Microencapsulation by Spray Drying: Influence of Emulsion Size on the Retention of Volatile Compounds

A. SOOTTITANTAWAT, H. YOSHII, T. FURUTA, M. OHKAWARA, AND P. LINKO

ABSTRACT: The influence of the mean emulsion droplet size on flavor retention during spray drying was studied. *d*-Limonene, ethyl butyrate, and ethyl propionate were used as the model flavors. Gum arabic, soybean water-soluble polysaccharides, or modified starch blended with maltodextrin, were used as the wall materials. The increasing emulsion droplet decreased the retention of flavors. The distribution curve containing larger emulsion droplets shifted toward a smaller size after atomization, indicating that the larger emulsion droplets would be changed in size during atomization and result in decreasing flavor retention. For ethyl butyrate and ethyl propionate, the retention had a maximum at the mean emulsion diameter of 1.5 to 2 and 2.5 to 3.5 μm, respectively.

Keywords: microencapsulation, spray drying, flavor retention, emulsions, volatiles

Introduction

The microencapsulation of flavor is the technology of converting liquid flavor materials into easy-to-handle solids. It also provides protection against degradative reactions and prevents the loss of flavor. In addition, it can be used to control the release of flavors during food processing and storage. Various encapsulation methods have been previously proposed (Dziezak 1988; Shahidi and Han 1993; King 1995; Gibbs and others 1999). Among them, spray drying is the most popular method of producing flavor powders, which presents the challenge of removing water by vaporization while retaining the flavors that are much more volatile than water. According to the selective diffusion concept (Thijssen and Rulkens 1968), the diffusion coefficient of flavor decreases at a higher rate than the diffusion coefficient of water during drying.

Numerous studies have been conducted to evaluate the retention of flavor during spray drying. The properties of the volatile compounds (Rulkens and Thijssen 1972; Reineccius 1988), the capsule wall material (Inglett and others 1988; Sheu and Rosenberg 1995; McNamee and others 1998, 2001; Buffo and Reineccius 2000), and the emulsion (Reineccius 1988; Risch and Reineccius 1988; Mongenot and others 2000; Liu and others 2000, 2001), along with the drying process conditions (Rulkens and Thijssen 1972; Zakarian and King 1982; Anker and Reineccius 1988; Chang and others 1988; Rosenberg and others 1990; Bhandari and others 1992; Finney and others 2002), and the powder morphology during and after drying (El-Sayed and others 1990; Moreau and Rosenberg 1993; Hecht and King 2000) have been already reported. Recently, the main emphasis of the microencapsulation of flavors has concentrated on preventing flavor losses during spray drying and extending the shelf life of the products. This is intended to produce high quality flavor powders. Buffo and Reineccius (2000) reported the optimization of the gum acacia/modified starch/maltodextrin blending. The attempt to replace commonly used gum arabic with other carbohydrates has been investigated by McNamee and others (2001). Furthermore, work has also been done on improving the properties of flavor (that is, combining flavor with additive materials). For example, Liu and others (2001) improved flavor retention by adding a weighting agent to the flavor. Finally, because process development should be carried out to control the loss of flavor, Finny and others (2002) studied the effects of the type of atomization and processing temperature on the properties of the encapsulated flavor.

The emulsion size in the feed liquid also influences flavor retention and the stability of the encapsulated flavors. Using gum Arabic or Amiogum 23 as the carrier, Risch and Reineccius (1988) studied the effect of emulsion sizes of orange peel oil (0.9 mm ~ 4.0 mm) on flavor retention and shelf life. Their results suggested that a smaller emulsion size yields a larger percentage retention of the orange oil with a smaller amount of surface oil, but did not produce a longer shelf life. Sheu and Rosenberg (1995) suggested that the retention of volatiles during microencapsulation by spray drying could be enhanced by reducing the mean emulsion size of the dispersed core material during emulsification. Ethyl caprylate retention was improved by reducing the mean emulsion size when a combination of whey protein and maltodextrin was used as the carriers. Furthermore, Ré and Liu (1996) correlated an improved eugenol retention by measuring the difference between the mean emulsion size and the mean particle size of the dry powder.

Scanning Electron Microscopy (SEM) techniques have been developed for the study of the outer and inner structures of food microencapsulation, including procedures for embedding and sectioning or polishing the embedded specimen by Rosenberg and others (1985). SEM techniques have since been further developed and become an important technique in studying microencapsulation as a tool for the selection of wall materials, for the study of core material distribution in microcapsules, and for elucidating the mechanisms of capsule formation.

The objective of this study was to find the reasons for decreasing emulsion size yielding a higher retention of orange oil. The en-

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capsulation of model flavors, *d*-limonene (insoluble flavor) in the emulsion state was investigated by spray drying, concentrating on emulsion droplet size in both the feed-liquid emulsion and in the spray-dried powder. The effect of emulsion droplet size on the flavor retention was also studied for the moderately soluble flavors, ethyl butyrate and ethyl propionate. The SEM technique was also used to investigate the inner structure of the encapsulated powder and the arrangement of flavor droplets in the microcapsules.

Table 1—Composition of the carrier solutions and their viscosities

	Maltodextrin (% w/w)	Gum Arabic (% w/w)	SSPS (% w/w)	HI-CAP 100 (% w/w)	Viscosity of solution (mPa·s) at 25 °C[a]
Blend GA-MD	30	10			96
Blend SSPS-MD	30		10		1500
Blend HI-CAP 100-MD	30			10	45

[a]measured for 2 h at the proper rotational speed; the uniform values were used.

Materials and Methods

Materials

d-Limonene, ethyl butyrate, ethyl propionate, and gum arabic (GA) were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Maltodextrin with 15-20 DE (MD, Amycol No. 1) and modified starch (HI-CAP 100) were gifts from Nippon Starch Chemicals Co., Ltd. (Osaka, Japan), and Nippon NSC Co., Ltd. (Tokyo, Japan), respectively. The basic properties and characteristics of soybean-soluble polysaccharide (SSPS), a new type of emulsifier which was extracted and refined from soybeans, were reported by Maeda (2000). In this study, SSPS (SOYAFIBE-S EN100) was also a gift from Fuji Oil Chemical Co., Ltd. (Osaka, Japan), which has been marketing SSPS under the brand name 'SOYAFIBE-S,' and sucrose acetate isobutyrate (SAIB) was a gift from Taiyo Kagaku Co., Ltd. (Mie, Japan). The organic chemicals used in the analysis were of analytical grade.

Preparation of a liquid flavor emulsion

d-Limonene, ethyl butyrate, and ethyl propionate were used as the model flavors. Based on a previous study (Liu and others 2000, 2001), the emulsion of ethyl butyrate and ethyl propionate with the GA emulsifier was unstable. Therefore, the weighting agent, SAIB (Chanamai and McClements 2000; Liu and others 2001), was blended with ethyl butyrate and ethyl propionate. The mixing mass ratio of the esters flavor to SAIB was 0.55 to 0.45 to regulate the density. The resulting densities were 0.98 ± 0.02 g/cm^3 for both the ethyl butyrate and ethyl propionate. The carrier solution was prepared by blending and rehydrating the solid powders in warm distilled water, followed by cooling to room temperature. The total concentration of dissolved solid was 40% w/w on a wet basis, which consisted of 10% emulsifier (GA, SSPS, or HI-CAP 100) and 30% additive wall materials, MD, as shown in Table 1. *d*-Limonene, the density-adjusted ethyl butyrate, or the density-adjusted ethyl propionate was added to the carrier solution to produce a flavor mass ratio to the total solid of 0.25 to 1. An emulsion was prepared by homogenizing the flavor with the carrier solution using a Polytron homogenizer (PT-10, Kinematica GA, Littau, Switzerland) and a Microfluidizer (Model 110T, Microfluidics Corp., Newton, Mass., U.S.A.) at 12000 psig (82.8 MPa). The rotational speed and time of the homogenization were controlled in order to vary the emulsion droplet size distribution. In general, a larger emulsion size was prepared at a low rotational speed (at dial 5 to 8 of the Polytron homogenizer) for 1 to 3 min. For preparing a fine emulsion, the emulsion solution made by Polytron homogenizer (at dial 8 for 3 min) was passed through the Microfluidizer. The size distribution of the liquid emulsion droplets was measured immediately after the homogenization.

Preparation of encapsulated flavor powders

The powders were obtained by spray drying the flavor emulsion in an Ohkawara-L8 spray dryer (Ohkawara Kakouki Co., Ltd., Yokohama, Japan) equipped with a centrifugal atomizer. The spray dryer was composed of a cylindrical chamber with an 800 mm I.D. and 560 mm height, followed by a conical chamber of 650 mm high with a 60 ° angle. The operational conditions of the spray drying were: air inlet temperature of 200 °C, air outlet temperature of 110 ± 10 °C, rotational speed of the atomizer of 30000 rev/min, feed rate of 45 mL/min, and air flow rate of 110 kg/h. The finished powder was stored in a hermetically sealed bottle at –30 °C until analysis.

Emulsion droplet size analysis

The droplet size distribution of the emulsions was measured by using a laser diffraction particle size analyzer (SALD-3000A, Shimadzu Corporation, Kyoto, Japan) connected to a flow sample unit cell. Distilled water was used as the dispersant. The refractive index was set to the standard value at 1.70 to 0.2i. Measurements were reported either as the full particle size distribution or as the mean diameter. In this study, the volume average lipid globule size, D_{43}, was used as the mean diameter based on the volume frequency. Each sample was analyzed in duplicate, and the data presented as an average. In order to determine the flavor droplet size distribution in the powders, the spray-dried powders were redispersed in distilled water at a concentration of 10% (w/w) by mixing with a magnetic stirrer for 30 min. Subsequently, the flavor droplet size (reconstituted emulsion size) was also determined by SALD-3000A.

Determination of flavor droplet size in emulsion after atomization

In order to investigate the change in the emulsion droplets during atomization, the emulsion size distribution in the atomized droplet was compared with the feed emulsion before the atomization. Plastic bags were used to cover the rotating atomizer in the drying chamber without air flow and heating in order to collect the atomized emulsion. The atomized emulsions were then determined for the emulsion droplet size by the laser scattering method as described above.

Powder particle size analysis

The size distribution of the spray-dried powders was determined by dispersing them in 2-methyl-1-propanol and analyzing by the laser light scattering method. A laser diffraction particle size analyzer with a batch cell unit was used. D_{43} was used as a mean diameter. Each sample was analyzed in duplicate and the data were reported as an average.

Rheological measurements

The viscosities of the emulsion and carrier solution were measured by a dynamic shear rheometer, Brookfield viscometer (Model DV-II, Brookfield Engineering Laboratories, Inc., Middleboro, Mass., U.S.A.), with a small sample adapter, SC4-18, and 8 mL sample volume. The samples were placed in the temperature-controlled measurement vessel and allowed to equilibrate to the required temperature (25 °C).

Total flavor content determination

One 10th of a gram of the spray-dried powder was dispersed in 4 mL of water in a glass bottle, and then 2 mL of hexane was added, followed by violent mixing with a vortex mixer for 1 min. To extract the flavor into the organic solvent, the mixture was heated in a heating block with intermittent shaking. The extraction time and temperature were 30 min and 90 °C, respectively. The extracted mixture was then centrifuged at 3000 rev/min for 10 min to separate the organic phase from the water. Two microliters of the organic phase were injected twice for each sample into a gas chromatograph (GC-14B, Shimadzu Corp., Kyoto, Japan) equipped with a PEG-20M packed column (2m × 3.2 mm). The chromatographic conditions were as follows: flame ionization detector (FID) at 230 °C with N_2 as the carrier gas. The column temperature was controlled at constant values of 120 °C, 100 °C, and 80 °C for *d*-limonene, ethyl butyrate, and ethyl propionate, respectively. The external standard method was used to calculate the flavor quantity. Two bottles of the standard 1 ml/mL of flavors in hexane were prepared, and 2 microliters of this standard were injected into the gas chromatograph twice for each bottle of standard. The average peak area was used to calculate the amount of flavor. To determine the solid content in the powder, 1 gram of spray-dried powder was dried in the vacuum dryer (ADVANTEC VR-320, Toyo Seisakusho Co., Ltd., Chiba, Japan) at 90 °C for 20 h and the flavors quantified in the same manner as mentioned above. The solid content in the spray-dried powder was calculated based on the assumption of a totally dried powder after vacuum drying. Flavor retention was defined as the ratio of the flavor in the powder on a dry basis to the original flavors in the feed emulsion. All of the samples were analyzed in duplicate and the data were presented as an average.

Surface oil determination

One 10th of a gram of powder was washed in 2 mL of hexane containing the internal standard cyclohexanone, 1 µl/mL, in a glass bottle. The mixtures were slowly mixed on a rotary shaker for the optimum time of 30 s at ambient temperature. The solvent was then filtered. The flavor content in the organic phase was measured by gas chromatography as described above. The results were the average of the duplicates in each sample.

Scanning electron microscopy (SEM)

A JSM 5800 model (JEOL Co., Ltd., Tokyo, Japan) scanning electron microscope was used to investigate the microstructural properties of the spray-dried microencapsulated products. The powders were placed on the SEM stubs using a 2-sided adhesive tape (Nisshin EM Co. Ltd., Tokyo, Japan). In order to examine the inner structure, the powders (attached to the stub) were fractured by attaching a 2nd piece of adhesive tape on top of the microcapsules and then quickly ripping it off (Moreau and Rosenberg 1993). Because of the weakness of this cutting method (only the weak particles, especially the hollow particles, might be cut), 5 specimen stubs were prepared for each sample using strong adhesive tape. In all cases, the specimens were subsequently coated with Pt-Pd using a Model MSP-1S magnetron sputter coater (Vacuum Device Inc., Tokyo, Japan). The coated samples were then analyzed using the SEM operating at 15 kV. Twenty pictures of each sample were taken to represent the structure of the powders.

Table 2—Properties of feed liquid emulsion and the spray dried powder for encapsulating *d*-limonene

Wall material system	D_{43} of feed emulsion size (µm)	Viscosity of emulsion[a] (mPa.s) at 25 °C	D_{43} of flavor in powder (µm)	Water content % (w/w)	Powder size (µm)
Blend GA - MD	1.05	180	1.55	0.88	42.68
	1.26	120	1.65	2.53	44.81
	2.97	180	2.62	2.51	47.19
	4.09	180	2.94	1.27	44.83
Blend SSPS - MD	0.88	3200	1.14	1.88	52.59
	0.99	2600	1.29	1.74	53.93
	1.55	2600	1.60	2.65	55.19
	2.95	2600	2.55	2.09	49.04
Blend HI-CAP 100 - MD	0.65	90	0.90	2.48	53.42
	0.90	65	0.91	1.35	42.99
	2.05	61	2.10	2.26	46.47
	4.07	60	2.21	1.79	44.88

[a]measured for 2 h at the proper rotational speed; the uniform values were used.

Moisture content determination

The moisture content of the spray-dried powder was determined using a MKS-510N Karl Fischer Titrator (Kyoto Electronics Manufacturing Co., Ltd., Kyoto, Japan). The powder sample, 0.03 to 0.08 g, was weighed and mixed with the Hayashi solvent FM containing 26% methanol and < 0.2 mg H_2O/mL (Hayashi Pure Chemical Ind., Co., Ltd., Osaka, Japan) and titrated against a 5 mg/mL Hydranal composite solvent (Riedel-de-Haën, Sigma-Aldrich, Seelze, Germany). The water content was reported in % w/w of sample. The samples were measured 3 times and the averages reported.

Statistical analysis

The effects of the emulsion droplet size were studied in 3 types of wall materials and 3 types of model flavors. The quantification of the flavor by gas chromatography, emulsion droplet, and powder size measurements, and the rheological measurements were done in duplicate for each treatment, except for determining the water content which was analyzed in triplicate. Average values were used for calculations and figures. The calculations and graphs were made using the computer program Microcal Origin 6.1 (Microcal Software Inc., Northampton, Mass., U.S.A.).

Results and Discussion

Effect of the feed emulsion size on the properties of encapsulated spray dried powder of insoluble flavor

Table 2 shows the properties of the encapsulated insoluble flavor (*d*-limonene) powder, including the water content and particle droplet size as a function of the initial mean emulsion size. The viscosity of the blend of SSPS-MD was much higher than the other 2 systems, but the fine emulsion and good properties of powder were also obtained. The water content of the powder was similar for each system. The results show no effect of the emulsion droplet size and type of wall materials on the water content properties of the powder that should directly relate to the drying conditions. Furthermore, the results also show that the powder size was similar in each system as related to the properties of the feed liquid emulsion, viscosity, density, and surface tension (Marshall 1954). These properties of the feed liquid will influence the size of the liquid droplet formation during atomization.

Figure 1 shows the influence of the feed emulsion droplet size on the retention of the insoluble flavor, *d*-limonene, during spray drying. For all combinations of the carrier solid, the increasing emulsion diameter resulted in a decreasing retention of *d*-limonene. Flavor retention markedly decreased, especially in the range of the 0.5 to 2.0 μm mean emulsion size. This implies that a fine emulsion is stable during both the atomization and spray drying, and also indicates that, for the proper wall materials, the emulsion droplet size is a significant factor for the retention of flavor. Risch and Reineccius (1988) have also shown in similar research that a smaller emulsion size yields a higher retention of orange oil.

In order to explain the decreasing *d*-limonene retention of the larger droplet emulsion, the emulsion droplet size distributions before and after atomization were investigated The flavor droplet distributions in the powder (emulsion droplet after drying) were also measured. Figure 2a shows the distribution curve of the initial coarse emulsion droplet size before and after atomization when a blend of GA and MD was used as the wall material. The distribution of the emulsion in the spray-dried powder is also shown in the figure. The distribution curve after atomization shifted toward a smaller size, while the distribution of the emulsion droplets after drying appeared unchanged compared with the droplets distribution after atomization. This implies that the larger emulsion droplets would be sheared into smaller droplets because of the large velocity gradient and the turbulence in the thin liquid film on the surface of the rotating atomizer. Some of the sheared droplets were then broken down and evaporated during atomization. These results explain the greater loss of flavor from the larger emulsion droplets during spray drying, as shown in Figure 1. On the other hand, the distribution curve of the fine emulsion before and after atomization and after drying are shown in Figure 2b. The distribution curve of fine emulsion droplet size seemed unchanged during the atomization, implying that the fine emulsion droplets were redistributed into a lower ratio than the coarse emulsion droplet size after atomization, thus resulting in higher retention.

In Figure 2, the emulsion droplet distributions after atomization seemed unchanged after spray drying. Therefore, the relationship between the mean flavor size in the feed emulsion and in the spray-dried powder for all combinations of wall materials was investigated as shown in Figure 3. The larger droplets became smaller after drying, especially the mean emulsion size which was greater than 2 mm. On the other hand, for the fine droplet size, the flavor droplet size remained unchanged after drying. These results also supported the reason for the lower retention of the coarse emulsion droplet as previously explained.

Effect of the feed emulsion droplet size on the surface oil content

The surface oil can be easily oxidized to form off-flavor compounds. The amount of surface oil in the spray-dried powder is quite important for stable storage. Figure 4 shows the amount of surface oil for different carrier solutions as a function of the flavor emulsion droplet size for *d*-limonene. The ordinate is the percentage of surface oil (flavor) to the total amount of flavor in the powder. The amount of surface oil increased with the increasing mean emulsion droplet size for most of the wall materials; that is, surface oil values were in the range of 0 to

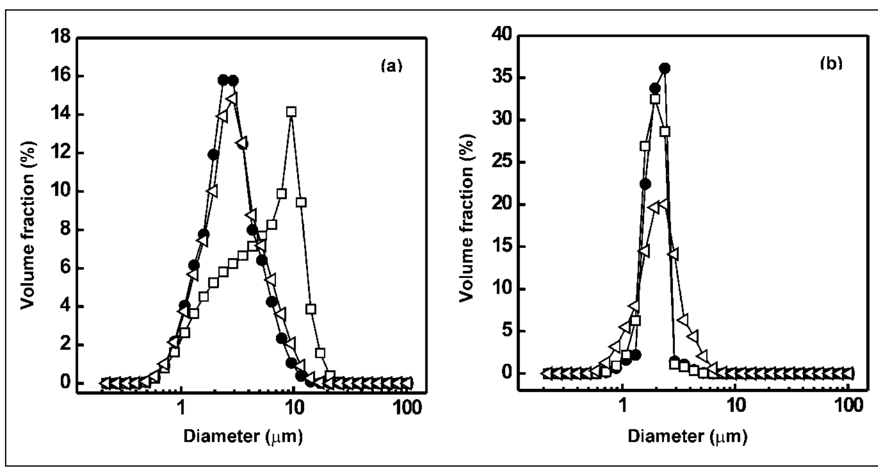

Figure 2—Change in distribution of emulsion droplet size: Wall materials: Blend GA-MD, Flavor: *d*-limonene (a) Coarse droplet size (b) Fine droplet size: □ Feed emulsion, ● Emulsion after atomization, △ Redispersed encapsulated powder

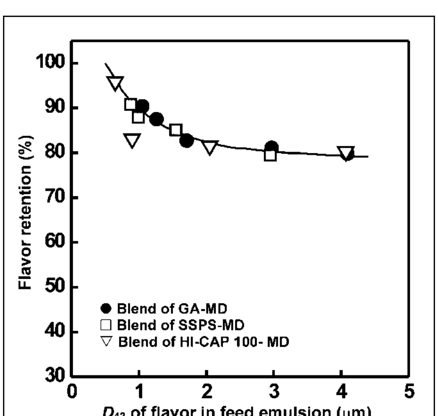

Figure 1—Effect of feed emulsion droplet size on the retention of *d*-limonene, an insoluble flavor, during spray drying

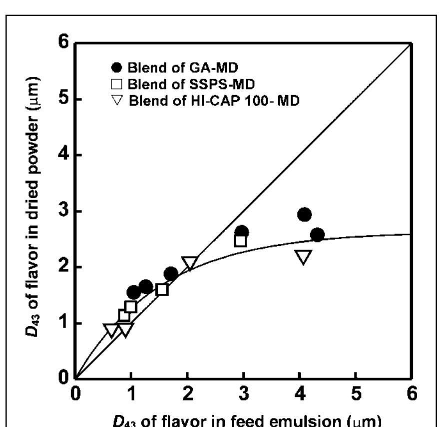

Figure 3—The relation between *d*-limonene flavor droplet size in the feed emulsion and after spray drying for the various types of wall materials

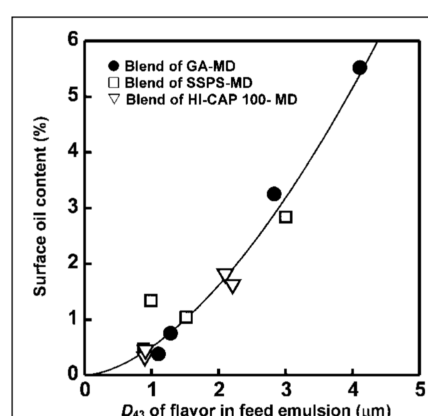

Figure 4—Effect of feed *d*-limonene emulsion droplet size on the amount of the surface oil after spray drying

6% of the total oil content with an emulsion size range of 0 to 5 mm. Risch and Reineccius (1988) have also shown similar results—that a larger emulsion size yielded a higher surface oil content. Higher remaining flavor on the surface of the atomized droplets might be explained by the breakdown of the large emulsion particles during atomization, as shown in Figure 2a.

Table 3—Physicochemical properties of flavors

	Molecular weight	Solubility (v/v)	Boiling temperature (°C)
d-limonene	136	insoluble	136
Ethyl butyrate	116	6.7x10-3	116
Ethyl propionate	102	1.7x10-2	102

Effect of the feed emulsion droplet size and the type of flavors on flavor retention during spray drying

Figure 5 shows the flavor retention during spray drying as a function of the emulsion size of *d*-limonene, ethyl butyrate, and ethyl propionate when a blend of GA and MD was used as the wall material. The physicochemical properties of each flavor are shown in Table 3. The results show that the flavor retention of *d*-limonene (80 to 90% flavor retention) was higher than the esters, ethyl butyrate (40 to 60% flavor retention), and ethyl propionate (40 to 50% flavor retention). The same results were also reported in our previous study (Liu and others 2000, 2001) with the lower retention of ester flavors. The lower stability of the ester emulsion was mentioned as the reason for the lower flavor retention during spray drying. They also showed the improvement of the flavor emulsion stability and flavor retention by adjusting the density of the ester flavor with a weighting agent, sucrose acetate isobutyrate (SAIB). However, although the stable emulsion with the adjusted density esters were used in this study, the retention of the ester flavor during spray drying was still lower than the retention of the stable emulsion of *d*-limonene. This indicates that there might be other factors which influence the loss of the ester flavor during drying. The molecular dimensions seem to play a significant role in the loss of flavor because they are directly related to the diffusion of molecules. Furthermore, the high volatile and high solubility of flavors might encourage a higher loss of flavor during spray drying. As Rosenberg and others (1990) commented in their study, the dissolved flavor can diffuse with water through the wall material matrix during the early stages of the drying process. They also said that, besides the loss from the molecular diffusion that controls retention, the loss of the water-soluble flavor should be a result of droplet stripping during the early stages of drying. Therefore, the dissolved flavors in the feed emulsion were easier to lose than the flavor droplets in the emulsion during the drying, especially during the semipermeable membrane formation period.

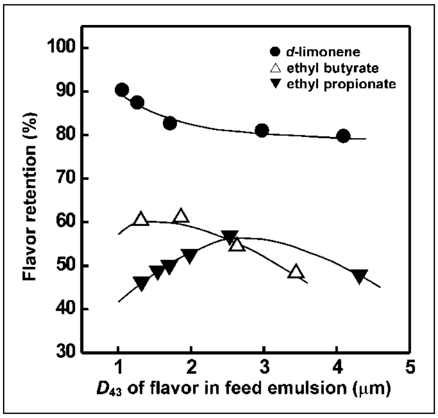

Figure 5—Effect of feed emulsion droplet size and properties of model flavors on the retention flavor during spray drying. Wall materials: Blend GA-MD

When the effect of the emulsion size is considered, the increasing emulsion diameter resulted in a decreasing retention of flavor during spray drying of the insoluble *d*-limonene, as already explained. Also, in the case of the moderately soluble ethyl butyrate and ethyl propionate, larger emulsion droplets decreased the retention. The retention had a maximum at the optimal value of the mean emulsion diameter, and a fine emulsion caused a decrease in the retention of both the ethyl butyrate and ethyl propionate. Ethyl butyrate showed a maximum of 60% retention at the mean emulsion size in the range 1.5 to 2.0 μm. In Figure 5, it was difficult to reach a conclusion about ethyl butyrate since there are few data points in the range of the fine small droplet size, 0.5 to 1.0 μm. However, the retention seemed to decrease in the range of the small droplets, although the small emulsion in the range of 0.5 to 1.0 μm could not be prepared. The emulsion droplet size was also limited by the emulsified properties of the carrier solution (blend of GA and MD at 40% w/w solid content). Moreover, ethyl propionate showed a maximum of about 55% retention for the mean emulsion size around 2.5 to 3.5 μm. This would be due to an increase in the surface area of the flavor droplets in the emulsion, resulting in an accelerated dissolution of the soluble flavor into the carrier solution and diffusion through the liquid to evaporate on the surface of the sprayed droplets during the early stage of the drying period as already explained. The difference in the optimal emulsion droplet size of the ethyl propionate and ethyl butyrate, which showed the highest retention, might be explained by the difference in their solubility as shown in Table 3. The solubility of ethyl propionate is 3 times greater than the solubility of ethyl butyrate.

Internal microstructure of encapsulated powder for different types of model flavor

The morphology of encapsulated flavor powders during spray drying affects some of their properties, such as the flavor release rate and the flow properties of the spray-dried powder. The flavor release characteristics depend upon the porosity, surface integrity, and the distribution of flavor droplets in the capsule which is directly related to the morphology of the atomized droplet during drying. The flow properties of spray-dried powders are also closely linked to the outer topography of the particles. Therefore, it is very important to characterize the outer and inner structures of the encapsulated flavor powders.

In this study, an SEM technique was used to investigate the inner microstructure of the encapsulated flavor powders. Figures 6, 7, and 8 show SEM photographs of the encapsulated powders of *d*-limonene, ethyl butyrate, and ethyl propionate in a GA and MD blended capsule, respectively. A central void was observed. Formation of the central void is related to the expansion of the capsule. This has been commonly observed in spray-dried powders and has been previously studied (Verhey 1972; Greenwald and King 1982). The mechanisms associated with the formation of these central voids are related to the expansion of the particles during the latter stages of the drying process.

Furthermore, the inner structure of the capsules indicated that the flavors were located in the form of small droplets embedded in the wall matrix. The inner structure of the capsules was similar to that reported in general for spray-dried flavor microcapsules (Chang and others 1988; Rosenberg and Young 1993; Sheu and Rosenberg 1995; Rei-

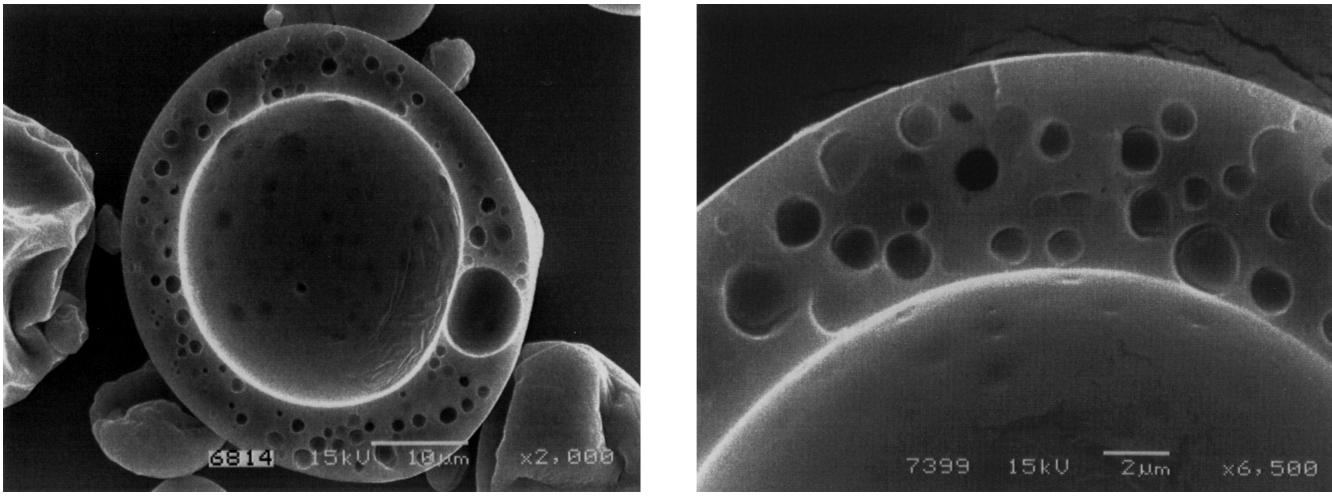

Figure 6—Internal microstructure of encapsulated *d*-limonene in dried powder. Wall materials: Blend GA-MD, D_{43} of flavor in feed emulsion: 1.71 µm, D_{43} of flavor in powder 1.88 µm

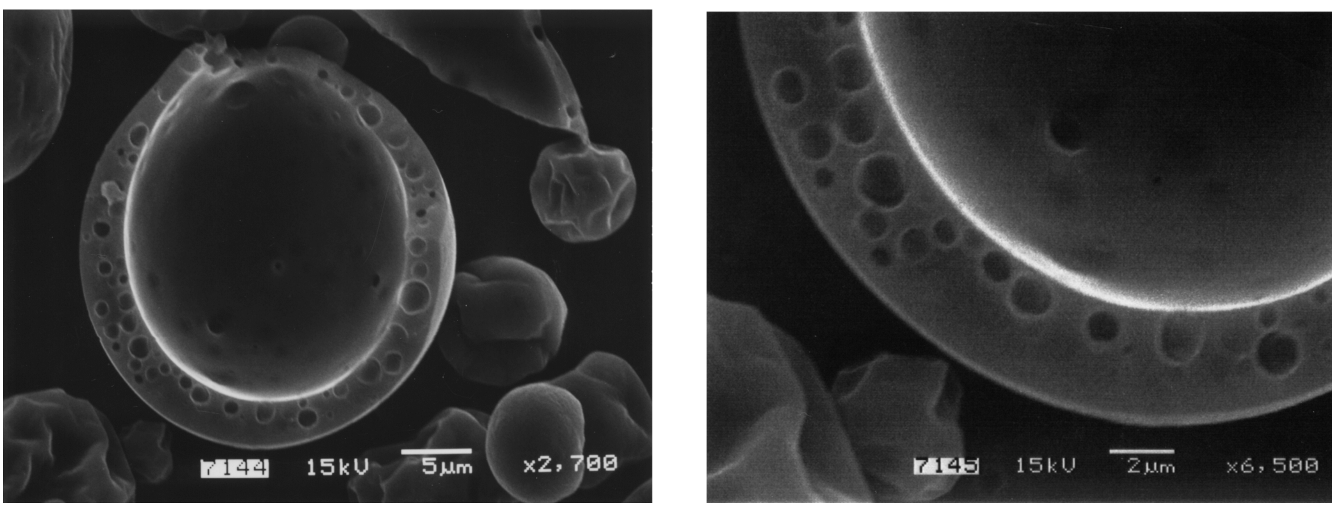

Figure 7—Internal microstructure of encapsulated adjusted density ethyl butyrate in dried powder. Wall materials: Blend GA-MD, D_{43} of flavor in feed emulsion: 1.31 µm, D_{43} of flavor in powder 1.35 µm

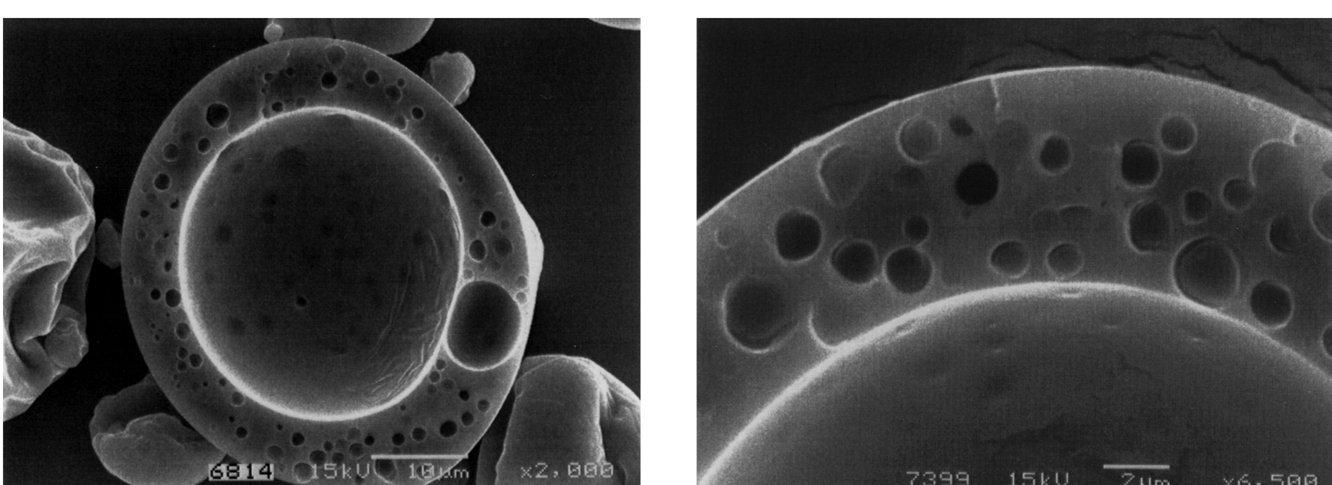

Figure 8—Internal microstructure of encapsulated adjusted density ethyl propionate in dried powder. Wall materials: Blend GA-MD, D_{43} of flavor in feed emulsion: 1.32 µm, D_{43} of flavor in powder 1.46 µm

neccius and others 1995; Kim and Morr 1996; Finney and others 2002). Figure 6 shows many *d*-limonene droplets embedded in the wall matrix and the high concentration of flavor droplets. On the other hand, for the moderately soluble flavors of ethyl butyrate and ethyl propionate, Figures 7 and 8 show a few of the encapsulated flavor droplets and a low concentration of the droplets, especially in the area near the outer surface of the powder. These observations support the assumption that the losses in soluble flavor might be enhanced by internal mixing that may bring the ester to the surface of the capsule and thus cause its partial loss to the drying air, especially during the early stage of the drying period resulting in the low retention of flavor. Rosenberg and others (1990) also mentioned the same assumption.

Conclusions

The emulsion droplet size influenced the retention of volatiles after encapsulation by the spray-drying method. The results indicate that there are advantages to creating a smaller emulsion for the insoluble flavor when preparing a solution for spray drying, even though larger emulsions are much easier to prepare and are less expensive. The smaller emulsion of the insoluble flavor shows the higher retention and lower surface oil content after the encapsulation. The change in the size of the larger emulsion droplet during atomization shows the major loss of flavors. However, for the moderately soluble flavor, the preparation of a smaller emulsion is not required in the process. The highest retention of an encapsulated moderately soluble flavor can be obtained at the optimal value of the mean emulsion droplet size.

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References

Anker MH, Reineccius GA. 1988. Influence of spray-dryer air temperature on retention and shelf life. In: Risch SJ, Reineccius GA, editors. Flavor encapsulation. Washington DC: Amer Chem Soc. p 78-86.
Bhandari BR, Dumoulin ED, Richard HMJ, Noleau I, Lebert AM. 1992. Flavor encapsulation by spray drying: Application to citral and linalyl acetate. J Food Sci. 57(1):217-21.
Buffo RA, Reineccius GA. 2000. Optimization of gum acacia/modified starch/maltodextrin blends for the spray drying of flavors. Perf & Flav 25:45-54.
Chanamai R, McClements DJ. 2000. Impact of weighting agents and sucrose on gravitational separation of beverage emulsions. J Agric Food Chem. 48:5561-5.
Chang YI, Scire J, Jacobs B. 1988. Effect of particle size and microstructure properties on encapsulated orange oil. In: Risch SJ, Reineccius GA, editors. Flavor encapsulation. Washington DC: Amer Chem Soc. p 87-102.
Dziezak JD. 1988. Microencapsulation and encapsulated ingredients. Food Technol. 42(4):136-51.
El-Sayed TM, Wallack DA, King CJ. 1990. Changes in particle morphology during drying of drops of carbohydrate solutions and food liquids. 1. Effect of composition and drying conditions. 2. Effect on drying rate. Ind Eng Chem Res. 29:2346-57.
Finney J, Buffo R, Reineccius GA. 2002. Effect of type of atomization and processing temperatures on the physical properties and stability of spray-dried flavors. J Food Sci. 67(3):1108-14.
Gibbs BF, Kermasha S, Alli I, Mulligan N. 1999. Encapsulation in the food industry: a review. Intl J of Food Sci and Nutr. 50:213-24.
Greenwald GC, King CJ. 1982. The mechanism of particle expansion in spray drying of food. AIChE Symp. Ser. Food Proc Eng. 78(218):101-10.
Hecht JP, King CJ. 2000. Spray drying: influence of developing drop morphology on drying rates and retention of volatile substances. 1. Single-Drop. Ind Eng Chem Res. 39:1756-65.
Inglett GE, Gelbman P, Reineccius GA. 1988. Encapsulation of orange oil: use of oligosaccharides from a-amylase modified starches of maize, rice, cassava, and potato. In: Risch SJ, Reineccius GA, editors. Flavor encapsulation. Washington DC: Amer Chem Soc. p 29-36.
Kim YD, Morr CV. 1996. Microencapsulation properties of gum arabic and several food proteins: spray-dried orange oil emulsion particles. J Agric Food Chem. 44:1314-20.
King AH. 1995. Evaluation of the mechanisms associated with the release of encapsulated flavor materials from maltodextrin matrices. In: Risch SJ, Reineccius GA, editors. Encapsulation and controlled release of food ingredients. Washington DC: Amer Chem Soc. p 1_{43}-160.
Liu XD, Furuta T, Yoshii H, Linko P. 2000. Retention of emulsified flavor in a single droplet during drying. Food Sci Technol Res. 6(4):335-9.
Liu XD, Atarashi T, Furuta T, Yoshii H, Aishima S, Ohkawara M, Linko P. 2001. Microencapsulation of emulsified hydrophobic flavors by spray drying. Drying Technol 19:1361-74.
Maeda H. 2000. Soluble soybean polysaccharide. In: Philips GO, Williams PA, editors. Handbook of hydrocolloids. Cambridge, UK: Woodhead Publishing Ltd. p.309-20.
Marshall WR. 1954. Drop-size distributions from spinning-disk atomizers. In: Marshall WR, editor. Atomization and spray drying. New York, N.Y.: AIChE, Chem Engr Progress, Monograph Series. No. 2. p.68-73.
McNamee BF, O'Riordan ED, O'Sullivan M. 1998. Emulsification and microencapsulation properties of gum arabic. J Agric Food Chem. 46: 4551-55.
McNamee BF, O'Riordan ED, O'Sullivan M. 2001. Effect of partial replacement of gum arabic with carbohydrates on its microencapsulation properties. J Agric Food Chem. 49:3385-88.
Mongenot N, Charrier S, Chalier P. 2000. Effect of ultrasound emulsification on cheese aroma encapsulation by carbohydrates. J Agric Food Chem. 48:861-7.
Moreau DL, Rosenberg M. 1993. Microstructure and fat extractability in microcapsules based on whey proteins or mixtures of whey proteins and lactose. Food Struct 12:457-68.
Risch SJ, Reineccius GA. 1988. Spray-dried orange oil—Effect of emulsion size on flavor retention and shelf life. In: Risch SJ, Reineccius GA, editors. Flavor encapsulation. Washington DC: Amer Chem Soc. p 67-77.
Reineccius GA. 1988. Spray drying of food flavors. In: Risch SJ, Reineccius GA, editors. Flavor encapsulation. Washington DC: Amer Chem Soc. p 55-66.
Reineccius GA, Ward FM, Whorton C, Andon SA. 1995. Development in gum acacias for the encapsulation flavors. In: Risch SJ, Reineccius GA, editors. Encapsulation and controlled release of food ingredients. Washington DC: Amer Chem Soc. p 161-8.
Ré MI, Liu YJ. 1996. Microencapsulation by spray drying: influence of wall systems on the retention of the volatiles compounds. Drying'96- Proceedings of the 10th Intl Drying Symposium, Kraków, Poland. p 541-9.
Rosenberg M, Kopelman IJ, Talmon YY. 1985. A scanning electron microscopy study of microencapsulation. J Food Sci. 50:139-44.
Rosenberg M, Kopelman IJ, Talmon Y. 1990. Factors affecting retention in spray-drying micro-encapsulation of volatile materials. J Agric Food Chem 38:1288-94.
Rosenberg M, Young SL. 1993. Whey proteins as microencapsulating agents: microencapsulation of anhydrous milkfat-structure evaluation. Food Struct 12:31-41.
Rulkens WH, Thijssen HAC. 1972. The retention of organic volatiles in spray-drying aqueous carbohydrate solutions. J Food Technol 7(1):95-105.
Shahidi F, Han XQ. 1993. Encapsulation of food ingredients. Crit Rev Food Sci Nutr. 33:501-47.
Sheu TY, Rosenberg M. 1995. Microencapsulation by spray drying ethyl caprylate in whey protein and carbohydrate wall systems. J Food Sci. 60(1):98-103
Thijssen HAC, Rulkens WH. 1968. Retention of aromas in drying food liquids. De Ingenieur. 47:45-56
Verhey JGP. 1972. Vacuole formation in spray powder particles: 1. Air incorporation and bubble expansion. Neth Milk Dairy J 26:186-202
Zakarian JA, King CJ. 1982. Volatiles loss in the nozzle zone during spray drying of emulsions. Ind Eng Chem Pro Des Dev. 21:107-13