Prilling process: an alternative for atomization and producing solid particles of emulsions

B.N. Dubey[*], M.R. Duxenneuner and E.J. Windhab
Laboratory of Food Process Engineering, Institute of Food, Nutrition and Health,
ETH Zürich, Switzerland.

Abstract

Emulsions are extensively used in food, flavor, cosmetic, pharmaceutical, and coating industries. Double emulsions have the ability to carry both polar and non-polar components due to their compartmentalized internal structure. Atomization of emulsions is a process method of interest for encapsulation of flavors, nutrients, or colors, applied in industrial scale. Present studies show the ability of different nozzle geometries to keep the microstructure of simple and multiple emulsions unchanged. The microstructure change of simple and multiple emulsions during spraying process (without chilling) were investigated for different air to liquid pressure ratios (A/L). The experimental results show that the droplet size decreases with increasing air pressure (maximum air pressure 4 bar) at constant liquid flow rate of 0.2 L/min. Viscosity and loss modulus of the emulsion increases with decreasing droplet size of the emulsion. In order to produce solid particles from emulsion, prilling process (spraying and chilling) was carried out for both emulsion system in a spraying tower having average temperature about -30 °C. The microstructure of the solid particles was investigated by cryo-scanning electron microscopy (Cryo-SEM). It shows that the structure differs from the initial emulsions (liquid), but it keeps some order of the core structure (encapsulation).

Introduction

Emulsions consist of a dispersed droplet in an immiscible liquid continuous phase. The dispersed phase can be either droplets of a single liquid (in the case of simple emulsion), or an emulsion (in the case of a double or multiple emulsion) [1]. Emulsions are often used in food, flavor, cosmetic, pharmaceutical, and coating industries. The wide usage reflects that emulsions can have either hydrophilic or lipophilic cores giving an opportunity to enclose both polar and non-polar components. Therefore, double emulsions offer advantages over simple emulsions for encapsulation, as they have the capacity to hold both polar and non-polar components, and to protect them from environmental impact [2]. Correspondingly, it enhances the control-release property of desired components in an appropriate environment. Several processes [3] can be used for the encapsulation such as spray drying, fluid bed drying, spray cooling, extrusion, coacervation, and molecular inclusion etc. However, atomization of emulsions in a controlled manner is a growing research field for food engineers, where encapsulation of food ingredients on the industrial scale is required.

The goal of the present study is the production of well-defined microstructured solid particles of simple and multiple emulsions through prilling process (spray and chilling). The produced solid particle should have well-defined microstructures or inner cores that can be filled with functional food components (such as nutrients or flavors). Towards to the target, the study discuss here will be mainly a demonstration of the influences of spray process parameters on the microstructure of the simple and double emulsions, and try to illustrate the method to keep the internal structure of the emulsion unchanged. On these studies, characteristics of the initial emulsions are an important to some extent for investigating the spray characteristics. However, the methods are already well known to produce emulsions of defined microstructure [4-12]. However, very few researchers investigated the break up of emulsions during spraying [13-15] and produced well-defined microstructured solid particles of emulsions. Present studies mainly dealing with common emulsions produced by rotor-stator or membrane emulsification rather than focusing to produce well-defined emulsions. Therefore, the studies are mainly concentrated on the effect of spraying rather than looking on different emulsification process to produce mono-disperse droplets.

---

* Corresponding author: Schmelzbergstrasse 9, LFO E21, 8092 Zurich, E-mail: bdubey@ilw.agrl.ethz.ch
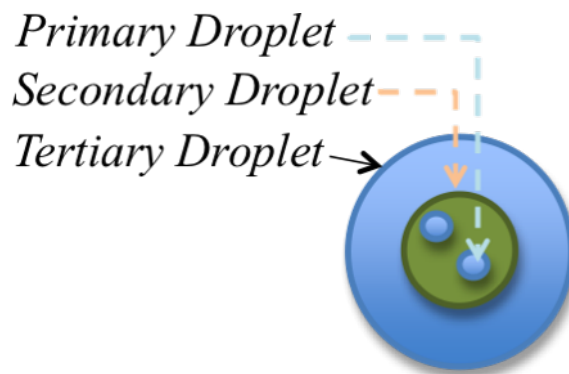
Figure 1. A spray droplet of a double emulsion with
having inner droplets (structure kept)

Present studies show the change of primary, secondary droplets of emulsions (Figure 1) during spraying with different spray nozzles (internal/external mixing nozzles) at different operating conditions. The microstructure change of simple and multiple emulsions during spraying process (without chilling) were investigated for different air to liquid (A/L) ratios. Later, the spraying of emulsion was also studied with chilling (so called prilling). The internal microstructure of produced solid particle was investigated by the cryo-SEM to compare with the initial sprayed emulsion. Further studies will be carried out to investigate the encapsulation capacity through prilling process.

Materials and Methods

Two different model emulsions as simple emulsion (O/W and W/O) were prepared, where continuous phase was sunflower oil (Florin AG.) containing 2%wt Span 20 (Fluka, Switzerland) as emulsifier and 5%wt PGPR (Polyglycerol polyricinoleate, DANISCO, Denmark) as stabilizer as well as emulsifier. On the other hand, the continuous phase, water, was containing 2%wt Tween 20 (Fluka, Switzerland) as emulsifier and 10%wt of PEG (Polyethylene Glycol; Clariant, Switzerland) as stabilizer. A rotor-stator device (Polytron PT6000, Kinematica AG.) was used to produce simple emulsion. The mean size of the droplets strongly depends on the power applied. Similarly, double emulsions (O/W/O and W/O/W) were prepared by a two-step method using the same emulsifier and stabilizer with different concentration so that the weighted HLB (hydrophilic-lipophilic balance) value is higher than 10 for W/O/W and lower than 8 for O/W/O [16].

At first, simple emulsions were produced by the rotor-stator device, where the size of the droplets was maintained as small as possible (mean size about 1 µm). In the second step, the double emulsions were produced by rotating membrane emulsification (ROME, Kinematica AG.). Double emulsions contain the simple emulsions (as prepared in the first step) as disperse phase and droplet size of the double emulsions mainly depends on the rotational speed of membrane at constant flow rates of continuous and disperse phase. Simple emulsions contain commonly 20%wt or 40%wt of dispersed phase of oil-in-water (O/W) and water-in-oil (W/O) emulsion and double emulsions (O/W/O and W/O/W) contain 30%wt dispersed phase, which contains 30%wt or 40%wt inner emulsion droplets (of O/W or W/O emulsion respectively).
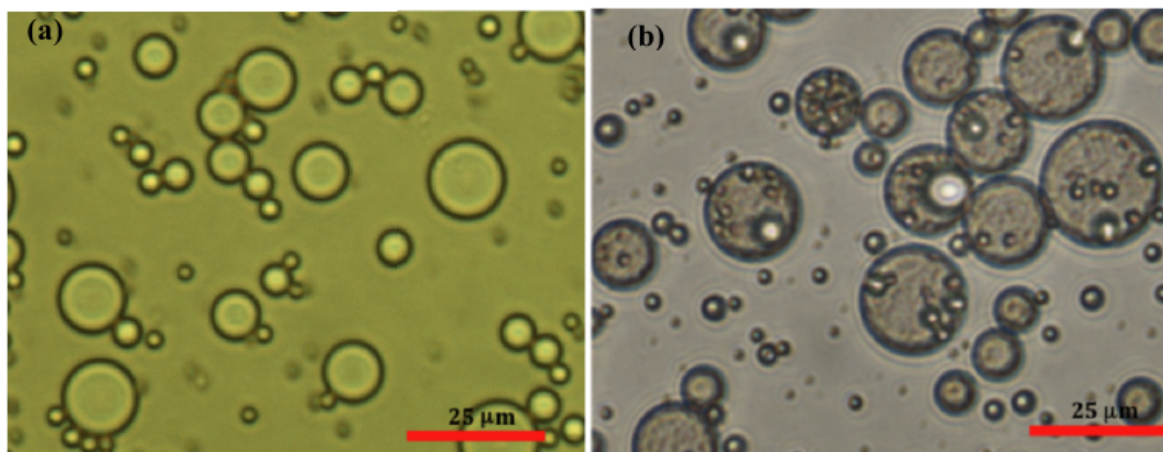

Figure 2. Inverse light microscopy pictures of (a) simple emulsion (W/O) and (b) double emulsion (W/O/W)

To study the characteristics of the emulsion system, emulsion breakup during spraying and the microstructure of solid particles (product from emulsions after prilling), several analytical techniques were applied. The characterization of emulsions consists of the size and size distribution of emulsion droplets, rheological characteristics of emulsion and microstructure of emulsion droplets. The direct and qualitative observation of the simple and double emulsions (before and after spraying) was done by the inverse light microscopy (max. mag. 60×; Nikon AG.). Typical light microscopic pictures of simple and double emulsions (before spraying) are shown in Figure 2. The droplet size and size distribution of the emulsions (before and after spraying of emulsion) were studied by the Laser Diffraction Particle Size Analyzer, LDPSA (LS 13320, Beckman Coulter, Inc.) applying the Fraunhofer model. The sizes of the double emulsions droplets (secondary droplet only) were estimated by LDPSA, while the sizes of the inner droplets (primary droplet) were measured separately in simple emulsions. Since the membrane emulsification is a gentle way for emulsion preparation [6], it was assumed that the droplet size of inner simple emulsion is not influenced during preparation of double emulsion.

The shear rate dependent viscosity of the simple and double emulsions (before and after spraying, without chilling) was measured using Physica MCR 300 (Couette geometry, measuring gap 1.13 mm) rheometer. The identical geometry was also used to measure dynamic moduli (storage and loss modulus) of the same emulsion systems by applying a deformation rate of 2 %. The Cryo-SEM (SEM Gemini 1530, Electron Microscopy ETH Zurich) was used for analyzing the internal microstructure of the solid particles (of simple and double emulsions) produced by prilling process. Analysis of the size and size distribution of solid particles of emulsions from prilling process were performed by sieving (equivalent mean sieve diameter of 40 to 2000 μm) method.

The internal diameter and height of the tower used for the prilling process was 1 m and about 4.5 m respectively [16]. On the other hand, an additional small spraying tower (length of square arm is 0.7 m, and height is 2 m) was constructed to observe the spraying (without chilling) of emulsion and monitoring the filament breakup of emulsions during spraying using a high-speed camera. Three different types of full cone nozzle geometries (Table 1) were used for the experimental investigations as shown in Figure 3.
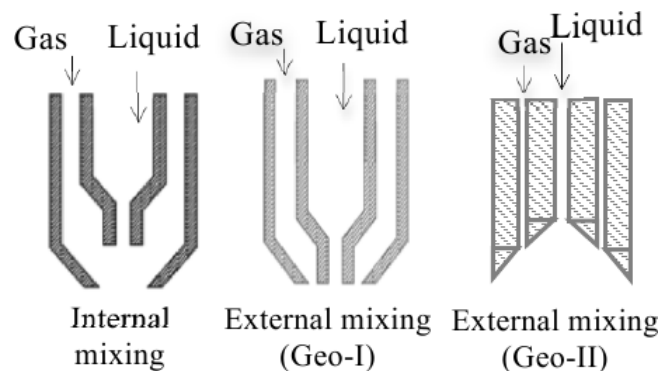
**Figure 3.** Sketches of different nozzle geometries

Table 1. Three different types of nozzle geometries and their specifications

| Nozzle Types	Specifications
Internal mixing	Internal diameter (mm): 0.5, 0.7 Serial: 1/4J-SS+SU12-SS-2850, Spraying Systems AG.
External mixing (Geo-I)	Internal diameter (mm): 0.5, 0.7 Serial: 1/4J-SS+SU2-SS-2850, Spraying Systems AG.
External mixing (Geo-II)	Internal diameter (mm): 0.9, 1.0 Serial: 150.150.005, Lechler GmbH

Results and Discussion

First series of experiments were carried out to investigate the influence of air pressure on primary and secondary droplets of emulsions (simple and double respectively) during atomization (without chilling) by different nozzle geometries (external and internal mixing). Emulsions were sprayed in the small tower (see materials and methods section) to make the experiments easier and to observe the influence of nozzle geometries (internal/external mixing) on microstructure of emulsions. The effect of air to liquid flow rate ratio (or/and air to liquid pressure ratio) was also studied employing these nozzles. The microstructure of the initial emulsion was well defined by measuring droplet size distribution (the mean droplet size of initial emulsion is marked in graphs at zero $P_{air}/$

P_{liq} or GLR), microscopic pictures as well as rheological measurements that can be easily compared with sprayed emulsions. In general, a higher-pressure ratio corresponds to smaller droplet of the sprayed emulsions as shown in Figure 4, 7 & 8.
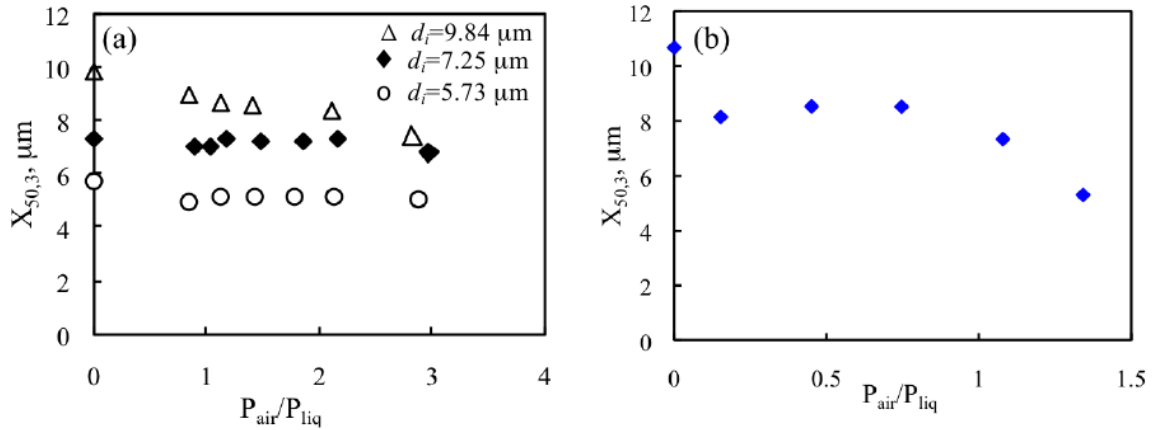
Figure 4. Influences of A/L pressure ratios on emulsion (40% O/W) droplet size for (a) the external mixing nozzle (geo-II), and (b) the internal mixing nozzle are shown

Figure 4a shows that when the droplet size (d_i) of emulsion (before spraying) is smaller (about ≤ 7 μm), then the droplet size of the emulsion is not much influenced by the A/L pressure ratio (maximum relative air pressure 4 bar) in the case of external mixing nozzle (geo-II). However, droplet size of the emulsions cannot be decreased further, because of insufficient stress applied. Indeed, the equilibrium mean droplet size of emulsion was smaller during production of the emulsion by rotor stator than the applied spraying stress. However, bigger initial droplet sizes (≈ 10 μm) of the emulsions were gradually decreased with increasing the A/L pressure ratio. On the other hand, the droplet size of the emulsion became much smaller by the internal mixing nozzle than the external mixing nozzle (geo-II) with increasing the A/L pressure ratio (Figure 4b). For both nozzle geometries, the droplet size distribution was moving to the smaller droplet sizes for the higher A/L pressure ratio as shown in
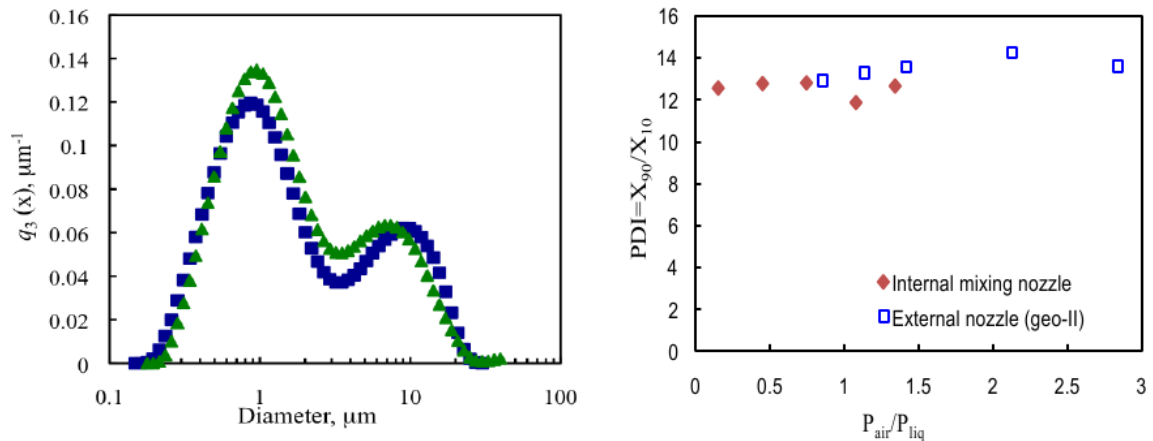

Figure 5. Influences of A/L pressure ratio on (a) emulsion (40% O/W) droplet size distribution (mean droplet size of the initial emulsion was about 9.84 μm) for external mixing nozzle (geo-II), and (b) PDI for external mixing nozzle (mean droplet size of the initial emulsion was about 9.84 μm) as well as internal mixing nozzle (mean droplet size of the initial emulsion was about 10.68 μm).

Figure 5a. In Figure 5a, only results for the external mixing nozzle (geo-II) are shown, even though the similar effect was also observed strongly for the internal mixing nozzle. However, the polydispersity index (PDI) was almost unchanged by the A/L pressure ratio for the both nozzle geometries (Figure 5b). Though the size distribution and polydispersity of emulsion droplets give sufficient information, we also measured the viscosity and loss modulus to observe the influences of A/L ratio on rheological behavior of emulsions. It was found that the viscosity of the emulsion was increased with decreasing droplet size (due to higher A/L pressure ratio) of the emulsion (Figure 6). The loss modulus of emulsions was also slightly increased with increasing A/L pressure ratio.

4

To start with, the simple emulsions were sprayed to investigate and for better understand of spraying of emulsion applying different nozzle geometries and operating conditions. Double emulsions are rather complex and therefore need thorough studies to implement the idea to prilling process.
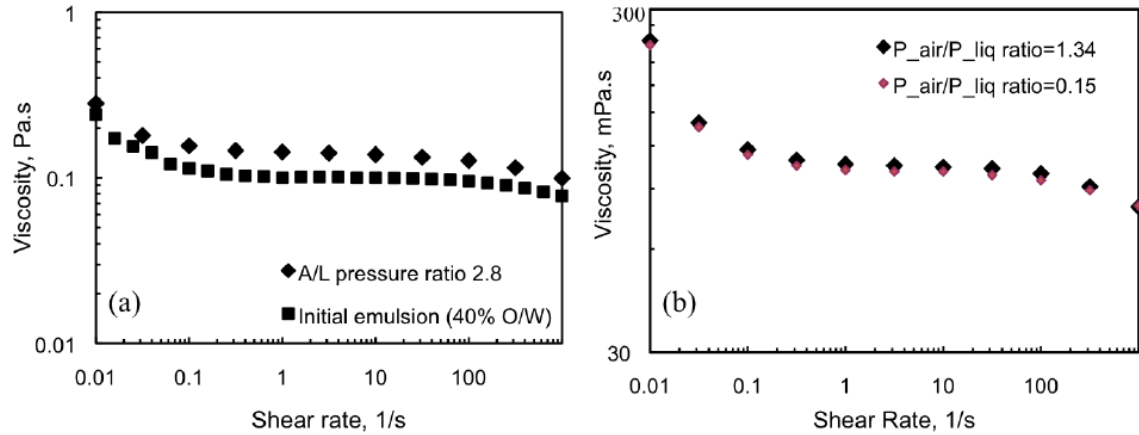
Figure 6. Influence of A/L pressure ratio on the viscosity of emulsion (40% O/W) using (a) an external mixing nozzle (geo-I) and (b) an internal mixing nozzle.
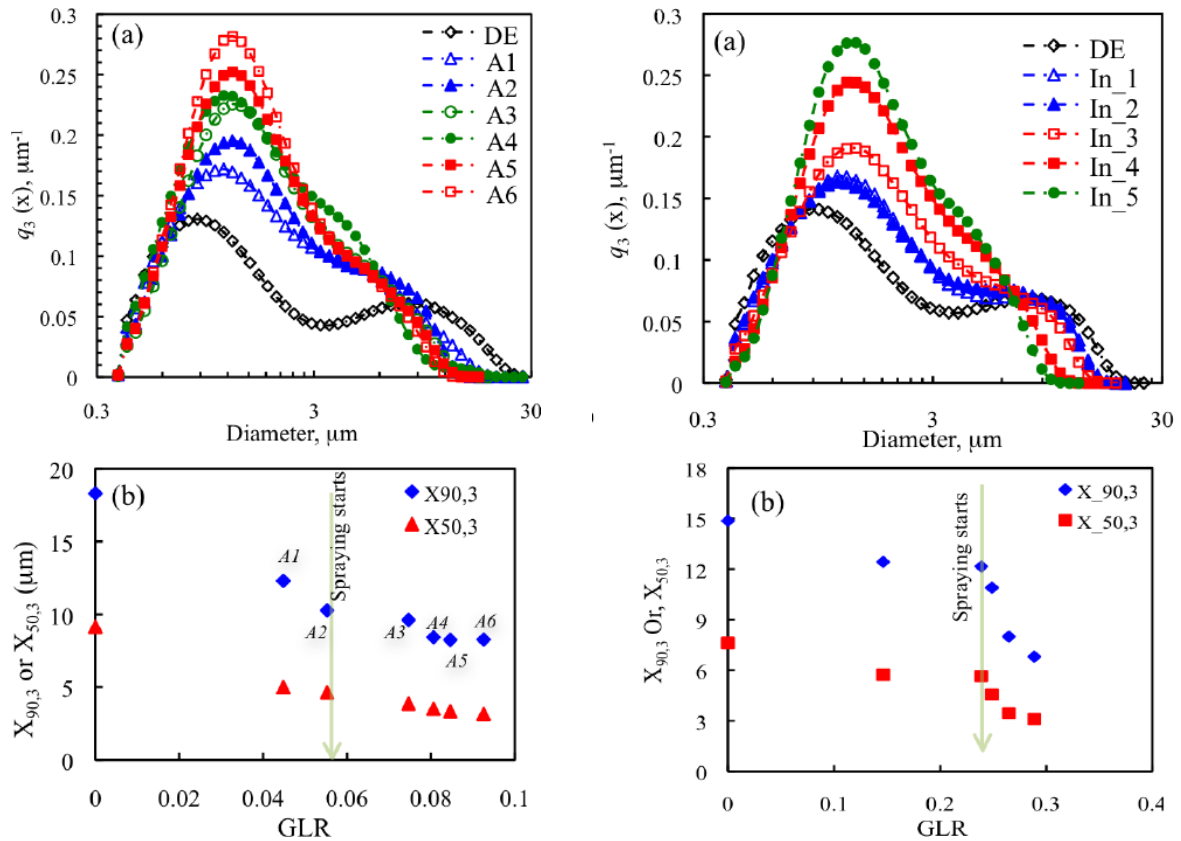

Figure 7. Spraying of double emulsion 30% (30% W/O)/W using an external mixing nozzle, (a) Size distribution of double emulsion (DE), and six different samples (A1 to A6) of double emulsion produced by spraying with different GLR values; (b) $X_{50,3}$ and $X_{90,3}$ changes with GLR
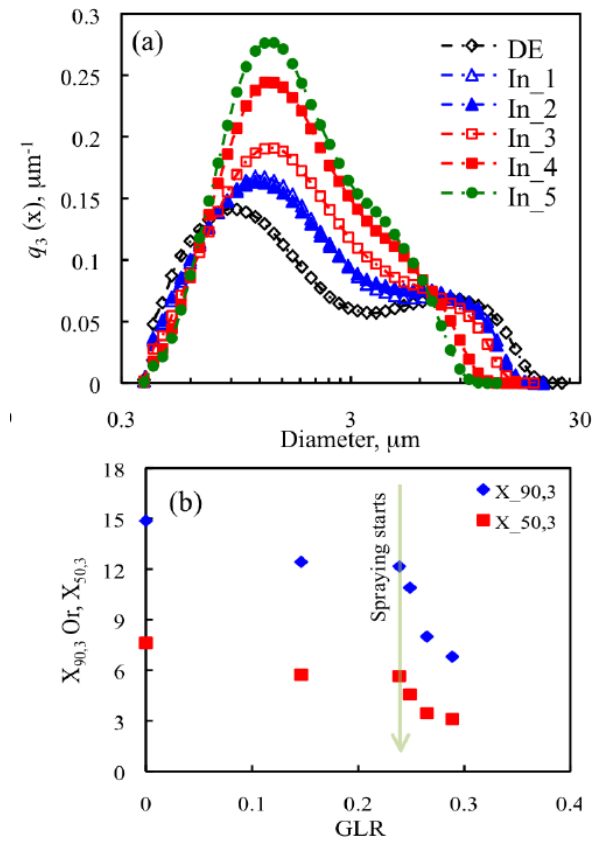
Figure 8. Spraying of double emulsion 30% (30% W/O)/W using an internal mixing nozzle, (a) Size distribution of double emulsion (DE), and five different samples (In_1 to In_5) of double emulsion produced by spraying with different GLR values; (b) $X_{50,3}$ and $X_{90,3}$ is a function of GLR

Similar to the experiments with simple emulsion (SE), double emulsions (DE) were also sprayed using two different nozzles (internal and external mixing nozzle) without chilling. Two different model systems of DE (W/O/W and O/W/O) were studied, but for both emulsion systems similar results were found. Here only the experimental results for 30%(30%W/O)/W emulsion are described. The influence of 'gas to liquid mass ratio' (GLR)

on size distribution of emulsion droplet was investigated. The size distribution of emulsion droplets (secondary droplets) was observed to be left shifted over increasing GLR value for both geometries with nozzle diameter 0.5 mm (Figure 7a and 8a). At higher GLR, the applied stress is high enough to break up the outer shell (secondary droplet) of the double emulsion leading to a left shift in the plot of the size distribution. However, using an external mixing nozzle, the emulsion droplet mean size, $X_{50,3}$ and $X_{90,3}$ were decreased gradually over increasing GLR (Figure 7b). On the other hand, mean size of the emulsion droplets $X_{50,3}$, and $X_{90,3}$ was decreasing fast above the critical GLR value (a critical GLR value is defined by eye observation, when the spraying is going to start) for the internal mixing nozzle (Figure 8b). In Figure 7b and Figure 8b, critical GLR value for starting the spraying were shown for both geometries. We observed that the internal mixing nozzle requires much higher GLR value (about 0.25) to initiate the spray of emulsion compared to external mixing nozzle (GLR ≈ 0.055). On the other hand, internal mixing nozzle produced narrower secondary droplets compared to external mixing nozzle at the higher-pressure region (Figure 9a).
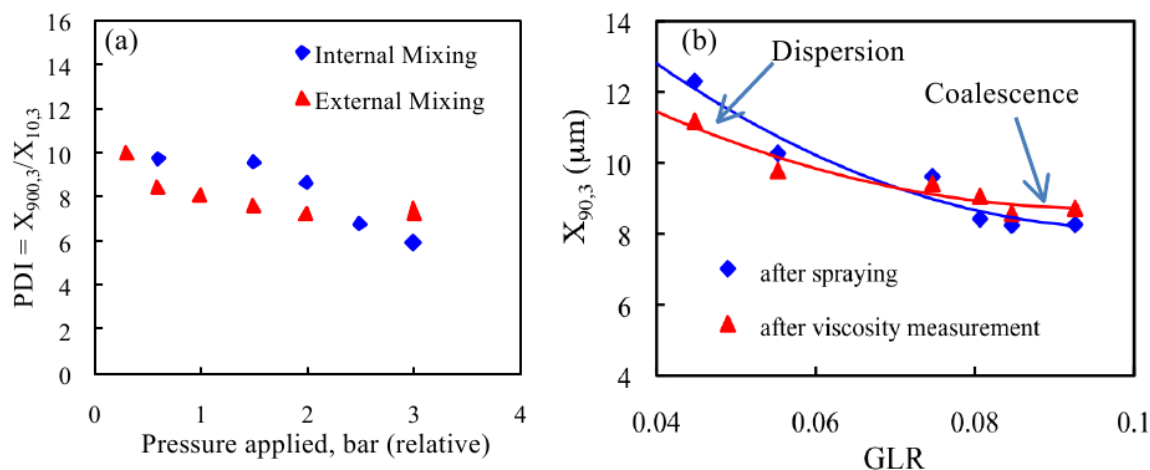

Figure 9. (a) PDI as a function of air pressure for internal and external mixing (geo-I), (b) The change in $X_{90,3}$ as a function of GLR and the same sample after shearing for shear rate dependent viscosity measurement (from 0.01 to 1000 s^{-1})

In this study, our aim is to keep the major microstructure in emulsion during spraying. However, a defined energy per unit volume is required for making spray-particles or particle with specified size. The corresponding stress is responsible for breaking the emulsion droplets. In Figure 9(b), the droplet size of the emulsion as $X_{90,3}$, and $X_{90,3}$ of same sample after shear rate dependent viscosity measurement (shear rate values from 0.01 to 1000 s^{-1} for up and down measurements) is plotted against GLR. At the lower GLR ranges, the droplet size ($X_{90,3}$) decreases further due to shear during viscosity measurements. The reason is that the applied energy per unit volume is higher due to shear inside the rheometer than during spraying at lower GLR value. Due to higher energy input, the droplets break up further to an equilibrium state of droplet size (dispersion). On the other hand, the droplet size is smaller after spraying at the higher GLR value than after shearing of the same sample by the rheometer.Due to lower applied energy (during viscosity measurement), the final droplet size approaches to an equilibrium, which was bigger than the droplet size produced by spraying at higher GLR (coalescence).

The viscosity and loss modulus was measured for all samples of emulsions before and after spraying. As the droplet size was varying with different GLR value, the viscosity and loss modulus also changed. Figure 10 shows the shear rate dependent viscosity and loss modulus of the samples (DE, A2, A6 as in Figure 7a). Due to decrease in droplet size of the disperse phase with increasing GLR value, the corresponding viscosity was increased (Figure 10a), and a small increase in the loss modulus was observed (Figure 10b).
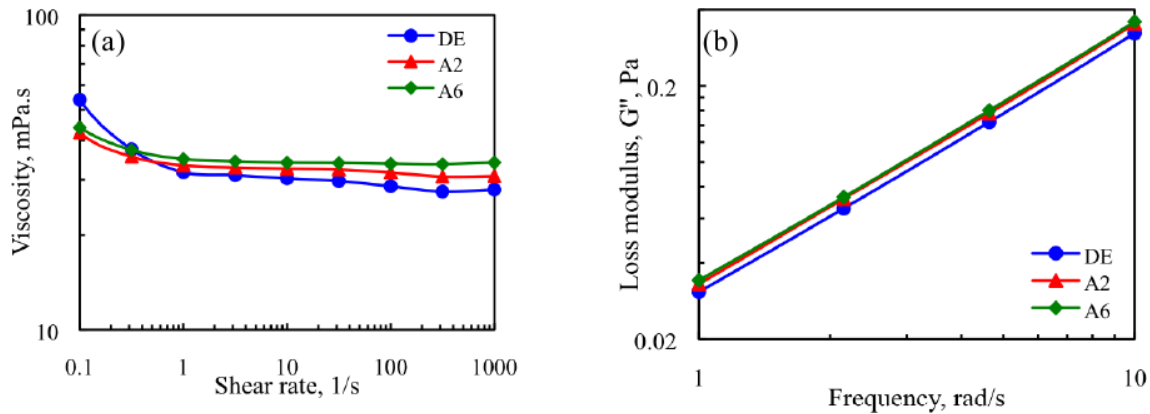
Figure 10. Rheological measurements of double emulsions with 30 % (30 % W/O)/W and sample produced by spraying using external mixing nozzle at 20 °C, (a) shear rate dependent viscosity versus shear rate, and (b) loss modulus versus frequency. (mean size and size distribution of samples are shown in Figure 7)

Experiments were also carried out for production of solid particles of simple and double emulsions through the prilling process. Inverse light microscopy picture of a double emulsion (W/O/W) containing 30% disperse phase (20% W/O simple emulsion having mean droplet size about 2 μm) is shown in Figure 11a. The emulsion was sprayed at 3 bar relative air pressure (relatively high pressure to ensure that the produced particles are small enough) with an external mixing nozzle (geo-II) at -30 °C of tower mean temperature.
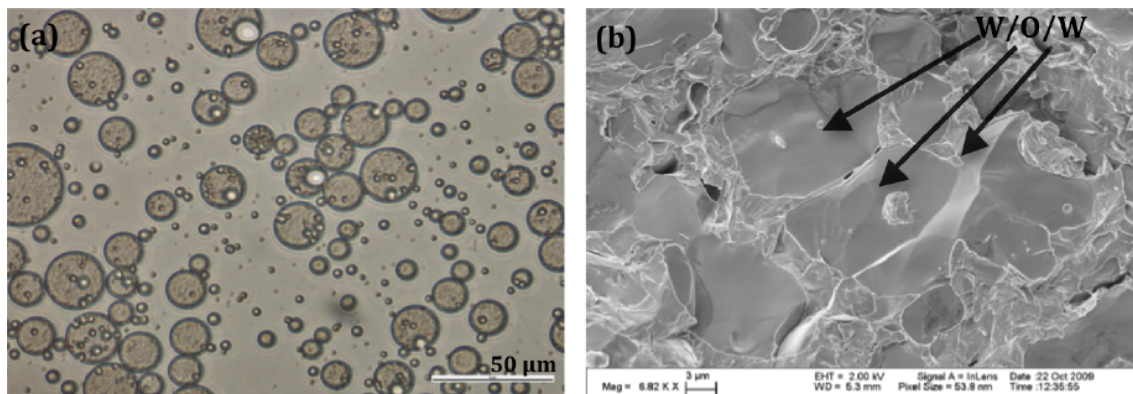
Figure 11. (a) Inverse light microscopy picture of an emulsion (W/O/W) prepared by ROME, (b) Cryo-SEM picture of the solid particle of double emulsion produced by prilling

The produced particles ($X_{50,3}$ about 250 μm) were analyzed by cryo-scanning electron microscopy (cryo-SEM) to observe the microstructure. In spite of higher applied pressure during spraying, the emulsion particles contained some inner cores (droplet of inner simple emulsion) that were clearly observed by the cryo-SEM pictures (Figure 11b).

Conclusion

The experimental results show that the air to liquid pressure ratio influences the change of microstructure of emulsions. The droplet (primary or secondary) size of emulsion decreases with increasing air pressure at constant liquid flow rate. Consequently, viscosity and loss modulus of the emulsion increases with decreasing droplet size of emulsion. However, in case of lower droplet size of the dispersed phase, the applied stress was not sufficient for further break up of the droplets using external mixing nozzle (geo-II). In case of double emulsion, the droplet size decreases more using an external mixing nozzle (geo-I) at lower GLR value than the internal mixing nozzle. However, the internal mixing nozzle is much efficient in terms of smaller droplet size and polydispersity of samples.

Prilling (atomization and chilling) experiments were done for production of solid particles. The microstructure of the produced solid particle was investigated by cryo-scanning electron microscopy (cryo-SEM) showing the received multiple emulsion structure in detail.

Acknowledgement
1. German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) for funding this project.
2. Electron Microscopy ETH Zurich (EMEZ) for giving the opportunity to use cryo-SEM instrument.

References
[1] Bibette, J., Calderon, F. L., Schmitt, V., and Poulin, P., *Emulsion science: basic principles: an overview*, Springer-Verlag Berlin, 2002, p.117-136.
[2] Hanson, J. A., Chang, C. B., Graves, S. M., Li, Z., Mason, T. G., and Deming, T. J., *Nature Letters*, 455, 85-89 (2008).
[3] Madene, A., Jacquot, M., Scher, J., and Desobry, S., *Int. J. of Food Sc. And tech.*, 41, 1-21 (2006).
[4] Eisner, V., Emulsion processing with a rotating membrane (ROME), *PhD thesis*, ETH-Zurich, 2007.
[5] Okushima, S., Nisisako, T., Torii, T., and Higuchi, T., *Langmuir*, 20, 9905-9908 (2004).
[6] Graaf, A. v. d., Schroön, C. G. P. H., Boom, R. M., *J. of Membrane Sc.*, 251, 7-15 (2005).
[7] Florence, A. T., and Whitehill, D., *J. of Colloid and interface Sc.*, 79, 243-256 (1981).
[8] Hakansson, A., Tragardh, C., and Bergenstahl, B., *Chemical Engineering Science*, 64, 2915-2925 (2009).
[9] Bibette, J., Calderon F. L., and Poulin, P., *Rep. Prog. Phys.*, 62, 969–1033 (1999).
[10] Maa, Y., and Hsu, C., *Journal of Controlled Release*, 38, 219-228 (1996).
[11] Israelachvili, J., *Colloids Surfaces A: Physicochem. Eng. Aspects*, 91, 1-8 (1994).
[12] Ficheux, M. F., Bonakdar, L., Calderon, F. L., and Bibette, J., *Langmuir*, 14,2702-2706 (1998).
[13] Broniarz-Press, L., Ochowiak, M., Rozanski, J., Woziwodzki, S., *Experimental Thermal and Fluid Science*, 33: 955–962 (2009).
[14] Tanner, F. X., Srinivasan, S., Althaus, T. O. , Feigl, K. A. and Windhab, E. J., *ICLASS 2009, 11th Triennial International Conference on Liquid Atomization and Spray Systems,* Vail, Colorado, USA, July 2009.
[15] Dubey, B. N., Duxenneuner, M. and Windhab, E. J., *SPRAY 2010*, Heidelberg, Germany, May 2010.
[16] Garti, N., *Lebensm. –Wiss. u. –Technol.*, 30, 222-235 (1997).