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Characterization and oxidation stability of spray-dried emulsions with omega-3 oil and buttermilk processed by ultra-high-pressure homogenization (UHPH).

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ABSTRACT

Integrating functional ingredients, such as buttermilk and omega-3 rich oils, in spray-dried emulsions (SDE) is a suitable way to incorporate these ingredients in dairy products to substitute dairy fat and increase their added value. Ultra-high-pressure homogenization (UHPH) processing of liquid emulsions considerably improves stability compared to the conventional homogenization (CH) process. With this premise, SDE were produced while comparing CH (30 MPa) and UHPH (100 or 200 MPa) processing of feeding emulsions. Emulsions were formulated with (50:50 chia:sunflower) oil, whole commercial buttermilk (BM), and maltodextrin (MD) as wall materials. Further spray drying of emulsions was then conducted. Obtained SDE were characterized in terms of water content, A_w (water activity), flowing properties, water solubility, encapsulation efficiency (EE), color, and microstructure. Oxidation stability of SDE was analyzed in accelerated oxidation conditions at 50 °C for one month for primary and secondary oxidation analysis evolution on days 1, 7, 14, and 31 of storage. Results showed better ability of BM as encapsulating agent in UHPH-processed emulsions with 7% of BM. This improvement was especially observed in the flowing properties and encapsulating efficiency. Seven percent BM UHPH-treated SDE showed the best primary oxidation stability during storage, while the 4% BM-UHPH-treated SDE exhibited better secondary oxidative stability.

1. Introduction

Substituting or enriching the lipid fraction of foods with oils rich in polyunsaturated omega-3 offers the opportunity to consumers to increase the daily intake of these components, which in general is insufficient in the diet of most of the population (Kris-Etherton, Harris, & Appel, 2002). In addition, if buttermilk (BM) is also incorporated in the emulsion as an emulsifier, which is also recognized as a biofunctional compound (Ali, 2019; Hernell, Timby, Domellöf, & Lönnerdal, 2016; Singh & Gallier, 2017; Vanderghem et al., 2010), the potential advantages of the obtained emulsion are multiple. BM is a by-product of butter production, with a market maintaining an average annual growth rate of 1.16% from 2013 to 2016 (Ali, 2019). Its use in the food industry includes the production dry mixes, bakery products, and dairy products such as cheese or yoghurt (Ali, 2019). Thus, BM may increase the added value of food products to which it is supplemented, such as, infant formulae. BM is rich in milk fat globule membrane (MFGM), composed mainly by phospholipids, sphingolipids, and glycoproteins, all of them responsible for giving BM functional value (He et al., 2017; Lopez et al., 2017). These compounds have shown beneficial health effects, such as lowering of cholesterol levels and improved brain development and cognitive function in infants, within others (He et al., 2017; Lopez et al., 2017; Spitsberg, 2005). The use of oil-in-water emulsions is common in the pharmaceutical and food industries for encapsulating bioactive lipids as delivery systems of lipophilic functional components. Spray drying is the most widely used technology in the food sector for the preparation of solid emulsions due to its wide availability, versatility, and low cost.

Microencapsulation of oil in SDE requires droplets to be surrounded by a coating in a homogeneous or heterogeneous matrix to give small capsules providing a physical barrier between the core compound and

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Abbreviations

a*	red-green color parameter
Aw	water activity
b*	yellow-blue color parameter
BM	butter milk
CH	conventional homogenization
CI	Carr's index
HR	Hausner Ratio
MD	maltodextrin
MDA	malondialdehyde
MFGM	milk fat globule membrane
EE	encapsulation efficiency
L*	luminosity
SDE	spray dried emulsion
UHPH	ultra-high-pressure homogenization
YI	yellowness index
WI	whiteness index

other components of the product. Thus, the combination of an emulsifying agent to adsorb at the oil-water interface and a polysaccharide with high solid content and low viscosity is required to create the matrix in which droplets are embedded. Both types of compounds, emulsifiers, and polysaccharides, are commonly called wall materials. Maltodextrin (MD) is one of the most widely used polysaccharides in SDE combined with an emulsifying material, in this case BM.

Although drying of emulsions is a good system for the protection and release of bioactive compounds, unsaturated fatty acids are susceptible to oxidation. However, as reported by Augustin et al. (2015) whole BM powder was found to be better to high heat skim milk powder as an encapsulant to produce recombined omega-3 oil powders, founding a lower oxidation in BM emulsions. Similarly, another study (Zhang et al., 2020) using algal oil encapsulated with 100% or 50% buttermilk mixed with 50% maltodextrin showed good EE and oxidation stability of spray dried emulsions.

Homogenization systems produce fine emulsions, which show different degrees of oil protection against oxidation. UHPH processing may work up to 400 MPa (Hebishy, Buffa, Juan, Blasco-Moreno, & Trujillo, 2017). Currently, the UHPH technology capable of reaching up to 400 MPa is under development. Therefore, it is considered an emerging technology with great potential for the food, pharmaceutical and other industries in which colloidal products require great physical stability, as well as a microbial reduction. Mechanisms acting in UHPH are great intensity physical forces on dispersed particles such as friction, compression, acceleration, and shear resulting in great size reduction of particles, including microorganisms. All this result in high physical stability of dispersions, and microorganisms' inactivation when compared with conventional high-pressure homogenization systems (Dumay et al., 2013; Fernandez-Avila, Arranz, Guri, Trujillo, & Corredig, 2015; Hebishy, Buffa, Guamis, Blasco-Moreno, & Trujillo, 2015). On the other hand, protein material usually used as emulsifiers in food emulsions, may also experience structural modifications to some extent, depending on the type of protein incorporated (Fernandez-Avila & Trujillo, 2016; Hebishy, Buffa, et al., 2017; Hebishy, Zamora, Buffa, Blasco-Moreno, & Trujillo, 2017), thus creating a thick interfacial layer in the oil-water interface which prevents against lipid oxidation (Fernandez-Avila & Trujillo, 2016). These studies showed that oil-in-water emulsions made with whey protein isolate and sodium caseinate and treated by UHPH exhibited a greater physical and oxidative stability than emulsions produced with conventional homogenization. With this premise and considering the good results in emulsion stability observed in a previous study (Aghababaei et al., 2020) with a similar formulation to the present study, it is expected that improved characteristics of SDE-UHPH-treated emulsions will be found compared to conventional homogenized ones. The effect of UHPH and its potential protection of spray-dried against oxidation, as well as the general characteristics of powders, could contribute to find new opportunities for this emerging technology, which has not yet been studied for this purpose. Hence, the main objective of this work was to characterize and evaluate the oxidative stability of spray-dried emulsions obtained from UHPH (100 and 200 MPa) and conventional (30 MPa) homogenized feeding emulsions formulated with 4 and 7% BM, 10% oil and 30% MD.

2. Material and methods

2.1. Materials

Glucidex® 19-Maltodextrin (MD) was purchased from Roquette Freres (Lestrem, France) with 19 DE. Buttermilk powder (BM) was obtained from Activa Food-Tech, S. A. (Girona, Spain) with the following composition: 30% protein, 7% fat, 52% lactose, less than 4% moisture and 7% ash. Crude chia oil (20% C-18:2, >56% C-18:3 according to the specifications) was obtained from Interfat, S. A. (Barcelona, Spain). Crude sunflower oil (4–9% C-16:0, 1–7% C18:0, 15–85% C18:1, 50–72% C18:2) was purchased from Gustav Heess (Barcelona, Spain). All other chemicals used were of analytical or better grade.

2.2. Emulsion preparation and analysis

Six different samples (Table 1) of emulsions were obtained. The preparation procedure is fully described elsewhere (Aghababaei, Cano-Sarabia, Trujillo, Quevedo, & Ferragut, 2021). After mixing of ingredients, coarse emulsions were further homogenized using conventional (CH) or UHPH treatments. CH was performed with a Homolab (FBF Italia, Sala Baganza PR, Italy) at 30 MPa. Subsequently, heat treatment of emulsions was made at 65 °C, 30 min. UHPH treatments at 100 and 200 MPa were processed in an Ypsicon equipment Model A-60, which is an ultra-high-pressure continuous device (60 L/h) (Ypsicon Advance Technologies, S.L., Barcelona, Spain) that works up to 300 MPa. Working temperatures of samples were the following: 40 °C inlet temperature; 60 ± 2 and 80 ± 3 °C, at the high-pressure valve, corresponding to 100 and 200 MPa respectively; and 25 °C outlet temperature, which was reached after a quick cooling by a heat exchanger connected to the UHPH equipment. Emulsions were collected in Pyrex bottles for further sampling and analysis. Emulsions were analyzed as fully described by Aghababaei et al. (2021) for particle size distribution, using a Mastersizer laser diffraction 2000 analyzer (Malvern Instruments Ltd., Worcestershire, UK) and confocal laser-scanning microscope (Leica TCS SP5, Leica Microsystems GmHB, Mannheim, Germany) was used to observe the structure of fresh emulsions (24 h after production).

2.3. Spray drying of emulsions

Emulsions were dried in a Mini Spray-Dryer B-290 (Büchi

Table 1
Emulsion formulations and treatments.

Sample name	H (MPa)	Oil % (w/w)	MD % (w/w)	BM % (w/w)	TS % (w/w)
4CH	30	10	30	4	44
4UH100	100	10	30	4	44
4UH200	200	10	30	4	44
7CH	30	10	30	7	47
7UH100	100	10	30	7	47
7UH200	200	10	30	7	47

H: homogenization conditions; CH: conventional homogenization treatment. UH: ultra-high-pressure homogenization treatment; Oil: 50:50, chia:sunflower. MD: maltodextrin; BM: buttermilk; TS: total solids.

Labortechnik AG, Flawil, Switzerland). The samples were tempered at 25 °C, and the drying working conditions were 150 °C inlet temperature, 80% aspiration (32 m^3/h), and 30% feed flow (9 mL/min). Spray-dried emulsions (SDE) were collected in aluminum bags for further analysis.

2.4. Spray-dried emulsion characteristics

2.4.1. Moisture content and Aw

Moisture content of SDE was determined gravimetrically by drying 2 g of powder until constant weight (AOAC standard method no. 990.20). Aw was determined using Aqualab equipment, Model Series 3 TE (Decagon Devices, Pullman, WA).

2.4.2. Flowing properties

The bulk (ρ_{bulk}) and tapped (ρ_{tapped}) densities were determined as described by Tatar, Tunç, Dervisoglu, Cekmecelioglu, and Kahyaoglu (2014), with minor modifications. About 5 mL of SDE was added into a 25 mL glass graduated cylinder, measured, and weighed. Then, the cylinder was gently tapped by hand fifty times and the volume was read directly from the cylinder. The weight of SDE divided by the volume was used to calculate respectively the bulk (non-compacted powder) and tapped (compacted) densities. The powder flowability was evaluated using Carr's Index (CI) and the Hausner Ratio (HR) (Turchiuli et al., 2005), which were calculated following equations (2) and (3), respectively:

$$CI = (\rho_{tapped} - \rho_{bulk})/\rho_{tapped} \times 100 \quad (2)$$

$$HR = \rho_{tapped}/\rho_{bulk} \quad (3)$$

2.4.3. Water solubility

Solubility of SDE was evaluated as described by Botrel, Borges, Fernandes, and Lourenço Do Carmo (2014) with minor modifications. The sample (1 ± 0.01 g) was weighed and added to a beaker with 20 mL of distilled water, while stirring at 200 rpm. When all the sample had been added, the stirring speed was increased to 1200 rpm for 3 min. Subsequent centrifugation at 1600 rpm for 15 min at 20 °C was performed. Then, 5 mL of the supernatant was shifted to a preweighed capsule and dried at 110 °C for 4 h until constant weight. The water solubility (WS) was calculated by equation (4):

$$WS\ (\%) = (s \times 4/m) \times 100 \quad (4)$$

where: s is the grams of solids in supernatant and m is the grams of sample.

2.4.4. Encapsulation efficiency

The EE, total oil content (TO), and surface oil content (SO) of SDE were determined as described by González, Martínez, Paredes, Leónn, and Ribotta (2016). Briefly, for TO determination, 4.0 ± 0.1 g of sample were extracted in a Soxhlet apparatus for 24 h, with 200 mL of n-hexane solvent. After complete evaporation of the solvent, the oil extracted was weighed and expressed as a percentage of oil (dry basis) of the SDE.

For SO determination, 2 ± 0.01 g of SDE were mixed with 30 mL of petroleum ether followed by shaking for 1 min at room temperature and filtered through Whatman no. 1 paper. Solids in the filter were washed with 10 mL hexane and organic phases were combined. The filtrated solution was then transferred to an oven at 105 °C for the complete evaporation of hexane. EE was determined by calculating the ratio of the total oil contained in the SDE (TO) and the free oil (SO) located on its surface, according to equation (5).

$$EE = (TO - SO) \times 100/TO \quad (5)$$

2.4.5. Color evaluation

Color parameters were assessed with a colorimeter Konica Minolta CR-410 (Konica Minolta, Osaka, Japan), using D_{65} light source and angle of 10° observer as references. ESD samples were placed in a 50 mL clear optical glass container filled up to 10 mm followed by a white stopper disk to standardize measurements. The bottom external surface was measured. Results were expressed in the CIE L*a*b* color space, where L* is the lightness, a* is the greenness-redness, and b* is the blueness-yellowness. The Whiteness Index (WI), Yellowness Index (YI), and total color difference (ΔE) were calculated using the following equations (6)–(8), respectively.

$$WI = 100 - [(100 - L^*) + a^{*2} + b^{*2}]^{0.5} \quad (6)$$

$$YI = 142.86 \times b^* \times L^{*-1} \quad (7)$$

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (8)$$

2.4.6. Morphology and size

The morphology of SDE was observed by SEM, using the Quanta ™ 650 FEG scanning electron microscope (FEI Company, Hillsboro, OR, USA), with an accelerating beam voltage (HV) of 5 kV. Samples were prepared by fixing a small amount of powder on metal discs with double-sided carbon tapes, which were then platinum-plated in a Leica EM ACE600 vacuum chamber (Leica Microsystems, Wetzlar, Germany). Mean diameter of particle size of SDE samples were analyzed by measuring 100 particles per sample on the SEM photographs using the microscope software.

2.5. Oxidation stability

The oxidative stability of SDE was determined by the peroxide value and by quantification of malondialdehyde as secondary oxidation product. SDE were stored at 50 °C for 31 days to accelerate the oxidation process. Primary and secondary oxidation were determined in SDE on days 0, 7, 15, and 31. Feeding emulsions of the corresponding SDE were also analyzed on day 0 to evaluate the effect of the drying process on primary oxidation.

2.5.1. Primary oxidation

The hydroperoxide concentration was determined according to the previously described method by Hu, McClements, and Decker (2003). SDE (1 ± 0.01 g) were reconstituted in 10 mL distilled water. A sample of 300 μL emulsion was taken in triplicate and mixed with 1.5 mL of an isooctane: 2-propanol solution (3:1) in glass tubes, and vortexed for 30 s (10 s × 3). The organic phase of the mixtures was separated by centrifugation at 1000 rpm at 20–25 °C for 2 min. 200 μL of the organic phase was added to 2.8 mL of a methanol: 1-butanol solution (2: 1). Then, 1 μL of 3.97 M ammonium thiocyanate and 15 μL of iron solution prepared with 0.132 M BaCl2 and 0.144 M FeSO4 were added continuously. Finally, the test tubes were vortexed (10 s), and, after 20 min, the absorbance of the solution was measured at a wavelength of 510 nm in a spectrophotometer Dinko UV 2310 (Dinko Instruments, Barcelona, Spain). Hydroperoxide concentrations were determined by means of a standard curve, made from cumene hydroperoxide, in a concentration range of 0.002–2 mM.

2.5.2. Secondary oxidation

Quantification of malondialdehyde was made according to the method proposed by Papastergiadis, Mubiru, Van Langenhove, and De Meulenaer (2012) by HPLC. For sample preparation, 5 mL of emulsion were taken and mixed with 15 mL of 7.5 g/100 mL TCA containing 0.1 g/100 mL EDTA and 0.1 g/100 mL propyl gallate into 50 mL conical centrifuge tubes, and shaken horizontally for 15 min. Subsequently, they were centrifuged at 3500 rpm for 15 min and then, 1 mL of the

supernatant was taken and added to glass tubes (with cap and screw) together with 3 mL of 40 mM TBA. The tubes were boiled for 40 min, then cooled to room temperature, and 1 mL of methanol was added to each one and vortexed for 10 s. Samples were placed in Eppendorf tubes and centrifuged at 3500 rpm for 15 min to avoid the presence of precipitates. The separation and quantification of malondialdehyde was carried out in an HPLC equipment composed of an automatic injector (Waters 717 Plus, Milford, Massachusetts, USA), a Perkin Elmer model 515 booster pump (Waltham, Massachusetts, USA), and a serial fluorescence detector 200 (Perkin Elmer). Aliquots (20 μL) of the sample were injected onto an Agilent Pursuit 3 C18 column (5 μm, 150 × 4.6 mm) at 40 °C analysis temperature. The mobile phase consisted of a 50 mM KH_2PO_4 buffer solution, methanol, and acetonitrile (72:17:11, pH 5.3) pumped isocratically with a flow of 0.8 mL/min. The fluorometric excitation and emission wavelengths were set at 525 and 560 nm, respectively. To quantify the amount of malondialdehyde, a standard curve was made from 1.1 to 3.3 tetraethoxypropane in a concentration range of 0.25–25 μM. Peak quantification was performed using Turbochrom TC6 software (Perkin Elmer).

2.6. Statistical analysis

Results are presented as mean ± standard deviation. SDE characterization was subjected to a one-way analysis of variance (ANOVA) test using the Minitab Express™ version 1.5.3 (Minitab, State College, PA, USA). Significant differences between means were determined by the Tukey test. A confidence level of 95% ($p < 0.05$) was used. At least two individual productions of each formulation and treatment were performed. All analysis were replicated three times.

3. Results and discussion

3.1. Characteristics of emulsions

Processing of feeding emulsion determines the characteristics of microcapsules produced by spray drying (González et al., 2016). BM concentration as well as homogenization treatment influenced the particle size distribution and microstructure of feeding emulsions (Fig. 1). In CH emulsions, mean particle size ($d_{4,3}$) was about 13 and 4.5 μm corresponding to 4CH and 7CH, respectively. The particle size distribution curves were bimodal, which corresponded to individual and aggregated oil droplets. This fact was especially present in 4CH emulsions. UHPH-processed emulsions showed a particle size reduction in comparison to CH emulsion in both 4UH and 7UH. In Fig. 1 the CLSM micrographs are inserted, in which the structure of oil droplets can be observed. The most remarkable characteristic of UHPH-processed emulsions, independently of the BM concentration, was the formation of oil droplets aggregates which were smaller in particle size than the individual oil droplets of the CH emulsions, which was associated to a higher emulsion stability of UHPH-processed emulsions (Aghababaei et al., 2021). The strong physical forces acting in UHPH have been described to cause partial protein denaturation (Fernandez-Avila et al., 2015; Floury, Desrumaux, & Legrand, 2002; Serra, Trujillo, Guamis, & Ferragut, 2009) and casein micelle disintegration (Sharma, Jana, & Chavan, 2012), which facilitates the aggregation by means of protein-oil and protein-protein interactions. This phenomenon has also been described in other emulsions treated by UHPH such as those formulated with 1, 3 and 5% sodium caseinate (Hebishy, Buffa, et al., 2017), in which aggregates were only observed at 3 and 5% of that emulsifier. In our emulsions, which were formulated for further spray drying, the presence of 30% of MD could lead to depletion flocculation, promoting the aggregation of individual oil droplets in presence of protein and carbohydrates, by their partial thermodynamic incompatibility (De Kruif & Tuinier, 2001).

3.2. Characteristics of spray-dried emulsions

In this study, spray-drying conditions were kept constant according to preliminary trials to make sure that the SDE were not sticky and flowability was good enough for an acceptable yield. Total solid content of SDE was 44% for formulations containing 4% BM and 47% for formulations with 7% BM. In Table 2, characteristics of SDE are shown. Moisture content varied from 2.06 to 3.19% in all SDE with few differences ($p < 0.05$) being observed among them. 4CH sample was the SDE with the lowest water content and 7UH100 that which showed the highest water content of SDEs. It appeared that both homogenization treatment and BM concentration influenced water content. Probably, in CH treatments, water was easier to eliminate by spray drying because of the lower particle volume fraction observed in these sample (Fig. 1). This behavior of CH compared to UH samples was observed for both BM concentrations, 4 and 7%. In addition, when comparing the BM concentration SDE series, 7% SDE showed higher water content, which could explain certain difficulty for water evaporation in the drying process. On the other hand, the different colloidal structures, big droplets in CH or small aggregates in UH SDE, may indicate a different protein distribution between the continuous and oil-water interface of the feeding emulsions, modifying water elimination during the spray drying process. However, in terms of powder stability during storage, as reported by Klaypradit and Huang (2008), dry foods with moisture content between 3 and 10% have a good behavior.

Aw values ranged from 0.130 to 0.191 with no significant differences ($p < 0.05$) between them, although the highest values observed corresponded to those with lower BM content, as expected. These values are considered adequate for dry foods since they guarantee microbiological stability (Comunian et al., 2019).

One relevant characteristic of powders is bulk density, which varied in a narrow range, from 430 to 455 kg/m^3 for all samples with no significant differences ($p < 0.05$) observed between them. These values are in the range of most of the spray-dried emulsions reported in literature, which may vary broadly depending on composition and drying conditions used. Our SDE bulk density values were similar to those found by other authors (Sarkar, Arfsten Golay, Acquistapace, & Heinrich, 2016;

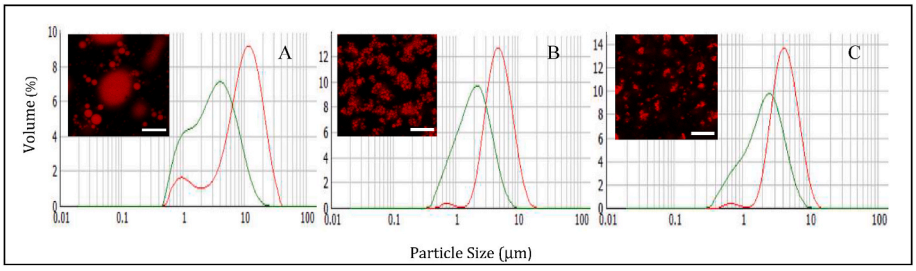

Fig. 1. Particle size distribution of 4% BM (red line) and 7% BM (green line) of emulsions processed by CH (A), UH100 (B) and UH200 (C). CLSM images correspond to oil droplets and aggregates observed in 7% BM at the different homogenization treatments applied, labelled with Nile Red (scale bar 7.5 mm). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Characteristics of SDE from feeding emulsions containing 4 and 7 (%) BM and processed by different homogenization systems (CH and UHPH).

Sample	Moisture	A_w	r_b	r_t	CI	HR	WS	EE	Size
	(%)		(kg/m^3)	(kg/m^3)			(%)	(%)	(μm)
4CH	2.06 ± 0.04^{c}	0.191 ± 0.01^{a}	455 ± 17^{a}	551 ± 11^{a}	17.3 ± 2.6^{a}	1.21 ± 0.03^{a}	94.1 ± 3.4^{a}	77.1 ± 2.6^{c}	10.3 ± 3.6
4UH100	2.64 ± 0.10^{b}	0.192 ± 0.01^{a}	438 ± 12^{a}	526 ± 17^{ab}	16.6 ± 1.1^{a}	1.20 ± 0.06^{a}	93.6 ± 2.9^{a}	83.0 ± 2.1^{b}	11.4 ± 5.5
4UH200	2.82 ± 0.30^{ab}	0.185 ± 0.01^{a}	454 ± 12^{a}	534 ± 10^{ab}	15.1 ± 0.7^{ab}	1.17 ± 0.01^{ab}	92.1 ± 3.3^{a}	84.1 ± 0.8^{b}	7.4 ± 6.3
7CH	2.76 ± 0.08^{ab}	0.130 ± 0.01^{a}	434 ± 09^{a}	470 ± 06^{c}	7.70 ± 0.7^{c}	1.08 ± 0.01^{cd}	96.8 ± 2.2^{a}	81.2 ± 1.3^{bc}	8.8 ± 5.2
7UH100	3.19 ± 0.06^{a}	0.151 ± 0.01^{a}	445 ± 13^{a}	506 ± 15^{b}	11.9 ± 1.1^{b}	1.13 ± 0.01^{bc}	91.7 ± 4.5^{a}	91.5 ± 2.5^{a}	6.3 ± 2.9
7UH200	3.07 ± 0.10^{ab}	0.131 ± 0.01^{a}	430 ± 07^{a}	465 ± 10^{c}	7.50 ± 1.0^{c}	1.08 ± 0.01^{d}	91.5 ± 1.3^{a}	89.4 ± 0.9^{a}	11.0 ± 4.5

Means in each column with different superscript letters were significantly different ($p < 0.05$). Values are mean and SD of three replications.
A_w: water activity; r_b: Bulk density; r_t: Tapped Density; CI: Carr Index; HR: Hausner Ratio; WS: Water Solubility; EE: Encapsulation Efficiency; Size: mean diameter of particle size analyzed.

Carneiro, Tonon, Grosso, & Hubinger, 2013) who also reported oil content similar to those used in this study. Some powders parameters related to bulk and tapped densities (eqs. (2) and (3)), were calculated: Carr's Index (Carr, 1965) is a scale of flowability (values ≤ 10 are excellent and values > 38, are awful). The Hausner Ratio (Hausner, 1967) is a scale of cohesiveness from 1 (excellent) to > 1.6 (awful). Thus, both parameters, CI and HR, can be used to determine powder properties during processing and storage conditions (Quispe-Condori, Saldaña, & Temelli, 2011; Sanchez-Reinoso & Gutiérrez, 2017). Flowing properties of the present SDE showed a significantly different ($p < 0.05$) behavior, mainly depending on BM concentration regardless of the homogenization system used; i. e., all 4% BM SDE were similar but different from 7CH and 7UH200, which exhibited lower values of CI and HR. As shown in Table 2, SDE with 4% BM had values in the range corresponding to a fair flowability and cohesiveness (CI = 16–20 and HR = 1.19–1.25, are considered as fair on their respective reference scales). In these samples, although no statistical differences were observed, CI and HR values decreased as homogenization pressure increased, indicating a certain influence of this technological treatment. SDE with 7% BM had values mostly in the range of excellent flowability and cohesiveness, thus exhibiting very good handling properties, and showing that BM is a good encapsulating agent capable of producing powder emulsions with high quality characteristics of handling and transport.

Solubility in water is a relevant quality parameter of dry powders which mostly depends on its chemical composition and physical state (Dhanalakshmi, Ghosal, & Bhattacharya, 2011). All SDE produced in this study showed high solubility in water at room temperature. They did not exhibit significant variations in their solubility ($p > 0.05$), which ranged between 91.5 and 96.8%. This parameter is strongly influenced by the nature of the wall materials (carbohydrates and proteins), which in this work were constituted by 30% MD and 4 or 7% BM, both with high solubility in water. Solubility values observed in this study were similar to those reported by other authors (Korma et al., 2019) in powder emulsions formulated with WPI and MD or inulin with 30% total solids.

The EE reflects the degree to which wall material can retain oil in microcapsules. Values of this parameter showed good encapsulation of oil, ranging between 77.1 and 91.5% in the different SDE. Both BM concentration and homogenization system influenced the results obtained. In formulations containing 4% BM, the UHPH treatment (100 or 200 MPa) improved significantly ($p < 0.05$) the capacity of oil retention of microcapsules compared to 4CH. On the other hand, SDE containing 4% BM and treated by UHPH showed similar values of this parameter than formulation 7CH, indicating the positive influence of BM concentration. The best EE was observed in 7UH100 and 7UH200 SDE, which showed similar values. Emulsifying properties of BM are attributed to its composition, rich in casein, whey proteins and phospholipids, which adsorbs at the oil-water interface exerting the desired covering of oil droplets. Thus, increasing BM content could improve the effective oil coverage, and in consequence, the EE as reported also by other authors (Wang, Che, Fu, Chen & Selomulya, 2016). On the other hand, as observed in the feeding emulsions, UHPH promoted the aggregation of oil droplets though protein-protein interactions. In consequence, oil could be hidden in those colloidal structures keeping better EE.

Color attributes are important characteristics for consumer acceptance. Table 3 summarizes the results of color measurements: CIE Lab parameters, color difference between homogenization treatments, and color difference between different BM concentrations for the same treatments of SDE. As well, two indexes used for near-white opaque materials (WI and YI) were calculated. L* did not show differences between treatments or BM concentration, ranging from 92.6 to 94.0. Red – green (a*) varied in a short range into the red tonality, while b* (yellow - blue), was the parameter that most contributed to the color differences and YI within samples, being formulations containing 7% BM those that showed the highest WI values ($p < 0.05$). Regarding color differences, by comparing the effect of homogenization treatment as well as the BM content, most of values were >1, which means that they can be classified as slightly noticeable (0.5–1.5) by the human eye (Sanchez-Reinoso & Gutiérrez, 2017).

Morphology of SDE examined by SEM are shown in Fig. 2. All the

Table 3
Color characteristics of SDE from feeding emulsions containing 4 and 7% BM processed by different homogenization systems (CH and UHPH).

Samples	L*	a*	b*	ΔE	WI YI	
4CH	92.9 ± 0.5^{ab}	3.70 ± 0.02^{a}	0.47 ± 0.22^{c}	–	95.4 ± 0.04^{e}	0.72 ± 0.34^{c}
4UH100	92.6 ± 0.1^{b}	3.60 ± 0.02^{b}	0.60 ± 0.07^{c}	1.60 ± 0.07^{a}	95.4 ± 0.02^{de}	0.93 ± 0.11^{c}
4UH200	93.4 ± 0.6^{ab}	3.57 ± 0.03^{b}	0.63 ± 0.07^{c}	1.86 ± 0.20^{a}	95.5 ± 0.06^{cd}	0.96 ± 0.11^{c}
7CH	94.0 ± 0.2^{a}	3.12 ± 0.03^{c}	1.33 ± 0.10^{b}	–	95.8 ± 0.02^{cd}	2.02 ± 0.15^{b}
7UH100	93.4 ± 0.3^{ab}	2.92 ± 0.01^{d}	1.86 ± 0.08^{a}	1.00 ± 0.20^{b}	95.6 ± 0.03^{de}	2.84 ± 0.12^{a}
7UH200	93.6 ± 0.1^{ab}	3.25 ± 0.03^{e}	1.20 ± 0.06^{b}	1.18 ± 0.03^{b}	95.7 ± 0.05^{cd}	1.84 ± 0.11^{b}
4CH–7CH				1.57 ± 0.78^{a}		
4UH100–7UH100				1.63 ± 0.30^{a}		
4UH200–7UH200				0.85 ± 0.26^{a}		

Means in each column with different superscript letters were significantly different ($p < 0.05$). Values are mean and SD of three replications. L*, a*, b*: CIELab color coordinates; ΔE: Color Difference between UHPH and CH treatments for each BM concentration formulation; WI: Whiteness Index; YI: Yellowness Index.

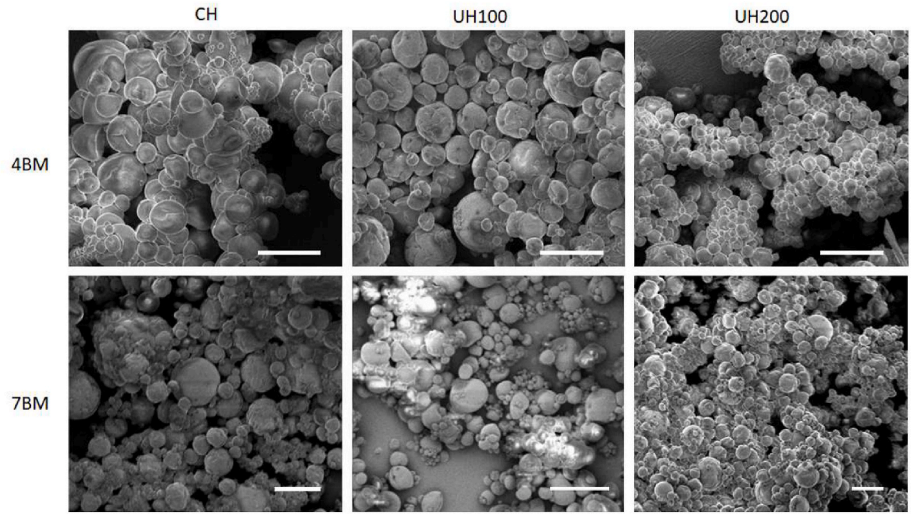

Fig. 2. SEM images of SDE containing 4 and 7% BM (lines) from feeding emulsions treated by CH and UHPH (columns). Scale bars correspond to 5 μm.

images always showed spherical particles, with apparent smooth surfaces without remarkable presence of fractures, although depression and superficial folds were observed in some microcapsules, probably due to the sudden contraction that occurs in the early stages of drying. The general aspect of all SDE were similar, regardless of the percentages of BM or homogenization treatments. Particle sizes were heterogenous, showing the presence of small and larger particles in the same sample, frequently aggregated to each other. In general, formulations containing 4% BM showed higher particle size (Table 2) than 7% BM formulations. However, it is difficult to establish any correlation since the variety observed in the particle size was often high. This aspect has also been observed in different studies (Benito-Román, de Paz, Melgosa, Beltrán, & Sanz, 2018; Carneiro et al., 2013) which is typical in spray-dried foods.

3.3. Oxidation stability of SDE

The stability of SDE against oxidation was evaluated in accelerated conditions of heating at 50 °C for one month, at days 1, 7, 14, and 31 of storage. The oxidation analysis was performed for primary and secondary oxidation. The effect of drying on primary oxidation developed in SDE samples was also estimated compared to the fresh emulsions as depicted in Fig. 3. As expected, the effect of drying caused an increase of hydroperoxide concentration in all samples, which varied in function of homogenization treatment and BM concentration. Regarding BM concentration, both fresh emulsions and SDE were more protected against oxidation with 7% BM. The effect of treatment was more accused in CH emulsions, which exhibited higher difference of hydroperoxides between fresh and SDE compared to those treated by UH. Probably, the fresh UHPH-treated emulsions were more exposed to pro-oxidant agents due to the high increase of oil surface droplets generated during UHPH treatment. However, the effect of BM concentration prevailed against treatment as the oxidative state of SDE on day 1 was quite similar in all the 7BM SDE series.

Fig. 4 shows the hydroperoxides concentration evolution during SDE storage. The pattern of the primary oxidation curves was similar in all samples. They were characterized by a subtle increase in the

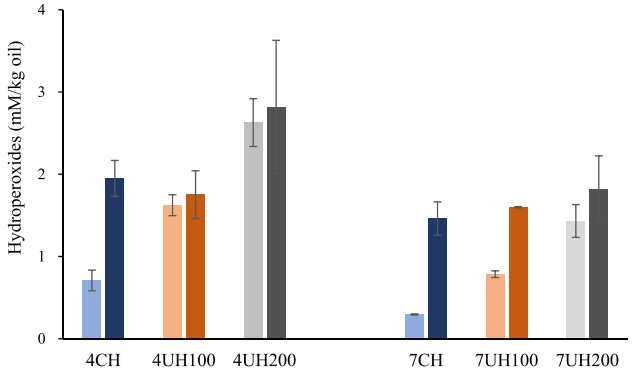

Fig. 3. Effect of drying process on primary oxidation in formulations containing 4 and 7% BM. Clear color (feeding emulsions on day 1), dark color (SDE on day 1 after drying). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

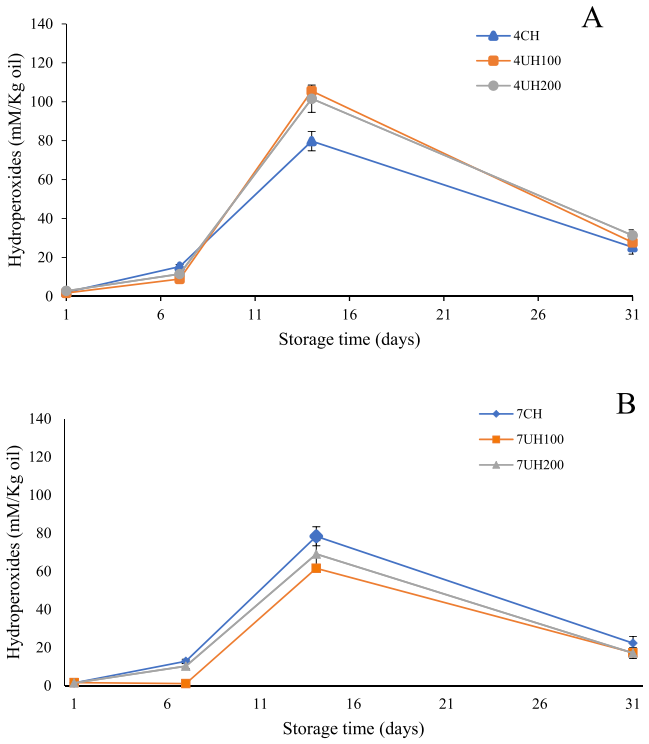

Fig. 4. Hydroperoxides concentration evolution during storage of SDE in accelerated conditions at 50 °C obtained from feeding emulsions treated by different homogenization systems (CH and UHPH) and BM concentration. 4% BM (A); 7% BM (B).

concentration between days 1 and 7, followed by a pronounced increase on day 14, and a noticeable decrease at day 31. This observed evolution of hydroperoxides is consistent with the kinetics of development of primary lipid oxidation, in which a latency period appears at the beginning followed by a propagation or exponential increase of the oxidation products (Kamal-Eldin, McAkinen, & Lampi, 2003). The decrease observed after the peak is due to the secondary oxidation products being formed from the primary products' degradation (Papastergiadis et al., 2012).

Considering BM concentration, hydroperoxide levels of 7% BM samples were lower during storage than those of 4% BM, exerting less protection by recovering the interface of small oil droplets and aggregates generated by UHPH treatment than 7% BM. Hebishy, Buffa, et al. (2017) in sodium caseinate emulsions treated by UHPH observed this dependence of protein concentration on the oil droplet protection against oxidation. Thus, at the lowest amount of emulsifier, the film formed is not dense enough to protect the oil from oxidation, allowing the diffusion of oxygen and pro-oxidants towards the oil droplets during storage (Sarkar, Arfsten, Golay, Acquistapace, & Heinrich, 2016).

The effect of BM concentration and homogenization treatment was consistent with the EE observed (Table 2). EE was higher in UHPH-treated samples containing higher BM concentrations. Zhang et al. (2020) showed a similar tendency in spray-dried emulsions produced by homogenization at 30 MPa (3 cycles), and formulated with different concentrations of BM, maltodextrin, and seaweed oil, finding that the formulations with the highest percentage of BM showed the lowest hydroperoxides, attributing this effect to higher EE.

Fig. 5 shows the evolution of secondary oxidation through the determination of malondialdehyde (MDA) concentration in SDE over time. In general, low levels of MDA were observed in most of the stored SDE with an MDA increase on day 31, which was especially marked in SDE containing 7% BM. This MDA increase coincided with the decrease in hydroperoxides mentioned above, confirming that as the end of accelerated storage approaches, oxidation state continues to advance. Regarding the higher MDA concentrations observed in 7% BM formulations, it could be explained based on the presence of some compounds of BM that could behave as pro-oxidants, especially if they were present in excess (Berton-Carabin, Ropers, & Genot, 2014). BM contains phospholipids that may have antioxidant effects. However, when they are in dehydrated dairy products, they can also behave as pro-oxidants due to the unsaturation presented by MFGM phospholipids such as phosphatidylcholine and phosphatidylethanolamine (Cui & Decker, 2016). As can also be seen in Fig. 5, emulsions treated at 100 MPa were generally those that presented lower MDA within the storage, compared with CH and UH200 treated emulsions. This significant difference observed, especially at day 31 of storage, may be due to the bigger size of the oil droplet aggregates formed at 100 MPa compared to 200 MPa treated samples. Although at the two UH pressures applied in this study, a high size reduction of individual oil droplets was observed (Aghababaei et al., 2021); reaggregation was produced, giving more stable emulsions with smaller particle sizes than those obtained with conventional technology. However, as can be seen in Fig. 1, UH100 emulsions had bigger aggregates, thus the effective exposure of oil to the oxidation catalyzers were lower by limiting their access to lipids. Further study of oxidation at ambient temperature could clarify the real behavior of those dried emulsions, given that storage temperature greatly determines the oxidation kinetics as reported by other authors (Escalona-García et al., 2016), being highly reduced at 25 °C in chia oil encapsulated with whey protein concentrate.

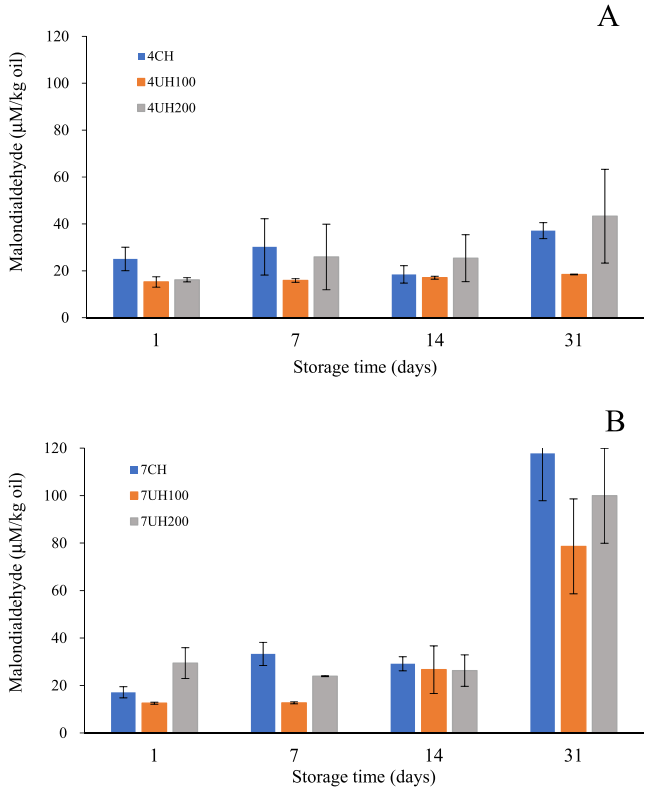

Fig. 5. Malondialdehyde concentration evolution during storage of SDE in accelerate conditions at 50 °C obtained from feeding emulsions treated by different homogenization systems (CH and UHPH) and BM concentration. 4% BM (A); 7% BM (B).

4. Conclusions

Incorporation of buttermilk (at 4 or 7%) has allowed the production of spray-dried products with good general properties such as optimal flowability and cohesiveness. In addition, when UHPH treatment was used compared to conventional homogenization, general properties of powders were similar or improved, such as the EE, which increased its performance as encapsulant in producing dried emulsions. Oxidative stability evolved in a similar direction regarding primary oxidation. However, the secondary products of oxidation were higher in 7% than in 4% buttermilk formulations, probably due to the higher concentrations of unsaturated phospholipids of buttermilk at the oil-water interface. This hypothesis is reinforced as the UHPH treatment at 100 MPa produced the best oxidative stability of spray-dried emulsions; probably it was caused by the microstructure of feeding emulsion obtained at these UHPH conditions, in which prevailed the oil droplets protected by buttermilk hidden inside the big aggregates observed in those emulsions.

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CRediT authorship contribution statement

Carolina Varela: Investigation, Data curation, Methodology, Writing – original draft, Formal analysis. **Fatemeh Aghababaei:** Investigation, Data curation, Formal analysis. **Mary Cano-Sarabia:** Visualization, Supervision, Resources. **Libni Turitich:** Investigation, Data curation. **Antonio J. Trujillo:** Project administration, Supervision, Conceptualization. **Victoria Ferragut:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

Authors declared that they have no conflicts of interest to this work.

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