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Spray drying of emulsions: Influence of the emulsifier system on changes in oil droplet size during the drying step

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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 $d_{90,0}$ 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.

1 | 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 (Gharsallaoui et al., 2007). Typical formulations include the oily phase to be encapsulated, a protein source (e.g., whey protein)

Abbreviations: β-LG, β-Lactoglobulin; $d_{90,0}$, 90%-value of number based distribution of droplet size; LMWE, low molecular weight emulsifier; MCT, medium-chain triglycerides; MoDi, mono- and diglycerides; ODSD, oil droplet size distribution; PSD, particle size distribution; SDSD, spray droplet size distribution; *SEM*, scanning electron microscopy; WPI, whey protein isolate.

acting as emulsifier (Prasad Reddy et al., 2019; Ramakrishnan et al., 2013), as well as a carbohydrate source (e.g., starch conversion product) acting as matrix material (Fang et al., 2019; Sanchez-Reinoso & Gutiérrez, 2017) after drying. Lipid-based, low molecular weight emulsifiers (LMWE) are also commonly added to formulations, as they are expected to improve the stability of emulsions during processing and storage by improving the characteristics of the adsorption layer around the oil droplets (Petrovic et al., 2010; Wang et al., 2017). LMWE commonly added to protein-based formulations include lecithins, mono- and diglycerides (MoDi), and esters of fatty acids (e.g., citrem; Danviriyakul et al., 2002; Drapala et al., 2017).

In the first step of a spray drying process, oil-in-water emulsions are atomized into fine droplets with a nozzle. In the subsequent drying step, the spray droplets are dried to powder upon contact with hot air (Barbosa-Cánovas et al., 2005; Hernandez Sanchez et al., 2015). The oil droplet size distribution (ODSD) in the powder influences the stability of the powder upon storage, as well as the functional properties of the reconstituted emulsion (Haas et al., 2019; McClements & Li, 2010), and is therefore an important quality parameter. In industrial processes, an emulsification step is applied prior to the spray drying process to adjust the ODSD to the desired product-specific value. However, previous studies have shown that changes in ODSD may take place during the spray drying process (Gharsallaoui et al., 2010; Serfert et al., 2013; Taneja et al., 2013). The addition of LMWE to protein based emulsifiers can greatly influence the extent of these changes. For example, (Drapala et al., 2017) observed a significant increase in the oil droplet size after spray drying of emulsions when combining whey protein hydrolysate (WPH) with a citrem or a lecithin, as compared to emulsions stabilized with WPH alone.

In the named studies, the changes in ODSD were investigated by comparing the ODSD before the complete spray drying process with the ODSD after the complete spray drying process and powder reconstitution. No study has been found in which the phenomena occurring during each step of the spray drying process, namely the atomization of the liquid followed by the drying of the spray droplets were studied separately. In our preceding study, the changes in ODSD occurring during the atomization step in dependence of the emulsifier system were investigated (Taboada et al., 2020). We focused on the effects of adding lipid-based LMWE (lecithin, citrem, MoDi) to whey protein stabilized emulsions. The results showed that oil droplet breakup takes place during the atomization step, almost independently of the emulsifier system. Immediately after breakup in the nozzle, coalescence of the newly created oil droplets may take place. These phenomena are largely influenced by the emulsifier system (Taboada et al., 2020). In the preceding study, the changes in oil droplet size during the drying step remained unaccounted for. But, during the drying step of spray drying, the oil droplets are forced close to each other due to water evaporation and volume reduction. Therefore, it is likely that coalescence of the oil droplets is further promoted. Coalescence during the drying step would lead to further changes in oil droplet size.

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,

Brabrand, Denmark) and mono- and diglycerides (Lamemul K 2000 K, BASF Personal Care and Nutrition GmbH, Monheim, Germany) were used as lipid-based LMWE. The citrem is a partially neutralized citric acid ester of mono-diglyceride with almost fully hydrogenated palm-based oil fatty acids. The mono- and diglyceride has fully hydrogenated fatty acids with head groups of 96% monoglyceride. The lecithin consists of a mixture of headgroups with decreasing percentage: phosphatidylcholine, phosphatidylinositol, phosphatic acid, and phosphatidylserine. As matrix material maltodextrin (C × DryTM MD 01910, Cargill, Haubordin, France) was chosen.

Emulsions were prepared following the procedure described in (Taboada et al., 2020). Briefly, emulsion premixes (50 wt.% oil) consisting of an aqueous WPI solution and MCT oil with LMWE (lecithin or citrem or MoDi) were prepared and homogenized in a colloid mill (IKA magic LAB, IKA-Werke GmbH & Co. KG, Staufen, Germany) operated at a gap width of 0.16 mm and a circumferential speed of 26 m/s. The emulsion premixes were then mixed with the continuous phase, namely a solution of maltodextrin in water, to obtain the emulsions for atomization and spray drying experiments. This procedure was performed to produce a large volume of emulsion with the exact oil droplet size ensuring constant start conditions for all experiments. The oil content in the final emulsions was 15 wt.% and the ratio of MCT oil to WPI and LMWE was 1:0.1:0.01. These concentration ratios are in the range for spray drying applications of emulsions (Drapala et al., 2015). The concentration of maltodextrin in the final emulsion was 24.8 wt.%. The reported mass fractions refer to the total emulsion. As comparison, emulsions without added lipid-based LMWEs were also prepared.

The oil droplet size of the emulsions was measured via laser diffraction (HORIBA LA950, Retsch Technology GmbH, Haan, Germany). The data were analyzed by the Mie theory with a standard optical model for MCT oil in water. The $d_{90,0}$ (90%-value of number based distribution) was chosen as characteristic value to analyze differences in oil droplet sizes. Viscosities of the emulsions were measured at 20°C by rotational rheometry (Physica MCR 101, Anton Paar, Graz, Austria) using a double gap geometry (DG26.7). A logarithmic shear rate-controlled ramp was performed between 1 and 1,000 s^{-1}. Emulsions were stored overnight (12 hr) before atomization or spray drying. Preliminary investigations showed that the oil droplet size remains constant for all emulsions during this time span.

2.2 | Atomization of emulsions

To determine the oil droplet size after atomization, experiments were performed in a pilot-scale spray test rig. A detailed description of the setup is provided elsewhere (Taboada et al., 2020). Briefly, a high pressure three-piston pump (Rannie LAB Typ 8.5, SPX FLOW Inc., Charlotte, USA) was used to supply the emulsions to a pressure swirl atomizer of the type SKHN-MFP SprayDry (core size 16, orifice diameter 0.34 mm, Spraying Systems Deutschland GmbH, Hamburg, Germany). 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 $p < .05$ using the software OriginPro 2018 (OriginLab Corporation, Northampton, USA). Scheffè'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. 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 mm^3 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 $d_{90,0}$ of the feed emulsions prior to atomization and spray drying are summarized in Table 1. Emulsions prepared only with WPI presented a slightly higher $d_{90,0}$ compared to emulsions prepared with WPI/LMWE, although the differences among WPI, WPI/Citrem, and WPI/MoDi are not significant. The lowest $d_{90,0}$ 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

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 system			
	WPI	**WPI/Lecithin**	**WPI/Citrem**	**WPI/MoDi**
Feed emulsion				
$d_{90,0}$ (μm)	3.99 ± 0.29^a	2.49 ± 0.10^b	3.34 ± 0.13^a	3.50 ± 0.37^a
Viscosity at 1,000 s^{-1} (mPa·s)	33.1 ± 0.5^a	32.3 ± 1.9^a	31.0 ± 0.3^a	31.56 ± 1.4^a
Powders				
Moisture content (%)	2.81 ± 0.52^a	2.69 ± 0.1^a	2.15 ± 0.49^a	2.46 ± 0.44^a
Water activity (–)	0.23 ± 0.01^a	0.21 ± 0.03^a	0.20 ± 0.04^a	0.23 ± 0.05^a

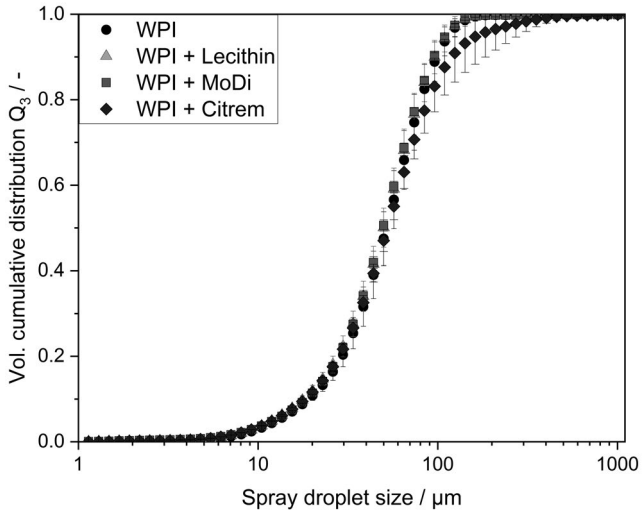

FIGURE 1 Droplet size distributions of spray droplets measured during atomization experiments with emulsions stabilized with whey protein isolate and WPI/LMWE

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.

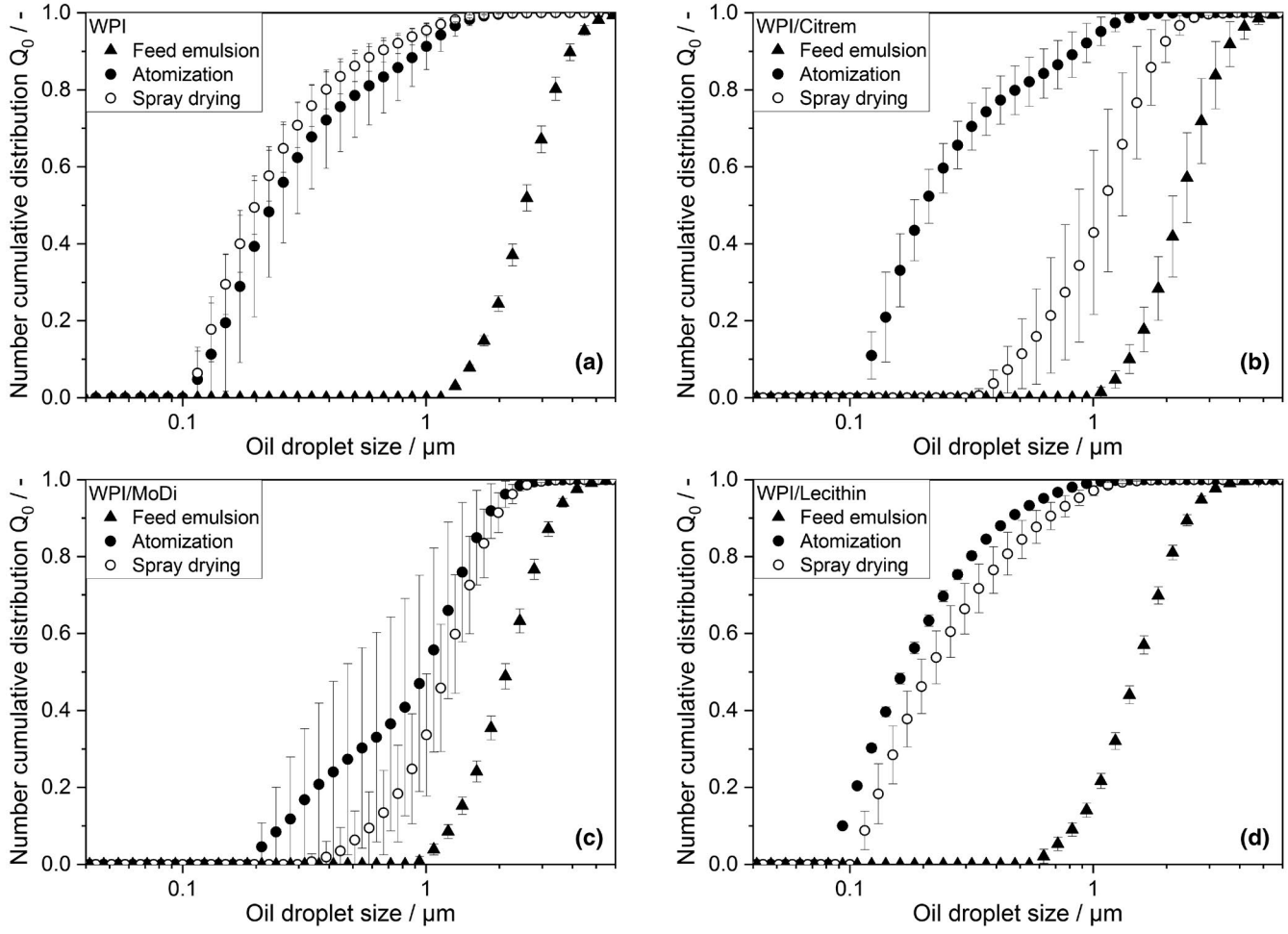

FIGURE 2 Number cumulative distributions of oil droplet size of emulsions stabilized with whey protein isolate and WPI/LMWE after atomization and spray drying. (a) whey protein isolate (b) WPI/Citrem (c) WPI/MoDi (d) WPI/Lecithin

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 ± 0.28^{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}

3.3 | Interfacial tension and dilatational rheology influenced by LMWE

With the knowledge of interfacial tension and phase angle of dilatational rheology, we aim to explain the interfacial mechanisms which are affecting the oil drop size during the drying step of spray drying. The measured values of interfacial tension and phase angle for systems with β-LG and β-LG/LMWE are summarized in Table 3. The dominating proteins in WPI are β-LG and α-lactalbumin (Foegeding et al., 2011). The interfacial tension of β-LG was 15.3 ± 0.2 mN/m whereby a similar value was reported earlier for the same interfacial system (Keppler et al., 2021). The interfacial tension of 0.1% α-lactalbumin at pH 7 against oil was reported to be 15 mN/m as well

	β-LG	β-LG/Lecithin	β-LG/Citrem	β-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

TABLE 3 Interfacial tension and phase angle of 0.1 % β-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

(Lam & Nickerson, 2015). 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 ± 0.7° 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 ± 0.5° (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 (Bylaite 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

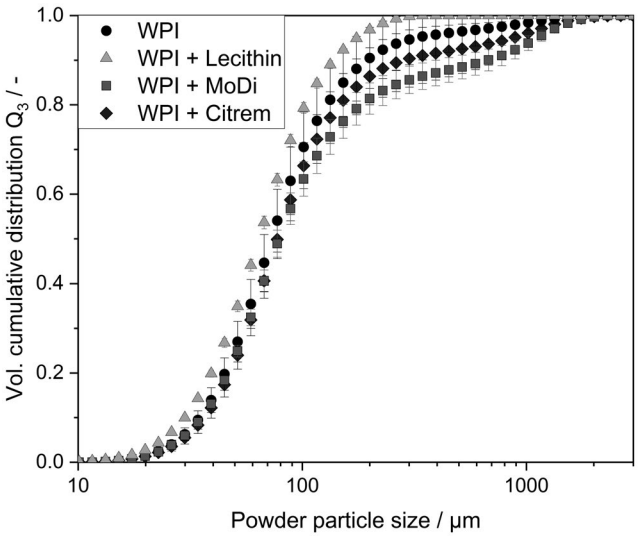

FIGURE 3 Particle size distributions of spray dried powders from emulsions stabilized with whey protein isolate and WPI/LMWE

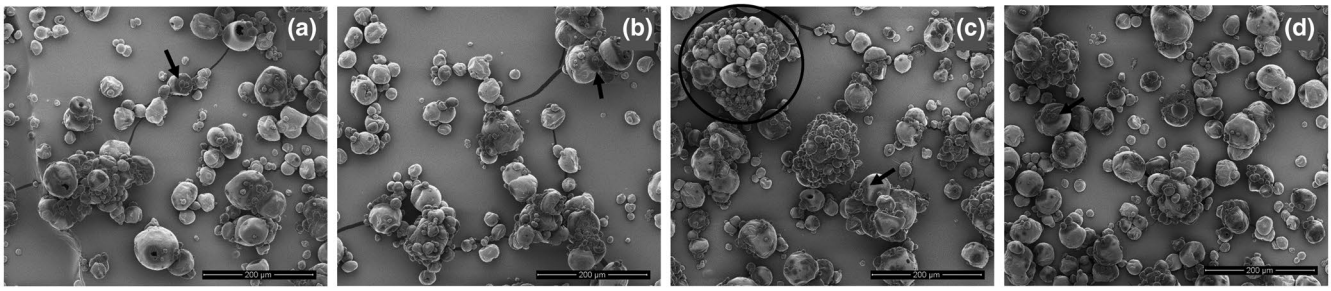

FIGURE 4 Scanning electron microscopy micrographs of spray dried emulsions stabilized with (a) whey protein isolate, (b) WPI/Lecithin, (c) WPI/MoDi, (d) WPI/Citrem. Magnification 500×

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.

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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*: Theresia Heiden-Hecht. *Supervision; Writing-review & editing*: Monika Brückner-Gühmann. *Funding acquisition; 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.

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