1 Introduction

1.1 The structure of instant coffee

Freeze-dried food products usually present an intricate internal porous structure. This structure is dependent on the type of pores forming it, where usually two types can be differentiated: 1) pores, left after sublimation of ice crystals and 2) gas pores, created by foaming the product before freezing. While gas pores show a spherical shape, ice crystal pores are more cylindrical, sometimes in the shape of platelets. Depending on the ratio between these two pore types and the overall porosity, predominantly closed or open-pore networks or a mixture of both can be created. In Figure 1.1 scanning electron microscopy images of freeze-dried coffee are shown. The structure of all materials is completely different depending on the process of creation and the applied process parameters.

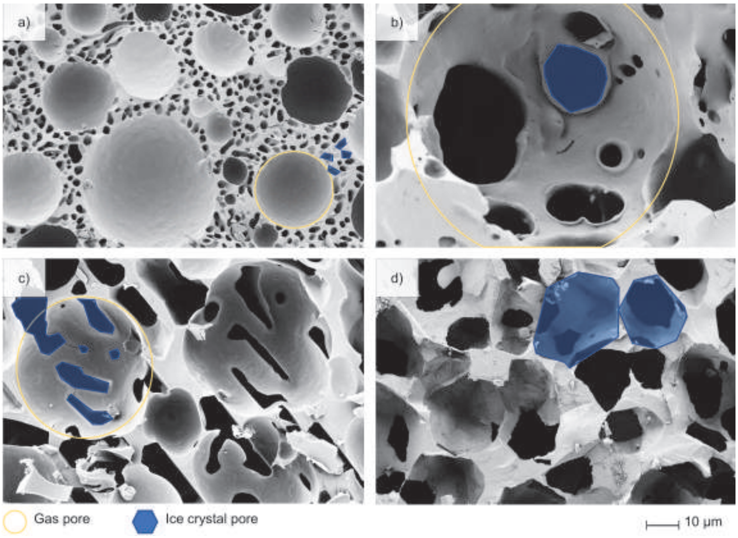

Figure 1.1: Freeze-dried coffee granules: a) with nitrogen, 100 % overrun, no interconnection between gas pores and ice crystal pores, b) with carbon dioxide, rapid drying, c) with nitrogen, 100 % overrun, 1 % polysorbate 20 and d) no foaming, only ice crystal pores. Ice crystal pores and gas pores are shown exemplarily.

Figure 1.1 a) shows gas pores between 20 µm to 50 µm, ice crystal pores are with 1 µm to 2 µm rather small. While the ice crystal pores create an open pore network, it is shown that the gas pores are not linked and therefore most of them are closed pores. Ice crystal size and pore size can be increased as shown in Figure 1.1 b) by changing the process gas, the freezing procedure or the drying conditions. Here an open pore structure can be observed. In Figure 1.1 c) the addition of a surfactant improves the pore interconnections, creating flat pores, where ice crystal pores seem to merge during the drying. Figure 1.1 d) shows the internal structure of an instant coffee granule, where only enlarged ice crystal pores in the range of 10 µm create an open pore structure. Thus, the aim of this work is to create an internal open pore network that enhances the mass transport. Further, the relationship between internal structure parameters and reconstitution kinetics needs to infered, with the final aim of improving the overall freeze-drying process and the product.

1.2 The process of soluble coffee production

The structure of the soluble coffee is dependent on the production process. After blending, roasting, milling and extraction the structure of the final soluble coffee powder gets defined. In the first step, the coffee extract gets partially frozen. Ice crystals are nucleated in a scraped surface heat exchanger (SSHE) and the coffee slurry is gassed. The process gases usually are either carbon dioxide or nitrogen, due to their cheap availability and food compliance. The foam produced is very dependent on the gas properties, especially its solubility and surface tension.

After controlled nucleation of ice crystals and the expansion of the coffee extract by injection of gas, the pumpable coffee slurry is frozen in a thin cake of several millimeter height under controlled conditions. The cake is broken, milled and sieved to the defined particle size and the granules are subsequently freeze-dried under vacuum. After freeze-drying, a free-flowing soluble coffee product is achieved which goes into packaging and can be reconstituted by the consumer. In Figure 1.2 the process of soluble coffee structuration and reconstitution is shown. The blending, roasting, bean milling and extraction is not part of this work and can be found elsewhere. As an alternative to freeze-drying also spray drying can be used, where the coffee extract is directly spray-dried and after structured in an agglomeration process for better handling and reconstitution. The spray drying process is not part of this work and was investigated and improved by other authors (Villegas-Santiago et al., 2019; Antonyuk, 2014; Al-Mansour et al., 2011). A comparison of the properties of both technologies was already supplied by Ghirişan et al. (2017). A combination of both processes, the spray-freeze-drying was also investigated by other authors (Padma Ishwarya et al., 2015; Anandharamakrishnan, 2019; Deotale et al., 2020).

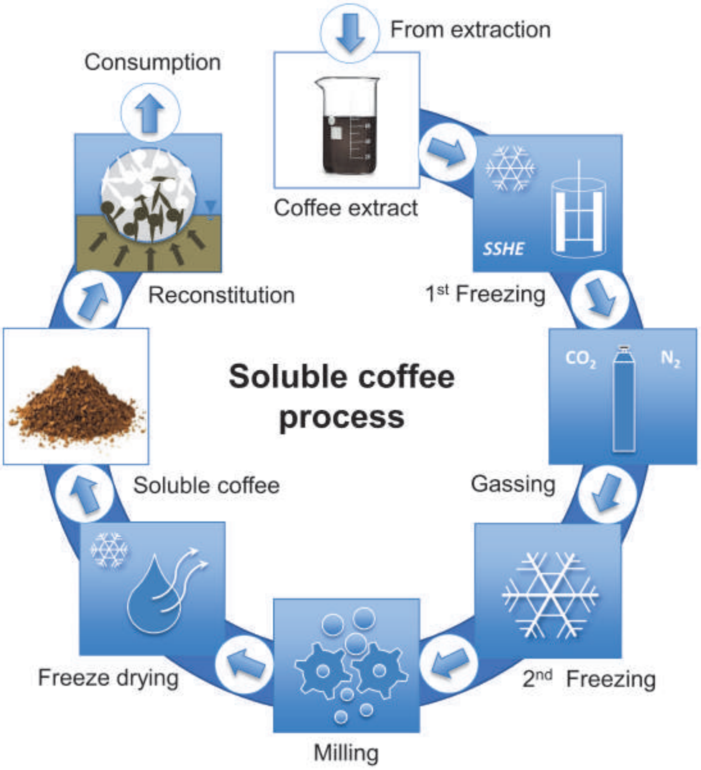

Figure 1.2: Process overview of soluble coffee production with focus on structuring and drying of the coffee extract and the final reconstitution of the instant powder.

The relevance of each production step on the structure and reconstitution properties is shown in the following sections. Specific attention is paid to the freezing process, which determines the size and shape of the ice crystals. The understanding and the design of the ice crystal network is crucial to achieve fast drying and reconstitution of instant coffee particles.

1.3 Freezing of concentrated solutions

As shown in the previous chapter the internal porous structure is dependent on ice crystal pores, gas pores and the interaction between each other. The following chapter deals with the mechanisms of ice crystal formation and growth for internal structure modification, along with a description of the necessary crystallization devices and a comparison with the current state of the art.

1.3.1 Physics and structure of crystals

The morphology of ice is manifold, depending on the way the ice crystals were formed and grown and the environmental conditions (e.g. temperature, pressure, presence of solutes) at which they were exposed. Since the morphology of ice plays a key role in food products and their processing, precise knowledge of the process parameters influence on ice morphology is needed. While ice cream is favored by small, rounded crystals for a good texture and mouthfeel (Cook et al., 2010; Donhowe et al., 1996; Petzold et al., 2009), an increase on ice crystal size is reportedly beneficial for the freeze-drying process, especially during the primary drying step (Searles et al., 2001; Petzold et al., 2009; Hottot et al., 2004). The freezing of water consists out of two steps: (1) decreasing the temperature below the melting temperature achieving a supercooling of the solution and (2) a first-order phase transition from liquid water to solid ice. During the crystallization three phenomena are observed: (1) the nucleation of ice crystals, where molecules order from the solution to a lattice structure, (2) crystal growth, where water adsorbed on the surface of a nucleus is freezing, progressively increasing the size of the crystal and (3) the recrystallization of the structure to minimize the energy state, e.g. by decreasing the surface of the crystal (Petzold et al., 2009). Thus, before a nucleus is created, the solution needs to be below melting temperature. If solutes are present, like in almost all food products, freezing-point depression needs to be considered. As soon as supercooling of the solution is observed, water molecules begin to attach loosely together. This group of molecules is very unstable and tends to break easily. The higher the supercooling the higher the chances for water molecules to order into a lattice, given the energy barrier to overcome at this sub-nucleus size. As soon as the grouped water molecules reach a critical size a stable interface is formed, resulting in a rapidly growing of this nucleus. Crystal growth is controlled by the ability to remove latent heat from the surface of the crystal and by the rate of mass transfer which includes the diffusion of water towards the crystal and the diffusion of solute away from the crystal surface. In systems which stay after freezing above glass transition temperature ice crystals are not stable in size and form due to the possible mobility of water and solute molecules and recrystallization can take place (Petzold et al., 2009; Schwartzberg, 1990). Recrystallization will be further discussed in subsection 1.3.3.

1.3.2 Crystallization in scraped surface heat exchangers

Controlled freezing is necessary to achieve a homogeneous crystallization of the ice crystals within the raw solution with maximal freeze concentration. Such requirement is mainly due two reasons: On the one hand, maximal freeze concentration will lead to the maximal amount of ice crystals, which is crucial to increase pore interconnections, resulting in an open pore network. On the other hand, it ensures the highest possible glass transition temperatures of the material, which allows higher temperature during primary drying without structural collapse, which enables faster drying kinetics. Freezing directly influences the product morphology in terms of interconnecting pore size and porosity and is therefore directly linked to the drying time. Since precooled tray freezing ususally results in broad ice crystal size distributions (Searles et al., 2001), the use of a scraped surface heat exchanger (SSHE) becomes paramount to finely control the crystal size. SSHE are very versatile in terms of use, being able to handle very viscous products in solution and suspension form, while keeping good heat transfer and mixing properties. A scraped surface heat exchanger consists of a barrel, where the walls can be cooled or heated by a double jacket. The radial scraper, consisting out of two or more blades, is continuously brushing against the wall. For crystallization processes, the wall is cooled by refrigerant and dendritic ice crystals nucleate at the wall. These ice crystals are continuously scraped off by the blades and broken by the forces of the stirrer. Due to the presence of a temperature gradient from the wall to the center of the device, small fragments start to melt, cooling down the solution. Bigger fragments tend to recrystallize to disc-shaped, hexagonal shape since it is energetically favored (Rao et al., 2006; Donhowe et al., 1996; Cook et al., 2010). The process is schematically shown in Figure 1.3. Petzold et al. (2009) argued that the crystal form is essential for high drying rates. Large dendritic crystals which are formed at low freezing rates result in higher mass transfer. The disc-shaped crystals are potentially less favorable for the freeze-drying process, but they are industrially easier to control and energetically more favorable.

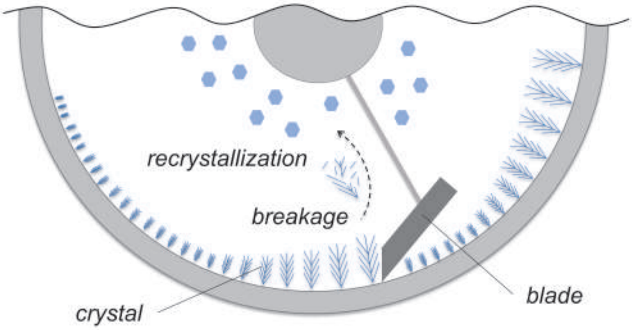

Figure 1.3: Crystallization process in a scraped surface heat exchanger. Crystals are nucleating and growing from the wall into the solution, are scraped off and broken by the blades, and tend to recrystallize towards the center of the barrel.

SSHEs for freezing are frequently used in the food industry. Margarine, coffee and tea extracts, sorbets, and ice cream are the moste renown products. For most freezing applications the ice crystal size plays an important role but the size requirements varies between the applications. For ice cream and sorbets small ice crystals are favored to ensure a smooth mouthfeel and a good creaminess. Thus, the parameters to control the crystal size are well known. The type of dasher, the dasher or scraper speed, the cooling rate, the degree of supercooling at the wall, residence time and throughput are important parameters to control the crystal size (Hottot et al., 2004; Cook et al., 2010; Petzold et al., 2009; Russell et al., 1999). Small crystals and narrow crystal size distributions are achieved by short residence times, high cooling rates, and moderate scraping speed. Long residence times, high shear rates, and low cooling rates are favorable to increase particle size, where especially the effect of recrystallization plays an important role (Rao et al., 2006). The size and amount of crystals are strongly dependent on the temperature difference between wall and solution. Common products such as ice cream have temperatures of around −6 °C to −7 °C when leaving the SSHE since viscosity is increasing dramatically with progressing crystallization. Below this temperature, the heat intake by agitation is greater than the amount removed by the heat exchanger. The use of higher cooling rates is a potential solution to circumvent this limitation. At these temperatures around 50 % of the available water is frozen, depending on the initial concentration and the freezing temperature of the product.

1.3.3 Hardening, crystal growth and recrystallization

After the first freezing step in the SSHE, a second freezing or hardening of the slurry, is usually performed at a temperature between −40 °C to −45 °C with the help of an air blast freezer. The goal is to freeze-concentrate the thinly distributed slurry to the maximum and create a stable intermediate product. 75 % to 80 % of the water is frozen after this stage, depending on the freezing kinetics. The rest of the water is the so-called bound water or non-freezable water which stays in the frozen coffee matrix. For more information refer to chapter 1.4.1 where the state diagram is further explained. The shape and size of the crystals during this step are dependent on the freezing rate (Sagara, 2001; Petzold et al., 2009). High freezing rates lead to a second crystallization step and usually results in a bimodal crystal size distribution (Levin et al., 2021). Low freezing rates lead to crystal growth since the diffusion of the water to the surface of existing ice crystals is fast enough, but not completely limited by the viscosity of the cryo-concentrated slurry.

Ice crystal size can also be influenced during storage where either elevated temperatures or temperature fluctuations lead to an increase in ice crystal size (Petzold et al., 2009). The closer the storage temperature is to the melting temperature or the higher the amplitude of the temperature fluctuations, the faster recrystallization takes place (Donhowe et al., 1996; Hartel, 1996) since the recrystallization rate is strongly affected by the molecular mobility of the water and solute molecules (Ablett et al., 2002; Adapa et al., 2000). For the recrystallization of ice in food systems migration and accretion of ice crystals were found to be the two driving mechanisms (Adapa et al., 2000), where migration or so called Ostwald ripening was found to be the dominant factor (Schwartzberg, 1990; Kahlweit, 1975). While accretion describes the merging of two adjacent ice crystals, Ostwald ripening is the melting of the smaller ice fraction due to their reduced melting temperature and growth of the larger ones. The dynamic of the recrystallization during Ostwald ripening can be described by:

$$d_{50} = d_{50,0} + \dot{\psi} \cdot t^{b}, \tag{1.1}$$

where d_{50} is the median pore diameter after a certain time t, $d_{50,0}$ is the median diameter before temperature fluctuations are applied, $\dot{\psi}$ is the dimensionless recrystallization rate and b is the power law-exponent. The power law-exponent was found to be in the range of 0.33 to 0.5 but is strongly dependent on the studied food system composition (Donhowe et al., 1996). The ice crystal size was determined inline by focused beam reflectance measurements (FBRM) in scraped surface heat exchangers (Arellano et al., 2012; Haddad Amamou et al., 2010) and during storage (Ndoye et al., 2015), by light microscopy in a cold room (Donhowe et al., 1996) or by indirect measurements of the pore size after conventional freeze-drying by SEM (Pardo et al., 2002).

Sagara (2001) found enhanced vapor permeability during freeze-drying with increasing ice crystallization time. According to their results, liquid material should be frozen slowly so that straight ice columns are formed directed in parallel to heat and mass transfer direction during the later drying process. In the pharmaceutical industry, directional freezing is frequently used (Qian et al., 2011). Searles et al. (2001) and Konstantinidis et al. (2011) found similar results stating that increased crystal size by controlling the ice nucleation temperature leads to an improvement of primary drying time. Kochs et al. (1991) confirmed that slow freezing rates reduce the primary drying time significantly. After hardening the thin frozen cake is broken, ground and all fines are removed before freeze-drying.

1.4 Foaming of concentrated solutions

The foam formation is essential for the production of freeze-dried instant coffee in order to reduce the energy consumption of the process and increase the throughput. Usually the coffee liquor is concentrated to 45 %w/w to 50 %w/w coffee but the amount of ice crystals in high concentrated frozen coffee is not sufficient to create an open pore network and drying would be too slow and the resulting product would surpass the density requirements for proper packaging and good reconstitution. The foaming allows a tuning of the porosity of the dried material as well as the desired bulk density for the packaging. Nevertheless, the structure of pores created by foam formation are differing from the pore structures that are left behind by ice crystals after drying. Thus, in the following section an overview of foam formation is given.

1.4.1 Physics and structure of foams

A foam is classically defined as a dispersion of gas in a liquid or solid that is thermodynamically unstable due to its high surface area (Hunter et al., 2008). This structure is affected by surface and gravitational forces separating the foam in a pure liquid phase at the bottom and a lighter gas phase at the top of the container. This effect can be reduced by increasing the viscosity of the continuous liquid phase or by lowering the surface tension at the gas-liquid interface. Several mechanisms are known to destabilize the foam (Walstra, 1989), mainly:

1. Ostwald ripening
2. Creaming / Liquid drainage
3. Coalescence
4. Flocculation

An overview of the mechanisms is shown in Figure 1.4. The mechanisms are explained in detail in the following.

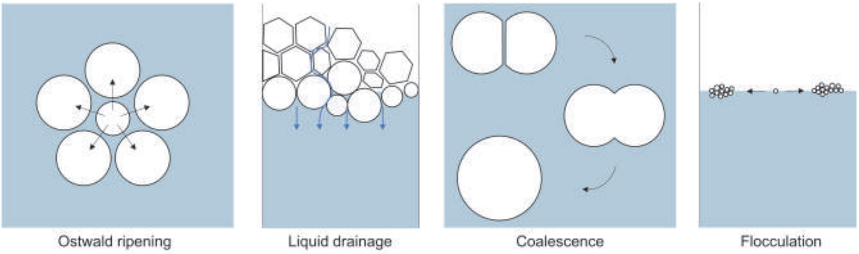

Figure 1.4: Mechanisms that destabilize foams: Ostwald ripening, liquid drainage, coalescence of gas bubbles and flocculation. The image was adapted from Denkov et al. (2020).

Ostwald ripening

This mechanism can be described as the growth of larger bubbles at the expense of smaller ones. This effect can be observed due to the higher solubility of a gas in small bubbles due to the higher pressure which can be expressed by the Kelvin equation (Powles, 1985), assuming the gas phase as ideal and the liquid phase as incompressible:

$$R \cdot T \cdot ln\left(\frac{p_{bs}}{p_{nbs}}\right) = \frac{(2 \cdot \gamma \cdot V_{mol})}{r}, \tag{1.2}$$

where R is the ideal gas constant, T is the temperature, p_{bs} and p_{nbs} are the vapor pressure over a bent surface and non-bended surface, respectively, γ is the interfacial tension, V_{mol} is the molar volume of the fluid and r is the radius. Same follows from the Young-Laplace equation (Young, 1805; Dullien, 2015), describing the difference in pressure Δp in dependence of surface tension σ and radius r of the bubble:

$$\Delta p = \frac{2 \cdot \sigma}{r}, \tag{1.3}$$

Therefore, smaller bubbles tend to decrease in size, whereas the dissolved gas diffuses to the bigger bubbles and leads to bubble growth. The shrinkage of the smaller bubbles depends strongly on the type of gas and the presence of surface-active components. Carbon dioxide foams are usually less stable because the solubility in water is comparably high (Cooney, 1974). In comparison, nitrogen shows a solubility decrease of fifty times resulting in much stabler foams (Saint-Jalmes, 2006).

Creaming and liquid drainage

Both effects are based on gravitational and capillary forces (Sun et al., 2008). Where creaming describes the rise of bubbles to the foam surface due to buoyancy effects, liquid drainage is the sinking of the liquid phase to the bottom of the foam (Saint-Jalmes, 2006). Therefore, at the top of the foam bubbles are packed closer and porosity is increasing while at the bottom a liquid phase builds up over time. For spherical bubbles in diluted dispersions, the creaming velocity v can be described by the Stokes equation (Lamb, 2006):

$$v = \frac{2g \cdot (\rho_l - \rho_g)}{9\eta} \cdot r^2, \tag{1.4}$$

where g is the acceleration of gravity, ρ_l and ρ_g are the density of the liquid phase and the gas phase, respectively, η is the viscosity of the continuous phase and r is the bubble diameter.

Coalescence

Coalescence describes the merging of two bubbles into one and is in most cases the dominant mechanism for foam destabilisation (Hunter et al., 2008). It occurs when the film between two bubbles gets thin enough to surpass the bubble surface tension. Reasons for the rupture of the lamella can be found during the foam formation (e.g. by high bashing of the foam, particles in the foam) or during the aging of the foam, where it starts to dry. For foams, the effect of coalescence takes place in parallel with the Ostwald ripening, creaming, and liquid drainage effects and is therefore quite complex and not fully understood (Langevin, 2019).

Flocculation

It describes the assembly of gas bubbles in groups over a long time due to surface energy effects and is occuring in dilute foam systems (Hunter et al., 2008). For dry foams, flocculation is of less interest since the bubbles are already closely packed.

1.4.2 Foaming process

Foams can be generated by two processes: (1) by supersaturation of a liquid with gas (e.g. under high pressure) and instant release of the pressure to reduce gas solubility and form gas nuclei or (2) by mechanical forces and high shear rates (e.g. by blowing gas into the liquid through narrow channels or dashing a gas into a liquid phase (Walstra, 1989)). A famous example of a food product, which creates a foam by supersaturation, is beer. In most processes, mechanical forces are used as in ice cream or sorbet production. The incorporated air in ice cream is typically around 100 % to 120 % overrun (Hartel, 1996), where sorbets usually reach up to 60 % overrun (Bolliger et al., 1998). This percentage is defined by the amount of gas (air) divided by the mass of all further ingredients. For solutions, it can be described by:

$$OR = \frac{V_g}{V_l}, \tag{1.5}$$

where OR is the overrun, V_g is the gas volume and V_l is the liquid volume. For food products like ice cream or instant coffee, the incorporation of gas takes place directly in the SSHE, in parallel to the crystallization process (Hartel, 1996).