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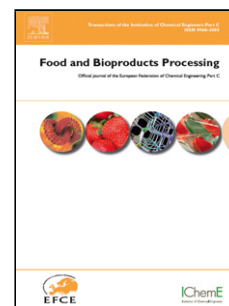
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**Encapsulation of citral in formulations containing sucrose or trehalose:
emulsions properties and stability**

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Abstract

The performance of formulations for citral encapsulation by spray drying was assessed. Focus was put on the emulsions properties and stability. Formulations contained sucrose or trehalose with or without maltodextrin and a modified starch as emulsifier. Viscosity, molecular mobility, microstructure, droplet size distribution, and stability were analyzed before and after spray-drying. Instability processes operated in the emulsions bulk, being flocculation the main one. Droplet size and viscosity influenced the emulsions stability. An increase in viscosity attained by the addition of MD delayed the global destabilization processes. Emulsion properties and stability were similar between the formulations containing sucrose or trehalose. Also, there were no differences regarding aroma retention or sensorial perception of citral. The mixture of maltodextrin and trehalose presented higher T_g values allowing to maintain the glassy state of the powder in broader temperature and relative humidity conditions. Trehalose presented a promising performance as an ingredient in the carrier formulation to encapsulate citric flavors.

Keywords: citral; encapsulation; emulsions; trehalose; sucrose; spray drying.

1. Introduction

Microencapsulation of flavors is of great importance in the flavoring and food industries. This process is carried out in order to obtain a dry flavor powder, which is easy to handle due to the advantage of the solid state. Flavor encapsulation can be accomplished by a variety of methods such as spray-drying, spray-chilling or spray-cooling, freeze-drying, extrusion, coacervation and molecular inclusion, among others. The choice of appropriate microencapsulation technique depends on the end use of the product and the conditions involved in the manufacturing process (Madene *et al.*, 2006). The two major industrial processes are spray-drying and extrusion (Beristain *et al.*, 1996; Goubet *et al.*, 1998; Yamamoto *et al.*, 2011), although freeze-drying (Yang *et al.*, 2011) and coacervation (Patrick, 2013) are also used.

The most common way to perform the microencapsulation of flavors is by spray drying, which is the transformation of a feed from a fluid state (solution, dispersion, emulsion) to a dried particulate form. This technology results suitable; not only in providing protection against degradative reactions and preventing the loss of flavor, but also in giving the controlled release of flavors.

The manufacturing and storage processes, packaging materials and ingredients present in foods often cause modifications in overall flavor by reducing aroma intensity or producing off-flavor components. On the other hand, many factors linked to aroma (soluble or not in water) affect the global quality of the food: a) the physico-chemical properties; b) the matrix affinity, since some flavors are more stable in carbohydrates based matrix carriers and others are more stable in lipid-based coatings; and c) the concentration and interactions of volatile aroma molecules with food components (Landy *et al.*, 1995).

Emulsions are complex two-phase systems, made by droplets dispersed in a continuous phase. They are inherently unstable due to the difference in specific gravity between these two phases. Specifically, oil in water emulsions (o/w) constitute colloidal systems in which small lipid droplets are dispersed in an aqueous medium and form the basis of many kinds of foods. The conversion of two separate immiscible liquids into an emulsion, or the reduction of the size of the droplets in a preexisting emulsion, is achieved by homogenization processes. Conventional methods to prepare emulsions rely on stirring equipment, colloid mills, homogenizers, ultrasonics or microfluidizers (Charcosset, 2009).

The retention during spray drying of flavors, insoluble in water, (Soottitantawat *et al.*, 2003) can be largely influenced by the emulsion droplets size. Soottitantawat *et al.* (2003) have found that a smaller emulsion size is needed for the higher retention of non soluble flavors (for a certain range of sizes).

For technologists, the ability to control the properties and stability of food emulsions is a key factor in the development of better products. In this contribution, focus was put on the encapsulation of citral flavor (non soluble in water). The choice of components for the carrier matrix was based on obtaining a stable powder capable of efficiently encapsulate citral. In this sense, a modified starch was incorporated as an emulsifier, due to its ability of lowering the surface tension at the oil–water interface and imparting viscosity to the aqueous continuous phase (Prochaska *et al.*, 2007). The addition of maltodextrin (MD) to the formulation provides a low cost, bland polysaccharide that is not particularly surface-active; and its main stabilizing action in oil-in-water emulsions is believed to be through viscosity modification or even gelation of the aqueous continuous phase surrounding the oil droplets when the used concentration is appropriate. Also, the high glass transition temperature (T_g) of low dextrose equivalent MD provides good physical stability to the dried powders (Bhandari and Hartel, 2005). Regarding the spray

drying process, it is well known that the type of carriers affects the flavor retention, for this reason, disaccharides, mainly sucrose, are sometimes included in commercial formulations to improve retention characteristics (Menting *et al.*, 1970). Concerning the powder stability, sucrose has some negative characteristics as it has a relatively low T_g , which has shown to affect the storage stability of orange and strawberry spray-dried flavors (Busso Casati *et al.*, 2007). On the other hand, trehalose could be used as an alternative to use in microencapsulation, as it shows higher T_g values compared to sucrose (Komes *et al.*, 2003). Komes *et al.* (2003) observed an improvement in aroma retention in dehydrated strawberry purees in the presence of trehalose compared to sucrose. In a previous work, no significant differences in the perception of citral flavor in emulsions containing trehalose or sucrose were observed (Sosa *et al.*, 2011). So, the potential use of trehalose as a component of the carrier formulation for citral encapsulation was assessed in the present contribution.

Therefore, the objective of this work was to comparatively determine the performance of four sugar based formulations for citral encapsulation by spray-drying. Emulsions attributes and stability were analyzed before, and after the spray-drying process (upon hydration of the powder with water).

Materials and methods

2.1. Materials

Sucrose and trehalose, of analytical grade, were purchased from Merk (Germany) and Cargill Inc. (Wayzata, MN, USA), respectively, and Maltodextrin (MD) with a dextrose equivalent of 12 was from Givaudan S.A. (Argentina). The commercial modified starch used as emulsifier was from Capsul (Gelfix, Argentina). The dispersed phase was

constituted by citral “Extra Fino” kindly given by Saporiti Sabores (Argentina). Deionized water was used in all cases.

2.2. Emulsions preparation

Premixtures were prepared by completely dissolving in water, the starch and either sucrose or trehalose, or a mixture (1:1) of MD plus S or MD plus T. These mixtures constituted the continuous phases of the emulsions, and after adding the required citral amount, will constitute forward in the text the so called S, T, SMD and TMD formulations. In all cases, the total mass of dry solids was 40 g per 100 g of emulsion. The exact mass of each dry component in the formulations is detailed in **Table 1**. 200 mL of each pre-emulsion were obtained by mixing the ingredients in a Griffin & George (Loughborough, UK) stirrer. This operation was carried out for 2 min, at 25°C and 750 rpm. Emulsions formation was completed by submitting the pre-emulsion to a high speed blender, Sorvall OMNI MIXER 17106 -OMNI Corporation International, Waterbury (CT, USA), operating at 16000 rpm for 10 min. The temperature increase was avoided by keeping the sample into an ice bath during stirring.

One set of samples were immediately spray-dried. These samples were destined to the study of reconstituted emulsions (RE). The remaining samples constituted the so called fresh emulsions (FE), which were immediately analyzed.

2.3. Spray-drying

The emulsions were spray-dried using a laboratory scale device, Mini Spray Dryer Büchi B290 (Flawil, Switzerland). The operational conditions of the drying process were: the co-current flow method, inlet air temperature $175 \pm 3^\circ\text{C}$, outlet air temperature $83 \pm 3^\circ\text{C}$, flow rate 8 mL/min, air pressure 3.2 bar, two-fluid nozzle diameter 1.5 mm. Once obtained, the powders were collected into sealed PVDC bags and then stored at -18°C

until analysis. The powders moisture (% in dry basis) was determined in duplicate by the Karl Fischer method, using a Mettler Toledo DL 31 titrator (Schwerzenbach, Switzerland). After spray-drying, the powders a_w values ranged between 0.098 and 0.183 with standard deviations lower than 0.005. The obtained moisture values were 4.30 ± 0.14 , 4.44 ± 0.07 , 3.82 ± 0.22 , and 4.69 ± 0.10 for S, T, SMD, and TMD emulsions, respectively. Dry powders were dissolved in deionized water to give the RE (keeping the original solids content 40%).

2.4. Viscosity determination

Apparent viscosity of emulsions was determined from the respective flow curves, whose points were collected with a cone and plate DV-LVT Brookfield viscometer (Middleboro, MA, USA) using a stainless steel cone 41, at room temperature 25 ± 1 °C. A shear rate range between 0.5 and 200 s^{-1} was applied (Kawakatsu *et al.*, 2001). The sample volume was 2 ml. All the determinations were made at least in duplicate.

2.5. Distribution and size of emulsion droplets

The droplet size of emulsions was measured by light scattering using a Mastersizer 2000 device with a dispersion unit Hydro 2000MU (Malvern Instruments Ltd, UK). Immediately after emulsions preparation, aliquots of each sample were poured into the dispersion unit. The pump speed was set at 1800 rpm. A refractive index (RI) of the disperse phase of 1.488, and its absorption parameter of 0.001 were used. Droplet size is reported as the volume–surface mean diameter or Sauter diameter ($D_{32} = \sum n_i d_i^3 / \sum n_i d_i^2$) and the equivalent volume–mean diameter or De Broucker diameter ($D_{43} = \sum n_i d_i^4 / \sum n_i d_i^3$), where n_i is the number of droplets of diameter d_i (Huang *et al.*, 2001; Leroux *et al.*, 2003). D_{32} is inversely proportional to the specific surface area of droplets, and provides a measure of the mean diameter where most of the particles fall. D_{43} is more sensitive

to changes in particle size involving destabilization processes (Relkin and Sourdet, 2005), and it was used for evaluation of emulsions structural stability (flocculation or coalescence). The droplets size is informed as the average and standard deviation of ten readings made on each of two independently prepared emulsions.

In other set of measurements, aliquots of each FE were poured into the dispersion unit containing 1.0% sodium dodecyl sulfate (SDS) (w/w) solution. Measurements in the presence of SDS allowed evaluating the individual droplet size without flocculation (Anton *et al.*, 2002).

2.6. Molecular mobility

A Bruker mq 20 Minispec pulsed nuclear magnetic resonance (NMR) instrument, with a 0.47T magnetic field operating at resonance frequency of 20 MHz, was used for measurements. 4 mL of each emulsion was placed into 10 mm diameter glass tubes prior to analysis. Proton transverse relaxation times T_2 associated to slow relaxing protons were measured using the Carr–Purcell–Meiboom–Gill pulse sequence (CPMG) $90^\circ x-(t-180^\circ y-t \text{ echo})_n$. The decay envelopes were fitted to bi-exponential behavior with the following Eq.1:

$$I = A_1 \exp(-t/T_{2-1-CPMG}) + A_2 \exp(-t/T_{2-2-CPMG}) \quad (\text{Eq.1})$$

where I represents the NMR signal intensity at time t . The relaxation time $T_{2-1-CPMG}$ corresponds to the protons in the less mobile water fraction. A_1 is proportional to the number of protons in the T_{2-1} state. The relaxation time $T_{2-2-CPMG}$ corresponds to the more mobile water fraction. A_2 is proportional to the number of protons in the T_{2-2} state. All determinations were performed in triplicate and the average and standard deviation are informed.

2.7. Emulsion stability upon time

The stability of FE and RE was analyzed using a Quick Scan vertical scan analyzer (Beckman Coulter, Fullerton, CA, USA). 7.0 mL of each sample was loaded into a cylindrical glass measurement cell and the backscattering and transmission profiles as a function of the sample height (total height = 10 cm) were obtained in quiescent conditions (25° C). In this way, the physical evolution of the destabilization process is followed without disturbing the fresh system and with good accuracy and reproducibility (Pan *et al.*, 2002). The Quick Scan head acquired backscattering and transmission data every 40 μm . Measurements were performed immediately after emulsion preparation and every 30 min during 2 h. Because of the importance of the stability maintenance in the RE, which may be used to design lemon flavor based beverages, data were also obtained 24 h after emulsions reconstitution.

2.8. Microstructure

The Olympus FV300 (Olympus Ltd, London, UK) confocal laser scanning microscope (CLSM) with a Ar gas laser ($\lambda = 488 \text{ nm}$) was used to collect the images. A 10X ocular was used, together with a 60X objective for a total visual magnification of 600X. The laser intensity used was 20%. Images were recorded by using confocal assistant Olympus Fluoview versión 3.3 software provided with the FV300 CLSM. The sample preparation was performed following the protocol of Herrera and Hartel (2001). Briefly, emulsions (5 mL) were kept under stirring, 0.5 μg of Nile Red stain powder was added one hour before the observation. The Nile Red stains the oil so that the oil droplets appear red in the micrographs and the aqueous phase appears dark.

2.9. Statistical analysis

Significant differences between samples properties were determined by analysis of variance (ANOVA) using the general linear model procedure. An alpha level of 95 % ($p < 0.05$) was used to determine significance. Statgraphics 3.0 software was used for these procedures.

2. Results and discussion

3.1. Emulsions characterization

The knowledge of the emulsions rheological properties results necessary to properly design unit operations like pumping systems, and to determine the organoleptic characteristics perceived by the consumers (Gabriele *et al.*, 2009). As many factors affect the rheology of food emulsions, the rheological properties cannot be predicted a priori, so experimental studies on food emulsions are necessary (Rao *et al.*, 1999).

The viscosity–shear rate relationship of emulsions can be used to provide information about the strength of the colloidal interactions between droplets (Hunter, 1993; Tadros, 1994). **Figure 1** shows the flow curves for the different fresh emulsions (FE) (**Fig. 1a**) and reconstituted emulsions (RE) (**Fig. 1b**). RE were prepared by dissolving each spray-dried powder in water, keeping the original solids/water ratio.

For all the emulsions, the shear stress increased linearly as the shear rate increased. Therefore, viscosity resulted constant upon shear stress variation, showing the Newtonian character of the analyzed emulsions, in the studied domain.

Figure 1c shows the viscosity values obtained for FE, RE, and their continuous phases, and also for pure citral. S and T formulations manifested viscosity values similar to those corresponding to their continuous phases. Citral viscosity (2,2 cp) seemed not to contribute to the global viscosity of the S and T emulsions.

S and T emulsions, both for FE and RE, presented viscosity values significantly lower than emulsions containing maltodextrin (SMD and TMD). As MD is a branched polysaccharide whose molecules expand into the aqueous solution, it exerts a remarkable viscous effect (Klinkesorn *et al.*, 2004). Therefore, TMD and SMD emulsions manifested viscosity values higher than those corresponding to single sugar emulsions. Another observation was the fact that before drying the polysaccharide containing emulsions presented higher viscosities than after drying, having RE similar values than their corresponding continuous phases. If such a fact had obeyed only to the MD presence, the viscosity values would have been similar. In the case of FE, flocs disruption during viscosity measurements could cause the increase in viscosity values observed for TMD and SMD. At this respect, Starov and Zhdanov (2003) pointed out that the effective viscosity increases with the degree of flocculation.

It is known that the droplet size distribution influences the properties of the emulsion in aspects such as rate of destabilization processes, long-term stability, resistance to creaming, texture and optical appearance, viscosity, physiological efficiency in emulsions destined to controlled delivery of compounds, and chemical reactivity (Jurado *et al.*, 2007). Risch (1988) and Soottitantawat *et al.* (2003) observed that the droplet size is an important parameter in the retention of encapsulated citric aromas.

Figure 2 illustrates the volume and number size distribution derived from the static light scattering (SLS) measurements made at room temperature 25 ± 1 °C and at initial times, for FE and RE formulations. All the studied emulsions presented a very similar droplet size distribution, with a multimodal pattern i.e. polydispersed populations. In the case of RE a peak between 100 and 1000 μm was detected. The apparition of these big droplets was attributed to bubbles formation generated during the size measurements (Murray *et al.*, 2009). The volume distribution could be converted to number distribution in order to compare the relative importance of each droplet size population into the

global distribution (**Fig. 2 insets**). The number distribution showed only one peak, which indicated the existence of only a dominant population, with average size around 0.15 μm both for FE and RE, which means that the majority of the emulsion droplets fell into the nano-scale.

The volume-surface mean diameter (D_{32}) and the equivalent volume-mean diameter (D_{43}), both derived from the droplet size distribution, were used to characterize the droplets diameters (**Figure 3**). S and T emulsions manifested the highest D_{32} values for FE (**Fig. 3a**). The MD-containing FE showed much lower D_{32} values, which were not significantly different from the values obtained for all the analyzed RE.

In the case of the attribute D_{43} , fresh emulsions presented higher values than their respective RE, and constituted significantly different groups among them (**Fig. 3b**). The large D_{43} values correspond to the occurrence of one or more destabilization processes operating into the emulsions bosom (Relkin & Sourdet, 2005; Palazolo, 2006). In general, RE formulations presented an important decrease in D_{32} and D_{43} values compared to those observed for the respective FE. This could be due to the disruption of emulsion droplets into smaller droplets during atomization in the spray-drying process, as it was previously reported (Soottitantawat *et al.*, 2003).

MD-containing emulsions showed a particular behavior. D_{32} values for FE were relatively low; however, D_{43} values were high. In the case of RE, both D_{32} and D_{43} resulted low. The D_{32} values for FE and RE did not present significant differences. However, the values obtained for FE were slightly higher, and this could indicate that the initial droplet size was big enough to favor destabilization. The emulsion's droplets association pattern was affected by the presence of MD upon drying and rehydration, generating a system with fewer tendencies to flocculate in comparison with MD containing FE.

In order to identify the type of droplets aggregation occurring in the FE (flocculation or coalescence), the determination of droplets sizes was also made in the presence of SDS (**Fig. 3b**). SDS acts dissociating any existing flocs, therefore, the particle size measured with SDS addition shows no change if the emulsion had coalesced, but it will show differences or will revert to the original particle size distribution if the destabilization had occurred by flocculation (Dickinson, 1992). A persistent droplet association was observed only for T emulsions, which indicated certain degree of coalescence. The S and MD-containing emulsions showed very low D_{43} values, indicating that practically no coalescence developed, and only reversible flocculation was present.

3.2. Molecular mobility

$^1\text{H-NMR}$ measurements were performed to estimate the molecular mobility in the different emulsions (**Figure 4**). Transverse relaxation times (T_2) were determined after the application of the CPMG pulse sequence. These T_2 values are associated to relatively slow proton relaxations, which in turn would be related to water molecules with little interactions with solids (Fullerton and Cameron, 1988; Kou *et al.*, 2000). Two populations having different molecular mobility were detected. The less mobile populations were represented by T_2 (T_{2-1}) values, of approximately 87 ms and 35 ms for the formulations containing pure sugars and mixtures with maltodextrin, respectively (**Figure 4a**). The populations with higher mobility were represented by T_2 (T_{2-2}) values, of approximately 500 ms for S and T, and 300 ms for SMD and TMD (**Figure 4b**). There were no differences in the T_2 values due to the sugars or between FE and RE. The main difference observed was due to the presence of MD which caused an important reduction in the water mobility, probably due to the high molecular weight and the high viscosity generated in the emulsions.

3.3. Emulsions stability upon time

The length of time that an emulsion must remain stable depends on the nature of the food product (Dickinson, 2003). Some emulsions are formed as intermediate steps during a manufacturing process and therefore only need to remain stable for a few seconds, minutes or hours, whereas others must remain stable for days, months or even years prior to consumption (Mc Clements, 1999). In the case presented here, it was required that the emulsions were stable during the time elapsed from their preparation up to their drying, i.e. a few minutes. Therefore, the stability studies were carried out for two hours, a period that exceeded the life time required.

Emulsions stability was studied by analyzing the back scattering profile as a function of time. This technique offers the advantage to allow the continuous evaluation of the global emulsion destabilization in quiescent conditions and without previous dilution (Palazolo *et al.*, 2005). According to Mengual *et al.* (1999) these profiles constitute the macroscopic fingerprint of the emulsion at a given time. The back scattering is a parameter directly dependent on the particle mean diameter (D) and on the particle volume fraction (ϕ), i.e. back scattering = $f(D, \phi)$ (Cerqueira *et al.*, 2007). The back scattering profiles as a function of tube length containing FE and RE obtained at room temperature are shown in **Figures 5** and **6** respectively. In general a regular back scattering pattern was observed all along the tube length, indicating the absence of creaming and sedimentation (Mengual *et al.*, 1999; Palazolo *et al.*, 2004) However, in the case of FE (**Figure 5**), a uniform decrease in the averaged back scattering curves was observed upon time, indicating slow flocculation occurrence (Palazolo *et al.*, 2004). In this case, the destabilization processes operated relatively fast, given that at 30 minutes there was an important decrease in the % back scattering and that the changes observed at longer times were less relevant. Probably the destabilization started in the

preparation process, which resulted coincident with the high D_{43} values observed at the initial times (**Figure 3b**). The back scattering analysis for the RE did not show important changes up to 2 hours of storage (**Figure 6**), which could be related to the relatively smaller droplet sizes (**Figure 3a**). However, it is important to note that the initial percentage of back scattering (at $t=0$) was approximately 10% lower for RE compared to FE. This fact indicates that there would be a certain degree of flocculation occurring in the RE formulations upon powders reconstitution. These results seem to be contradictory with the data obtained by the SLS measurements (**Figure 6**), unless we consider that the flocs could be linked by very weak bonds with no possibility to resist the shear and dilution imposed by the dispersion unit of the static light laser device.

In order to clarify this behavior we analyzed micrographs obtained by CSLM for all the formulations at the initial time (**Figure 7**). FE displayed a homogeneous droplets aspect for all the studied formulations (**Figure 7a,c,e,g**). The pictures confirm the presence of highly packed systems with the smallest droplets occupying the free spaces between the biggest ones. Meanwhile RE (**Figure 7b,d,f,h**) showed the presence of aggregates with droplets that suffered a certain degree of deformation, especially in MD containing emulsions. The observation of these micrographs allowed the visualization of the flocs indicating that flocculation could occur as a consequence of emulsions drying and concomitantly with the later reconstitution process. The reconstituted emulsion can be considered mainly to see the evolution of oil droplets size from original emulsion to after spray drying in powder.

As a potential technological application for the citral powders could be their incorporation into dehydrated citric juices, which need to be hydrated to consume, it would be desired that the product stability would last at least one day after the powder reconstitution. Then, back scattering profiles corresponding to 24 h of storage were also included for RE (**Figure 6**). After one storage day, a back scattering decrease at the

bottom part of the tube with a back scattering increase occurring at the top can be seen for T and S emulsions (**Figure 6a, b**). This phenomenon was indicative of creaming (Mengual *et al.*, 1999; Palazolo *et al.*, 2004; Cerdeira *et al.*, 2007). On the other hand, after 24 h storage, SMD and TMD emulsions showed a certain degree of flocculation, and also the rising of flocs indicated by a back scattering increase in the top part of the tube (**Figure 6c, d**). These results show that the presence of the polysaccharide helped to avoid the extended creaming. Also, the higher molecular mobility observed in T and S formulations (**Figure 4**) contributed to the higher destabilization developed in these systems.

3.4. Spray-dried powders properties

In a previous work we analyzed several properties of the spray dried powders: the water content, the glass transition temperature (T_g), the T_2 relaxation times (as an estimation of molecular mobility) and the percentage of citral retention (determined by GC) (Sosa *et al.*, 2011). Being a water activity (a_w) value of 0.11 appropriate for powder storage in order to minimize physical deterioration, the above mentioned properties (**Table 2**) were evaluated at this a_w value (determinations were made on samples equilibrated at 11 % relative humidity for 14 days at 23 °C. In these conditions all the powders were in the glassy state). Water content values were lower for sucrose containing formulations than for trehalose ones, as reflected by lower T_2 values. Also, trehalose containing formulations showed higher T_g values than those observed for sucrose containing powders. As expected, maltodextrin caused an increase in T_g values for both sugars formulations. The higher citral retention was observed for TMD, being quite similar for the rest of the formulations.

3. Conclusions

During atomization in the spray-drying process some disruption of emulsion droplets occurred, leading, in general, to smaller droplets sizes. The obtained size was small enough to assure certain stability (at short storage times) independently of the formulation's composition. This suggests that there would be a threshold droplets size to achieve stability that does not depend only on emulsions viscosity; i.e. T and S emulsions having lower viscosity values than MD-containing emulsions presented similar droplet size after reconstitution.

The results shown in this work indicate that emulsion properties and stability are similar between the formulations containing sucrose or trehalose. Also, the spray-dried powders did not show significant differences regarding aroma retention or sensorial perception of citral. Then, trehalose could be used as a replacement for sucrose without introducing deleterious characteristics in the emulsions prepared to encapsulate this kind of citric aromas. However, it would be advisable to use sugar-MD mixtures since creaming processes were detected in quiescent conditions in single sugar reconstituted emulsions. Besides, the mixture of maltodextrin and trehalose presented higher T_g values, suggesting that it is the best formulation among the analyzed in this work, to maintain the glassy state in broader temperature and relative humidity conditions for powder storage. It can be concluded that trehalose presented a promising performance as an ingredient in the carrier formulation to encapsulate oil flavors.

Today new technologies are being developed to reduce the size of the droplets emulsions and thus extending their uses in industry, principally those concerning to flavor encapsulation. Among the recent trends in this field, mixed systems constituted by different carrier matrices are studied in order to obtain better physical-chemical properties, allowing more efficient encapsulation both for protection and controlled release of the active ingredient. Our conclusions are based on the use of certain

components (matrices, emulsifiers), at certain total solid content, and specific spray drying conditions. The study was made at a pilot stage; other conditions will be studied in the near future.

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Table legends

Table 1. Dry components (g /100 g dry matter) of the formulations containing citral, trehalose (T), sucrose (S), trehalose-maltodextrin (TMD), sucrose-maltodextrin (SMD).

Table 2. Properties of the spray-dried powders containing encapsulated citral at $a_w = 0.11$: water content (WC), glass transition temperature (T_g), transversal relaxation time (T_2), citral retention by sensorial analysis (perception), and citral retention (by GC).

Figure legends

Figure 1: Flow curves for (a) fresh emulsions (FE), and (b) reconstituted emulsions (RE): Trehalose (■), Sucrose (●), Trehalose-Maltodextrin (□) and Sucrose-Maltodextrin (○). (c) Viscosity values for FE, RE and the components of the continuous phases (corresponding to the formulations T, S, TMD, SMD) and dispersed phase (citral). Means with a different letter are significantly different ($p < 0.05$).

Figure 2: Droplet size distribution for Trehalose (a), Trehalose-Maltodextrin (b), Sucrose (c), and Sucrose-Maltodextrin (d) FE (■) and RE (□). Measurements were made at initial times. Each point corresponds to the mean of ten readings made on each of independently prepared emulsions.

Figure 3: Parameters obtained from static light scattering: (a) volume surface mean diameter (D_{32}), and (b) equivalent volume mean diameter (D_{43}) for FE and RE. Means with a different letter are significantly different ($p < 0.05$).

Figure 4: T_2 relaxation times obtained by ^1H RMN after the application of the CPMG pulse sequence for FE and RE. T_{2-1} values correspond to the less mobile populations (a) and T_{2-2} values to the populations with higher mobility (b). Means with a different letter are significantly different ($p < 0.05$).

Figure 5: Back scattering profiles as a function of the tube length (arrow denotes time) in quiescent conditions for FE (a) Trehalose, (b) Sucrose, (c) Trehalose-Maltodextrin, and (d) Sucrose-Maltodextrin. Each curve represents the mean value of two independently prepared samples.

Figure 6: Back scattering profiles as a function of the tube length (arrow denotes time) in quiescent conditions for RE (a) Trehalose, (b) Sucrose, (c) Trehalose-Maltodextrin, and (d) Sucrose-Maltodextrin reconstituted emulsions. Each curve represents the mean value of two independently prepared samples.

Figure 7: Confocal laser scattering microscopy (CLSM) images of FE: S (a), T (c), SMD (e), TMD (g); and RE: S (b), T (d), SMD (f), TMD (h).

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Table 1. Dry components (g /100 g dry matter) of the formulations containing citral, trehalose (T), sucrose (S), trehalose-maltodextrin (TMD), sucrose-maltodextrin (SMD).

Formulations	% of dry components				
	Citral	Modified Starch	Trehalose	Sucrose	Maltodextrin
T	12.5	7.5	80.0	-	-
S	12.5	7.5	-	80.0	-
TMD	12.5	7.5	40.0	-	40.0
SMD	12.5	7.5	-	40.0	40.0

Table 2. Properties of the spray-dried powders containing encapsulated citral at $a_w=0.11$: water content (WC), glass transition temperature (T_g), transversal relaxation time (T_2), citral retention by sensorial analysis (perception), and citral retention (by GC). The values are mean values \pm SD, $n=3$.

Formulations	WC (% b.s.)	T_g (°C)	T_2 (μ s)	Perception (%)	Retention (%)
T	4.68 \pm 0.01	52.60 \pm 0.50	7.11 \pm 0.09	54.40 \pm 4.81	73.04 \pm 0.16
S	2.98 \pm 0.01	28.12 \pm 0.10	6.35 \pm 0.04	60.80 \pm 4.80	75.92 \pm 0.27
TMD	4.47 \pm 0.24	54.75 \pm 1.02	7.44 \pm 0.07	57.60 \pm 4.80	81.36 \pm 0.90
SMD	3.56 \pm 0.16	44.31 \pm 0.47	6.77 \pm 0.05	64.00 \pm 4.79	75.44 \pm 0.29

Highlights

Emulsion properties and stability were similar between samples with different sugars

The droplets size was small enough to assure stability no matter the composition

Trehalose could be used as a substitute of sucrose for citral encapsulation

Maltodextrin/trehalose/starch was better for the glassy state maintenance in storage

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