D_{[3,2]}$) and the specific surface area (ASF) were determined. To obtain information about the width of the size distribution, the interquartile range (IQR) was calculated according to equation 3-1. Here, $d_{(0.75)}$ is the 75th percentile, i.e., the diameter below which 75% of the volume of particles are found and $d_{(0.25)}$ is the diameter below which 25% of the volume of particles are found.

$$IQR = d_{(0.75)} - d_{(0.25)} \quad (3-1)$$

The SP68 Sphere Spectrophotometer (X-Rite Europe GmbH, Regensdorf, Switzerland) was used to determine the color of the raspberry puree before and after homogenization treatment. The color difference (ΔE) was calculated as follows:

$$\Delta E = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad (3-2)$$

where L_0^* , a_0^* and b_0^* were the values of the untreated sample, and L^* , a^* and b^* were the values of the homogenized samples.

3.2.2.6 Foam formation and characterization

For foam formation, 150 g sample solution were whipped for 10 min at room temperature using the Artisan stand mixer 5KSM150 (KitchenAid, Strombeek Bever, Belgium) at 220 rpm. For foam characterization, foam samples were carefully filled into plastic cups, thereby, ensuring that no air inclusions occurred. The top of the cups was leveled with a plastic spatula to obtain a plane surface and to ensure a constant volume.

In order to investigate the gas volume incorporated into the sample solutions, the overrun was determined according to the method described by Kreuß et al. (2009) and calculated according to equation 3-3.

$$\text{overrun, \%} = \frac{m_{\text{solution}} - m_{\text{foam},0\text{min}}}{m_{\text{foam},0\text{min}}} \times 100 \quad (3-3)$$

The stability of the foam refers to a foam age of 30 min. Following the method described by Bals and Kulozik (2003), the foam filled plastic cups were left at room temperature for 30 min. Then, the drained liquid was decanted and the weight of the foam ($m_{\text{foam}, 30\text{min}}$) was measured. Foam stability was calculated as follows:

$$\text{foam stability, \%} = \frac{m_{\text{foam},30\text{min}}}{m_{\text{foam},0\text{min}}} \times 100 \quad (3-4)$$

According to the method of Bals and Kulozik (2003), bubble size distributions (BSD) were examined using the optical microscope Axiovert 135 (Carl Zeiss AG, Oberkochen, Germany) at ten-fold magnification. The foam samples were applied to a microscope glass slide and images of the bubbles were taken at different positions of the foam. Data analysis comprised the bubble diameters of at least 300 bubbles per sample.

Foam rheological measurements were carried out following the method described by Lexis and Willenbacher (2013). To determine apparent yield point, shear rheological measurements were performed with the Modular Compact Rheometer MCR 302 (Anton Paar GmbH, Graz, Austria) using a parallel plate geometry (PP50, Anton Paar GmbH, Graz, Austria) with a diameter of 50 mm. To minimize wall slipping effects, the plates were covered with abrasive paper (grain size 40) and the gap was set to 5 mm. Foam samples were sheared with a logarithmically increasing shear stress (1-1000 Pa) within 90 s. The yield point τ_y was defined as the shear stress at which the linear-elastic region merges into the flow region of the flow curve.

3.2.2.7 Ascorbic acid

Ascorbic acid (AA) was determined by RP-HPLC according to the method of Chebrolu et al. (2012) with slight modifications. In detail, for ascorbic acid extraction, 2 g of fruit puree or foam sample and 18 g of MPA (meta phosphoric acid, 3%, Sigma-Aldrich

Chemie GmbH, Steinheim, Germany) were firstly homogenized for 30 s using the Ultra-Turrax T 25 (IKA®- Werke GmbH & Co. KG, Staufen, Germany). Then, the samples were shaken at room temperature for 30 min at 1,000 rpm with the Multi Reax (Heidolph Instruments GmbH & Co. KG, Schwabach, Germany). Afterwards, the solutions were centrifuged for 10 min at 6,000×g (Multifuge 1S-R, Heraeus Holding GmbH, Hanau, Germany). To determine the free AA content, the supernatants were passed through 0.45 µm cellulose acetat syringe filters (VWR International GmbH, Darmstadt, Germany) and analyzed by RP-HPLC using an Agilent 1100 series chromatograph (Agilent Technologies, Santa Clara, USA) equipped with a binary pump, an auto sampler, and a VW detector. Separation of AA was achieved using a Zorbax 300 SB-C18 column (Agilent Technologies, Santa Clara, United States). Injection volume was 10 µL. Eluent A consisted of 100% ultrapure MilliQ water (MilliQsystem, Millipore, USA) and 0.2% trifluoroacetic acid (Honeywell International Inc., Morris Plains, USA), whereas eluent B contained 100% acetonitrile (J.T. Baker, Gliwice, Poland) and 0.2% trifluoroacetic acid (Honeywell International Inc., Morris Plains, USA). Elution was performed at a flow rate of 0.8 mL/min using a gradient starting with isocratic elution at 0% B for 5 min, increasing to 100% B at 5.5 min, isocratic elution at 100% B for 1 min, decreasing to 0% B at 7 min and isocratic elution at 0% B for 5 min. The detection of AA was carried out at 243 nm. Analyses were performed with the OpenLAB CDS ChemStation (Agilent Technologies, Santa Clara, USA) software. The reduction of dehydroascorbic acid (DHA) to AA was achieved by the addition of 250 µl TCEP (tris(2-carboxyethyl)phosphine, 5 mM, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) to 250 µl of filtrate. After 30 min at room temperature, the solutions were analyzed as described for free AA.

3.2.2.8 Anthocyanins

An RP-HPLC method was established for the determination of anthocyanins, which allowed for the quantification of cyanidin-3-sophoroside, cyanidine-3-rutinoside and cyanidine-3-glucoside in the fruit puree or foam samples. For this, 2 g of sample and 18 g of HCl (1%, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were homogenized for 30 s using the Ultra-Turrax T 25 (IKA®- Werke GmbH & Co. KG, Staufen, Germany) and then shaken at room temperature for 180 min at 1,000 rpm with the Multi Reax (Heidolph Instruments GmbH & Co. KG, Schwabach, Germany). After the solutions

were centrifuged for 10 min at 6,000×g (Multifuge 1S-R, Heraeus Holding GmbH, Hanau, Germany), the supernatant was passed through a 0.45 µm cellulose acetate syringe filter (VWR International GmbH, Darmstadt, Germany) and analyzed by RP-HPLC. An injection volume of 20 µL per sample was analyzed using an Agilent 1100 series chromatograph (Agilent Technologies, Santa Clara, USA) equipped with a binary pump, an auto sampler, and a VWD detector. For quantification, standard solutions of cyanidin 3-O-β-sophoroside (Polyphenols AS, Sandnes, Norway), cyanidin 3-O-β-rutinoside (Polyphenols AS, Sandnes, Norway) and cyanidin 3-O-glucoside chloride (Extrasynthese, Genay Cedex, France) were used. Separation of the anthocyanins was carried out using a Phenomenex Luna® C18(2) column (Phenomenex Ltd. Deutschland, Aschaffenburg, Germany). Eluent A consisted of 100% ultrapure MilliQ water (MilliQsystem, Millipore, USA) and 0.2% trifluoroacetic acid (Honeywell International Inc., Morris Plains, USA). Eluent B comprised 100% acetonitrile (J.T. Baker, Gliwice, Poland) and 0.2% trifluoroacetic acid (Honeywell International Inc., Morris Plains, USA). Eluents contained trifluoroacetic acid to ensure that no pH shift of the anthocyanins occurred during chromatography procedure. Elution was performed at a flow rate of 0.5 mL/min using a gradient starting with 15% B, increasing to 25% B at 18 min, increasing to 100% B at 19 min, isocratic elution at 100% B for 1 min, decreasing to 15% B at 20.5 min and isocratic elution at 15% B for 3 min. The anthocyanin peaks were detected at 520 nm and analyses were carried out by OpenLAB CDS ChemStation (Agilent Technologies, Santa Clara, USA) software.

3.2.2.9 Statistical analysis

In total, two batches of each sample condition were prepared and each sample was analyzed in triplicate. Thus, a six-fold determination was carried out. Mean values are presented; error bars indicate the standard deviation.

3.2.3 Results and discussion

3.2.3.1 Impact of single hydrocolloids

Foaming properties, i.e., the formation and composition of interfaces in foams, are influenced by the concentration and properties of the proteins present in the solution. Due to intermolecular interactions, proteins form a network at air/water interfaces and thus, stabilize the foam system. Referring to the process of foam-mat drying, the quality

of the final product is strongly affected by the stability of the foam before and during drying. As the pure fruit often yields only a temporal foam stability, the addition of hydrocolloids can lead to an increase in viscosity and thereby, improve foam stability due to the high water-binding capacity and the thickening properties. In Fig. 3-7, the overrun in dependence of MD (a) and P (b) concentration is illustrated. For both, a decrease of overrun with increasing hydrocolloid concentration was observed. An increase in hydrocolloid concentration and thus, a higher viscosity of the aqueous phase led to a more difficult incorporation of air and a less rapid diffusion of the protein in the vicinity of the interface (Lau and Dickinson, 2005). With decreasing PPI concentration lower absolute values of the overrun were obtained.

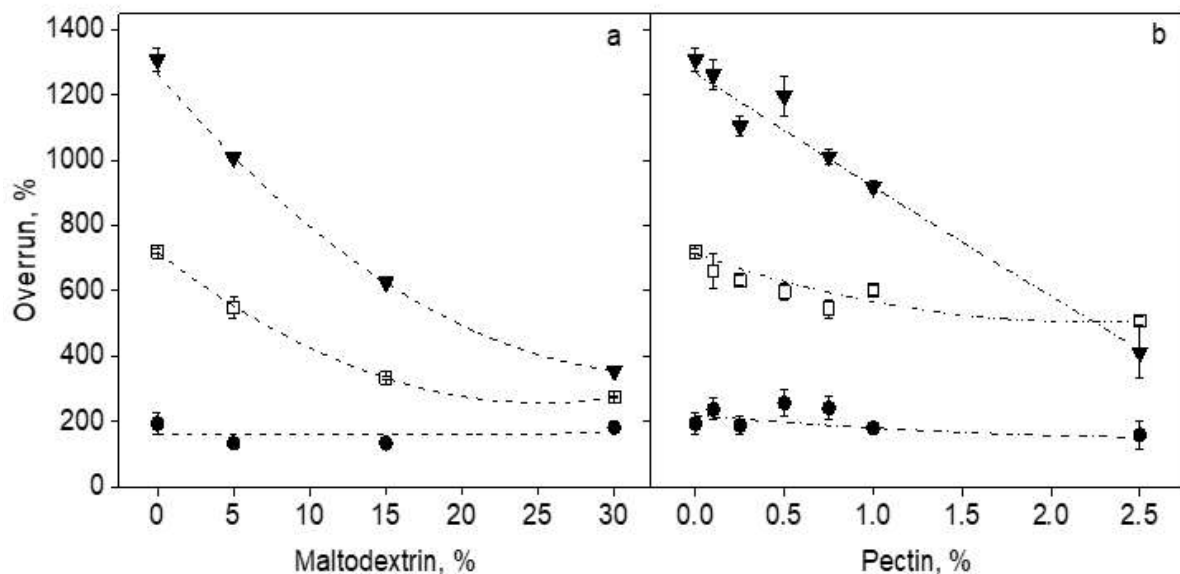


Fig. 3-7. Effect of maltodextrin (a) and pectin (b) concentration on overrun of aerated raspberry puree containing (●) 2.5% (w/w), (□) 5% (w/w) and (▼) 10% (w/w) PPI. Vertical bars represent standard deviation.

Moreover, with increasing MD and P concentrations the dispersion of smaller bubbles became more uniform (Fig. 3-8). Lau and Dickinson (2005) reported that a more viscous medium offers higher stabilization to the newly formed air bubbles, and thus, more small bubbles are found in the samples with high hydrocolloid concentration.

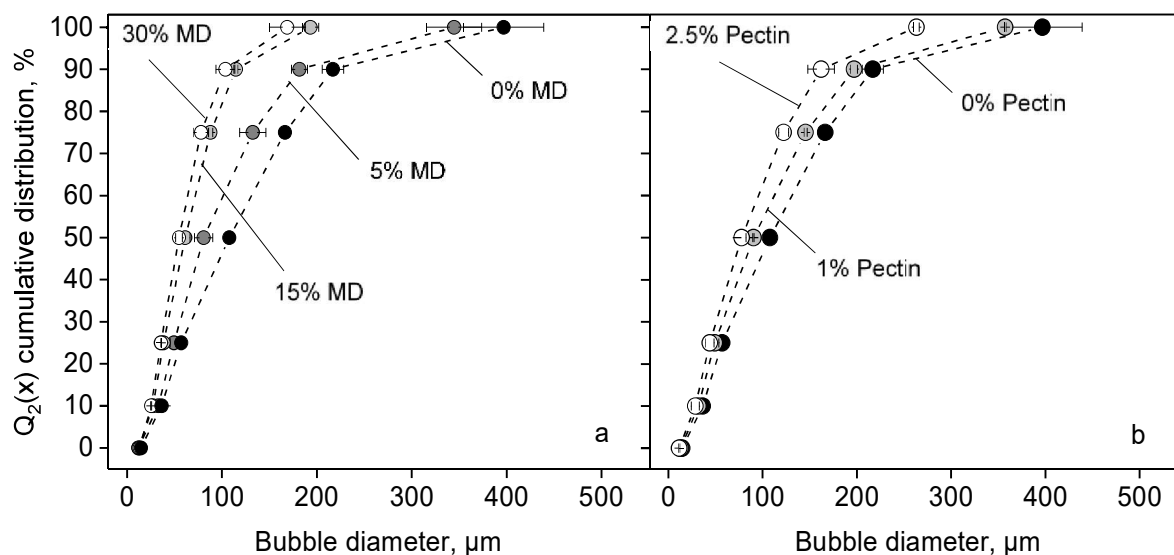


Fig. 3-8. Effect of maltodextrin (a) and pectin (b) concentration on bubble size distribution of aerated raspberry puree whipped with 5% (w/w) PPI. Horizontal bars represent standard deviation.

Increasing hydrocolloid concentration led to enhanced foam stability (Fig. 3-9). With increasing PPI concentration enhanced foam stability was found. At a PPI concentration of 10%, no influence of MD or P concentration on foam stability was determined. Foam stability at these conditions was maximal and achieved values at or close to 100%.

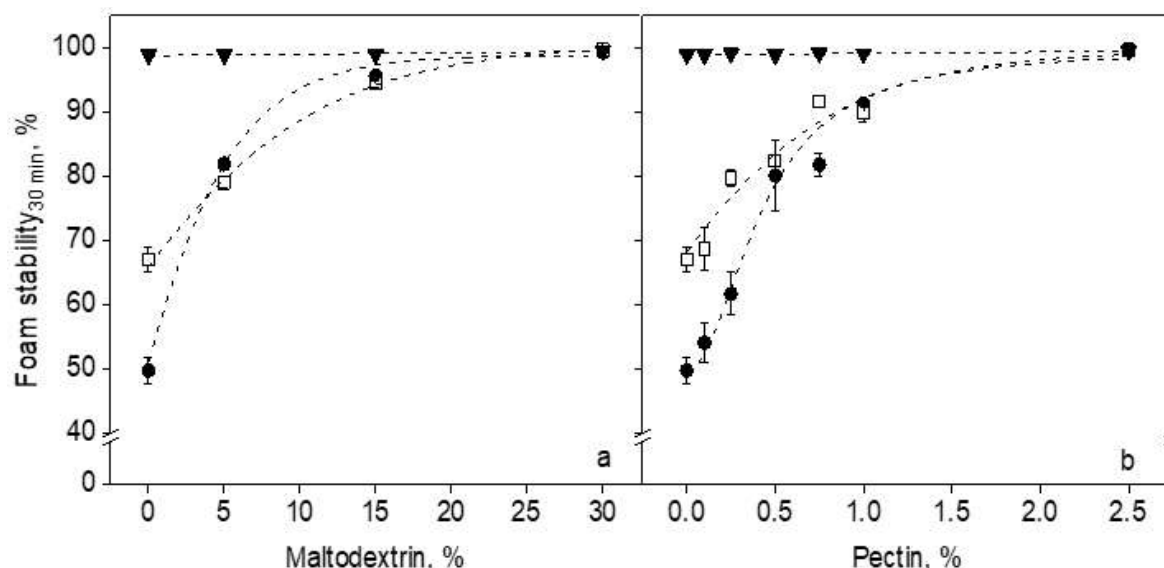


Fig. 3-9. Effect of maltodextrin (a) and pectin (b) concentration on foam stability of aerated raspberry puree containing (●) 2.5% (w/w), (□) 5% (w/w) and (▼) 10% (w/w) PPI. Vertical bars represent standard deviation.

Protein-pectin interactions, which are favored by increasing protein concentration (Schmidt et al., 2010), seem to be an explanation why foams with lower absolute concentrations of P (2.5%) showed the same behavior as foams with higher absolute concentrations of MD (30%). This assumption was also reflected in the results of foam rheology (Fig. 3-10). While increasing MD concentration led to reduced yield points, P showed an opposite trend. However, for both hydrocolloids, increased PPI concentration resulted in higher yield points. P showed higher absolute values of yield point than MD for the same protein concentration due to a higher serum viscosity, which presumably resulted from the formation of protein-pectin complexes (Sadahira et al., 2016).

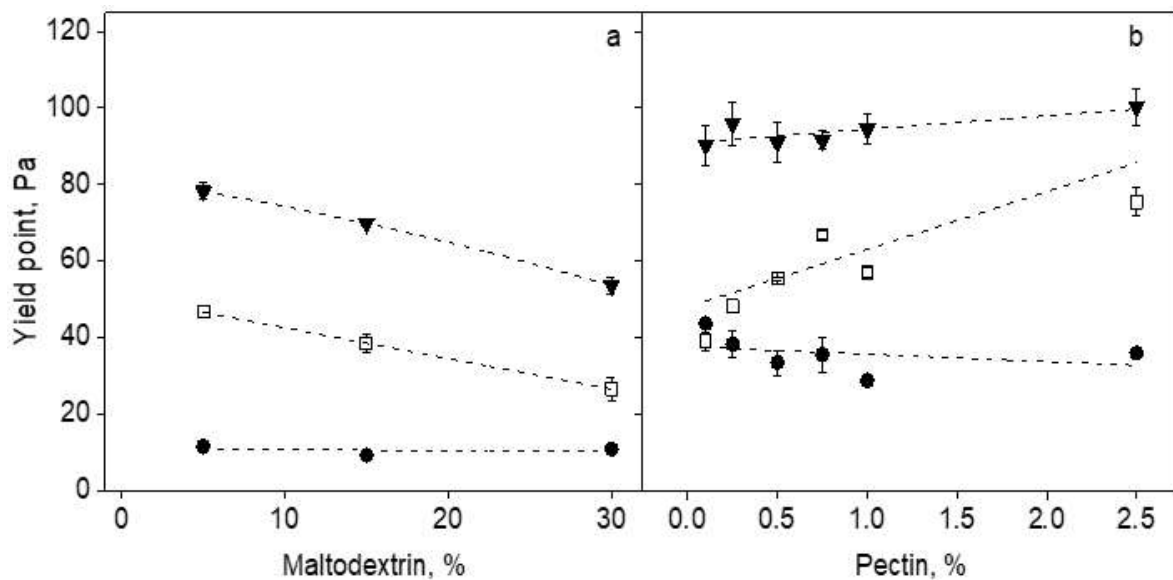


Fig. 3-10. Effect of maltodextrin (a) and pectin (b) concentration on yield point of aerated raspberry puree containing (●) 2.5% (w/w), (□) 5% (w/w) and (▼) 10% (w/w) PPI. Vertical bars represent standard deviation.

3.2.3.2 Impact of hydrocolloid mixtures

The impact of different PPI:P:MD ratios on the foaming properties was investigated with the aim of achieving higher foam stabilities as compared to the addition of single hydrocolloids. Simultaneously, concentrations of individual components should be reduced. In particular, the reduction of MD, might matter in terms of producing healthy natural fruit snacks, and to prevent a possible negative sensory perception due to the addition of high concentrations of solids content. In the following, the results of the combination of different MD and P concentrations on the overrun and foam stability

are examined in detail. The overrun of raspberry puree foamed with 2.5% PPI as a function of P and MD concentration is shown in Fig. 3-11a. Results for 10% PPI are shown in Fig. 3-11b. The increase in viscosity caused by the addition of MD and P led to a decrease of over-run for all protein concentrations tested. The combination of both polysaccharides resulted in an additional decrease of the overrun compared to the addition of single P or MD. For 10% PPI foams, the influence of P concentration decreased with increasing MD concentration. The increase of P concentration from 0.1 to 2.5% resulted in a reduction of overrun from ~1000% to ~450% at 5% MD and from ~400% to ~300% at 30% MD. The decrease of P impact on the overrun with increasing MD concentration was less pronounced for 2.5% PPI foams than for foams whipped with 10% PPI as the decrease in overrun for 2.5% PPI foams was, with approx. 50%, relatively independent of MD concentration. The same trend was observed for the impact of MD concentration. While for 2.5% PPI the decrease of overrun with approx. 35% with increasing MD concentration from 5 to 30% was relatively independent of P concentration, foams with 10% PPI showed a stronger decrease of MD impact on the overrun with increasing P concentration.

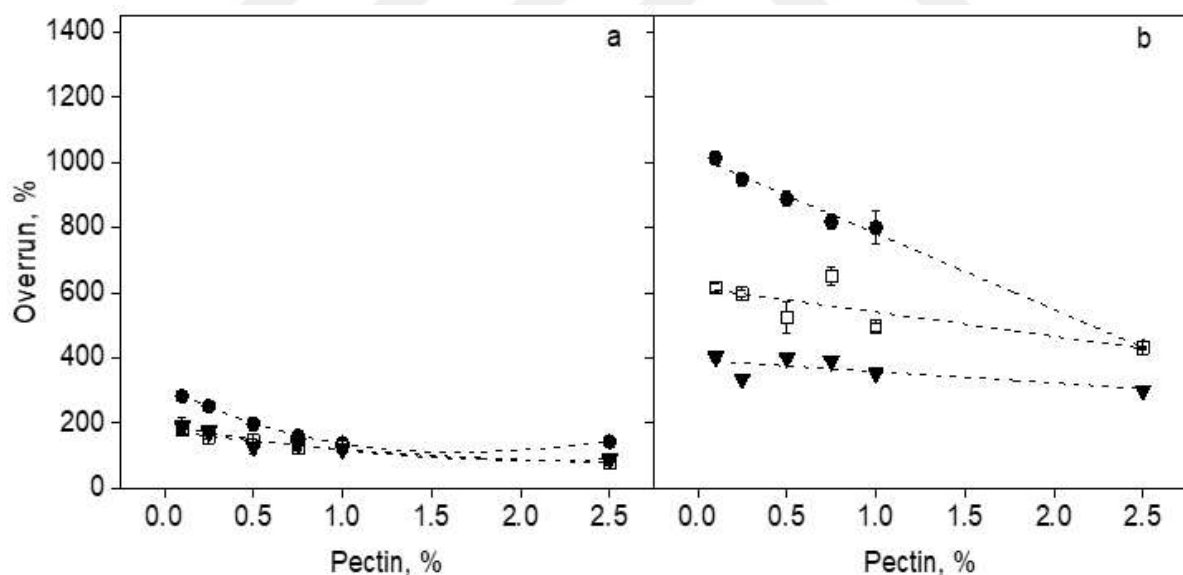


Fig. 3-11. Effect of maltodextrin (● 5%, □ 15%, ▼ 30%) and pectin concentration on overrun of aerated raspberry puree whipped with (a) 2.5% (w/w) and (b) 10% (w/w) PPI. Vertical bars represent standard deviation.

Sadahira et al. (2016) observed that at protein:pectin ratios from 40:1 to 63:1, mixtures of egg white and pectin in a high sugar content system showed high foaming capacity,

and the resulting foam elastic and solid behaviour. Furthermore, they observed a decrease of foaming capacity with increasing relative pectin concentration (protein:pectin ratio < 35:1) and less elastic and solid foams. Thus, the authors assumed that protein:pectin ratios lower than 35:1 lead to the formation of insoluble complexes between the biopolymers, resulting in reduced protein availability that may hinder the incorporation of air. Besides the previously mentioned viscosity effect, which is probably more attributed to the addition of MD, the formation of protein-pectin complexes could be an additional explanation for the results shown in Fig. 3-11. This is also confirmed by Schmidt et al. (2010), who showed that increasing the protein concentration favors protein-pectin interactions (see Section 3.2.3.1).

Regarding foam stability, increasing MD concentration from 5 to 30% led to 40% enhanced stabilities of raspberry foams whipped with 2.5% PPI and 0.1% P (Fig. 3-12a). A decrease of MD impact with increasing P concentration was observed as the foam with 2.5% P showed maximum stability independent of the maltodextrin concentration. Increasing P concentration from 0.1 to 2.5% led to 40% enhanced stabilities of foams whipped with 2.5% PPI and 5% MD. A decrease of P impact with increasing MD concentration was observed as the addition of 30% MD resulted in maximum foam stabilities independent of P concentration. Sadahira et al. (2016) reported higher foam stability with increasing relative pectin concentration in a high sugar content system. Besides the increase in viscosity due to high sugar addition, the formation of soluble complexes between protein and pectin increases the viscosity of the serum phase and thus, enhances the stability towards liquid drainage. With increasing protein concentration, enhanced foam stabilities for 5 and 15% MD and 0.1 to 1.0% P were found. For fruit foams whipped with 10% PPI (Fig. 3-12b), the behavior of protein regarding foam stability was predominant as the stability was independent of P and MD concentration and consistently at maximum.

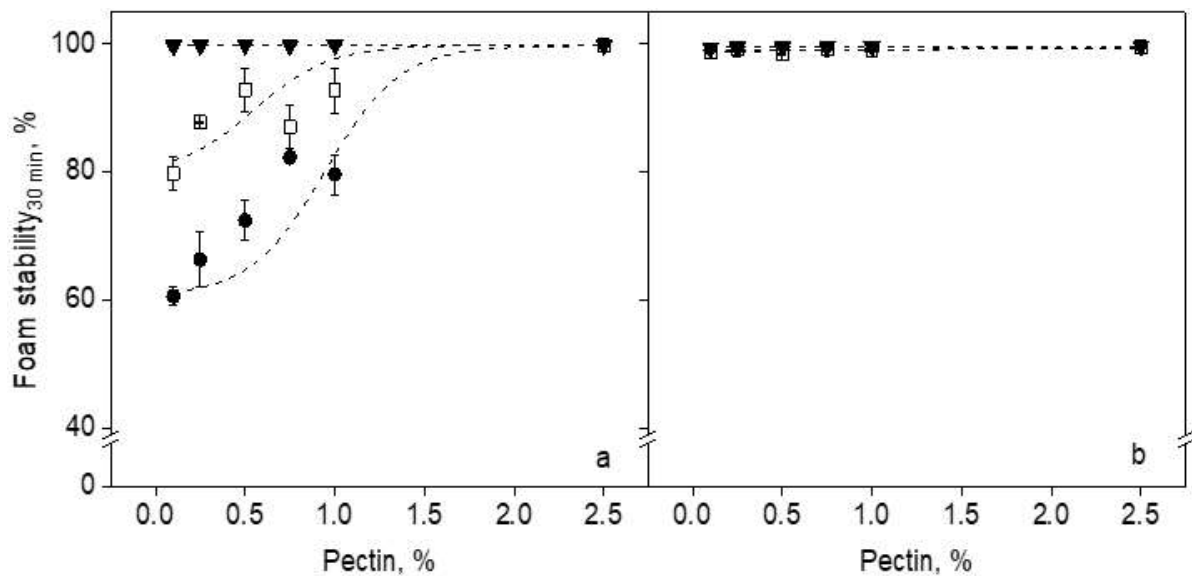


Fig. 3-12. Effect of maltodextrin (● 5%, □ 15%, ▼ 30%) and pectin concentration on foam stability of aerated raspberry puree whipped with (a) 2.5% (w/w) and (b) 10% (w/w) PPI. Vertical bars represent standard deviation.

The yield point of raspberry foam whipped with 2.5% PPI as a function of P and MD concentration is shown in Fig. 3-13a. Results for 10% PPI are shown in Fig. 3-13b. The increase in MD concentration led to reduced yield points. For 5% MD, at lower P concentrations (0.1–1.0%) the yield point was reduced with increasing P concentration, and then increased again at 2.5% P. For 15% and 30% MD, the yield point seemed to be independent of P concentration. Increasing the PPI concentration led to increased yield points. However, comparing the results of the mixtures and the single addition of hydrocolloids, the respective effects of MD and P seem to compensate each other in mixtures.

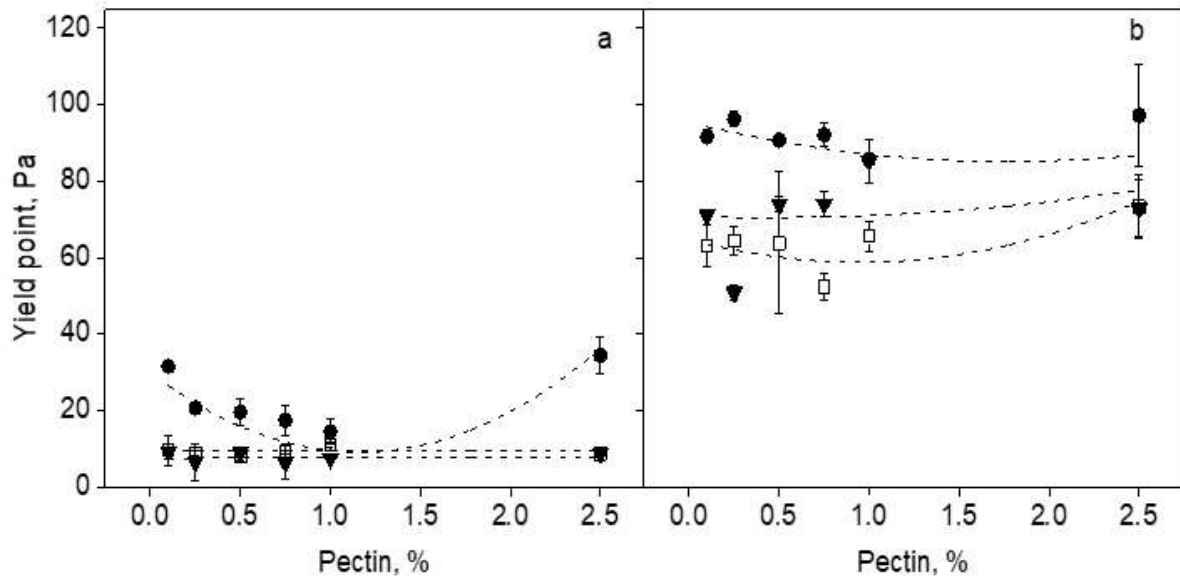


Fig. 3-13. Effect of maltodextrin (● 5%, □ 15%, ▼ 30%) and pectin concentration on yield point of aerated raspberry puree whipped with (a) 2.5% (w/w) and (b) 10% (w/w) PPI. Vertical bars represent standard deviation.

3.2.3.3 Effect of homogenization treatment

Homogenization treatment reduced the mean particle diameters based on volume ($D_{[4,3]}$) and surface ($D_{[3,2]}$) of the control sample significantly from 266 μm and 64 μm to 175 μm and 32 μm at 13,000 rpm (Table 1). The reduction in $D_{[3,2]}$ between the control sample and the sample homogenized at 13,000 rpm ($\sim 50\%$) was higher than in $D_{[4,3]}$ ($\sim 34\%$). This higher reduction in $D_{[3,2]}$ was also observed between samples of each speed adjustment. As the $D_{[4,3]}$ is highly influenced by large particles and the $D_{[3,2]}$ is more affected by the presence of smaller particles (Bengtsson and Tornberg, 2011; Lopez-Sanchez et al., 2011), the results indicated that disruptions occurred preferentially in smaller particles and a substantial increase in the number of small particles was determined, when the puree was homogenized. The $D_{[3,2]}$ of the untreated sample was four times higher than the $D_{[4,3]}$ indicating a polydisperse system with a higher amount of large particles. These results were confirmed by the data of the PSD (Tab. 3-2). With increasing revolution speed, $d_{(0.1)}$, $d_{(0.5)}$ and $d_{(0.9)}$ were reduced. The IQR, providing information about the particle size distributional width, decreased with increasing revolution speed, indicating a narrower distribution for samples treated with higher speeds. Moreover, the reduction in the diameters of the suspended particles led to an increase in the particle surface area (Tab. 3-2).

Tab. 3-2. Particle characteristics of raspberry puree treated in a colloid mill at 3,000, 8,000 and 13,000 rpm.

Revolution speed (rpm)	D _[4,3] (μm)	D _[3,2] (μm)	d _(0.1) (μm)	d _(0.5) (μm)	d _(0.9) (μm)	IQR (μm)	A _{SP} (m ² /g)
0 (control)	266±13 ^a	64±4 ^a	48±2 ^a	129±5 ^{ab}	741±25 ^a	239±48 ^a	0.09±0.01 ^a
3000	262±13 ^a	58±3 ^a	46±1 ^a	122±1 ^a	750±38 ^a	218±40 ^a	0.10±0.01 ^a
8000	218±21 ^{ab}	44±2 ^b	38±1 ^b	114±2 ^b	601±85 ^{ab}	155±29 ^a	0.14±0.01 ^b
13000	175± 3 ^b	32±0 ^c	17±1 ^c	107±2 ^c	442±24 ^b	127±1 ^a	0.19±0.00 ^c

^{a, b, c} Means in the same column with different letters indicate significant differences ($P < 0.05$). IQR: Interquartile range.

Fig. 3-14a shows the apparent viscosity of raspberry puree processed at increasing revolution speed as a function of shear rate. Apparent viscosity decreased with increasing shear rate from 1 to 100 s⁻¹, indicating non-Newtonian behavior. The viscosity of raspberry puree at a constant shear rate of 100 s⁻¹ is shown in Fig. 3-14b. It is obvious that the untreated sample (control) showed a higher apparent viscosity than the homogenized samples. Increasing revolution speed resulted in a decrease in apparent viscosity of the treated samples. The decrease was linked to a reduced particle size. However, the rheological behaviour of the puree after mechanical processing is influenced by changes in both the particles of the dispersed phase and the properties of the serum (Augusto et al., 2012; Tanglertpaibul and Rao, 1987).

Besides the effect on particle size and viscosity, homogenization treatment induced a color modification of the samples. Color differences were detected between the untreated sample and the sample homogenized at 13,000 rpm as the L*, a* and b* values increased significantly (Tab. 3-3). Due to the higher ability of small sized particles to scatter light, samples after homogenization appeared brighter.

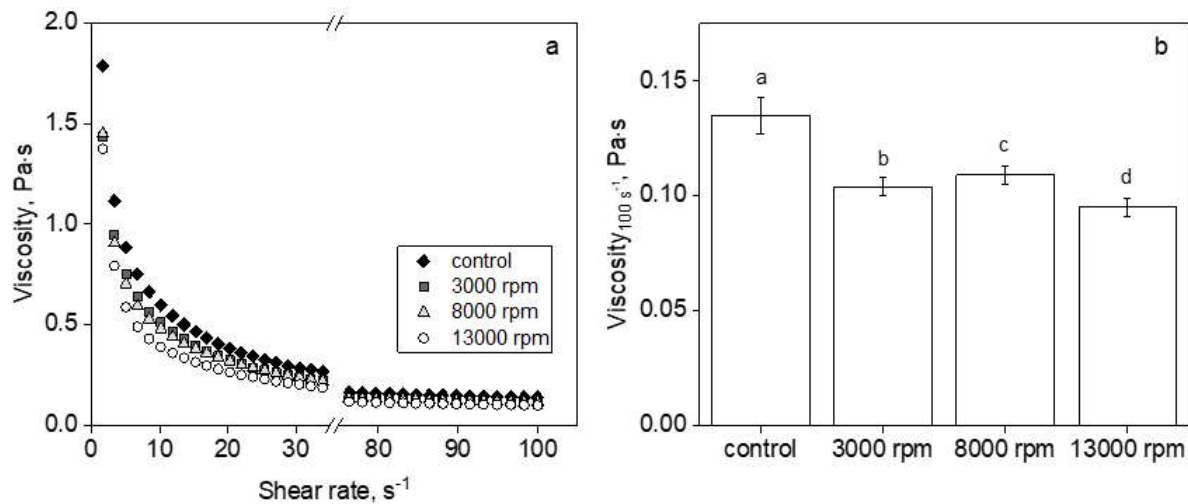


Fig. 3-14. (a) Apparent viscosity of non-homogenized and homogenized (3,000 rpm, 8,000 rpm, 13,000 rpm) raspberry puree as an effect of varying shear rate (1-100 s⁻¹). For clarity, standard deviation was omitted. **(b)** Viscosity of raspberry puree homogenized at increasing revolution speed at a constant shear rate of 100 s⁻¹. Vertical bars represent standard deviation; means with different letters indicate significant differences (P < 0.05).

For 8,000 rpm and 13,000 rpm an increase in the red (a*) and yellow (b*) color in comparison to the control sample was observed. ΔE values indicated that rotational speeds of 3,000 rpm and 8,000 rpm induced medium color differences, which were visible to an un-trained eyed ($\Delta E > 2$), while 13,000 rpm caused obvious color differences ($\Delta E > 4$).

Tab. 3-3. Color values for raspberry puree treated in a colloid mill at 3,000, 8,000 and 13,000 rpm.

Revolution speed (rpm)	Color			
	L*	a*	b*	ΔE
0 (control)	35.18 ± 1.01 ^a	21.85 ± 1.18 ^a	12.16 ± 0.77 ^a	-
3000	34.13 ± 1.61 ^a	21.36 ± 1.77 ^a	11.63 ± 1.27 ^a	2.24 ± 1.52 ^{ab}
8000	36.15 ± 0.92 ^{ab}	23.20 ± 1.20 ^{ab}	13.22 ± 0.95 ^{ab}	2.35 ± 0.85 ^{ac}
13000	37.76 ± 0.46 ^b	24.62 ± 0.93 ^b	14.52 ± 0.91 ^b	4.54 ± 0.87 ^{bc}

a, b, c Means in the same column with different letters indicate significant differences (P < 0.05).

Due to the increase in specific surface area, it was assumed that oxidation processes would increase with smaller particle sizes. Hence, the impact of homogenization treatment on ascorbic acid and anthocyanin stability was analyzed. Tab. 3-4 shows the relative content of valuable ingredients for puree samples treated at different revolution speeds. For all samples, no changes were observed as the ascorbic acid and anthocyanin contents remained equal for each examined revolution speed.

Tab. 3-4. Ascorbic acid and anthocyanin content of raspberry puree and foam.

		Revolution speed (rpm)			
		0(control)	3000	8000	13000
Ascorbic acid, puree (C_t/C_0)	Free AA	1.00	1.00±0.01	1.00±0.02	0.98± 0.01
	DHA	1.00	1.08±0.17	0.95±0.14	1.17± 0.16
Ascorbic acid, foam (C_t/C_0)	Free AA	1.00	0.97±0.00	0.85±0.14	0.90± 0.01
	DHA	1.00	1.17±0.00	1.56±0.40	1.60± 0.25
Anthocyanins, puree (C_t/C_0)	Cyanidine-3-sophoroside	1.00	1.01±0.01	1.00±0.00	1.00± 0.01
	rutinoside	1.00	1.00±0.00	0.99±0.01	0.99± 0.00
	glucoside	1.00	0.98±0.04	0.96±0.04	0.96± 0.02
Anthocyanins, foam (C_t/C_0)	sophoroside	1.00	1.01±0.01	1.00±0.02	1.01± 0.00
	rutinoside	1.00	1.02±0.01	1.01±0.02	1.01± 0.00
	glucoside	1.00	1.02±0.00	1.02±0.02	0.98± 0.00

The effect of homogenization on foamability and foam stability of raspberry puree is shown in Fig. 3-15. The non-homogenized sample showed significant higher foam stability than the homogenized purees due to its higher viscosity, as described previously. Because of the more coherent fruit tissue, foam lamellae were assumed to be blocked. Thereby, drainage was reduced and thus, the foam stability was increased.

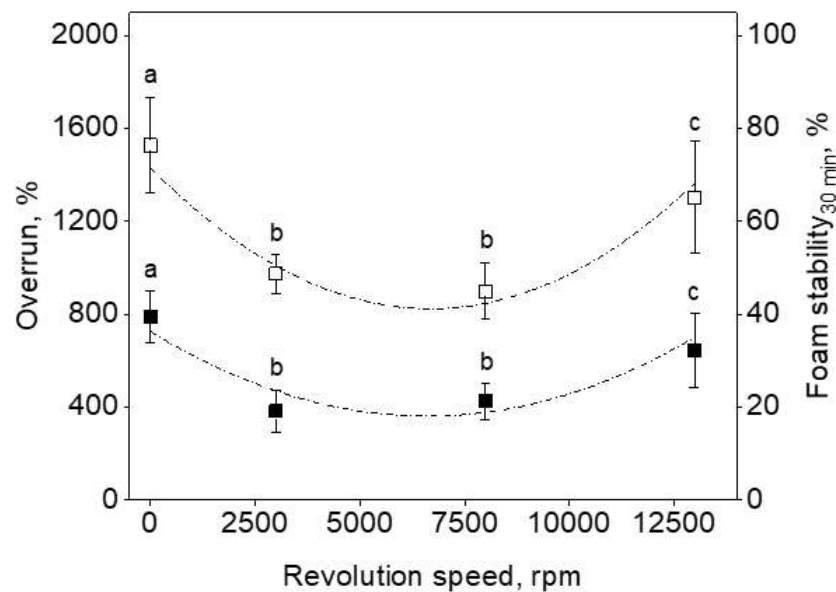


Fig. 3-15. Effect of revolution speed on overrun (■) and foam stability (□) of aerated raspberry puree whipped with 5% (w/w) PPI. Vertical bars represent standard deviation; means with different letters indicate significant differences ($P < 0.05$) for the same parameter.

As a result of the destruction of the coherent tissue structure and the associated reduction of viscosity, drainage could flow more easily from the foam lamellae and thus, foam stability decreased. The increase in speed from 3,000 rpm to 8,000 rpm showed no significant changes in overrun and foam stability, which is in accordance with the viscosity values described above. Increasing revolution speed from 8,000 rpm to 13,000 rpm led to a significant increase in overrun, which can possibly be explained by an improved convective transport of the proteins to the interface due to the decreased viscosity. Simultaneously, an increase in foam stability was observed, which was presumed to be attributed to the formation of complexes that are assumed to stabilize the interface. Cell disruption can expose and release cell wall constituents, such as pectin and proteins, and thus, triggering particle-particle and particle-serum interactions (Augusto et al., 2012). Moreover, the reduction in particle size and thus, the strongly increased particle surface area (Tab. 3-2) could improve interparticle interactions. As can be seen in Tab. 3-4, the content of free AA in the foams was slightly decreased with increasing revolution speed. During foaming a small percentage of free AA was converted to DHA. Anthocyanin content of the foams was not affected by the homogenization treatment. However, foaming properties of the raspberry puree were

significantly affected by the conducted homogenization treatment due to occurred structural changes.

3.2.4 Conclusion

The aim of this study was to investigate the impact of hydrocolloid addition or homogenization treatment on the foaming properties of raspberry fruit puree intended for the application as dried, aerated fruit snacks. Foaming per se was achieved by PPI. As foam-mat drying, in general, requires time-stable foam structures (i.e., high foam stability as well as small and narrow bubble size distribution), which could not be achieved by PPI alone, maltodextrin and pectin were evaluated for their capability to meet these requirements. It was shown that the addition of maltodextrin and pectin led to an enhancement of foam stability, a decrease of overrun and narrower bubble size distribution. Even though pectin was used in considerably smaller concentrations, maltodextrin and pectin showed similar behavior. However, in terms of foam rheology clear differences were observed: while the increase in maltodextrin concentration led to lower yield points, the increase in pectin concentration resulted in higher yield points. Stabilizing effects of maltodextrin were traced back to an increase in bulk viscosity and thus, a retardation of gravitational drainage. Conversely, stabilizing effects of pectin were explained by the formation of protein-pectin complexes, which in turn also enhanced bulk viscosity and thus, retarded gravitational drainage. Compared to single hydrocolloid systems, the use of pectin and maltodextrin mixtures led to a further enhancement of foam characteristics. However, the respective effects of both hydrocolloids seemed to compensate each other within the mixtures. Homogenization treatment of the fruit puree as alternative to hydrocolloid addition led to reduced particle sizes and lower viscosity, which in turn was reflected in a modification of foaming properties. Due to the increased specific surface area (ASF), enhanced oxidative processes were presumed. However, degradation of ascorbic acid and anthocyanins was not observed.

Summing up, the practical meaning of the results of this study is that the foaming properties of raspberry puree can be improved by chemical as well as mechanical options. With knowledge about these aspects, foam-mat drying processes of fruit foams may be optimized regarding enhanced product quality.

3.2.5 Acknowledgments

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3.3 Foam drying: Conventional *versus* microwave freeze drying

3.3.1 Conventional freeze drying (FD)

The primary objective of this study was to establish an applicable microwave drying process for obtaining a fast, gentle, energy-efficient alternative for producing fruit foams with a specific end product structure. Conventional freeze drying (FD, also known as lyophilization) is a state-of-the-art technology that provides the best quality of food material compared with other drying methods. However, because of conductive heating, diffusion limitations occur in heat and mass transfer. Therefore, long drying times are required with a high energy demand. A critical step in the freeze-drying process is the passage of the product from the frozen state to the dried state where there is a wide variation in water content as well as temperature (Marin, 2003). An increase in temperature is an appropriate method to reduce the drying time; however, an optimum temperature has to be defined to avoid melting. Specifically, the foam structure can easily collapse because of decreased viscosity above the glass transition temperature, where structural loss occurs because of the incapability of the material to bear its own weight (Harnkarnsujarit and Charoenrein, 2011). Therefore, different shelf temperatures were tested in this study to find an optimal temperature setting that can be applied for both FD and MWFD methods. The tested shelf temperatures and drying times with regard to the success of drying are given in Tab. 3-5 for 100 g raspberry foam.

Tab. 3-5. Tested shelf temperatures at 0.1 mbar chamber pressure for freeze drying of raspberry foam containing 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P.

–: collapsed, nonuniform, +: non-collapsed, uniform

Shelf temperature (°C)	Drying time (h)	Drying uniformity (collapsed/non-collapsed structure)
20	24	–, remaining local ice and liquid
30	16	+, gentle drying
40	14	–, local melting of ice, collapsed structure located at the center
50	10	–, melting of ice, collapsed structure, dried by evaporation mostly

The low values of pressure and temperature, which depend on the material, tend to preserve the structure of the frozen product. The lowest possible pressure of 0.1 mbar was chosen in this study for both FD and MWFD processes. The foam structure dried at 20°C shelf temperature for 24 h was initially expected to be dried according to the average moisture content of the sample. However, it was not uniformly dried, and ice remained in the core of the sample where solid water was partially surrounded by liquid water. This phenomenon might be due to the lack of sublimation energy where the drying rate was too low, causing melting and a long drying time. This shows the importance of drying time besides the low shelf temperature for gentle drying. To obtain a completely dried sample, the drying time was kept longer than 30 h. However, the core of the sample was still spongy, and the structure collapsed because of local ice melting. Temperatures above 30°C resulted in collapsed structures as well. The ice was consequently melted, and the foam was dried partially by evaporation rather than by sublimation. In particular, the portions of the sample that were in direct contact with the heated shelves at the highest temperatures for a long time via conduction showed structural deformation, as shown in Fig. 3-16. Drying under sub-optimal conditions led to a collapse in the foam structure (Ratti, 2001).

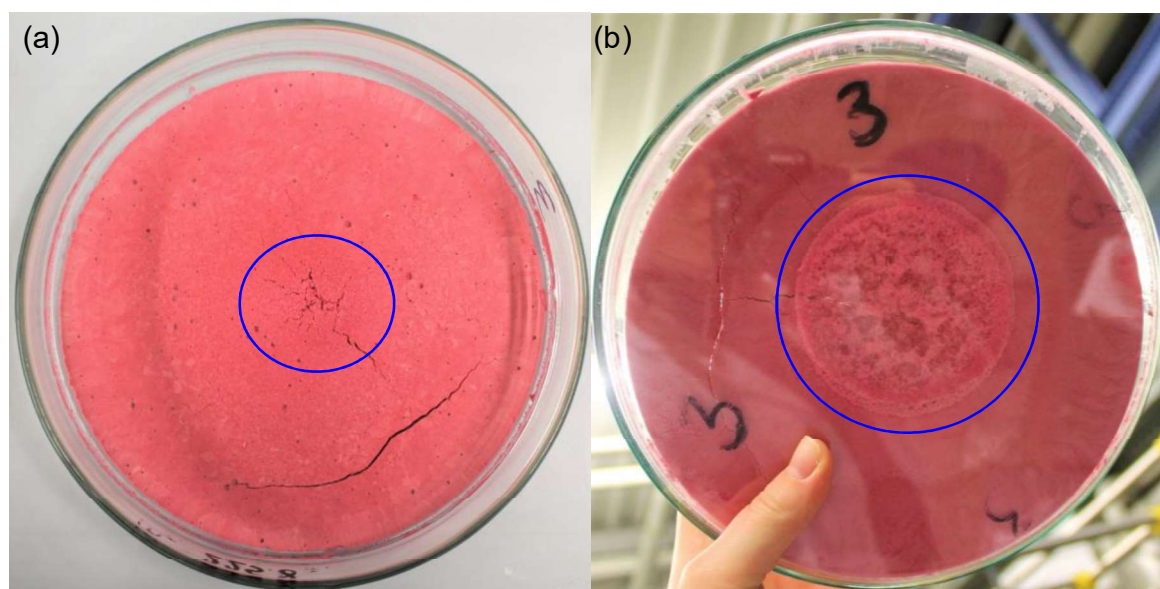


Fig 3-16. (a) Top and (b) bottom views of the dried foam subjected to conventional freeze drying at 0.1 mbar chamber pressure and 40°C shelf temperature. Both images revealed an uneven texture and collapsed structure with pronounced heterogeneity over the bottom surface of the sample.

A shelf temperature of 30°C was found to be suitable in terms of drying uniformity (no melting/recrystallization and no collapse), total drying time, and organoleptic product

quality. Therefore, the chamber pressure and the shelf temperature/maximum product temperature were set 0.1 mbar and 30°C, respectively, for both FD and MWFD. The condenser temperature was set at -50°C.

3.3.2 Microwave-assisted freeze drying (MWFD)

A microwave field generated using a magnetron was used in FD which improved the drying efficiency (Fan et al., 2017). Building on this, the first aspect is to offset the limitations of the process. A well-designed MW system is crucial for successful processing; however, each and every food material needs individual process parameters for a stable and gentle drying process. Microwave drying has some drawbacks including difficulties in temperature control and uneven and/or overheating which result in possible textural damages with an occurrence of hot spots, corona, and plasma discharge (Zhang et al., 2006).

The most frequent problem of the MWFD process is arching, which involves corona/plasma discharge that can adversely affect the quality of the product or damage the critical components of the system; for example, the Teflon parts can turn black (Duan et al., 2010b; Gaukel et al., 2017). Therefore, it is vital to delimitate the microwave power for the foam structure in this study. There are two critical phases where these phenomena possibly occur: at the beginning of the process where the product is completely in the solid state and toward the end of drying process when the water content is very low. Generating plasma under a low-pressure environment is extremely risky. Therefore, it is very important to transfer a reasonable microwave density matching the product load (Ozcelik and Püschner, 2017). At an applied pressure of 0.1 mbar, different specific microwave power inputs were tested at different product loads for specifying the applicable microwave power range. The applied microwave power input range was 100 to 250 watt for product loads of 80, 100, and 120 g. Knowing that the thickness and the exposed area of the material are important factors for a stable process, the product loads were tested in glass jars with different diameters such as 150, 190, 200, and 230 mm. Then, the drying process was examined in terms of process stability considering arching or plasma occurrence. The 190-mm diameter glass jars were found to be the most appropriate not only for drying stability but also in terms of practicality for sample preparation. The jars were suitable for both FD and MWFD

methods. Therefore, 190-mm glass jars were used in this study. The tested conditions are summarized in Tab. 3-6.

Tab. 3-6. Occurrence of plasma at different tested microwave power input values and product load at 0.1 mbar chamber pressure in terms of drying process stability. The tested raspberry foam contains 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P and the glass jar diameter is 190 mm.

0: no plasma, +: plasma, ++: arching and intense plasma

Product load (g)	Microwave power (Watt)			
	100	150	200	250
80	0	+	++	++
100	0	0	0/+	++
120	0	+	++	++

Hundred grams of sample with a foam thickness of approximately 1 cm was found to be suitable for a stable process. At a microwave power of 2.0 W g^{-1} , arching was reduced the most. Arching occurred at the beginning of the process when the microwave was first introduced, following which the process was stable. Microwave power above 2.0 W g^{-1} was not applicable because arching was too intense and it interrupted the process. The solid structure (ice) was not capable of absorbing the intense microwave energy; hence, the process was stopped. Because solid water is almost transparent to the microwaves, the dielectric heating is mainly driven by the organic product itself (Ozcelik and Püschner, 2017). Thus, it is not possible to apply excessive energy input because it cannot be simultaneously absorbed by the product. Therefore, microwave power input was limited to 2.0 W g^{-1} because of corona and plasma discharge. However, plasma occurrence depended on the formulation as well where the dense structure resulted in structural collapses. For instance, an intense plasma was occurred for the foam containing 2.5% (w/w) protein, 15% (w/w) MD and 2.5 (w/w) pectin, a very dense structure (0.63 g cm^{-3}), dried at MW power input of 1.5 and 2.0 W g^{-1} (See Fig. 3-17). Related results are discussed in more detail in Section 3.4 and 3.6. The intense plasma that occurred was a clear sign of the collapse and hot spots. Because the applied energy was too intense for a dense structure, energy excessively heated some regions, causing ice melting. At such regions, temperature increased suddenly and the rest of product was still in the solid state. Thus, the inhomogeneity of the product where

the moisture content changes from piece to piece led to uneven alteration of the electric field (Duan et al., 2010a).



Fig. 3-17. Plasma discharge during the MWFD at 2.0 W g^{-1} . The foam sample contained 5% (w/w) PP, 30% (w/w) MD, and 2.5% (w/w) P and was subjected to drying at a 0.1-mbar chamber pressure and 30°C maximum product temperature.

Another challenge of MWFD is overheating and nonuniform temperature distribution, which can be avoided by application of a pulsed microwave (Wang et al., 2013). When microwave energy is applied continuously, the generated heat within the product causes a rapid increase in temperature, especially when there is not much water left in the product that cannot absorb the applied energy (Gunasekaran, 1999). To solve the uneven and excessive-heating problems, intermittent application of microwave energy with temperature control was applied, thus guaranteeing the uniformity of microwave heating. When the maximum desired product temperature was reached, microwave energy was applied using an on–off cycle strategy until no more water could be removed from the material. Therefore, the sudden temperature rise could be eliminated, and the product could be maintained at the desired temperature throughout the entire process. The software of the dryer $\mu\text{WaveCAT}$ allows setting of the desired temperature and pressure profiles to achieve precise control of the overall drying process.

Fig. 3-18 presents an applied pulsed microwave drying profile. To establish the process parameters of drying, microwave power input, maximum product surface temperature, height, and amount of the samples were studied. A drying profile with a maximum product temperature of 30°C was programmed with an automatic regulation of microwave input.

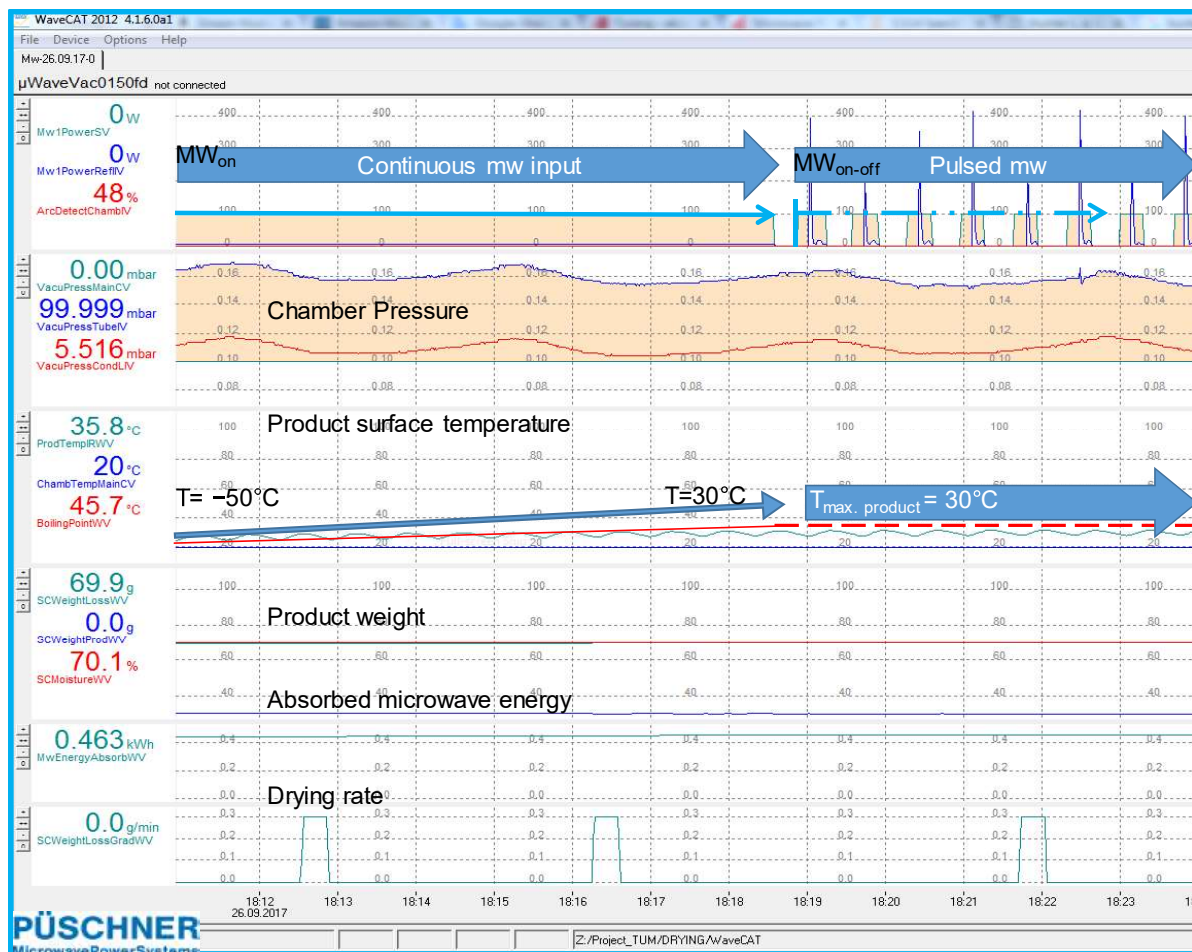


Fig. 3-18. Drying profile applied with pulsed microwave input (1.0 W g^{-1}) depending on the maximum product temperature (30°C) at 0.1 mbar chamber pressure (the screenshot was taken after the end of entire drying process therefore, actual process parameters appeared to be zero) (μ WaveCAT, Püschner Microwaves, Schwanewede, Germany).

3.4 Impact of hydrocolloid addition and microwave processing conditions on drying behavior of foamed raspberry puree

Summary and contribution of the doctoral candidate

Foams made out of fruit purees can subsequently be dried and consumed as snacks. Fruit foams produced by microwave-assisted freeze drying have a more porous and cellular structure, which makes them favorable compared to the foams obtained by conventional drying of fruit puree. It is well known that freeze drying is one of the leading methods to obtain high quality products. However, it requires long drying times, which result in high energy consumption and thus proportionally high production costs. To make such fruit snacks affordable for the consumer, a gentle but simultaneously fast drying process has to be applied. The primary objective of this study was to investigate the drying characteristics of foamed raspberry puree. Therefore, we evaluated the impact of varying hydrocolloid formulations and the microwave input power on the drying characteristics of raspberry foams during microwave-assisted freeze drying. Conventional freeze drying was performed as a reference.

To evaluate drying behavior, the concentrations of single compounds were varied while those of others were kept constant. Based on the investigated foam formulations (Chapter 3.2.) while the highest foam stability was concerned for a gentle drying process. Potato protein was applied as a foaming agent, and its concentration was varied (2.5, 5, 7, and 10%) while those of MD (15%) and pectin (2.5%) were kept constant. For the variation of MD (5, 15, and 30%), a constant protein (5%) and pectin (2.5%) concentration was applied. Based on the preliminary experiments, a 2.0 W g⁻¹ power input was determined to be the maximum microwave power input. Three different microwave power levels (1.0, 1.5, and 2.0 W g⁻¹) were tested.

A gentle and fast drying process of raspberry foam was characterized via microwave-assisted freeze-drying process. Drying speed was positively correlated with MD concentration and thus bubble size and size distribution. MD concentration significantly influences temperature change during the drying process. A moderate foam overrun is advantageous for efficient drying, thus providing a compromise between a high internal surface area and thin lamellae. Varying microwave power did not significantly influence the total drying time. However, the microwave freeze drying process at 1 W g⁻¹ yielded a 3–4-fold decrease in total drying time in comparison to conventional freeze-drying.

Overall, there was a considerable correlation between the fresh foam characteristics and the drying behavior of foamed raspberry puree.

The doctoral candidate developed the concept of experiments and established the methods. This comprised the conception and design of the experiments, based on a critical literature review, and a major conduction of the preliminary experiments and data analysis including statistical evaluation and data interpretation. In addition, the doctoral candidate wrote and revised the manuscript. Co-authors contributed to the experimental part or to the discussion of the results and provided input to the drafted publication prior to the submission.



*Adapted original manuscript*³

Impact of hydrocolloid addition and microwave processing condition on drying behavior of foamed raspberry puree⁴

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Highlights

- A microwave-aided freeze-drying process was applied to a heat-labile fruit foam.
- Effects of the foam stabilizers maltodextrin and potato protein and microwave power on the drying kinetics were investigated.
- A gentle and fast drying process of raspberry foams was achieved.
- The technology proposed proved to be an efficient alternative to the conventional freeze-drying for the production of fruit foams.

Abstract

In this study, foamed raspberry puree was dried by microwave-assisted freeze drying (MWFD). The combined use of microwaves and a foamed structure was intended to accelerate the drying process, while creating an innovative product structure with intense aroma impact for consumption as a snack. The influence of potato protein as foaming agent, maltodextrin as foam stabilizer and microwave (MW) power on the drying characteristics of raspberry foams during MWFD was investigated. Conventional freeze drying (FD) experiments were performed as a reference. MD concentration was shown to significantly influence product temperature. As higher MD concentrations yielded smaller bubbles and a more uniform bubble size distribution, lower drying temperatures were needed to reach the same final moisture content. Varying MW power did not significantly influence the drying time. MWFD at 1.0 W g⁻¹ yielded a 3 to 4-fold decrease in total drying time as compared to FD. The addition of 10% protein

³Adaptions refer to formatting aspects: e.g., numbering of sections, figures, tables and equations, abbreviations, manufacturer specifications, axis labeling, figure captions and style of citation.

⁴ Originally published in: Journal of Food Engineering (2019), Vol. 240, pp. 83-91. Permission for reuse of this article was granted by Elsevier.

led to the most gentle drying at high MW power input due to structural changes enabling a lower resistance against water vapor mass transfer. There was a high correlation between the foam characteristics and the drying behavior. An overrun above 450% led to gentle drying at all tested microwave power input levels. Foam bubble size and bubble size distribution correlated well with drying velocity. Overall, MWFD was shown to be a much faster and more gentle alternative to FD for the production of fruit foams.



3.4.1 Introduction

Raspberries have achieved great popularity within consumers as they contain high concentrations of ascorbic acid and anthocyanins. Along with the rising demand for convenience foods, there has been a clear trend toward the production of healthy snack products in recent years. In general, a modern snack product is expected to provide high-quality nutrition combined with an attractive appearance and a pleasant mouthfeel. In line with increasing health awareness, vegan food products have gained popularity, and this has triggered an increase in demand for fruit-based products. Further, the consumer generally expects a minimally processed product with a natural and intense taste close to that of unprocessed food. One way of producing dried snack products is freeze drying (FD), a method considered non-damaging, and which yields products with an almost natural appearance. However, FD is slow and therefore expensive, and products (e.g., dried whole fruit such as raspberries) rehydrate slowly. As an alternative to dried whole fruit, an attractive fruit product concept could be achieved by first converting whole fruit into pulp or puree then whipping these into a foam. Such foamed pulps could subsequently be dried. Thereby, a snack product could be produced with a highly porous structure, exhibiting a new and intense sensory perception during chewing as the aroma is released instantaneously (Carvalho et al., 2017).

The foamed structure could also lead to a faster drying process, since the open structure creates a lower resistance to the escape of water vapor during drying (Huang et al., 2015). Liquid or semi-liquid food is whipped to a mechanically and thermodynamically stable foam using foaming agents and foam stabilizers, such as hydrocolloids. A specific foam stability is important, especially when a foam structure is to be dried; an unstable foam could collapse before or during the drying process. In order to obtain a stable fruit foam, various foaming and stabilization agents such as egg albumen, soy protein isolate, methyl cellulose, or milk proteins have been reported in the literature (Abbasi and Azizpour, 2016; Franco et al., 2015; Kadam et al., 2011; Karim and Wai, 1999; Rajkumar et al., 2007; Sankat and Castaigne, 2004; Thuwapanichayanan et al., 2008). Recently, food producers have shown great interest in replacing animal proteins with plant proteins (Glusac et al., 2018). Among plant proteins, hypoallergenic, high-quality potato proteins have gained interest. Due to its functional properties potato protease inhibitors, one of the essential fractions of the soluble potato protein was used

as a foaming agent. Particularly at low pH ranges PPI is stable against Ostwald ripening at pH 3 which is the pH of raspberry (van Koningsveld et al., 2002). For enhanced foam stabilization, carbohydrates such as maltodextrin can be used due to their neutral taste and high solubility (Jafari et al., 2017). Hydrocolloids, mainly used as gelling agents when dispersed in water (Saha and Bhattacharya, 2010), are also used. Typically, a gelling agent such as pectin can help to stabilize a foam and prevent drainage, coalescence, the rupture of the film between bubbles, Ostwald ripening and other destabilizing events.

Drying of foams, also known as foam mat drying, has been investigated since the 1920s. It has become popular because liquid or semi-liquid products can be dried faster this way than via conventional methods (Ratti and Kudra, 2006). Increased efficiency is achieved because the air bubbles increase the inner surface area and create a structure less resistant to mass transport of water vapor resulting in the removal of evaporated water much faster than in a non-foamed liquid structure. Building on this, (Brygidyr et al., 1977) and (Thuwapanichayanan et al., 2012) reported that foam drying could be achieved at lower temperatures; and foams hardly experience overheating and, thus higher product quality can be achieved (Ng and Sulaiman, 2018). It has also been noted that foaming and stabilizing agents may help to avoid bubble collapse during drying, since they increase the glass transition temperature of the sample (Ratti and Kudra, 2006).

It appears that foam mat drying of fruits is one of the most efficient methods to dry sticky and highly dense fruit purees. It has been applied to different fruits and fruit products, such as mango (Lobo et al., 2017), jambolan (de Carvalho et al., 2017), cowpea (Falade et al., 2003) and muskmelon (Sangamithra et al., 2015a). However, foam mat drying of raspberry has not been reported in the literature to date.

As mentioned above and as demonstrated by a number of researchers (Jiang et al., 2011; Michalska et al., 2016; Monteiro et al., 2015), freeze-drying is the best method for obtaining high-quality dried food products since the drying process is run at very low temperatures in an oxygen-free environment. However, the lower drying rates observed during freeze-drying result in high energy consumption and thus lower energy efficiency (Ratti, 2001; Zhang et al., 2006). Dehnad et al. (2016) emphasized that the

best for functional properties are a compromise between the drying time and temperature. Consequently, there is a distinct need for an equally gentle drying process, which can yield fruit products with comparable quality, but higher process efficiency. Microwave-assisted freeze-drying (MWFD) emerges as a promising method. Since the electromagnetic radiation of microwaves heats the product in bulk volumetrically without direct contact, the application of microwave (MW) energy to a freeze-drying process yields higher drying rates and accordingly shorter overall processing times. However, there are still some difficulties with the implementation of MWFD on industrial scale due to non-uniform temperature distribution. It is critical to regulate microwave power and chamber pressure to avoid hot spots during the process (Fan et al., 2019).

To the best of the authors' knowledge, no work has been reported in the literature on foaming characteristics of raspberry puree and its behavior during drying with microwaves. The hypothesis of this work was that freeze-drying of foamed fruit puree could be accelerated by the application of microwave energy, resulting in a high-quality product and a specific end product structure.

The primary objective of this study was to investigate the drying characteristics of raspberry foams. We evaluated the influence of potato protease inhibitors (PPI) as a foaming agent, the concentration of MD as a foam stabilizer, and MW input power on drying behavior to determine the optimal MWFD conditions for fruit foams. The MWFD process was compared with conventional FD as a reference.

3.4.2 Materials and methods

3.4.2.1 Foam preparation

Frozen Willamette cultivar raspberries from Serbia were supplied by Mainfrucht (Gochsheim, Germany). The required quantity of frozen raspberries was defrosted for 2 h at 20°C. Then a puree was produced using a food mill. PPI were used as a foaming agent. Maltodextrin (DE 6) (MD) and pectin (P) were used as foam stabilizers. Tables 3-4 and 3-5 list the foam formulations, all of which had been found suitable for a stable drying process in preliminary tests. The mixture of raspberry puree, foaming agent, and stabilizers was whipped by a KitchenAid mixer (Model Arti-san 5KSM150, St. Joseph, MI, USA) at the maximum speed of 220 rpm for 10 min.

3.4.2.2 Foam properties

The foam overrun indicates the amount of air that was able to be incorporated into the foam by mechanical whipping. Foam overrun increases with increasing foam porosity. To measure foam density (kg m^{-3}), a measuring cylinder was filled to the top with foam, its surface was smoothed with a spatula, and the weight taken. Foam overrun was calculated by following equation:

$$\text{Overrun} [\%] = \frac{\left(\frac{1}{\rho_f} - \frac{1}{\rho_l}\right)}{\frac{1}{\rho_l}} \times 100 \quad (3-5)$$

where ρ_f is the foam density (kg m^{-3}) and ρ_l is the solution density (kg m^{-3}).

Foam stability is the ability of a foam to hold air for a given period of time. Drainage volume is the rate at which liquid drains from foam. Drainage volume was measured by weighing the liquid that had dripped out of the foam after 30 min at room temperature. An increase in drainage decreases the stability of a foam. The stability of the foam was calculated based on the difference between the initial foam weight and weight of the drained liquid after 30 min. Foam stability was calculated according to equation (3-6):

$$\text{Foam stability} [\%] = \frac{m_{\text{foam},30 \text{ min}}}{m_{\text{foam},0 \text{ min}}} \times 100 \quad (3-6)$$

where $m_{\text{foam},0 \text{ min}}$ is the generated foam weight and $m_{\text{foam},30 \text{ min}}$ is weight of the foam after 30 min. The bubble size distribution was measured with a microscope (Model Axiovert 135, Carl Zeiss, Jena, Germany). After spreading samples onto glass slides, images were examined and the diameter of 300 bubbles was measured. From the bubble diameter data the 10, 25, 50, 75, and 90 percentiles were calculated. AxioVision Rel.4.8. (Carl Zeiss, Jena, Germany) software was used for characterization of bubble size and bubble size distribution.

3.4.2.3 Experimental set-up

For the foam drying trials, single compounds were varied in different concentrations while the others were kept constant. According to literature, foam stability is an important factor in foam drying and should be as high as possible (Ratti and Kudra, 2006).

As foam stabilities of all tested concentrations in preliminary experiments were very high (above 90%), all ingredient concentrations were generally applicable for drying trials.

In order to retain the intense raspberry taste, the usage of high maltodextrin concentration was aimed to be avoided. Therefore, 15% MD was chosen for testing varying PPI concentration (2.5, 5, 7.5, 10%). For the variation of maltodextrin (5, 15 and 30%), a protein concentration of 5% was applied as very stable foams were achieved at this concentration. Further, sensory perception was still not influenced much by the protein addition. As pectin was found not to influence the foam characteristics significantly, it was kept constant for all trials.

3.4.2.4 Drying equipment

Freeze drying

Freeze drying (FD) experiments were conducted to establish a reference for the study. Accordingly, all samples were freeze dried and the results were compared to those obtained from the samples subjected to microwave-assisted freeze-drying (MWFD). The freeze drying process was conducted in a pilot-scale freeze dryer Christ Gamma 1-20 (Osterode, Germany). The samples were heated via conduction through the shelves. The samples were dried at a chamber pressure of 0.1 mbar, an ice condenser temperature of -50°C and a shelf temperature of 30°C .

Microwave freeze drying

For the MWFD experiments, a pilot-scale microwave freeze dryer (Model $\mu\text{Vac0150fd}$, Püschner Microwaves, Schwanewede, Germany) was used. Microwave radiation was generated with a 1000 W magnetron at 2.45 GHz. Each sample was placed on a polypropylene/polytetrafluoroethylene (PP/PTFE) turntable rotating at 1 rpm during the drying process. The drying kinetics of the samples were monitored by continuously measuring their weight. A balance (5 kg; precision: 0.1 g) connected to the turntable was used for online monitoring of the sample. Product surface temperature was measured continuously using an infra-red camera mounted at the chamber wall above the sample. The chamber pressure was adjusted by means of a rotary vane pump. The condenser temperature was -50°C . The $\mu\text{WaveCAT}$ dryer software allowed the setting, recording and monitoring of the desired temperature and pressure profiles to

achieve precise control of the overall drying process. The drying variables, including pressure, product surface temperature, product weight, drying rate, and absorbed and reflected MW energy were recorded at 1 s intervals. The maximum product temperature was controlled automatically based on the sample's surface temperature measured by an infrared temperature sensor (Heitronics, Wiesbaden, Germany). By pulsing the microwave power, product surface temperature was limited to a maximum of 30°C; as soon as the surface temperature reached 30°C, microwave input was regulated to a pulsed heating mode. Further details of the drying equipment are given in Ambros et al. (2016).

The maximum possible MW power available was determined to be 2.0 W g⁻¹ based upon preliminary experiments. Three levels of MW power (1.0, 1.5 and 2.0 W g⁻¹) were tested. For comparison purposes, the chamber pressure and the maximum product temperature were set to match those for FD at 0.1 mbar and 30°C, respectively. For both FD and MWFD methods, foam samples weighing 100 g were placed into 190 mm diameter glass dishes. Each sample was spread over the bottom surface of the dish forming a smooth layer and frozen at -80°C for 24 hours prior to drying.

A target residual water content ranging from 3.5 ± 1% (w.b.) was applied in all drying experiments as the criterion to terminate the drying process. All samples were evaluated for their residual water content and water activity immediately after the drying processes had terminated.

3.4.2.5 Moisture content

The initial moisture content of samples was measured gravimetrically by using Smart Turbo 6 (CEM Corp., Germany). Dried raspberry foam samples were ground by a mortar and pestle. Residual moisture content of the dried samples was measured by Karl-Fischer titration (Schott, Mainz, Germany). The analysis was conducted using an automatic titrator Titro Line KF (Schott, Mainz, Germany). A 0.1 g dried sample was used for each measurement. All reagents used for the analysis were purchased from Sigma-Aldrich (Steinheim, Germany).

3.4.2.6 Water activity

The water activity of dried raspberry foam powder was determined at 25°C using a water activity meter AW Sprint (Novasina AG, Lachen, Switzerland) with a sensitivity

of 0.001. Standard salt solutions (Novasina) of known water activity were used for calibration of the sensor at the measuring temperature.

3.4.2.7 Evaluation of drying characteristics

Moisture ratio

For a better comparison of the drying kinetics between foams with different initial water content, the mass of product moisture was normalized to a moisture ratio value. The moisture ratio at a certain time point of drying, $MR(t)$, was calculated according to equation (3-7):

$$MR(t)[-] = \frac{M_t - M_e}{M_0 - M_e} \quad (3-7)$$

where M_t is the product mass at time t (kg kg^{-1}), M_e is the equilibrium mass (kg kg^{-1}) and M_0 is the mass at the beginning of the drying (kg kg^{-1}).

Drying rate

The drying rate was calculated by equation (3-8) from the change in moisture ratio over drying time as:

$$\text{Drying rate}[\text{min}^{-1}] = \frac{MR_{t1} - MR_{t2}}{t2 - t1} \quad (3-8)$$

where MR_{t1} and MR_{t2} are the moisture ratios obtained at the beginning and the end of a time interval $t2-t1$ (min).

3.4.2.8 Statistical analysis

For each sample two batches were prepared, and all analyses were performed in triplicate. In total, a six-fold determination was conducted and were reported as means and standard deviations, calculated using Excel (Microsoft, Redmond, USA). To test for significant differences between MD and PPI treatments, Tukey test was performed with initial moisture content, final water activity, foam thickness, overrun and foam stability and different concentrations of MD and PPI as factors. All data analyses were done using R software (version 3.5.0) using the package "car" (Fox and Weisberg, 2011).

3.4.3 Results and discussion

In this section we report on the MWFD drying behavior of raspberry fruit foams containing varying concentrations of agents affecting foam formation and foam stabilization. In Section 3.4.3.3, we compare MWFD drying speed against that for conventional FD.

3.4.3.1 Impact of varying MD concentration, PPI concentration and MW power on drying behavior

3.4.3.1.1 Drying kinetics

Drying curves of raspberry foams with varying MD concentrations are shown in Fig. 3-19a. After a relatively steep initial drop, all three curves flatten out at ~ 0.04 MR at the bound water point. The 5% MD foam reached this point after 305 min, while it took 272 min for the 15% MD foam and 76 min for the 30% MD foam. In this last step, only bound water was removed. The initial fall in MR for foam with 30% MD was greatest. Lower MD concentrations resulted in longer drying times.

We studied the impact of PPI on the drying kinetics of raspberry foams containing fixed concentrations of MD (15%) and P (2.5%). Fig. 3-19b shows moisture ratio change over time for foams containing four different PPI concentrations (2.5%, 5%, 7.5% and 10%). Raspberry foams containing 2.5% PPI dried slightly faster than foams with higher concentrations of PPI. The effect of different PPI concentrations on drying time appeared to be minor.

The effect of MW input power on the drying behavior of raspberry foams containing 15% MD is shown in Fig. 3-19c. An increase in MW power resulted in a shortened drying time. Regarding different microwave levels at varying MD concentration, an explicit desorption phase was evident at all microwave levels for the sample with 5% MD. Samples with higher MD concentration only showed desorption at or above 1.0 W g^{-1} . Higher applied MW power resulted in faster heating and more vibration of molecules and, thus, a higher vapor pressure build-up in the sample. This could accelerate water removal. Furthermore, it can be seen that doubling the MW power input did not double the drying rate. This is due to the fact that energy absorption of the product, especially in MWFD, is severely limited by the low loss factor of ice, and also by the less flexible organic molecules, which can absorb MW energy to a certain extent. When the product

is frozen, the dielectric loss factor of the product is very low and drying is mainly driven by the dielectric properties of the organic molecules such as carbohydrates (Ozcelik and Püschner, 2017). This obviously plays an important role in MW energy absorption, and thus, in volumetric heating. With higher MD concentration, the influence of the MW power input became less significant. This may be due to the higher loss factor of the foam at higher MD concentrations. The impact of MD concentration on drying behavior is therefore more pronounced than that of MW power input.

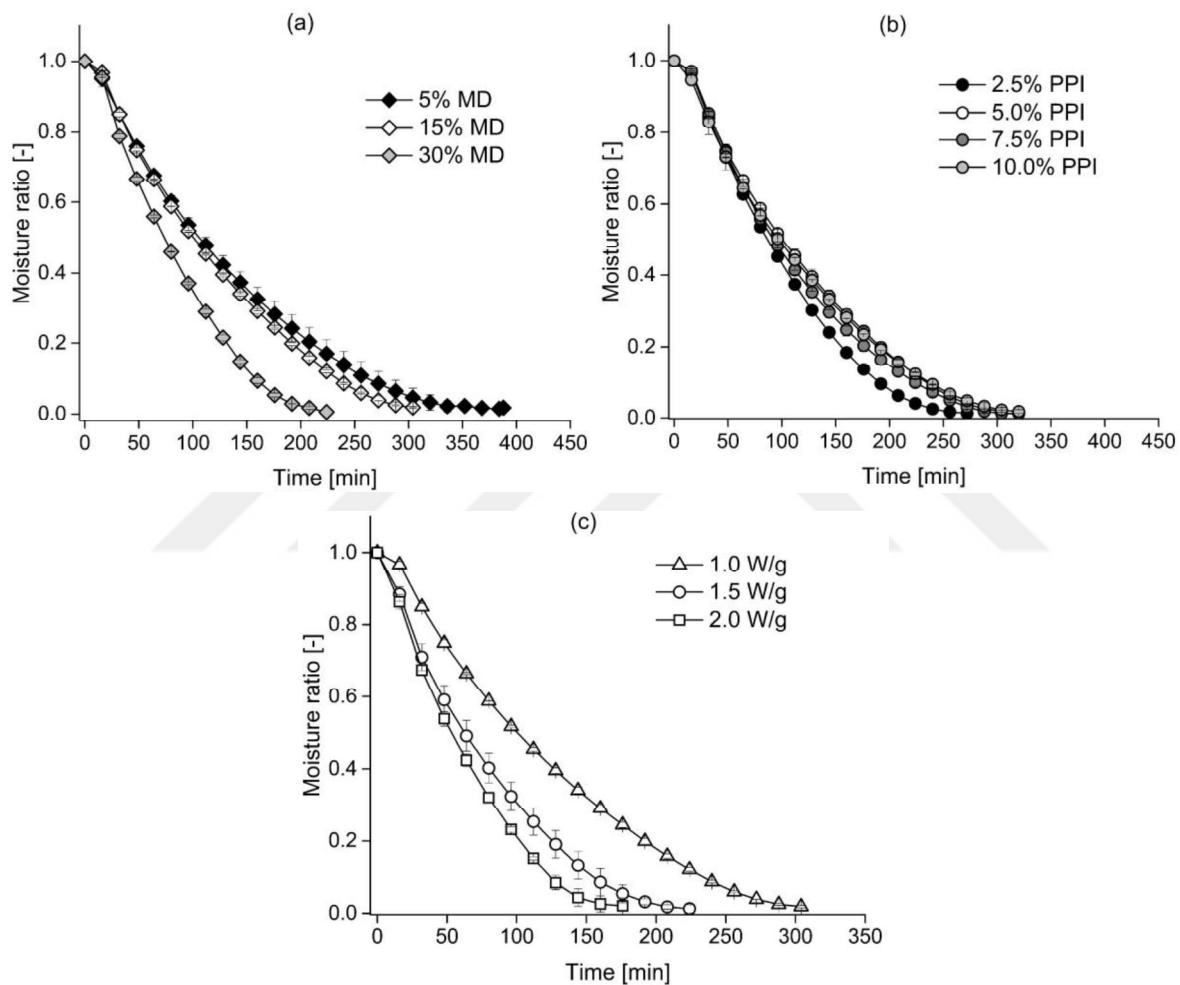


Fig. 3-19. Drying curves of raspberry foams at 0.1 mbar chamber pressure and 30°C maximum product temperature. **(a)** 5% (w/w) PPI + 2.5% (w/w) P with different MD concentration at 1.0 W g⁻¹ microwave power level, **(b)** 15% (w/w) MD + 2.5% (w/w) P with different PPI concentrations at 1.0 W g⁻¹ microwave power level, **(c)** 5% (w/w) PPI + 15% (w/w) MD + 2.5% (w/w) P foam at different microwave power inputs (1.0, 1.5 and 2.0 W g⁻¹).

3.4.3.1.2 Bubble size distribution

Bubble size distribution narrowed as MD concentration increased (Figure 3-20). Higher MD concentrations result in smaller bubbles with a more uniform size distribution. In a consequence, highly porous structure provides less diffusional resistance thus the diffusivity of moisture increased.

A more homogeneous foam structure is likely to facilitate faster drying, and this aspect is discussed further below in conjunction with the effect on drying rate.

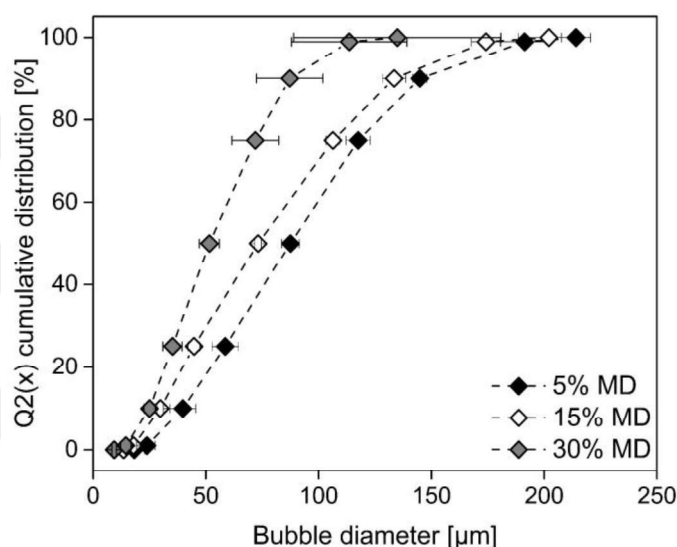


Fig. 3-20. Bubble size distribution of fresh raspberry foams containing 5% (w/w) PPI + 2.5% (w/w) P with different MD concentrations.

3.4.3.1.3 Drying rate

Fig. 3-12a shows the drying rate of the raspberry foams with varying MD concentration. The drying rate curves show an increase to a maximum value at high moisture ranges early in the process. Due to the high moisture content at the beginning, drying could proceed very fast, as expected. Immediately beyond the peak the drying rate decreases steadily; there are no periods during which the rate of drying is constant. As the water content decreased, there was also a marked decrease in the drying rate since the outer layers had already been dried and sublimation was occurring mainly in the inner regions of the foam. Moreover, the drying rates were higher at higher MD concentrations with lower initial moisture content. The abovementioned drying behavior of foams with varying concentrations of MD could be explained by the bubble characteristics present in the foam structure (Fig. 3-20). The bubble size and bubble size

distribution appear to affect the MWFD behavior. Drying rates of foams containing different PPI concentrations are shown in Figure 3-21b. Although the foam with 2.5% PPI initially exhibited a higher drying rate, there was no marked difference among the tested samples for the remainder of the drying period. The protein concentration did not appear to significantly affect the drying behavior at a power input of 1.0 W g^{-1} . Of note is that samples with higher MD concentration had reduced foam height after freezing, despite the fact that the overrun prior to freezing was almost identical at all MD concentrations (Tab 3-4).

Tab. 3-4. Tested foam recipes with varying maltodextrin concentration all with 5.0% (w/w) potato protease inhibitors and 2.5% (w/w) pectin, fresh foam characteristics, initial moisture content (%) and final water activity of FD and MWFD at 1.0 W g^{-1} .

Samples	MD (%,w/w)	Foam thickness (cm)	Overrun (%)	Foam stability (%)	Initial moisture content (%)	Water activity (-)	
						FD	MWFD (1.0 W g^{-1})
5% MD	5.0	1.15 ± 0.14^a	214.20 ± 11.88^a	94.84 ± 3.07^a	76.93 ± 0.24^a	0.165 ± 0.007^a	0.226 ± 0.05^a
15% MD	15.0	1.02 ± 0.06^{ab}	218.69 ± 9.79^a	92.98 ± 2.97^a	70.67 ± 0.13^b	0.116 ± 0.030^b	0.149 ± 0.04^b
30% MD	30.0	0.92 ± 0.04^b	214.60 ± 2.22^a	99.64 ± 0.04^b	62.97 ± 0.32^c	0.073 ± 0.004^c	0.094 ± 0.09^c

Consequently, this reduces the moisture diffusion pathway to the surface. In general, the pore structure facilitates the dehydration process due to increased inner surface area. Mass transfer resistance then decreases because of the capillary effect of lamellae, which eventually enables a fast drying process (Prakotmak et al., 2010; Sangamithra et al., 2015b).

A second point to consider regarding MWFD behavior is the dielectric properties of the raspberry foam. It is likely that a high MD concentration significantly increases the dielectric loss factor of the foam. Thereby, a foam can absorb more MW energy, which in turn accelerates drying. In addition, a denser, more compact foam structure is likely to have improved conductive heat transfer within the foam domain, which is likely responsible for the relatively high drying rate toward the end of the desorption phase.

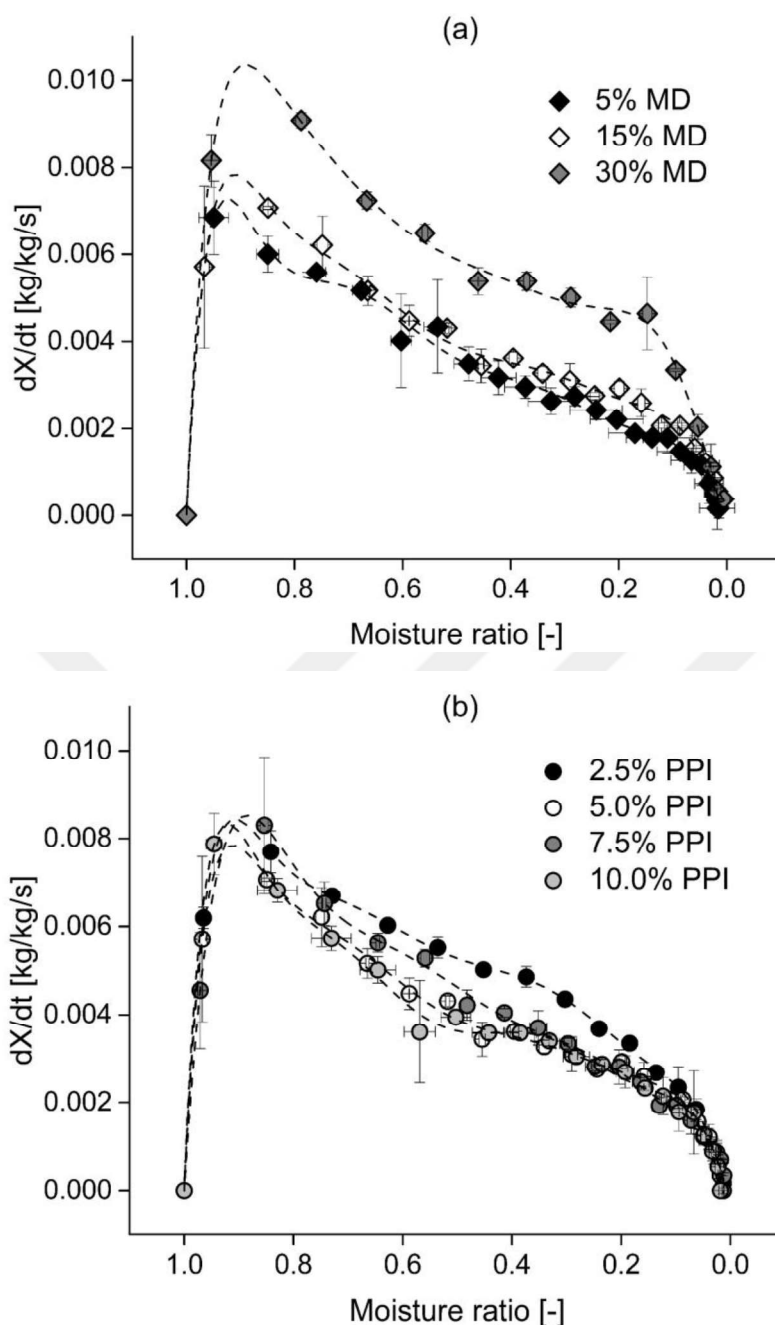


Fig. 3-21. Drying rate as a function of product moisture ratio of raspberry foams at 0.1 mbar chamber pressure and 30°C maximum product temperature. **(a)** 5% (w/w) PPI + 2.5% (w/w) P with different MD concentrations at 1.0 W g⁻¹ microwave power level, **(b)** 15% (w/w) MD + 2.5% (w/w) P with different PPI concentration at 1.0 W g⁻¹ microwave power level.

3.4.3.2 Impact of varying MD, PPI concentration, and MW power on temperature changes during drying process

Fig. 3-22a show surface temperature of the raspberry foams plotted against the moisture ratio for three different MD concentrations. At the beginning of the drying process, soon after MW input began, product temperature swiftly increased from -50°C to

-20°C. Once a moisture ratio of approximately 0.6 was reached, surface temperature was always higher for foam samples with lower MD concentrations. Thus, with a lower MD concentration, a higher surface temperature occurred at any given moisture ratio, except at the start and end of the drying period. The temperature of the 30% MD sample remained below zero until the beginning of the desorption phase. It can be seen from the figure that at the higher MD concentration most of the drying process took place below 0°C; by the time the temperature had risen to 0°C the residual moisture content was observed to be ~10%. It appeared that the MWFD of the sample with 30% MD showed the most uniform drying. The fact that a high MD concentration leads to drying with a sublimation phase taking place mostly below zero is of great importance as far as the structural integrity of the product is concerned. One explanation of this relatively uniform drying is the existence of a uniform bubble size distribution at the highest MD level. However, all three curves showed a steep increase toward the end of drying which corresponds to the low water content range. Removal of bound water toward the end of drying occurred at high temperature (but not exceeding 30°C) since more energy was needed for the evaporation of bound moisture. The MD concentration had a significant influence on sample temperature during the drying process.

The surface temperature of raspberry foams with different PPI concentrations is shown Fig. 3-22b. The temperature profiles follow a similar trend in all cases except for the foam with the lowest PPI concentration; the surface temperature of the foam with 2.5% PPI remains longer in the negative range than the other samples. This observation can be attributed to the lower dielectric loss factor and, thus, to the very low energy uptake. On the other hand, it may indicate that the sublimated water vapor is effectively transported to the surface due to the weaker protein network.

The level of MW input power, however, has no significant effect on the surface temperature profile (Fig. 3-22c). For the 30% MD foam, slightly higher temperatures were recorded at higher MW input powers. In particular, the level of MW power did not affect the product temperature in the sublimation phase. In this phase, the majority of the absorbed MW energy is known to be converted into sublimation enthalpy. Toward the end of drying, slightly higher temperatures were recorded at higher MW power due to sudden sublimation and subsequent hot spots.

It should be noted that in foams with 2.5% PPI at microwave powers of 1.5 and 2.0 W g⁻¹, hot spots occurred during drying. The reason for this is the very dense foam structure and thus impeded diffusion of the water vapor formed in the interior of the product.

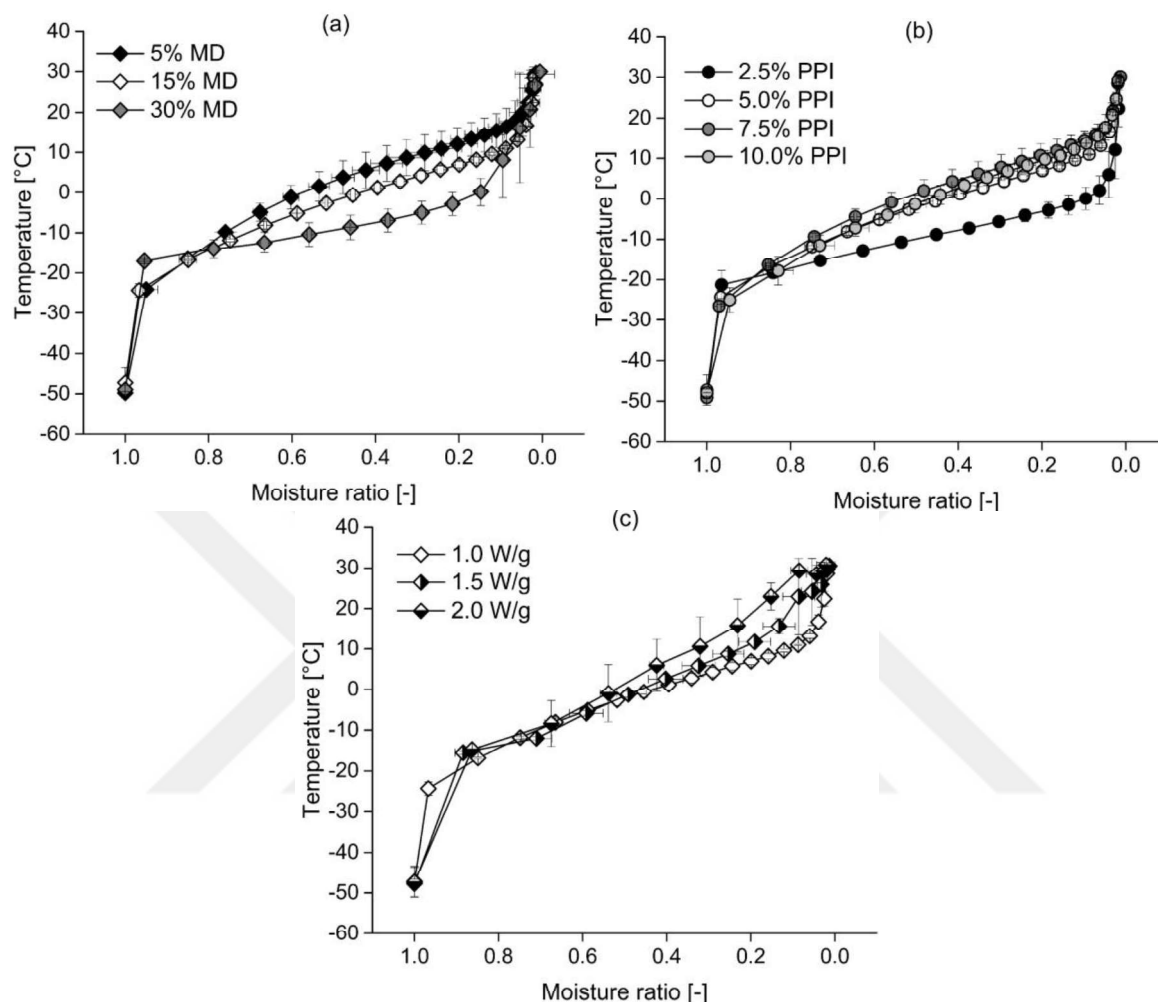


Fig. 3-22. Maximum product surface temperature as a function of product moisture ratio of raspberry foams at 0.1 mbar chamber pressure and 30°C maximum product temperature. **(a)** 5% (w/w) PPI + 2.5% (w/w) P with different MD concentrations at 1.0 W g⁻¹ microwave power level, **(b)** 15% (w/w) MD + 2.5% (w/w) P with different PPI concentrations at 1.0 W g⁻¹ microwave power level **(c)** 5% (w/w) PPI + 15% (w/w) MD + 2.5% (w/w) P foam at different microwave power inputs (1.0, 1.5 and 2.0 W g⁻¹).

For the foam samples containing higher PPI concentrations (5, 7.5, and 10%), the surface temperature was independent of the changes in MW power. Temperature profiles also were very similar. These results suggest that the most gentle drying can be achieved at low PPI concentrations with a low MW power input. Like an unfoamed liquid layer, a dense foam structure makes it almost impossible to obtain high performance since the product heats up quickly and hot spots are produced.

3.4.3.3 Impact of varying MD, PPI concentration, and MW power on drying time

All samples were dried using FD to establish a reference. The total drying time for FD of various samples including raspberry splits, puree, and foams are depicted in Fig. 3-23. The longest drying time was 72 h for the puree, while the raspberry splits required 54 h to reach a residual water content of less than 4% (w.b.). The drying times for the foam samples ranged from 10–20 h, significantly shorter than those for the puree and raspberry splits. The variation in drying times can be attributed to the structural differences among the raspberry splits, pulp, and foams, although it should be noted that the initial water content of the samples was different at the beginning of the drying.

Fig. 3-23a. shows the drying time of raspberry foams with different MD concentrations. MWFD required 3.5 to 5 min g⁻¹ evaporated water, while FD required between 8.8 min g⁻¹ and 15.8 min g⁻¹. The faster drying at higher MD concentrations can be attributed to the low initial water content and faster diffusion of moisture through the thin foam lamellae and gas bubbles to the surface. As explained in Subsection 3.4.3.1, smaller bubbles and a narrower bubble size distribution accelerate the drying.

Tab. 3-5. Tested foam recipes with varying potato protease inhibitors concentration all with 15.0% (w/w) maltodextrin and 2.5% (w/w) pectin, fresh foam characteristics, initial moisture content (%) and final water activity of FD and MWFD at 1.0 W g⁻¹.

Samples	PPI (%, w/w)	Foam thickness (cm)	Overrun (%)	Foam stability (%)	Initial moisture content (%)	Water activity (-)	
						FD	MWFD (1.0 W g ⁻¹)
2.5% PPI	2.5	0.58±	79.19 ±	99.79 ±	72.22 ±	0.083 ±	0.197 ±
		0.11 ^a	6.37 ^a	0.02 ^a	0.52 ^a	0.003 ^a	0.008 ^a
5.0% PPI	5.0	1.02±	218.69 ±	92.98 ±	70.67 ±	0.116 ±	0.149 ±
		0.06 ^b	9.79 ^b	2.97 ^b	0.13 ^a	0.030 ^a	0.004 ^b
7.5% PPI	7.5	1.30±	379.20 ±	98.26 ±	69.18 ±	0.099 ±	0.141 ±
		0.04 ^c	14.38 ^c	3.84 ^a	0.19 ^b	0.013 ^a	0.016 ^b
10.0% PPI	10.0	1.44±	447.48 ±	99.51 ±	67.76 ±	0.090 ±	0.105 ±
		0.01 ^c	25.22 ^d	0.14 ^a	0.19 ^c	0.001 ^a	0.020 ^c

Figure 3-23b. shows the drying time of raspberry foams with different PPI concentrations. The total drying time increased slightly with increasing PPI concentration. A

higher protein concentration leads to an increase in the overrun (Tab. 3-5), therefore shorter drying times could be expected.

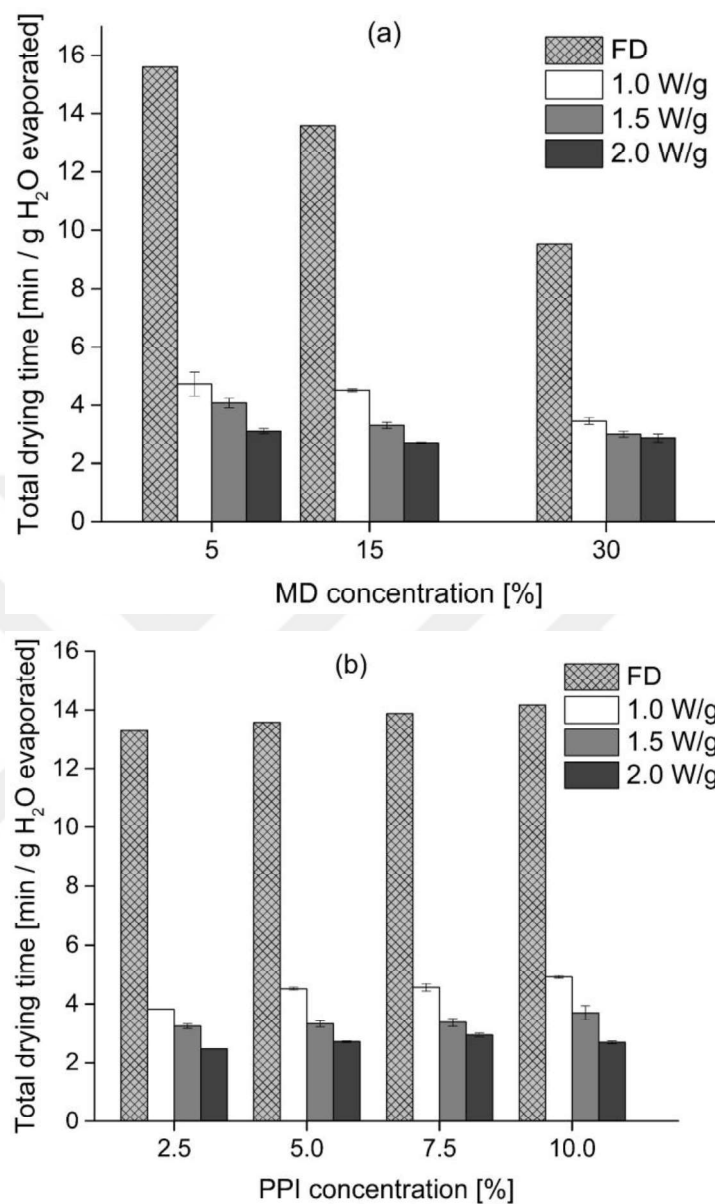


Fig. 3-23. Drying time for freeze and microwave freeze-dried raspberry foams as a function of varying concentrations at different microwave power inputs (1.0; 1.5; 2.0 W·g⁻¹), 0.1 mbar chamber pressure and 30°C maximum product temperature **(a)** 5% (w/w) PPI + 2.5% (w/w) P with different MD concentration **(b)** 15% (w/w) MD + 2.5% (w/w) P with different PPI concentration.

Normally, faster drying can be achieved at a higher overrun since the effective diffusion is increased (Kadam and Balasubramanian, 2011; Thuwapanichayanan et al., 2012).

A higher protein concentration may also lead to a better formation of the protein network. Partially unfolded proteins or even aggregates could interact more with each other and build a stable network.

This might inhibit the water vapor diffusion from the product. Though higher overrun allows higher microwave power input without hot spot occurrence, it was shown (Subsection 3.4.3.2) that a higher overrun can adversely affect the drying speed. Since a higher foam density is associated with a higher loss factor, foams with lower overrun can absorb more MW energy per unit volume.

3.4.3.4 Absorbed microwave energy

For a better prediction of the efficiency of a microwave process, it is important to evaluate the MW energy absorbed by the product. Figure 3-24a shows the absorbed MW energy relative to 1 g of removed water as a function of the microwave input and MD concentration.

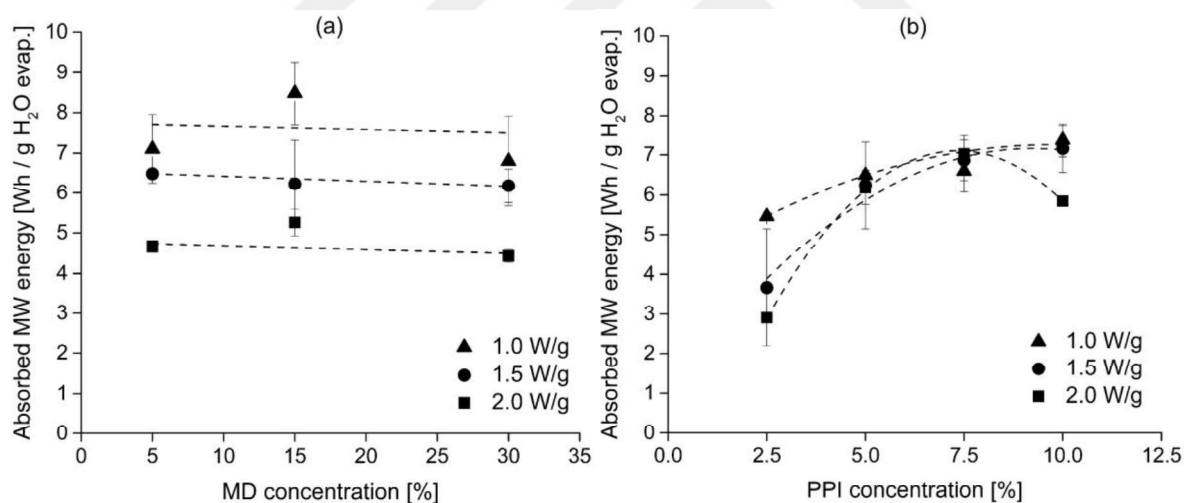


Fig. 3-24. Absorbed microwave energy at different microwave power inputs (1.0; 1.5; 2.0 W g⁻¹), 0.1 mbar chamber pressure and 30°C maximum product temperature (a) 5, 15, 30% (w/w) MD concentrations (b) 2.5, 5.0, 7.5, 10% (w/w) PPI concentrations.

Absorbed MW energy at 5%, 15% and 30% MD concentration at 1.0 W g⁻¹ power resulted approximately 4.9 Wh g⁻¹. Here, the MD concentration does not affect the absorbed MW energy. However, with increasing MW power, absorbed MW energy rises. For all MD concentrations, the absorbed MW energy was increased to 7 Wh g⁻¹ at 2.0 W g⁻¹. This can be mainly explained by the shortening of the drying time at higher MW levels, which, in these experiments, led to an increase in drying efficiency. The effect

of MW power on the absorbed MW energy of the foam samples with four different PPI concentrations is shown in Figure 3-24b. Regardless of the input power level, the absorbed MW energy increases as the PPI concentration is increased from 2.5% to 5%. A further increase in the PPI concentration did not result in a pronounced change in absorbed MW energy. At 2.5% PPI, absorbed MW energy was significantly reduced (from 5.5 to 3 Wh g⁻¹) with increasing input MW power from 1 W g⁻¹ to 2 W g⁻¹. At higher PPI concentrations, however, the level of MW power did affect the absorbed energy significantly. These values are also related to shorter drying times at lower protein concentrations.

3.4.4 Conclusion

Our results indicate that a moderate foam overrun is advantageous for efficient drying, providing a compromise between a high internal surface area and thin lamellae. The diffusion limitation which typically occurs in very dense structures, especially toward the end of drying, can thus be circumvented. From this perspective, it is important to find a favorable concentration for the foaming agent in order to achieve an open, porous, yet stable foam for the highest possible drying speed. The character of a foam also has another purpose beyond acceleration of drying. It also contributes to a novel fruit product structure with a crispy mouthfeel. However, since a dried raspberry fruit pulp foam is hygroscopic, a stable, crisp product for longer periods of shelf life can only be obtained if separated from the humid air environment. Otherwise, the dried foam would absorb moisture and become soft. Tightly sealed packaging would be required to preserve the product and maintain its crisp texture and related sensorial characteristics, including rapid induction of aroma and flavor release upon chewing. Drying speed was positively correlated with MD concentration, and hence with bubble size and bubble size distribution. MD concentration significantly influences temperature change during the drying process. Therefore, proper bubble size and bubble size distribution have to be found. In this study the foam was created using a bulk whipping device, but the impact of the type of shearing device (batch or continuous), the defined gas/liquid volume ratio chosen, and other related processing conditions have still to be studied. These aspects, together with an assessment of the sensorial effect of a foamed fruit pulp in comparison to a freeze-dried whole fruit, are part of investigations currently being conducted by the authors of this study. Overall, the creation of an appropriate foam provided faster drying with an open pore structure. The incorporation

of MW energy to the freeze-drying process improved efficiency and produced foam with the same characteristics as FD.

3.4.5 Acknowledgments

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3.5 Impact of dielectric properties on microwave drying process

The occurrence of hot/cold spots, which influences the product quality, was further investigated in terms of dielectric properties of the tested recipes. We observed that the occurrence of hot spots, especially at high microwave power levels, strongly depends on the formulations. Therefore, the effect of different concentrations of ingredients on the dielectric behavior was examined. For the measurement of dielectric properties, a dielectric measurement kit (*μWaveAnalyser*, Püschner Microwaves, Schwanewede, Germany) was used.

The open-ended coaxial cavity method described in Section 1.5.1 was used for determination of dielectric properties. Water was used as the reference, and raspberry puree was used as a blank sample. The foam recipes were chosen considering different drying behaviors of different foam formulations (Ozcelik et al., 2019b; Ozcelik et al., 2019a). The PPI concentration was fixed at 5% (w/w) while varying the concentrations of MD (5, 15, and 30%, w/w). The pectin concentration was kept constant at 2.5% (w/w). The raspberry puree, foaming agent, and stabilizers were mixed. Fig. 3-25 shows the dielectric properties of water and the raspberry puree.

The dielectric behavior of raspberry puree was similar to that of water, but it exhibited a lower dielectric constant and a higher dielectric loss factor. To understand the impact of each ingredient on raspberry puree, samples were prepared and measured under varying temperatures for their dielectric properties.

Fig 3-26 displays the dielectric properties of varying pectin, MD and protein concentrations as a function of temperature.

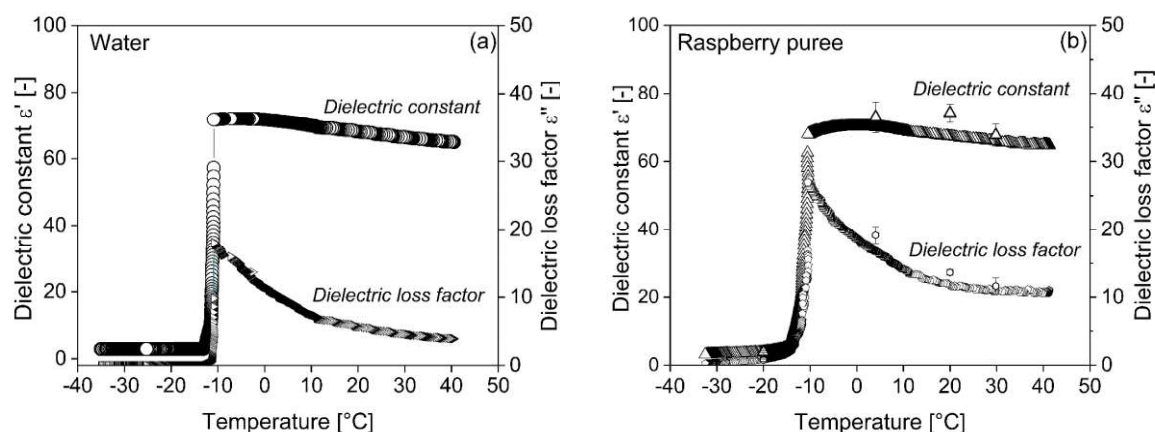


Fig. 3-25. Dielectric constant and loss factor of (a) water and (b) raspberry puree at varying temperatures.

Increasing protein concentration in the raspberry puree decreased the dielectric properties compared to pure raspberry puree. This might be because of the binding of free water by the reactive side chains of the protein. Even though PPI is highly soluble in water, at high concentrations, PPI exhibits protein–protein interactions and even covalent bonds between side chains that lead to a protein structure. The water enclosed in this structure is highly restricted in its movement, thereby lowering the dielectric properties (Schmidt et al., 2018a). However, a higher concentration of protein leads to the highest dielectric loss factor at the same temperature. This behavior might be because of the added ions in the protein. (Ahmed et al., 2008) reported similar behavior for soy protein isolate. Notably, higher dielectric loss factor than ice was achieved with higher protein concentrations. This agrees well with the abovementioned hypothesis of the drying behavior of protein foams discussed in Sections 3.2 and 3.3. Higher protein concentrations increase the dielectric loss factor; thus, more energy can be absorbed and is easily converted to heat. Gentle drying was therefore achieved at higher MW power inputs (Ozcelik et al., 2019b). The varying concentration of MD significantly influenced the dielectric constant rather than loss factor. This might be because of the binding of water to the hydroxyl groups of MD (Wang et al., 2011).

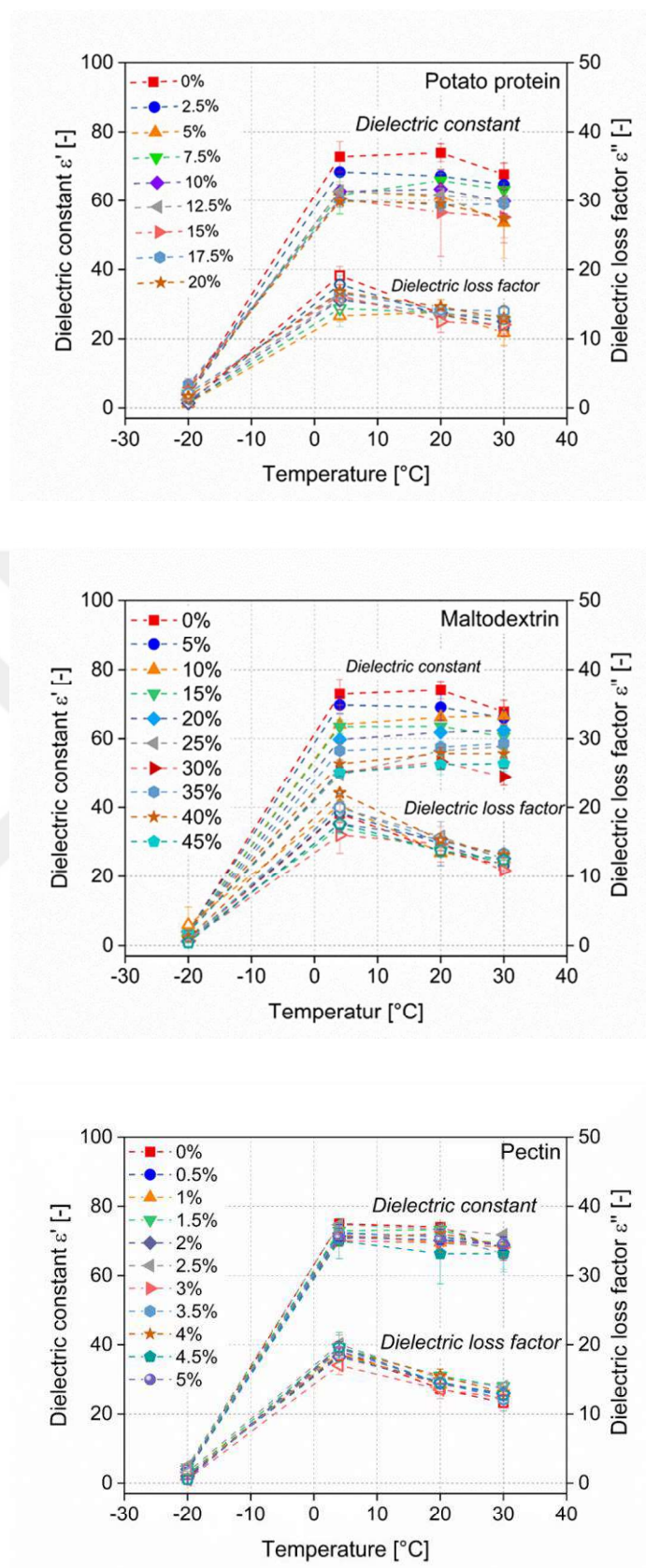


Fig. 3-26. Dielectric constant and loss factor of varying ingredient concentrations **(a)** potato protein isolate, **(b)** maltodextrin, and **(c)** pectin.

The higher dielectric constant means more energy could be stored within the material. Because of the higher stored energy that can easily be converted to heat because the dielectric loss factor of MD mixtures is higher than that of ice could have been a reason for higher drying rates (Fig. 3-26b). Varying pectin concentration did not have a significant impact on dielectric properties (Fig. 3-26c). (Venkatesh and Raghavan, 2005) reported that carbohydrates do not show appreciable dipole polarization at microwave frequencies.

Moreover, to better understand MWFD behavior of the tested foam compositions, samples were further examined compared to raspberry puree (without additives) with respect to dielectric properties. The related results are displayed in Fig. 3-27 and 3-28.

Fig. 3-27 depicts the dielectric constant of foams with varying MD concentrations in comparison with that of raspberry puree. Increasing MD concentration resulted in a lower dielectric constant. However, the dielectric loss factor of the tested foams was not significantly different.

The loss factor slightly increased with increasing PPI concentration (Fig. 3-28) which might be caused by the additional polar side chains in the protein in addition to dipolar rotation.

The binding of water to the hydroxyl groups of the carbohydrates is suspected to be the main cause of this phenomenon. Slight inhomogeneity of the sample could affect the dielectric properties of the material. Furthermore, during the drying process, the dielectric properties also vary depending on the moisture content and whether the water is in the free or bound state. The polar molecules of water in the free state react more freely than those of bound water.

However, the differences in drying behavior of the different recipes is defined by structural aspects rather than by the dielectric properties. Further research should be conducted on dielectric properties, and in particular, the loss factor should be examined in more detail during the drying process to help better understanding.

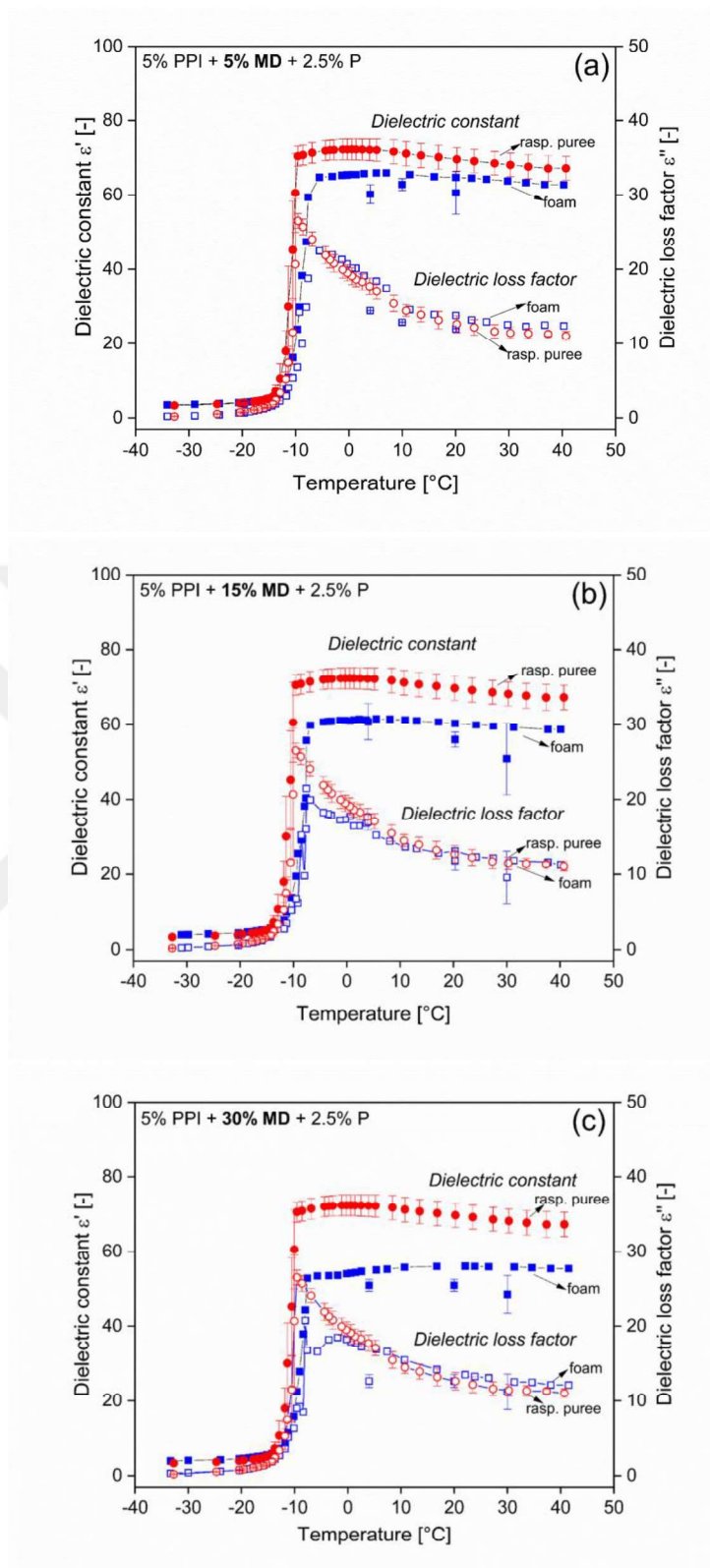


Fig. 3-27. Dielectric constant and loss factor of foams containing 5% (w/w) PPI + 2.5% (w/w) P with different MD concentrations.

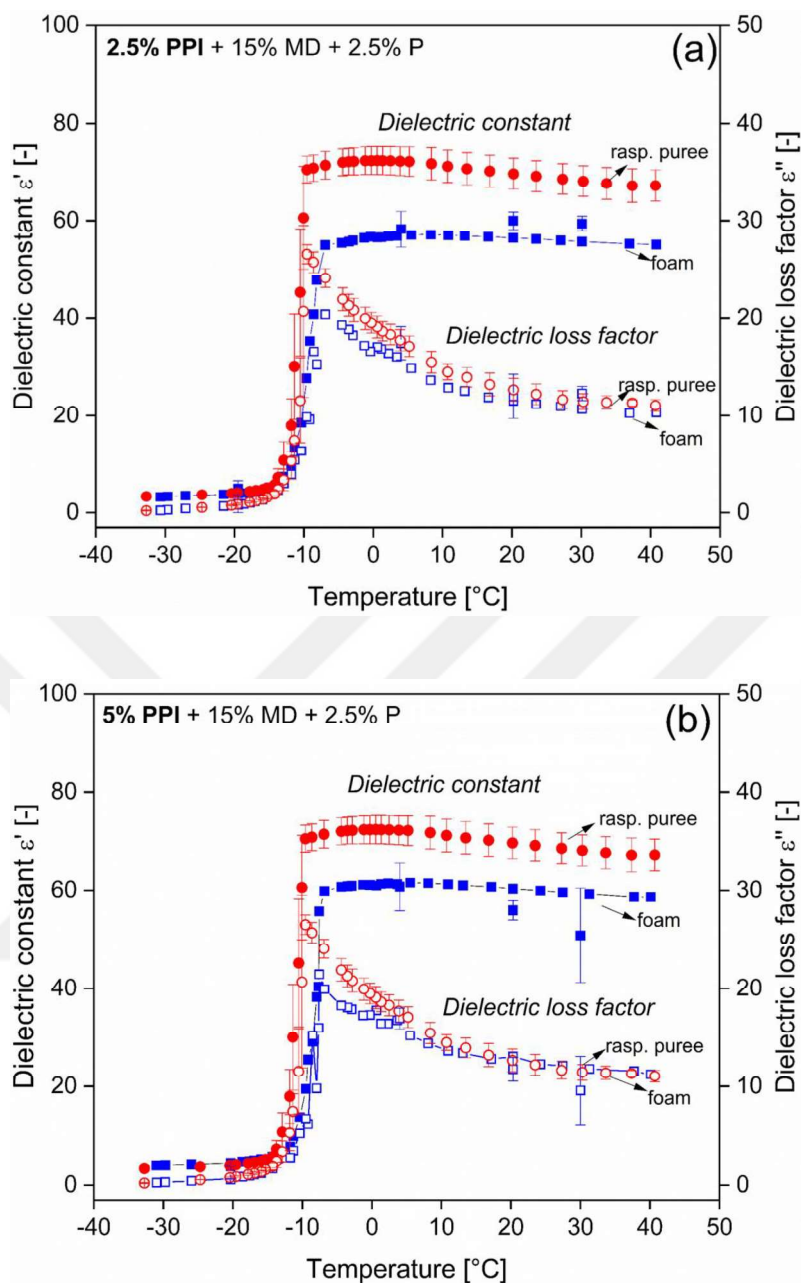


Fig. 3-28. Dielectric constant and loss factor of foams containing 15% (w/w) MD + 2.5% (w/w) P with different protein concentrations. **a)** 2.5% (w/w) PPI **b)** 5% (w/w) PPI.

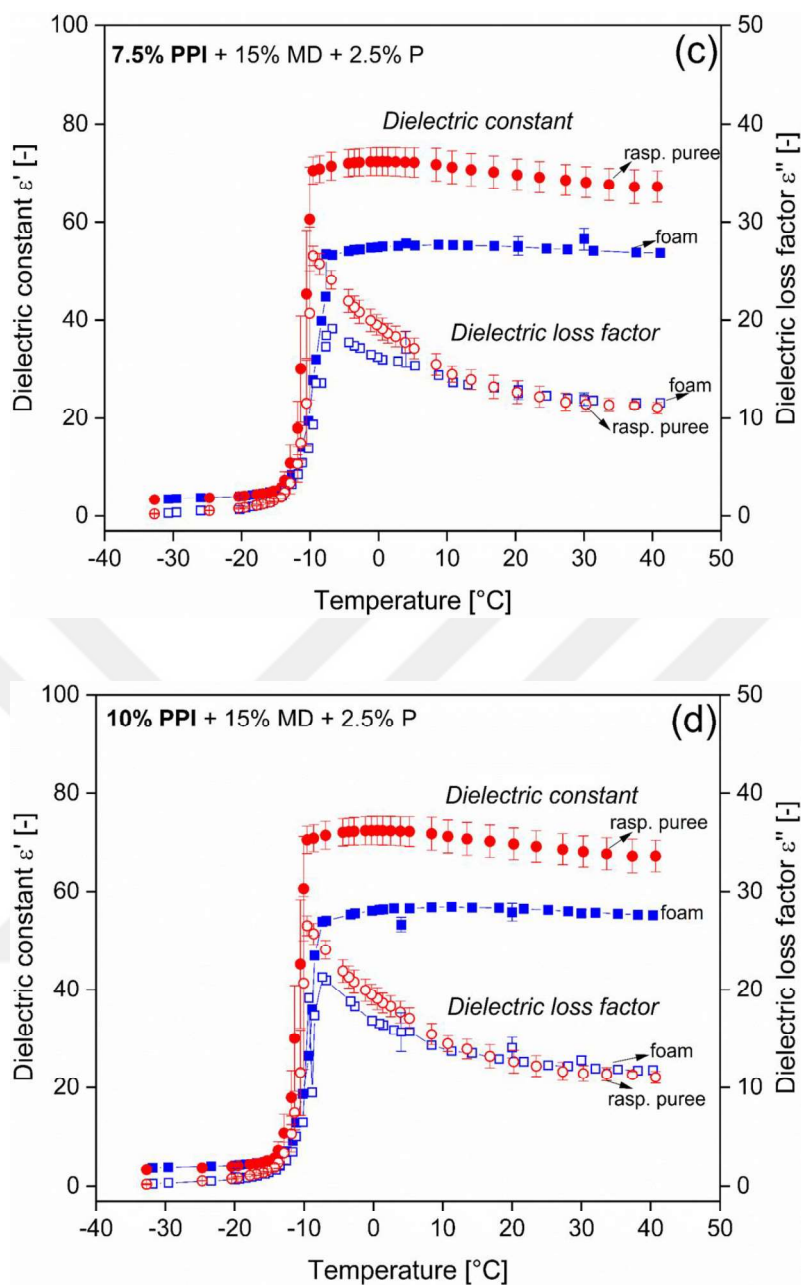


Fig. 3-28 (continued). Dielectric constant and loss factor of foams containing 15% (w/w) MD + 2.5% (w/w) P with different protein concentrations. **c)** 7.5% (w/w) PPI **d)** 10% (w/w) PPI.

3.6 Effect of hydrocolloid addition and microwave-assisted freeze drying on the characteristics of foamed raspberry puree

Summary and contribution of the doctoral candidate

The creation of a proper fruit foam provided fast drying with an open pore structure. Furthermore, the incorporation of MW energy to the freeze-drying process improved the efficiency of the drying process. The character of foam also has another purpose beyond acceleration of the drying process. It also promotes a novel fruit product structure with a crispy mouthfeel. Such dried foams can disintegrate very quickly upon contact with the saliva in the mouth, leading to a spontaneous release of flavor. Therefore, this study compares the characteristics of foamed raspberry puree dried via microwave-assisted freeze drying and conventional freeze drying.

To this end, we determined the factors that promoted the degradation of sensitive substances. The effect of potato protein concentration as a foaming agent, MD concentration as a foam stabilizer, and microwave power input on the retention of ascorbic acid (AA), anthocyanins (ACY), color, and structure was evaluated. The microwave-assisted freeze dried products were compared to products obtained by conventional freeze drying.

Results indicated that the raspberry puree yielded 20% higher AA and 18% higher anthocyanin content than the unprocessed fruit. The foaming step had no significant effect on the sensitive substances. Both drying methods resulted in 66%–81% retention of AA and 53%–84% retention of total ACY. High retention of sensitive substances was achieved owing to the oxygen-free, low temperature environment and high drying rates. Uniform heating with microwave drying is indispensable for gentle drying. Uniform drying was obtained at 1.0 W g^{-1} .

Scanning electron microscopy confirmed that identical products were obtained via microwave-assisted freeze drying compared with those obtained via conventional freeze drying. The application of microwave energy to the freeze-drying process intensely (8-fold) decreased the total drying time; thus, the energy demand was drastically minimized. The total energy consumption for evaporating 1 g of water was 2.1 kWh for microwave-assisted freeze drying and 6.2 kWh for conventional freeze drying. In contrast, no linear correlation was observed between microwave power input and energy demand for the microwave system alone.

Overall, it could be concluded that microwave-assisted freeze drying, as an energy-efficient method, can be used for producing snack foods while preserving the nutritional content, textural quality, and appealing colors of the product.

The most significant contribution to this manuscript was made by the doctoral candidate. This comprised designing the experiments, critically reviewing the literature, and performing data analysis and data interpretation including the statistical evaluation. In addition, the doctoral candidate wrote and revised the manuscript. Co-authors contributed to the experimental part or to the discussion of the results and provided input to the drafted publication prior to the submission.



Adapted original manuscript⁵

Effect of hydrocolloid addition and microwave-assisted freeze drying on the characteristics of foamed raspberry puree⁶

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Highlights

- Nutritional product obtained via microwave-freeze drying process was investigated.
- High drying rates enhanced the preservation of ascorbic acid and anthocyanins.
- Product identical to those of conventional freeze drying was obtained.
- Ascorbic acid content can be preserved by 80% via microwave-freeze drying.

Abstract

Foamed fruit purees can be dried and consumed as snacks. This study compares the characteristics of foamed raspberry puree dried via microwave-assisted freeze drying and conventional freeze drying. The effect of potato protein (PP) (as a foaming agent), maltodextrin (MD) (as a foam stabilizer), and microwave power on the product characteristics was investigated. The puree contained 18%–20% higher content of anthocyanins and ascorbic acid than unprocessed raspberries. The retention of ascorbic acid and anthocyanins increased with increasing concentrations of MD and PP. Both drying methods resulted in 66%–81% retention of ascorbic acid and 53%–84% retention of total anthocyanins. The higher drying rates obtained at higher maltodextrin concentrations resulted in higher ascorbic acid and anthocyanin retention. The total color difference was significantly higher for the foam with 30% MD (w/w) at 2.0 W g⁻¹, accounting for the formation of hot spots. Protein concentration did not have a considerable effect on product color. Increasing the maltodextrin concentration yielded a harder foam structure, while increasing the protein concentration had the opposite effect. Overall,

⁵Adaptions refer to formatting issues: e.g., numbering of sections, figures, tables and equations, abbreviations, manufacturer specifications, axis labeling, figure captions and style of citation.

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microwave-assisted freeze drying was found to be a promising alternative to conventional freeze drying, as it offers a more efficient drying process with comparable product quality.



3.6.1 Introduction

Snack foods have become widespread, sought-after grocery items. This rise in popularity is mainly because snack food products meet the convenience demands of people who have a busy lifestyle. Snack food products are expected to have a crispy texture, making them attractive to consumers; at the same time, products with healthful characteristics are also in demand. These requirements could be fulfilled by dried fruit foams. These products have high nutritional value and are rich in bioactive compounds such as dietary fibers, vitamins, minerals, and phytochemicals (e.g., anthocyanins). In addition, dried fruit foam emits a strong aroma, which is appealing to consumers, due to its highly porous structure. Raspberries are very popular, as they have beneficial effects on health, an attractive color, and a unique flavor (Kähkönen et al., 2001; Lee et al., 2012).

Most fruits and vegetables are seasonal and perishable and thus are not available in the market year-round. Raspberries are extremely perishable, as they have a highly sensitive skin and a soft texture. To extend their shelf life and reduce food waste, raspberries are commonly processed to make juice, jam, or jelly or they are frozen or dehydrated. Dehydration is a commonly used method for preserving fruit. However, retention of its nutritional value requires particular attention and special conditions during processing by dehydration. Convective drying (CD) and freeze drying (FD) are the two most commonly used drying methods in the food industry. FD is known to be the most popular drying method for obtaining products of high quality (Megías-Pérez et al., 2014). However, both methods have their drawbacks. CD takes place in an oxygen-rich, high-temperature environment and generally requires long drying times. Therefore, CD causes the loss of volatile compounds, substantially degrading product quality (Wojdyło et al., 2009; Yongsawatdigul and Gunasekaran, 1996). Conventional FD, involving the sublimation of a frozen product, requires very long drying times because heat conductivity is impeded at the low pressures required in this process. The resulting low throughputs makes this drying method very expensive (Ambros et al., 2018; Ratti, 2001; Zhang et al., 2006).

Microwave-assisted freeze drying (MWFD) lacks the major drawbacks of the CD and FD methods and provides a compromise between these methods by accelerating the process while creating an oxygen-free, low-temperature, “benign” drying environment.

In this respect, the MWFD method provides for fast drying while producing tasty food products of quality comparable to that achieved by FD. Microwaves penetrate deep into foods via electromagnetic radiation, ensuring overall heating of large parts of the product, known as “volumetric heating.” This result is in stark contrast to conventional FD, in which sublimation occurs only on the thin sublimation surface, not throughout the entire volume of the product (Ozcelik and Püschner, 2017). During the processing of raspberry puree into a foam, the drying rates are increased considerably by the addition of microwave (MW) energy to the FD process (Ozcelik et al., 2019a). MWFD drying is likely to yield products of quality equivalent to or even better than those obtained via conventional FD (Ambros et al., 2018).

However, once a foam is created by whipping it must remain stable during drying to maintain its structure. Therefore, unstable products must be supported by foaming and stabilizing agents. Potato protein can be used as a foaming agent, and maltodextrin can be used to increase viscosity and stabilize the foam (Ozcelik et al., 2019a). The use of proper foaming agents at optimal concentrations is very important to obtaining a stable foam throughout the drying process.

Color and texture are important organoleptic food properties that directly affect consumer perceptions of product quality. Anthocyanins are natural, water-soluble phenolic/flavonoid substances present in raspberries. The glycosides of anthocyanidins produce a red color under acidic conditions (Khoo et al., 2017; Rababah et al., 2005). The most abundant anthocyanins in raspberries, in a descending order by weight, are cyanidin-3-sophorosid, cyanidin-3-glucoside, and cyanidin-3-rutinoside (Michalczyk et al., 2009). Raspberries also contain ascorbic acid (AA), an important antioxidant with a wide variety of health-promoting properties (Cetojević-Simin et al., 2015; Martí et al., 2018).

Inappropriate use of foaming agents or disproportionate amounts of foaming agents results in a soft texture with collapsed bubbles in the end product (Thuwapanichayanan et al., 2012). Of the textural properties, crispness/hardness is one of the most desirable features of snack products. Because subjective interpretation of textural characteristics is inconsistent, standardized mechanical tests are used to evaluate product texture quantitatively (Jakubczyk et al., 2017; Jeltema et al., 2016).

Foam mat drying of several fruits is reported to yield a high quality product (Falade et al., 2003; Rajkumar et al., 2007). Conventional drying methods have been applied to seabuckthorn berry (Kaushal et al., 2013), Tommy Atkins mango (Lobo et al., 2017), jacon juice (Franco et al., 2015), muskmelon (Sangamithra et al., 2015a), jambolan (de Carvalho et al., 2017), cherry (Abbasi and Azizpour, 2016), beetroot (Ng and Sulaiman, 2018), star fruit (Karim and Wai, 1999), and lime fruit (Dehghannya et al., 2018b). In addition, supplemental microwave energy has been used in the drying of guava pulp, blue honeysuckle, and black currant (Qadri and Srivastava, 2015; Sun et al., 2012; Zheng et al., 2011). Furthermore, (Darniadi et al., 2017) observed that foam mat FD of blueberry juice was suitable for retaining most of the characteristics of the original juice.

The number of studies comparing the quality of foamed fruits prepared by MWFD and conventional FD is very limited. To the best of the authors' knowledge, no work has been reported in the literature on the product characteristics of foamed raspberry puree dried with microwaves. The hypothesis of this work is as follows: (1) Puree production under atmospheric conditions oxidizes AA and anthocyanins as a result of cell destruction; (2) The quality of the foamed fruit puree (end product) obtained by MWFD will be better or at least comparable to that of FD because the amount of thermal stress induced by these two drying methods is equivalent. We believe that MWFD can provide high quality food products (e.g., raspberry foam) using an oxygen-free, low-temperature drying environment with high drying rates.

This study aims to investigate the product characteristics of raspberry foams. To this end, we determined which factors promoted the degradation of sensitive substances. We further evaluated the effect of PP concentration as a foaming agent, maltodextrin (MD) as a foam stabilizer, and MW power input on the retention of AA, anthocyanins, color, and structure. The MWFD products were compared to products obtained by conventional FD.

3.6.2 Materials and methods

3.6.2.1 Raspberry puree and foam preparation

Frozen Willamette cultivar raspberries from Serbia were supplied by Mainfrucht (Gochsheim, Germany). Preliminary tests determined that characteristics causing variations in the final product included degree of ripeness, growth conditions, climate, and size of berries. To eliminate bias caused by such variations, 50 kg of frozen raspberries were crushed in the frozen state, and raspberry splits were thoroughly mixed. Frozen raspberries were thawed at room temperature and seedless raspberry puree was produced using a food mill (GEFU GmbH, Eslohe, Germany) with perforated disks having mesh sizes of 3, 2 and 1 mm. This puree was used as the raw material for producing raspberry foam. The potato protease inhibitor Solanin300 (PP) (Veendam, Netherlands) was used as a foaming agent. Maltodextrin (DE 6) (MD) (Nutricia, Erlangen, Germany) and highly esterified citrus pectin (P) (degree of esterification 68%–76%) (Herbstreith & Fox, Neuenbürg/Württ, Germany) were used as foam stabilizer. The mixture containing defined concentrations of PP, MD and P were referred to as “non-foamed”. The foam recipes were chosen with consideration of the drying behavior of different foam formulations reported by Ozcelik et al. (2019a). The MD concentration was fixed at 15% (w/w) while testing various PP concentrations (2.5, 5, 7.5, and 10%, w/w). A range of MD concentrations (5, 15, 30%, w/w) then was tested while keeping the PP concentration constant at 5% (w/w). The pectin concentration was kept constant at 2.5% (w/w) in all recipes. The raspberry puree, foaming agent, and stabilizers were mixed before whipping. To completely hydrate the powders in the raspberry puree, the mixture was stirred gently for 30 min at room temperature. After cooling for 24 h at 4°C, the mixture was whipped using a commercial planetary mixer equipped with a wire whisk geometry (KitchenAid Artisan 5KSM150, St. Joseph, Michigan, USA) at a maximum speed of 220 rpm for 10 min at 20°C. At the end of whipping, the entire liquid volume was incorporated into the foams and was referred to as “foamed.” To evaluate the influence of drying conditions on product quality parameters, each sample was analyzed before and after drying. Samples were not stored prior to the analysis to avoid the storage effect. The schematic diagram of experimental method is presented in Fig. 3-29.

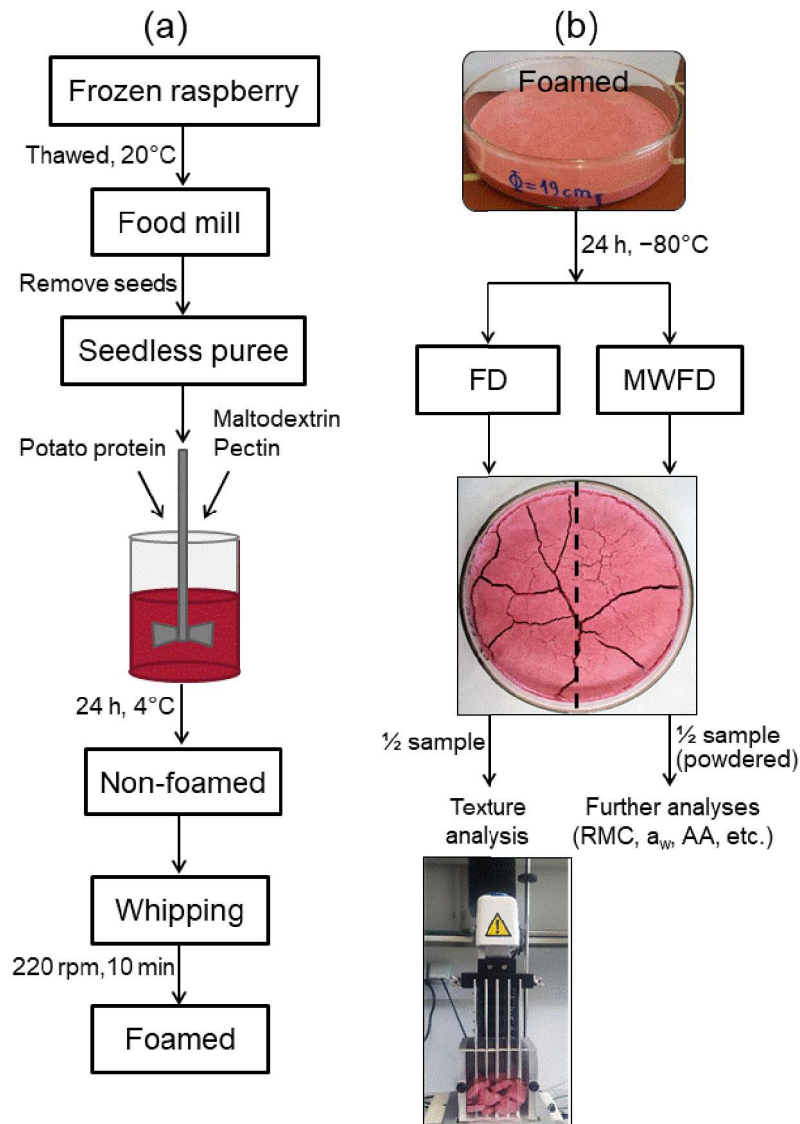


Fig. 3-29. Schematic of the experimental method: **(a)** foam preparation, **(b)** foam drying.

3.6.2.2 Foam density

The density of the foam was measured using a graduated cylinder having a volume of 100 cm^3 . The cylinder was filled to the top level with foam, its top surface was smoothed with a spatula, and the mass measurement was taken. The density of the raspberry foam was calculated using the following equation:

$$\text{Foam density} = \frac{\text{Foam Mass}}{\text{Foam volume}} \left[\frac{\text{g}}{\text{cm}^3} \right] \quad (3-9)$$

3.6.2.3 Drying equipment

3.6.2.3.1 Freeze drying

FD experiments were conducted to establish a reference for the study. Accordingly, all samples were freeze dried, and the results were compared to those obtained from the samples subjected to MWFD. The FD process was carried out in a pilot-scale freeze dryer (Christ Gamma 1-20, Osterode, Germany). The samples were heated via conductive heating on the shelves and dried at a chamber pressure of 0.1 mbar, an ice condenser temperature of -50°C , and a shelf temperature of 30°C . From preliminary trials, the total drying time was obtained for each sample by trial and error method. When the desired residual moisture content was obtained, the drying process was terminated.

3.6.2.3.2 Microwave freeze drying

MWFD experiments were performed in a pilot-scale microwave freeze dryer (Model $\mu\text{Vac0150fd}$, Püschner Microwaves, Schwanewede, Germany). The drying kinetics and the residual water content of the samples can be determined continuously by means of a balance with a maximum load of 5 kg and a precision of 0.1 g. The balance connected to the turntable was used for online monitoring of the sample. The $\mu\text{Wave-CAT}$ software of the dryer allowed the set-ting, recording, and monitoring of the desired temperature and pressure profiles to achieve precise control of the overall drying process. The drying variables, including pressure, product sur-face temperature, product weight, drying rate, and absorbed and reflected MW energies, were recorded at 1 s intervals. Details of the process are given in Ozcelik et al. (2019a). The condenser temperature was kept at -50°C . By pulsing the microwave power, the product surface temperature was limited to a maximum of 30°C . As soon as the surface temperature reached 30°C , the microwave input was set to the pulsed heating mode, with MW power set to 1.0, 1.5, and 2.0 W g^{-1} . For comparison purposes, the chamber pressure and the maximum product temperature were set to match those used in FD at 0.1 mbar and 30°C , respectively.

For both FD and MWFD, foam samples weighing 100 g were placed into 190-mm diameter glass dishes. Each sample was spread over the bottom surface of the dish, forming a smooth layer, and frozen at -80°C for 24 h before drying. The size of the

sample did not significantly change after the FD and MWFD processes. The thickness of the foams varied between 0.92–1.15 cm at varying MD concentration and 0.58–1.44 cm at varying PP concentration (Ozcelik et al., 2019a). It is important to reduce the residual moisture content below 5% which prevents microbial spoilage and deleterious enzymatic reactions in dried products. It was possible to reduce the residual moisture content down to 3% (w.b.) for the tested samples. Therefore, a target residual water content of $3.5 \pm 1\%$ (w.b.) was sought in all drying experiments as the criterion for termination of the drying process. All samples were evaluated for their residual water content and water activity immediately after the drying processes was terminated.

3.6.2.4 Moisture content

The initial moisture content of all samples was measured gravimetrically using Smart Turbo 6 (CEM, Germany). Dried samples were ground using a mortar and pestle. The residual moisture content of the samples was measured by Karl–Fischer titration (Schott, Mainz, Germany) according to the method described by Ozcelik et al. (2019a).

3.6.2.5 Water activity

The water activity of dried sample powder (approx. 2.5 g) was measured using a water activity meter AW Sprint (Novasina, Lachen, Switzerland) with a sensitivity of 0.001 a_w values were recorded at 25°C after reaching an equilibrium.

3.6.2.6 Determination of ascorbic acid content

The content of AA was determined chromatographically using the RP-HPLC Agilent 1100 series chromatograph (Agilent Technologies, Santa Clara, CA, USA) equipped with a binary pump, an auto sampler, and a VW detector. AA was isolated using a Zorbax 300 SB-C18 column (Agilent Technologies). The analysis was performed as described by Chebrolu, Jayaprakasha, Yoo, Jifon, & Patil (2012), with slight modifications. Samples were mixed using the Ultra-Turrax T 25 (IKA Werke, Staufen, Germany) with meta phosphoric acid (3% solution) (Sigma-Aldrich Chemie, Steinheim, Germany). The samples then were shaken at room temperature for 30 min at 1000 rpm using the Multi Reax shaker (Heidolph Instruments, Schwabach, Germany), followed by centrifugation for 10 min at $6000 \times g$ (Multifuge 1S-R, Heraeus, Hanau, Germany). The supernatants were passed through syringe filters (VWR International, Darmstadt,

Germany) for the determination of free AA. The reduction of dehydroascorbic acid (DHA) to AA was achieved by the addition of TCEP (tris[2-carboxyethyl]phosphine, 5 mM) (Sigma-Aldrich) to the filtrate. The detection of AA was carried out at 243 nm. Chromatograms were evaluated using the OpenLAB CDS ChemStation software (Agilent Technologies). The method is described in more detail elsewhere Dachmann et al. (2018).

3.6.2.7 Determination of anthocyanin content

Cyanidin-3-sophoroside, cyanidine-3-rutinoside, and cyanidine-3-glucoside were quantified as the representative raspberry anthocyanin using RP-HPLC. The sample was homogenized for 30 s using Ultra-Turrax T 25 (IKA Werke, Staufen, Germany), mixed with 1% HCl (Sigma-Aldrich Chemie), and shaken at room temperature for 180 min at 1000 rpm. After the solutions were centrifuged for 10 min at 6,000 × g (Multifuge 1S-R, Heraeus), the supernatant was passed through a syringe filter (VWR International, Darmstadt, Germany) and analyzed by RP-HPLC. Standard solutions of cyanidin 3-O- β -sophoroside (Polyphenols AS, Sandnes, Norway), cyanidin 3 O β -rutinoside (Polyphenols AS, Sandnes, Norway), and cyanidin 3 O glucoside chloride (Extrasynthese, Genay Cedex, France) were used for quantification. Anthocyanins were separated using a Phenomenex Luna C18(2) column (Phenomenex, Aschaffenburg, Germany). The anthocyanin peaks were detected at 520 nm, and chromatograms were evaluated using OpenLAB CDS ChemStation (Agilent Technologies) software. The method is described in more detail by Dachmann et al. (2018). To evaluate the influence of drying conditions on the retention of AA and ACY, each sample was analyzed before and after drying, and the amount of retention was calculated.

3.6.2.8 Color analysis

Before- and after-drying color evaluations were performed using a color analyzer SP68 (X-Rit, Regensburg, Germany), with the results reported in CIELAB color scales. The measurements were performed using a D 65 standard illuminant. According to the CIELAB color coding, the L^* value represents lightness of color from 0 (black) to 100 (white), the a^* value represents the degree of redness (0 to 60) or greenness (−60 to 0), and the b^* value represents the degree of yellowness (0 to 60) or blueness (−60 to 0) of the specimen. The total color difference ΔE was calculated as follows:

$$\Delta E = \sqrt{(L_0^* - L^{**})^2 + (a_0^* - a^*)^2 + (b_0^* - b^{**})^2} \quad (3-10)$$

where L_0^* , a_0^* and b_0^* are the color parameters of the reference sample and L^* , a^* and b^* are the color parameters of the tested sample. FD samples were used as references. Higher ΔE values indicate greater differences from the reference sample (Nsonzi and Ramaswamy, 1998).

3.6.2.9 Texture analysis

The texture of dried samples was analyzed using the TA.TXplus texture analyzer (Stable Micro Systems, Godalming, UK) equipped with a 50-kg load cell and the Kramer shear cell. The five-bladed Kramer shear cell (KSC) was chosen because it is suitable for analyzing multi-particle products. The analysis was performed such that the dried samples were subjected to a combination of compression, shearing, and extrusion. The Kramer shear cell (KSC), designed and first proposed by (Kramer and Twigg, 1960) was designed for multi-dimensional products representing a remarkably non-uniform configuration from piece to piece, such as, breakfast cereals, fruits, snack foods or filled pasta. The primary issue of using multi-dimension products is that they are usually of varying sizes or are of non-homogeneous nature. In order to obtain repeatable results from the tests performed with Kramer shear cell, it is important to take a certain number (or amount) of sample and perform a bulk compression and/or shearing test creating an averaging affect (Carvalho et al., 2017; Liu et al., 2019; Paula and Conti-Silva, 2014; Sánchez-Alonso et al., 2012). We calculated the density of the foam samples as they have varying concentrations. In order to obtain repeatable test results, we determined that filling approximately 50% of the load cell, especially for the samples that do not have a uniform shape, is very important. We tested samples of varying amounts (5, 10, 15 g) under the same test conditions. Each amount was tested with 3 replicates and each replicate of sample was measured 3 times, making a total of 9 measurements for each tested amount, for each recipe. The standard deviations in the data gathered from 3 replicates were determined to be low, showing that the data possess statistically acceptable confidence levels. We determined that a sample amount of 10 grams yields repeatable results. Height calibration was performed before the measurements, and the distance was set to 8.5 cm. The dried foam samples were

brittle and a half of dried foam was used for analysis. The dried samples cracked naturally because of the drying process. Samples were carefully broken into small pieces of similar dimensions (approximately $25 \times 35 \times 10$ mm) for determining their texture (Fig. 3-17b). For each test, 10 g of sample was placed in the cell, and the crosshead speed was adjusted to 2 mm s^{-1} . The force versus time data were obtained from the dedicated software *Exponent 32* (Stable Micro Systems) for the test equipment. The maximum peak force value is expressed in terms of “hardness” (N) of the sample.

3.6.2.10 Microstructure analysis

A field emission scanning electron microscope (FE-SEM) (Zeiss Sigma, Carl Zeiss Microscopy, Jena, Germany) was used to investigate the microstructure of the dried samples. The sample was coated with 10 nm of gold palladium and imaged using an SEM in high vacuum mode using a secondary electron detector. An accelerating voltage of 5 kV was used.

3.6.2.11 Statistical analysis

All experiments were conducted in triplicate, and all data are presented as the mean $\pm$ standard deviation. Analysis of variance (ANOVA) was performed on the collected data to evaluate differences between the samples. Differences were considered significant for $p < 0.05$. Statistical analysis of data was carried out using R software (Fox and Weisberg, 2011).

3.6.3 Results and discussion

3.6.3.1 Effect of foam manufacturing on ascorbic acid, anthocyanins, and color

3.6.3.1.1 Ascorbic acid and anthocyanins

AA and anthocyanins are principal indicators of the overall nutritional quality of a product. Both were quantified by HPLC. AA is known to be very sensitive to both heat and oxygen. Oxygen is the main factor that degrades AA into dehydroascorbic acid. We investigated the AA content after each step of processing to identify steps that had significant effects on the concentration of this nutrient (Fig. 3-30). We expected high

AA and anthocyanin content in the unprocessed raspberry fruits. Surprisingly, unprocessed raspberries had significantly lower AA and anthocyanin content than did raspberry puree (Fig. 3-30a, b).

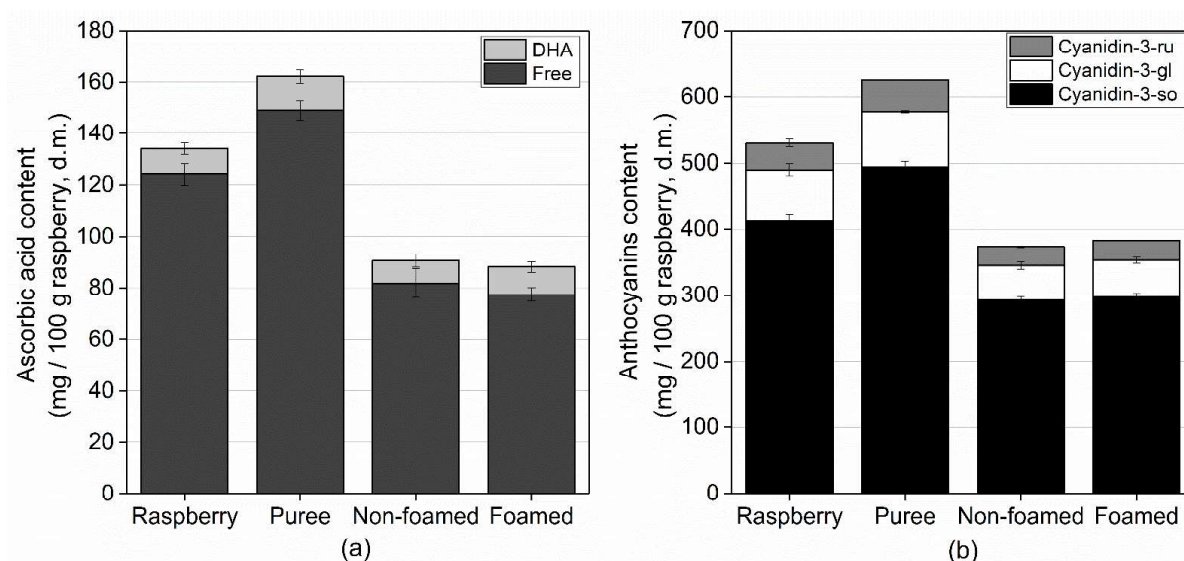


Fig. 3-30. Ascorbic acid and anthocyanin content of raspberry samples at progressive stages of processing. The samples are in the form of unprocessed raspberries, puree, non-foamed, and foamed. Non-foamed and foamed samples contain 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P.

Compared to the unprocessed fruit, raspberry puree had 20% higher AA and 18% higher anthocyanin content. We expected a decrease in these nutrients due to oxidation during processing. The production of puree requires disintegration of berry cells via mechanical crushing or straining through a sieve, which releases liquid and solutes from the berries. Anthocyanins are predominantly located in the skins. Their higher content in the puree than could be attributed to the disruption of cells and tissue, which releases molecules bound to cell walls. Additionally, straining of the crushed berries through the sieve also might have increased anthocyanin extraction by prolonged enzymatic activity (Weber and Larsen, 2017). Similarly, Tomas et al. (2015) reported a 28% increase in anthocyanins after pressing during black mulberry juice production.

The effect of the hydrocolloids PP and MD used for converting the raspberry puree into foam on the content of AA and anthocyanins was evaluated. Of the different recipes, the 15% (w/w) MD foam was chosen as an example. The AA and anthocyanin content of the mixture was analyzed before and after foaming to evaluate the influence of the foaming step (Fig. 3-30a, b). After the addition of hydrocolloids to the raspberry puree, the mixture was kept at 4°C for 24 h. During this step, the AA content decreased by

44% and the content of anthocyanins decreased by 40%. The decrease in the content of anthocyanins can be caused by the storage of sample.

In contrast, the foaming step does not have a significant effect on the AA and anthocyanins contents (Fig. 3-30a, b). This result further emphasizes that the effects of oxygen are dependent on time and temperature. The foam was prepared at room temperature (20°C) in a short time (10 min). Our results show that the exposure time to oxygen is of great importance to the extent of AA and anthocyanin degradation.

3.6.3.1.2 Color

Color data were determined in raspberry samples ranging from fresh fruit to wet foams (Fig. 3-31). All color parameters were significantly higher in processed forms than in raspberries, with raspberry puree yielding the deeper red color. The least significant difference was observed in the L^* value (lightness) of the puree. A higher a^* value (tending toward red rather than green) of the puree is mainly due to the higher anthocyanin concentration, which is responsible for the red color.

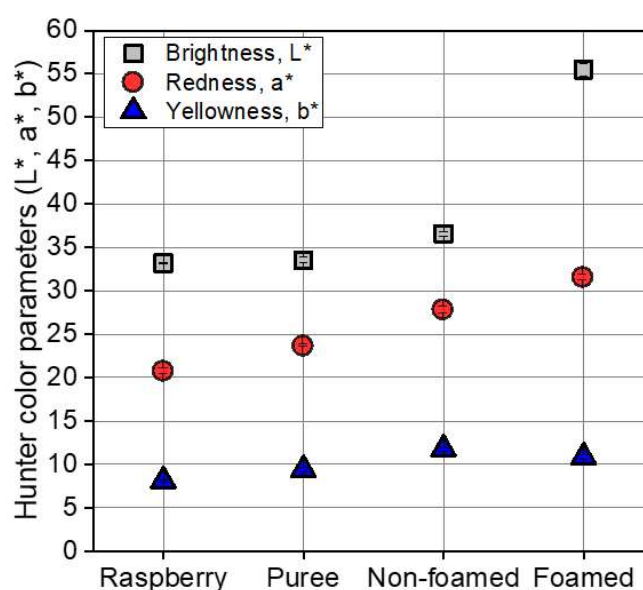


Fig. 3-31. Hunter color parameters for a range of raspberry samples having different form. The fresh samples are in the form of raspberry, puree, non-foamed, and foamed. Non-foamed and foamed samples contain 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P.

The addition of hydrocolloids increased all color parameters compared to the puree, as expected. The foaming process significantly increased the L^* and a^* parameters, while the b^* value (degree of yellow) decreased compared to that of the non-foamed

sample. Air bubbles trapped in the foam structure during the whipping process are likely to be responsible for the brighter color and higher L^* values.

3.6.3.2 Effect of drying on the retention of ascorbic acid, anthocyanins, and color

3.6.3.2.1 Retention of ascorbic acid and anthocyanins

To evaluate the quality of the product, we focused on the uniformity of drying. In our previous study, we reported that MD and PP strongly correlated with drying speed and MW power, respectively (Ozcelik et al., 2019a). The occurrence of hot/cold spots, which influences the product quality, was further investigated here. The water activity of all tested samples, with either drying method under varying MW power inputs, ranged from 0.073 to 0.227, values at which microbiological and structural deterioration is prevented. The effect of MD and PP concentrations and the MW power input on the retention of AA and anthocyanins is summarized in Fig. 3-32.

AA retention increases with higher concentrations of MD and PP. However, only 5% (w/w) MD and 2.5% (w/w) PP differed significantly ($p < 0.05$) from the other recipes using FD. Concerning the influence of on the retention of AA, the 30% (w/w) MD foam retained $81.3 \pm 0.9\%$ of the AA at 1.0 W g^{-1} using microwave radiation and $73.6 \pm 7.6\%$ using FD. This slightly higher retention of AA in 30% (w/w) MD foam results from the shorter drying times. Ozcelik et al. (2019a) reported that foam samples containing 30% (w/w) MD dried faster in MWFD due to the higher porosity of the foam. Moreover, when the product temperature reached 0°C , the drying was nearly complete. Sublimation was dominant throughout the drying process. On the other hand, the maximum product temperature approached the set temperature of 30°C toward the end of the drying process. The slight decrease in the AA content might have occurred at the end of the drying process. These authors reported the retention of AA in 10% (w/w) PP foam as $77.6 \pm 1.1\%$; most of the water was removed below 0°C (Ozcelik et al., 2019a).

Gómez Ruiz et al. (2018) reported that the degradation reaction increased at high temperature and the effect of oxygen was temperature dependent. Temperatures of 50°C – 60°C and an increase in partial pressure showed no effect on AA degradation. However, a significant effect was found at higher temperatures (70°C – 90°C), increasing the degradation of AA. These findings suggest that the low-temperature

(30°C), oxygen-free environment (0.1 mbar) and short drying times offered by MW-assisted FD helps to preserve the AA content.

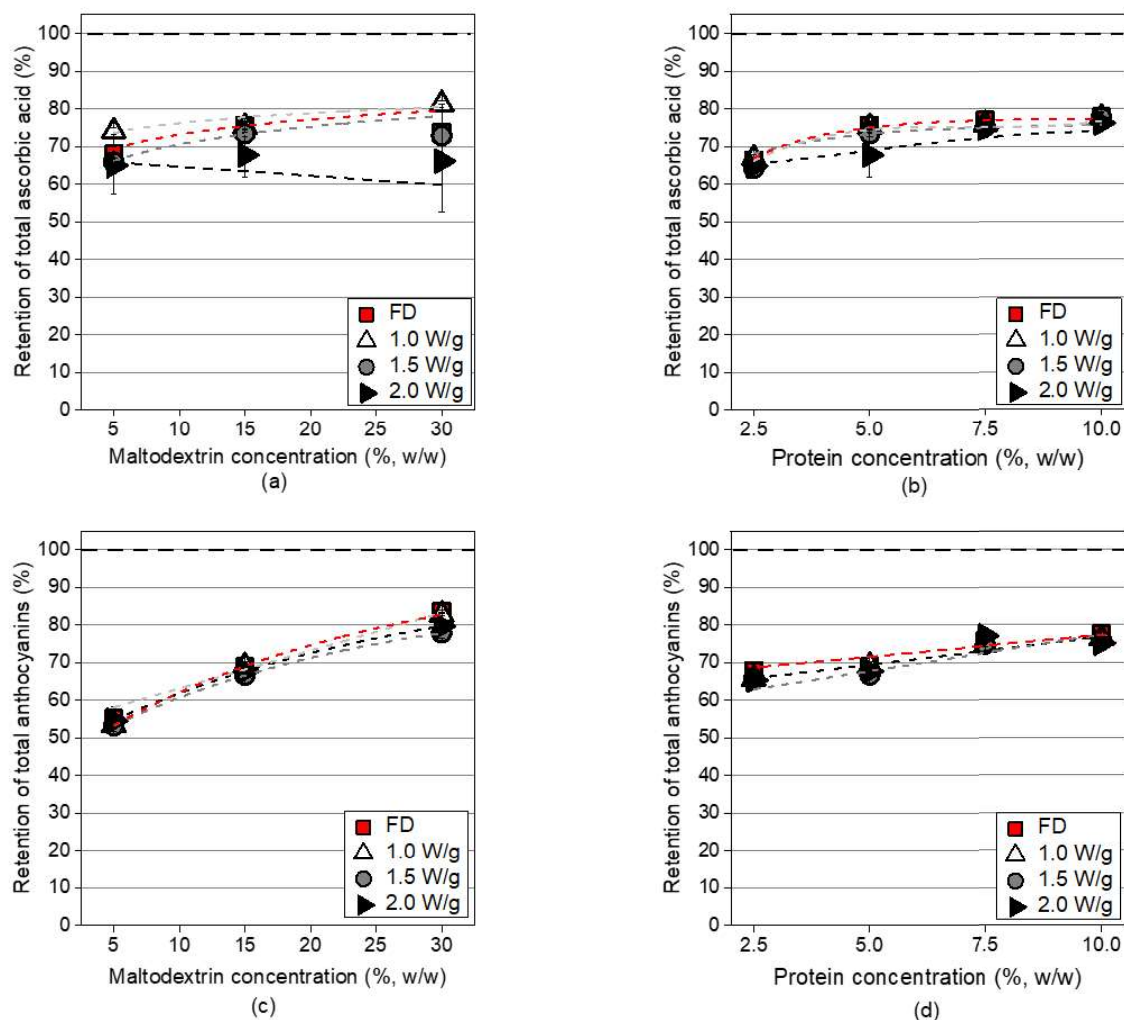


Fig. 3-32. Comparison of % retention of ascorbic acid (AA) and total anthocyanin content (ACY) (Cyanidin-3-sophoroside + Cyanidin-3-glucoside + Cyanidin-3-rutinoside) according to foaming agent (PP, potato protein) and foam stabilizer (MD, maltodextrin) concentrations at different MW power levels with FD. All samples were subjected to drying at 0.1 mbar chamber pressure and 30°C maximum product temperature. **(a)** % retention of AA versus MD concentration of foam [5% (w/w) PP + 2.5% (w/w) P] at different MW power levels, **(b)** % retention of AA versus PP concentration of foam [15% (w/w) MD + 2.5% (w/w) P] at different MW power levels, **(c)** % retention of ACY versus MD concentration of foam [5% (w/w) PP + 2.5% (w/w) P] at different MW power levels, and **(d)** % retention of ACY versus PP concentration of foam [15% (w/w) MD + 2.5% (w/w) P] at different MW power levels.

However, it is important to note that the faster drying at higher MW input power did not result in high retention because of hot spots. The 30% (w/w) MD foam retained $66.1 \pm$

13.4%, with a drying time of 183 min at 2.0 W g^{-1} and 218 min at 1.0 W g^{-1} . The higher standard deviations in the data, especially at higher MD concentrations, probably indicate the occurrence of hot spots.

The formation of ice is of great importance in MWFD, with the dielectric behavior of a material affecting its heating characteristics. The dielectric loss factor describes energy conversion to heat (Sosa-Morales et al., 2010; Tulasidas et al., 2016). While solid water (ice) has a low dielectric loss factor and is almost transparent to microwaves, the dielectric loss factor of liquid water is very high. The chemical composition of a substance also affects its dielectric properties. In this regard, ice crystals in some regions of a sample will sublime quickly, but a dense structure entraps water vapor, leading to melting in the surrounding regions. As a result, more MW energy is absorbed by the product, causing further melting. Such non-uniformity was not observed using an IR-probe, which only measures the product surface temperature. For a given relatively high electromagnetic field intensity (2.0 W g^{-1}), a dramatic increase in dielectric loss with temperature results in a thermal runaway phenomenon in which certain areas of a sample are overheated while other areas remain frozen. Comparison of the 30% (w/w) MD foam dried at different MW powers is shown in Fig. 3-33.

Uniform drying achieved at 1.0 W g^{-1} is shown in Fig. 3-33a, b, and c, while the occurrence of hot spots at 2.0 W g^{-1} are shown in Fig. 3-33d, e, and f. A small region of hot spots taken from a 30% (w/w) MD foam sample dried at 2.0 W g^{-1} was further examined for AA content, which was $48.7 \pm 1.3\%$. Increasing PP concentration did not significantly affect AA retention. The standard deviation of AA retention at increasing PP concentrations along with increasing MW power was negligible. This observation is attributed to the gentle drying that is achieved at higher PP concentrations. Uniform drying is very important for achieving higher retention. All tested recipes yielded the same or slightly higher retention of AA with MWFD at 1.0 W g^{-1} than with FD.

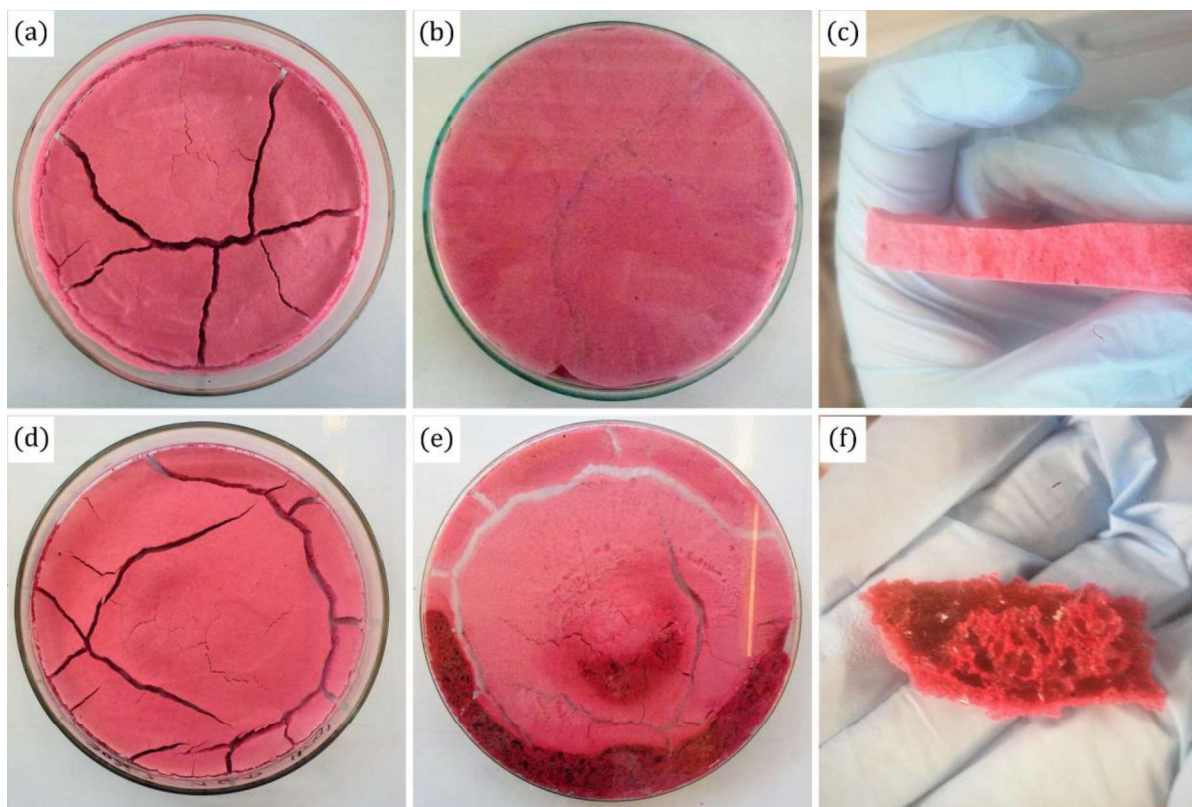


Fig. 3-33. Top and bottom views of the dried foams subjected to MWFD at 1.0 W g^{-1} (a, b and c) and 2.0 W g^{-1} (d, e and f) MW power levels. Both foam samples contained 5% (w/w) PP, 30% (w/w) MD, and 2.5% (w/w) P and were subjected to drying at 0.1 mbar chamber pressure and 30°C maximum product temperature. Images a, b and c depict uniformly-dried foam, revealing an even color distribution throughout the sample with an appealing texture. Images d, e, and f show a non-uniformly-dried foam, revealing an uneven color distribution with pronounced heterogeneity over the bottom surface of the sample. Note that the peripheral and central regions of the bottom surface show localized darker regions termed “hot spots.”

The retention of anthocyanins at varying MD and PP concentrations and MW power levels is shown in Fig. 3-32c and 3-32d. Anthocyanin retention increased significantly with increasing MD concentration ($p < 0.05$). This result suggests that MD stabilizes the anthocyanins because of the reduced water content. These results agree with a previous study by Ahmed et al. (2009), who reported that the MD-supplemented purple sweet potato flour had higher anthocyanin content than did flours without MD. The main reason for this higher anthocyanin retention is the shorter drying time (Abbasi and Azizpour, 2016). Anthocyanin retention increased with increasing PP concentration, although the retention with 7.5% and 10% (w/w) PP did not differ significantly. The MD concentration was 15% (w/w) for several PP recipes. Thus, high PP concentration may result in higher retention in the presence of some amount of MD in the mixture. Faster drying might also be responsible for this higher retention. The effect of MW

power input on anthocyanin retention is shown in Fig. 3-32c and 3-32d. No significant difference was observed between MW, at any of the power inputs tested, and FD.

Overall, no significant differences were observed between the MWFD and FD processes. This result is similar to the findings reported by (Xu et al., 2014) who observed no significant loss in total anthocyanin or vitamin C content after microwave treatment of red cabbage.

3.6.3.2.2 Color

The effect of different concentrations of ingredients and MW power input on color parameters is summarized in Table 3-6. As expected, the L^* value increased with increasing ingredient concentrations. Because the MD, PP, and pectin have a white/yellowish color, their addition to the recipe lightens the color of the mixture by dilution of raspberry puree pigments. The a^* and b^* values decreased with increasing MD concentration. The 30% (w/w) MD foam was significantly brighter than the other samples ($p < 0.05$). Overall, these results show that MD has a greater effect than the other ingredients on all color parameters.

In addition to evaluating each color parameter individually, we calculated the total color difference (Eq. 3-10) using the FD data as a reference to better understand the effect of MWFD on the total product color. Fig. 3-34a and b depict the total color difference (ΔE) between foams with different MD and PP concentrations at different MW power levels. Of interest is whether the hydrocolloids change the color under the different drying conditions.

Tab. 3-6. Color parameters of raspberry foam according to recipe.

Raspberry foam recipes	L*					a*					b*				
	1.0 W g ⁻¹	1.5 W g ⁻¹	2.0 W g ⁻¹	2.0 W g ⁻¹	1.0 W g ⁻¹	1.0 W g ⁻¹	1.5 W g ⁻¹	1.5 W g ⁻¹	2.0 W g ⁻¹	2.0 W g ⁻¹	1.0 W g ⁻¹	1.0 W g ⁻¹	1.5 W g ⁻¹	1.5 W g ⁻¹	2.0 W g ⁻¹
5% PP + 5% MD + 2.5% P	58.5 ± 0.1 ^a ₁	57.2 ± 0.5 ^a ₂	56.6 ± 0.6 ^a ₂	31.9 ± 0.2 ^a ₁	31.0 ± 0.8 ^a ₁	31.0 ± 1.5 ^a ₁	6.0 ± 0.3 ^a ₁	6.4 ± 0.0 ^a ₁	7.0 ± 0.7 ^a ₁						
5% PP + 15% MD + 2.5% P	59.4 ± 0.7 ^a ₁	59.7 ± 0.2 ^b ₁	58.7 ± 1.7 ^a ₁	29.6 ± 0.5 ^b ₁	29.9 ± 0.3 ^a ₁	29.5 ± 0.4 ^{a,b} ₁									
5% PP + 30% MD + 2.5% P	64.0 ± 0.7 ^b ₁	63.6 ± 0.3 ^c ₁	62.2 ± 0.6 ^b ₂	28.1 ± 0.7 ^c ₁	28.1 ± 0.1 ^b ₁	27.8 ± 0.5 ^b ₁	3.5 ± 0.1 ^c ₁	3.5 ± 0.1 ^c ₁	4.4 ± 0.4 ^b ₂						
2.5% PP + 15% MD + 2.5% P	57.9 ± 0.5 ^a ₁	58.5 ± 0.4 ^d ₁	57.8 ± 0.4 ^a ₁	30.5 ± 0.7 ^{a,b} ₁	30.0 ± 0.1 ^a ₁	29.9 ± 0.3 ^a ₁	5.7 ± 0.1 ^{a,b} ₁	5.7 ± 0.1 ^d ₁	5.8 ± 0.1 ^{a,b} ₁						
5.0% PP + 15% MD + 2.5% P	59.4 ± 0.7 ^a ₁	59.7 ± 0.2 ^b ₁	58.7 ± 1.7 ^a ₁	29.6 ± 0.5 ^b ₁	29.9 ± 0.3 ^a ₁	29.5 ± 0.4 ^{a,b} ₁									
7.5% PP + 15% MD + 2.5% P	61.4 ± 0.9 ^c ₁	61.3 ± 0.5 ^e ₁	61.5 ± 0.4 ^b ₁	28.6 ± 0.4 ^{b,c} ₁	28.8 ± 0.3 ^b ₁	28.6 ± 0.3 ^b ₁	3.9 ± 0.2 ^c ₁	4.0 ± 0.1 ^e ₁	3.9 ± 0.1 ^b ₁						
10.0% PP + 15% MD + 2.5% P	62.5 ± 0.5 ^{b,c} ₁	63.0 ± 0.5 ^f ₁	62.3 ± 0.9 ^b ₁	27.7 ± 0.1 ^f ₁	27.8 ± 0.3 ^b ₁	27.9 ± 0.1 ^b ₁	3.2 ± 0.1 ^f ₁	3.2 ± 0.2 ^f ₁	3.3 ± 0.1 ^b ₁						

Data are presented as the mean ± standard deviation; n = 3. Different superscript letters in the same column indicate a significant difference (p<0.05) between recipes. Different subscript numerals in the same row within L*, a* and total color change indicate a significant difference (p<0.05) between MW power levels.

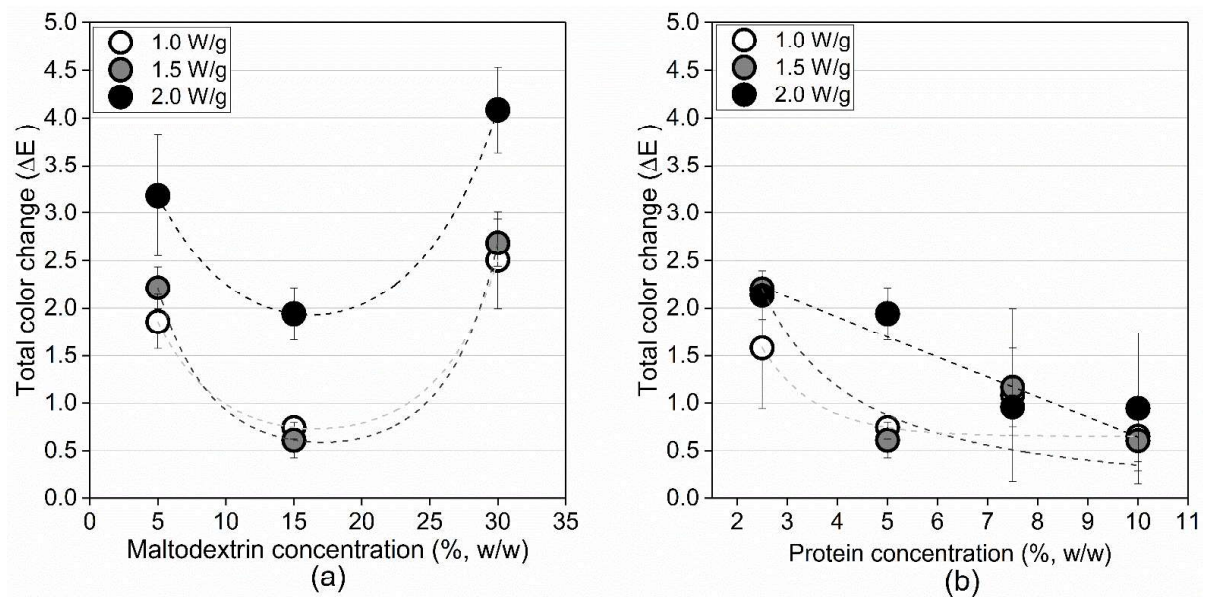


Fig. 3-34. Total color change with concentration of several ingredients in raspberry foam. All recipes contain 2.5% (w/w) P. The MD concentration varies, while PP concentration was kept at 5% (w/w); PP concentration varies while MD concentration was kept at 15% (w/w). FD samples were used as a reference for the total color difference. **(a)** varying MD concentration **(b)** Varying PP concentration.

The MW power level did not significantly affect the a^* value of the samples at the tested MD concentrations. The 30% (w/w) MD foam resulted in significantly higher b^* values at 2.0 W g⁻¹ than at the other MW power levels ($p < 0.05$). The total color difference of the tested MD foams was differed significantly between 2.0 W g⁻¹ and 1.0 W g⁻¹. Specifically, the significant differences were in the L^* and b^* values for the foam containing 30% (w/w) MD, which could be caused by the hot spots shown in Fig. 3-33d, e and f).

Contrary to the effect of MD on color parameters, varying PP concentration resulted in no significant difference between color parameters at all power inputs. Additionally, we observed a positive correlation between PP concentration and ΔE values. The results also show that uniform drying can be achieved at higher MW power levels at higher protein concentrations, supporting our previous observation that gentle drying can be achieved at high MW power input with high overrun (Ozcelik et al., 2019a). The color retention of all tested samples was identical between FD and MW at 1.0 W g⁻¹.

3.6.3.2.3 Structural properties

Texture

The textural characteristics of a dried foam depend on the amount of trapped air, the size of the air bubbles and the drying conditions. During whipping, an unknown amount of air trapped in the liquid is broken into small bubbles by the mechanical agitation (Sangamithra et al., 2015b). Foams that contain a high volume of air (low density) are expected to have a softer texture.

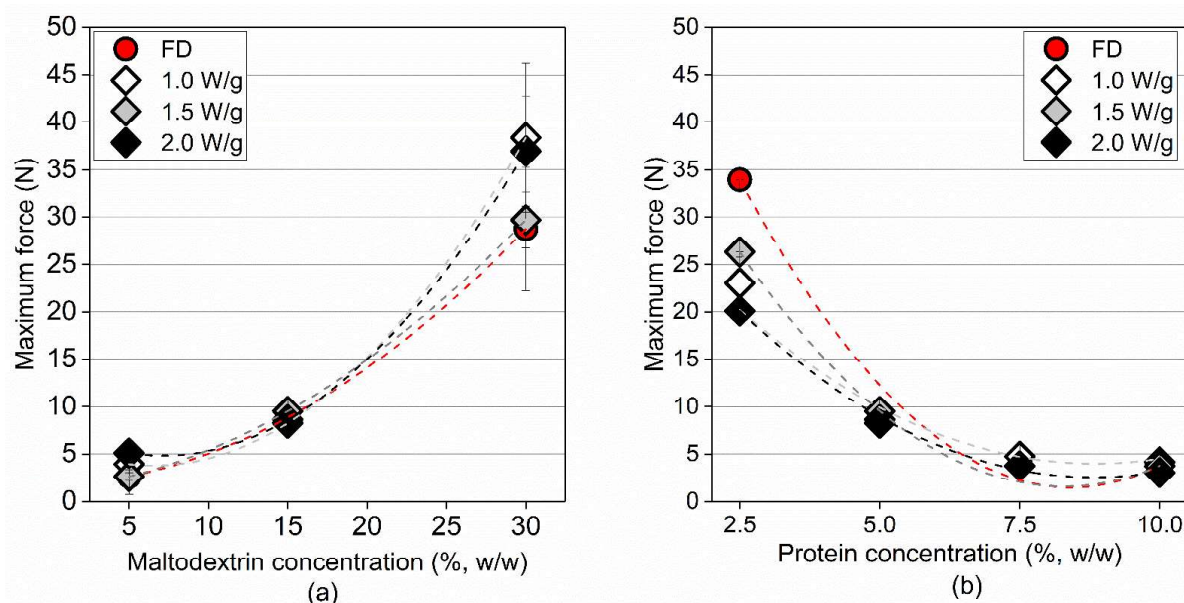


Fig. 3-35. Variation in the maximum force (as a measure of sample hardness) with concentrations of foaming agent (PP, potato protein) and foam stabilizer (MD, maltodextrin) at different MW power levels and FD. All samples were subjected to drying at 0.1 mbar chamber pressure and 30°C maximum product temperature. **(a)** Maximum force versus MD concentration of the foam [5% (w/w) PP + 2.5% (w/w) P] at different MW power levels and FD, **(b)** Maximum force versus PP concentration of the foam [15% (w/w) MD + 2.5% (w/w) P] at different MW power levels and FD.

The hardness of the foam was observed to increase with increasing MD concentrations (Fig. 3-35a). The densities of the different foams are shown in Table 3-7.

Tab. 3-7. Initial foam density of foam recipes containing 2.5% (w/w) pectin.

Tested foam recipes	Foam density (g cm ⁻³)
5% PP + 5% MD + 2.5% P	0.39 ± 0.01 ^a
5% PP + 15% MD + 2.5% P	0.38 ± 0.01 ^a
5% PP + 30% MD + 2.5% P	0.42 ± 0.00 ^b
2.5% PP + 15% MD + 2.5% P	0.63 ± 0.04 ^c
5.0% PP + 15% MD + 2.5% P	0.38 ± 0.01 ^a
7.5% PP + 15% MD + 2.5% P	0.30 ± 0.01 ^d
10.0% PP + 15% MD + 2.5% P	0.24 ± 0.01 ^e

Data are presented as the mean ± standard deviation; n = 3. Different superscript letters in the same column indicate a significant difference (p<0.05) between recipes.

While the densities of the 5% and 15% (w/w) MD foams did not differ significantly, the hardness of these foams differed. Likewise, the density of the 30% (w/w) foam was slightly higher than that of the foams with other MD concentrations, while the hardest foam was obtained with 30% (w/w) MD. This discrepancy between the density and hardness indicates that the bubble size and distribution (Ozcelik et al., 2019a) greatly affects the hardness of the samples, beyond the effect on the density. A small, uniform pore structure requires a higher force to shear and compress the foam, leading to harder foams (Sham et al., 2001). Additionally, due to the higher drying rates, most water was removed below 0°C in the foams with higher MD concentration. Thus, the tissue of the foams with higher MD concentrations was not damaged during drying. Accordingly, it can be argued that a harder sample can be obtained for a given density if a uniform bubble size and distribution can be maintained.

We observed that the density of the foam significantly decreased with increasing PP concentration (p < 0.05) (Fig. 3-22b). While the density of raspberry puree is 0.67 g cm⁻³, a higher foam density of 0.63 g cm⁻³ was obtained at 2.5% (w/w) PP concentration. A very dense structure resulted in foam collapse and hot spots at higher MW levels because the applied energy excessively heated some regions, causing the melting of ice crystals and expansion. The occurrence of structural collapse altered the hardness at different power inputs for the 2.5% (w/w) PP foam. Thus, the hardness decreased with increasing MW power input level. Increasing the PP concentration yielded softer foams, and the effect of MW power level was insignificant. The softest

foam was obtained at 10% (w/w) PP, which is also the foam with the lowest density (0.24 g cm^{-3}).

In general, the hot spots and collapsed foam cells, which occur specifically at higher MW input power levels, had higher standard deviations. However, the FD and MWFD samples did not differ significantly ($p > 0.05$).

SEM micrographs

The influence of foaming and drying on the sample structure was further examined with the aid of a field emission scanning electron microscope (FE-SEM). The FE-SEM images of several samples obtained at $250\times$ are depicted in Fig. 3-36.

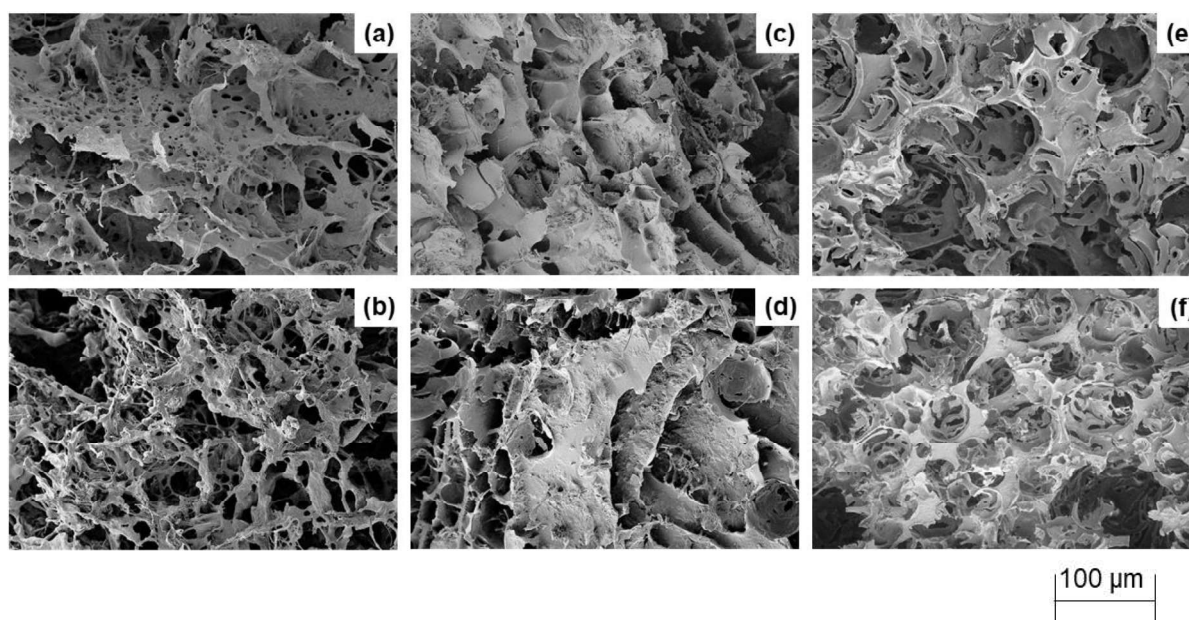


Fig. 3-36. Field emission scanning electron micrograph images of dried samples ($\times 250$). Raspberry puree (a) FD and (b) MWFD, non-foamed puree containing 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P (c) FD and (d) MWFD, foamed puree containing 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P (e) FD and (f) MWFD.

The raspberry purees had a higher number of small round pores distributed in a 3-dimensional network. The puree dried via MWFD had a more irregular network of pores than did that dried via FD. The microstructure of MWFD puree (Fig. 3-36b) was more amorphous, with fewer pores than puree samples dried via FD (Fig. 3-36a). The microstructures of the dried puree samples exhibited a compact texture regardless of the drying method. The non-foamed samples had a honeycomb network with a few round pores. The bubbles were most likely formed during the mixing of the puree with the

hydrocolloids. MWFD of the non-foamed sample resulted in a surface of fine particles, yielding a more rigid and compact structure.

The foams possessed a layered network of larger pores in a regular, repeating pattern (Fig. 3-36e and f). In foam drying, the resistance to mass transfer is lower, as the exposed surface area is proportionally greater in conjunction with the thin lamellae of the foam. This structure imposes considerably lower diffusion limitations; such that water can be removed more readily than in non-foamed structures. Due to the lower thermal conductivity of the air voids compared to liquid, heat transfer from the heated shelves to the sublimation front inside the product is very limited. With MWFD, the structure becomes more open during drying; thus, FD results in a more layered structure than does MWFD (Fig. 3-36e). In this context, the addition of microwaves to the FD process provides an additional benefit. Besides high diffusivity, microwaves directly generate heat inside the product. According to the SEM micrographs, bubbles break up during the drying process, especially in MWFD, so that the water can more readily escape from the product. The foam samples dried via MWFD (Fig. 3-36f) had a homogenous pore distribution with no collapsed cells or ruptured tissue. We determined that the foam samples maintained the air bubbles throughout the drying process, regardless of the drying method used.

3.6.4 Conclusion

We determined that obtaining a tasty snack food product with high nutritional value while mitigating the drawbacks of the FD process is possible. To achieve uniform heating and better process control, which are indispensable for gentle drying, temperature-controlled, pulsed MW is used in MWFD. High retention of AA and anthocyanins was achieved owing to the oxygen-free, low-temperature “benign” drying environment and high drying rates. Uniform drying was obtained at 1.0 W g^{-1} , and the drying time could still be shortened by as much as 70% with the aid of MW energy. Hence, the drying time for MWFD is almost 8-fold less than that of FD. Because of the shorter drying times and high efficiency, the total energy consumption of MWFD was 2.1 kWh per 1 g evaporated water at 1.0 W g^{-1} as compared to 6.2 kWh for FD. The MW applied system consumed 10% of the energy, while the remaining 90% was consumed by the pump and condenser. The energy demand decreased slightly because the drying time

was shorter with higher MW power, but we observed no linear correlation between MW power input and energy demand for the MW system alone.

The efficiency of the process could be increased even further by increasing the MW power in a stepwise manner to compensate for the moisture loss in successive stages of the drying process. This alteration might also help to keep the temperature more stable and eliminate the occurrence of hot/cold spots. The optimal storage condition for fruit foams remains a research topic for further investigation.

Microwave FD can be used as an energy-efficient method for producing snack foods while preserving their nutritional content, textural quality, and appealing colors of the product. We confirmed our hypothesis and showed that microwave FD outweighs its popular alternative—the FD method—in energy consumption and yields products of equivalent quality.

3.6.5 Acknowledgments

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3.7 Storage stability of dried raspberry foam as a snack product: effect of foam structure and microwave-assisted freeze drying on the stability of plant bioactives and ascorbic acid

Summary and contribution of the doctoral candidate

The shelf-life of a food product is an important criterion not only for consumers but also for the manufacturer. A stable food product is one that can retain acceptable quality from the safety and organoleptic perspective. Thus, there are three main elements that could affect the storage stability of the product: formulation, processing, and storage conditions.

So far, we have evaluated the formulation, processing, and process conditions of dried foamed raspberry puree. In this study, we aimed to investigate the storage behavior of raspberry fruit in different structural forms, namely foamed and non-foamed puree, with potato protein and hydrocolloids. The impact of hydrocolloids, porous structure, and microwave energy on the stability of the dried fruit foam was compared to those of conventional freeze dried products during 12 weeks of storage at 37°C. Dried samples were vacuum packed. The plant bioactives, namely ACY and AA, and color during storage were investigated. Water sorption and glass transition temperature were also measured.

The results suggested that the structure of the fruit preparation is a critical parameter and plays an important role in preserving quality. Raspberry puree without hydrocolloids was not stable during storage because of its critical level of T_g , which triggers negative changes in the AA and ACY, thus adversely affecting the color of the samples. Results showed that the addition of hydrocolloids stabilized the raspberry puree stored at high temperature. The foam structure provided better storage stability based on the tested parameters. It can be concluded that the matrix composition helped prevent the detrimental reactions and enhanced storage stability.

The most significant contribution to this manuscript was made by the doctoral candidate. This comprised the conception and design of experiments based on a previous critical literature review as well as major conduction of data analysis and data interpretation. In addition, the doctoral candidate wrote and revised the manuscript. Co-authors contributed to the experimental part or to the discussion of the results and provided input to the drafted publication prior to the submission.

Adapted original manuscript⁷

Storage stability of dried raspberry foam as a snack product: effect of foam structure and microwave-assisted freeze drying on the stability of plant bioactives and ascorbic acid⁸

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Highlights

- Studied storage stability of raspberry puree post microwave-freeze drying process.
- Raspberry puree became be a healthy foam snack with aid of hydrocolloids.
- Freeze-dried puree enhanced the preservation of plant bioactives during storage.
- The main plant bioactives in raspberry puree were anthocyanins and ascorbic acid.

Abstract

We compared the effects of the use of microwaves during freeze drying with conventional freeze drying on the structure and storage behavior of dried raspberry puree foam. The effects of hydrocolloids, such as potato protein (as a foaming agent), maltodextrin, pectin (as foam stabilizers), and the impact of foam structure on the stability of plant bioactives (namely anthocyanins and ascorbic acid) and color during storage was investigated. Dried samples were vacuum-packed and stored at 37°C for 12 weeks. Water sorption and glass transition temperatures were also measured. The results suggest that the raspberry puree is not as stable as the foamed structure. Storage stability of microwave-assisted freeze-dried samples revealed equivalent or even slightly better characteristics when compared with those produced via the conventional freeze-drying method. It can be concluded that microwave freeze drying does not induce specific detrimental changes during storage as compared to the freeze-drying technology used as control.

⁷ Adaptions refer to formatting issues: e.g., numbering of sections, figures, tables and equations, abbreviations, manufacturer specifications, axis labeling, figure captions and style of citation.

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3.7.1 Introduction

Functional food concepts are becoming more important in the snack food market owing to the ever-increasing health awareness of consumers. Dried fruit-based products have attracted attention due to their healthy reputation. Compared with other fruits, raspberries possess high concentrations of plant bioactives, including anthocyanins and vitamin C.

Since raspberries are extremely perishable, they are commonly processed into jam, jelly, puree, or dehydrated products to prolong their shelf life. The physical and chemical stability of a food material essentially depends on its glass transition temperature (T_g) during storage. Foods are very stable when they are stored below their T_g , which corresponds to a highly viscous state where the rate of chemical reactions is very low due to the limited mobility of molecules. Dried raspberry products are usually rich in sugars, and therefore have a low T_g and require low storage temperatures (Jakubczyk et al., 2010). The average concentration of total sugars of fresh raspberries was reported to be 4.4 g/100 g (Rao and Snyder, 2010). The dominant sugars are fructose, glucose, and sucrose in mass fractions of 2.4, 1.9, and 0.2 g/100 g, respectively (Rao and Snyder, 2010). The T_g values of fructose, glucose and sucrose in mango puree were reported to be -5°C , 32°C , and 62°C , respectively (Jaya and Das, 2004). To overcome the disadvantages of low glass transition temperatures of sugars, hydrocolloids are commonly used to improve the quality attributes and shelf-life stability of food preparations.

Foam-mat drying is one way to create a dried snack product while retaining the characteristics of a healthy food and its functional constituents. Foam drying is particularly suitable for drying of sticky and heat-labile products because the open porous structure enhances heat transfer. Thus, faster drying rates can be achieved at lower temperatures (Karim and Wai, 1999). In this context, while conventional freeze drying (FD) is state-of-the-art, the addition of microwave (MW) energy to the freeze-drying process has been shown to be an efficient alternative to produce fruit foams with comparable or even better characteristics (Ozcelik et al., 2019b; Ozcelik et al., 2019a; Ozcelik and Püschner, 2017).

A foam structure can be defined as the metastable form of a whipped liquid or semi-liquid. Due to their functional properties, proteins are often used as a foaming agent by adsorbing to the interface between air and liquid (Schmidt et al., 2018b). Considering their ability to increase viscosity, hydrocolloids are often used as foaming agents and foam stabilizers. In addition to this capacity, maltodextrin (MD) is often used as a drying agent, which can help to stabilize the product thanks to its high T_g . Pectin (P), one of the most widely used gelling agents among the hydrocolloids, has been used to further stabilize the foam (Saha and Bhattacharya, 2010), and it has been used potato protein isolate (PP) as a foaming agent. Due to its good foaming properties, it is a suitable alternative to proteins of animal origin (van Koningsveld et al., 2002).

Deteriorations in the quality of a food product during storage occur, in general, as a result of a series of chain reactions triggering one another. Chemical deterioration is based mainly on the interplay between water activity, water adsorption, and glass transition temperature. Water activity is related to the chemical potential of water and is responsible for the reactions, since water is the most important plasticizer for food components (Levine and Slade, 1988). On the other hand, temperature promotes the mobility of the reactants due to the phase shift dictated by the T_g . A highly viscous material becomes soft and rubbery, and thus the mobility of reactants increases. This phenomenon results in several quality losses in the product (Bell and Hageman, 1994). These negative effects include textural softening, color changes due to non-enzymatic browning, and degradation of ascorbic acid (AA) and anthocyanins (ACY). Greater mobility of oxygen, which is an indispensable reaction partner in the degradation of AA and ACY, causes faster and greater degradation (Herbig and Renard, 2017).

3.7.2 Material and methods

3.7.2.1 Raspberry puree and sample preparation

Frozen raspberry puree was supplied by Mainfrucht (Gochsheim, Germany). Total soluble solids of the puree were 8.0° Brix, and pH was in the range of 2.90–3.50. Frozen raspberry puree was thawed at 4°C and then adjusted to 20°C in a water bath. This puree was used as the raw material for the production of raspberry foams. PP, consisting of the low molecular-weight fraction of the potato protease inhibitor (Solanic300,

Veendam, Netherlands), was used as a foaming agent. Maltodextrin DE 6 (MD) (Nutricia, Erlangen, Germany) and highly esterified citrus pectin (P) (degree of esterification 68%–76%) (Herbstreith & Fox, Neuenbürg/Württ, Germany) were used as foam stabilizers. The foam recipe was chosen with consideration of the drying behavior and product characteristics of foamed raspberry puree of different foam formulations reported by Ozcelik et al. (2019a) PP, MD and P concentrations of 5% (w/w), 15% (w/w) and 2.5% (w/w), respectively, were used. The raspberry puree, foaming agent, and stabilizers (where used) were mixed before whipping. To completely hydrate the powders in the raspberry puree, the mixture was stirred gently for 24 h at 4°C. From this point, this mixture will be designated as the “non-foamed sample”. The mixture was kept at 20°C for 30 min prior to the whipping. The non-foamed preparation was then whipped using a KitchenAid mixer (Artisan 5KSM150; St. Joseph, MI, USA) at a maximum speed of 220 rpm for 10 min at 20°C. Raspberry puree, non-foamed and foamed samples were subsequently dried to make preparations for storage trials. More details of the experimental methodologies are presented in Ozcelik et al. (2019a).

3.7.2.2 Drying techniques and equipment

Drying experiments were performed according to the uniform drying settings reported by Ozcelik et al. (2019a). For both FD and MWFD, samples of 100 g were placed into 190-mm diameter glass dishes. Samples were frozen at –80°C for 24 h before drying. A target residual water content of $3.5 \pm 1\%$ (w.b.) was sought in all drying experiments as the criterion for termination of the drying process. All samples were evaluated for their residual water content and water activity immediately after the drying processes was terminated.

3.7.2.2.1 Freeze drying

FD experiments were conducted with all samples to establish a reference for the study. The FD process was carried out in a pilot-scale freeze dryer (Christ, Model: Gamma 1-20; Osterode, Germany). The samples were heated via conductive heating on shelves at 30°C. Chamber pressure was set to 0.1 mbar and the ice condenser temperature was run at –50°C.

3.7.2.2.2 Microwave-assisted freeze drying

MWFD experiments were performed in a pilot-scale microwave freeze dryer (Model μ Vac0150fd; Püschner Microwaves, Schwanewede, Germany). Microwave radiation was generated by a 1000 W magnetron at a frequency of 2.45 GHz. Details of the system are given in Ozcelik et al. (2019a). The condenser temperature was -50°C . The μ WaveCAT dryer software (Püschner Microwaves) was used for programming the drying process. As soon as the surface temperature reached 30°C , the microwave input was set to the pulsed heating mode, with MW power set to 1.0 W g^{-1} . For comparison purposes, the chamber pressure and the maximum product temperature were set to 0.1 mbar and 30°C , respectively, to match those used in FD.

3.7.2.3 Packaging and storage condition

Dried samples were placed into glass bottles and closed with a perforated lid. Then the bottles were sealed under vacuum (Multivac Sepp Haggenueller, Wolfertschwenden, Germany). The packaging materials used were light-proof multi-layered aluminum vacuum pouches consisting of 12 μm thick PET, 12 μm thick aluminum and 75 μm thick low-density polyethylene (LDPE) (Long Life for Art, Eichstetten, Germany). Samples were always kept in the dark and were vacuum sealed. Each sample was packed and stored independently at $37\pm 1^{\circ}\text{C}$ for up to 12 weeks in order to accelerate the storage effects. Samples were analyzed every four weeks starting from week 0, which represents the results from samples immediately after the drying process, to week 12.

3.7.2.4 Residual moisture content

Samples were ground using a mortar and pestle and the powder was analyzed. The residual moisture content of the samples was measured by volumetric Karl–Fischer titration (V20S; Mettler Toledo, Greifensee, Switzerland).

3.7.2.5 Water activity

The determination of water activity (a_w) in dried sample powder was performed using a water activity meter AW Sprint (Novasina, Lachen, Switzerland) with a sensitivity of 0.001. The a_w values were recorded at 25°C and measurement was finished after reaching an equilibrium.

3.7.2.6 DVS water vapor isotherms

Water vapor isotherms were determined using the DVS equilibrium method at 25°C according to the method of Bingol et al. (2012) with slight modifications. Approximately 30 mg of powder of each sample was transferred to the sample pan of the DVS device (Surface Measurement System Ltd, London, UK). The samples were exposed to a humidity range of 0–90% RH, 90–0% RH (cycle) with increments of 10% RH. Equilibrium was considered to be reached when the change in mass with time (dm/dt) was lower than 0.0005 mg/min for 10 min. The sorption curves were plotted on a dry weight basis moisture content as a function of water activity. The experimental sorption data were fitted to a theoretical regression model. The Guggenheim-Anderson-de Boer (GAB) model, which is most commonly used to fit experimental water sorption values, including fruit products, was applied to describe dm/dt (Shafiur Rahman, 2007). The GAB model was applied here as it has been proven to best fit water desorption and adsorption by foods over a wide range of water activities (Radosta, 1985). The isotherms were fitted according to the following equation:

$$M = \frac{M_0 k C a_w}{(1 - k a_w)(1 + (C - 1)k a_w)} \quad (3-11)$$

where M is equilibrium moisture content (g/100 g); M_0 is the monomolecular layer moisture content; C is the surface energy constant, and k is a constant correcting the properties of the multilayer molecules with respect to the liquid.

3.7.2.7 Color analysis

Color evaluations were performed using a color analyzer SP68 Sphere Spectrophotometer (X-Rite Europa GmbH, Regensdorf, Switzerland), with the results reported in CIELAB color scales. The measurements were performed using a D 65 standard light source. According to the CIELAB color coding, the L^* value represents lightness of color from 0 (black) to 100 (white), the a^* value represents the degree of redness (0 to 60) or greenness (–60 to 0), and the b^* value represents the degree of yellowness (0 to 60) or blueness (–60 to 0) of the specimen. The total color difference ΔE was calculated as follows:

$$\Delta E = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad (3-12)$$

where L_0^* , a_0^* and b_0^* are the color parameters of the reference sample and L^* , a^* and b^* are the color parameters of the test sample. The results from week 0 of each sample were used as reference. Higher ΔE values indicate greater differences from the reference sample.

3.7.2.8 Determination of ascorbic acid concentration

The concentration of AA was determined chromatographically using the reversed-phase high-performance liquid chromatography (RP-HPLC) Agilent 1100 series chromatograph (Agilent Technologies, Santa Clara, CA, USA) equipped with a binary pump, an auto sampler, and a variable wavelength detector. AA was isolated using a Zorbax 300 SB-C18 column (Agilent Technologies). The analysis was performed as described by Chebrolu et al. (2012), with slight modifications. The sample was mixed using a Ultra-Turrax T 25 homogenizer (IKA Werke, Staufen, Germany) with meta phosphoric acid (3% v/v solution) (Sigma-Aldrich Chemie, Steinheim, Germany). The sample was then shaken at 20°C for 30 min at 1,000 rpm using the Multi Reax shaker (Heidolph Instruments, Schwabach, Germany), followed by centrifugation for 10 min at $6,000 \times g$ (Multifuge 1S-R, Heraeus, Hanau, Germany) at 20°C. The reduction of dehydroascorbic acid (DHA) to AA was achieved by the addition of TCEP (tris[2-carboxyethyl]phosphine, 5 mM) (Sigma-Aldrich Chemie, Steinheim, Germany) to the supernatant. The detection of AA was carried out at a wavelength of 243 nm. Chromatograms were evaluated using the OpenLAB CDS ChemStation software (Agilent Technologies). The method is described in more detail elsewhere (Dachmann et al., 2018).

3.7.2.9 Determination of anthocyanin concentration

Cyanidin-3-sophorose, cyanidin-3-rutinoside, and cyanidin-3-glucoside were quantified as the representative raspberry anthocyanins, using RP-HPLC (Subsection 2.8). Samples were homogenized for 30 s using an Ultra-Turrax T 25 homogenizer (IKA Werke, Staufen, Germany), mixed with 1% v/v HCl (Sigma-Aldrich Chemie), and shaken at room temperature for 180 min at 1,000 rpm. After the solutions were centrifuged for 10 min at $6,000 \times g$ (Multifuge 1S-R, Heraeus), the supernatant was collected and used to determine anthocyanin concentration. Standard solutions of cyanidin 3-O- β -sophorose (Polyphenols AS, Sandnes, Norway), cyanidin 3-O- β -

rutinoside (Polyphenols AS, Sandnes, Norway), and cyanidin 3 O glucoside chloride (Extrasynthese, Genay, France) were used for quantification. Anthocyanins were separated using a Phenomenex Luna C18(2) column (Phenomenex, Aschaffenburg, Germany). The anthocyanin peaks were detected at 520 nm, and chromatograms were evaluated using OpenLAB CDS ChemStation (Agilent Technologies) software. The method is described in more detail by Dachmann et al. (2018). To evaluate the influence of storage on the retention of AA and ACY concentrations, each sample was analyzed immediately after drying, and at 4, 8 and 12 weeks, and the amount of active product retained was calculated.

3.7.2.10 Statistical analysis

All experiments were replicated three times and the summary statistics of each variable were presented as the mean $\pm$ standard deviation. Analysis of variance (ANOVA) was performed on the collected data in order to evaluate differences between the samples. Differences were considered to be significant if $p < 0.05$.

3.7.3 Results and Discussion

3.7.3.1 Effect of structural basis on residual moisture content, water activity, sorption behavior, and glass transition temperature of dried samples

3.7.3.1.1 Residual moisture content and water activity

The residual moisture content (RMC) and water activity (a_w) are the two most critical parameters to be considered with regard to food safety and quality preservation of dried products. The residual water content of dried fruits is expected to be low and a maximum water activity of 0.6 or below should be ensured to assure high storage stability (Hui & Barta, 2006).

The dried samples were sealed under vacuum immediately after the drying process in order to avoid moisture uptake. Samples from week 0 were analyzed immediately after drying. The RMC and a_w results of the MWFD samples are summarized in Table 3-8.

The RMC of raspberry puree tended to rise over the storage period, whereas the non-foamed and foamed structures resulted in more stable RMC results. The a_w values of dried samples showed significant variation ($p < 0.05$), starting from 0.13 to 0.29. As

water activity was below 0.6 for all samples during the entire storage period, microbiological stability was ensured.

Tab. 3-8. Residual moisture content and water activity of raspberry puree, non-foamed, and foamed raspberry puree. Non-foamed and foamed samples contained 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P. All samples were dried via MWFD at 1.0 W g⁻¹ microwave power input, 0.1 mbar chamber pressure and 30°C maximum product temperature. Samples were stored in the vacuumed pack at 37°C in the dark.

Storage time, weeks	Residual water content (%)			Water activity (-)		
	<i>Puree</i>	<i>Solution</i>	<i>Foam</i>	<i>Puree</i>	<i>Solution</i>	<i>Foam</i>
Week 0	2.87	3.30	2.97	0.14	0.13	0.14
	± 0.84 ₁ ^a	± 0.55 ₁ ^{ab}	± 0.01 ₁ ^a	± 0.04 ₁ ^a	± 0.00 ₁ ^a	± 0.02 ₁ ^a
Week 4	3.81	2.56	2.89	0.19	0.21	0.26
	± 0.45 ₁ ^a	± 0.01 ₁ ^a	± 0.38 ₁ ^a	± 0.01 ₁ ^{ab}	± 0.00 ₂ ^b	± 0.00 ₃ ^b
Week 8	4.05	3.23	3.05	0.22	0.25	0.25
	± 0.28 ₁ ^a	± 0.01 ₁ ^{ab}	± 0.27 ₁ ^a	± 0.00 ₁ ^{ab}	± 0.00 ₁ ^c	± 0.01 ₁ ^b
Week 12	4.58	5.13	3.67	0.26	0.29	0.28
	± 0.34 ₁ ^a	± 0.90 ₁ ^b	± 0.02 ₁ ^a	± 0.00 ₁ ^b	± 0.01 ₂ ^d	± 0.00 ₁₂ ^b

Data are presented as the mean ± standard deviation; n = 3. A common superscript letter in the same column indicates no significant difference (p>0.05) between storage time. A common subscript numeral in the same row within residual moisture content and water activity indicates no significant difference (p>0.05) between structures.

3.7.3.1.2 Water sorption behavior

Fig. 3-37 depicts the water (ad-)sorption isotherms obtained at 25°C. The desorption profiles indicated a similar trend to that of the adsorption profiles, with a negligible hysteresis. The sorption isotherm data were fitted to a regression based on the GAB model. The calculated GAB model parameters are listed in Table 3-9. The monolayer moisture content, which specifies the amount of water adsorbed on the surface of the sample, varied from 0.08 to 0.32 g water per g solid. The constant parameters of k and C depended on the molar sorption enthalpies. The C values obtained ranged from 0.38 to 1.43. According to Blahovec (2004), this relationship between k and C defines the type of isotherm as type III, where $0 < k \leq 1$ and $0 < C < 2$. Similar sorption behavior had been observed previously for apple puree, pineapple, apricot, star apple, mango and blueberries (Djendoubi Mrad et al., 2012; Falade and Aworh, 2004; Jakubczyk et al., 2010; Lim et al., 1995; Viganó et al., 2012).

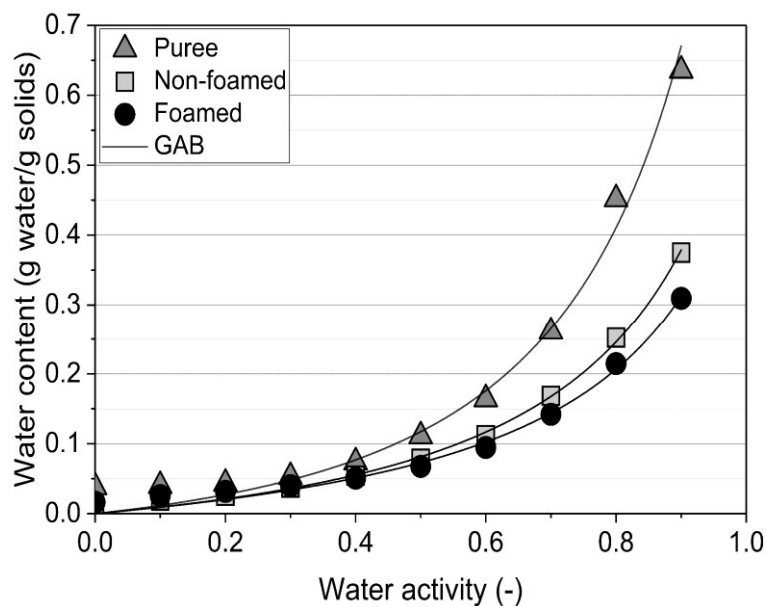


Fig. 3-37. DVS (dynamic vapor sorption) behavior of the tested samples at 25°C. The samples are in the form of raspberry puree, non-foamed and foamed samples. Non-foamed and foamed samples contained 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P. All samples were dried via MWFD at 1.0 W g⁻¹ microwave power input, 0.1 mbar chamber pressure and 30°C maximum product temperature. Samples were stored in the vacuumed pack at 37°C in the dark. (GAB: The Guggenheim-Anderson-de Boer model).

The curves obtained are typical of those for fruit-like, sugar-rich foods which adsorb a comparatively small amount of water at low a_w levels. The composition, structure, and also the size of the molecules of complex food materials influence their sorption behavior. Raspberry sugars are mainly mono- and disaccharides such as fructose (53%), glucose (42%), and sucrose (5%) (Bobinaité et al., 2016).

Tab. 3-9. Calculated GAB model parameters for the adsorption isotherms of raspberry puree, non-foamed, and foamed raspberry puree at 25°C. Non-foamed and foamed samples contain 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P. All samples were dried via MWFD at 1.0 W g⁻¹ microwave power input, 0.1 mbar chamber pressure and 30°C maximum product temperature.

Samples	Parameters			
	M_0 (g H ₂ O/g solid d.m.)	$k(-)$	$C (-)$	$R^2(-)$
Raspberry puree	0.32 ± 0.14	0.83 ± 0.34	0.38 ± 0.32	0.99
Non-foamed	0.18 ± 0.13	0.79 ± 0.08	0.54 ± 0.41	0.99
Foamed	0.08 ± 0.03	0.87 ± 0.06	1.43 ± 0.89	0.99

Water interacts only via hydrogen bonds with the hydroxyl groups on the surface of the crystal. Consequently, the simple sugar molecules can adsorb more water due to the

increased surface area per g, allowing more hydroxyl groups to be exposed (Radosta, 1985). The sorption curves of all samples intersected at the transition between the low and intermediate a_w range ($a_w < 0.6$), where they exhibited relatively low water uptake (Fig.3-37). This is because of the weak interactions between water and sugar molecules that cannot break the interactive forces between water and small sugar molecules. The raspberry puree exhibited the highest equilibrium moisture content because of its high fructose content. Thus, it was more hygroscopic than the other samples containing high molar mass additives (Ramón et al., 2017). Since the sugars are the main components of dried raspberry puree, higher adsorption occurs because of the relatively high sugar dissolution. Furthermore, the adsorption of water can convert a glassy material into a rubbery material (Radosta, 1985).

The steep curves of the increase in water adsorption of all samples above a water activity of 0.6 can be attributed to the overall water-sugar interactions. These interactions increased sufficiently to cause fragmentation of sugar-sugar interactions, so that water could penetrate into the crystal and consequently dissolve the sugar molecules. Hence, the moisture content increased considerably, because a solution was created. The raspberry matrix could be stabilized efficiently by using proteins in conjunction with MD and pectin. The hydrated protein consists of many sites with which water molecules can interact by hydrogen bonding (Radosta, 1985). In addition, hydrocolloids may cause redistribution of water upon gelation and cross linking (Taub and Singh, 1998). The additional hydrocolloids might have a dilution effect on the sugar composition of the puree, which provides the higher water-binding capacity at higher a_w ranges. The amount of water adsorbed to the food structure with the addition of MD was higher, where the water molecules interact *via* hydrogen bonds with the hydroxyl groups of the glucose molecules of the MD (Cano-Higueta et al., 2015). Pectin could act as both a water binder and a stabilizer. In addition to the additives, the foamed structure affected the sorption behavior. There was a significant difference between the non-foamed and the foamed samples, when both consisted of the same amount of hydrocolloids. The foamed sample was shown to be less hygroscopic than the non-foamed sample, with the foamed sample having a higher volume and hence providing a higher adsorption capacity. This observation suggests that the porosity of the sample plays an important role in determining the sorption characteristics. In the range of intermediate to high a_w values, all samples tended to increase the water adsorption due to the crystalline sugar

dissolution (Falade and Aworh, 2004). At the end of the desorption cycle, all samples retained less than 5% water. The puree retained significantly higher moisture than did the other samples and the samples were not caked at the end of the DVS run. The RMC and a_w data from the storage period correlated well with their water sorption behaviors.

3.7.3.2 Effect of structural basis on the retention of ascorbic acid and anthocyanins of dried samples

3.7.3.2.1 Ascorbic acid

AA, also known as vitamin C, is a water-soluble vitamin that turns into dehydroascorbic acid (DHA) by losing two protons under oxidative conditions. As this reaction is reversible, the DHA can be recycled to AA (Chebrolu et al., 2012). Fig. 3-38a depicts the percent retention of AA during storage. The AA results are presented as the sum of free AA and DHA.

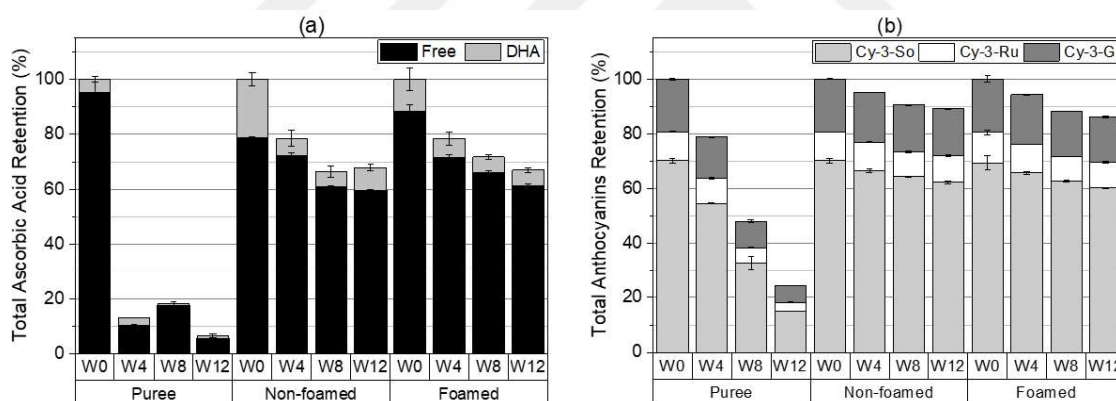


Fig. 3-38. Percentage retention of (a) ascorbic acid and (b) anthocyanins in dried raspberry samples having different structures during a 12-week storage time. The samples are in the form of raspberry puree, non-foamed and foamed samples. Non-foamed and foamed samples contained 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P. All samples were dried via MWFD at 1.0 W g⁻¹ microwave power input, 0.1 mbar chamber pressure and 30°C maximum product temperature. Samples were stored in the vacuumed pack at 37°C in the dark. (Free: Free ascorbic acid; DHA: Dehydroascorbic acid; Cy-3-So: Cyanidin-3-sophoroside; Cy-3-Ru: Cyanidin-3-rutinoside, and Cy-3-Gl: Cyanidin-3-glucoside; W: Week).

The determined values were normalized based on those obtained from week 0 samples, which were considered to be 100%. The impact of the drying process on AA and

ACY was evaluated in our previous study (Ozcelik et al., 2019b). The retention of AA is intensely affected by the structure of the sample. A marked decline of AA to 87% was observed in the raspberry puree after 4 weeks of storage, while 94% were observed at the end of the 12-weeks storage. Aaby et al. (2018) reported that, after 35 days of storage, almost no vitamin C was left in strawberry puree due to the activity of degrading enzymes. It is well known that the degradation of AA is mainly caused by conditions of high temperature, high levels of oxygen, moisture, and light. Although the samples were kept in sealed bags in the present study, exposure to the ambient oxygen prior to the sample preparation for analysis might have been responsible for the observed degradation. Furthermore, the oxygen trapped in the cells might have been released during storage at relatively high temperatures. The combination of high storage temperature and slight increases in the RMC and a_w during storage could have had a triggering effect on degradation. Relatively rapid drying of sugar-rich fruit may cause an amorphous metastable state, which is sensitive to high storage temperatures and to the changes in the moisture content of the dried puree (Telis and Martínez-Navarrete, 2009). The water plasticization effect, due to the critical glass transition temperature of the puree, occurred at around $40 \pm 5^\circ\text{C}$. However, the DHA did not increase during storage as was to be expected. Although oxidation might have occurred, part of the DHA could have been restored to AA. This could be attributed to the reversible interaction between DHA with AA.

The non-foamed and foamed samples were much more stable than the puree. After four weeks of storage, 21% loss was determined from both the non-foamed and the foamed samples. In the following weeks, the loss rate of AA slowed. At the end of week 8, the loss was 34% for the non-foamed and 28% for the foamed sample. Carbohydrates, such as maltodextrin, might have acted as an oxygen barrier at the lamella surface wall matrix of the structure during storage and could have formed a protective layer for the functional compounds, including AA and ACYs (Domian et al., 2017). The MD could protect these valuable substances from oxidation thanks to its film-forming capacity which contributes to increased stability during long-time storage (Telis and Martínez-Navarrete, 2009). Dried lamellae in the foam/porous structure around the pores resembles a glassy membrane structure. This structure protected the entrapped bioactive compounds, such as AA, from oxidation. As a consequence, slightly higher retention values were obtained for the foamed than for the non-foamed

samples. Raharitsifa and Ratti (2010) reported that the retention of vitamin C in non-foamed apple juice was higher than that in foamed products, which contained 3% egg white and 1% methylcellulose and were stored at 4°C under vacuum. Yet, both non-foamed and foamed structures ended up with a 33% loss of AA at the end of the 12-week storage period.

3.7.3.2.2 Anthocyanins

The initial concentration of anthocyanins (ACYs) was determined immediately after drying. The storage results were normalized based on the results obtained after drying. Fig. 3-38b presents the percent retention of ACYs during storage at 37°C. The concentrations of three different ACYs gradually decreased throughout the storage period, as expected. The cyanidin-3-sophoroside (Cy-3-So) was the major ACY pigment (comprising 70% of ACYs), which contributes to the red color of the raspberry. The content of cyanidin-3-glucoside (Cy-3-Gl) and cyanidin-3-rutinoside (Cy-3-Ru) pigments were 19% and 11% (= week 0), respectively.

Of particular importance was the loss of the ACYs in the puree samples, which experienced the greatest loss of all samples. At the end of the 12-week storage period at 37°C, the loss of the ACYs in the raspberry puree reached 76%. The loss of ACYs in the puree was gradual through-out the storage time, as shown in Fig. 3-38b. With 11–14% declines, the loss of ACYs in non-foamed and foamed samples was much lower on a percentage basis than in the puree. Fang and Bhandari (2011) reported that the loss of ACYs from spray-dried bayberry powder reached 94% when stored at 40°C. The Cy-3-So seems to be the least stable of the ACY pigments. The puree exhibited a 40% loss in Cy-3-So at the end of the 8-week period, with the loss reaching 79% toward the end of the 12-week storage period. This result suggests that the rapid loss of Cy-3-So could be responsible for the color degradation, especially for the lower redness values in the puree samples (see Subsection 3.7.3.3), as higher losses are unavoidable at high storage temperatures if the glass transition temperature is exceeded. In particular, for the puree, it was critical that the T_g might decrease during storage since the RMC was slightly increased. It is also important to note that the T_g of raspberry puree was $40 \pm 5^\circ\text{C}$ when the storage temperature was 37°C. Within the temperature range of 35–37°C, the amorphous solid puree turned into a rubbery state. Thus, the molecular mobility of the food matrix and the reactants were greatly

accelerated, which triggers the occurrence of physicochemical alterations (Bhandari and Howes, 1999).

By the end of the storage period, the loss of the Cy-3-GI pigment was 69%, 11% and 15% for the raspberry puree, non-foamed and foamed samples, respectively. In the literature, the Cy-3-GI pigment is reported to be one of the most reactive ACYs during processing, while Cy-3-Ru shows the greatest stability against thermal treatment (Ancos et al., 2000; Patras et al., 2010). However, in the present study the Cy-3-GI pigment was not the most reactive one during storage. The degradation trend of Cy-3-GI was similar to that of the Cyn-3-Ru pigment.

Overall, the results from both AA and ACY studies revealed that combinations of hydrocolloids (PP, MD and P) acted as a protective shield by stabilizing the raspberry puree during a high-temperature, long-term storage period. One would have expected that the porous structure of the puree would have caused more deterioration of the bioactives due to the increased surface area, allowing greater interaction with oxygen.

3.7.3.3 Effect of structural basis on color characteristics of dried samples

Color is a critical quality indicator in food materials and its variation can be considered to be a predictor of other quality measures. The color parameters determined in the samples are listed in Table 3-10.

There was no significant difference ($p>0.05$) in the L^* value among all samples by the end of storage. One of the most important color measures of raspberry preparations is redness (a^*), which is mainly determined by the ACYs. The puree showed a significant decrease in the a^* value over the entire storage period. In contrast to the puree, the a^* values of the non-foamed and foamed samples containing hydrocolloids were very stable ($p>0.05$). Similar behavior was observed in the b^* values. The b^* value of the raspberry puree significantly ($p<0.05$) increased over time, while no significant difference ($p>0.05$) was observed between the non-foamed and foamed samples at the end of storage.

Tab. 3-10. Hunter color parameters for a range of raspberry puree samples having different structures. The samples are in the form of raspberry puree, non-foamed, and foamed samples. Non-foamed and foamed samples contained 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P. All samples were dried via MWFD at 1.0 W g⁻¹ microwave power input, 0.1 mbar chamber pressure and 30°C maximum product temperature. Samples were stored in the vacuumed pack at 37°C in the dark.

Storage time, weeks	L*			a*			b*		
	<i>Puree</i>	<i>Solution</i>	<i>Foam</i>	<i>Puree</i>	<i>Solution</i>	<i>Foam</i>	<i>Puree</i>	<i>Solution</i>	<i>Foam</i>
Week 0	53.7 ± 0.3 ^a ₁	60.2 ± 2.1 ^a ₂	59.1 ± 0.1 ^a ₁₂	25.4 ± 0.9 ^a ₁	23.2 ± 0.9 ^a ₁₂	21.4 ± 0.6 ^a ₂	7.7 ± 0.3 ^a ₁	4.8 ± 0.4 ^a ₂	4.5 ± 0.3 ^a ₂
Week 4	51.0 ± 0.3 ^a ₁	60.0 ± 0.1 ^a ₂	59.7 ± 0.1 ^a ₂	21.6 ± 0.5 ^b ₁	23.3 ± 0.1 ^a ₂	22.5 ± 0.1 ^a ₁₂	7.1 ± 0.2 ^{ab} ₁	5.0 ± 0.0 ^a ₂	5.0 ± 0.1 ^a ₂
Week 8	53.2 ± 0.4 ^a ₁	60.4 ± 0.1 ^a ₂	59.7 ± 0.4 ^a ₂	19.5 ± 0.2 ^c ₁	22.5 ± 0.1 ^a ₂	22.1 ± 0.2 ^a ₂	8.4 ± 0.1 ^a ₁	4.2 ± 1.1 ^a ₂	5.1 ± 0.3 ^a ₂
Week 12	53.4 ± 0.0 ^a ₁	60.0 ± 0.1 ^a ₂	59.6 ± 0.3 ^a ₂	16.5 ± 0.1 ^d ₁	23.0 ± 0.1 ^a ₂	22.2 ± 0.1 ^a ₃	10.3 ± 0.0 ^c ₁	5.4 ± 0.0 ^a ₂	5.4 ± 0.1 ^a ₂

Data are presented as the mean ± standard deviation; n = 3. Different superscript letters in the same column indicate a significant difference (p<0.05) between storage times. Different subscript numerals in the same row within L*, a* and b* a significant difference (p<0.05) between the structures. L* value denotes lightness, the a* value denotes the degree of redness, and the b* value denotes the degree of yellowness of the specimen.

The main factors influencing color stability in stored fruit preparations are the concentration of ACYs and other phenolic compounds, and other factors, such as temperature, oxygen, sample structure, light and pH (Sun et al., 2010). A decrease in the a* value with an increasing b* corresponds to a visible color change toward a darker product, which appears as browning of the product. Visually detectable color changes were observed in the puree. The browning might occur due to several mechanisms in the food matrix. One of the most common phenomena is the non-enzymatic browning reaction, called the Maillard reaction. Reducing sugars in a product can interact with the amino groups of a protein, especially under high storage temperatures and acidic conditions (Taub and Singh, 1998). Monosaccharides, such as fructose or glucose, are reducing sugars. Because of their free aldehyde and ketone groups, they are more reactive than the disaccharides (sucrose). After the drying process, raspberry puree was found to be hygroscopic and very sticky. This is a common characteristic of sugar-rich fruits, where the plasticizing effect of low molecular-weight sugars depresses the

T_g (Roos and Karel, 1991). Even a small amount of water adsorption by a sample can cause a dramatic decrease in the T_g . This can be attributed to an increase in the mobility of reactants and oxygen diffusion as a result of an increase in RMC and a_w , which, in turn, causes a further increase in the mobility of the reactants and oxygen diffusivity. On the contrary, no browning was observed in the non-foamed and foamed samples supplemented with hydrocolloids such as PP, MD and P. The rate of browning can be controlled by diffusion inhibition of the reactants (Roos and Himberg, 1994). Additionally, Bodelón et al. (2013) reported that the color deterioration of strawberry puree was prevented during storage due to the high amount of the antioxidant AA. Accordingly, rapid loss of AA, occurring at early stages of the storage period, may explain the color deterioration observed in the raspberry puree in the current study.

The total color difference (ΔE) is a measure widely used to quantify color variations in a product. The dried samples (= week 0) were taken as reference. Fig. 3-39 shows the total color changes in response to storage time.

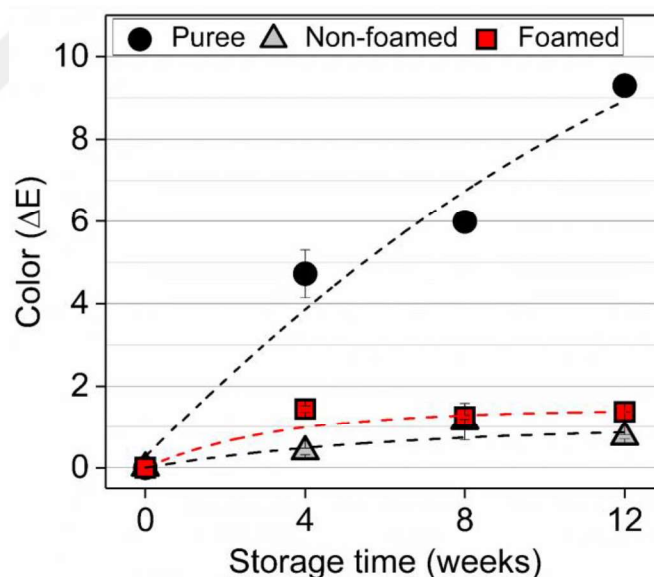


Fig. 3-39. Total color change of microwave-assisted freeze-dried (MWFD) raspberry samples in three different structures during a 12-week storage period. The samples were in the form of raspberry puree, non-foamed and foamed samples. Non-foamed and foamed samples contained 5% (w/w) PP + 15% (w/w) MD + 2.5% (w/w) P. All samples were dried via MWFD at 1.0 W g⁻¹ microwave power input, 0.1 mbar chamber pressure and 30°C maximum product temperature. Samples were stored in the vacuumed pack at 37°C in the dark (Reference: Week 0 of each sample).

The puree samples showed a steep increase in ΔE by the end of week 4. Higher ΔE values correlated with the extent of degradation during the storage period. The ΔE value of the puree reached 9.3 by the end of 12 weeks of storage, while the corresponding values were 0.8 and 1.1 for the non-foamed and foamed samples, respectively. The color behavior of raspberry puree corresponded with the findings reported by Ochoa et al. (1999). The fact that the total color changes in the non-foamed and foamed samples were negligible pointed out that these structures are comparably much more stable than was the puree during storage at high temperature (37°C).

3.7.3.4 Effect of drying method on the storage stability of dried samples: MWFD versus FD

The characteristics of foamed raspberry puree dried via MWFD or FD were compared with the results obtained in our previous study (Ozcelik et al., 2019b). Overall, differently dried puree samples did not show a considerable difference in their storage behavior. Fig. 3-40 depicts the water activity, ascorbic acid and anthocyanin retention, and the total color difference of samples dried via MWFD or FD. The results obtained by the end of 12 weeks of storage are presented in a comparable manner.

Of particular interest was to determine whether MWFD affects the characteristics of dried samples during storage. The water activity of the samples dried via the two different techniques was found to be slightly different (Fig. 3-40a). However, the a_w values of all samples remained below 0.3.

The retained AA of the samples dried via MWFD was found to be slightly higher than the AA values of the samples dried via FD (Fig. 3-40b). The difference, however, was not significant ($p>0.05$).

ACY retention in the samples dried via MWFD was significantly higher ($p<0.05$) than those determined in the FD samples (Fig. 3-40c). The MWFD puree retained 40% of the ACYs, while the corresponding value was 24% for the FD samples. Using either drying method, the foamed samples retained more ACYs than did the non-foamed samples. The foam dried via MWFD retained 98% ACYs significantly ($p<0.05$) higher compared with 86% in the samples dried via FD.

The total color difference results of the samples are shown in Fig. 3-40d. The puree samples dried via MWFD yielded significantly ($p < 0.05$) lower ΔE values than those dried via FD. On the other hand, the drying method had no discernible impact on ΔE values of non-foamed and foamed samples during storage.

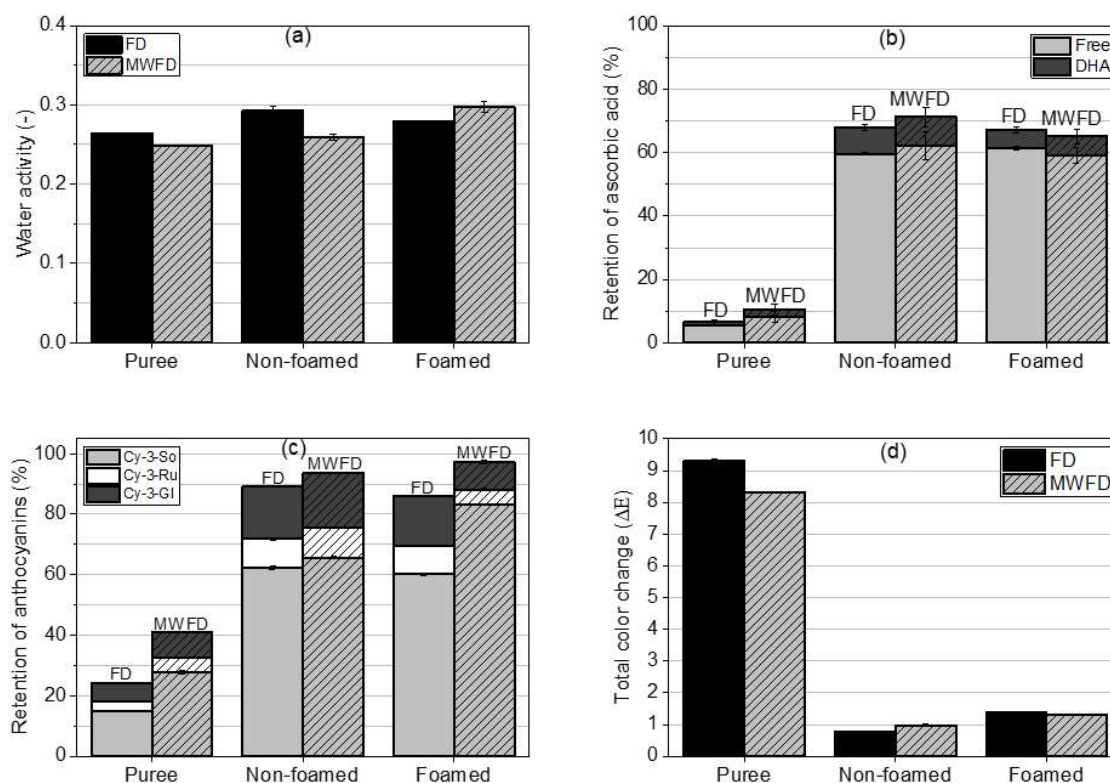


Fig. 3-40 (a) Water activity, (b) ascorbic acid, (c) anthocyanins, and (d) total color change data of the FD and MWFD samples in three different forms at the end of the 12-week storage period. Samples were stored in the vacuumed pack at 37°C in the dark. (Free: Free ascorbic acid; DHA: Dehydroascorbic acid; Cy-3-So: Cyanidin-3-sophoroside; Cy-3-Ru: Cyanidin-3-rutinoside, and Cy-3-Gl: Cyanidin-3-glucoside; W: Week).

Additionally, the findings on the glass transition temperature and sorption behavior of samples dried via FD were further evaluated. The samples did not reveal significant differences in their sorption behavior or their glass transition temperature, regardless of the drying method. In their study with apple puree, Jakubczyk et al. (2010) reported comparable results for the samples subjected to MW convective drying or FD.

3.7.4 Conclusion

We found that the structure of the fruit preparation is a critical parameter and plays an important role in preserving the quality of dried fruit material during storage. In general,

it is difficult to store dried raspberry puree because of its high sugar content. T_g is the key factor which impacts the storage stability of the food matrix. We determined for the raspberry puree, without supplementary hydrocolloids, that the critical level of the T_g triggers negative changes in the bioactive constituents such as AA and ACYs, which adversely affect the color of the preparation. Addition of hydrocolloids stabilized the raspberry puree stored at high temperature. It turned out, in contrast to our hypothesis, that the foam structure provided a better storage stability based on the tested parameters. Although an open porous structure could generally be expected to lead to higher rates of deteriorating reactions, the matrix composition helped here to prevent these reactions. The MWFD process was determined to be an efficient alternative to the conventional FD method. We found in our previous research (Ozcelik et al., 2019b; Ozcelik et al., 2019a) that MWFD out-performed FD was more efficient in terms of energy consumption and yielded products of comparable quality. The present study showed that MWFD can be used to produce fruit products which exhibit a storage stability comparable to or even slightly better than those produced via the FD method.

3.7.5 Funding

This Industrial Collective Research (IGF) Project (AiF 19015 N) of the FEI was supported by AiF under the programme for promoting the IGF of the German Ministry of Economic Affairs and Energy (BMWi), based on a resolution of the German Parliament.

3.7.6 Acknowledgments

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4 Overall discussion

Fruits and fruit derivatives have been dried conventionally using drying methods such as air drying and freeze drying, resulting in low drying rates. In contrast, the long drying times at relatively high temperatures cause degradations and undesirable product quality. Freeze drying is generally used to produce heat-labile products with excellent end quality for obtaining high value-added products. Comprehensive research has been conducted for enhancing the efficiency of the freeze-drying process by the aid of microwaves, and the product characteristics have been investigated to devise an efficient alternative drying method. Microwaves penetrate directly into the products, causing rapid internal heating. Despite of its unique advantages the complexity of microwave processing of foods is still challenging because of its volumetric heating. However, no research has been conducted on microwave-assisted fruit foam drying yet. Therefore, the objective of this study was comprehensive miscellaneous characterization of foam of raspberry as a model fruit and to identify approaches for the drying characteristics of microwave-assisted freeze-drying technique. The process conditions of microwave-assisted freeze drying for a uniform and energy-efficient process for the production of fruit snacks with high nutritional quality were also defined. Thus, it was aimed at finding proper foam formulations for the relevance between fresh foam characteristics and drying characteristics as well as the product characteristics. Another aspect was to evaluate the storage behavior of the dried foam for a long period of time under several storage conditions.

Overall, the microwave-assisted-freeze-drying process for producing dried fruit foams while preserving their nutritional and textural quality yielded short drying times because of the higher drying rates and efficiency in terms of energy consumption compared with the conventional freeze-drying process.

Based on the obtained results, a remarkable contribution was made to the field of research on innovative fruit-based products in conjunction with fast and energy-efficient drying processes. A more detailed discussion will be carried out in the following sections, based on the findings of this thesis (Section 3).

4.1 Foam matrix formulations

The main objective of this study was to characterize fruit foam matrix to establish an efficient drying process assisted by microwaves. Drying hard-to-dry materials including all types of fruits and fruit juices requires gentle processing conditions to obtain a high-quality end product. High-quality processed food can be defined as products that show fresh fruit-like characteristics (i.e., vitamins, bioactive compounds, color, aroma compounds, and flavor). An important approach, therefore, is to convert the sugar rich, heat-sensitive materials into a foamed matrix with the help of hydrocolloids, thus providing lower temperatures quicker during drying in comparison to un-foamed materials. The metastability of liquid foams causes instabilities due to the unbalanced forces at the liquid-gas interface (Ratti and Kudra, 2006). Instabilities such as drainage, Ostwald ripening, and coalescence have been explained in detail in Subsection 1.2.1. These instabilities lead to disappearance of bubbles (Wilson, 2013). The stability of foam, therefore, must be guaranteed prior to the drying process by composing stable foam formulations. As pure fruit often has temporal foam stability, additional hydrocolloids are required to enhance foam stability because of high water-binding capacity and thickening properties. Finally, the appropriate foaming agent and foam stabilizers can form and stabilize the bubbles, thus preventing successful drying. Proteins are amphiphilic molecules that are widely used as foaming agents considering their two important functional properties—their ability to form and stabilize foams. It is clear that soluble proteins can differ widely in their ability to adsorb and unfold at the interface for foam formation under given conditions. Parameters as such protein concentration, pH, temperature, and whipping conditions dictate the foam formation and structure. Proteins in the food industry or in previous research are mostly of animal origin. Because plant-based nourishment has gained more importance because of health and environmental concerns and because of the high surface activity, potato protein (PP) was applied in this study. The acidic nature of raspberry (pH 3) is also another important factor to be considered. However, when the functionality of potato protein and its competitors, egg white and whey protein isolate (WPI), was compared under the same conditions (at pH 3.2, 20°C, 220 rpm, 10 min), PP achieved higher overrun and foam stability (See Subsection 3.1.1). Varying concentration of protein was also evaluated to define the maximal applicable concentration range. No significant changes were observed in foam formation and stability above a protein concentration of 10%.

In contrast, foaming via whipping by rotor-stators greatly influences the capacity of foam formation by the foaming conditions. In particular, the rotational speed, whipping time, and distribution of air depend on the shear forces applied by mechanical energy (Schmidt et al., 2018a). To make an air-liquid dispersion, a large amount of mechanical energy must be supplied to increase the interfacial area (Rodríguez Patino et al., 2008). Hence, increasing whipping time increases the volume of gas incorporated into the foam matrix and consequently the overrun because more and smaller bubbles can be formed. However, when whipping is performed for more than 10 min, the foam volume decreases. This might be because of the continuous surface expansion and protein desorption due to bubble breakage, which may cause extensive protein unfolding, leading to a decrease in the effective molar protein concentration (van Koningsveld et al., 2002). Therefore, 10-min whipping time was found to be optimal for this study (Subsection 3.1.2). Furthermore, during foam formation, foam decay needs to be retarded with the help of stabilizers. On the other hand, polysaccharides such as maltodextrin and pectin, are hydrophilic in nature and increase the viscosity of continuous aqueous phases, thus controlling the rheology of the food system as a stabilizing agent (Ghosh and Prasun, 2012). Polysaccharides and proteins both contribute to the structural and textural properties of foam matrix by changing the rheology through the gelling networking system (Dickinson, 1992). Hence, based on the intuitive theoretical considerations, any macromolecule acting as an ideal steric stabilizer should not only be strongly attached to the interface (like an amphiphilic protein) but also be strongly solvated by the aqueous continuous phase (like predominantly hydrophilic polysaccharide) (Dickinson and Izgi, 1996). This shows that foam stability should be substantially enhanced by the presence of interfacial protein-polysaccharide complexation. Protein and polysaccharide complex formation is mainly driven by various non-covalent interactions, like electrostatic, hydrophobic, and steric interactions and H-bonding, (Kruif and Tuinier, 2001). In biopolymer mixing systems, two possible trends occur depending on the nature of bio-polymers. As explained earlier (Subsection 1.2.4), segregative (thermodynamic incompatibility) or associative interactions occur between polysaccharides and proteins. Therefore, concentration of mixing polysaccharides and the ratio between proteins and polysaccharides as well as the pH plays an important role toward the solubility of hydrocolloids. Therefore, the formulations of raspberry pulp with varying concentrations of single hydrocolloids, MD (varied between 0% to 30%), P (varied between 0%-2.5%), and protein (PP) concentration (varied between 2.5%-10%) of

foamed matrix were evaluated in terms of their foam characteristics: overrun, foam stability, and bubble size distribution. Increasing hydrocolloid concentration led to a decrease in overrun. Because of the increased viscosity of the continuous phase, hardly any air is incorporated in the vicinity of the interface (Lau and Dickinson, 2005). In addition, increasing MD and P lead to smaller bubbles and enhanced foam stability, which in turn forms more uniform bubble size distribution. A clear different trend was observed between MD and P on shear rheology. Increasing MD concentration led to lower yield points, while increasing P concentration resulted in higher yield points. Stabilizing effects of MD in turn increase in bulk viscosity and thus cause a retardation of gravitational drainage. Conversely, the stabilizing effects of pectin are caused by the formation of protein-pectin complexes, which in turn also enhance bulk viscosity and retard gravitational drainage. Compared to single hydrocolloid systems, the use of pectin and maltodextrin mixtures leads to further enhancement of foam characteristics. However, the respective effects of both hydrocolloids seemed to compensate for each other in the mixtures (Dachmann et al., 2018).

On the other hand, raspberry pulp preparation includes an additional homogenization step, which was further examined for the possible effect of mechanical stress on the foaming behavior. It was therefore hypothesized that the tissue and cell disruption during homogenization leads to structural alterations, which affect the foaming properties of the pulp. Moreover, it was assumed that oxidative processes increase during homogenization and increased the specific surface area (A_{SF}), thus changing the contents of sensitive ingredients (ascorbic acid and anthocyanins). However, the results led to no significant degradation in ascorbic acid and anthocyanin contents. Apparent viscosity decreased with increasing shear rate from 1 to 100 s^{-1} , indicating non-Newtonian behavior. The untreated samples showed a higher apparent viscosity than the homogenized ones. Increasing revolution speed resulted in a decrease in apparent viscosity of the treated samples caused by a reduced particle size. Foam stability of non-homogenized pulp was significantly higher than that of homogenized pulp because of its higher viscosity. Because of the more coherent fruit tissue, foam lamellae were assumed to be blocked. Therefore, drainage was reduced, and thus, the foam stability was higher. In conclusion, homogenization treatment of the fruit puree as an alternative to hydrocolloid addition led to reduced particle sizes and lower viscosity, which in turn was reflected in a modification of foaming properties (Dachmann et al.,

2018). Overall, the raspberry foam matrix formulated with protein (PP) (2.5% to 10%), maltodextrin (MD) (5%-30%), and pectin (P) (0.1%-2.5%) led to high foam stability with small bubbles and uniform bubble size distribution thus assuring subsequent stable foam drying.

4.2 Microwave-foam drying

The concept of microwave technology in the drying applications is based on higher energy efficiency, better quality, small footprint, and lower environmental impact through lower water and energy consumption. Microwave drying or microwave assisted vacuum drying have already been applied by many researchers to various food-stuff. Microwave foam drying dates back to 1977 for the drying of tomato paste (Brygidyr et al., 1977). Even though conventional FD is still regarded as a reference method for obtaining a high-value food owing to high physical, chemical, and nutritional quality, MWFD has gained interest. Reviews on MWFD were presented by King (1970), Karel (1974), Goldblith (1975), and recently, Fan et al. (2019). The unique volumetric heating of microwaves can overcome the drawbacks of FD while maintaining at least the same quality. However, microwave-freeze-foam drying has not been focused on, except for milk foam drying by MWFD (Sochanski et al., 1990). As explained earlier, the challenges of MWFD are mainly due to the inhomogeneous temperature distribution, arching and/or plasma formation, and hot/cold spot occurrence, consequently leading to poor quality. Therefore, appropriate process parameters and their control are the key to successful implementation of MWFD. Thus, the obtained foam formulations were examined for subsequent drying processes. Importantly, the freezing rate is an important aspect for MWFD rates. Because MFWD rates are limited by mass transfer, the rate of freezing has a significant influence on the subsequent drying rate. Impact of freezing rate may have an adverse effect on the texture of the dehydrated product (Sunderland, 1980); therefore, a -80°C freezing cabinet was used for freezing the samples prior to drying processes.

4.2.1 Definition of process conditions in conventional freeze drying and microwave freeze drying

Comparison of FD vs. MWFD techniques; therefore, at first, conventional FD was established as a reference. The process parameters, namely chamber pressure and temperature including the mass/height of the samples, were considered for both techniques (see subsection 3.3.1). The microwave penetration depth (D) is also important criterion for determining the effective size of the dried material during MWFD (Duan et al., 2010a). Additional process parameters for FD are MW power input for the MWFD process. For FD, local melting was observed above 30°C because of conductive heating through plates. On the other hand, for MWFD, depending on the formulation, the drying process was completed below 40°C. Therefore, it was clear for both drying techniques and all foam formulations that the maximum product temperature was 30°C. According to literature, the temperature of the frozen core can be controlled by chamber pressure. The lower pressures also provide greater driving forces for mass transfer and reduce the fraction of unfrozen water (Sunderland, 1980). Therefore, the chamber pressure was set to 0.1 mbar to prevent plasma discharge in MWFD (Duan et al., 2010a). In MWFD, heat generation is proportional to the dielectric properties of a material (Fan et al., 2019). Indeed, the uniformity of the sample is of great importance because inhomogeneity of the sample can lead to variations in dielectric properties. Note that the dielectric properties depend on the composition moisture content, state of the water, and product temperature; therefore, they simultaneously change during the drying process. The applicable MW power input level has to be defined considering foam characteristics. Roughly, there are three major stages that are critical for determining the MW power input. *In the first drying stage (pre-sublimation stage)*, poor coupling of the frozen samples occurs with the electromagnetic field. The sample is an ice block. Solid water (ice), which is the case in this research, is transparent to microwaves due to the low dielectric loss factor (0.003 at -20°C), and dielectric heating is mainly driven by the organic product itself (Ozcelik and Püschner, 2017). Thereby, applied microwave power input is critical because the product can only absorb a limited amount of energy rather than an excessive amount of energy, which is then reflected. *In the second drying stage (sublimation stage)*, the temperature increases from minus to 0°C, and sublimation heat for ice provided by MW. If the applied MW power density is close to the threshold value this may cause corona discharge. MW energy can be absorbed

by frozen food and may lead to energy dissipation in the dry zone, to the extent that bound water is left behind by retreating sublimation front (King, 1970). This can cause local ice melting and thus hot spot occurrence.

In the final stage (desorption stage), the temperature of the sample increases faster from 0 to 30°C because the unfrozen water in the dried samples in this stage has a higher dielectric loss factor, and product temperature rapidly increases. At this point, the cyclic on-off MW field strategy can be used for regulating the MW power to avoid overheating. The advantages of intermittent application of MW have already been suggested from several researchers (Cao et al., 2017; Dehghannya et al., 2018a; Mothibe et al., 2014; Wang et al., 2013; Wang et al., 2018). Therefore, a temperature controlled on-off cyclic MW profile (See subsection 3.3.2) was applied at a maximum product surface temperature of 30°C.

4.2.2 Drying characteristics of raspberry foam

The primary objective of this study was to investigate the drying characteristics of raspberry foams. After defining the foam formulations and the drying process conditions, the influence of varying hydrocolloid concentrations and MW power input were investigated on drying behavior to determine the optimal MWFD conditions for fruit foams. It was hypothesized that freeze-drying of foamed fruit puree is accelerated by the application of MW energy, resulting in a high-quality product and a specific end product structure.

4.2.2.1 Impact of varying foam formulations

Increasing MD concentrations from 5% to 30% decreased the total drying time, while the effect of varying PPI concentrations on drying time appeared to be minor. Moreover, the drying rates were higher at higher MD concentrations; this behavior can be linked to the fresh foam characteristics attributed to the bubble size and size distribution. Based on the results obtained Ozcelik et al. (2019a), bubble size and size distribution highly affects drying rates in MWFD. However, there was no marked impact of varying PPI concentrations on the drying rates. At higher MD concentrations, most drying processes took place below 0°C; by the time the temperature had risen to 0°C, the residual moisture content was observed to be ~10%. It appeared that the MWFD of the sample with 30% MD led to the most uniform drying. The fact that a high MD

concentration leads to drying with a sublimation phase taking place mostly below 0°C is of great importance as far as the structural integrity of the product is concerned. This relatively uniform drying can also explain the existence of a uniform bubble size distribution at the highest MD level which led to uniform heat distribution. The temperature profiles follow a similar trend for varying PPI concentrations except for the foam with the lowest PPI concentration; the surface temperature of the foam with 2.5% PPI remains longer in the negative range than the other samples. This observation can be attributed to the lower dielectric loss factor, and thus, to the very low energy uptake. On the other hand, it may indicate that the sublimated water vapor is effectively transported to the surface due to the weaker protein network.

4.2.2.2 Impact of varying microwave power input

An increase in MW power resulted in shorter drying times. Higher applied MW power (2.0 W g^{-1}) accelerated heating; the molecules are more excited by MW, thus leading to a higher vapor pressure build-up in the sample which can accelerate drying. However, a linear correlation was not observed between MW power and drying time. It can be seen that doubling the MW power input did not double the drying rate. This is due to the fact that energy absorption of the product, especially in MWFD, is severely limited by the low loss factor of ice and also by the less flexible organic molecules, which can absorb MW energy to a certain extent. The level of MW input power, however, has no significant effect on the surface temperature. For the 30% MD foam, slightly higher temperatures were recorded at higher MW input powers toward the end of drying, and slightly higher temperatures were recorded at higher MW power due to sudden sublimation and subsequent hot spots. It should be noted that in foams with 2.5% PPI at microwave powers of 1.5 and 2 W g^{-1} , hot spots occurred during drying. The reason for this is the very dense foam structure and thus the impeded diffusion of the water vapor formed in the interior of the product. For samples containing higher PPI concentrations (5, 7.5, and 10%), the surface temperature was independent of the changes in MW power. High concentration (10%) of protein led to the most gentle drying at high MW power input due to structural changes enabling a lower resistance against water vapor mass transfer.

In conclusion, there was a high correlation between the foam characteristics and the drying behavior. An overrun above 450% led to gentle drying at all tested MW power

input levels. Foam bubble size and bubble size distribution were found to be well correlated with drying velocity.

4.2.3 Effect of foam manufacturing on the characteristics of fresh foam

It was hypothesized that puree production under atmospheric conditions oxidizes AA and anthocyanins as a result of cell destruction. Unprocessed raspberries had significantly lower AA and anthocyanin contents than raspberry puree. Compared to unprocessed fruit, raspberry puree had 20% higher AA and 18% higher anthocyanin content. A decrease was expected in these nutrients due to oxidation during processing. The production of puree requires disintegration of berry cells via mechanical crushing by straining through a sieve, which releases liquid and solutes from the berries. Anthocyanins are predominantly located in the skins. Their higher content in the puree could be attributed to the disruption of cells and tissue, which releases molecules bound to cell walls. Of the different recipes, the 15% (w/w) MD foam was chosen as an example. The AA and anthocyanin content of the mixture was analyzed before and after foaming to evaluate the influence of the foaming step. After the addition of hydrocolloids to the raspberry puree, the mixture was kept at 4°C for 24 h. During this step, the AA content decreased by 44% and the content of anthocyanins decreased by 40%. The decrease in the content of anthocyanins can be caused by the storage of the sample. In contrast, the foaming step does not have a significant effect on the AA and anthocyanin contents.

4.2.4 Product characteristics of dried raspberry foam

We hypothesized that the quality of the foamed fruit puree (end product) obtained by MWFD will be better or at least comparable to that of puree obtained by FD because the amount of thermal stress induced by these two drying methods is equivalent.

A high quality can be expected with uniform drying. As already mentioned, hot/cold spots directly influence quality. Increasing hydrocolloid concentrations increased the retention of AA. 30% MD foam dried via MWFD at 1 W g⁻¹ retained higher AA compared to FD due to faster drying. However, importantly, faster drying at higher MW power input did not result in high retention because of hot spots. Increasing MD concentration significantly increased the ACY retention.

Based on the previously obtained results, higher PPI (10%) concentration was favored for all MW power inputs because the drying uniformity was assured and the product characteristics such as AA, ACY, color, and texture did not differ at varying MW power inputs. However, varying MD concentrations at 2 W g^{-1} clearly resulted in hot spots which in turn significantly decreased the product quality in terms of AA and color. Overall, no significant differences were observed between the MWFD and FD processes.

In conclusion, uniform drying was obtained at 1.0 W g^{-1} , and the drying time could still be shortened by as much as 70% with the aid of MW energy. Hence, the drying time for MWFD is almost 8-fold less than that of FD. Because of the shorter drying times and high efficiency, the total energy consumption of MWFD was 2.1 kWh per 1 g evaporated water at 1.0 W g^{-1} as compared to 6.2 kWh for FD.

4.3 Storage stability of dried raspberry foam

Storage stability of foods is important in drying processes aimed at preserving foods by removal of water. However, quality deteriorations occur more during the time of storage rather than during the drying process. Therefore, storage stability is an important indicator of success of the drying process as well as the food matrix. Therefore, the stability of both FD and MWFD was assessed together with the composition and structure of different raspberry products. Storage evaluation was performed for 12 weeks of storage, and the samples were stored at 37°C under vacuum-packed conditions.

Regarding water binding, raspberry pulp without hydrocolloids was the most hygroscopic when compared with other samples containing hydrocolloids. There was a significant difference between foamed and non-foamed samples with the same quantity of hydrocolloids. Non-foamed samples were less hygroscopic than foamed samples because foamed structures have a higher volume which provides a higher adsorption capacity. This behavior indicates that the porosity plays an important role in the sorption characteristics. The contents of AA and ACY, which are sensitive to heat and oxygen, were significantly affected by the structure. Raspberry pulp was the least stable during storage. Indeed, 94% of AA was degraded, while 76% of ACY was degraded at the end of storage. In contrast, foamed and non-foamed samples consisting of hydrocolloids were highly stable. Both structures retained 70% of AA and 90% of ACY.

Carbohydrates acting as an oxygen barrier at the lamellae surface wall matrix of the structure during storage therefore act as a protective layer for sensitive substances (Domian et al., 2017). Specifically, MD with a high film-forming capacity contributes to increased stability during storage (Telis and Martínez-Navarrete, 2009). A similar trend was observed for the color of the samples. The color of raspberry puree was significantly degraded, and the puree became dark brown at the end of storage. Because the color of raspberry is related to ACY, this degradation was not a surprising result.

Clearly, hydrocolloids play an important protective role for sensitive substances. The interaction between reducing sugars (fructose or glucose) and amino groups of protein in raspberry, especially at relatively high storage temperature, is called Maillard reaction, which leads to browning.

The considerable instability of raspberry puree was associated with its low glass transition temperature, which was found to be $40 \pm 5^\circ\text{C}$; therefore, a high storage temperature (37°C) might be critical, especially for raspberry puree. In highly hygroscopic raspberry puree, the plasticizing effect of water as well as the low molecular weight sugars reduce the T_g . Therefore, the amorphous structure changes from glassy to rubbery with a marked decrease in the matrix viscosity. Addition of MD with a high T_g value increases the T_g of the foamed and non-foamed samples

Therefore, the foam structure provided better storage stability. Although an open porous structure could generally be expected to lead to higher rates of deteriorating reactions, the matrix composition helped to prevent these reactions.

Regarding the drying techniques based on the obtained results, MWFD led to a storage stability comparable to or even slightly better than the FD method (Ozcelik et al., 2020).



5 Conclusions

In this research we examined the drying of fruit pulps with varying degrees of cell disruption with and without the addition of hydrocolloids with the aim of obtaining fruit foams with intensive sensory impact due to their open pore structure, while at the same time avoiding aroma loss. Foams that are more porous in structure present a larger surface area such that diffusion limitations can be overcome. Furthermore, microwaves can overcome the low heat transfer of convective or conductive heating, and when employed in oxygen-free and low-temperature conditions, product quality including nutritional quality is preserved.

Healthy fruits such as raspberries may be converted into functional food using hydrocolloids and microwave freeze drying (MWFD). The rapid drying process is time and energy efficient and results in dried foams of superior physical (color, texture), chemical (ascorbic acid, anthocyanins) and sensorial quality. The foam matrix structure also ensures storage stability.

A stable raspberry fruit foam made with the addition of hydrocolloids (protein-carbohydrates) benefits from the functional properties of potato protein, which is responsible for the air bubbles. Carbohydrates, namely maltodextrin and pectin, help to stabilize the bubbles. More specifically, maltodextrin controls the size and distribution of the air bubbles through the foam structure. At higher maltodextrin concentrations small and more homogeneously distributed bubbles are obtained. The fruit foam structure can be adjusted by changing the hydrocolloid concentration.

One risk with MWFD is non-uniform temperature distribution which, should it occur, may cause hot spots and a subsequent reduction in product quality. Foam density, bubble size and size distribution have direct impacts on MWFD outcomes. Foam density is the key parameter enabling gentle drying. Crucially, microwave power level must be low (1.0 W g^{-1}) and chamber pressure must be as low as possible (0.1 mbar) to prevent arcing and ensure uniform drying.

The matrix composition of the foam structure plays an important stabilizing role during storage, providing foam stability even at high storage temperatures (37°C).

Microwave freeze foam drying of heat-labile fruits is superior to the popular alternative (FD) in terms of energy consumption and it yields a product of equivalent quality. This study is the first to report on microwave freeze foam drying of fruit pulp utilizing potato protein, a process that provides an efficient way to meet the requirements for innovative products. Our results form the basis for the utilization of microwaves for the drying of fruit pulps, and will be of value in the research environment and food industry.



6 Summary / Zusammenfassung

6.1 Summary

Functional foods have attained significant popularity in the snack food market, not least for their potential positive health benefits. A modern snack food product is not only expected to be practical but also to possess healthy characteristics alongside a crispy texture, attractive appearance and pleasant mouthfeel. Fruits are excellent candidates for health food products. Fruit pulps can be converted into fruit foams by exploiting the functional properties of hydrocolloid (protein-polysaccharide) additives that facilitate the production of dried, long-lasting fruit snacks. The drying of foams in the form of so-called foam-mats is generally carried out using convective hot air (CD) or conventional conductive freeze drying (FD), but both methods have crucial disadvantages. The relatively high temperatures involved during air drying drastically reduce the quality of the product compared to the original food. On the other hand, freeze drying results in products of excellent quality due to the absence of liquid water and low temperatures during processing, but drying times are long and therefore expensive. The aim of this research was to bridge the “drying efficiency gap” without sacrificing quality. To this end, freeze drying assisted by microwaves (MWFD) featuring volumetric heat generation was investigated as an efficient alternative to conventional freeze drying.

First, to characterize a stable foam prior to and during the drying process, raspberry pulp to which varying concentrations of hydrocolloids had been added was examined. Potato protein (PP) acted as a foaming agent, while maltodextrin (MD) and pectin (P) acted as foam stabilizers. Parameters measured were foaming ability, foam stability and bubble size. Homogenization has the potential to cause structural alterations due to tissue and cell disruption that might in turn affect foaming properties and nutritional compounds, therefore, homogenization treatment effects were also investigated. Results from this work informed raspberry foam formulation parameters for the subsequent drying process.

The drying characteristics of raspberry foams via MWFD were explored. The impact of PP and MD formulation and differing microwave power input levels were examined on drying behavior and compared to FD as a reference. A moderate foam volume (overrun above 450%) was found to be advantageous for efficient and gentle drying, providing

a compromise between a high internal surface area and thin lamellae. Under these conditions diffusion limitations, especially toward the end of drying, are circumvented. Drying speed was correlated with MD concentration and hence bubble size and bubble size distribution. MWFD at 1 W g^{-1} yielded a 3–4-fold decrease in total drying time compared to FD. A protein concentration of 10% yielded the gentlest drying at high microwave power input due to structural changes conferring low resistance to water vapor mass transfer. Overall, the creation of an optimal foam with an open pore structure provided faster drying. Augmenting the conventional FD process with MW energy improved efficiency and produced foam with the desired characteristics.

Next, the characteristics of dried raspberry foams produced by FD and MWFD were compared based on physical (color, texture, microstructure) and chemical (ascorbic acid and anthocyanins) factors. Both drying methods resulted in 66%–81% retention of ascorbic acid and 53%–84% retention of total anthocyanins, though higher drying rates were obtained at higher MD concentrations with the result that ascorbic acid and anthocyanin levels were higher. Increasing MD concentration yielded a harder foam texture while increasing PP had the opposite effect. Foam with 30% MD dried at 2 W g^{-1} exhibited color differences which accounted for the formation of hot spots, though uniform drying was obtained at 1 W g^{-1} . Drying time was very significantly shortened with the aid of MW energy to almost 8-fold less than that for FD. MWFD was plainly superior to FD in energy consumption and yielded products of equivalent quality.

Finally, stability and color after storage for 12 weeks at 37°C were investigated. Raspberry puree was prepared with formulations of MD, PP and P. Then, samples of plain raspberry puree (control), and non-foamed and foamed puree containing stabilizer and foaming agent, were dried using MWFD and FD, stored, and their properties compared. The structure of the dried fruit preparation was found to be crucial to preserving quality during storage. The foamed structure provided better storage stability based on the parameters tested. Interestingly, although an open porous structure could generally be expected to lead to more rapid deterioration, the matrix composition helped to prevent unfavorable reactions. After storage, the stability of samples dried via MWFD was comparable to or even slightly better than that of samples produced via FD.

6.2 Zusammenfassung

Von einem Snack-Lebensmittel wird nicht nur erwartet, dass es praktisch ist, sondern neben einer knackigen Textur, einem attraktiven Aussehen und einem angenehmen Mundgefühl auch gesunde Eigenschaften aufweist. Hier erweisen sich Früchte als ausgezeichnetes Ausgangsmaterial für einen gesunden Snack. Aus Fruchtpulpen können unter Ausnutzung der funktionellen Eigenschaften von Hydrokolloid-Additiven aus Proteinen und Polysacchariden getrocknete, haltbare geschäumte Fruchtsnacks hergestellt werden. Die Trocknung von Schäumen in Form von sogenannten „foam-mats“ erfolgt in der Regel mit konvektiver Heißluft (CD) oder konduktiver Gefriertrocknung (FD). Beide Verfahren weisen aber entscheidende Nachteile auf. Die relativ hohen Temperaturen bei der Lufttrocknung mindern die Qualität des Produkts im Vergleich zum Ausgangsprodukt drastisch. Andererseits führt die Gefriertrocknung aufgrund der Trocknung im festen Zustand und niedrigen Temperaturen zu Produkten mit ausgezeichneter Qualität. Allerdings sind die Trocknungszeiten lang und die Trocknung daher teuer. Ziel dieser Arbeit war es, einen effizienten Trocknungsprozess zu gestalten, ohne die Qualität des Endprodukts zu beeinträchtigen. Zu diesem Zweck wurde die Gefriertrocknung mit Hilfe von Mikrowellen (MWFD), die sich durch eine volumetrische Wärmeentwicklung auszeichnen, als effiziente Alternative zur konventionellen Gefriertrocknung untersucht.

Um einen stabilen Schaum vor und während des Trocknungsprozesses zu charakterisieren, wurde zunächst Himbeerpulpe untersucht, der unterschiedliche Konzentrationen an Hydrokolloiden zugesetzt wurden. Kartoffelprotein (PP) fungierte als Schaumbildner, während Maltodextrin (MD) und Pektin (P) als Schaumstabilisatoren eingesetzt wurden. Die gemessenen Parameter waren Schäumbarkeit, Schaumstabilität und Blasengröße. Die Homogenisierung der Fruchtpulpen hat das Potenzial, strukturelle Veränderungen durch Gewebe- und Zellaufschlüsse hervorzurufen, die wiederum die Schaumbildung und die Nährstoffzusammensetzung beeinflussen können. Daher wurde der Einfluss der Homogenisierungsbehandlung auf die Schaumeigenschaften untersucht. Die Ergebnisse dieser Versuche lieferten Parameter für Himbeerschaum-Formulierungen für den anschließenden Trocknungsprozess.

Das Trocknungsverhalten und die Eigenschaften der Himbeerschäume während der MWFD wurden untersucht und mit FD als Referenzverfahren verglichen. Der Einfluss

von PP- und MD-Konzentration und unterschiedlichen Mikrowellenleistungseinträgen auf das Trocknungsverhalten wurde analysiert. Ein moderates Aufschlagvolumen (Overrun > 450%) erwies sich als vorteilhaft für eine effiziente und schonende Trocknung, die einen Kompromiss zwischen einer hohen inneren Oberfläche mit dünnen Lamellen und einer guten Stabilität des Schaums unter Vakuumbedingungen darstellt. Unter diesen Bedingungen werden Diffusionslimitierungen, insbesondere gegen Ende der Trocknung, vermindert. Die Trocknungsgeschwindigkeit wurde mit der MD-Konzentration, der Blasengröße und Blasengrößenverteilung korreliert. Die MWFD bei 1 W g^{-1} ergab eine 3-4-fache Verkürzung der gesamten Trocknungszeit im Vergleich zur FD. Bei hohen Mikrowelleneinträgen zeigten Schäume mit einer Proteinkonzentration von 10% die geringsten Veränderungen während der Trocknung aufgrund der sehr offenen porigen Struktur, die nur einen geringen Widerstand für den Wasserdampftransport darstellt. Insgesamt resultierte die Bildung eines optimalen Schaums mit einer offenen Porenstruktur in einer schnelleren Trocknung. Die Ergänzung des konventionellen FD-Prozesses mit MW führte daher zu einem effizienteren Prozess und der Herstellung von Schäumen mit den gewünschten Eigenschaften.

Anschließend wurden die Eigenschaften der mittels FD und MWFD hergestellten getrockneten Himbeerschäume anhand physikalischer (Farbe, Textur, Mikrostruktur) und chemischer (Ascorbinsäure und Anthocyane) Faktoren verglichen. Beide Trocknungsmethoden führten zu 66%-81% Retention der Ascorbinsäure und 53%-84% Retention der gesamten Anthocyane. Bei höheren MD-Konzentrationen wurden höhere Trocknungsraten erzielt, sodass die Ascorbinsäure- und Anthocyan Spiegel höher waren. Die Erhöhung der MD-Konzentration führte zu einer härteren Schaumstruktur, während die Erhöhung von PP den gegenteiligen Effekt bewirkte. Der Schaum mit 30% MD, der bei 2 W g^{-1} getrocknet wurde, zeigte Farbunterschiede, die die Bildung von Hot Spots verursachten, während ein Mikrowelleneintrag von 1 W g^{-1} zu einer gleichmäßigen Trocknung führte. Die Trocknungszeit konnte mit Hilfe von MW-Energie sehr deutlich auf ca. $1/8$ gegenüber der FD verkürzt werden. MWFD war der FD in Bezug auf den Energieverbrauch deutlich überlegen und lieferte Produkte mit vergleichbarer Qualität.

Schließlich wurden Stabilität und Farbe nach 12-wöchiger Lagerung bei 37°C untersucht. Himbeerpüree wurde mit Formulierungen von MD, PP und P hergestellt. Anschließend wurden Proben aus reinem Himbeerpüree (Kontrolle) und ungeschäumtem

und geschäumtem Püree, die Stabilisator und Schaumbildner enthielten, mittels MWFD und FD getrocknet, gelagert und ihre Eigenschaften verglichen. Die Struktur der Trockenfruchtzubereitung erwies sich als entscheidend für die Erhaltung der Qualität während der Lagerung. Die geschäumte Struktur sorgte für eine bessere Lagerstabilität basierend auf den getesteten Parametern. Interessanterweise, obwohl eine offenporige Struktur im Allgemeinen zu einem schnelleren Abbau wertgebender Inhaltsstoffeführen könnte, half die Matrixzusammensetzung, ungünstige Reaktionen zu verhindern. Die Lagerstabilität der mit Hilfe von MWFD getrockneten Proben war vergleichbar oder sogar etwas besser als die der mittels FD hergestellten Proben





7 Wider perspectives and future work

The research presented in this thesis has raised more questions than it has answered. There are several lines of research arising from this work which should be pursued.

Firstly, from chapter 3.7, the storage behavior of varying structures was studied in this thesis. The foam structure was the most stable owing to the hydrocolloids and more specifically because of protective role of maltodextrin. The intention was to thoroughly investigate the effects of varying hydrocolloid concentrations on storage stability of raspberry foams to evaluate quality parameters, namely ascorbic acid, plant bioactives, texture, and color. It was already reported that higher storage stability of dried products with low molecular weight sugars can be achieved by increasing the glass transition temperature. In future work, we hope to clarify the protective role of carbohydrates and analyze whether their concentration increases the storage stability of foams. Furthermore, we plan to examine the samples under various storage conditions as such at room temperature and at 4°C as well as under vacuum and non-vacuum packed storage to provide another perspective to the published work.

Another aspect is to assess the foams for a longer period of time. We analyzed raspberry foams samples stored for 12 weeks, and our results revealed good quality of product. However, because snack foods are expected to have a long shelf life, long term storage can provide an additional insight both for science and the industry.

This interpretation all together will provide a wider perspective to understand the storage behavior of the dried raspberry foams. Once this is completed, the understanding of the storage behavior of fruit foams will be greatly improved and will be useful from the industrial perspective for producing snack foods.

A second line of research is to investigate the aroma compounds in the different structures obtained from raspberry. As has been already emphasized earlier in this thesis, dried foams are expected to disintegrate very quickly upon contact with saliva in the mouth, leading to a spontaneous flavor release. In contrast, processing potentially causes greater aroma losses. Due to the larger surface area, drying of foam structures can lead to greater aroma loss than that of the whole fruit. In addition, a foamed fruit puree may alter flavor release because mechanical stress of cell disruption can cause an increase in formation of other aroma components compared with whole fruit.

Thereon, additional drying stress can also affect the aroma profile of both foamed raspberry puree and condensate, which are different from whole fruit. Volatile compounds can easily be entrained through the vacuum environment, inducing aroma loss of the dried material (Álvarez et al., 2000). In contrast, loss can be recovered from the condensate. In addition to vacuum stress, the applied microwave energy can cause further stress on the aroma compounds. The impact of microwave drying on raspberry aroma-active compounds and the recovery of aroma-active compounds in the condensate have not been studied till date. Therefore, another important aspect is to understand the final aroma profile of dried products containing protein-polysaccharides as well as whether the incorporation of microwaves into FD can cause undesirable aroma losses.



8 References

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9 Appendix

The publications and presentations are listed in chronological order. Publications being part of this thesis are marked in bold.

9.1 Peer reviewed publications

- 1- Dachmann, E., Hengst, C., **Ozcelik, M.**, Kulozik, U., & Dombrowski, J. (2018). Impact of Hydrocolloids and Homogenization Treatment on the Foaming Properties of Raspberry Fruit Puree. *Food and Bioprocess Technology*, 111(4), 570. <https://doi.org/10.1007/s11947-018-2179-1>
- 2- **Ozcelik, M.**, Ambros, S., Heigl, A., Dachmann, E., & Kulozik, U. (2019a). Impact of hydrocolloid addition and microwave processing condition on drying behavior of foamed raspberry puree. *Journal of Food Engineering*, 240, 83–98. <https://doi.org/10.1016/j.jfoodeng.2018.07.001>
- 3- **Ozcelik, M.**, Heigl, A., Kulozik, U., & Ambros, S. (2019b). Effect of hydrocolloid addition and microwave-assisted freeze drying on the characteristics of foamed raspberry puree. *Innovative Food Science & Emerging Technologies*, 102183. <https://doi.org/10.1016/j.ifset.2019.102183>
- 4- **Ozcelik, M.**, Ambros, S.; Morais, S.I.Freitas; Kulozik, U. (2020): Storage stability of dried raspberry foam as a snack product. Effect of foam structure and microwave-assisted freeze drying on the stability of plant bioactives and ascorbic acid. In *Journal of Food Engineering* 270 (109779). DOI: 10.1016/j.jfoodeng.2019.109779.

9.2 Book chapters

- 1- Ozcelik, M., & Püschner, P.-A. (2017). Microwave plant requirements and process control for advanced applications. In H. Schubert & M. Regier (Eds.), *Woodhead Publishing Series in Food Science, Technology and Nutrition. The microwave processing of foods* (pp.350–380). Oxford: Woodhead Publishing. <https://doi.org/10.1016/B978-0-08-100528-6.00016-4>.

9.3 Patents

- 1- Ozcelik, M., Haboglu M.F., A manufacturing method that can be used for the production of stuffed pasta. EP2791603 (A2)-2014-10-22, patent.

9.4 Non reviewed publications

- 1- Ozcelik, M., Gentle microwave vacuum drying for fresh fruits, 14th International Conference on Microwave and High Frequency Heating, Nottingham, UK, September 17-19, 2013.
- 2- Ozcelik, M., Masatcioglu, M.T., Koksel, H., Utilization of drum wheat flour in extrusion cooking, 15th International Cereal and Bread Congress, Istanbul, Turkey, April 18-21, 2016.
- 3- Ozcelik, M., Ambros, S., Kulozik, U. (2017): Application of texture analysis method to foamed fruit snacks. Jahresbericht zur Milchwissenschaftlichen Forschung am Zentralinstitut für Ernährungs- und Lebensmittelforschung (ZIEL). ISBN 978-3-947492-00-8, 63-65.
- 4- Ozcelik, M., Ambros, S., Kulozik, U., Microwave-freeze-drying of fruit foams for the production of healthy snacks, IMPI 52nd Annual Microwave Symposium, Long Beach, California, USA, June 26-28, 2018.
- 5- Ozcelik, M., Ambros, S., Kulozik, U., Microwave-freeze-drying of fruit foams for the production of healthy snacks, 21st International Drying Symposium, Valencia, Spain, September 11-14, 2018.
- 6- Ozcelik, M., Deborah Kracheletz, Sabine Ambros, Kulozik, U. (2018). Dielectric properties of raspberry foams. Jahresbericht zur Milchwissenschaftlichen Forschung am Zentralinstitut für Ernährungs- und Lebensmittelforschung (ZIEL). ISBN 978-3-947492-10-7, 70-72.

9.5 Oral presentations

- 1- Ozcelik, M., Gentle microwave vacuum drying for fresh fruits, 14th International Conference on Microwave and High Frequency Heating (AMPERE), Nottingham, UK, September 17-19, 2013.
- 2- Ozcelik, M., Masatcioglu, M.T., Koksel, H., Utilization of durum wheat flour in extrusion cooking, 15th International Cereal and Bread Congress, Istanbul, Turkey, April 18-21, 2016.
- 3- Ozcelik, M., Ambros, S., Kulozik, U., Microwave-freeze-drying of fruit foams for the

production of healthy snacks, IMPI 52nd Annual Microwave Symposium, Long Beach, California, USA, June 26-28, 2018.

- 4- Ozcelik, M., Ambros, S., Kulozik, U., Microwave-freeze-drying of fruit foams for the production of healthy snacks, 21st International Drying Symposium (IDS), Valencia, Spain, September 11-14, 2018.
- 5- Ozcelik, M., Ambros, S., Kulozik, U., Microwave-freeze-drying of fruit foams for the production of dried snacks, Process Net Annual Meeting, Jahrestreffen der Fachgruppen Lebensmittelverfahrenstechnik, Rheologie und Trocknungstechnik, Lausanne, Switzerland, March 5-7, 2019.

9.6 Professional service

- 1- Reviewer for Journal of Food Chemistry, Elsevier.
- 2- Reviewer for Journal of Food Processing and Preservation, John Wiley&Sons.
- 3- Reviewer for Journal of Drying Technology, Taylor&Francis.
- 4- Reviewer for Journal of Langmuir, American Chemical Society.

Abstract

Freeze drying of whole fruits takes a long time and results in sensorially unattractive quality. Instead, fruits were macerated to produce pulps. Fruit pulps were converted into foams stabilized by hydrocolloids (protein-polysaccharide) and drying process enhanced by microwave heating was applied. Both the foam structure as well the vacuum microwave drying process led to a tremendous acceleration of water removal due to faster heat and mass transfer. The stabilization of foamed pulp was preserved throughout the process so that a new product concept result from this research.

