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## Redispersible dry emulsions stabilized by plant material: Rapeseed press-cake or cocoa powder

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## ABSTRACT

This work aimed at valorizing by-products of the agrifood industry: powders deriving from rapeseed press-cakes and cocoa. Novel oil-in-water emulsions stabilized by these vegetal powders were formulated and were dehydrated by freeze-drying and spray-drying. Dry emulsions of at least 40% oil content and with a moisture content below 2.6 wt% were obtained. Dry-emulsions did not exhibit any clumping even after several months of storage at room temperature, and were redispersible in water. To compare the ability of the drying process to preserve the state of dispersion, the size distributions of the oil droplets were compared before dehydration and after redispersion of the dry emulsions in an aqueous phase. Several oil-to-vegetal powder weight ratios were probed, and the impact of a solid filler –lactose– was investigated.

### 1. Introduction

Vegetable oils are oils or fats extracted from plant seeds. Under conventional conditions, seeds are crushed and pressed, thus generating liquid oil and a solid press-cake. The increase in oil production worldwide implies a proportional increase in oil mill wastes. Therefore, immediate attention is required to manage mill waste materials in order to minimize their environmental impact and to recycle them as value-added ingredients or functional materials for various domains including the food industry (Chandrasekaran & Shine, 2012, chap. 13). Press-cakes are very often exploited for composting or animal feeding. While valuable, such type of valorization has low technological and economical value. Most biomass waste is a complex and variable mixture of molecules, and separation is a key issue. A complication comes from the fact that both the bio-waste and the materials to be separated are solid. Therefore, separation frequently involves organic solvents and/or harsh processing conditions. In the current regulatory climate, the chances of introducing new stabilizers into foods that rely on the use of harsh chemicals or large quantities of organic solvents are very small. For obvious economic, regulatory and environmental reasons, applications requiring a minimum level of bio refinery are highly sought after. Here, we highlight the possibility to valorize press cakes as inexpensive, renewable, and abundantly available stabilizers for the fabrication of dry

emulsions.

Emulsions are liquid-liquid (oil-water) metastable colloids generally obtained in the presence of surface-active molecules like surfactants, amphiphilic polymers or proteins. Solid amphiphilic particles can also be used as emulsion stabilizers. Following the seminal studies by Pickering and Ramsden (Pickering, 1907; Ramsden, 1903), solid-stabilized emulsions are commonly referred to as “Pickering emulsions”. In this kind of system, large solid particles (from 1 nm to several microns) are irreversibly anchored at the oil–water interface (Binks, 2002). Their kinetic stability is generally enhanced, compared to conventional surfactant-stabilized emulsions, owing to the formation of a thick and rigid interfacial layer. To adsorb at the interface, particles are required to be wetted by both immiscible liquids, *i.e.* they must exhibit amphiphilic properties. As a matter of fact, the emulsion type (oil-in-water (O/W) or water-in-oil (W/O)) is mainly determined by the relative wettability of the particles, as stated by the empirical Finkle's rule (Finkle, Draper, & Hildebrand, 1923): hydrophilic (resp. hydrophobic) particles will preferentially stabilize oil (resp. aqueous) drops dispersed in water (resp. oil).

Pickering emulsions based on solid particles of biological origin are of great interest. Using these biomass-based particles to stabilize emulsions meets consumers' demand for a replacement of synthetic surface-active agents by environmentally friendly compounds. For

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**Table 1**

Composition of the parent emulsions and main droplet size characteristics (percentages are relative to the overall mass of emulsion).

| Formulation  | Powder content (wt%) | Lactose content (wt%) | Oil content (wt%) | $D_v$ ( $\mu\text{m}$ ) | $D_s$ ( $\mu\text{m}$ ) | P                    |
|--------------|----------------------|-----------------------|-------------------|-------------------------|-------------------------|----------------------|
| A (rapeseed) | 7.5                  | 7.75                  | 15                | $1.40 \pm 0.07^c$       | $1.14 \pm 0.06^c$       | $0.35 \pm 0.05^c$    |
| B (rapeseed) | 7.5                  | 0                     | 15                | $1.93 \pm 0.10^b$       | $1.41 \pm 0.07^b$       | $0.41 \pm 0.05^{bc}$ |
| C (rapeseed) | 7.5                  | 7.75                  | 30                | $2.57 \pm 0.13^a$       | $2.28 \pm 0.11^a$       | $0.29 \pm 0.05^c$    |
| D (cocoa)    | 7.5                  | 7.75                  | 15                | $1.96 \pm 0.10^b$       | $1.23 \pm 0.06^{bc}$    | $0.56 \pm 0.05^b$    |
| E (cocoa)    | 7.5                  | 15.5                  | 15                | $2.46 \pm 0.12^a$       | $1.25 \pm 0.06^{bc}$    | $0.90 \pm 0.07^a$    |

Values with the same letter in one column are not significantly different (ANOVA, Tukey HSD,  $p < 0.05$ ).

instance, many studies have been directed towards emulsions stabilized by food-grade particles. These include fat and wax crystals, starches (Yusoff & Murray, 2011), chitin nanocrystals, cellulose fibers (Campbell, Holt, Stoyanov, & Paunov, 2008), flavonoids (Luo et al., 2011) and protein microgels (Destribats, Rouvet, Gehin-Delval, Schmitt, & Binks, 2014). Gould, Vieira, and Wolf (2013) and Joseph et al. (2019) explored the functionality of cocoa particles as emulsion stabilizers through the mechanism of Pickering stabilization.

Compared to conventional emulsions, dry emulsions have many technological assets: increased shelf life, lack of bacteriological growth owing to the very low water activities, facilitated transport, and improved oil stabilization against oxidation (Gu, Decker, & McClements, 2004; Klinkesorn, Sophanodora, Chinachoti, McClements, & Decker, 2005; Shaw, McClements, & Decker, 2007). To avoid oil droplets from merging into a macroscopic separated oil phase, either during the drying process or during the storage of the dry powder, a hydrophilic wall material is generally added to the aqueous phase. Typical examples of species used as wall materials are glucose, lactose, maltodextrin, starch, and cellulose. Once water is evaporated, this wall material, together with the emulsifier used to stabilize the emulsion, forms a solid phase that immobilizes the droplets, thus avoiding their recombination (coalescence). The amount of solid hydrophilic wall material needed ranges in general between 30 and 80 wt% of the total final powder (Gu et al., 2004; Jost, Dannenberg, & Rosset, 1989; Klinkesorn et al., 2005). Alternative strategies to the introduction of this solid wall materials have been explored. These include the formation of viscoelastic layers based on polyelectrolyte complexes (Gu et al., 2004; Klinkesorn et al., 2005; Moreau, Kim, Decker, & McClements, 2003; Mun, Decker, & McClements, 2005), cross-linked whey proteins (Cho, Shim, & Park, 2003; Jost et al., 1989; Kellerby, Gu, McClements, & Decker, 2006; Romoscanu & Mezzenga, 2005; Sarkar, Arfsten, Golay, Acquistapace, & Heinrich, 2016), protein-polysaccharide complexes induced by Maillard reaction (Li, Woo, Patel, & Selomulya, 2017). The intrinsic stiffness of the interfacial layers, possibly combined with the excess polymeric material efficiently protects droplets against recombination.

In the present work, we propose a facile and cost-effective solution to valorize mill wastes and/or by-products of the agrifood industry. We fabricated O/W emulsions based on an oil currently used in the food industry, sunflower oil, stabilized by delipidated and finely crushed powders of vegetal origin, cocoa powder and rapeseed press-cake. These latter were selected because they are abundant and because of their large content in surface-active species like proteins (Lecumberri et al., 2007; Leming & Lember, 2005). Two processes were implemented to dehydrate the emulsions and to produce fine powders: freeze-drying and spray-drying. The redispersability of the powders in water was examined. To compare the ability of the drying process to preserve the state of dispersion, the size distributions of the oil droplets were compared before dehydration and after redispersion of the powders in an aqueous phase. Several oil-to-vegetal powder weight ratios were probed, and the impact of the added wall material – lactose – was investigated.

## 2. Materials and methods

### 2.1. Materials

The oil phase of the emulsions consisted of sunflower oil (Rustica, France, density:  $920 \text{ kg m}^{-3}$ ) purchased from a local supermarket. Cocoa powder is generally obtained after grounding the cocoa beans and crushing the obtained paste by a hydraulic press to extract cocoa butter. In that respect, cocoa powder is reminiscent of a press-cake. Cocoa powder was from VanHouten (France). It contained 22 wt% lipids, 20% wt% proteins and its ash content after calcination was 8.6 wt% (determined gravimetrically according to NF ISO 6884). The powder was delipidated with hexane according to NF EN ISO 734-1. An almost fully delipidated rapeseed press-cake was supplied by OLEAD (France). It contained 2.2% residual oil, 38 wt% proteins and its ash content after calcination was 7.7 wt%. The water used in the experiments was deionized with a resistivity close to  $0.15 \text{ M}\Omega \text{ m}$  at  $20^\circ\text{C}$ . Lactose was from Sigma-Aldrich (France).

### 2.2. Preparation of parent emulsions stabilized by plant material

The aqueous phase containing cocoa powder or rapeseed press-cake and lactose (several proportions were probed, see Table 1), was first ground using a bead mill (Dyno-Mill Multi Lab, Willy A Bachofen-WAB, France), equipped with chrome accelerators (DYNO-Accelerators, Willy A Bachofen-WAB, France). The grinding chamber (0.6 L) was previously filled with water and  $8 \times 10^{-4} \text{ m}$  zirconium beads (Zyrmill Y, Willy A Bachofen-WAB, France) at the maximum level of bead filling (65% v/v). Milling was run in continuous mode in one single pass. The liquid was pumped at a flow rate of  $0.1 \text{ kg/min}$  ( $1.67 \times 10^{-3} \text{ kg/s}$ ) with a rotational speed for the grinding media of  $10 \text{ m/s}$ . The dispersion was cooled with water circulating in the jacket of the grinding chamber.

The aqueous dispersion deriving from the bead milling step was then agitated using an Ultra-Turrax® mixer (rotor-stator system, T25 digital, dispersing element S25 N-25F, IKA, Germany) working at 12 000 rpm (1257 rad/s) for 2 min. The stirring speed was then increased up to 16 000 rpm and the required amount of sunflower oil was slowly added to the water phase under agitation (around 5 min). Mixing was then extended for 10 min at 20 000 rpm (2095 rad/s). The system was finally homogenized using a single-chamber high-pressure homogenizer (ALM, Pierre Guérin, FRANCE), operating at a pressure of 265 bars. The whole emulsion volume was submitted to 2 passes through the homogenizing chamber.

### 2.3. Parent emulsions characterization

#### 2.3.1. Optical microscopy

An Olympus BX51 optical microscope (Olympus, Japan) fitted with a digital color camera (Color View, Olympus, Japan) was used to gain qualitative information about the emulsions in terms of characteristic droplet size and aggregation state. All the emulsions prepared in this study were observed and characteristic images with be provided in subsequent sections. To facilitate the observation, emulsions were always diluted by dispersing  $200 \mu\text{L}$  ( $2 \times 10^{-7} \text{ m}^3$ ) of emulsion in  $1 \text{ 500 } \mu\text{L}$  ( $1.5 \times 10^{-6} \text{ m}^3$ ) of deionized water. Samples were deposited on

a glass slide and were covered by a cover slip. A specific configuration was adopted in order to avoid sample damage. Indeed, we observed that the shear applied upon spreading of the confined liquid sometimes provoked droplet coalescence on the glass substrate. To avoid this phenomenon, cavity microscopy slides (well slides) with single ground and polished spherical cavities (Marienfeld, Germany) were adopted for observations. The samples were placed in the cavity zone before the cover slip was carefully deposited.

### 2.3.2. Droplet size measurements

Surfactant-stabilized emulsions droplets are commonly analyzed using light-scattering. In solid-stabilized emulsions, both particles and droplets are detected and consequently the scattering signal is not directly exploitable. A specific treatment was applied to our emulsions to get rid of particles present both in the bulk phase and at the oil/water interface, following the method presented by Joseph et al. (2019).

The emulsions were submitted to a 4-fold dilution in a 10 wt% SDS solution. The system was then stirred with a magnetic bar for 10 h. The emulsions diluted in the SDS solution were then centrifuged for 5 min at 220g (Rotanta 460 RF Centrifuge, Hettich Lab Technology, Germany),  $g$  being the earth gravity constant, in order to separate the particles (sediment) from the oil droplets (cream). The resulting creams were milky and colorless, indicating that cocoa or rapeseed particles were not present anymore. In their seminal work, Joseph et al. (2019) proved that this protocol led to droplets separation/disaggregation. After careful inspection of the droplets under the microscope before and after SDS treatment, they concluded that the droplets sizes were apparently preserved. They also observed the emulsions by fluorescence microscopy and particles were not detected anymore at the interfaces after SDS treatment. This low molecular weight surfactant is known to displace species with high interfacial adsorption energies like proteins (Mackie, Gunning, Wilde, & Morris, 2000; Pradines, Krägel, Fainerman, & Miller, 2008).

The creams were collected, diluted 50 times in deionized water and analyzed. The size distributions were measured using the Mastersizer 2000 apparatus (Malvern Instruments, France). Static light-scattering data were transformed into size distribution using Mie Theory. The droplet refractive index was 1.47 and that of the aqueous phase was 1.33. A small volume of sample was introduced under stirring at 1600 rpm (168 rad/s) in the dispersion unit containing a solution of SDS at 0.2 wt%. Each measurement was performed in triplicate. The droplets distributions were described in terms of their volume-averaged diameter,  $D_v$ , surface-averaged diameter,  $D_s$ , and polydispersity,  $P$ , defined as:

$$D_v = \frac{\sum N_i D_i^4}{\sum N_i D_i^3}; \quad D_s = \frac{\sum N_i D_i^3}{\sum N_i D_i^2}; \quad P = \frac{1}{\bar{D}} \frac{\sum N_i D_i^3 (\bar{D} - D_i)}{\sum N_i D_i^3} \quad (1)$$

where  $\bar{D}$  is the median diameter, *i.e.* the value for which the cumulative undersized volume fraction is equal to 50%, and  $N_i$  is the total number of particles with diameter  $D_i$ .

### 2.3.3. Analysis of soluble compounds

Hereafter, the term “particles” will refer to the water-insoluble fraction of the cocoa powder or of the rapeseed press-cake. Being denser than water, such fraction can be separated from the soluble one upon centrifugation.

A 10 wt% dispersion of vegetal powder dispersed in deionized water was centrifuged for 1 h at 100 000 g (Aventi J-301 Centrifuge, Beckman Coulter, USA). The supernatant containing the soluble fraction was collected and freeze-dried for mass measurement. The same procedure was performed on a 10 wt% dispersion of vegetal powder processed in the bead mill. After re-dissolution of the freeze-dried supernatant, water-soluble carbohydrates, proteins and polyphenols were quantified. Carbohydrates were titrated using the anthrone-sulfuric acid assay (Leyva et al., 2008). Briefly, carbohydrates were hydrolyzed (150  $\mu$ L

(1.5  $\times 10^{-7}$  m<sup>3</sup>) of reagent at 1 g/L (1 kg/m<sup>3</sup>) for 50  $\mu$ L (5  $\times 10^{-8}$  m<sup>3</sup>) of sample, 30 s of stirring, 20 min at 100 °C) and the resulting furfuralic compounds were assayed at 620 nm using a glucose calibration curve from 0 to 100 mg/L (0–0.1 kg/m<sup>3</sup>). Proteins were quantified using Bradford reagent (or Coomassie brilliant Blue) (150  $\mu$ L (1.5  $\times 10^{-7}$  m<sup>3</sup>) for 5  $\mu$ L (5  $\times 10^{-9}$  m<sup>3</sup>) of sample), which is known to form light-absorbing complexes in the presence of proteins. Complexes were titrated at 595 nm using a Bovine Serum Albumin (BSA) calibration curve from 0 to 500 mg/L (0–0.5 kg/m<sup>3</sup>) (Noble & Bailey, 2009). Polyphenols were quantified using Folin-Ciocalteu reagent (100  $\mu$ L (10<sup>-7</sup> m<sup>3</sup>) for 20  $\mu$ L (2  $\times 10^{-8}$  m<sup>3</sup>) of sample). This yellow-colored acid turns to blue upon phenol oxidation. Polyphenol quantification was performed using a gallic acid calibration curve from 0 to 100 mg/L (0–0.1 kg/m<sup>3</sup>) (Zhang et al., 2006).

Water-soluble compounds within the emulsions were also analyzed and quantified. Emulsions were centrifuged for 1 h at 100 000 g (Aventi J-301 Centrifuge, Beckman Coulter, USA), in order to induce particles sedimentation and droplets creaming. The intermediate aqueous phases were carefully sampled and centrifuged a second time for 5 min at 4600 g to remove residual droplets prior to freeze-drying and analysis.

## 2.4. Emulsion drying

The dehydration of O/W emulsions is a process employed in the pharmaceutical, cosmetic, and food arenas to obtain solid-like powders. The most frequently methods employed to evaporate water rapidly are spray-drying and freeze-drying (Hernandez Sanchez, Cuvelier, & Turchiuli, 2015; Marefati, Rayner, Timgren, Dejmeck, & Sjöo, 2013). Spray-drying is a unit operation in which the emulsion is pumped, atomized and dried in contact with a hot air current. Freeze-drying is a process where water is crystallized at low temperature and then sublimated directly from the frozen state into vapor by decreasing the pressure. Parent emulsions were dried just after fabrication using 2 different techniques.

**Freeze drying:** emulsions were stored at least 12 h at  $-80$  °C and then introduced into a freeze-dryer (FTS Systems, Dura-Dry, USA) at a pressure of 0.1 mbar for 24 h.

**Spray-Drying:** the emulsions were dried in a pilot-scale spray dryer (Niro Mobile Minor, GEA, Denmark) equipped with a rotary atomizer. The emulsions were fed into the spray tower at a feed flow rate of 1.5 L/h (4.2  $\times 10^{-7}$  m<sup>3</sup>/s). Inlet and outlet air temperatures were 220 °C and 90 °C, respectively.

The obtained powders were stored at room temperature.

## 2.5. Characterization of dry emulsions

### 2.5.1. Moisture content

The residual moisture content of dry emulsions was determined gravimetrically with a moisture analyzer (Moisture Series, Fischer Scientific, US) by drying the samples at 90 °C until a constant weight was reached. Values were expressed on a wet basis.

### 2.5.2. Oil encapsulation efficiency

During the drying process oil can be macroscopically released. The oil encapsulation efficiency is defined as the fraction of oil which remains embedded in the grains matrix after the drying process. The oil content of spray-dried emulsions was determined using the normalized method of Soxhlet extraction with hexane (NF EN ISO 734-1), and was compared to the theoretical oil content assuming that only water was eliminated during the drying process (no oil leakage).

### 2.5.3. Bulk density

To determine the average bulk density, a 6 mL-glass test tube was totally filled with the dry emulsion powders. The tube was tapped vertically against a bottom solid surface to pack the powder and eliminate voids. The initial height was restored by adding powder and the

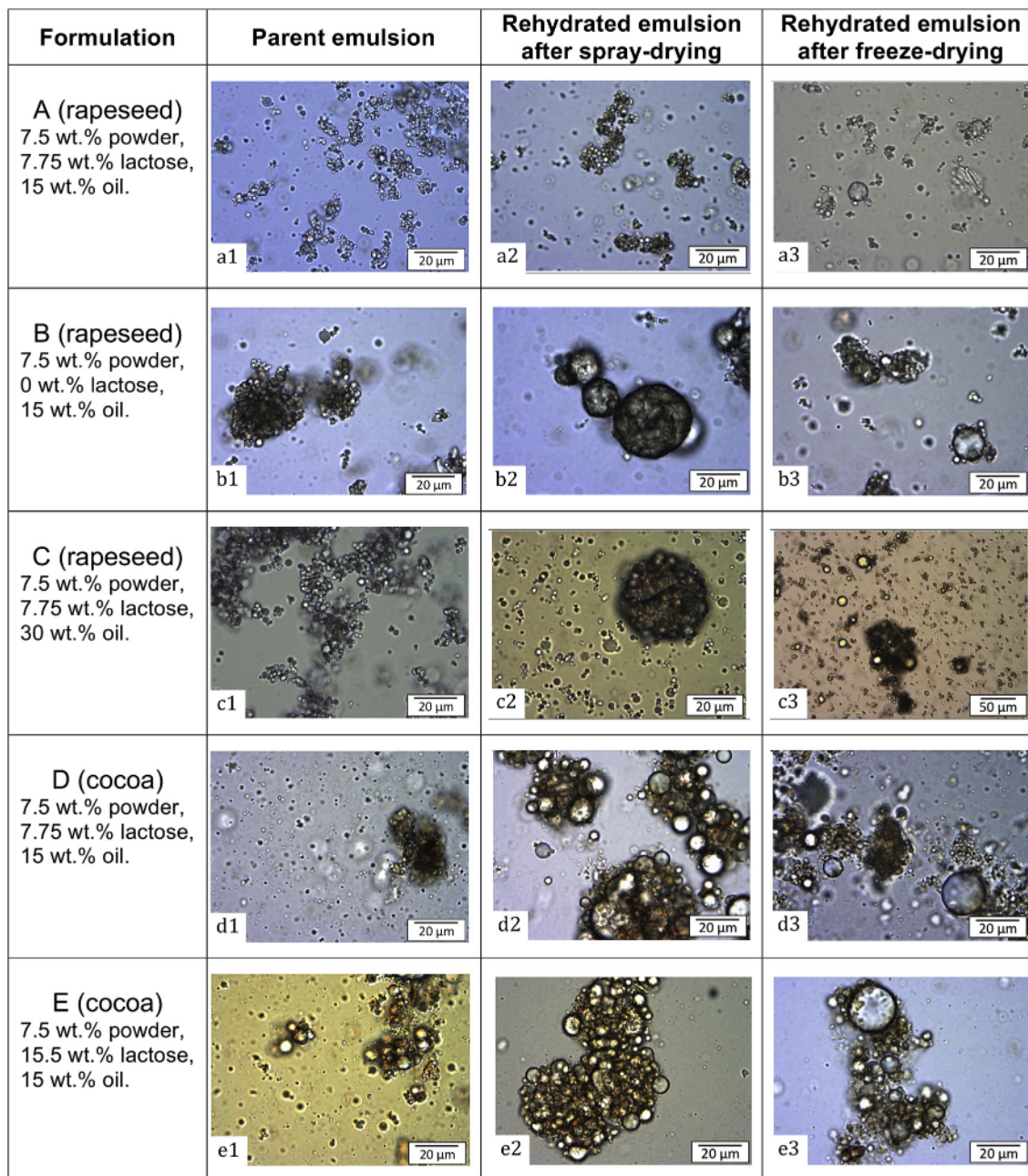


Fig. 1. Microscopic images of parent and rehydrated emulsions for all formulations.

process was repeated until no further variation of the volume was noticed after tapping.

#### 2.5.4. Optical microscopy

Microscope observations were performed in order to identify potential differences in grain morphologies, depending on the drying technique (Olympus BX51 optical microscope, Olympus, Japan). Dry emulsion powders were directly spread on a glass slide and observed in air, without cover slip, to avoid compression of the grains that would produce oil leakage.

## 2.6. Rehydrated emulsions

### 2.6.1. Redispersion of dry emulsions in water

The powders were redispersed by mixing them with the amount of distilled water required to restore the same composition as that of the

parent emulsions. The amount of water  $m_w$ , to be added to a mass  $m_d$  of dry emulsion is given by equation (2):

$$m_w = m_d \left( \frac{1}{DE_0} - 1 \right) \quad (2)$$

where  $DE_0$  is the dry extract (wt%) of the parent emulsion, *i.e.* the summation of the vegetal powder, lactose and oil contents indicated in Table 1. The redispersion was made the same day the emulsions were dehydrated and after an 8-month storage period at room temperature ( $20 \pm 3^\circ\text{C}$ ).

The powders were gently dispersed by manual shaking using a spatula until the samples became homogeneous. In all cases, the redispersion process took less than 1 min.

### 2.6.2. Optical microscopy and droplet size measurements

Rehydrated emulsions were observed following the method

**Table 2**

Soluble fraction of vegetal powder dispersions after bead milling. The contents are expressed as weight percentages of the initial powder mass.

|                                | Total soluble fraction    | Carbohydrates (eq. Glucose) | Proteins (eq. BSA)       | Polyphenols (eq. Gallic acid) |
|--------------------------------|---------------------------|-----------------------------|--------------------------|-------------------------------|
| Cocoa dispersion               | 23.3 ± 0.5 % <sup>a</sup> | 4.7 ± 0.5 % <sup>a</sup>    | 0.5 ± 0.1 % <sup>a</sup> | 0.6 ± 0.1 % <sup>a</sup>      |
| Rapeseed press-cake dispersion | 52.6 ± 0.9 % <sup>b</sup> | 19.8 ± 2.0 % <sup>b</sup>   | 8.7 ± 0.4 % <sup>b</sup> | 0.8 ± 0.1 % <sup>a</sup>      |

Values with the same letter in one column are not significantly different (ANOVA, Tukey HSD,  $p < 0.05$ ).

described in section 2.3.1. Droplet size distributions were measured using exactly the same protocols as for their parent emulsions, after SDS treatment (section 2.3.2).

We define  $R_v$  -respectively  $R_s$ -, as the ratio between the droplet volume-averaged diameter -respectively the surface-averaged- of the rehydrated emulsion and of the parent emulsion. Provided oil leakage after the drying process is insignificant, the ratios are expected to be larger than unity if coalescence between the droplets occurs during the drying process. The smaller these ratios (the closer to unity), the better the protection against coalescence.  $R_s$  reveals the relative evolution of the oil/water interfacial area. Indeed, the total surface area of the droplets is given by  $S = \frac{6V_d}{D_s}$ , where  $V_d$  is the volume of the dispersed phase and  $D_s$  is defined by Eq. (1).  $R_v$  is a good indicator for assessing the extent of droplet coalescence, as the volume-averaged diameter provides pronounced statistical significance to large droplets (see Eq. (1)).

### 2.7. Statistical analysis

All the above-mentioned analyses (average droplet size measurements, soluble compounds, moisture content, oil encapsulation efficiency, bulk density of dry emulsions) were performed at least in triplicate and the values are expressed as means ± mean deviations. Statistical analyses based on ANOVA + test post hoc Tukey HSD were performed using R freeware through the Rstudio interface.

## 3. Results and discussion

### 3.1. Parent emulsions

The compositions of parent emulsions were selected so as to find the best compromise between two antagonistic constraints: (i) good kinetic stability upon drying, which is facilitated by a large amount of vegetal powder and wall material, and (ii) low viscosity of the emulsions to be sprayed in the atomizer, which is generally obtained at low dried extracts. Table 1 indicates the selected compositions of all parent emulsions as well as their main droplet size features deduced from light scattering ( $D_w$ ,  $D_v$  and  $P$ ). The powder content was kept constant in the experiments, while the powder origin (cocoa or rapeseed), the lactose content and the oil content were varied. In all cases, the average diameters were in the micrometer range. Fig. 1 (a1, b1, c1, d1, e1) show characteristic microscope images of the emulsions, revealing their strong aggregated state. Droplets form large and dense flocs, in which they are totally immobilized (they are not submitted to Brownian motion). Joseph et al. (2019) described emulsion stabilization as being due to surface-active moieties of particles adsorbed at the interface, and network stabilization due to physical trapping of droplets in the particles network. Vegetal particles being relatively large (from 0.1 to several tens of microns), they act as “collectors” likely to attach two or more oil droplets on their periphery. This bridging configuration favors the formation of large droplet flocs. The emulsions were kinetically stable since no macroscopic oil leakage was observed at the top of the recipients and the mean diameters did not evolve after several months of storage at 4 °C (data not shown). Due to the strong aggregated state, the emulsions were highly viscous, even gelled in some cases, which delayed gravity driven phenomena. Only a slight creaming phenomenon was observed after a few days of storage but it had no influence on

the size distribution. We would like to stress here that the measured size distributions are relative to individual droplets, and not to aggregates, since the adopted sizing protocol ensured full detachment of the particles from the interfaces and disaggregation of the droplets (see § 2.3.2).

The emulsions are stabilized by the particles (insoluble fraction of the powder, Joseph et al., 2019) and also potentially by surface-active species initially dissolved in the continuous phase. One of the most important roles of emulsifiers is to facilitate the formation of small emulsion droplets during homogenization. An effective emulsifier should rapidly adsorb to the freshly formed droplet surfaces, reduce the interfacial tension to facilitate droplet break-up under shear and provide a protective coating that prevents the droplets from aggregating with their neighbors (Leal-Calderon, Schmitt, & Bibette, 2007). The phospholipids of cocoa beans are important as surface-active compounds in chocolate products. It is generally admitted that the phospholipid level in the common varieties of cocoa beans is relatively constant at 0.3 to 0.5 wt% (Parsons, Keeney, & Patton, 1969). In rapeseeds, the phospholipid content is of the order of 1 wt% (Ambrosewicz-Walacik, Tańska, & Rotkiewicz, 2015). Proteins are also very efficient stabilizers due to their amphiphilic nature, their ability to adsorb at the oil/water interface at relatively fast rates and to protect droplets against coalescence under different conditions (McClements, 2004). Rapeseed powder has a significantly larger overall protein content than cocoa powder: ~35 wt% vs. ~20 wt% (Lecumberri et al., 2007; Leming & Lember, 2005). The composition of soluble compounds in terms of carbohydrates, polyphenols and proteins was measured for both powders and the results are reported on Table 2. Proteins contained in both powders are mostly insoluble. It is likely that particles are adsorbed at the oil/water interfaces via surface-active moieties deriving from insoluble proteins (attached to the particles), protein aggregates, polyphenol-protein or polyphenol-polysaccharide complexes (Foegeding, Plundrich, Schneider, Campbell, & Lila, 2017; Liu, Ma, Gao, & McClements, 2017) and phospholipids. Owing to their small size (and consequently their intrinsically large mobility), soluble proteins may rapidly adsorb at the interfaces and may also significantly contribute to emulsion stabilization.

### 3.2. Properties of dry emulsions

Parent emulsions were dried following the two techniques described in section 2.4. Table 3 indicates the theoretical composition of dehydrated emulsions. This latter was calculated assuming that the total amount of water was evaporated and that all other components were fully recovered. Dry emulsions were characterized right after their preparation in terms of oil content, residual moisture content and bulk

**Table 3**

Theoretical composition of dry emulsions.

| Formulation  | Powder content (wt %) | Lactose content (wt %) | Oil content (wt%) |
|--------------|-----------------------|------------------------|-------------------|
| A (rapeseed) | 24.8                  | 25.6                   | 49.6              |
| B (rapeseed) | 33.3                  | 0                      | 66.7              |
| C (rapeseed) | 16.6                  | 17.1                   | 66.3              |
| D (cocoa)    | 24.8                  | 25.6                   | 49.6              |
| E (cocoa)    | 19.7                  | 40.8                   | 39.5              |

**Table 4**  
Properties of spray-dried and freeze-dried emulsions.

| Formulation   | Drying method | Oil content (wt%)       | Moisture content (wt%)    | Bulk density (g.cm <sup>-3</sup> ) |
|---------------|---------------|-------------------------|---------------------------|------------------------------------|
| A* (rapeseed) | Spray-drying  | 46.4 ± 1.5 <sup>b</sup> | 1.98 ± 0.10 <sup>b</sup>  | 0.59 ± 0.03 <sup>abc</sup>         |
| B* (rapeseed) |               | 67.5 ± 2.0 <sup>a</sup> | 1.48 ± 0.07 <sup>d</sup>  | 0.52 ± 0.03 <sup>cde</sup>         |
| C* (rapeseed) |               | 68.4 ± 2.2 <sup>a</sup> | 1.49 ± 0.07 <sup>d</sup>  | 0.56 ± 0.03 <sup>bcd</sup>         |
| D* (cocoa)    |               | 50.8 ± 1.5 <sup>b</sup> | 0.91 ± 0.05 <sup>e</sup>  | 0.62 ± 0.03 <sup>ab</sup>          |
| E* (cocoa)    |               | 37.6 ± 1.0 <sup>c</sup> | 1.86 ± 0.09 <sup>bc</sup> | 0.68 ± 0.03 <sup>a</sup>           |
| A* (rapeseed) | Freeze-drying | 49.5 ± 0.7 <sup>b</sup> | 1.90 ± 0.09 <sup>bc</sup> | 0.36 ± 0.02 <sup>f</sup>           |
| B* (rapeseed) |               | 66.8 ± 1.0 <sup>a</sup> | 1.63 ± 0.08 <sup>cd</sup> | 0.28 ± 0.02 <sup>f</sup>           |
| C* (rapeseed) |               | 66.1 ± 1.0 <sup>a</sup> | 1.63 ± 0.08 <sup>cd</sup> | 0.50 ± 0.02 <sup>de</sup>          |
| D* (cocoa)    |               | 49.5 ± 0.8 <sup>b</sup> | 1.83 ± 0.09 <sup>bc</sup> | 0.57 ± 0.03 <sup>bcd</sup>         |
| E* (cocoa)    |               | 39.2 ± 0.6 <sup>c</sup> | 2.54 ± 0.1 <sup>a</sup>   | 0.46 ± 0.02 <sup>e</sup>           |

Values with the same letter in one column are not significantly different (ANOVA, Tukey HSD,  $p < 0.05$ ).

\*Composition of the parent emulsion: A: 7.5 wt% powder, 7.75 wt% lactose, 15 wt% oil; B: 7.5 wt% powder, 0 wt% lactose, 15 wt% oil; C: 7.5 wt% powder, 7.75 wt% lactose, 30 wt% oil; D: 7.5 wt% powder, 7.75 wt% lactose, 15 wt% oil; E: 7.5 wt% powder, 15.5 wt% lactose, 15 wt% oil.

density, and the results are reported in Table 4. The measured values of the oil content (Table 4) are very close to the theoretical ones reported in Table 3 (the differences are within the error bars), indicating that the oil loss was insignificant during the drying process.

In emulsified formulations meant to be spray-dried, the oil content relative to dried matter generally remains below 33 wt% (Carneiro, Tonon, Grosso, & Hubinger, 2013; Ixtaina, Julio, Wagner, Nolasco, & Tomás, 2015; Shamaei, Seiedlou, Aghbashlo, Tsotsas, & Kharaghani, 2017). A few studies reported significantly higher oil contents (Mezzenga & Ulrich, 2010; Sarkar et al., 2016). Our systems containing between 40 and 68 wt% oil are thus in a relatively high range compared to current investigations. The powders remained kinetically stable under quiescent conditions, with no apparent oil leakage even after several months of storage at room temperature. However, upon shearing between fingers, oil was progressively released providing a smooth feel. This simple experiment reveals that oil delivery can be produced by applying a mechanical stress. Irrespective of the drying technique, the moisture contents are between 0.9 and 2.6 wt%, within the prescribed regulations for dried powder in the food industry ( $< 3-4$  wt%) (Klinkesorn et al., 2005).

Bulk density is an important property as it determines the ability of the powder to be packed. This parameter is influenced by the grain size distribution, the grain shape, the state of aggregation of the grains and the moisture content (Goula, Adamopoulos, & Kazakis, 2004). On Table 4, it appears that for each formulation, powders deriving from the freeze-drying process have lower bulk densities than those obtained by spray-drying. Fig. S1 (supplementary material) shows the visual (macroscopic) aspect, as well as typical microscope images of the systems. Spray-dried emulsions are made of well-defined large spheroidal grains, whose diameter is of the order of several tens of micrometers. On the contrary, powders deriving from freeze drying are coarse. They are made of irregularly shaped and strongly aggregated grains. Thus, it can be stated that the two drying techniques generate different grain morphologies and aggregation states, which impacts their average bulk densities.

For both drying techniques, powders had the same macroscopic appearance after several months of storage. Neither oil leakage nor clumping were noticed, reflecting efficient stabilization of the encapsulated oil droplets by the solid components.

### 3.2.1. Rehydrated emulsions

Powders were redispersed the same day they were dehydrated ( $t_0$ ) using pure water in order to restore the composition of the parent emulsions. We never observed any oil layer residing at the top of the

**Table 5**  
Properties of spray-dried and freeze-dried emulsions after redispersion.

| Formulation   | Drying method | $R_s$                    | $R_v$                     |
|---------------|---------------|--------------------------|---------------------------|
| A* (rapeseed) | Spray-drying  | 1.05 ± 0.05 <sup>a</sup> | 1.20 ± 0.06 <sup>h</sup>  |
| B* (rapeseed) |               | 1.39 ± 0.07 <sup>b</sup> | 2.57 ± 0.13 <sup>f</sup>  |
| C* (rapeseed) |               | 1.34 ± 0.07 <sup>b</sup> | 1.65 ± 0.08 <sup>g</sup>  |
| D* (cocoa)    |               | 6.54 ± 0.30 <sup>c</sup> | 7.77 ± 0.40 <sup>c</sup>  |
| E* (cocoa)    |               | 2.12 ± 0.10 <sup>c</sup> | 2.62 ± 0.13 <sup>f</sup>  |
| A* (rapeseed) | Freeze-drying | 1.27 ± 0.07 <sup>b</sup> | 3.92 ± 0.20 <sup>c</sup>  |
| B* (rapeseed) |               | 1.94 ± 0.10 <sup>c</sup> | 9.63 ± 0.50 <sup>b</sup>  |
| C* (rapeseed) |               | 2.14 ± 0.10 <sup>c</sup> | 8.04 ± 0.40 <sup>c</sup>  |
| D* (cocoa)    |               | 2.90 ± 0.15 <sup>d</sup> | 11.74 ± 0.60 <sup>a</sup> |
| E* (cocoa)    |               | 2.09 ± 0.10 <sup>c</sup> | 5.93 ± 0.30 <sup>d</sup>  |

Values with the same letter in one column are not significantly different (ANOVA, Tukey HSD,  $p < 0.05$ ).

\*Composition of the parent emulsions: A: 7.5 wt% powder, 7.75 wt% lactose, 15 wt% oil; B: 7.5 wt% powder, 0 wt% lactose, 15 wt% oil; C: 7.5 wt% powder, 7.75 wt% lactose, 30 wt% oil; D: 7.5 wt% powder, 7.75 wt% lactose, 15 wt% oil; E: 7.5 wt% powder, 15.5 wt% lactose, 15 wt% oil.

emulsions, confirming the absence of macroscopic oil leakage. We first compare formulations A and D which are identical, albeit based on two different vegetal sources. Table 5 indicates the values of the size ratios  $R_s$  and  $R_v$  and Fig. 1 (a2, a3, d2, d3) shows selected micrographs of the rehydrated emulsions. The corresponding size distributions are given in Fig. 2. Rehydrated emulsions are aggregated, as the parent emulsion. Formulation A based on rapeseed press cake provides very good performances. The size ratios  $R_s$  and  $R_v$  are close to unity for the powder deriving from spray-drying (Table 5). By comparing Fig. 1-a1 and a2, we deduce that parent and rehydrated emulsions are almost identical and this is confirmed by the size distributions in Fig. 2. For the system processed by freeze-drying, the size distribution becomes broader, with a new mode at large diameters, around 20  $\mu\text{m}$  (Fig. 2), reflecting droplet coalescence. This agrees with the observations under the microscope (Fig. 1-a3). One can notice in the image of formulation D on Fig. 1-d3 that droplets larger than the average are present, thus confirming the existence of the supplementary mode.

Powders based on cocoa could also be redispersed in pure water but both drying pathways induced substantial droplet coalescence, as revealed by the size ratios  $R_s$  and  $R_v$ , which were significantly larger than unity (Table 5). Interestingly, the emulsion deriving from spray-drying had a size distribution narrower than that deriving from freeze-drying (Fig. 2).

Redispersion in water was also achieved after a storage period of 8 months at room temperature for the systems deriving from spray-drying. In Fig. S2 (supplementary material) we compare the volume-averaged diameter of the parent emulsions, the dry emulsions rehydrated at  $t_0$  and the dry emulsions rehydrated after 8 months. The average diameters of the rehydrated emulsions measured at  $t_0$  and at  $t = 8$  months are comparable, which confirms that dry emulsions remain kinetically stable over a long period of time.

To sum up, rapeseed press cake provides better performances than cocoa powder. This could be explained by the overall largest content in amphiphilic species in the rapeseed source (see section 3.1), providing better anchoring and coverage capabilities. These species include phospholipids, polyphenols complexes and proteins, these latter being the most abundant ones. Our results also reveal that emulsions processed by spray-drying are less prone to coalescence than those submitted to freeze-drying. This latter technique induces cryo-concentration of the droplets, likely to compress them and to provoke coalescence events (Marefati et al., 2013).

### 3.3. Influence of the lactose content

Lactose is currently used as an edible filler (Ixtaina et al., 2015; R.

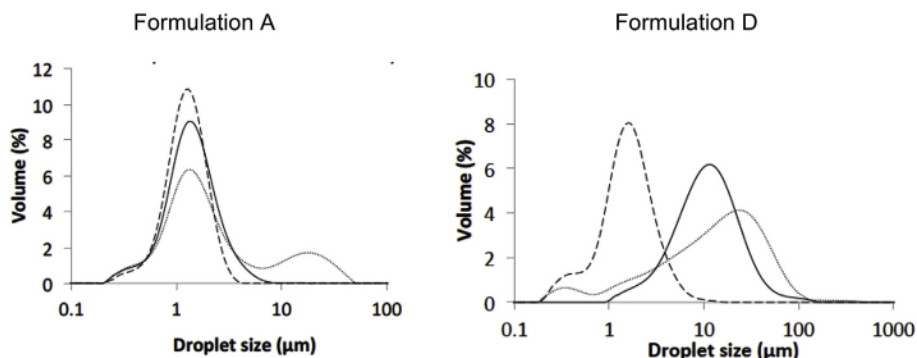


Fig. 2. Size distributions of parent and rehydrated emulsions for formulations A and D. (---) Parent emulsion; (—) Rehydrated emulsion after spray-drying; (· · · · ·) Rehydrated emulsion after freeze-drying.

Li, Roos, & Miao, 2017; Maher, Auty, Roos, Zychowski, & Fenelon, 2015). The positive effect of lactose is generally attributed to the formation of a protective (against coalescence) continuous glass phase in which the droplets are embedded (Rosenberg & Sheu, 1996).

### 3.3.1. Rapeseed-stabilized emulsions

The highly performing formulation A containing 7.5% lactose was compared to formulation B devoid of lactose. The macroscopic aspects of the powders obtained from formulations A and B are identical (see S1, supplementary material). Table 5 indicates the characteristic size ratios and some typical micrographs of the rehydrated emulsions (at  $t_0$ ) are reported in Fig. 1 (a2,a3,b2,b3). Unlike formulation A, rehydrated emulsions deriving from formulation B exhibit significantly larger droplet average diameters than their parent emulsion for both drying techniques. This is confirmed by the size distributions of Fig. 3. Once again, among the two techniques, spray-drying provides better performances, reflected by smaller  $R_s$  and  $R_v$  values. Spherical aggregates can be clearly distinguished in Fig. 1-b2. These latter are reminiscent of the grains (i.e. aerosol particles) observed in the dry powder (S1-b1, supplementary material), indicating that the grains were not fully dispersed in the rehydrated emulsion.

These results underline the ability of lactose to protect droplets against coalescence during the drying process. During the spray-drying process, the implementation of elevated air temperatures accelerates water evaporation from the aerosol particles surface. This results in the fast formation of a hard crust which provides a semi-permeable membrane around the particles, allowing further evaporation, while preventing leaching of oil droplets to the surface (Gaiani et al., 2010). In addition, protein-carbohydrate conjugates formed as a result of the Maillard reaction between the amino groups of the proteins and the carbonyl group of lactose might have a significant effect on the crust formation (Aghbashlo, Mobli, Madadlou, & Rafiee, 2013).

### 3.3.2. Cocoa-stabilized emulsions

Because of the rather poor performance of formulation D (see section 3.2.1), the amount of lactose was raised up to 15.5 wt% in formulation E. The macroscopic aspect of the powders deriving from

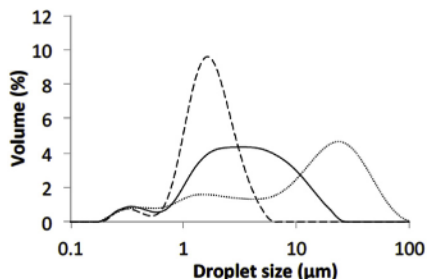


Fig. 3. Size distributions of parent and rehydrated emulsions for formulation B. (---) Parent emulsion; (—) Rehydrated emulsion after spray-drying; (· · · · ·) Rehydrated emulsion after freeze-drying.

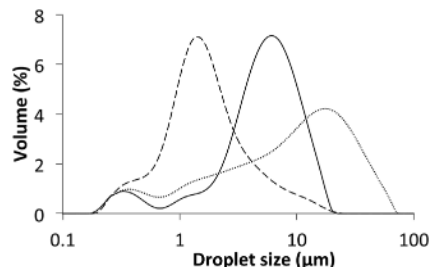


Fig. 4. Size distributions of parent and rehydrated emulsions for formulation E. (---) Parent emulsion; (—) Rehydrated emulsion after spray-drying; (· · · · ·) Rehydrated emulsion after freeze-drying.

formulation E is shown in S1 (e2, e4) (supplementary material). The powder obtained by freeze-drying is again coarser than that deriving from spray-drying. Emulsions were rehydrated at  $t_0$  and the main characteristics are given in Table 5 (size ratios), Fig. 1 (e2, e3) (typical micrographs) and Fig. 4 (size distributions). The droplets form dense aggregates whose size exceeds several hundred microns. By comparing these data with those corresponding to formulation D (Table 5, Fig. 1 (d2, d3), Fig. 2), it turns out that the increase in lactose concentration has a protective effect against coalescence.

### 3.4. Influence of the oil/vegetal powder ratio

Dry solid powders are available today mainly in formulations that comprise a relatively high weight percentage of non-oily compounds. The minimum amount of solid hydrophilic carrier needed is in general between 30 and 80 wt% of the total final powder (Gu et al., 2004; Jost et al., 1989; Klinckesorn et al., 2005). Dry solid powders comprising a high content of oil compounds would bring several significant advantages and are highly sought after.

In formulation C, the fraction of oil is twice as large as in formulation A. The increase in the oil/solid ratio is generally detrimental to the stabilization, since there is proportionally fewer wall material. Actually, the powder obtained by spray-drying exhibits good resistance to coalescence. Indeed, the size ratios  $R_s$  and  $R_v$  have low values, close to 1.5 (Table 5), and the evolution of the size distributions is moderate, with only a slight widening towards higher sizes (Fig. 5). The powder deriving from freeze-drying is more prone to coalescence. The corresponding rehydrated emulsion (at  $t_0$ ) becomes polydisperse, with two main modes centered on 5 and 50  $\mu\text{m}$ . Thus, a dry powder comprising two thirds of oil (Table 4) can be obtained, preferentially by spray-drying. The powder exhibits no clumping or oil leakage (see S1, supplementary material) and its rehydration leads to an emulsion without oil leakage as well.

## 4. Conclusion

In this paper, we investigated the possibility to produce novel

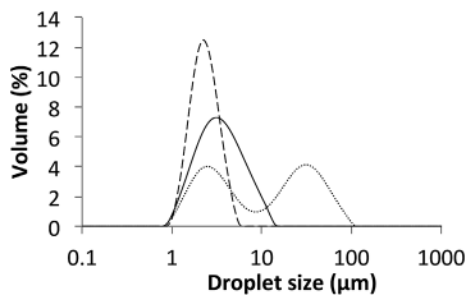


Fig. 5. Size distributions of parent and rehydrated emulsions for formulation C. (---) Parent emulsion; (—) Rehydrated emulsion after spray-drying; (.....) Rehydrated emulsion after freeze-drying.

redispersible powders based on Pickering oil-in-water emulsions stabilized by plant material, and processed by freeze-drying and spray-drying. Powders of at least 40% wt% oil and with a moisture content below 2.6 wt% were easily achieved, without any loss. Fine and easily handleable dry powders were obtained. The study investigated the impact of the drying process and of several formulation parameters, including the filler/wall (lactose) content, the oil content, the vegetal origin of the stabilizing material (rapeseed and cocoa), on the overall properties of rehydrated emulsions. Compared to their parent emulsions, rehydrated emulsions exhibited larger average droplet sizes due to the occurrence of coalescence phenomena during the drying process. Yet, the size distribution remained generally in the colloidal range ( $< 100 \mu\text{m}$ ), and macroscopic release was not observed. Formulations based on rapeseed press-cake provided excellent performances, since after spray-drying, the redispersed emulsion had almost the same features as the parent emulsion in terms of size distribution. Strictly speaking, no additional hydrophilic filler compound was required. However, the stability against coalescence was significantly enhanced in presence of lactose. Spray-drying had less impact than freeze-drying on the evolution of the size distribution and rapeseed material was more performant than cocoa powder.

Pickering emulsions based on plant material represent a versatile and promising route to formulate powders that can find applications in the food industry. Such powders are a complete foodstuff as they contain lipids, proteins, fibers and polyphenols. They could be used as intermediary products to be incorporated in aqueous formulations (instant drinks, vegetal milks, soups).

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.lwt.2019.108311>.

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