Encapsulation of Hydrophilic and Hydrophobic Flavors by Spray Drying

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The encapsulation of flavors is the important process in food industry. The encapsulation of flavors with spray drying and the flavor release from spray-dried powder were reviewed. The hydrophobic flavor was in the form of emulsion before spray drying. Therefore, the researches were mainly related to the forming of emulsion which wall material containing emulsifier properties are required. On the other hands, the hydrophilic flavor was mainly related to the antioxidant and coloring flavor powder. The hygroscopicity of powder and their stickyness during the spray dryer were important points to improve which the remaining of hydrophilic flavors were less concerned. The morphologies, and flavor release behavior are important physical properties of the flavor encapsulated powder. Especially, the correlation equations for the flavor release are summarized in the relation with Avrami or Weibull equation. The glass transition temperature is important to estimate the collapse of the powder and the permeation of the powder matrix to flavor compounds. The flavor release (mass transfer of flavor) rate is affected by temperature difference (T−Tg). In this review, recent researches are summarized in the flavor encapsulation in spray drying, especially for tropical flavor encapsulation.

Keywords: flavor, encapsulation, spray drying, powder, controlled release

1. Introduction

Tropical fruits are of increasing interest to consumers worldwide. Fabiano et al reviewed the drying of exotic tropical fruits and indicated the drying method affected the quality of fruits such as the content of vitamins [1]. The tropical fruits are exotic in flavor. Flavor contents in the fruits were affected also by the drying conditions and method. Flavor (aroma) is one of the most important attributes that affects the consumption of fruit from the tropics and subtropics. In food industry, various core compounds, such as volatile compounds, essential oils, and oleoresins, are encapsulated with some specific concerns, such as safety usage of solvent and wall material. The most common and economical way to carry out microencapsulation to retain and protect chemically reactive or flavor compounds is spray drying so that it is widely used in commercial scale. Many research works related to encapsulation of liquid flavors by spray drying have been reported [2–5]. Several researchers investigated the volatile flavor constituents of tropical fruits and flavor behaviors at storage. Pino and Marbot [6] investigated the volatile constituent of acerola fruits. Tietel et al. [7] evaluated the flavor and quality of ‘Or’ and ‘Odem’ mandarins after 4 weeks of storage. Rouseff et al. [8] reviewed historical review of citrus flavor research during the past 100 years. Bicas et al. [9] investigated volatile constituents of exotic fruits from Brazil. They pointed the flavor in these fruits was a very important factor. Perez-Cacho and Rouseff [10] reviewed processing and storage effects on orange juice aroma. They indicated the flavor compounds were labile compounds and unstable during the storage. One method is the encapsulation to form stable flavor form. Madene et al. [4] reviewed the flavor encapsulation and controlled release. They summarized the flavor release mechanism from the powder with diffusion, swelling, melting and degradation. Gibbs et al. [11] reviews also the encapsulation in the food industry. They showed encapsulation in foods is also utilized to mask odours or tastes. Various techniques are employed to form the capsules, including spray drying, spray chilling or spray cooling, extrusion coating, fluidized bed coating, liposome entrapment, coacervation, inclusion complexation, centrifugal extraction and rotational suspension separation. Powder formation of these flavors is one interesting process of food industry. Zuidam and Heinrich [12] edited the book of “Encapsulation Technologies for active food ingredients and food processing”. The aroma encapsulation were
summarized in the book. Spray drying has been playing a vital role in the encapsulation and microencapsulation of functional compounds in food.

The losses of both hydrophilic and hydrophobic flavors during the spray drying were reported in each step of process. The losses of flavors were occurred first during the atomization step. The flavors and water are evaporated with the hot inlet air at initial period of drying. The loss of flavors especially the high volatile flavors (with low boiling point temperature) was expected in this period with the temperature of droplet increase. In the second step with the constant drying periods, the formation of crust was occurred. The crust was the selective membrane allows the higher diffusion rate of water than the flavors resulted the higher remaining of flavor in the droplet. However, the high solubility flavor as well as hydrophilic flavor was lost in the higher amount than in the hydrophobic flavor. The dissolved flavors were loss during the drying as the water molecule. After the solid droplets were formed, the loss of flavors was expected to occur with the change of powder morphology. However, the losses in this step were less amount comparing to the first and second steps.

In this paper, the hydrophobic and hydrophilic flavors encapsulation focusing on tropical flavor by spray drying especially the work published in last decade were reviewed including the flavor release mechanism as well as the oxidation of encapsulated flavors.

2. The encapsulated hydrophobic flavors

To encapsulate the hydrophobic flavors by spray drying, the emulsion of flavors will first to produce under the wall materials solution. Therefore, the wall materials with emulsifier properties or the additional of surfactant are required. Then the flavor emulsion is spray dried to form the encapsulated flavors powder. The flavor is in the form of droplet inside the shell wall of powder as the multi core encapsulated powder. In the past decade, the research works are studied the effects of each factors on the flavor retention during spray drying. During the storage with various conditions, the water, oxygen and flavor itself can diffuse through the shell wall. The stability of encapsulated flavors during the storage is also widely investigated.

2.1 Wall materials

Wall materials are one of the most important factors on the properties of encapsulated flavor powder. The widely used of wall materials to encapsulated hydrophobic flavor by spray drying is gum arabic (also known as arabic gum or acacia gum) and n-octenyl succinic anhydride (OSA)-modified starch since both of them have the emulsifier properties. The maltodextrin was also used to blend with the emulsifier wall materials as the drying aid which was also prevent the losses of flavor during the spray drying process. The higher solid content increased the flavors retention because the rate of crust formation around the atomized droplet as the selective diffusion membrane for the flavors is increased. The surfactants were also added to stabilize the emulsion with less used methods. The used surfactants are mostly in the form of viscous and sticky liquid affected to the physical properties as well as the yield of product. The surfactant can stabilize the emulsion but it cannot cover the flavor droplet during the drying periods.

There are some of works that reported the new wall materials with the emulsifier properties comparing to the conventional materials of gum arabic and OSA-modified starch. Drusch [13] reported a novel emulsifying wall component of sugar beet pectin. Beristain et al. [14-15] showed the application of mesquite gum with the high retention. Xie et al. [16] reported the addition of peach gum in the emulsion system resulted the smooth surface of spray dried powder. Hogan et al. [17] used the whey protein concentrate to encapsulate the soya oil. The whey protein concentrate offered the surface active properties required to stabilize emulsion. Hogan et al. [18] showed the encapsulation with sodium caseinate/maltodextrin blends. Charve and Reineccius [19] evaluated the potential of selected proteins (sodium caseinate, whey and soy protein isolates) as alternative materials for flavor comparing to the gum arabic and modified starch. The highest flavor retention in gum arabic was reported but protein materials effectively limited limonene oxidation. Calvo et al. [20] studied the microencapsulation of extra-virgin olive oil by spray-drying with proteins (sodium caseinate and gelatin), gum arabic and maltodextrin. A better microcapsule yield, efficiency, and internal–external fat ratio were achieved when a combination of proteins and polysaccharides was used as the wall component. Liu et al. [21] used the soybean soluble polysaccharide to encapsulate the hydrophobic flavors. The increasing of flavor retention with addition of gelatin to the emulsion was also reported. The volatile compounds were retained in dry emulsions stabilized by pea protein isolate/pectin complex. The pectin was able to preserve the β-sheet secondary structure of pea protein.
when pea globulins/pectin complexes are heated. Drusch et al. [22] and Gharsallouai et al. [23] described the fundamental physical characteristics of spray-dried carrier matrices based on sodium caseinate and casein hydrolyzate. Surface accumulation of proteins at the air-water interface led to a modified surface composition of spray-dried carrier matrix particles for microencapsulation. However, the interfacial elasticity was markedly altered when using hydrolyzed casein as emulsifier, which is related to a decrease in microencapsulation efficiency. Lipid oxidation during storage of the microencapsulated oil increased with the protein content in the formulation. Excess protein led to an increase in free volume elements and is suspected to increase oxygen diffusion.

Klinkesorn [24] used the two-layered interfacial membranes of lecithin-chitosan to emulsify the tuna oil combination with the maltodextrin as drying aid materials. The high oil retention levels (>85%) was obtained. Loksuan [25] showed the modified tapioca starch as potential wall material for encapsulation of β-cryptoxanthin. The efficacy of pullulan as stabilizer to achieve a stable emulsion of turmeric oleoresin and its subsequent microencapsulation was investigated. Kshirsagare et al. [26] and Yang et al. [27] used the konjac glucomannan (KGM) which have the excellent film forming capability to encapsulate orange oil. The KGM was hydrolyzed before used to decrease the viscosity of carrier solution. Because of the lack of emulsifier properties, the surfactant or gum arabic or OSA-modified starches have to add in the system.

Furthermore, the combination of encapsulation methods between the inclusion complex and spray drying were also reported. The cyclodextrins and their derivatives was used to form the inclusion complex of hydrophobic flavor and then following by spray drying to form the dry products. Liu et al. [28] showed the encapsulated of menthols in β, α and γ-cyclodextrin following with the single droplet drying process to simulate the loss of flavor during spray drying process. Kawakami et al. [29] showed the encapsulation of rice flavor in α-cyclodextrin and highly branched cyclic dextrin by spray drying.

### 2.2 Type of hydrophobic flavors

Numerous of works have reported the encapsulation of flavors as well as the tropical flavors in both of model flavors and natural extracted flavors. Bylaitë et al. [30] encapsulated the caraway essential oil in mixtures of whey protein concentrate and malodextrins matrix by spray drying. Partanen et al. [31] reported the microencapsulation of caraway extract in β-cyclodextrin and modified starches. The inclusion complex seemed to protect volatile substances more efficiently during storage, whereas microcapsules with modified starches as wall material were more heat tolerant. Encapsulation of extracted sea buckthorn kernel oil and the stability of the products were also investigated. Encapsulation of extracted sea buckthorn kernel oil in maltodextrin and emulsifying starch derivative and the stability of the products were investigated [32]. Teixeira et al. [33] encapsulated swiss cheese flavor in conventional wall materials of gum arabic and maltodextrin. The rose oil which composed of 2-phenylethanol (50.22%), nerol (22.34%) and citronellol (19.40%) was also encapsulated gum arabic and maltodextrin wall materials. The yield of encapsulated rose oil varied with wall materials (64–70%) [34]. The model flavor of menthol was also encapsulated in gum arabic and modified starch. The re-crystallize to form whisker of menthol during storage was discussed [35]. Krishnan et al. [36] reported the microencapsulation of cardamom oleoresin using binary and ternary blends of gum arabic, maltodextrin, and OSA-modified starch as wall materials. Bixin was encapsulated by spray-drying with gum arabic or maltodextrin [37]. Dzondo-Gadet [38] reported the encapsulation of safou pulp oil in maltodextrins(DE=6). Baranauskiene et al. [39] reported the encapsulation of natural flavorings of oregano, citronella and marjoram into skimmed milk powder and whey protein concentrate. Vaidya et al. [40] reports on the microencapsulation of cinnamon oleoresin by spray drying using binary and ternary blends of gum arabic, maltodextrin, and modified starch as wall materials. Shaikh et al. [41] reports on microencapsulation of black pepper oleoresin (piperine) by spray-drying, using gum arabic and OSA-modified starch as wall materials. The encapsulation of peppermint oil in modified starch was also reported with the encapsulation efficiency about 80 percent [42]. About 60 percent encapsulation efficiency of cold pressed avocado oil using whey protein and maltodextrin was reported [43]. Bae et al. [43] and Jimenez et al. [44] reported the encapsulation of conjugated linoleic acid in whey protein concentrate and gum arabic. Ahn et al. [45] studied the encapsulation of high oleic sunflower oil. The lipid oxidation of encapsulated sunflower oil was remarkable decreased with the addition of the mixed natural antioxidants extract to the system. Natural Canthaxanthin was encapsulated in soybean soluble polysaccharides. The results showed the oxida-
tion was more suppressed for the microcapsules prepared from the emulsion having smaller droplets [46]. Touré et al. [47] reported the microencapsulation of ginger oil in maltodextrin (DE=18)/whey protein isolate with the application of the higher pressure homogenization. The best conditions for higher retention at 93 percent were found. The influence of some process conditions on the microencapsulation of flaxseed oil (vegetable sources of ω-3) in gum arabic by spray drying was reported [48]. Rodea–González [49] reported the encapsulation of chia essential oil in whey protein concentrate–polysaccharide matrices. Ko et al. [50] produced the encapsulated allyl isothiocyanate (AITC) in gum arabic and chitosan materials via spray drying. Lim et al. [51] investigated the influence of the composition of the wall material on the encapsulation and stability of microencapsulated red–fleshed pitaya seed oil by spray drying. The study on oil retention revealed that sodium caseinate > whey protein > gum arabic as effective wall materials for pitaya seed oil encapsulation. Rubilar et al. [52] prepared the formulation of soup powder enriched with ω-3 fatty acids of linseed oil in gum arabic/maltodextrin mixture. Recently, the encapsulation of multiflavors bergamot oil in gum arabic and modified starch were studied. The transformation among each flavor to give the retention higher than 100 percent was discussed [53].

3. The encapsulated hydrophilic flavors

To encapsulate the hydrophilic flavors, the aqueous solution of flavor and carrier solid was prepared. Then, the aqueous mixture was spray dried. The flavors are dispersed and encapsulated in the dried carrier solid in the form of matrix type.

The researches work is now aim to improve the physical properties of the powder. The main problem of the natural hydrophilic flavors is the content of the soluble solid as low molecular of saccharide in the extract aqueous flavor which is a cause of the stickyness and the high hygroscopicity. Therefore, the research is aim to improve the hygroscopicity of product as well as to decrease the sticky of obtained powder during the spray drying. The maltodextrin was normally used as the drying aid agents to the system. The higher maltodextrin content decreased the stickyness and hygroscopicity of the product. The gum arabic was also used because of its excellent film forming properties even the emulsifier properties are not required in this system. However, the quality of the product as the flavor concentration in dry basis was decreased. Numerous works was done to improve these problems rather than the retention of flavor in the powder products.

3.1 Wall materials

Some new wall materials and wall materials systems were applied to solve the stickyness and hygroscopic properties problems with high flavor content. Oliveira et al. [54] showed the potential using of cashew tree gum to partially replace the conventional maltodextrin as drying aid agent in spray drying of cashew apple juice. The retention of ascorbic acid was increased with the decreasing of powder hygroscopicity especially when the ratio of cashew tree gum to maltodextrin is higher than 50%.

Recently, the protein compounds were added to the feed solution in the small amount to increase the hygroscopic properties instead of adding high content of maltodextrin. Jayasundera et al. [55] reported the powder recovery up to 80% of amorphous fructose and sucrose powder with the addition of sodium caseinate at 7.89% and 0.13% respectively. The protein compounds in the emulsion were reported to form the film and crust around atomized droplet during the drying process. Kim et al. [56] reported the surface composition of spray dried of milk powder. The results showed that the surface composition is very much different from the bulk composition of powders. A maltodextrin/apple pectin based matrix was used to encapsulate the plant extracts. The bioactive polyphenols and moisture content of the particles or the antioxidant activity appeared significantly modified [57].

3.2 Type of hydrophilic flavors

There are numerous of works reported the encapsulated hydrophilic flavors such as juice powder and colorant powder. In general, for the hydrophobic and hydrophilic flavors which have the close molecular weight and normal boiling point, the retention of hydrophilic flavors during the spray drying are lower than the retention of hydrophobic flavors as the mechanism explained above. However, the low amount of remaining flavor in the powder is enough for the application of juice powder as well as the colorant product. As mention before, almost of the works done in encapsulate hydrophilic flavor the stickyness and hygroscopicity of product are concerned with a few reported of colorant retention. Amaranthus betacyanin extracts were spray-
dried using a range of maltodextrins (DE10–25) and starches (native/modified) as carrier and coating agents. Adding maltodextrins and starches significantly reduced the hygroscopicity of the betacyanin extracts and enhanced storage stability [58]. The extracted 2-acetyl-1-pyrroline odor of rice flavor was encapsulated in gum arabic and maltodextrin [59]. Shiga et al. [60] developed the encapsulated extracted shiitake flavors powder by spray drying. The mixture between cyclodextrin and maltodextrin was used as carrier. A heat treatment to increase the lenthionine before the spray drying was recommended. Cactus pear juice powder was produced with maltodextrin with different DE values. The retention of vitamin C as well as the powder properties was also reported [61]. Cano-Chauca et al. [62] investigated the induction of crystallization on powder mango juice during the process of spray drying and the correlation of the microstructure of the powder obtained with the functional properties of stickiness and solubility. The maltodextrin, gum arabic and waxy starch were used as wall materials with the additional of cellulose. They reported that the cellulose as a substance that induces crystallization of sugar is not suitable. Immature acerola juice powder was prepared by spray drying with maltodextrin and gum arabic. The ratio of juice solid to carrier was 1:1. The glass transition temperature and the stickiness of the powder was discussed [63]. The raisin juice powder was produced with maltodextrins as drying aid agents. It was shown that the lower the DE of the maltodextrin used, the lower the temperature of drying air at the inlet and the lower the concentration of drying aid in the feed were required for successful powder production [64]. The watermelon powder was produced with maltodextrin. Addition of maltodextrin reduced the stickiness of the products and altered the physicochemical properties of the spray-dried powders. The loss of lycopene and carotene occurred at higher inlet temperatures [65]. Microencapsulation of anthocyanin pigments of black carrot by spray drying with maltodextrin (DE 10, 20, 30) was reported. The highest anthocyanin content powder was found in DE20 of maltodextrin. The higher air inlet temperature the higher anthocyanin losses [66]. Gong et al. [67] produced the instant bayberry powder by spray drying following with the agglomeration process. Tonon et al. [68] studied the influence of spray drying conditions on the physicochemical properties of açai powder with maltodextrin DE 10 as carrier. The curcumin pigments was also produced by spray drying using porous starch and gelatin [69]. A powder food colorant was obtained by spray drying of puntia stricta fruit juices with glucose syrup (DE 29) as drying aid. Color was retained during the drying process (>98%) and drying yield was high (58%) [70]. Moreira et al. [71] assessed the impact of some processing parameters on moisture content, flowability, hygroscopicity and water solubility of spray dried acerola pomace extract using maltodextrin and cashew tree gum as drying aids. Bakowska–Barczak and Kolodziejczyk [72] prepared the encapsulated black currant berries in maltodextrin (DE 11, 18 and 21) and inerlin by spray drying. The retention of black currant polyphenol compounds and their antioxidant activity was investigated. The DE11 of maltodextrin had not only higher drying yield but also offered better protection for phenolics during storage. Pomegranate bioactive compounds (polyphenols and anthocyanins) of juice were encapsulated with maltodextrin or soybean protein isolates by spray drying. The polyphenols encapsulating efficiency was significantly better in soybean protein isolates matrix whereas for anthocyanins was in maltodextrin matrix [73]. Kha et al. [74] reported a good quality gac powder in terms of colour, carotenoid content and total antioxidant activity can be produced by spray drying at low inlet temperature (120 °C) and adding maltodextrin concentration at 10% w/v. Chin et al. [75] reported the stability of encapsulated durian powder by spray drying. Gum arabic, maltodextrin and N–Lok were used as wall materials. The retention of maker volatile compounds (two esters and two sulfides) was investigated during spray drying and storage. The retention of flavors was in the rage of 20–70%. The study demonstrated that volatiles with larger molecular weight tended to retain better during spray drying. However, the stability during storage was still low. Nayak and Rastogi [76] reported that maltodextrin is an effective drying aid for production of microencapsulated anthocyanin from gacoria indica. Addition of gum acacia and tricalcium phosphate further reduced the hygroscopicity as well as increasing the stability of the pigments. Goula and Adamopoulos [77] investigated the development a new technique for spray drying orange juice concentrate using dehumidified air as drying medium and maltodextrin as drying agent. They indicated the hygroscopicity and degree of caking decrease with an increase in inlet air temperature and maltodextrin concentration and a decrease in maltodextrin dextrose equivalent and the combination of maltodextrin addition and use of dehumidified air as drying medium seems to be an effective way of producing a free–flowing orange powder. The pro-
duction of bayberry polyphenols powder with MD (DE10) by spray drying with the retention of phenolic content and total anthocyanins after spray drying at about 95% was reported [78]. The water extract of the mountain tea was spray-dried by using β-cyclodextrin, gum arabic and maltodextrins as carrier materials. The product yield increased with the addition of the carrier materials whereas decreased at higher drying temperatures [79]. Suhaimi et al. [80] carried out to determine the effect of different ratios of pineapple juice to maltodextrin as a carrier agent. These results suggested that the ratio of pineapple juice solid to maltodextrin at 40:60 produced the highest powder output at 84.85% recovery. Yousefi et al. [81] reported the pomegranate juice was diluted to 12° Brix and carriers (maltodextrin, gum arabic, waxy starch) were added with varying concentrations of cellulose before being reduced to powder by spray drying. The gum arabic still showed the most effective carriers. The production of pomegranate juice powder with DE6 of maltodextrin was also investigated. The results showed that inlet temperature had a great influence on the physicochemical properties of the spray-dried powders. The antioxidant capacity of the sample increased with increasing air inlet temperature. However, the total phenolics content of the samples was not affected by temperature [82]. Furthermore, also to produce the pomegranate juice powder, Vardin and Yasar [83] showed the optimization of pomegranate juice spray–drying as affected by temperature and maltodextrin content. Solval et al. [84] developed a cantaloupe juice powders from fresh cantaloupe fruit by spray drying. The 10 wt% maltodextrin solution was used as a carrier. The results indicated that the inlet air temperature of the spray dryer can affect vitamin C and β-carotene contents of cantaloupe juice powders. Caparino et al. [85] showed the effect of drying methods (refractance window drying, freeze drying, drum drying and spray drying) on the physical properties and microstructures of mango powder. The maltodextrin was used as carrier for the spray drying technique. The higher porosity or lower bulk density in spray-dried mango powder was due to the addition of maltodextrin. The spray dried powder showed the least hygroscopic comparing to other types of drying. Wang and Zhou [86] characterized of spray-dried soy sauce powders using maltodextrins. Maltodextrin concentration and DE value greatly influenced the caking strength of the soy sauce powders.

4. Effects of related factors on the retention of the flavor and properties of encapsulated powder

The properties of wall materials, flavors, emulsion as well as the spray drying parameters have been reported to affect the retention and properties of obtained encapsulated flavor powder. In this paper, some of the works that reported to each property were reviewed. Mongenot et al. [87] showed the ultrasound emulsification on cheese aroma encapsulation. The use of ultrasound is particularly effective to obtain a stable emulsion with maltodextrin as support, which is known for poor emulsification properties. Buffo et al. [88] study the effect of agglomeration process of fluidization on the retention of flavor in the powder. Flavors retention was not adversely affected by the secondary processing as long as agglomeration did not promote structure collapse. Finney et al. [89] report the effects of type of atomization and processing temperatures on the physical properties and stability of spray-dried flavors. Type of atomizer and inlet air temperature did not affected to the total oil content. However, the centrifugal atomizer gave the higher surface oil content than spray nozzle type. This study added factual evidence to strengthen the hypothesis that shelf life depends primarily on the porosity of dried particles and confirmed that surface oil is not a significant determinant of shelf life. Cho and Park [90] showed the double encapsulation of limonene powder by coating the powder with wax oil. The double encapsulated limonene was consistently stable without the oxidation. Soottitantawat et al. [91] reported the effect of flavor emulsion size on their retention after spray drying. The large emulsion size gave the low flavor retention in both of non-soluble and partly-soluble flavors because the droplet was sheared during the atomization process. However, for the small emulsion size give the higher retention of non-soluble flavor but give the lower retention in the case of partly-soluble flavor. Microencapsulation by spray drying of multiple emulsions containing carotenoids was reported to improve their properties [92]. Turchiuli et al. [93] investigated the feasibility of encapsulation of a vegetable oil used as a model into a mixture of maltodextrin and acacia gum. Encapsulation was completed in three stages, i.e. emulsification, spray drying and fluid bed agglomeration. Agglomeration did not change oil encapsulation properties of the spray-dried powder but considerably improved its wettability. Chegini and Ghobadian [94] investigated the effects of the feed ratio, atomizer speed,
and inlet air temperature on properties of spray-dried orange juice powders basing on a full factorial experimental design. Tan et al. [95] reported the effect of marine oil loading on the encapsulation efficiency when modified starch was used as wall materials. The higher oil loading increased the droplet size of emulsions formed resulted the higher surface content and lower production yield. The encapsulation of vegetable oil as the model in MD and GA was studied. The direct agglomeration process was used to increase the size of the particle to improve the flowability and wettability [96]. A cool chamber wall spray dryer was used to increase the production of yield of lime juice powder because of the decreasing of particles stickiness on the wall [97]. The different emulsifying ingredients (Tween 20, modified starch or whey protein concentrate) were used to produce sub-micron emulsions by high pressure homogenizer. The biopolymers were not efficient ingredients to produce very small emulsion droplets compared with small molecule surfactants because of their slow adsorption kinetics [98]. However, it was not possible to produce a fairly stable microfluidized emulsion with surfactants for encapsulation purposes. The influence of particle morphology of spray dried powders obtained by using different carriers on the efficiency of microencapsulation of rosemary aroma is investigated. The efficiency of encapsulating aroma inside the capsules depended on the size of obtained particles and the apparent density of powders. An increase in the average diameter and decrease in the apparent density of powders decreased the quantity of microcapsulated aroma [99]. Serfert et al. [100] investigate the impact of the emulsifying carrier matrix constituent, n-octenylsuccinate derivatised (OSA)-starch, and process conditions on physical characteristics and oxidative stability of microencapsulated fish oil. The highest oxidative stability was observed for fish oil microencapsulated in OSA-starch with the lowest average molecular weight. In terms of spray-drying under inert conditions and in the presence of air, lipid oxidation of microencapsulated fish oil was rather attributed to oxygen availability in the feed emulsion than in the drying gas. The present study indicates that also discrete air inclusion may accelerate lipid oxidation of microencapsulated oils. To produce low-salt fish sauce powder, the effect of electrodialysis pretreatment on physicochemical properties and morphology of powder was investigated. Without the additional carrier materials, the lower hygroscopicity of the low salt fish sauce powder with the low product recovery was reported. The salt concentration of not lower than 14 wt% was recommended [101]. Paramita et al. [102] developed the high content of encapsulated of d-limonene powder. The medium-chain triglyceride was mixed to the d-Limonene to make the emulsion in the OSA-modified starch carrier solution before spray drying. Goula et al. [77, 103] reported an effective way of increasing lycopene encapsulation and reducing residue formation of spray dried orange juice concentrate by using dehumidified air as the drying medium.

5. Morphology of spray-dried powder

Spray drying is the process by which a solution or slurry is transformed into a dry powder by spraying the fluid feed material into a hot drying medium. The morphology of the spray-dried particle has been studied extensively by Walton and Mumford [104] and Walton [105] using a suspended droplet drying techniques. They classified the morphology of the droplet into 3 categories; agglomerate, skin-forming, and crystalline. Figure 1 shows four powder photos of scanning electron microscope, milk proteins (a), spray-dried fat with maltodextrin (b), mannitol (c) and α-cyclodextrin (d). Several spray-dried powders have aggregates as shown in Fig. 1(a), which were formed at the outlet gas temperature above glass transition temperature. The crystalline in spray-dried powder with mannitol and cyclodextrin were observed. Higher content fat in wall material could be observed smooth surface in spray-dried powder.

Morphologies of the powder particle by spray drying

![Fig. 1 Morphologies of spray-dried powders.](a) Spray-dried milk powder (x140), (b) Spray-dried powder with maltodextrin and fat (x800), (d) spray-dried mannitol (x1500), (d) Spray-dried α-cyclodextrin]
Affects upon the porosity, the surface integrity and flow properties of spray dried powder. Figure 2 shows dextrose equivalent (DE) of maltodextrin affects the surface integrity. Surface crinkle structure might depend on the drying rate. The powders produced with higher maltodextrin concentrations were less hygroscopic and had a lower moisture content after drying.

Hecht and King [106] investigated the morphology changes of the particle by using single droplet. Rogers et al. [107] investigated particle shrinkage and morphology of milk powder made with a monodisperse spray dryer. They suggest the surface crust (initially spherical) is viscoelastic and deforms in response to drying stresses. They also investigated the modelling of the formation of insoluble material for a monodisperse spray dryer. Alamilla-Beltrán et al. [108] investigated the morphological changes of particles during spray drying and concluded the particle changes are related to moisture content of the material and operating drying temperatures. Abadio et al. [109] investigated physical properties of powdered pineapple (ananas comosus) juice in the effect of maltodextrin concentration and atomization speed. They showed the powder density could be correlated with atomizing speed and maltodextrin concentration. Bhandari et al. [110] investigated spray drying of concentrated fruit juices. They obtained the optimal ratio of maltodextrin to the juice. In the morphology of the spray dried powder, the coagulation of the particles is important to evaluate the powder properties. The stickiness problem of sugar products such as fruit juices has been related to their low glass transition temperature ($T_g$) and water-induced plasticization.

6. Release of flavor from spray-dried powder

Spray drying is the most commonly used technique for the production of dry flavorings. Zuidan and Heinlich [111] summarized encapsulation of aroma. Morphologies of the encapsulant depend on the flavor release behavior as well as wall material. The release mechanism comparison may be carried out using model independent or model dependent methods [112]. In order to investigate the release mechanism, several different models have been employed for outlining the release mechanism from matrices. The analysis of flavor release from spray-dried powder is complex and difficult, since the phenomena of flavor release take place with intrinsically overlapping mechanisms, mainly by dissolution and subsequent diffusion of flavors and water as well as flavor oxidations. The release rates, that are achievable from single microcapsule, are generally 0, 0.5, or 1st order. Zero–order release relation can be used to describe the flavor release of several types of modified release flavor dried powders, as in the case of some transdermal systems, as well as matrix particles with low soluble flavor, coated forms, osmotic systems, etc. When the core is a pure material and release through the wall of the reservoir microcapsule as a pure material, the release rates might indicate the zero–order. Half order release kinetics occurs with matrix particles. Diffusion is controlled by the solubility of a flavor in the matrix and the diffusivity of the flavor through the matrix [113]. A simple equation of Avrami equation has been proposed for the correlation of the release time–course of a spray-dried ethyl-n-butylate powder during storage [5].

![Fig. 2 Surface morphologies of spray-dried particle with various DE of maltodextrin.](image-url)
Where $R$ is the retention of flavor in the powder, $t$ is the storage time, $k_R$ is the release rate constant, $n$ is a parameter representing the release mechanism. This equation is also called the Weibull distribution function, which has been successfully applied to describe the shelf-life failure. A general empirical equation described by Weibull [114] could be adapted to the dissolution/release process. Figure 3 shows the release time–course of ethyl butyrate from spray-dried powder with the mixture of gum arabic and maltodextrin, and soluble soybean polysaccharides and maltodextrin. The mechanism values of $n$ depend also on the wall material. The release time–course of ethyl butyrate fitted well to the Avrami’s equation. This Avrami equation is essentially analogous to the equation of Kohlraush–William–Watt (KWW) [115]. Taking a logarithm of both sides of equation 1, we can get the parameter $n$ as slope by plotting $\ln[-\ln R]$ vs. $\ln t$ and release rate constant $k$ from the interception at $\ln t = 0$. For $n$ of value, $n = 1$ represents the first-order reaction, $n = 0.54$ represents the diffusion–limiting reaction kinetics. Table 1 shows the proposed equation for various $n$ values. Flavor release rate are strongly affected by the environmental humidity and temperature since the humidity as water vapor pressure influence the degree of plasticization of wall material and emulsion stability in spray-dried powder. Soottitantawat et al. [116] showed the release of $d$-limonene from emulsified $d$-limonene in spray-dried powder was closely related to water activity of the powder.

### 7. Collapse of spray-dried powder

Most amorphous carbohydrate systems are not in equilibrium and can be metastable with slow kinetics for changes, or unstable with physical changes occurring on practical time scale. Dried fruits and vegetable juices are convenience foods that have long storage life at ambient temperature. However, environmental humidity affected the physical structure of the powder. Stickiness is a major reason that limits the spray drying of various sugar–rich food products. The main constituents of fruit juices are low molecular weight sugars such as sucrose,

![Fig. 3 Effect of gelatin on the release time–course of ethyl butyrate.](image)

### Table 1 Comparison of mechanism value of $n$ with the release model equation in Avrami equation.

<table>
<thead>
<tr>
<th>Value of $n$</th>
<th>Release mechanism</th>
<th>Model equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.54</td>
<td>Diffusion controlled (sphere)</td>
<td>$\left[1 - R^{1/3}\right]^3 = kt$</td>
</tr>
<tr>
<td>0.57</td>
<td>Diffusion controlled (cylinder)</td>
<td>$R \ln R + 1 - R = kt$</td>
</tr>
<tr>
<td>0.62</td>
<td>Diffusion controlled (tablet)</td>
<td>$(1 - R)^2 = kt$</td>
</tr>
<tr>
<td>1.00</td>
<td>First-order mechanism</td>
<td>$-\ln R = kt$</td>
</tr>
<tr>
<td>1.07</td>
<td>Moving interface mechanism (sphere)</td>
<td>$1 - R^{1/3} = kt$</td>
</tr>
<tr>
<td>1.11</td>
<td>Moving interface mechanism (disk)</td>
<td>$1 - R^{1/2} = kt$</td>
</tr>
<tr>
<td>1.24</td>
<td>Zero–order mechanism</td>
<td>$1 - R = kt$</td>
</tr>
</tbody>
</table>
glucose, fructose, and some organic acids. Jaya and Das [117] investigated the glass transition and sticky point temperatures and stability/mobility diagram of fruit powders. They showed glass transition temperature of the fruit powders were interpreted in terms of the Gordon–Taylor model (Eq (2)) for verification and glass transition and sticky point temperatures were compared by plotting them in a graph against moisture content.

\[
T_{gm} = \frac{X_s T_{gs} + k X_w T_{gw}}{X_s + k X_w}
\]

(2)

where \(T_{gm}, T_s,\) and \(T_w\) are the glass transition temperature (°C) of the mixture, solids, and water respectively, \(X_s\) and \(X_w\) are the mass fraction of solids and water (wet basis), and \(k\) is the Gordon–Taylor parameter. In the equation, the value of ‘\(k\)’ depends on moisture content and the empirical equations derived for ‘\(k\)’ of three different fruits were different from each other. The empirical constant ‘\(k\)’ of power equations for different fruit powders are [117]:

\[
k = a X_w^{-b}
\]

(3)

where \(a\) and \(b\) are parameters for powder (\(a=0.548, 0.642,\) and \(1.294\) for mango, pineapple, and tomato powder, \(b=0.628, 0.5571,\) and \(0.4474\) for mango, pineapple, and tomato powder, respectively). Foster et al. [118] investigated glass transition related cohesion of amorphous sugar powders and indicated the rate of cohesiveness development is proportional to the \((T-T_g)\) value, that is, the greater the temperature above the \(T_g\), the quicker the powders will develop liquid bridges which may result in caking. Mosquera et al. [119] investigated the water content–water activity–glass transition temperature relationships of commercial spray–dried borojó powder, as related to changes in color and mechanical properties. They showed the changes in the mechanical properties of borojó powder related to collapse development started when the sample moved to the rubbery state and began to be significant at about \(10^\circ C\) above \(T_g\). Collapse has been found to occur in amorphous system above \(T_g\), where its rate affected by temperature difference \((T-T_g)\) [120]. Soottitantawat et al. [116] indicated the flavor release rates and oxidation rate of \(d\)-limonene from spray–dried powder could be correlated with the temperature difference \((T-T_g)\). In their results, flavor release rate constant increased with an increase in \(T-T_g\) and reached a maximum at roughly \((T-T_g)\) equals to zero, which is analogous to the oxidation rate constant. Moisture sorption properties of dry food products and ingredients are critical in their overall processing, storage stability, and application performance. Dronen and Reineccius [121] investigated rapid analysis of volatile release from powders using dynamic vapor sorption atmospheric pressure chemical ionization mass spectrometry and indicated the system demonstrated differences in volatile release as a function of volatile compound, relative humidity, and food polymer. Mortenson and Reineccius [122] investigated dynamic real-time analysis to determine how carrier material affects menthol release characteristics from various spray–dried powders. They showed DVS–P&T–GC methodology proved to be a useful screening tool to select samples for the more precise DVS–PTR–MS analysis.

Table 2 The theories linked with the physical state of carbohydrate matrix affecting oxidation of matrix-embedded flavors and lipids.

<table>
<thead>
<tr>
<th>Observation</th>
<th>Theory</th>
<th>Uncertainties/Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (A_w) affects lipid oxidation rate</td>
<td>Monolayer theory – best stability at monolayer moisture</td>
<td>Assumption of equilibrium, sorption the only material property considered</td>
</tr>
<tr>
<td>2. Oxygen is needed for hydroperoxide formation</td>
<td>Oxygen transfer is rate–limiting for oxidation</td>
<td>Shown for glassy system at ambient/ high temperature, but may depend on oil susceptibility</td>
</tr>
<tr>
<td>3. Diffusion of small molecules is facilitated due to plasticization</td>
<td>Glass transition theory</td>
<td>Diffusion not coupled with viscosity in the transition region</td>
</tr>
<tr>
<td>4. Dry starch is a good oxygen barrier</td>
<td>Role of water as solvent, solubility of (O_2) in dry carbohydrate limits permeation</td>
<td>Solubility data only for solutions of sugar alcohols, extrapolated to low–water systems</td>
</tr>
<tr>
<td>5. Average volume of the voids between polymers increases gradually with increasing water content</td>
<td>Glassy state swelling affects diffusion of small permeants in carbohydrate matrices</td>
<td>Also molecular packing affects as demonstrated for glucose syrup in comparison to maltose as length of jump distances</td>
</tr>
<tr>
<td>6. Oxidative stability of oil in carbohydrate and protein matrices is oppositely affected by water</td>
<td>More intense structural re–organization of the protein matrix in the presence of water due to hydrophobicity</td>
<td>Antioxidativity of proteins at high humidity may affect oxidative stability</td>
</tr>
</tbody>
</table>
Recent advances in understanding the nano-scale structures, and thus packing, of carbohydrate matrices [123, 124] should lead to better control over diffusion of small permeants in glassy state. Also the role of water has been re-assessed not only affecting as plasticizer, but also as a solvent e.g. to oxygen [125, 126]. The theories linked with the physical state of carbohydrate matrix affecting oxidation of matrix-embedded lipids and the permeation of small components are briefly summarized in Table 2.

8. Conclusion

The microencapsulation of tropical flavors by spray drying is reviewed with the recently published papers. Spray drying is a useful method to encapsulate extracted flavors or liquids of the tropical fruits in powder form. The selection of wall materials and emulsifier, as well as the process conditions are very important to form the suitable powder in food industry. The stability and release of flavor are affected with the glass transition temperature of the wall materials, and presumably by the nano-scale structure of the formed powder matrix. Storage conditions have a major role in both physical and chemical stability of the powders. Basic mass-transfer phenomena of flavor release and stability during spray drying and storage at different humidity conditions are currently under investigation using the latest analytical instruments.

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噴霧乾燥による親水性,または疎水性フレーバーの包括粉末化

スーチンタワット アビナーン, リッタ パータネン, ネオ ツールーン, 吉井英文

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食品の香りのコントロールは,食品素材の付加価値を大きく高める技術として注目され,フレーバーの徐放制御特性などの新しい機能を付与した機能性粉末を作製する研究が行われている。食品工業において,フレーバーの包括粉末化は重要なプロセスである。本総説において,噴霧乾燥によるフレーバーの包括粉末化と噴霧乾燥粉末からのフレーバー徐放挙動についてまとめた。疎水的フレーバーは,一般的にオイルにフレーバーを溶解させたもの,またはフレーバーオイルそのものを,界面活性剤,賦形剤を溶解した溶液に添加後乳化した溶液を噴霧乾燥機で粉末化する。親水性フレーバーは,噴霧乾燥粉末内に均一に分散するため包括率は賦形剤に大きく依存する。これらのそれぞれの粉末作製における賦形剤,フレーバーのタイプについて,既往の研究をまとめた。噴霧乾燥粉末は,粉末が凝集したものや,凹凸の山が多い粉末,粉末内部が中空や繊維が析出したものといった様々な形態の粉末がある。この粉末の形態は,粉末内機能性物質の安定性や粉末の流動性に大きく影響する。食品粉末のフレーバーの保持,徐放特性は,粉末の品質の点から非常に重要である。フレーバーの徐放に関する多くの研究が行われており,粉末からのフレーバー徐放特性が貯蔵温度における相対湿度と密接に関係していることが報告されている。乳化フレーバー噴霧乾燥粉末の緩和現象の係わる事項として,貯蔵中の賦形剤の相変化,粉末からのフレーバーの移動,酸化,賦形剤中の酸素移動,水分の移動といった諸現象の経時変化がある。フレーバー粉末の徐放性に関する研究のほとんどは,恒温恒湿環境下（静的条件）における粉末からのフレーバー徐放特性から評価されている。乳化フレーバー粉末やフレーバー包括シクロデキストリンからのフレーバー徐放挙動は,次式のアブラミ式で良好に相関できる。

\[ R = \exp \left( - (kt)^n \right) \]  (1)

ここで, \( R \) は粉末中のフレーバー残留率, \( k \) は徐放速度定数 (s⁻¹), \( t \) は時間 (s), \( n \) は徐放機構定数である。このアブラミ式（Weibull式）は,結晶成長を相関する速度式で多くの事象を解析するのに用いられている。異なる \( n \) の値を用いて,多くのフレーバー徐放機構に対応しフレーバー徐放挙運動を相関できることから,この式は非常に有用な相関式である。フレーバー粉末が球で賦形剤中の拡散速度によりフレーバー徐放速度が決まる場合は,徐放機構定数 \( n \) は 0.54 付近の値をとる。アブラミ式を用いて噴霧乾燥香料粉末からのフレーバー徐放速度定数の温度依存性（ガラス転移温度依存性）をみた結果,ガラス転移温度 \( T_g \) と徐放環境温度 \( T \) の差 \( (T-T_g) \) に依存していた。