Application Note

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Microencapsulation of Flavors and Fragrances by Spray Drying

1. Introduction

Recently, encapsulation of active ingredients in powder has gained much attraction. This technology could enable novel formulations for products in many fields, such as pharma, biology, food and cosmetics.[1] The main purpose of encapsulation is to protect the sensitive compound in a solid matrix against the damage of the surrounding environment during the shelf life. Encapsulation has also been employed for sustained, controlled or targeted release of encapsulated products.

In food and cosmetic industries, flavor and fragrance compounds are rather volatile liquids and generally thermally and/or chemically labile, considerable sensitive to air, light and irradiation.[2] An effective approach for protection of the precious compounds is encapsulation of flavor and fragrance into a carrier matrices. The advantages of encapsulation are listed in Figure 1. Examples of commonly used encapsulated flavors and fragrances are fish oil, sunflower oil, peppermint oil and limonene oil, as well as sulfur aroma.[3-7] As produced particles with a diameter ranging from sub-micrometer to millimeter are called microcapsules.[8]

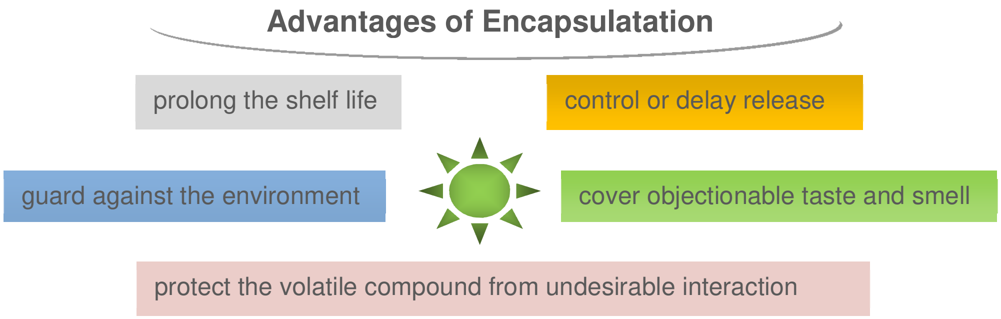

Figure 1: The advantages of encapsulation of flavor and fragrance.

Various encapsulation techniques have been used to produce microcapsules, like spray drying, fluidized bed, extrusion, freeze drying, co-crystallization and coacervation, organic phase separation.[9]
Comparing to other methods, spray drying is simple in operation, highly reproducible, low in production costs and easy to scale-up. Hence, encapsulation of flavor and fragrance by spray drying is often the first choice and has been exploited by several studies.[10]
Normally, multiple-core microcapsules are produced, the core material is dispersed throughout the carrier to form the effective protection shell. Microcapsules with this structure usually have a core material loading of 20-30 % based on total solids of the emulsion.[9]

Here, we highlight recent research progress in spray drying encapsulation of flavor and fragrance including discussions about the influence of emulsion characters and parameter setting on the final dried powder.

2. Spray drying technology

Spray drying is a widely applied technology to convert aqueous or organic solutions, emulsions, dispersions and suspensions into a dry powder. It is a quick and single step process that makes it advantageous in terms of lower costs, easy scale-up and operation. Importantly, temperature sensitive and volatile materials, such as enzymes, proteins, antibiotics, flavor and fragrance could be spray dried without loss of activity. The reason is that the mean residence time of particles in the process is in the range of a few seconds only.

Usually, the BUCHI Mini Spray Dryer B-290, the instrument with the highest market share in laboratory scale spray drying, is employed for researches and feasibility studies. In Figure 2, a scheme of the Spray Dryer B-290 is shown. The liquid sample with a maximum viscosity of 300 mPa·s is fed to the nozzle by a peristaltic pump. Due to the so-called atomization at the nozzle tip, the liquid sample is dispersed into fine droplets. The drying air is heated-up by an electrical heater, and circulated through the system by an aspirator. The droplets fall through the heated drying chamber where the solvent evaporates rapidly. The cyclone, located downstream the drying chamber, separates the dried particles from the gas stream and the dried product falls into a collection vessel. The outlet filter captures very fine particles, preventing them from leaving the system. This avoids environmental pollution, protects the operator and the instrument from possible corrosion and abrasion of the aspirator by these fine particles.

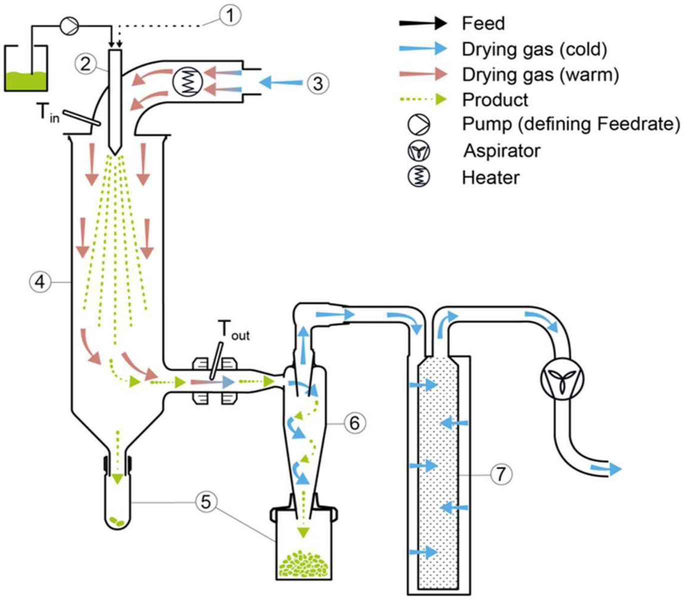

Figure 2: Scheme of the BUCHI Mini Spray Dryer B-290.

Three nozzle designs, could be installed to BUCHI Mini Spray Dryer B-290, i) the two-fluid nozzle, ii) the three-fluid nozzle and iii) the ultrasonic nozzle (Figure 3).

The two-fluid nozzle has two concentric channels in which pressurized air and emulsion flow separately. For non-aqueous mixture or highly reactive substances, inert gas is used instead of nitrogen gas. The pressurized air is provided to obtain rapid expansion. It's mixed with the liquid feed within the nozzle body (internal mixing) or at its tip (external mixing). Many researchers used the two-fluid nozzle to produce microcapsules containing flavor or fragrance with excellent results.[4, 11]

The three-fluid nozzle has been developed to spray dry two immiscible samples without emulsify them prior to feeding. Therefore, it could be used for encapsulating the flavor or fragrance material into shell material. Three separate channels are available, one for core liquid, shell solution and atomizing gas.

Finally, the ultrasonic nozzle is the third nozzle option. It converts electrical energy to mechanical vibratory energy, at the atomizing surface. Compared to the first two nozzle types, it produces more uniform microcapsules with a narrower size distribution. The produced microcapsule size is in the range of 10-60 µm with similar shape and good flowability. This nozzle set-up requires an ultrasonic controller in addition.

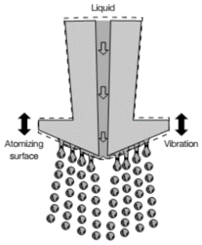

Figure 3: The ultrasonic nozzle, applied to produce microcapsules in the range of 10-60 µm.

3. Influential factors in flavor & fragrance powder manufacturing

3.1. Flavor and fragrance

Normally, the properties of the flavor and fragrance are non-water soluble, volatile and sensitive to the environment, such as fish oil, vegetable oil, sulfur aroma, d-limonene phytosterols, walnut oil, chia oil and more.

3.2. Carrier material

A variety of carriers or matrix materials could be chosen for the encapsulation process. The properties should be water soluble, film forming ability, emulsify capability, low viscosity, low hygroscopicity, low cost, bland taste, stable etc. Taking into account these prerequisites the optimum carrier material or carrier combination has to be chosen. Common carrier material are:

(1) Carbohydrates: maltodextrin, pectin, sucrose, cellulose (e.g.: Hydroxypropyl methylcellulose(HPMC)), gum arabic, cyclodextrins, modified starches (e.g.: Hi-CAP100, N-LOK, CAPSUL, ENCAPSUL855, CRYSTAL TEX 627, CIEmCAP12633, CIEmCAP12634, CIEmCAP12635 etc.).
(2) Proteins: whey protein concentrate (WPC), whey protein isolate(WPI), soy protein, caseinates.
(3) Other materials: skimmed milk powder (SMP), gelatin, wax.

3.3. Emulsion characterization

In microencapsulation, it is aimed to control the release and retention of the embedded compound. A key step in encapsulation of flavor and fragrance is the preparation of the initial feed emulsion. It is an important factor determining the retention of volatiles and encapsulation efficiency of the active compound.[9]
With an effective emulsion, the carrier is adsorbed on the oil droplet surface reducing the interfacial tension, and preventing droplet coalescence due to the formation of a protective membrane around them.[12]

Here we discuss emulsification conditions, such as solid concentration, emulsion viscosity, emulsion stability, emulsion droplet size D [3, 2], that were shown to affect the quality of the encapsulated product.

Solids concentration (Carrier Material)
The effect of solids concentration depends on the type of core material, hence the flavor or fragrance to be encapsulated. There is an optimum solid concentration value for the drying process. For example, Liu et al. found that the retention of menthol increased with increasing concentration of carrier material maltodextrin.[13] Furthermore, Goula et al. observed that increased solids concentration caused an increase in encapsulation efficiency. It could be explained that highest possible solids content reduces the required time to form a semi-permeable membrane at the surface of the drying particle. A fast formation of a solid surface could be associated with low levels of surface oil content as there is less opportunity for the core material droplets to come onto the particle surface.[14]

Viscosity
The viscosity of the initial feed emulsion to be spray dried should be lower than 300 mPa.s. High viscosities could prolong the atomization process and form semi-permeable membrane rapidly. This will suppress the internal circulations and oscillations of droplets, decreases the surface oil and improves the retention.[15] However, increasing the viscosity exceeding a certain a value could not help to further retain volatile compound, due to a larger exposure during atomization and difficulties in droplet formation.[9]

Emulsion stability

Emulsion stability should be observed, i.e. the emulsion should retain stable during the whole spray drying period. According to Noello et al., the emulsion stability could be analyzed by the creaming index. After 24 h standing, an emulsion stabilized by whey protein concentrate and maltodextrin 10 DE separate to an oil phase and a water phase that could not be used for feeding. However, the whey protein concentrate and pectin emulsion with added maltodextrin was stable for 24 h and could be used for spray drying.[12] The reason was that the protein-polysaccharide complexes can generate higher droplet density, which reduces the density difference between the oil and aqueous phase, decreasing the driving force that causes phase separation.

Initial emulsion droplet size

The Sauter mean D [3,2] is used for statistical calculation of the initial emulsion droplet size. The final dried product specifications e.g. particle size, encapsulation efficiency, surface oil and volatile retention are usually affected by the emulsion droplet size.
Goula et al. found that the encapsulation efficiency increased as emulsion D [3,2] decreased. It proved that small emulsion droplets will be enclosed and embedded more efficiently within the final microcapsules.[14]

Baranauskiene et al. described that peppermint essential oil was better retained in smaller emulsion particles than in larger ones. Conversely, the flavor could evaporate more easily from large emulsion particles during atomization. High volatility and solubility of flavor compounds might also lead to a higher loss during spray drying.[3]

The morphology of emulsions could be observed using an optical microscope. In general, we can conclude that a narrow droplet size distribution is beneficial to the spray drying process.[12]

3.4. Spray drying parameters

Successful encapsulation of compounds by spray drying is highly dependent on the correlation and interdependency of the process parameters. Thus, optimization of the parameters, including inlet temperature (Inlet T), outlet temperature (Outlet T), feed rate, dry air flow and atomization gas, is important to obtain the desired microcapsules.

Inlet temperature and outlet temperature

The Inlet T is set to a value where temperature gradient between the wet droplet surface and hot saturated gas leads to an evaporation of the solvent. The maximum Inlet T that can be set on the BUCHI Mini Spray Dryer B-290 is 220 ℃. The more energy is put to the system the faster the water is evaporated which in turn increases the drying efficiency. Furthermore, quick drying leads to a rapid formation of a semi-permeable membrane on the droplet surface that retains the core material in the microcapsule.

However, the droplet could inflate or breakdown when the boiling point of the liquids is exceeded. Liu et al. found that the retention of d-limonene was increased between inlet T of 40 to 100 ℃, but the retention of ethyl butyrate and ethyl propionate were decreased when the inlet T was higher than 115 ℃.[16] Roccia et al. reported that Inlet T(109 ℃, 130 ℃, 165 ℃ and 200 ℃) had positive linear effects on solid yield, as shown by above 95 % confidence interval for the significant coefficients (the design of the regression fitting model).[6]

In spray drying the outlet T cannot be set, it is a function of the inlet T, the feed rate, the dry air and atomization gas performance.

Feed pump rate

The peristaltic pump feeds the emulsion to the nozzle. In general and while holding the other parameters constant, an increased feed rate result in bigger particle size, better separation and higher yield.

Drying air and atomization gas

The BUCHI Mini Spray Dryer B-290 has a maximum drying air flow rate of approximately 35 m^3/h when set the aspirator to 100 %. The atomized droplet coming out from the nozzle will be dried in the drying cylinder within 1-2 seconds. This time is short enough to retain the activity of the encapsulated compound in the droplet and to keep the volatile flavor. According to response surface methodology (RSM), Goula observed that by increasing the drying air flow rate, the encapsulation efficiency will be increased. This effect can be attributed to a lower relative humidity in the whole system.[14]

As described above, a small emulsion particle size is desired and can lead to a better mixing of atomization gas and emulsion. It will retain the volatiles due to a more rapid heat and mass transfer associated with the drying process, i.e. more rapid drying process.

4. Recent flavor and fragrance microencapsulation applications

Many applications aiming to encapsulate flavor or fragrance into a carrier material leading to high yields, long shelf-life and effective encapsulations have been investigated by several research groups. Most publications rely on BUCHI Spray Dryers for laboratory scale spray drying. In Table 1 we highlight recent publications in the field of microencapsulation together with the application.

Table 1: Applications list of spray dried microcapsules using BUCHI Spray Dryers.

Flavor and fragrance	Carrier material	Findings and Benefits
Sulfur aroma[7]	Arabic, maltodextrin or their mixture	Obtained good retention, high yield; Storage stability improved.
Peppermint essential oil[3]	Eight different modified starches	Compared different carriers on retention of peppermint essential oil during spray drying process.
Caraway essential oil[2]	WPC, SMP, and their mixtures with maltodextrin	Proved WPC per se and in combination with carbohydrates can be successfully used as wall materials. WPC exhibited better encapsulating properties than SMP.
Limonene oil[5]	Gum Arabic, WPC, and their mixtures with cassava starch	Created microcapsule morphologies with uniform surfaces and without cracking, offered adequate protection to limonene oil.
Coconut oil[1] (containing Vitamin A)	Arabic gum	Exhibited spherical form and rough particle surfaces. Particle size in the range of 3.5 and 10.4 µm. Protect and stabilize vitamin A in the capsules.
Chia seeds oil[12]	WPC/pectin+maltodextrin WPC+Hi-Cap®100	Compared different carriers for encapsulation. And the final microcapsules increased the induction time and have enhanced stability.
Fish oil[17]	WPI	Examined the effect of nozzle type and design (2-fluid nozzle, 3-fluid nozzle and ultrasonic nozzle) on fish oil encapsulation

		efficiency and microcapsule properties.
Pomegranate seed oil[14]	SMP	Optimum operating conditions to achieve high encapsulation efficiency of 95.6 %.
Canola oil[15]	Lentil protein isolate and maltodextrin	Encapsulate canola oil in most effective encapsulation wall material with protection against degradative oxidative reactions.
Walnut and chia oil[18]	HPMC; maltodextrin	Protective effect to walnut oil and to chia oil with microencapsulation process.
Phytosterols[11]	Arabic gum and maltodextrin	Phytosterol microparticles were formulated and developed by spray drying with good characteristics.
Sunflower oil[6]	HPMC; maltodextrin	Based on RSM method to develop optimized encapsulation process.

5. Characteristic features of the microcapsules

An ideal encapsulation process of flavor or fragrance results in a dried powder with low moisture content, uniform particle size, minimum surface oil content, high yield and maximum retention of core material. Here, we discuss these important product requirements.

5.1. Moisture content and water activity

Moisture is known to influence the oil oxidation, flavor retention and microstructure of the particles.[7, 12, 15] Usually, the moisture content of the microparticles was quantified by a thermogravimetric method.[6-7, 12, 18] Martinez et al. showed that the moisture content varied between 0.95 and 2.13 % for walnut or chia oil encapsules.[18] Roccia et al. reported that it was in the range of 2.35-4.86 % for the sunflower oil powder.[6]

The water activity is usually associated to the moisture content, which could be measured by a water activity meter.[2, 12] It will influence the release of the flavor, due to it could change the coating matrix structure. Low water activities slows down the release of volatiles and inhibits microbial spoilage. At the higher water activity levels, the matrix may start to plasticize, hence, increasing the release rates of mobile flavors.[3] This effect was reported by Baranauskiene et al. They showed that losing of peppermint essential oil volatiles during storage was more pronounced at a higher water activity levels.[3]

5.2. Particle size, distribution and microstructure

The particle size, distribution and microstructure of the final powder are also important factors for processing and handling of a product. They could affect the flavor, color, texture and odor of the product, as well as the flowability and dispersibility.[7] Usually, a uniform, homogeneous and round particle morphology is desired.

The possible particle diameter range is 1-25 µm for BUCHI Mini Spray Dryer B-290 when using the two fluid nozzle, and 10-60 µm with the ultrasonic nozzle. Legako et al. studied the effect of three nozzle designs to the final powder. They found that average diameter of fish oil microcapsules produced with the two fluid nozzle were the smallest at 7.3 µm followed by the ultrasonic nozzle and the three fluid nozzle at 11.3 and 12.0 µm. In addition, it was revealed that the ultrasonic nozzle could produce the most narrow size distribution, compared to the other two type nozzles.[17]

In general, the microcapsules with a smooth surface, few concavities and wrinkles have beneficial effects on encapsulation efficiency, and of course on stability.[14] The microstructure could be observed using SEM. It was shown that the combination of lentil protein isolate, maltodextrin, and sodium alginate as wall material to cover canola oil, the final microcapsule had strong wall structure to protect the core material.[15] Furthermore, for coconut oil microcapsules (containing vitamin A) presenting a spherical form and rough surface with 15 % and 20 % concentrations wall material were beneficial to efficiently protect and stabilize the encapsulated vitamin A.[1]

5.3. Yield

The yield could be calculated by dividing the weight of microcapsules solid mass by the total of solid mass to be spray dried. It is significantly affected by many factors, such as the core and wall material, the ratio of core and shell, the surfactant, inlet temperature, feed concentration etc. Normally, the yield is up to 70 % for the BUCHI Mini Spray Dryer B-290. Goula et al. discussed the effect of four factors on the yield, i.e. the core to wall material ratio, the feed solid concentration, the inlet temperature, and the drying air flow rate.[14] It was found that by decreasing the feed solids concentration and increasing core to wall material ratio, the yield increased. In addition, the yield increased by increasing the inlet air temperature.[6]

5.4. Total oil content, surface oil and encapsulation efficiency

The total oil content of the microcapsules includes the surface oil and encapsulated oil. The presence of oil on the powder surface is an undesirable property that will influence the storage stability.[3]

The encapsulation efficiency is calculated by subtracting surface oil content from the total oil retained after spray drying or by hydrodistillation of essential oil from the matrix after washing out surface oil by organic solvent.[2]

Noello et al. got a high encapsulation efficiency for chia oil microcapsules, of more than 99 %, hence, the oil loss to the surface is less than 1 %.[12] Baranauskiene et al. reported the encapsulation efficiency of peppermint essential oil into different modified starches varied from 39.2 % to 97.4 % depending on the character of the wall material.[3] Obviously, when the highest encapsulation efficiency is achieved, i.e. the lowest oil content on the surface of the microcapsule, the encapsulated compound is best protected the surrounding environment.

5.5. Storage stability

In the storage period, the microcapsules containing flavor and fragrance could be oxidized resulting in odor deterioration. Storability is one of the most important factors to determining the encapsulation efficiency.

Chang et al. determined the storage stability by testing the peroxide value (PV) and 2-Thiobarbituric acid reactive substances (TBARS). Lentil protein-maltodextrin-alginate microcapsules containing canola oil showed better oxidative stability than free canola oil which proved a strong benefit of the encapsulation. The microcapsules had a significantly lower PV over a 30 day storage period. Even after 25 days, the TBARS value didn't change much compared to first days after the microcapsule preparation.[15] Furthermore, Martinez et al. proved that the carrier could be an effective barrier against chia oil oxidative degradation. After a 90 day storage period, the PV of microencapsulated oil was considerable lower than the non-encapsulated oil.[18]

6. Conclusion

The spray drying technology has already received much attention and is widely used in the encapsulation of flavor and fragrance. It enables the production of high quality encapsulated powders and extends the shelf life of the products.

This application note summarizes the properties of carriers, emulsion characteristics, and spray drying parameters that are influential factors affecting the dried microcapsules.

The BUCHI Mini Spray Dryer B-290 provides a reliable and popular solution for many customers to support their microencapsulation research. Products developed using this instrumentation are and will be incorporated into a wide range products e.g. supplements to enhance the delivery of healthy oils.

Additionally, the lab-scale experiments can easily be scaled-up according to well-known transfer parameters.

7. Reference

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