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Microencapsulation by Spray Drying

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3 Microencapsulation by Spray Drying

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3.1 INTRODUCTION

Spray drying is a well-established process to encapsulate volatile, sensitive, and functional ingredients. The transformation from a liquid medium into a dry powder stabilizes the sensitive core materials in a closed matrix of the shell material. Since the core material is homogeneously distributed within the encapsulating matrix, the resulting type of capsule is usually referred to as matrix capsule. Air inclusion may occur in the particle in the form of a central void (Figure 3.1). With respect to applications in the food or pharmaceutical sector, spray drying of an emulsion is performed to encapsulate non–water-soluble core materials such as oils, vitamins, or flavors. Depending on the type of flavor, the process results in a high flavor retention above 95%, and a similar retention for encapsulation of nutritional oils.

Encapsulation by spray drying offers protection to adverse environmental conditions such as oxygen or light as well as protection against undesired reactions with other constituents or ingredients. For this purpose, a carbohydrate-based matrix is usually used. A critical issue related to the process is to preserve the physical properties of the emulsion during drying. Since microcapsules are frequently redissolved before ingestion, the dried emulsions need to be physically stable after dissolution. To create a certain functionality, more sophisticated structures may be build up in the emulsion-like bilayer formation at the interface or creation of fibrillar structures, and these structures should not be negatively affected during spray drying.

The release mechanism of carbohydrate-based matrix capsules prepared by spray drying is solvent activated, which means that the powder readily dissolves upon contact with water. This release mechanism has limited the range of applications to dry products in the past. However, through selection of the matrix constituents and buildup of more sophisticated physical structures, a controlled release of encapsulated ingredients can be achieved. This is of particular importance with respect to the release of pharmaceutical or food ingredients, which need to be delivered to specific parts of the gastrointestinal system.

3.2 GENERAL DESCRIPTION OF THE PROCESS OF SPRAY DRYING

Spray drying is a continuous process, which can be described in four stages. The first stage is the atomization where the liquid feed is transformed into droplets, the spray. By creating droplets, the surface of the fluid is greatly increased, which is important to ensure a fast and efficient evaporation...
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of the moisture from the drying droplet. The impact of droplet size reduction on the surface area is shown in Table 3.1.

The second stage is the spray-air contact when droplets meet the drying medium. Most commonly hot, dry air is used as drying medium. In case of very sensitive or reactive materials, nitrogen may be used. At this stage, the best conditions of contact between droplets and air must be achieved. Evaporation or drying, and thus particle formation within the drying chamber, is the third stage of the process followed by the product separation. The products can be directly recovered from the bottom of the drying chamber or in the case of fine particles through separation from the air with cyclones. Depending on the chemical and physical properties of the feed, the dryer design and operation, products can be powders, granules, or agglomerates. The typical setup of a one-stage spray drier is given in Figure 3.2.

In a two-stage drying process, final drying of the product is performed in a fluidized bed. Since the last traces of residual moisture are difficult to remove, the particles are dried to a moisture content of 2%–5% above the final moisture content in the first stage. The remaining moisture is removed during fluidized bed drying, where the product is in contact with dry air at moderate temperature. Apart from a more efficient drying process, particle agglomeration can be achieved, since particle collisions occur in the fluidized bed with sufficient moisture available for agglomeration through interparticle bridges. Three-stage drying involves transfer of the second drying stage into the base of the spray drying chamber and having the final drying and cooling conducted in the third stage located outside the drying chamber.

3.2.1 Atomization

Atomizer and nozzles are used to supply energy to the feed to form a spray. The feed can be a solution, emulsion, suspension, or paste, which needs to be pumpable. There are different types of
atomizers; among them the most common types are pressure nozzles, two-fluid nozzles or pneumatic nozzles, and mechanical atomizers (Figure 3.3). The selection of an atomizer depends on the product requirements. On one hand the physical properties of the feed need to be taken into consideration, while on the other hand the selection of an atomizer may affect the final particle properties. In general, a high viscosity, high total solids content, high surface tension, and high feed rate lead to an increase in droplet size. Finally, economic aspects play a crucial role in industrial applications. Mechanical atomization is less expensive than two-fluid nozzles since the supply of pressurized air in the latter system affects the costs in use.

Pressure nozzles are usually operated with a feed pressure of 30–200 bar and lead to a certain flow velocity at the orifice of the nozzle. The feed is forced into rotation in a swirl chamber within the nozzle resulting in a cone-shaped spray at the nozzle orifice. It readily integrates into a spray as it is unstable. An increase in the feed rate leads to a less homogeneous and coarse spray with an increase in the width of the droplet size distribution. The mean size of droplets is indirectly proportional to pressure up to 690 bar (680 atm) and directly proportional to feed rate and feed viscosity. Working with pressure nozzles results in a particle size diameter between 50 and 500 µm.

Two-fluid nozzles or pneumatic nozzles have pressurized air or steam as energy supply, whereas the feed has a comparably low velocity. Operating pressure of two fluid nozzles is low, up to 7 bar. The feed and the pressurized air are separately conducted to the nozzle orifice. Two-fluid nozzles may show an internal or external mixing zone. In a two-fluid nozzle with internal mixing, the air stream is rotating and contacting the feed within the nozzle. Part of the energy of the pressurized air is consumed through the mixing process. The major part of the energy is used during disruption of the liquid by rapid gas expansion at the orifice. Recently, effervescent atomization has gained attention for application in spray drying of foods and microencapsulation of food ingredients. It is a special type of internal mixing pneumatic atomizer being distinct in the formation of a two-phase flow prior to the nozzle orifice outlet, in which gas is introduced into the feed stream through holes in the inner channel. In nozzles with external mixing zone, the liquid emerges from the nozzle orifice and meets with the flowing gas. The atomization is achieved through frictional shearing forces between
the liquid surface and the air having a high velocity. A characteristic parameter affecting the drop-
let size is the air liquid ratio, which is the relation of air mass flow rate to feed flow rate. Two-fluid
nozzles have much likelihood of occluded air content within the particles and a low production per
drying units. The resulting particles have a mean size with a diameter of \( \leq 50 \mu m \).20

Mechanical atomizer use mechanical oscillation or rotating discs or wheels to accelerate the
feed. They form a low-pressure system and work with centrifugal energy. The feed is supplied cen-
trally to the wheel or onto the disc at rotating speed. In the case of a rotating disk, the liquid flows
outwards over the surface, accelerates to the periphery, and disintegrates into a spray of droplets.
To prevent liquid slippage over the surface, the friction between fluid and disc surface is increased.
Atomizer wheels can be high or wide and can have straight or curved vanes or channels. In the latter
case, the liquid exits the channel at the outer side of the wheel in the form of a liquid jet. Mechanical
atomizers are frequently used in food industry and particularly in encapsulation by spray drying.
They are operated at rotational speed up to 30,000 rotations per minute, produce a wide range of
particle size, and are easy to scale up and produce low costs. It is a continuous process with mild
conditions and no plugging.22 The particle size is directly proportional to feed rate and viscosity and
indirectly proportional to the wheel speed and wheel diameter. Rotary atomizer can handle high
feed rates, fluctuating feed rates, abrasive feed stocks, or feed stocks with high viscosity. The mean
size of particles is 30–200 \( \mu m \).17,20

### 3.2.2 Spray-Air Contact

At the moment of atomization, the liquid droplets come into contact with the drying medium. The
most common drying medium is hot air at an air inlet temperature between 150°C and 200°C.
In some applications inert gas, namely nitrogen, is used. Inert gas prevents the risk of explosion when flammable organic or explosive solvents are involved as well as oxidation in the case of products, which are particularly sensitive to oxygen. In this case, a closed system is required, in which the inert gas is reused. In the case of hot air in an open system, the filtered air can be exhausted to the atmosphere.

The droplet-air contact determines drying kinetics and the properties of the resulting powder particles. In this context, the positioning of the atomizer unit and the air supply, and thus the air flow pattern within the drying chamber, are of major importance. Generally, there are three droplet-air flow patterns: cocurrent, countercurrent, and the mixed flow. In the cocurrent flow dryer, the spray and the hot drying medium enter the drying chambers at the same point, most frequently the top of the drying chamber. The liquid spray meets the drying medium at its highest temperature, and, therefore evaporation of moisture is rapid. Since the droplet is cooled by the evaporating air, the wet bulb temperature of the particle is comparably low. In countercurrent flow the air enters at the opposite end of drying chamber. This offers excellent heat utilization, since the almost dry powder comes into contact with the hot and dry air. As a consequence, a low-residual moisture content may be achieved, but the thermal impact on the encapsulated core material is higher than in cocurrent air flow. Furthermore, the upward stream of the air reduces the velocity of the large droplets and thus increases the residence time in the drying chamber. This system is not recommended for heat-sensitive products, but for the production of coarse products with high bulk density. They also have a low porosity because of the reduced tendency of the droplet to expand rapidly and fracture during drying. Finally, a mixed flow pattern is a combination of cocurrent and countercurrent flow. The air enters at the top, and the spray is produced at the bottom of the drying chamber. The droplet is initially exposed to moderate temperature, meets the hottest air at an intermediate stage in the upper zone of the drying chamber, and is further dried on the way downward to the bottom of the drying chamber.

### 3.2.3 Evaporation and Particle Formation

Evaporation of water from the droplet or drying particle occurs on its surface. As mentioned earlier, the particle is cooled by the evaporating water. During the first stage of the drying process, the drying rate is constant. During this period, a solid structure develops in the interior of the drying droplet and transport of water through capillaries to the particle surface starts. At the end of this phase, moisture content at the surface of the particle has decreased to the moisture content that develops upon contact with saturated humidified air (maximum hygroscopic moisture content). In the second stage of the drying process, moisture content at the particle surface further decreases to an equilibrium state with the drying air. Heat conduction in the product takes place at this stage and negatively affects the drying rate. In this period of the drying process, moisture bound by sorption starts to be removed from the particle. Finally, in the third stage of the drying process drying rate further decreases due to a decrease in the difference of vapor pressure between the particle interior and the air.23,24

With respect to microencapsulation by spray drying, integrity of the particle is a prerequisite to achieve stabilization of the core material. If the drying process is too fast, particularly in the early stages of the drying process, particle ballooning may occur.25 The phenomenon is well described in the literature, for example, for sucrose, maltodextrins, or emulsions.26–28 Due to fast evaporation of the water from the particle surface, a crust develops. Through formation of the crust, transport of water to the particle surface is blocked. Since no evaporation occurs any longer, the drying particle heats up to the temperature of the air, which is above 100°C at that stage. Inside the particle, steam formation leads to inflation and particle ballooning occurs. If the internal pressure reaches a critical value, the crust bursts and steam is released from the inside. The particle may undergo this cycle for several times until the particle structure is completely fixed (Figures 3.4 and 3.5).
**FIGURE 3.4** Scheme on the mechanism leading to particle ballooning during spray drying.

**FIGURE 3.5** Scanning electron micrographs of microencapsulated fish oil prepared with different types of modified starch (medium viscosity: a,b; low viscosity: c,d) and dried at 210°C/90°C (a,c) or 160°C/60°C (b,d). (Reproduced with permission from Drusch, S. and Schwarz, K., *Eur. Food Res. Technol.*, 222, 155, 2006.) (Continued)
Another critical issue with respect to encapsulation is the fact that the particle undergoes a significant change in its composition during the process of particle formation. Approximately 40%—60% of the mass is lost since water is removed. On one hand, this means that the chemical environment constantly changes in ionic strength, pH, and content of other constituents dissolved in the aqueous phase. On the other hand, in case of dispersed systems, the emulsified or suspended core material droplets or particles come into close proximity. Stabilizing effects through steric hindrance or electrostatic repulsion are affected by the change in environmental conditions and aggregation or coalescence may occur (Figure 3.6), which in turn negatively affect encapsulation efficiency and physical stability of the redispersed system. Therefore, success in microencapsulation by spray drying can only be achieved, if the complex interplay between formulation, process design, functionality, and final application is analyzed. In the following section, critical aspects are described using the encapsulation of nutritional oils as an example.

**FIGURE 3.5 (Continued)** Scanning electron micrographs of microencapsulated fish oil prepared with different types of modified starch (medium viscosity: e,f; low viscosity: g,h) and dried at 210°C/90°C (e,g) or 160°C/60°C (f,h). (Reproduced with permission from Drusch, S. and Schwarz, K., *Eur. Food Res. Technol.*, 222, 155, 2006.)
3.3 EXAMPLE: MICROENCAPSULATION OF NUTRITIONAL OILS BY SPRAY DRYING

Among the group of nutritional oils, oils rich in polyunsaturated fatty acids are of major importance. Based on the multitude of physiological functions recommendations for a daily intake exist, which amount up to 650 mg.\textsuperscript{29–35} In the past, a range of epidemiological studies has shown that the intake in the population is much lower than the recommendation.\textsuperscript{36,37} For this reason, nutritionist nowadays still recommend supplementation of foods with oils rich in polyunsaturated fatty acids to ensure an adequate supply. In this context, the sensitivity of long-chain polyunsaturated fatty acids against oxidation limits the applicability, and encapsulation is required to protect the oils. For more than a decade, it is well accepted that encapsulation of the core material in an amorphous matrix reduces the mobility of the reactants and slows down the rate of oxygen diffusion.\textsuperscript{38} Thus, microencapsulation by spray drying is one of the suitable techniques for protection of oils rich in polyunsaturated fatty acids. Spray granulation is an alternative technique,\textsuperscript{39} which offers the possibility to limit air inclusion, but process time and thus thermal impact are higher than in spray drying. Additional processing like agglomeration or coating may negatively affect the microencapsulation efficiency since rewetting of the particle surface occurs.\textsuperscript{40,41}

A wide range of empirical studies on the performance of different matrix constituents in microencapsulation by spray drying are available.\textsuperscript{42–49} However, the understanding of the complex interplay between formulation, process conditions, and functionality in terms of protection of the core material has significantly improved during the last decade. The influences of the emulsifier, other carrier matrix constituents, and the process parameters on the physical characteristics of spray-dried microcapsules have been investigated using octenylsuccinate-derivatized starch and proteins. Particle ballooning as described earlier has been described in addition to oxidative damage of the oil during drying of emulsions with high viscosity due to high thermal impact in this drying scenario.\textsuperscript{50} Differences in the drying temperature resulted in significant differences in particle density in microcapsules based on octenylsuccinate-derivatized starch and maltodextrin as determined by mercury porosimetry and helium pycnometry. The impact of inlet air temperature on process-induced oxidation has been confirmed by Tonon et al.\textsuperscript{51} Based on these results, it was hypothesized that structural differences in the pico- to micrometer range determine the gas diffusivity and thus the long-term stability of encapsulated nutritional oils.\textsuperscript{52} The hypothesis was supported by the observation of Keogh et al.,\textsuperscript{52} who described a relationship of vacuole volume and off-flavor development during storage of microencapsulated oil rich in polyunsaturated fatty acids.

In the following years, nanostructural differences in the particle morphology and thus differing gas diffusivity was identified as the cause of a different oxidative stability of microencapsulated nutritional oils. When using a octenylsuccinate-derivatized starch with a high proportion of low molecular weight disaccharides, a significant inhibition of autoxidation compared to a carrier...
system with higher molecular weight starch fragments was achieved. Using positron annihilation lifetime spectroscopy, Townrow et al. showed that nanometer-sized defects in amorphous maltodextrin systems exist, and that these defects are reduced with an increase in low molecular weight maltose in the system. The impact of these defects, the free volume elements, on the stability of encapsulated oils as shown in Figure 3.7 has been confirmed. Furthermore, it was shown that also the protective effect of protein glycosylation on the oxidation of an encapsulated oil may not be attributed to an antioxidative effect of the conjugates, but rather a shift in the molecular weight profile in the carrier matrix.

Furthermore, it is important to consider that the distribution of the core material in the matrix is very heterogeneous as it has been shown by confocal laser scanning microscopy. The surface itself and pores close to the surface are filled with nonencapsulated or poorly encapsulated core material, which is easily oxidized. Microencapsulation efficiency is therefore without a doubt a critical factor. There is sufficient evidence that the surface area is inversely related to oxidative stability in oil-in-water emulsions. In a study of Rusli et al., microcapsules with a low proportion of nonencapsulated oil had a lower stability compared to microcapsules with a high proportion of nonencapsulated oil. The authors hypothesized that a reduced oil droplet size in microcapsules with high microencapsulation efficiency was the reason for the decreased stability. A small oil droplet size is related to a high surface area and at a given amount of wall material subsequently with a thinner film of encapsulating material. Furthermore, removal of water during rapid drying can result in conformational changes of high molecular weight emulsifying agents like proteins. Subsequently, destabilization of the emulsion and an increase in oil droplet size may occur. Low-molecular-weight carbohydrates like glucose syrup with a dextrose equivalent of 36 may compensate this effect by stabilizing the protein during dehydration.

In this context, Let et al. suggested that the composition of the interface may be more important than the total surface area itself. In recent years, research focused on modification of the oil-water-interface with the aim of physical stabilization of the interface during dehydration and/or modification of the release of the encapsulated core material. A well-described system is stabilization of the interface through bilayer formation using lecithin as emulsifier and chitosan as oppositely charged polymer for bilayer formation. Due to the cationic surface of the droplet, surface repulsion

FIGURE 3.7 Development of the hydroperoxide content of fish oil microencapsulated into matrices with different molecular weight profile upon storage at 20°C and 33% relative humidity. (Reproduced with permission from Drusch, S. et al., Food Biophys., 4, 42, 2009.)
of prooxidative metal ions leads to an increase in oxidative stability of nutritional oils in liquid emulsions with bilayer-covered interface. However, it has recently been shown that the bilayer is not stable during the process of spray drying due to the change in the composition of the aqueous phase. The instability is reflected in an increase in oil droplet size and a decrease in encapsulation efficiency and oxidative stability. In contrast, bilayer formation using either pea protein or β-lactoglobulin and pectin is suitable for production of emulsions, which are stable during the process of spray drying. Using interfacial dilatational rheology, Serfert et al. showed that bilayer formation strongly increases the viscoelastic modulus of the film at the interface, and thus its resistance against mechanical stress and disruption. Finally, very promising results on the physical and chemical stabilization of nutritional oils have been achieved using β-lactoglobulin-based fibrils as emulsifying agent in spray-dried microparticles.

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