



Flavoring properties that affect the retention of volatile components during encapsulation process

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methyl cinnamate-E (PubChem CID: 637520)
hexenyl butyrate, 3Z- (PubChem CID: 5352438)
linalyl acetate (PubChem CID: 8294).

ABSTRACT

Flavorings are widely used in food and beverage industries and spray drying is the most cost-effective encapsulation technique to deliver stable products. Generally, the same slurry is used to encapsulate both hydrophilic and hydrophobic flavors which led sometimes to lower retention. The same slurry formulation composed by Modified Starch and Maltodextrin 20DE was loaded with 35% of two different flavorings (orange and passion fruit) and, spray dried under the same conditions. The flavorings selected had different octanol/water partition coefficients and their composition affected the emulsion stability. Orange flavoring presented clearly better emulsion stability than passion fruit flavoring, confirmed by size distribution and Turbiscan Stability Index (TSI orange \ll TSI passion fruit). A key learning from this work is that the best infeed emulsion achieved by the most hydrophobic flavoring, presented the lowest droplet size and yielded in final bigger particle size and the best encapsulation efficiency result (>92%).

Introduction

Flavorings are commonly applied into various food and beverage formulations and present a major influence on food sensory attributes and, consequently, on the satisfaction of final consumers (Gupta et al., 2016). Most aromatic chemicals are volatile compounds with relatively low molecular mass, becoming susceptible to evaporation and degradation reactions during the industrial processes or environmental conditions such as variations in pH, presence of light, oxygen and high temperatures (Bangs & Reineccius, 1982; Madene et al., 2006). To preserve added flavorings, microencapsulation by spray drying has been employed since a long time and during the last decades by food and flavoring industries (Gary A. Reineccius, 1989; Voilley, 1985). Encapsulation evolves the emulsification in a carbohydrate solution and ideally creates a protective environment for the flavoring compounds

that both reduces their volatility and mobility and preserves them from oxidative reactions by increasing the resistance to mass transfer.

However, losses observed during manufacture, storage or preparation depend on the classes of flavorings employed (Goubet et al., 1998), since they are composed of a mixture of aromatic chemicals with different solubility, sensory threshold, relative volatility and carried by solvents with different natures. These factors modify the thermodynamic and kinetic aspects of the entrapped flavoring e.g., partitioning and mass transport rate (Saifullah et al., 2019) which makes it difficult to create a unique and efficient formulation that ultimately results in the desired flavor blend after encapsulation. Numerous studies have been conducted in order to determine the main factors that influence the loss of flavoring components during encapsulation including spray drying operating parameters and formulation as well. The spray dryer infeed solids content, emulsion droplet size and processing conditions

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associated with various wall materials and emulsifiers represent some of most investigated parameters (Bangs & Reineccius, 1982; Frascarelli et al., 2012; Goubet et al., 1998; Gupta et al., 2016; Jafari et al., 2008; Landy et al., 1995; A. Sootitawat et al., 2003; Voilley, 1985). However, the properties of the core flavoring materials are also crucial in determining the final encapsulated aroma composition and hence, sensory quality. Fundamental studies have been conducted to understand the influence of such properties on the flavor retention using homologous and heterologous series of flavoring compounds (Bangs & Reineccius, 1982; Voilley, 1985). As a result, it is recognized that in concentrated carbohydrate matrices, there is a tendency to have greater retention with certain chemical groups (generally acids < aldehydes < esters ≤ ketones ≤ alcohols (Le Thanh et al., (1992), Goubet et al., (1998)), and because the retention is determined by a selective diffusion process (Thijssen et al., 2007) greater molecular masses represent greater retentions in the matrix. The conclusion is that small, very volatile and hydrophilic flavorings have lower retention than the larger, less volatile and hydrophobic flavorings when microencapsulated by spray drying (Reineccius, 2007; Reineccius, 2009).

Several works have demonstrated that volatility of the pure compound can only partially influence losses of volatiles during drying of food materials. In addition to this matter, since carbohydrate matrices are highly hydrophilic, the polarity of the flavoring influences its solubility and mainly can lead to the formation of two-phase systems, or not, within the matrix, creating, or not, an additional barrier to mass transfer. There are few studies dedicated to understand the influence of hydrophilicity and hydrophobicity of the active compound (Covarrubias-Cervantes et al., 2004; Gupta et al., 2016; Apinan Sootitawat et al., 2015) on the final performance of encapsulation efficiency and stability of the entrapped flavoring.

Aiming to contribute to the understanding of flavoring retention, in this study the same carrier material was used to encapsulate two flavorings with different characters, and the retention was followed during the encapsulation steps, i.e., emulsion phase and immediately after spray drying. The main objective of this study was to understand which stage of flavor particle formation has the greatest effect on process efficiency and volatile retention.

Material and Methods

Natural identical orange and passion fruit flavoring were supplied by Symrise Flavor and Fragrances Ltda (Cotia, São Paulo, Brazil). As carrier materials, Maltodextrin (DE20) and Modified Starch (Capsul™) were provided by Ingredion (Mogi Guaçu, São Paulo, Brazil). Diethyl ether, Methanol, Pentane, and *Tert*-butyl methyl ether were purchased from Merck (Darmstadt, Germany). 2-Nonanol (N30307-25G, purity 99%, Sigma-Aldrich, Steinheim, Germany) was used as the internal standard for chromatographic analysis. Sodium chloride and Sodium sulphate were purchased from Synth (Diadema, São Paulo, Brazil). MilliQ water was used in all experiments.

Flavoring concentration in the liquid phase - GC-MS analysis

The composition of each flavoring was determined using a GC/MS/FID (Agilent 7890/5977, Agilent Technologies, California, United States) equipped with a fused silica capillary column (VF-WaxMS column, Length: 30 m, Diameter: 0.25 mm, Film Thickness: 0.25 μm; Part# CP9205), the column flow was split between both detectors and simultaneous signals were obtained. MS was used to identify the compounds and FID was used for quantification, with the addition of an internal standard (2-Nonanol). The oven temperature was programmed to increase from 60 °C to 240 °C at a rate of 3 °C min⁻¹ with initial and final holding times of 2 and 23 min, respectively. The injection port and detector temperatures were set at 250 °C.

Mass spectra were obtained with electron ionization (EI) mode, at 70 eV. The identification of compounds was carried out based on the

comparison of their retention index (calculated using *N*-Alkanes from C6 to C30) and by comparing the mass spectra with a computer database (NIST MS Search 2.0, Mass Spectral Library NIST17 - National Institute of Standards and Technology) and with reference to published data in an internal library from Symrise. Data acquisition was performed using a computer software (Mass Hunter Software Rev.B.07.02.1938, Agilent Technologies, Inc.). Evaluation of the results was performed on the software ChemStation (Agilent Technologies, version: F.01.01.2317) and using an Amdis (version: V2.71) deconvolution tool.

The analysis of liquid flavoring was realized after dilution of 1.5 g of liquid flavoring sample with 8.5 mL distilled water. The dispersion was mixed and then 1 mL was taken and mixed with 4 mL of acetone containing the Internal Standard. After rest 1 h the mixture was filtered to remove water residue (PVDF syringe filter with Sodium Sulfate) and an aliquot (1 μL) of the diluted sample was injected on split mode using helium as carrier gas with a flow rate of 1.2 mL/min.

Emulsion preparation

A slurry is the mixture prepared for spray drying and it can be an emulsion or a dispersion. The wall materials (350 g of Capsul and 300 g of Maltodextrin) were dispersed in deionized water (1000 g) and stirred for 20 min for rehydration. Coarse emulsions were prepared by high-shear mixing orange or passion fruit flavoring at 35% wt (350 g) in relation to total solids. Homogenization was performed under 7800 rpm (Silverson Machine Ltda, model L4R, Bucks, England) for 90 s.

Stability of emulsion

The stability of the emulsions was evaluated immediately after preparation by laser backscattering scanning technique using the Turbiscan Lab® Expert (Formulaction, L'Union, France).

This instrument measures two different parameters: backscattering and transmission, which depend both on size and concentration of droplets in the samples. The fresh emulsion was placed in a cylindrical glass tube (0.140 m, height; 0.016 m, diameter) and measurements of backscattered light intensity were performed hourly for 5 h, and then after 24 h. The wet phase destabilization was analyzed using backscattering (BS) profiles, with scans at 880 nm. A plot of these results was produced with BS on the y-axis and the sample height (H, mm) on the x-axis. A sample height of H = 0 mm corresponds to the bottom of the measurement cell. The Turbiscan Stability Index (TSI) also was used to quantify simultaneously the destabilization processes in the emulsion. This index (Eq. (1)) is a statistical factor, and its value is calculated as the sum of all the destabilization processes in the measuring cell and it is given by:

$$TSI = \sum_0^j |scan_{ref}(h_j) - scan_i(h_j)| \quad (1)$$

Where, $scan_{ref}$ and $scan_i$ are the initial backscattering value and the backscattering value at a given time, respectively, h_j is a given height in the measuring cell and TSI is the sum of all the scan differences from the bottom to the top of the vial. This analysis was performed in duplicate.

Droplet size

The particle size distribution of the emulsions was determined using a Laser Scattering Particle Size Distribution Analyzer (LA- 950, Horiba, Kyoto, Japan). The emulsions were dispersed in water until reaching the desired obscuration level of the equipment. The refractive index values adopted for the oil and aqueous phases were 1.45 and 1.33, respectively. Sauter mean diameter ($D_{3,2}$) was employed to describe the mean diameter of droplets. This analysis was performed in triplicate.

Rheology

Viscosity measurement was performed by determining the flow curves. The tests were done on a Physica MCR301 rheometer (Anton Paar, Graz, Austria). The measurements were made in triplicate, in parallel plate geometry of 75 mm in diameter, with temperature-controlled at 25 °C per Peltier and Gap 0.5 mm system. The emulsions were evaluated 1 h after preparation. The obtained curves were evaluated according to empirical mathematical models and the emulsion apparent viscosity was calculated as the ratio between the stress and deformation. This analysis was performed in triplicate.

Encapsulation by Spray Drying

The fresh prepared slurries were spray dried with pilot scale Niro Spray Dryer (Model P-6.3, 316 Stainless Steel, Niro, Soeborg, Denmark), which was equipped with a rotary disc atomizer and had a water evaporation capacity of 5 l/h when operated under the conditions of this research (inlet temperature: 185 ± 5 °C and outlet temperature: 85 ± 5 °C). The slurries were fed into the main drying chamber through a peristaltic pump and the feed flow rate was controlled by the pump rotation speed.

Encapsulation Efficiency

This parameter is related to the efficiency of the process to entrap the different volatile compounds. Encapsulation efficiency (EE) was calculated as the percent of the volatiles found in the flavoring after powder extraction in relation to the original flavoring employed to produce the powder (Eq. 02).

The flavoring entrapped in the spray dried powder was free from the wall material. By weighting 1.5 g of the powder into an Erlenmeyer flask and adding 8.5 mL of water. The flask was stirred until the powder was completely dissolved. After mixing, immediately 1 mL was taken out of this solution and put into a second vial. On top of this solution, under stirring and slowly, 4 mL of acetone containing internal standard (ISTD) was added. The samples were held for 1 h and then 2 µL were directly injected into the GC.

The concentration of flavoring components in the acetone solution was then determined by GC-MS as described above.

Surface oil: The oil on the powder surface was recovered for analysis by dispersing the spray dried powder in an organic solvent and then analyzing the solvent for volatiles. In an assay tube with a cap, 2 g of the powder sample was mixed with 4 mL of Pentane/Diethyl Ether (2:1), 200 ppm of the internal standard was added, and then agitated for 10 min in a shaker. Then the resulting mixture was passed through a Syringe Filter (Pall, PTFE, 0,2 µm, 13 mm) into a GC vial for GC-MS analysis.

The amount of flavoring encapsulated inside particles is indirectly given by equation (2):

$$\text{EncapsulationEfficiency}(\%) = \frac{(\text{Encapsulatedflavoring})}{\text{Theoreticalload}} \quad (2)$$

Where, the theoretical load represents the calculated amount of flavoring in the dry particle assuming no loss of flavoring. All amounts determined by GC-MS represent the sum of analytics detected (in ppm) per gram of dry particles.

Stability after Spray Drying

Flavoring stability (rate of oxygen consumption) during shelf-life was estimated by Oxygen bomb methodology. 20 g of sample was placed in a cylindrical glass (height = 10 cm; diameter = 5 cm) and then in an Oxipres apparatus (Mikrolab Aarhus A/S, Højbjerg, Denmark) for 48 h. The apparatus is composed of a hermetically closed iron vessel and it was initially set at 5 N/m² of pressure (from oxygen added) and the

internal temperature was kept at 60 °C. The pressure variation resulted from oxygen consumption by the particles was recorded and the results were converted to volume of consumed oxygen, as follows in Eqs. (3) and (4):

$$n = \frac{\Delta P \cdot V}{R \cdot T} \quad (3)$$

$$V_{O_2} = \frac{n \cdot MM}{d_{O_2}} \quad (4)$$

where n is the variation of the number of moles (consumed O₂ mol), P is the pressure difference (N/m²), R is the gas constant (8.314 J/mol.K), T is the temperature (60 °C = 333.15 K) and V is the free volume in the iron vessel, which is given by the difference between the total volume (1.96 × 10⁻⁴ m³) and the volume occupied by the sample (V_{total} - V_{particle}), V_{O₂} is the consumed O₂ volume (m³), MM is the molar mass of oxygen (0.032 kg/mol), d_{O₂} is the O₂ density (1.33 kg/m³). This analysis was performed in duplicate.

Statistical analysis

All measurements were carried out on two or three separately prepared samples and using a statistical software package GraphPad Prism (GraphPad Software, San Diego, CA). The mean values were compared using the test t-student to determine significant differences at 95% (p < 0.05).

Results and Discussion

Characterization of the flavorings

The composition of the orange and passion fruit flavorings was determined by GC-MS analysis and the identified aroma compounds that contributed to make up >90% in weight are presented in Table 1. The molecular weight (MW), vapor pressure (VP) and octanol/water partition coefficient (log P_{ow}) of the main aroma compounds were employed to understand the aroma retention in a carbohydrate matrix. A weighted average of each component is also calculated and presented below.

The release behavior of flavors is normally treated in the literature by regarding individual components and many works have justified differences in the retention based on molecular weight of such molecules, even within a very low range of MW variation (Goubet et al., 1998; Landy et al., 1995; Rosenberg et al., 1990). The general rule is that, regardless of the interaction with the matrix, the higher the molecular weight of the molecule, the lower the diffusion through the matrix, and higher retention can be expected. Landy et al. (1995) reached this conclusion after evaluating individually the retention of four ethyl esters from a homologous series in sodium caseinate aqueous phase. Rosenberg et al. (1990) emulsified different esters into a continuous phase and spray dried under the same conditions. They determined that ethyl caproate (MW = 144 g/mol) was better retained than ethyl butyrate (MW = 116 g/mol). More complex mixture of flavors was employed by (Voilley, 1985). Despite the author evaluating 16 flavor compounds, the conclusions about retention as function of MW in different matrices were taken from the behavior of 4 flavor compounds. All these articles evidence the complexity of analysis when complex mixtures are adopted.

Reineccius (2004) stated that since molecular weight represents the molecular size of an individual component, it is an important factor that may drive the diffusion through the membrane of wall materials. Thus, larger molecular sizes would lower the diffusion rate and volatiles might not reach the particle surface for evaporation. However, the author also pointed out the importance of the vapor pressure of flavoring components as it is directly correlated to volatility of aroma compounds. The vapor pressure should indicate the tendency of the free compound to

Table 1

Characterization of orange and passion fruit flavorings by GC–MS analysis.

Orange Flavoring					Passion fruit Flavoring				
Aroma compound	*Total %	**MW (g/mol)	**VP(mmHg)	***Log P	Aroma compound	*Total %	**MW (g/mol)	**VP(mmHg)	***Log P
D-Limonene	77.10 ± 0.43	136.23	1.64	4.50	Triacetin	23.72 ± 1.74	218.20	< 0.01	0.40
Triacetin	8.22 ± 0.13	218.20	0.00	0.40	Ethyl butyrate	21.21 ± 0.89	116.16	12.80	1.80
α-Terpineol	2.50 ± 0.01	154.25	0.04	3.17	Styrallyl acetate	13.23 ± 0.31	164.20	0.20	2.70
Ethyl butyrate	2.07 ± 0.01	116.16	12.80	1.80	Ethyl propionate	9.64 ± 2.81	102.13	35.85	1.32
Hexanal	1.78 ± 0.01	100.16	11.26	2.37	Methyl butyric acid	8.07 ± 0.33	102.13	0.49	1.47
Myrcene	1.36 ± 0.01	136.23	2.01	4.32	Methyl cinnamate-E	4.03 ± 0.13	162.18	< 0.01	2.58
Dimethoxyethane	1.26 ± 0.01	90.12	171.20	4.44	Hexenyl butyrate	3.16 ± 0.34	170.25	< 0.01	3.18
Linalool	0.88 ± 0.005	154.25	0.16	2.68	Linalool	2.22 ± 0.06	154.25	0.16	2.68
Ethyl acetate	0.55 ± 0.03	88.11	93.20	0.74	Maltol	2.16 ± 0.22	126.11	0.00	0.24
Weighted average values		135.84	4.43	3.80	Linalyl acetate	1.74 ± 0.34	196.29	0.11	4.03
					Furaneol	1.44 ± 0.44	128.13	0.01	0.33
					Weighted values		139.53	6.24	1.42

*Total % = The total amount of each component in the flavor formulation is being followed by the standard deviation value. **MW = Molecular weight of aroma compound and VP = Vapor pressure of aroma compound at 25 °C (PubChem, 2021). ***Log Pow = logarithm of the ratio of the equilibrium compound concentration in octanol and in water; calculated values (EPI, 2000, estimation Programs Interface V3,10: database).

evaporate before an impermeable crust is formed on the surface of the drying droplet and would also determine retention during the encapsulation process.

The rules governing the retention of volatile compounds in a free form would be different when it is put in an emulsion. In O/W emulsions, both the oil phase and the emulsifiers can inhibit flavor release, while some emulsifiers can interact with flavor compounds in the water phase or the interfaces of O/W emulsions (Tamaru et al., 2019). Therefore, it is not possible to associate the retention of flavoring molecules during manufacture only with their molecular weight or volatility (i.e., pure vapor pressure) when several parallel mechanisms can affect these parameters from emulsion preparation to the spray drying process.

Since the current work deals with flavorings that are very complex systems, the basis of our discussion will be done in relation to the general behavior instead of the migration of individual compounds. The weighted average values depicted in Table 1 demonstrate the general character of the two flavorings. Losses of volatile molecules from the free liquid flavoring will occur based on the relation of their vapor pressure and the external pressure. But, once encapsulated, in a matrix structure, moist or dried, the losses of flavoring to the environment will be mainly determined by the partition coefficient between the different phases (continuous, dispersed and air) and rate of diffusion through the bulk matrix to the exterior (Reineccius, 2004). Orange flavor had a slightly lower weighted average molecular weight (MW = 135.84 g/mol) than passion fruit flavoring (MW = 139.53 g/mol) which may not have an overall impact in the retention. The partition coefficient between the emulsion and environment (air) estimates the preferential distribution of flavor compounds between the phases and therefore the release from emulsions. A good correlation of this coefficient with partition coefficients octanol–air, and water–air was previously found (Tamaru et al., 2018). Moreover, in O/W emulsions, it is considered that flavor compounds are transferred from oil droplets to a water (aqueous) phase (log P_{ow}) prior to release from the water phase into the air (vapor) phase (Tamaru et al., 2019).

The weighted average partition coefficient of orange oil (log P_{ow} = 3.80) indicates the tendency of the flavoring to be dispersed in a biphasic system. Beyond d-limonene (log P_{ow} = 4.5), orange flavoring includes different chemical groups such as an alcohol (α-terpineol), aldehydes (hexanal, dimethoxyethane), and other flavor components common to essential oils (e.g., linalool and myrcene), which also have high partition coefficients. In contrast, while there is just one compound representing 77% of the composition for orange flavoring, this same percentage was reached only with a sum of 5 compounds in the passion fruit flavoring mixture. The weighted average value of log P_{ow} for passion fruit flavoring was calculated as 1.42, which means that this flavoring has less hydrophobic character than the orange flavoring. This value is consequence of esters (ethyl butyrate, styrallyl acetate, ethyl

propionate, methyl cinnamate-E, hexenyl butyrate, linalyl acetate), and acids (methyl butyric acid) present in the passion fruit flavoring which have more miscibility with triacetin (Log P_{ow} = 0.40), a common solvent in flavoring compositions. A small fraction of flavoring substances such as linalool, furaneol and maltol; when combined with esters, results in a typical tropical fruit flavoring mixture. Although triacetin has a low log P value which might indicate that this material is more water-soluble. Triacetin is not particularly water soluble, but eventually hydrolyzes to form glycerol and acetic acid (Wright, 2011).

Stronger hydrophobic interactions may be expected with higher partition coefficient (log P_{ow}), which favors retention (Nishinari & Fang, 2021). In general, the values of these partition coefficients depend on the chemical functional groups present and the lengths of the carbon chains in the compound (Buttery et al., 1971) and increased values of Log P_{ow} represent a less polar substance. For this reason, the oily component employed in the slurry can improve the retention of flavor compounds (Rabe et al., 2004). For orange flavoring, the oily phase is the d-limonene in which only the esters (ethyl butyrate and ethyl acetate) with low log P_{ow} will have more limited partition. For passion fruit flavor, many of flavor components present will have a good partition into triacetin and it is expected a reasonable retention even for this “hydrophilic” flavoring.

Stability of the dried infeed emulsion

The stability of an emulsion is dependent upon its formulation which may contain a variety of different hydrophobic and hydrophilic components, including flavoring, oils, essential oils, esters, alcohols, triacylglycerol oils, oil-soluble vitamins, polymers and different solvents (Piorkowski & McClements, 2014) contributing synergistically or not, to the film stabilization around droplets of oil/flavoring. In the current study, emulsion stability was evaluated immediately after preparation (up to 24 h) and these results are presented in Fig. 1.

The global destabilization kinetics of the passion fruit emulsion was significantly (p < 0.05) greater than in the orange flavoring during the stability test (from 1 h to 24 h). Low TSI values were kept for the orange emulsion (TSI < 1) up to the 5th hour after its preparation. After 24 h, the maximum destabilization index was also still very low (TSI = 2, approximately) for the citric flavor. Conversely, passion fruit emulsion promptly presented much higher destabilization kinetics, increasing the TSI from 4.5 at the 1st hour up to TSI 6.2 at the 5th hour testing and after 24 h, TSI value 9 was reached.

The emulsion destabilization process (e.g. flocculation, creaming and coalescence); leads to changes in the droplet size and also in the profile of droplet concentration along the gravity axis which may affect intensity of transmittance (Zhao et al., 2018). According to Gomes & Kurozawa (2020), a visual test is commonly used, but it cannot detect a

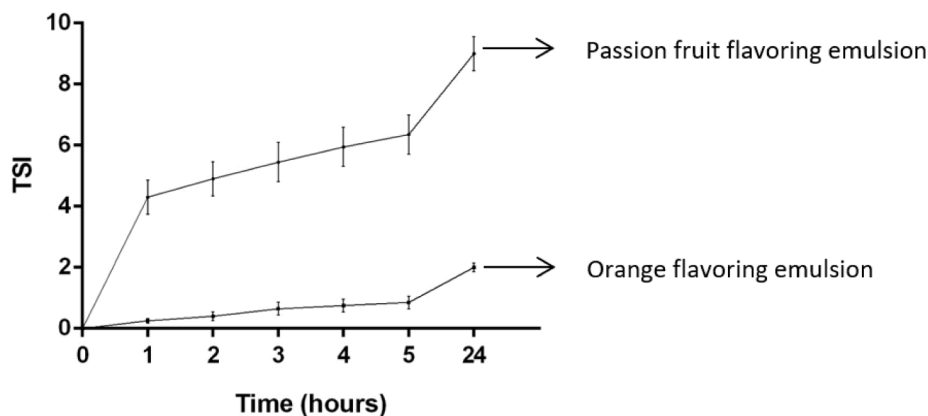


Fig. 1. Global destabilization kinetics (TSI - Turbiscan Stability Index) of orange and passion fruit slurries by Turbiscan.

stability issue at real time in the emulsion. The Turbiscan is a non-destructive method and any variation in droplet distribution size or diameter can affect the Backscattering (BS) signals. Then, the analysis of the BS profiles can provide additional information about the stability processes in the emulsions. Fig. 2 shows BS of the orange and passion fruit slurries during 24 h of stability test.

The BS profile is the reflection of waves or signals back in the direction from which they came. Thus, the less opaque the emulsion, the higher is its BS profile. The studied emulsions have significantly different BS profiles from each other. In the middle part of the emulsion, the BS of passion fruit emulsion changed from about 15% at $t = 0$ h to 6% after 24 h of emulsion preparation, while the orange emulsion showed a lower BS value change with time, being very close to 53% during the whole test (in all parts of the emulsion - bottom, middle, top). Considering bottom and top differences in Fig. 2, the highest deviation happened in the first hour test for passion fruit emulsion, where the BS

varied from 12% at 4 mm (bottom portion) to 16% at 38 mm (top portion) of the tube. No BS difference between bottom, middle and top part was observed for orange flavoring emulsion.

Both emulsions are composed of the same wall material mixture and the differences in emulsion stability are due to the ability of the flavor phase to be dispersed into droplets and to the wall materials to adsorb onto flavor droplet surface. To understand the correlation between BS and droplet distribution, the mean droplet size and viscosity of each dryer infeed emulsion is shown in Table 2.

Immediately after emulsion preparation ($t = 0$ h) the mean particle size of the passion fruit emulsion was statistically higher than that of the orange oil emulsion. Moreover, the analysis of the size distribution profile highlights the difference between particle size from the top and bottom part of the emulsion for both emulsions, although for orange emulsion these values were always below $1 \mu\text{m}$.

Normally, commercial emulsions are polydispersity systems and

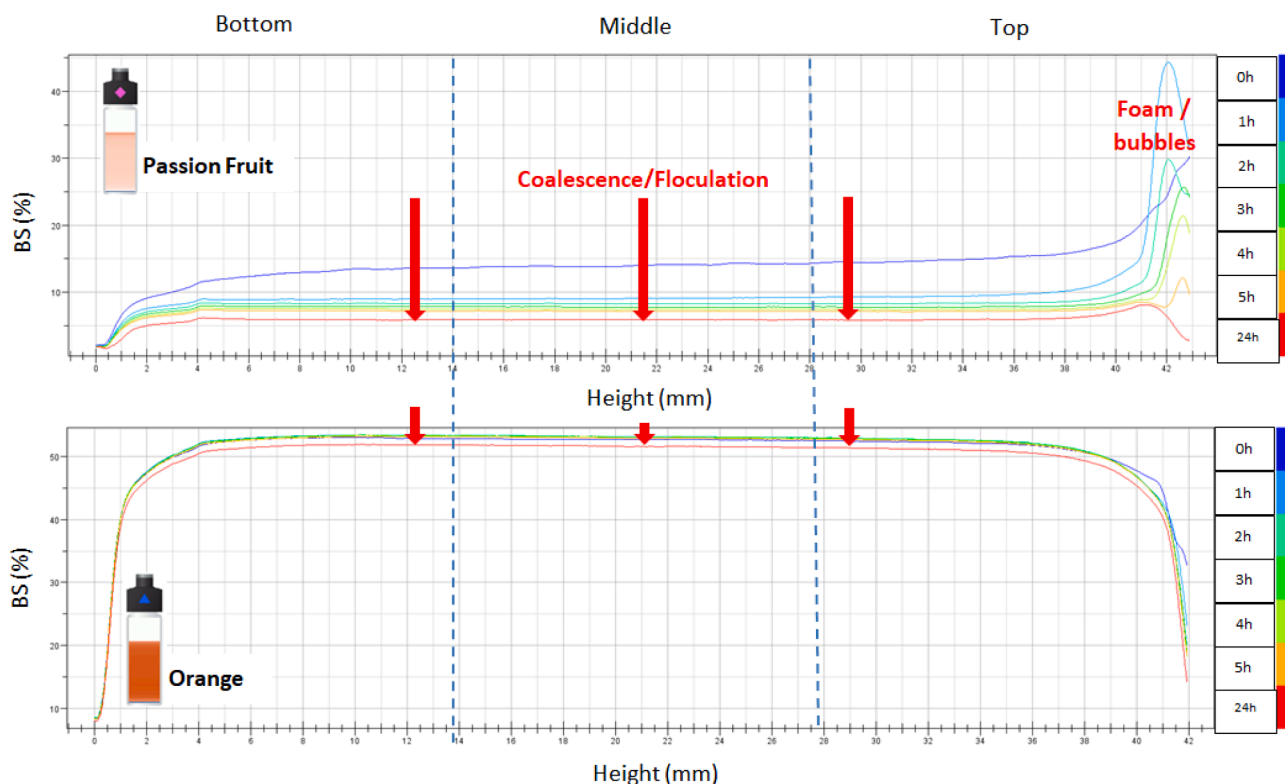


Fig. 2. Backscattering (% BS) profiles of orange and passion fruit emulsions (bottom - middle - top) through the height (mm) of the tube containing such products. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Droplet sizes and viscosities of flavoring emulsions.

Emulsion Time - Source	Mean Size ($D_{3,2}$)		Viscosity (Pa.s)	
	Orange flavoring	Passion fruit flavoring	Orange flavoring	Passion fruit flavoring
Global			0.117 ± 0.004 ^a	0.096 ± 0.001 ^a
t = 0 h - Bottom	0.65 ± 0.01 ^c	1.36 ± 0.04 ^d		
t = 0 h - Top	0.62 ± 0.02 ^e	1.83 ± 0.71 ^f		
t = 5 h - Bottom	0.81 ± 0.04 ^g	5.00 ± 0.69 ^h		
t = 5 h - Top	0.83 ± 0.05 ^g	7.35 ± 1.55 ⁱ		

Statistically difference, 95% level ($p < 0.05$): first row comparing orange and passion fruit viscosities; the other rows comparing orange and passion fruit droplet sizes from bottom and top parts of emulsion (in their respective columns); each column for comparing effect of time.

flavoring emulsion producers seek to develop a final product with a narrow monomodal distribution since it usually provides the best long-term stability (Piorkowski & McClements, 2014). Still, considering the emulsion right after its preparation ($t = 0$ h), the orange emulsion presented monomodal profiles for the top and bottom part and relatively low polydispersity (< 1.0). The passion fruit emulsion at analyzed at the same time as orange presented also monomodal profiles, although for the top part of such emulsion, the polydispersity was relatively high (> 1.0) showing a tendency to destabilization (Table 3).

As largely known, the hydrophobic nature of orange flavoring is crucial to forming an emulsion (Walstra, 1993). An emulsion with small droplet size distribution and high viscosity favors the better stability of the system, once small droplets have less mobility in a viscous dispersed phase (more resistance). If those droplets don't move, at least not fast; they have less chances of meeting and coalesce, flocculate or just separate by gravitational separation.

After 5 h standing, the droplet size distribution for orange emulsion increased but there was no difference between bottom and top positions (Table 2). On the other hand, the droplet size of passion fruit flavoring increased significantly ($p < 0.05$) for bottom and top parts of the emulsion ($p < 0.05$). Moreover, the profile of distribution size also changed for passion fruit, becoming bimodal, after 5 h standing.

As previously discussed, the behavior observed for passion fruit emulsion can be more related to the coalescence and/or flocculation of droplets. The increased size of oil droplets led to the modification of light transmittance (or backscattering) through the height, and it can be caused by the lack of superficial tension between passion fruit flavor and the matrix which can generate stability issues as shown in Fig. 2 by the distance between BS at 0 h and 5 h.

Destabilization kinetics will be influenced by gravitational forces, to which Stoke's law is applied to demonstrate the parameters involved in such destabilization:

$$v_{Stokes} = \frac{2gr^2(\rho - \rho_0)}{9\eta} \quad (5)$$

Where: v_{Stokes} = creaming/sedimentation velocity [m/s], g = gravity acceleration [m/s^2], r = radius of oil droplets [m], ρ = density of particulate phase [g/m^3], ρ_0 = density of continuous phase [g/m^3] and η = viscosity of the system [$g/m.s$].

The destabilization kinetics, therefore, are highly dependent on the viscosity of the coarse emulsion: the viscosity of passion fruit emulsion (0.096 Pa.s), although lower than orange emulsion (0.117 Pa.s) (Table 2, was not significantly different at $p < 0.05$). The behavior of both emulsions was Newtonian, and this allows directly calculating the dynamic viscosity of the phases, according to George Stokes, the British Scientist who developed this relationship in 1851. Despite an increase in viscosity reduces the creaming rate of the particles, the stability of orange emulsion can be not attributed to this small difference in the

viscosity values. Creaming in the present case is the upward movement of particles since both flavorings had a lower density than the aqueous phase (Piorkowski & McClements, 2014). The oil phases used in this study consists mostly of D-Limonene ($\rho_{orange\ flavoring} = 0.8930\ g/cm^3$) and mix of esters with triacetin ($\rho_{passion\ fruit\ flavoring} = 1.0081\ g/cm^3$), indicating a tendency of high velocity of creaming for orange emulsion droplets.

The contribution of the oil droplet radius to creaming is exponentially greater than viscosity or density differences. Therefore, the creaming velocity of passion fruit emulsion would be much higher than that of the orange emulsion, confirming the differences observed among such samples, from 1 to 24 h (Fig. 1).

Although lower in impact, the viscosity also affects the stability of the emulsion since lower viscosities favor internal mixing during the drying process which delays the formation of a semipermeable surface leading to greater flavoring losses during early encapsulation. Thus, a higher infeed viscosity can improve volatile retention (Reineccius, 2004). However, increasing the viscosity too much will slow the formation of discrete particles during atomization which promotes volatile losses. Thus, there is an optimum infeed viscosity for the retention of volatiles.

Flavoring retention analysis in the particles

As initially mentioned, some intrinsic properties of the aroma compound are determinant in flavoring retention (Goubet et al., 1998; Rosenberg et al., 1990) and chemical interactions between volatile compounds and the components of the matrix can occur at the wet stage, increasing the retention in the final particle.

Both flavorings were prepared using the same slurry formulation and under very similar preparation conditions. Aroma retention during drying was measured in powder obtained from the whole emulsion atomized right after slurry preparation ($t = 0$ h) and the bottom and top portions atomized after 5 h of slurry preparation ($t = 5$ h). Flavor retention determined by GC-MS is presented in Table 4.

The time necessary to dry an emulsion in a laboratory will depend on the amount of material and capacity of the equipment. In the current case, the drying process took about 20 min to be completely done. This time is too short to observe any consequence of emulsion destabilization, since there was not enough time for this to happen. If we do not consider any standing time between the preparations of emulsions and drying, the encapsulation efficiency of orange emulsion was 92.7% and of passion fruit emulsion 86.2% (statistically different, $p < 0.05$).

The slurry formulation used for orange and passion fruit flavorings was quite effective in markedly avoiding losses of flavoring compounds considering that the drying happened right after emulsion preparation. We know that in a real process or industrial scale, the timing of drying may be quite long reaching up to 12 h drying, depending on batch size and productivity. Although it is recommended to keep the emulsion under constant agitation during the whole drying process, interruptions or unscheduled shutdowns may occur. That is why it is important to work with stable emulsions to avoid any deviation when this type of circumstance happens.

From the stability test it was possible to see a clear destabilization curve for passion fruit formulation after the first hour of its preparation (Fig. 1). Destabilization measured by Turbiscan Stability Index (TSI), up to the fifth hour, was close to 1 for orange flavoring, while the TSI value for passion fruit emulsion was above 6. Considering these results, after standing for 5 h without agitation, the emulsions were spray dried and the encapsulation efficiency was determined by GC-MS. Encapsulation efficiency was determined on the powder obtained by separately spray drying the top and bottom parts of the emulsion in order to check if there was any difference in the encapsulation efficiency.

Table 3 shows that there was no significant difference between the encapsulation efficiencies when the bottom versus the top part of the orange emulsion was spray dried. However, a significant difference in

Table 3
Profiles of flavoring emulsion's distribution sizes.

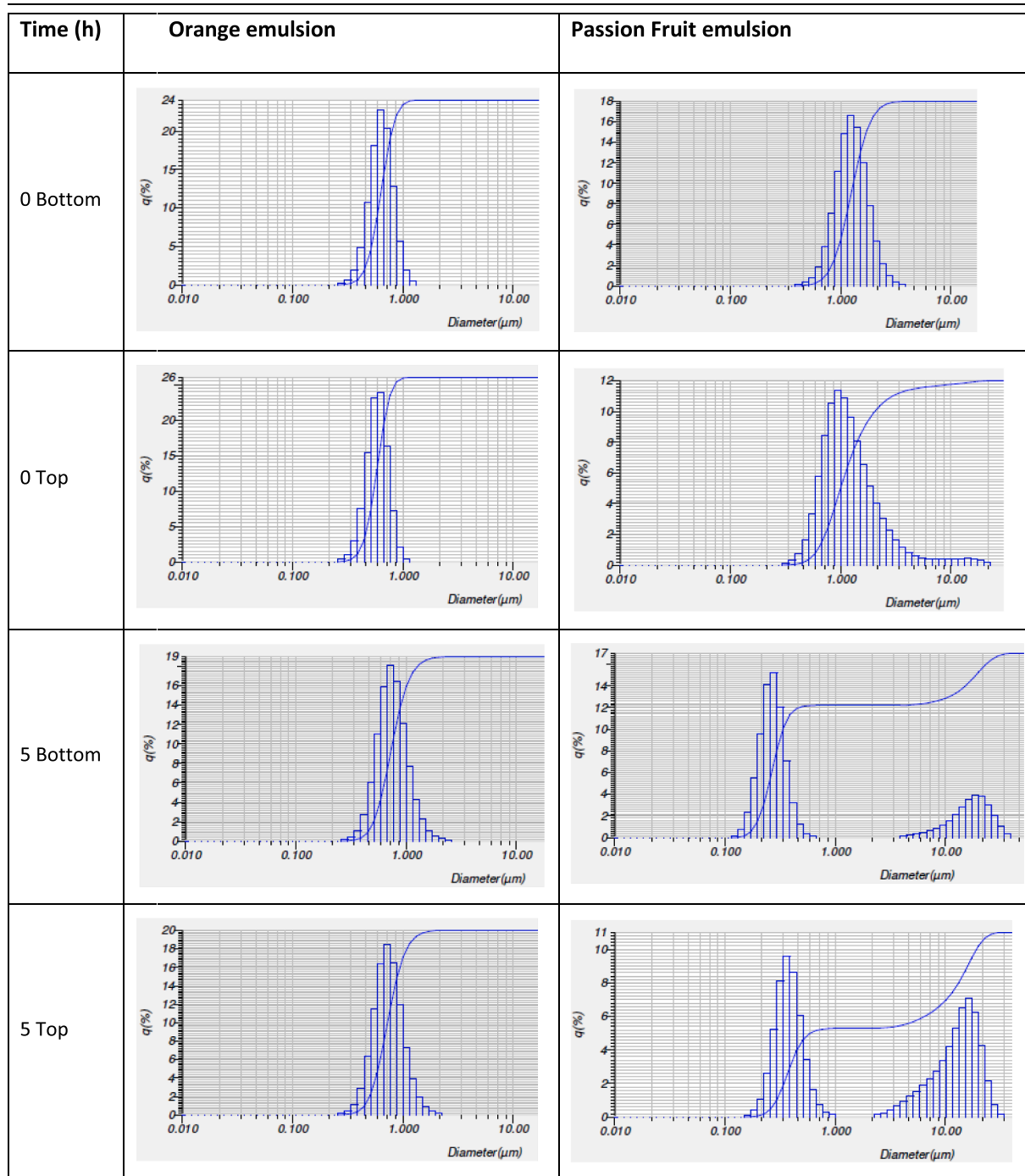


Table 4
Encapsulation efficiency of both emulsions – one made from a freshly made slurry (0 h) and the other from a 5th hour old emulsion.

Time (h)	Encapsulation Efficiency by CG-MS (%)	
	Orange flavoring	Passion fruit flavoring
t = 0 Global	92.7 ± 1.2 ^a	86.2 ± 1.1 ^b
t = 5 Bottom	93.0 ± 0.1 ^a	86.8 ± 0.2 ^b
t = 5 Top	92.2 ± 4.0 ^a	88.4 ± 0.3 ^c

Statistically difference, 95% level ($p < 0.05$): each row; second and third row comparing orange bottom and top and passion fruit bottom and top (in their respective columns); each column for comparing effect of time.

retention was determined in the passion fruit emulsion (top part better than bottom part). This difference is probably related to the destabilization event detected in the emulsion phase and discussed previously in the stability test. There was consistent high encapsulation efficiency for orange flavoring from zero up to 5 h standing (>92%). The orange flavoring particles presented significantly ($p < 0.05$) better encapsulation efficiency than passion fruit flavoring particles during the whole process, supporting the previous discussion about how different nature of flavorings and also different stability of their slurries can affect the encapsulation process.

The loss of volatiles during drying for both flavor systems happens during the time to form the protective crust around the drying droplet in

the constant period of drying (Menting & Hoogstad, 1967). The hydrophobic compounds from orange oil tend to be in the small emulsion droplets being separated from the continuous phase by the tense active molecule (biphasic organization). The aroma released from such droplets enclosed by the matrix will face more resistance than the passion fruit flavoring that has some hydrophilic chemicals, which are probably only mixed, after stabilization by drying, and that can contribute to higher exposure to drying conditions before the crust to be formed.

Not surprisingly, emulsions are commonly used to protect flavoring compounds in fluid food products, and efforts are constantly realized to create more robust interfacial properties (Given, 2009; Hu et al., 2003; Longyuan et al., 2010). Many of the food and beverage products containing volatile flavorings compounds are oil-in-water (O/W) emulsions, which consist of small lipid droplets dispersed in an aqueous medium. Flavorings contain components that range from ionic and polar hydrophilic species to nonpolar hydrophobic species. In the case of passion fruit flavoring, which has less hydrophobic character, as shown by its partition coefficient (log P), the interface that should separate oil phase and aqueous phase may be weak and permeable for some hydrophilic components. This also corroborates with the better interaction of the hydrophobic flavoring with the emulsifier of the matrix, while the hydrophilic components are simply dispersed in the system with higher exposure to the air phase. According to Bhandari et al. (2001), the greater solubility of polar components in water results in higher diffusivity through the hydrophilic matrix compared with nonpolar components. In this context, clearly the incorporation of flavoring into polymeric matrices shows that the emulsion already has a role in reducing the volatility of the flavorings.

The higher vapor pressure of the passion fruit flavorings compounds as well as the greater solubility of polar components in water should solubilize and distribute the flavoring throughout the slurry thereby reducing the gas phase concentration. Furthermore, an increased resistance to mass transfer can be expected in case of orange flavoring due to its partition between the hydrophobic droplet phase and the hydrophilic dispersed phase (Gunning et al., 1999).

Among the very limited number of chemical functions reviewed, alcohols are usually the best retained compounds by carbohydrates. This tendency was observed by Bangs & Reineccius (1982) with vapor pressure in such growing order: alcohol > aldehyde > ketone for Maltodextrin DE10, which can indicate an interaction with the matrix that the partition coefficient could not explain.

The encapsulation efficiency for orange flavoring can be separated by groups (t = 0 h): d-limonene and myrcene, both with MW = 136.23 g/mol, with about 94% each, terpineol-alpha and linalool (both, MW = 154.25 g/mol) with about 92% (E.E.), ethyl butyrate (MW = 116.16 g/mol) and hexanal (MW = 100.16 g/mol) with 69% and, finally, the lowest value was reached by ethyl acetate (MW = 88.11 g/mol) with about 68% (E.E.). There is a large difference in encapsulation efficiency between d-limonene and ethyl acetate. It is easy to see a relationship between the molecular weight of the volatiles and retention. The alcohols terpineol-alpha, linalool, d-limonene and myrcene have the highest MWs and the highest E.E.s. The differentiation of d-limonene and myrcene from other volatiles is their high Log P values, 4.50 and 4.32, respectively. The hydrophobic character of these chemicals can positively affect their retention as already mentioned. A similar comparison is terpineol-alpha and linalool with 3.17 and 2.68 log P values while the ethyl acetate has a log P value of 0.74. The hydrophobic character of the orange flavor components is proposed as the main driver for the high encapsulation efficiency of the whole profile.

For passion fruit flavoring, the encapsulation efficiency was more related to molecular weight and vapor pressure values of individual components, than to chemical groups or log P values. The hexenyl butyrate,3Z- (MW = 170 g/mol) and methyl cinnamate-E (162.18 g/mol) presented the best retentions, with 97.7% and 100% encapsulation efficiencies. The worst retentions in this flavoring were of ethyl butyrate (MW = 116 g/mol), ethyl propionate (MW = 102 g/mol) and ethyl

acetate (MW = 88.11 g/mol), with about 63.7%, 47.5% and 66.3% encapsulation efficiency, respectively. Vapor pressure is inversely related to volatile retention, where the lowest vapor pressure values (<0.01 mmHg). Hexenyl butyrate,3Z- and methyl cinnamate-E had the best encapsulation efficiency. Ethyl acetate, one of the lowest encapsulation efficiencies, has a vapor pressure value of 93.2 mmHg, followed by ethyl propionate with 35.85 mmHg and ethyl butyrate with 12.80 mmHg.

Gharsallaoui et al. (2012) evaluated the retention of ethyl esters with low log P during spray drying and it was confirmed that for these classes of compounds there was an inverse correlation between volatility and retention. This behavior can be explained by the diffusion process within the particle matrix. As the molecular weight of a volatile compound increases, its molecular sizes also increases and the diffusion rate decreases (Goubet et al., 1998; Reineccius, 2004).

As mentioned at the beginning of the discussion, the correlation of volatiles retention with molecular weight or any other independent factor will depend on various aspects. Since carbohydrate matrices are highly hydrophilic, the polarity of the flavoring influences its solubility and can lead to the formation of two-phase systems, or not, within the matrix, creating, or not, an additional barrier to mass transfer.

In the current work, regardless of the interaction with the matrix, the losses observed must be related to the solubility of the aromatic chemicals in water as well as to the lack of protection of an interfacial film in case of passion fruit (less hydrophobic flavorings) which are reflected in an unstable emulsion.

Physical stability of spray-dried particles

A primary purpose of flavoring microencapsulation or any other sensitive active products is to protect the material and then to improve shelf life and efficiency of the process. Numerous factors affect the results when different wall materials, emulsion characteristics and drying parameters are used. However, it is well documented that smaller emulsion droplet sizes are very good to retain volatile compounds and for efficiency as well, as less flavoring components are lost during the process, reducing also cost of manufacturing (Gupta et al., 2016).

The particle size distribution of the spray dried passion fruit flavoring was significantly smaller ($D_{4,3} = 36.9 \mu\text{m}$) than orange flavoring ($D_{4,3} = 44.1 \mu\text{m}$) under $p < 0.05$. The orange emulsion presented a much smaller flavor droplet distribution size (Table 2 with great emulsion stability and this system generated bigger final spray dried particles ($D_{4,3}$) than passion fruit emulsion and the highest encapsulation efficiency (Table 4. Several works in the literature have reported that must be possible to improve encapsulation efficiency and volatile retention by increasing the difference between droplet size and particle size (considering that there is an optimum value for particle size) (Chang et al., 1988; Fang et al., 2005; Jafari et al., 2007; Rulkens & Thijssen, 1972).

Oxygen consumption is an indication of degradation by an oxidative reaction. Both flavoring powders indicated good stability during the simulated shelf life as almost no oxygen (<0.1 ppm) was consumed during the tests. This behavior can be explained by the reduced surface area to volume ratio of the particles resulting in a decrease in the effective surface area for volatiles to release and react with oxygen. The most reactive products in this type of analysis are the ones that are exposed on the surface of the particles, i.e., non-encapsulated flavoring compounds. Although orange flavoring presented significantly better encapsulation efficiency than passion fruit, the surface oil calculated by GC-MS for both flavorings was very small and lower than 0.5%. This leads to the conclusion that for these flavorings, the main stability issue happens during emulsion stabilization, because once this product is dried taking out available water for chemical reactions, the spray dry products seem to be similarly stable during shelf-life.

It is important to highlight that orange profile is the susceptible flavoring to oxidation reaction. The good emulsion stability and great

result of encapsulation efficiency of this citric flavoring can prove that this encapsulation method was effective in order to protect the degradation of this flavoring when exposed to high concentration of oxygen.

There is not a conclusive correlation between the spray dried powder particle size and flavoring retention in the literature.

Conclusion

From this study it was possible to verify that the slurry preparation is a crucial step for improving the retention of flavoring components during encapsulation. Emulsion droplet size and emulsion's viscosity influenced the physical stability of the emulsions before drying. The smaller droplet size and higher viscosity (orange emulsion) generated better encapsulation efficiency with lower loss during the whole encapsulation process than passion fruit flavoring. Passion fruit flavoring having less hydrophobic character formed a poorer and less stable emulsion (larger droplet size). Our results show that unstable drier infeed emulsions should be dried quickly after emulsion preparation in order to improve the retention of volatiles. As the main stability issue happened in the infeed emulsion, it is recommended to design different slurry for hydrophilic (or less hydrophobic) flavorings. Good emulsion stability can be reached by increasing viscosity and reducing droplet size; and consequently, it will generate bigger particle size and an improvement on the retention of volatile components in the final spray dried powder.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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