INTRODUCTION

A wide variety of food powder products with encapsulated oily components are produced via spray drying of oil-in-water emulsions. Examples include infant formula, instant dairy powders and products with encapsulated flavors and functional lipids (Gharallaoui et al., 2007). Typical formulations include the oily phase to be encapsulated, a protein source (e.g., whey protein) stabilized by emulsifiers like lecithin, mono- and diglycerides (MoDi), and citrem. The changes in oil droplet size occurring during spray drying affect the quality of the final product, thus understanding the influence of formulation components on these changes is crucial.

Abstract

The goal of this study was to investigate the influence of the emulsifier system on the changes in oil droplet size occurring during the drying step of spray drying of emulsions. Atomization and spray drying experiments were performed with emulsions stabilized with whey protein isolate (WPI) alone or in combination with low molecular weight emulsifiers (lecithin, mono- and diglycerides (MoDi), and citrem). Oil droplet coalescence was observed for the systems WPI/Citrem and WPI/MoDi, as the d90,0 increased from 0.86 ± 0.16 and 1.67 ± 0.35 µm after atomization to 1.83 ± 0.24 and 1.90 ± 0.17 µm after drying, respectively. Oil droplets stabilized with WPI or WPI/Lecithin remained stable during drying. Measurements of dilatational rheology of the interfacial film showed that phase angle values increase in the order WPI/Lecithin < WPI < WPI/Citrem = WPI/MoDi. Therefore, in the studied system oil droplet coalescence during drying increases when the elastic behavior of the interfacial film decreases.

Practical applications

Spray drying of emulsions is a widely used process in the food industry for production of, for example, infant formula, dairy powders, and encapsulated aroma and coloring compounds. The oil droplet size in the resulting powder determines sensory aspects and stability of the final product. This study deepens the understanding of the changes in oil droplet size occurring during spray drying as affected by the formulation components, allowing therefore a better control of the quality of spray dried food emulsions.
The changes in oil droplet size during drying are expected to be strongly influenced by the interfacial behavior of the emulsifier system and by the viscoelasticity of the interfacial film. Proteins and LMWE show differences in interfacial stabilization. Proteins may form a viscoelastic layer at the interface which operates as a physical barrier against coalescence (Wilde et al., 2004). Therefore, we expect that oil droplets stabilized with WPI remain better protected against coalescence during the drying step. When proteins are aggregated, they can also stabilize emulsions by forming pickering emulsions (Burgos-Díaz et al., 2020). In this study, we focused on native proteins as raw material and therefore this mechanism is not further considered. LMWE have a higher interfacial activity than proteins, but do not form viscoelastic layers (Bos & van Vliet, 2001).

In general, a mixed interfacial film of LMWE and protein tends to show a reduced viscoelasticity compared to protein films, which can be explained by protein displacement and loss in interfacial interactions (Murray & Dickinson, 1996). Thus, increased coalescence is expected during the drying step with combinations of WPI/LMWE. However, a combination of both emulsifier types may result in more complex interfacial mechanisms influenced by interfacial activity, electrostatic and hydrophobic effects (Dan et al., 2013; Kotsmar et al., 2009), which influence the interfacial tension and viscoelasticity of the interfacial film. Therefore, the effects on the interfacial tension and viscoelasticity are not straightforward. The effects of proteins and LMWE on viscoelasticity of interfacial films can be estimated with dilatational rheology. In these measurements, the interfacial film is characterized by response of the interfacial area to expansion and compression (Lucassen-Reynders, 1993).

The goal of the present study was to investigate the influence of the emulsifier system (WPI vs. WPI/LMWE) on the changes in oil droplet size during the drying step of spray drying process. For this, atomization and spray drying experiments were performed in pilot scale with emulsions stabilized with WPI or combinations of WPI/LMWE. By comparing the ODSD after atomization and after spray drying, the changes in oil droplet size were quantified. Furthermore, the observed changes were explained via changes of interfacial tension and viscoelasticity of the interfacial film, characterized with pendant drop tensiometry and dilatational rheology.

2 | MATERIAL AND METHODS

2.1 | Model emulsions: Preparation and characterization

Oil-in-water emulsions were prepared for the investigations. Medium-chain triglycerides oil was used as dispersed phase (MCT oil, WITARIX MCT 60/40, IOI Oleo GmbH, Hamburg, Germany). Whey protein isolate (WPI, Lacprodan DI-9224, Sønderhøj, Denmark) served as protein emulsifier. The WPI composition was as follows: 89.5% protein, <0.05% lactose, 0.1% fat, 5% moisture, and <4% ash. A soybean lecithin (Metarin, Cargill, Hamburg, Germany), a citrem (GRINDSTED CITREM N12, DuPont Nutrition & Biosciences,
Emulsions were tempered to 20°C and atomized at a pressure of 100 bar and a corresponding volume flow rate of 28.8 L/h. During atomization, a sample of the spray was taken with a beaker 25 cm below the nozzle.

The spray test rig was also equipped with an in-line laser diffraction spectroscope (Spraytec, Malvern Instruments GmbH, Herrenberg, Germany) which allowed the measurement of the spray droplet size distribution (SDSD) during atomization. Spray droplet sizes were measured 25 cm underneath the nozzle exit for 30 s. A time-average SDSD was calculated. SDSD are of great relevance for the drying behavior as they determine the area for heat and mass transfer during the drying process.

Atomization experiments were performed in duplicate trials with two separately prepared emulsions. Two samples were taken at each trial, resulting in six independent samples for analysis.

### 2.3 Spray drying of emulsions

Spray drying experiments were performed in a pilot-scale spray dryer (Werco SD20, Hans G. Werner Industrietechnik GmbH, Germany) using the same atomization conditions as in the atomization experiments. The spray dryer was operated with an inlet and outlet temperature of 195 and 75°C, respectively. The corresponding air volume flow was 580 kg/h. The resulting powders were collected and stored in air-tight containers until analysis. Spray drying experiments were performed in duplicate with two separately prepared emulsions. Comparison of ODSD in emulsions after atomization (from Section 2.2) with ODSD after spray drying allows the quantification of the effect of the drying step on the oil droplet size.

#### 2.3.1 Powder analyses

To determine the oil droplet size after spray drying, powders were dispersed in water under gentle magnetic stirring (0.1 g/ml). The oil droplet size of the reconstituted emulsion was determined via laser diffraction as described in the previous section. Scanning electron microscopy (SEM, FEI Quanta 650 ESEM) was further used to study the powder microstructure.

Powders were also characterized by their particle size distribution (PSD), moisture content, and water activity. PSD of the powders were measured by a laser diffraction spectroscope with powder dispersion unit (HORIBA LA950, Retsch Technology GmbH, Haan, Germany). In this device, the powder was dispersed in the measurement chamber with a gas flow at a pressure of 2.5 bar. Moisture content was analyzed by weight loss after oven drying at 105°C to constant mass. Water activities were measured by a dedicated instrument (LabMaster-aW Neo, Novasina, Switzerland).

All measurements were performed in triplicate. The data was analyzed by 1-way-ANOVA with a significance level of $p < 0.05$ using the software OriginPro 2018 (OriginLab Corporation, Northampton, USA). Scheffé’s test was used for mean comparison.
2.4 Dilatational rheology

The interfacial behavior of the emulsifier system was characterized by determination of the interfacial tension and viscoelasticity of the interfacial film. Therefore, a pendant drop tensiometer (PAT1 M, Sinterface Technologies e.K., Berlin, Germany) with a high-speed camera was used at 22°C.

For these experiments, the major component of WPI—β-lactoglobulin—was utilized as model protein to ensure a high accuracy and precision of the results by reducing the noise in the measurements caused by the other numerous components in WPI. Typical values of β-lactoglobulin content in commercial WPI are between 45% and 69% (Foegeding et al., 2011). β-lactoglobulin (β-LG) was isolated from WPI (Bipro, Agropur Dairy Cooperative Inc., Minnesota, USA) with a purity of 98.11% (analysed according to (Keppler et al., 2014)). The protein was used at its critical interfacial concentration to provide a monolayer of protein at the interface (Tamm et al., 2012). LMWE and MCT-oil were utilized as described in Section 2.1. The LMWE were used below their critical micelle concentration to provide a monolayer of protein at the interface. Since LMWE are able to displace proteins from the interface (Wilde et al., 2004), it was assured that both emulsifiers share the same interface. The applied concentration ratio was the same as in the emulsions for spray drying experiments. The MCT-oil was purified via magnesium silicate adsorption (Florisil, Carl Roth GmbH, Karlsruhe Germany) to remove interfacial active substances.

The protein solutions were prepared at pH 7. Therefore, the protein was dissolved and stirred in distilled water for approximately 2 hr. The pH was adjusted to 7 with 1 M NaOH. The LMWE were solubilized in purified MCT oil to obtain a concentration of 0.005 wt.%. During the measurement, a drop of protein solution with a volume of 30 mm³ was formed in purified MCT oil with or without addition of LMWE. The drop was equilibrated for 14 hr and the interfacial tension was recorded. Afterwards, a frequency sweep (2.8% amplitude, 0.001 to 0.1 Hz) was performed. In this study, the results of dilatational rheology are expressed with the phase angle (ϕ) as important key parameter for elastic and viscous behavior. A phase angle of 0° indicates only elastic behavior of the interfacial film. If there is a phase angle of 90°, the interfacial film reacts only viscous. A value between 0° and 90° shows a viscoelastic behavior of the film.

3 RESULTS AND DISCUSSION

3.1 Feed emulsions characteristics and spray drying performance

The characteristic oil droplet sizes d90.0 of the feed emulsions prior to atomization and spray drying are summarized in Table 1. Emulsions prepared only with WPI presented a slightly higher d90.0 compared to emulsions prepared with WPI/LMWE, although the differences among WPI, WPI/Citrem, and WPI/MoDi are not significant. The lowest d90.0 was obtained for emulsions prepared with WPI/Lecithin. This is consistent with studies that showed that addition of lecithin to protein stabilized emulsions lead to smaller droplet sizes after homogenization (Wang et al., 2017). Viscosity values at a shear rate of 1,000 s⁻¹ are also presented in Table 1. As expected, no significant differences are observed between all emulsions. All emulsions presented a Newtonian behavior.

SDSD during atomization are depicted in Figure 1. Emulsions stabilized with different emulsifier systems presented similar SDSD. This is expected as SDSD are dominated by emulsion viscosity and atomization conditions (e.g., nozzle type and pressure) (Lefebvre & McDonell, 2017). All these parameters were held constant for the different formulations. Similar spray droplet sizes indicate that the emulsions were subjected to similar stresses during atomization. Also, similar SDSD ensure that the surface area for heat and mass transfer was the same for all emulsions during the spray drying process. As the air temperature and volume flow were kept constant during spray drying, the same drying behavior is expected for all emulsions. These results implicate that any differences observed in oil droplet size (see Section 3.2) are due to different emulsifiers and not due to the drying process. Values of moisture content and water activities of the resulting powders were measured and are depicted in Table 1. As expected, no significant difference in the values are observed for the different

| Emulsifier system | WPI | WPI/Lecithin | WPI/Citrem | WPI/MoDi |
|-------------------|-----|--------------|------------|----------|
| Feed emulsion     |     |              |            |          |
| d90.0 (µm)        | 3.99 ± 0.29ᵃ | 2.49 ± 0.10ᵇ | 3.34 ± 0.13ᵃ | 3.50 ± 0.37ᵃ |
| Viscosity at 1,000 s⁻¹ (mPa·s) | 33.1 ± 0.5ᵃ | 32.3 ± 1.9ᵃ | 31.0 ± 0.3ᵃ | 31.56 ± 1.4ᵃ |
| Powders           |     |              |            |          |
| Moisture content (%) | 2.81 ± 0.52ᵃ | 2.69 ± 0.1ᵃ  | 2.15 ± 0.49ᵃ | 2.46 ± 0.44ᵃ |
| Water activity (⁻) | 0.23 ± 0.01ᵃ | 0.21 ± 0.03ᵃ | 0.20 ± 0.04ᵃ | 0.23 ± 0.05ᵃ |

Table 1 Characteristics of feed emulsions and spray dried powders prepared using different emulsifier systems. For each characteristic, different letters indicate significant differences (p < 0.05)
emulsifier systems. Also, the values of moisture content and water activities are in a desirable industrial range to ensure product stability (Duckworth, 1975).

### 3.2 Oil droplet size after atomization and spray drying

The ODSD of the feed emulsions, the emulsions after atomization and the reconstituted emulsions after spray drying are depicted in Figure 2a-d for the different combinations of WPI/LMWE. In all cases the ODSD of the atomized emulsions (filled circles) is shifted toward lower values compared to their respective feed emulsions (filled triangles). These results indicate oil droplet breakup during atomization, which is consistent with previous studies (Taboada et al., 2020).

In the case of emulsions stabilized with WPI alone (Figure 2a), the ODSD of emulsions after atomization presents a bimodality.

---

**FIGURE 1** Droplet size distributions of spray droplets measured during atomization experiments with emulsions stabilized with whey protein isolate and WPI/LMWE.

**FIGURE 2** Number cumulative distributions of oil droplet size of emulsions stabilized with whey protein isolate and WPI/LMWE after atomization and spray drying. (a) whey protein isolate (b) WPI/Citrem (c) WPI/MoDi (d) WPI/Lecithin.
This bimodality is the result of oil droplet coalescence taking place during the atomization step, directly after droplet breakup (Taboada et al., 2020). When comparing the ODSD and the \(d_{90.0}\) after atomization and after spray drying (Table 2), no significant differences are observed. These results indicate that the oil droplets were stable during the drying step for this emulsion.

A different behavior is observed for emulsions stabilized with WPI/LMWE. In the case of emulsions stabilized with WPI/Citrem (Figure 2b), a bimodality is also observed in the ODSD of the emulsion after atomization, with a proportion of relatively small droplets (sizes between 0.1 and 0.3 µm) and larger droplets with sizes up to 1.1 µm. The bimodality is also the result of droplet coalescence during atomization (Taboada et al., 2020). The ODSD of the emulsion with WPI/Citrem after spray drying is shifted toward larger values, compared to the emulsion after atomization. In this case, oil droplet sizes start at 0.4 µm and range up to 2 µm. The value of \(d_{90.0}\) after spray drying is significantly higher than the value after atomization (Table 2). These results indicate that coalescence of oil droplets takes place during the drying step with the system WPI/Citrem.

For emulsions stabilized with WPI/MoDi (Figure 2c), the ODSD after atomization also presents a bimodality, with a relatively small proportion of submicron droplets (sizes between 0.2 and 0.8 µm) and larger droplets with sizes up to 2 µm. Thus, the oil droplets after atomization are evidently larger compared to the oil droplets after atomization with the other emulsifier systems. In our previous study, we demonstrated that these large oil droplets are the result of droplet coalescence directly after oil droplet breakup during atomization (Taboada et al., 2020). When considering the ODSD of the emulsion after spray drying it can be seen that the proportion of small droplets is reduced compared to the ODSD after atomization, with the smallest oil droplets being around 0.4 µm. Both the ODSD after atomization and spray drying presents large standard deviations. These large deviations are most probably a result of droplet coalescence, which is known to be a stochastic process (Neumann et al., 2018). Although the differences in \(d_{90.0}\) after atomization and after spray drying are not significant (Table 2), the results on the ODSD suggest that the combination of WPI/MoDi further promotes coalescence during the drying step.

The results with the systems WPI/Citrem and WPI/MoDi suggest that addition of these LMWE is detrimental for oil droplet stabilization against coalescence during the drying step. Other studies have also reported increased oil droplet coalescence by addition of monoglycerides and fatty acid esters to protein stabilized emulsions (Danviriyakul et al., 2002; Drapala et al., 2017; Matsumiya et al., 2014). We can expect that during atomization and directly after oil droplet breakup, LMWE adsorb faster at the interface than whey protein (Bos & van Vliet, 2001). Once at the interface, competitive adsorption with the protein may hinder the formation of the viscoelastic film at the interface (Bos & van Vliet, 2001), resulting in less stabilization against coalescence. Further details in interfacial mechanisms are explained in Section 3.3.

ODSD of emulsions after atomization and spray drying for the system with WPI/Lecithin are shown in Figure 2d. Differently to the other emulsifier systems of WPI/LMWE, the ODSD after atomization does not present a bimodality. In this case and as explained in our previous work, the combination WPI/lecithin prevents coalescence directly after oil droplet breakup during atomization (Taboada et al., 2020). Furthermore, the ODSD after spray drying is only slightly shifted to higher values and the distribution remains monomodal. In contrast with the emulsions with WPI/Citrem and WPI/Modi, oil droplets as small as 0.1 µm remain stable after spray drying in the emulsions with WPI/Lecithin. The results suggest that the oil droplets are well-protected against coalescence during the drying step with the combination WPI/Lecithin. An improved oil droplet stabilization by combination of whey proteins with lipid-based lecithin has also been reported in the literature (Bylaite et al., 2001; Wang et al., 2017).

### TABLE 2 Values of \(d_{90.0}\) after atomization and after spray drying of emulsions stabilized with whey protein isolate (WPI) and WPI/LMWE. For each system, different letters indicate significant differences (\(p < 0.05\)).

| Emulsifier system | \(d_{90.0}\) after atomization (µm) | \(d_{90.0}\) after spray drying (µm) |
|-------------------|-----------------------------------|-----------------------------------|
| WPI               | 0.89 ± 0.2\(^a\)                 | 0.68 ± 0.14\(^a\)               |
| WPI/Lecithin      | 0.47 ± 0.02\(^a\)                | 0.66 ± 0.11\(^b\)              |
| WPI/Citrem        | 0.86 ± 0.16\(^a\)                | 1.83 ± 0.24\(^b\)              |
| WPI/MoDi          | 1.67 ± 0.35\(^a\)                | 1.90 ± 0.17\(^a\)              |

### TABLE 3 Interfacial tension and phase angle of 0.1 % \(\beta\)-LG with addition of 0.005 % Lecithin, Citrem or MoDi at MCT-oil/water interface after 14 h drop ripening and at 2.8 % amplitude and 0.01 Hz

|          | \(\beta\)-LG | \(\beta\)-LG/Lecithin | \(\beta\)-LG/Citrem | \(\beta\)-LG/MoDi |
|----------|--------------|-----------------------|---------------------|------------------|
| Interfacial tension (mN/m) | 15.3 ± 0.2 | 8.4 ± 0.1 | 15.0 ± 0.2 | 15.2 ± 0.2 |
| Phase angle (°) | 6.9 ± 0.7 | 5.1 ± 0.5 | 9.5 ± 0.9 | 10.0 ± 1.0 |
The values of interfacial tension (Table 3) are comparable with the values reported in our previous study for systems with WPI and WPI/LMWE (Taboada et al., 2020). Therefore, it is expected that the viscoelastic behavior of the systems reported in Section 3.2 is well-modeled by the systems containing β-LG. 

β-LG shows a viscoelastic behavior (Table 3) comparable to previous studies (Böttcher et al., 2017; Keppler et al., 2021). The phase angle of $6.9 \pm 0.7^\circ$ indicates a high elastic portion in the interfacial film. This viscoelastic behavior is expected to increase the stability of emulsion droplets during processing steps (Bos & van Vliet, 2001; Lam & Nickerson, 2013). These results can explain the effects shown in Figure 2a. Directly after oil droplet breakup during atomization there is some coalescence due to the slow kinetics of the protein (Lam & Nickerson, 2013). However, once the protein is adsorbed at the interface, the highly elastic interfacial film protects the oil droplets against coalescence during the drying step. The high viscoelasticity is a result of high intermolecular interactions of protein molecules at the interface.

In general, LMWE adsorb faster at the interface than proteins (Bos & van Vliet, 2001) and hinder the formation of the viscoelastic film (Wilde et al., 2004). For a system consisting of β-LG and citrem or MoDi, the interfacial tension barely changes compared to β-LG alone (Table 3) which is attributed to the comparatively low interfacial activity for citrem and MoDi as LMWE. The phase angle increases with addition of citrem and MoDi to around 10.0°. The increase in phase angle indicates a loss in elastic portion of the interfacial film. This loss in viscoelastic behavior was expected for an interfacial film with protein and LMWE and corresponds to previous literature (Wilde et al., 2004). By this, the increase of droplet size during the drying step with WPI/Citrem and WPI/Modi compared to the system with WPI alone can be explained. It is expected that directly after oil droplet breakup, the LMWE adsorbs fastly at the interface (Bos & van Vliet, 2001) and hinders the formation of the viscoelastic film. Therefore, these films show less intermolecular interactions which results in an incomplete protection of the oil droplets against coalescence when forced in close contact during the drying step. The fewer interactions might be attributed to non-attractive interactions between the protein and citrem or MoDi. For a system containing citrem and β-LG, under neutral conditions both molecules are negatively charged due to the reported pka value and isoelectric point (Lam & Nickerson, 2013; Whitehurst, 2004). The repulsive forces between both molecules reduce the film elasticity which has been also reported by (Wilde et al., 2004). Under neutral conditions, for the non-ionic MoDi, no attractive interactions to the protein are expected.

In comparison, the addition of lecithin lowers the interfacial tension and shifts the interfacial behavior to a more elastic response with a phase angle of $5.1 \pm 0.5^\circ$ (Table 3). This behavior can be explained by the high hydrophilic portion and thus high interfacial activity of the molecule (Murray & Dickinson, 1996; Whitehurst, 2004). The high interfacial activity of the lecithin molecule and the mutual high reduction in interfacial tension (Table 3) can explain that the smallest oil droplets were present in the feed emulsion (Table 1) and after atomization (Table 2). The high interfacial activity increases the elastic response by Gibbs-Marangoni-mechanisms (Murray & Dickinson, 1996; Wilde et al., 2004) which is attributed to the ability of lecithin to stabilize fastly unoccupied interfacial parts. This ability prevents coalescence of the oil droplets from the beginning of the spray drying process. The increased elastic behavior of the film in the presence of lecithin makes the oil droplets less prone to coalescence when forced in close contact during drying. Synergetic effects between β-LG and several oil soluble LMWE, leading to higher interfacial stabilization have also been reported in the literature (Bylait et al., 2001; Chen & Dickinson, 1995). The detailed mechanisms at the interface are not easy to predict due to the mixed molecular structure of LMWE. Also, the different time scales of the phenomena occurring during atomization and drying and the presented measurements complicates the direct transfer of the observed effects. However, the results showed that LMWE and β-LG interact at the interface and lead to changes in the film viscoelasticity, even when the interfacial tension does not change. These effects go along with the observed coalescence of the oil droplets during the drying step. Therefore, the presented mechanisms give a better comprehension of the impact of interactions of emulsifiers on the changes of oil droplet size during spray drying.

3.4 Powder particle size distributions and microstructure

Powder particle size distributions (PSD) after spray drying are depicted in Figure 3. Up to a value of around 100 µm, all powders presented very similar PSD. Only the PSD corresponding to the emulsion with WPI/Lecithin presented a monomodal distribution, with maximum values of around 200 µm. Powders with other emulsifier systems presented bimodal distributions and large particles up to 1,000 µm. As all emulsions presented the same SDSD during
atomization (Figure 1), and no values of spray droplet sizes close to 1,000 µm were measured, these large particle sizes cannot correspond to the primary size of the powder particles. These high values can only be explained by the formation of clumps or agglomerates in the powder, which were not destroyed by the dispersing gas during the measurements. From Figure 3 it is also noticeable that the powders with WPI/MoDi presented the largest particle sizes, followed by WPI/Citrem and WPI.

Powders clumps can also be detected in SEM micrographs (Figure 4). In agreement with the results shown in Figure 3, the largest clumps are observed in the case of the powders with WPI/MoDi (see circle in Figure 4c). Furthermore, dark areas corresponding to regions with free, non-encapsulated oil are also detected in all the powders (see arrows). It is well-known that free surface oil can lead to the formation of liquid bridges between the particles (Nijdam & Langrish, 2006), leading to extensive clumping of the powders (Taneja et al., 2013). The amount of free surface oil has been previously correlated with coalescence of oil droplets during spray drying (Drapala et al., 2017; Drusch & Berg, 2008). With this knowledge it is obvious to assume that the systems with the most oil coalescence during the spray drying process (WPI/MoDi and WPI/Citrem) present the highest amount of non-encapsulated oil and have the highest tendency to clump formation. A detailed investigation on the free, non-encapsulated oil and the resulting storage characteristics of the investigated powders will be presented in a separate study.

4 | CONCLUSIONS

In the present study, the influence of addition of LMWE to WPI-stabilized emulsions on the changes in oil droplet size during the drying step of spray drying was investigated. No changes in ODSD after atomization and after spray drying were observed for emulsions stabilized with WPI. In the case of WPI/Lecithin, very small oil droplets remained stable after atomization and spray drying. The presence of lecithin seems to increase the stability of the interfacial film, making the oil droplets less prone to coalescence when forced in close contact during drying. These results go along with a lower interfacial tension and an increased elastic response of the interface with this system, as compared with protein alone. In contrast, emulsions with WPI/Citrem and WPI/MoDi presented an increase in oil droplet size during the drying step. A decrease in the elastic portion of the viscoelastic film by addition of these LMWE was observed. By this, the interfacial film of the oil droplets is less protected against coalescence when forced into close contact. Interestingly, significant differences in oil droplet coalescence and film viscoelasticity were observed between protein and mixed interfaces of protein with Citrem and MoDi, even when the interfacial tension was unchanged. By this, powders with significantly different characteristics, for example, clumping tendency, are obtained. The influence of the emulsifier system on the amount of free, non-encapsulated oil and on the storage stability of spray dried powders is currently being investigated. The results of this study are of high relevance to control the quality of whey/dairy-based food powder products. For an improved understanding of the effects, further studies are required in which a systematic approach is applied with LMWE of defined fatty acid and head group composition and so defined hydrophilic-lipophilic balance. Also, the effect of emulsifier concentrations should also be investigated.

ACKNOWLEDGMENTS

This IGF project of the FEI was supported via AiF within the programme for promoting the Industrial Collective Research (IGF) of the German Ministry of Economic Affairs and Energy (BMWI), based on a resolution of the German Parliament. Project 19312 N. The authors express their gratitude to Doll Chutani, Tammy Huberty, Pascal Hauns, and Andrea Butterbrodt for the experimental support in the atomization and spray drying experiments, and to Volker Zibat for the support with the SEM micrographs.

CONFLICT OF INTEREST

The authors have declared no conflicts of interest for this article.

AUTHOR CONTRIBUTIONS

Conceptualization; Investigation; Methodology; Writing-original draft: Martha L. Taboada. Investigation; Methodology; Writing-original draft: Monika Brückner-Gühmann. Funding acquisition; Supervision; Writing-review & editing: Theresia Helden-Hecht. Supervision; Writing-review & editing: Heike P. Karbstein. Funding acquisition; Supervision; Writing-review & editing: S. Drusch. Funding acquisition; Supervision; Writing-review & editing: Volker Gaukel.
DATA AVAILABILITY STATEMENT
Research data are not shared.

ORCID
Martha L. Taboada https://orcid.org/0000-0001-5011-2404

REFERENCES
Barbosa-Canovas, G. V., Ortega-Rivas, E., Juliano, P., & Yan, H. (2005). Food powders: Physical properties, processing, and functionality. Kluwer Academic/Plenum Publishers.

Bos, M. A., & van Vliet, T. (2001). Interfacial rheological properties of adsorbed protein layers and surfactants: A review. Advances in Colloid and Interface Science, 91(3), 437-471. https://doi.org/10.1016/S0001-8686(00)00077-4

Böttcher, S., Keppler, J. K., & Drusch, S. (2017). Mixtures of Quillaja sapo

Burgos-Díaz, C., Opazo-Navarrete, M., Soto-Añual, M., Leal-Calderón, F., & Bustamante, M. (2020). Food-grade pickering emulsion as a novel astaxanthin encapsulation system for making powder-based products: Evaluation of astaxanthin stability during processing, storage, and its bioaccessibility. Food Research International (Ottawa, Ont.), 134, 109244. https://doi.org/10.1016/j.foodres.2020.109244

Bylaite, E., Nylander, T., Venskutonis, R., & Jönsson, B. (2001). Emulsification of caraway essential oil in water by lecithin and β-lactoglobulin: Emulsion stability and properties of the formed oil-water interface. Colloids and Surfaces B: Biointerfaces, 20(4), 327-340. https://doi.org/10.1016/S0927-7765(00)00212-5

Chen, J., & Dickinson, E. (1995). Surface shear viscosity and protein-surfactant interactions in mixed protein films adsorbed at the oil-water interface. Food Hydrocolloids, 9(1), 35-42. https://doi.org/10.1016/0952-6671(95)00018-P

Dan, A., Gochev, G., Krägel, J., Aksenenko, E. V., Fainerman, V. B., & Miller, R. (2013). Interfacial rheology of mixed layers of food proteins and surfactants. Current Opinion in Colloid and Interface Science, 18, 302-310. https://doi.org/10.1016/j.cocis.2013.04.002

Danviriyakul, S., McClements, D. J., Decker, E., Nawar, W. W., & Chinchotti, P. (2002). Physical stability of spray-dried milk fat emulsion as affected by emulsifiers and processing conditions. Journal of Food Science, 67(6), 2183-2189. https://doi.org/10.1111/j.1656-2242.2002.tb09524.x

Drapala, K. P., Auty, M. E. A., Mulvihill, D. M., & O’Mahony, J. A. (2017). Influence of emulsifier type on the spray-drying properties of model infant formula emulsions. Food Hydrocolloids, 69, 56-66. https://doi.org/10.1016/j.foodhyd.2016.12.024

Drapala, K. P., Auty, M. E. A., Mulvihill, D. M., & O’Mahony, J. A. (2015). Influence of lecithin on the processing stability of model whey protein hydrolysate-based infant formula emulsions. International Journal of Dairy Technology, 68(3), 322-333. https://doi.org/10.1111/1471-0307.12256

Drusch, S., & Berg, S. (2008). Extractable oil in microcapsules prepared by spray-drying: Localization, determination and impact on oxidative stability. Food Chemistry, 109(1), 17-24. https://doi.org/10.1016/j.foodchem.2007.12.016

Duckworth, R. B. (1975). Water relations of foods. Food science and technology. Academic Press.

Fang, S., Zhao, X., Liu, Y., Liang, X., & Yang, Y. (2019). Fabricating multilayer emulsions by using OSA starch and chitosan suitable for spray drying: Application in the encapsulation of β-carotene. Food Hydrocolloids, 93(4), 102-110. https://doi.org/10.1016/j.foodhyd.2019.02.024

Foedinging, E. A., Luck, P., & Vardhanabhati, B. (2011). Milk protein products – Whey protein products. In J. W. Fuquay (Ed.), Encyclopedia of dairy sciences (2nd ed., pp. 873–878). Academic Press.

Gharsallou, A., Roudaut, G., Chambin, O., Voilley, A., & Saurel, R. (2007). Applications of spray-drying in microencapsulation of food ingredients: An overview. Food Research International, 40(9), 1107-1121. https://doi.org/10.1016/j.foodres.2007.07.004

Gharsallou, A., Saurel, R., Chambin, O., Cases, E., Voilley, A., & Cayot, P. (2010). Utilisation of pectin coating to enhance spray-drying stability of pea protein-stabilised oil-in-water emulsions. Food Chemistry, 122(2), 447–454. https://doi.org/10.1016/j.foodchem.2009.04.017

Haas, K., Obernberger, J., Zehetner, E., Kiesslich, A., Volkert, M., & Jaeger, H. (2019). Impact of powder particle structure on the oxidation stability and color of encapsulated crystalline and emulsified carotenoids in carrot concentrate powders. Journal of Food Engineering, 263, 398-408. https://doi.org/10.1016/j.jfoodeng.2019.07.025

Hernandez Sanchez, M. D. R., Cuvelier, M.-E., & Turchiuli, C. (2015). Design of liquid emulsions to structure spray dried particles. Journal of Food Engineering, 167(1), 99–105. https://doi.org/10.1016/j.jfoodeng.2015.07.036

Keppler, J. K., Heyse, A., Scheidler, E., Uttinger, M. J., Fitzner, L., Jandt, U., Heyn, T. R., Lautenbach, V., Loch, J. I., Lohr, J., Kieserling, H., Günther, G., Kempf, E., Grosch, J.-H., Lewinski, K., Jahn, D., Lübbert, C., Peukert, W., Kulozik, U., … Biedendieck, R. (2021). Towards re-combinantly produced milk proteins: Physicochemical and emulsifying properties of engineered whey protein beta-lactoglobulin variants. Food Hydrocolloids, 110, 106132. https://doi.org/10.1016/j.foodhyd.2020.106132.

Keppler, J. K., Sönöncichsen, F. D., Lorenzen, P.-C., & Schwarz, K. (2014). Differences in heat stability and ligand binding among β-lactoglobulin variantic variants A and B using 1H NMR and fluorescence quenching. Bioclima Et Biophysica Acta (BBA) – Proteins and Proteomics, 1844(6), 1083–1093. https://doi.org/10.1016/j.bbapap.2014.02.007

Kotsmar, C. S., Pradines, V., Alahverdjieva, V. S., Aksenenko, E. V., Fainerman, V. B., Kovalchuk, V. I., Krägel, J., Leser, M. E., Noskov, V. A., & Miller, R. (2009). Thermodynamics, adsorption kinetics and rheology of mixed protein – Surfactant interfacial layers. Advances in Colloid and Interface Science, 150, 41-54. https://doi.org/10.1016/j.cis.2009.05.002

Lam, R. S. H., & Nickerson, M. T. (2013). Food proteins: A review on their emulsifying properties using a structure-function approach. Food Chemistry, 141(2), 975–984. https://doi.org/10.1016/j.foodchem.2013.04.038

Lam, R. S. H., & Nickerson, M. T. (2015). The effect of pH and temperature pre-treatments on the structure, surface characteristics and emulsifying properties of alpha-lactalbumin. Food Chemistry, 173, 163-170. https://doi.org/10.1016/j.foodchem.2014.09.078

Lefebvre, A. H., & McDonell, V. G. (2017). Atomization and sprays (2nd ed.). CRC Press. https://doi.org/10.1201/9781351512091

Luccassen-Reyners, E. H. (1993). Interfacial viscoelasticity in emulsions and foams. Food Structure, 12(1), 1–12.

Matsumiya, K., Takahashi, Y., Nakanishi, K., Dotsu, N., & Matsumura, Y. (2014). Diglycerol esters of fatty acids promote severe coalescence between protein-stabilized oil droplets by emulsifier–protein competitive interactions. Food Hydrocolloids, 42, 397–402. https://doi.org/10.1016/j.foodhyd.2014.03.002

McClements, D. J., & Li, Y. (2010). Structured emulsion-based delivery systems: Controlling the digestion and release of lipophilic food components. Advances in Colloid and Interface Science, 159(2), 213–228. https://doi.org/10.1016/j.cis.2010.06.010

Murray, B. S., & Dickinson, E. (1996). Interfacial rheology and the dynamic properties of adsorbed films of food proteins and surfactants. FSTI (Food Science and Technology International), 2(3), 131-145. https://doi.org/10.3136/fsti.959619798.2.131
Neumann, S. M., van der Schaaf, U. S., & Karbstein, H. P. (2018). Investigations on the relationship between interfacial and single droplet experiments to describe instability mechanisms in double emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 553, 464–471. https://doi.org/10.1016/j.colsurfa.2018.05.087

Nijdam, J. J., & Langrish, T. A. G. (2006). The effect of surface composition on the functional properties of milk powders. *Journal of Food Engineering*, 77(4), 919–925. https://doi.org/10.1016/j.jfoodeng.2005.08.020

Petrovic, L. B., Sovilj, V. J., Katona, J. M., & Milanovic, J. L. (2010). Influence of polymer-surfactant interactions on o/w emulsion properties and microcapsule formation. *Journal of Colloid and Interface Science*, 342(2), 333–339. https://doi.org/10.1016/j.jcis.2009.10.077

Prasad Reddy, M. N., Padma Ishwarya, S., & Anandharamakrishnan, C. (2019). Nanoencapsulation of roasted coffee bean oil in whey protein wall system through nanospray drying. *Journal of Food Processing and Preservation*, 43(3), e13893. https://doi.org/10.1111/jfpp.13893

Ramakrishnan, S., Ferrando, M., Aceña-Muñoz, L., Mestres, M., de Lamo-Castellví, S., & Güell, C. (2013). Influence of emulsification technique and wall composition on physicochemical properties and oxidative stability of fish oil microcapsules produced by spray drying. *Food and Bioprocess Technology*, 6(8), 1561. https://doi.org/10.1007/s11947-013-1187-4

Sanchez-Reinoso, Z., & Gutiérrez, L.-F. (2017). Effects of the emulsion composition on the physical properties and oxidative stability of Sacha Inchi (*Plukenetia volubilis*) oil microcapsules produced by spray drying. *Food and Bioprocess Technology*, 10(7), 1354–1366. https://doi.org/10.1007/s11947-017-1906-3

Serfert, Y., Schröder, J., Mescher, A., Laackmann, J., Rätzke, K., Shaikh, M. Q., Gaukel, V., Moritz, H.-U., Schuchmann, H. P., Walzel, P., Drusch, S., & Schwarz, K. (2013). Spray drying behaviour and functionality of emulsions with β-lactoglobulin/pectin interfacial complexes. *Food Hydrocolloids*, 31(2), 438–445. https://doi.org/10.1016/j.foodhyd.2012.11.037

Taboada, M. L., Leister, N., Karbstein, H. P., & Gaukel, V. (2020). Influence of the emulsifier system on breakup and coalescence of oil droplets during atomization of oil-in-water emulsions. *ChemEngineering*, 4(3), 47. https://doi.org/10.3390/chemengineering4030047

Tamm, F., Sauer, G., Scampicchio, M., & Drusch, S. (2012). Pendant drop tensiometry for the evaluation of the foaming properties of milk-derived proteins. *Food Hydrocolloids*, 27(2), 371–377. https://doi.org/10.1016/j.foodhyd.2011.10.013

Taneja, A., Ye, A., Jones, J. R., Archer, R., & Singh, H. (2013). Behaviour of oil droplets during spray drying of milk-protein-stabilised oil-in-water emulsions. *International Dairy Journal*, 28(1), 15–23. https://doi.org/10.1016/j.idairyj.2012.08.004

Wang, S., Shi, Y., Tu, Z., Zhang, L., Wang, H., Tian, M., & Zhang, N. (2017). Influence of soy lecithin concentration on the physical properties of whey protein isolate-stabilized emulsion and microcapsule formation. *Journal of Food Engineering*, 207, 73–80. https://doi.org/10.1016/j.jfoodeng.2017.03.020

Whitehurst, R. J. (Ed.) (2004). *Emulsifiers in food technology*. Blackwell Publishing.

Wilde, P., Mackie, A., Husband, F., Gunning, P., & Morris, V. (2004). Proteins and emulsifiers at liquid interfaces. *Advances in Colloid and Interface Science*, 108–109, 63–71. https://doi.org/10.1016/j.cis.2003.10.011

---

**How to cite this article:** Taboada, M. L., Heiden-Hecht, T., Brückner-Gühmann, M., Karbstein, H. P., Drusch, S., & Gaukel, V. (2021). Spray drying of emulsions: Influence of the emulsifier system on changes in oil droplet size during the drying step. *Journal of Food Processing and Preservation*, 00, e15753. https://doi.org/10.1111/jfpp.15753