

Review

# Extending Applications of High-Pressure Homogenization by Using Simultaneous Emulsification and Mixing (SEM)—An Overview

Vanessa Gall <sup>1,\*</sup>, Marc Runde <sup>2</sup> and Heike P. Schuchmann <sup>1</sup>

- <sup>1</sup> Institute of Process Engineering in Life Sciences, Section I: Food Process Engineering, Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany; heike.schuchmann@kit.edu  
<sup>2</sup> mixolutions engineering, Oskar-von-Miller-Str. 23, 60314 Frankfurt, Germany; marc.runde@mixolutions.de  
\* Correspondence: vanessa.gall@kit.edu; Tel.: +49-721-608-42196

Academic Editor: Andreas Håkansson

Received: 30 September 2016; Accepted: 17 November 2016; Published: 26 November 2016

**Abstract:** Conventional high-pressure homogenization (HPH) is widely used in the pharmaceutical, chemical, and food industries among others. In general, its aim is to produce micron or sub-micron scale emulsions with excellent product characteristics. However, its energy consumption is still very high. Additionally, several limitations and boundaries impede the usage of high-pressure homogenization for special products such as particle loaded or highly concentrated systems. This article gives an overview of approaches that have been used in order to improve the conventional high-pressure homogenization process. Emphasis is put on the ‘Simultaneous Emulsification and Mixing’ process that has been developed to broaden the application areas of high-pressure homogenization.

**Keywords:** high-pressure homogenization; mixing; process modifications; process intensification; energy efficiency

## 1. Introduction

Emulsions are systems of at least two immiscible liquids in which one of the liquids is dispersed in the other as small droplets. They can be produced by using different emulsification systems such as rotor-stator systems, membrane systems, ultrasonic systems, and high-pressure systems [1–3]. High-pressure homogenizers are widely used in the pharmaceutical, chemical, and food industries [4]. They consist of a high-pressure pump and a disruption unit and enable a continuous homogenization. In general, only high-pressure systems can achieve the energy density needed to produce submicron emulsions [2,5,6] while at the same time providing the high throughputs required in industrial processes. Small droplet sizes lead to retarded creaming or sedimentation and improve product characteristics such as creaminess, texture, viscosity, color, bioavailability of active ingredients, and shelf life stability [4,7–9].

As the industry increasingly demands emulsions with smaller mean droplet diameters and narrower droplet size distributions, the objectives of the current research are:

- Enhancing the stabilization of the disrupted droplets [2,10,11].
- Decreasing the required energy input [2,10,11].
- Implementing more durable materials for the construction of the disruption unit which is commonly prone to wear by cavitation and particle abrasion [12].
- Enhancing the understanding of the HPH process in order to increase its efficiency [11].

Furthermore, conventional high-pressure homogenizers do have specific limitations and boundaries:

- The composition of an emulsion to be processed is limited. For example, particle-loaded systems such as particle stabilized emulsions (Pickering emulsions) and particle containing nano-carrier systems can cause abrasion in the disruption unit [13,14].
- Coalescence and agglomeration can occur at higher volume fractions of the disperse phase (e.g., in dairy homogenization) [10,15]. In general, coalescence is more likely to occur in high-pressure homogenizers compared to rotor-stator-systems because of the high energy input at extremely short residence times [16].
- Emulsifiers need to meet specific criteria such as fast adsorption kinetics in order to fulfill their purpose in high-pressure homogenizers [17]. Some of the emulsifiers typically used in the food industry (biopolymers or proteins), for example, are heat- or pressure sensitive [1,7] which complicates the production of emulsions at higher temperatures.

One potential approach for overcoming these limitations and boundaries is the ‘Simultaneous Emulsification and Mixing’ (SEM) process. This process is based on a modified disruption unit which combines the unit operations mixing and emulsification by inserting a micromixer shortly after the disruption unit [4,18,19].

This article will focus on the properties and possible applications of the SEM process, but will also introduce other approaches made in order to improve the conventional homogenization process. It will begin with providing some theoretical background of the topic (Chapter 2). Chapter 3 will focus on the improvements of the high-pressure process that have been developed in the last years including the SEM process. Some applications of the SEM process will be discussed in Chapter 4. Finally, Chapter 5 will provide a short summary and outlook.

## 2. Theoretical Background

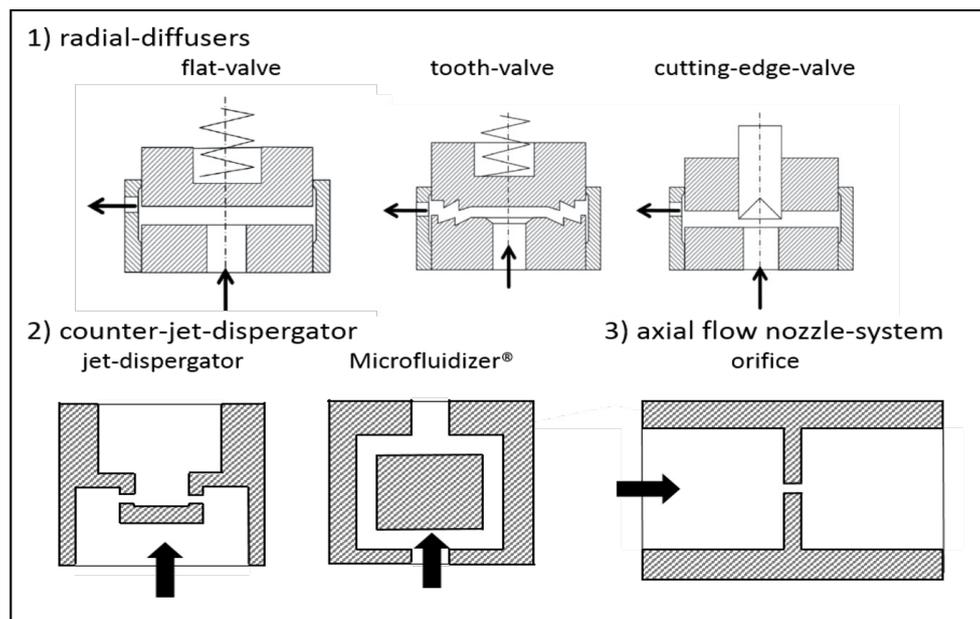
This chapter will give an introduction into the process of high-pressure homogenization (HPH).

Furthermore, it will summarize the most important characteristics of mixing, since those are important for the operating principle of the SEM process discussed later on.

### 2.1. High-Pressure Homogenization

Usually, HPH is conducted in two steps. First, a coarse emulsion is produced. Then the droplet sizes are reduced in a high-pressure homogenizer [15]. The idea of combining a high-pressure pump with a disruption unit in order to produce small-scale emulsions dates back to 1899 [20]. Piston pumps with pressure ranges between 20 and 4000 bar are most commonly used [3]. The high-pressure pump builds up energy that is then relaxed after the disruption unit and therefore leads to droplet disruption [16]. The energy input during droplet size reduction can be expressed as the energy density  $E_v$  that describes the average energy input per emulsion volume [21,22]. In case of high pressure homogenization processes, the energy density equals the pressure drop in the disruption unit. The obtained droplet diameter decreases with increasing pressure difference [21]—or increasing energy density—unless coalescence occurs [23].

The achievable droplet sizes also depend on the disruption unit as they influence the flow pattern which in turn determines droplet breakup. Disruption units can be divided by their flow guidance into radial diffusers, counterjet dispersators, and axial nozzle aggregates [2]. Typical representatives of these types are shown in Figure 1.



**Figure 1.** Disruption units in high-pressure homogenization. (1) radial-diffusers (reproduced with the permission from [3]; Behrs Verlag, 2012); (2) examples for counter-jet-dispergator: jet-dispergator adapted from [24], Microfluidizer® adapted from [25]; (3) axial flow nozzle-system.

Radial diffusers contain an axially mobile valve seat [21,26] which enables the variation of the flow rate by varying the slit width. Counterjet dispergators include a collision area of two or more opposed jets of the emulsion [16,21]. Both the counterjet dispergators and the axial flow-nozzle-systems contain no movable parts which makes them suitable for very high pressures [2]. Nozzle aggregates can be distinguished by their axial flow direction. Simple orifices usually consist of round holes of 0.1–2 mm diameter [10]. It has been reported that different disruption units lead to different droplet sizes when the same energy density is applied. For example, flat valves are less energy efficient than orifices or the Microfluidizer geometries, esp. for oil in water (o/w)-emulsions containing high viscosity oil [23,26].

Different mechanisms can cause droplet breakup: laminar shear or elongation stresses, turbulent stresses, and cavitation. According to recent reports, droplet breakup occurs after passing the disruption valve. In orifices, for example, the droplets are first elongated in the inlet area [10] and then disrupted in the turbulent and cavitating flow in the discharge area [26,27]. On top of that, the components of the emulsions influence the flow regimes and thus the mechanisms predominantly responsible for droplet breakup [28–31]. Further information on droplet breakup can be found in our second paper in this journal.

## 2.2. Mixing

Mixing is a unit operation of process engineering in which several substances, that differ in at least one property, are distributed in a defined volume. Its goal is to achieve homogeneity in order to improve product quality, chemical or biological conversions, or heat- and mass-transfer [32]. In theory, ideal mixing occurs when all starting materials are equally distributed instantly. In reality, however, this rarely occurs, so that either the time needed for complete mixing (mixing time) or the degree of mixing after a certain time (mixing quality) is used for characterization of the mixing quality [18].

Macromixing is the rate-determining step in most mixing processes and is caused by the largest scales of motion in the fluid. On the other hand, mixing on the smallest scale of motion and the final scales of molecular diffusivity is called micromixing [33].

Continuous mixers are often used in continuous processes and can be classified by their residence time, by their residence-time behavior, and by the way in which the mixing energy is introduced.

The required residence time and residence time behavior are influenced by process conditions, reaction kinetics (in case of biological or chemical reactions), and other factors [33].

Furthermore, the mixing energy can either be introduced by moving parts such as stirrers or it can be withdrawn directly from the flowing medium like in the jet mixer, for example [33,34]. The jet mixer can achieve rapid mixing in a short length of pipe mostly in turbulent flow regimes [33]. At least one component has to be added to the main stream with a considerably higher velocity than the main stream. The same working principle is used in the SEM process.

### 3. Developments in High-Pressure Homogenization

Several ideas to improve the conventional HPH process have been investigated in the last years. These can be classified as follows: geometrical modifications of the disruption valve, inserting a second homogenization step, and including a micromixer in the disruption unit. It should be mentioned that in this paper, only systems based on the conventional HPH process containing a high-pressure pump and a disruption unit are discussed in detail. However, desired droplet size distributions could also be produced by alternative concepts such as jet homogenizer [35,36] or microfluidic systems [37]. Furthermore, this article will not go into detail on the possibilities of post-homogenization treatment, since these are already discussed in [38].

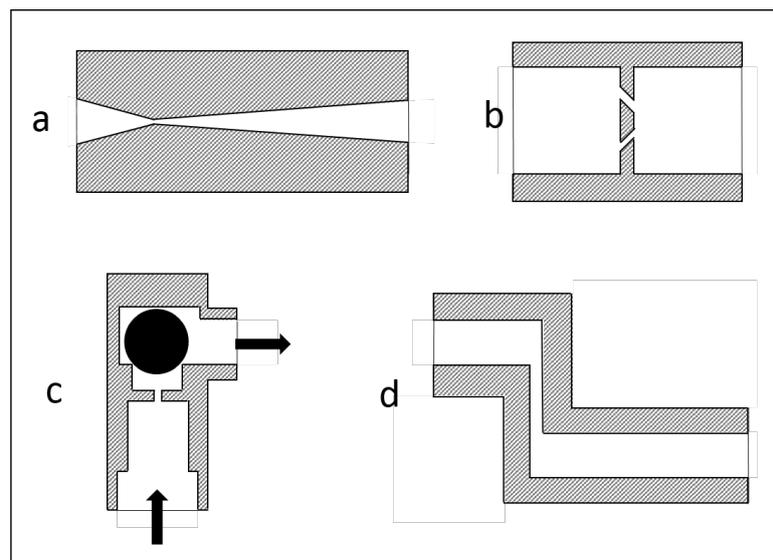
#### 3.1. Geometrical Modifications of the Disruption Valve

Flat valves can be divided into three generations. While the first generation had a flat valve seat and stamp, the valve seat in the second generation was designed in a conical shape which induced extended elongation and reduced total pressure loss. The third generation flat valve is characterized by a wider valve diameter at a smaller homogenization gap [10]. Droplet disruption could be improved in the second and third flat valve generation while applying the same energy density or pressure loss compared to a first generation flat valve [15].

Stansted Fluid Power Ltd. (Stansted, UK) developed a modified flat valve made of ceramic material that enables much higher levels of pressure (3500 bar) than a conventional flat valve [6]. Both the conventional and the Stansted valve consist of a valve piston and a valve seat, but the flow directions through the valve are reversed. First, the fluid passes the mobile valve piston and is then accelerated by the narrow gap between the piston valve and the piston seat [39]. Although very high pressures could be realized, the achieved droplet sizes were limited due to coalescence.

Modifications of orifices have been constructed in order to influence flow conditions and thus also to influence the mechanisms causing droplet breakup. Conical and circular inlets influence the elongation of the droplets, while conical outlets enhance the stabilization of the droplets while at the same time decreasing the pressure loss [27]. A modified orifice with two diagonal bores affects the intensity and distribution of turbulence after the homogenization unit. It has been shown that these orifices, also called two beam jet valves, result in smaller droplet sizes of an (o/w)-emulsion compared to conventional orifices [40]. The smallest droplet sizes were found at angles of 60° in relation to the direction of flow. A similar principle is used in the Y-chamber of the Microfluidics® (Westwood, MA, USA) disruption units [25]. Turbulence in the discharge area of the orifice can also be influenced by inserting an impact bead [41] or by using a redirecting valve [42,43]. These modified orifices are displayed in Figure 2.

However, according to Aguilar et al. [28], the geometry of the orifice should be adapted to the material characteristics of the emulsion. The authors report that at low viscosity ratio between the disperse and the continuous phase, droplets are easily elongated but also tend to relax faster after elongation. Therefore, emulsions of low viscosity ratio require a fast build-up of turbulent flow, with the intensity of turbulence being more important for efficient droplet breakup than the time scales over which droplets are subjected to turbulent stresses. The opposite is true for emulsions of high viscosity ratios.



**Figure 2.** Modifications of orifices. (a) Conical orifice adapted from [27]; (b) Two beam jet valve adapted from [44]; (c) Valve with impact bead adapted from [41]; (d) Redirecting valve adapted from [43].

### 3.2. Inserting a Second Homogenization Step

In industrial homogenizers, a double stage process is often installed in order to increase the emulsification efficiency of the HPH. Here, a second homogenization unit is inserted in line after the first one. With regard to flow conditions, the second unit applies a back-pressure and thus influences the pressure drop over the first device. This has implications particularly for the occurrence of cavitation [45,46]. The ratio of back-pressure and inlet pressure is defined as a Thoma number ( $Th$ ) [46,47]. It is reported that cavitation decreases with increasing  $Th$  and disappears at Thoma numbers of  $0.3 < Th < 0.5$  [48]. The Thoma numbers that also influence droplet breakup and minimum droplet sizes were found at  $0.15 < Th < 0.35$  [48–50], depending on the high pressure unit and the emulsion composition. Nevertheless, it was pointed out that only the first homogenization unit is responsible for droplet breakup. Therefore, the second homogenization unit can also be replaced by other process units inducing back-pressure, such as a needle valve or a pressure vessel [46]. In dairy homogenization, the second homogenization unit is also responsible for deagglomerating fat globule aggregates that result from casein bridging in the first homogenizing step [10,51].

The two homogenization units can be realized as two simple orifices or as modified valves. Displacing the second homogenization unit axially can intensify the turbulent flow in the discharge area of the first orifice [52]. Kolb et al. [5] stated that this new type of homogenization valve can reduce droplet sizes compared to a Microfluidizer or a flat valve due to reducing coalescence in the turbulent area between the two orifices. Karasch and Kulozik [53] proposed a double valve consisting of two beam jet valves for dairy homogenization.

### 3.3. Simultaneous Emulsifying and Mixing

The basic idea of the ‘Simultaneous Emulsification and Mixing’ process is to combine the unit operations mixing and emulsification in order to create synergies between them [18]. It should be noted that the SEM process is also named ‘High Pressure Post Feeding’ (HPPF) process in some publications [13,54,55]. Just as in the conventional process, a high-pressure pump is combined with a disruption unit. The SEM disruption unit however combines a simple homogenization orifice and a micromixer [4]. Two streams enter the SEM disruption unit (Figure 3): one stream which creates a turbulent jet and an additional mixing stream [18]. The first one, passing the valve or orifice, is often called the ‘homogenization stream’ as it is responsible for setting up flow conditions responsible for

droplet or filament breakup. It is also often called ‘main stream’ as it is placed centrally even if its throughput may be lower than that of the ‘mixing stream’ or ‘side stream’. The desired synergies between emulsification and mixing can only be achieved when the mixing stream is induced shortly after the disruptive unit where the disruptive flow conditions are fully built up [4,17,56,57].

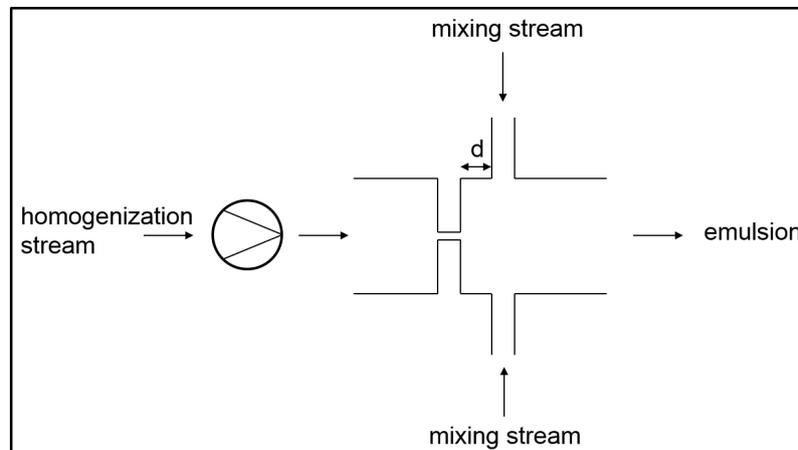


Figure 3. Function principle of SEM process.

The emulsion morphology produced by SEM can be influenced by geometrical parameters as well as process and material parameters [4,18,56,57]. According to Köhler [18], the SEM process can be operated in seven different operational modes (Figure 4). The type of operational mode depends on whether pure phases or premixes are used and whether these phases are applied in the homogenization or mixing stream [17,18].

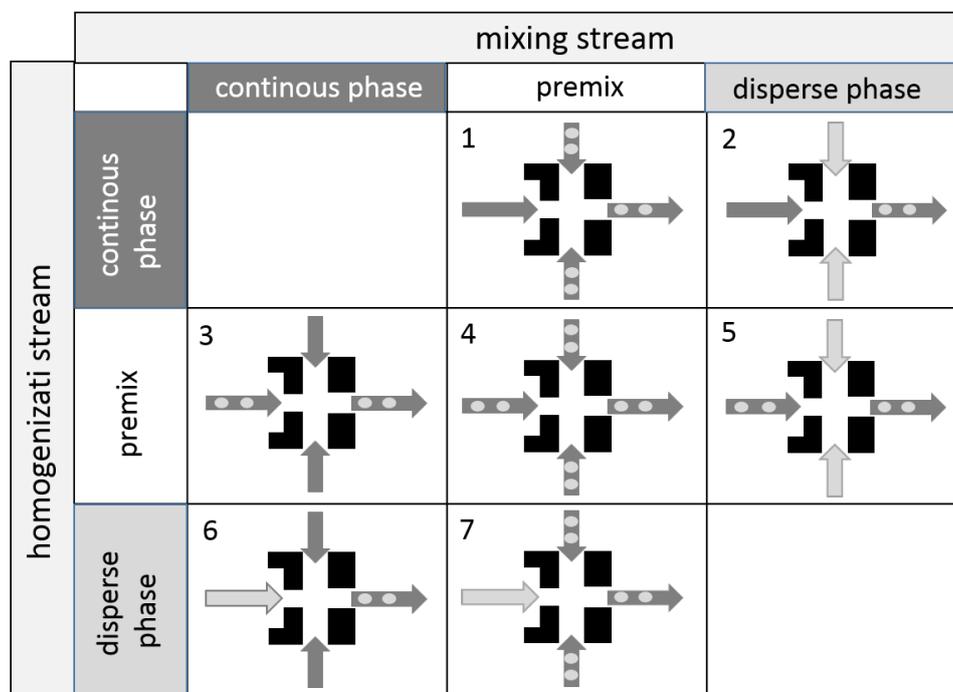


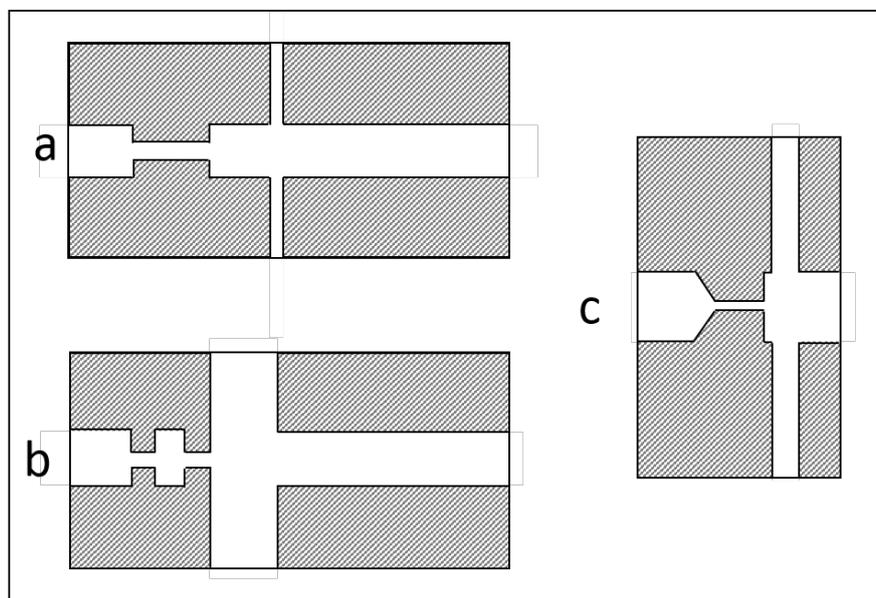
Figure 4. Operational modes of SEM adapted from [19]. The different phases (continuous phase, premix, disperse phase) are displayed in different colors according to the axes.

The operational modes of SEM can be classified as follows [18]:

- In the operational modes 2 and 6, pure phases are mixed in the micromixer. Primary droplets are produced due to the turbulent current after the orifice. These operational modes can also be referred to as simultaneous primary emulsification and mixing (SpEM).
- In the operational modes 1, 3, and 4, the already existing droplets of the premixes are disrupted into smaller droplets. These operational modes can also be referred to as simultaneous homogenization and mixing (SHM).
- In the operational modes 5 and 7, primary and secondary droplet breakup occurs since both pure disperse phase and emulsion premix are inserted into the homogenizer.

The operational modes in which the disperse phase does not pass the orifice itself are based on the idea that the homogenization stream delivers the local flow conditions required for emulsifying the disperse phase and mixing both streams [58].

The operating principle of the SEM process can be realized using different disruption units. Figure 5 illustrates some of the SEM valves that have been presented in the literature. They can either be simple orifices, modified orifices, or even double orifices. SEM flat valves have also been designed [18,59], but most of the recent research was conducted with orifices.



**Figure 5.** SEM valves. (a) orifice SEM valve adapted from [4]; (b) double SEM valve adapted from [58]; (c) SEM valve with modified inlet geometry adapted from [55].

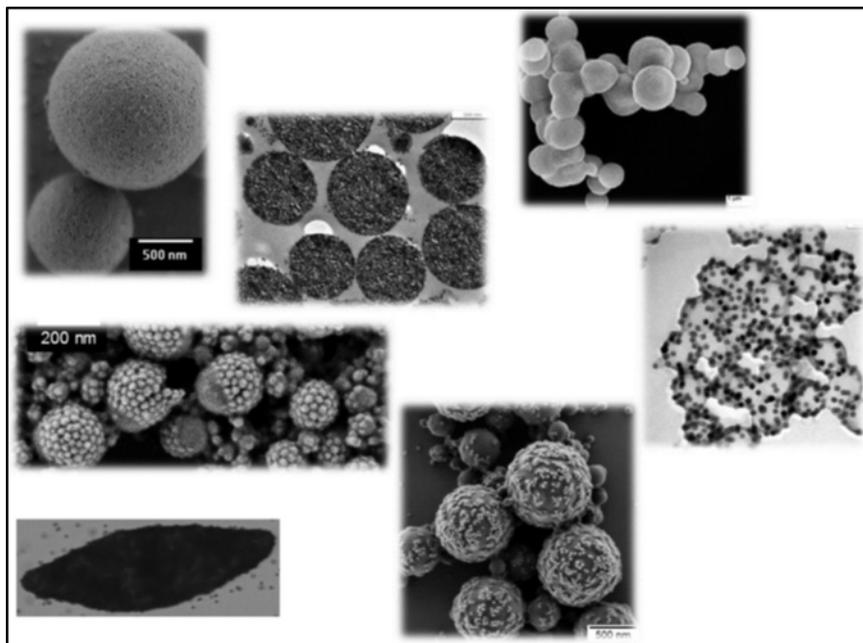
#### 4. Applications of SEM Homogenization

The SEM process has been tested in various application fields. This chapter will give an overview over the conducted research.

##### 4.1. Preparation of Hybrid Nanoparticles

Hybrid nanoparticles are of scientific and industrial interest as they can be used for several applications—e.g., paints of high color intensity [60–62], electronic devices [63,64], and medical applications [65–67]. Hybrid nanoparticles can be prepared by miniemulsion polymerization in a two-stage process [68–70]: first, a nanoparticle-in-monomer suspension is emulsified in a continuous phase and then the polymerization of the filled submicron-sized monomer droplets is conducted [55]. Hecht et al. consider high-pressure homogenizers to be the most suitable device to produce small sizes for particle filled monomer droplets at a high throughput [55]. Figure 6 displays some nanostructured particles produced in dynamic high-pressure processes via miniemulsions [11].

In the past, ultrasonic systems have been used to produce particle loaded droplets [71–73]. Since nanoparticles can cause abrasion in homogenization valves [12], Hecht et al. used the SEM process for the miniemulsion polymerization especially with regard to a high degree of nanoparticle filling (up to 60 wt %) [55]. As disruption unit, a simple orifice (Figure 5a) was used. To avoid abrasion of the orifice, operational mode 1 (see Figure 4) was chosen: pure continuous phase was pumped through the orifice, while the premix emulsion containing the nanoparticle-in-monomer-droplets was inserted as mixing stream. Droplets of the desired size range (<500 nm) were produced, which demonstrates that the particle-loaded droplets did not require an elongation prior to their break-up [55]. Winkelmann et al. [44] used a similar SEM process to produce zinc oxide nanoparticles by miniemulsion precipitation. Experimental investigations and computational fluid dynamics (CFD) simulations showed that different factors influence the mixing quality: the homogenization pressure, the disruption unit geometry, and the distance between the outlet of the disruption unit and the inlet of the second feed stream. Mixing quality was shown to be responsible for the size of precipitated nanoparticles especially when the process was run in the single-emulsion-mode. Here, precursor 1 of the particles to be precipitated is dissolved in the miniemulsion droplets, while precursor 2 is mixed into the continuous phase. Its transport into the miniemulsion droplet starts precipitation. On top of that, SEM homogenizers can also be efficiently used to disperse nanoparticles in a liquid [13].



**Figure 6.** Nanostructured particles produced in dynamic high-pressure processes via miniemulsions. Reproduced with the permission from [11]; Woodhead Publishing, 2016.

#### 4.2. Particle Stabilized Emulsions

Particle stabilized emulsions (PSE), also called Pickering emulsions, use small particles to stabilize the interface of emulsions [74,75]. They have regained interest in scientific literature [76] as the availability of suitable particles has increased [58]. Since the energy supplied during emulsification determines the droplet break-up for emulsions including PSE [77], HPH of PSE could be of great interest [58], although the particles may cause abrasion as already discussed.

By using an SEM process in which the stabilizing particles are added in the mixing stream, this problem can be reduced. Köhler et al. investigated the influence of process parameters, composition and operational mode on the homogenization results of (o/w)-emulsions prepared in the SEM process which were stabilized by Stober silica particles [58]. The investigated operational modes were numbers

1, 3, and 6 (see Figure 4). In all operational modes, the particles were added in the mixing stream. First experiments in the operational mode 3 revealed that small particles in the range of 12 nm were needed to achieve fast stabilization kinetics. Larger particles in the range of 200 nm resulted in significantly larger droplet sizes. At lower homogenizing pressures (100–500 bar), the obtained droplet sizes in all operational modes were comparable to emulsions stabilized by a conventional homogenizer. At higher pressures (800–1000 bar) however, droplet sizes could not be further reduced since the stabilization kinetics of the particles was apparently not fast enough and droplets re-coalesced.

#### 4.3. Dairy Homogenization

For decades, drinking milk and dairy products have been homogenized either in full-stream or partial-stream processes [51]. Homogenization reduces the milk fat globule diameter from around 4  $\mu\text{m}$  to 0.6–0.7  $\mu\text{m}$  [78]. The lower droplet size is crucial to prevent e.g., creaming of the fat droplets within the shelf life of milk. In the partial-stream process, the milk is first separated into cream and skim milk, before both are mixed again to yield a fat content of maximum 17 vol % [10,51] and homogenized. In full-stream homogenization, the fat content is adjusted to the final fat content (e.g., 3.5 vol %) upstream the homogenization step and the whole volume is homogenized.

The partial-stream homogenization process allows a fat content up to 17 vol % upstream of the homogenization step, which results in saved energy due to the reduced over-all processed volume. In a downstream standardization step, the fat content is then adjusted to the final fat content.

Raising the fat content during milk homogenization above 17 vol % is the key to save energy during homogenization [79]. Nevertheless, in conventional partial stream milk homogenization the fat content cannot exceed 17 vol % due to coalescence and aggregation of the fat droplets [4] after the homogenization step.

Köhler et al. [4] used SEM homogenization in order to enable the homogenization of cream with up to 42 vol % fat content which corresponds to the concentration at which cream exits the separation process in conventional dairy processing lines. In this case, the operational mode 3 and therefore a SpEM process was used. The homogenized cream was diluted with skim milk, also coming from the separation process, in the micromixer unit instantly after droplet breakup. Using this setup, fat globule aggregation could be prevented while still allowing for the homogenization of increased fat contents. Since the product volume to be pressurized was reduced, energy and investment costs could be cut. Furthermore, it was possible to simplify the process line because two mixing units could be eliminated. From the application point of view, the SpEM process allows an increase of the throughput of a dairy process line by a factor of up to 8 without investment in new high-pressure pumps [10,79].

In order to further improve the SpEM process of milk homogenization, Köhler et al. [4] investigated the influence of the distance between the exit of the orifice and the inlet of the mixing stream (distance  $d$  in Figure 3) on the milk fat globule size and mixing quality. Both experiments and CFD simulations of the process indicated that there is an optimal distance for the injection of the skim milk as mixing stream. Short distances improve the mixing quality while long distances enable an undisturbed disruption process. As compromise, the mixing stream was inserted after a distance  $d = 5$  mm in order to obtain the smallest droplets possible.

In subsequent experiments, Köhler et al. [57] found that the required product quality can be maintained by homogenizing cream with 32–42 vol %. Compared to conventional dairy HPH, the aggregation rate was rather low, even for those high fat contents. However, it must be stated that Köhler et al. found no further reduction of droplet sizes by increasing the homogenization pressure over 200 bar, which indicates that coalescence could not be fully prevented. On top of that, it was shown that using the SEM process provides the opportunity to increase the cream temperature, as the heat-sensitive milk proteins are mainly included in the skim milk [53]. In this way, homogenization results can be further improved as the droplet viscosity decreases with increasing temperature which simplifies droplet deformation and break-up [10]. According to Köhler et al. in [56], both the length

of the mixing zone and the geometrical shape of the flow channel had no significant influence on the homogenization results.

The experiments on the homogenization of milk in the SEM process described so far had been conducted using orifices as disruption units. However, in industrial dairy processes, flat valves are used instead [51]. Schlender et al. developed a modified flat valve allowing for SEM processing of e.g., drinking and chocolate milk [79]. The working principle of the SEM flat valve set-up is shown in Figure 7. The flat valve was successfully integrated in an industrial homogenization process with 1000 L/h throughput in operational mode 3. At 29 vol % fat content and 220 bar homogenization pressure, the droplet size distribution was comparable to commonly homogenized milk. Based on energy consumption data from this production line, 70%–80% energy could be saved in plants of similar dimensions. Furthermore, the authors also managed to further decrease fat globule droplet size for ESL (extended shelf life) dairy products, and to produce a cocoa drink that fits the standards of quality by adding a cacao mixture in the mixing stream.

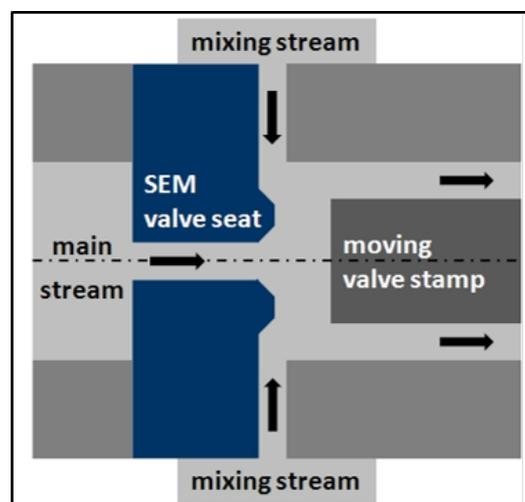


Figure 7. Principle of SEM flat valve for dairy homogenization.

#### 4.4. Melt Emulsification

Nowadays, small particles of wax are commonly produced by wet milling [16]. Using a melt emulsification process instead of wet milling can lead to shorter process times, energy savings, and new product characteristics [16]. The new product characteristics result from the spherical shape of the particles obtained by the melt emulsification process [18]. The process consists of three main steps: melting the disperse phase, emulsification, and producing a suspension by cooling [80]. One of the main challenges is finding a suitable emulsifier that can stabilize the emulsion at higher and lower temperatures as well as the suspension [18].

Köhler et al. showed that it is possible to produce monomodal particle size distributions in the order of 1  $\mu\text{m}$  [7] using a SEM melt emulsification process in operational mode 3. Different waxes were homogenized at pressures between 100 and 1000 bar. Cold water of 20°C was used as a side stream to realize an instant cooling of the droplets. Due to the instant cooling, it was possible to stabilize the droplets and maintain their spherical shape without any emulsifier added to the formulation [81].

#### 4.5. SEM Process for Research Purposes

To date, there are still open questions concerning the droplet breakup and stabilization of droplets in HPH process. For this reason, Kempa et al. used an SEM process to separately investigate the influence of the emulsifier on droplet deformation and coalescence in HPH [54]. This was realized by adding the fast adsorbing emulsifier SDS in the mixing stream, while the homogenization stream

consisted of an oil-in-water-emulsion without any emulsifier. Compared to emulsions produced with conventional high-pressure homogenization, no differences in the droplet size distributions could be found when the emulsifier was added in the first millimeters after the homogenization valve. However, droplet sizes increased with increasing distance of emulsifier addition. The authors could link the region of no emulsifier influence to those of high turbulent energy dissipation in the free jet. As a result, it became clear that the emulsifier had no influence on the droplet deformation in the orifice and on the disruption of the filaments in the following turbulent free jet. The role of the emulsifier is solely restricted to stabilizing emulsion droplets after breakup.

#### 4.6. Economical Interest

The SEM technology opens up opportunities in several operational fields like process costs, new products, and process design for all industrial sectors. The following economical aspects focus mainly on the dairy and beverage industry. Beside the already mentioned (Section 4.3) energy optimization with 30%–80% savings of mechanical energy cf. conventional processes, advantages in maintenance are expected too. Due to the effective dispersion after the homogenization gap, wear intensive additives like cocoa, sugar, or others can be added to the product with the mixing stream. By that, abrasion of the high-pressure unit can be minimized. Depending on its application, SEM homogenization provides potential energy and maintenance cost benefits of up to 70 vol %.

When the existing machinery is replaced, the equipment size could be reduced. This results in optimized investment and maintenance needs. Existing older and energy inefficient equipment can be upgraded to an economically profitable production level.

In case of process design, the usage of SEM processes results in new levels of freedom in product development, process configuration, and plant design. Besides a flexible product flow management for a cost optimized process design, rapid product changeover by in-line adjustment of mixing ratios between main and mixing stream are the focus of industrial interest. A further potential economical benefit can be achieved by developing new products with enhanced properties. As examples, the gentle treatment of shear- or temperature sensitive ingredients and additives while adding them to the mixing stream can be named. In other industrial sectors, production improvements of emulsions based products are often limited by batch processes. By using an SEM based continuous process instead, the production performance might be increased significantly. Especially in case of melt emulsification not only the production performance and process variability can be increased. The possible ultra-high cooling rate between the main and mixing stream also allows developing new product properties and can reduce the addition of environmentally questionable additives to a minimum. Here, a solvent-free production process can be reached [82].

## 5. Summary and Outlook

Several improvements to the HPH process have been successfully developed to lower its energy consumption and broaden its range of application. Geometrically improved disruption orifices and valves, as well as double orifices and valves, can increase the energy efficiency of the process when adapted to the emulsion composition. Special emulsions such as particle loaded or melt emulsions can be processed in high pressure homogenizers using SEM valves. In this way, abrasion or clogging of the homogenization valve can be avoided. On top of that, the mixing stream of the SEM valve can be used to include additional functions such as instant cooling, addition of reaction precursors, or dilution into the HPH process. A first application in dairy industry underlines its economic interest.

Nevertheless, further research is needed for a broad implementation of the SEM process in industrial applications. Most of the experiments have been conducted on a lab scale with a simple orifice while a flat valve based design is developed for higher tonnages. Even though most of the shown examples show the high potential of SEM processes, it also became clear that local flow conditions are critical for process design. Different applications require different designs and finding those is done today by experience-based trial-and-error. Future work will thus concentrate on an improved

understanding of the mixing characteristics of SEM units and their interference with droplet disruption. This will help in extending the possibilities of future HPH based processes.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Santana, R.; Perrechil, F.; Cunha, R. High- and low-energy emulsifications for food applications: A focus on process parameters. *Food Eng. Rev.* **2013**, *5*, 107–122. [[CrossRef](#)]
2. Schultz, S.; Wagner, G.; Urban, K.; Ulrich, J. High-pressure homogenization as a process for emulsion formation. *Chem. Eng. Technol.* **2004**, *27*, 361–368. [[CrossRef](#)]
3. Köhler, K.; Schuchmann, H.P.; Tesch, S.; Freudig, B. Emulgieren in Hochdruckhomogenisatoren. In *Emulgiertechnik*; Köhler, K., Schuchmann, H.P., Eds.; Behrs Verlag: Hamburg, Germany, 2012.
4. Köhler, K.; Aguilar, F.A.; Hensel, A.; Schubert, K.; Schubert, H.; Schuchmann, H.P. Design of a Microstructured System for Homogenization of Dairy Products with High Fat Content. *Chem. Eng. Technol.* **2007**, *30*, 1590–1595. [[CrossRef](#)]
5. Kolb, G.; Wagner, G.; Viardot, K.; Ulrich, J. Zur Herstellung von Feinemulsionen mittels Hochdruckdispergiereinheiten. *Chem. Ing. Technik* **2001**, *73*, 84–87. [[CrossRef](#)]
6. Floury, J.; Legrand, J.; Desrumaux, A. Analysis of a new type of high pressure homogeniser. Part B. Study of droplet break-up and recoalescence phenomena. *Chem. Eng. Sci.* **2004**, *59*, 1285–1294. [[CrossRef](#)]
7. Köhler, K.; Hensel, A.; Kraut, M.; Schuchmann, H.P. Melt emulsification—Is there a chance to produce particles without additives? *Particuology* **2011**, *9*, 506–509. [[CrossRef](#)]
8. Stang, M.; Schuchmann, H.P.; Schubert, H. Emulsification in High-Pressure Homogenizers. *Eng. Life Sci.* **2001**, *4*, 151–157. [[CrossRef](#)]
9. Thiebaud, M.; Dumay, E.; Picart, L.; Guiraud, J.P.; Cheftel, J.C. High-pressure homogenisation of raw bovine milk. Effects on fat globule size distribution and microbial inactivation. *Int. Dairy J.* **2003**, *13*, 427–439. [[CrossRef](#)]
10. Köhler, K.; Karasch, S.; Schuchmann, H.P.; Kulozik, U. Energiesparende Homogenisierung von Milch mit etablierten sowie neuartigen Verfahren. *Chem. Ing. Technik* **2008**, *80*, 1107–1116. [[CrossRef](#)]
11. Schuchmann, H.P. Advances in Hydrodynamic Pressure Processing for Enhancing Emulsification and Dispersion. In *Innovative Food Processing Technologies: Extraction, Separation, Component Modification and Process Intensification*; Knoerzer, K., Ed.; Woodhead Publishing Series in Food Science, Technology and Nutrition; Woodhead Publishing: Cambridge, UK, 2016; Number 302; pp. 387–412.
12. Hecht, L.L.; Schlender, M.; Köhler, K.; Schuchmann, H.P. Abrasion in high-pressure homogenization orifices: A new method to quantify the impact of particle loaded fluids. *Wear* **2012**, *289*, 138–144. [[CrossRef](#)]
13. Sauter, C.; Schuchmann, H.P. Materialschonendes Hochdruckdispersieren mit dem High Pressure Post Feeding (HPPF)-System. *Chem. Ing. Technik* **2008**, *80*, 365–372. [[CrossRef](#)]
14. Sauter, C.; Schuchmann, H.P. High pressure for dispersing and deagglomerating nanoparticles in aqueous solutions. *Chem. Eng. Technol.* **2007**, *30*, 1401–1405. [[CrossRef](#)]
15. Freudig, B. *Herstellen von Emulsionen und Homogenisieren von Milch in modifizierten Lochblenden*; Universität Karlsruhe (TH): Karlsruhe, Germany, 2004.
16. Schuchmann, H.P.; Danner, T. Emulgieren: Mehr als nur Zerkleinern. *Chem. Ing. Technik* **2004**, *76*, 364–375. [[CrossRef](#)]
17. Köhler, K.; Schlender, M.; Schuchmann, H.P. Hochdruckemulgieren—Neue Prozesse und Produkte. *Process* **2011**, *7/8*, 68–72.
18. Köhler, K. *Simultanes Emulgieren und Mischen*; Logos Verlag: Berlin, Germany, 2010.
19. Köhler, K.; Schuchmann, H.P. Simultanes Emulgieren und Mischen. *Chem. Ing. Technik* **2012**, *84*, 1538–1544. [[CrossRef](#)]
20. Gaulin, A. Appareil et Procédé pour la Stabilisation du Lait. Patent Brevet 295596, 23 May 1899.
21. Schuchmann, H.P. Tropfenaufbruch und Energiedichtekonzept beim mechanischen Emulgieren. In *Emulgiertechnik*; Köhler, K., Schuchmann, H.P., Eds.; Behrs Verlag: Hamburg, Germany, 2012.
22. Schuchmann, H.P.; Karbstein, N.; Hecht, L.L.; Gedrat, M.; Köhler, K. High-Pressure Homogenization for the Production of Emulsions. In *Industrial High Pressure Applications, Processes, Equipment and Safety*; Eggers, R., Ed.; Wiley-VCH Verlag: Weinheim, Germany, 2012; pp. 97–118.

23. Karbstein, H. Untersuchungen zum Herstellen und Stabilisieren von Öl-in-Wasser-Emulsionen. Ph.D. Thesis, Universität Karlsruhe (TH), Karlsruhe, Germany, 1994.
24. Klinksiek, B.; Koglin, B. Herstellung von Pharmazeutischen oder Kosmetischen Dispersionen. Patent EP0101007 B1, 11 May 1988.
25. Cook, E.J.; Lagace, A.P. Apparatus for Forming Emulsions. U.S. Patent 4,533,254, 6 August 1985.
26. Stang, M. *Zerkleinern und Stabilisieren von Tropfen Beim Mechanischen Emulgieren*; Universität Karlsruhe (TH): Karlsruhe, Germany, 1998.
27. Tesch, S. *Charakterisieren Mechanischer Emulgiervverfahren: Herstellen und Stabilisieren von Tropfen als Teilschritte beim Formulieren von Emulsionen*; Universität Karlsruhe (TH): Karlsruhe, Germany, 2002.
28. Aguilar, F.A.; Köhler, K.; Schubert, H.; Schuchmann, H.P. Herstellen von Emulsionen in einfachen und modifizierten Lochblenden: Einfluss der Geometrie auf die Effizienz der Zerkleinerung und Folgen für die Maßstabsvergrößerung. *Chem. Ing. Technik* **2008**, *80*, 607–613. [[CrossRef](#)]
29. Kelemen, K.; Schuch, A.; Schuchmann, H.P. Influence of flow conditions in high pressure orifices on droplet disruption of O/W emulsions. *Chem. Eng. Technol.* **2014**, *37*, 1227–1234. [[CrossRef](#)]
30. Kelemen, K.; Crowther, F.E.; Cierpka, C.; Hecht, L.L.; Kähler, C.J.; Schuchmann, H.P. Investigations on the characterization of laminar and transitional flow conditions after high pressure homogenization orifices. *Microfluid. Nanofluid.* **2014**, *18*, 599–612. [[CrossRef](#)]
31. Kelemen, K.; Gepperth, S.; Koch, R.; Bauer, H.-J.; Schuchmann, H.P. On the visualization of droplet deformation and breakup during high-pressure homogenization. *Microfluid. Nanofluid.* **2015**, *19*, 1139–1158. [[CrossRef](#)]
32. Pahl, M. Mischtechnik, Aufgaben und Bedeutung. In *Mischen und Rühren: Grundlagen und Moderne Verfahren*; Kraume, M., Ed.; Wiley-VCH: Weinheim, Germany, 2005; pp. 1–19.
33. Kraume, M.; Merz, C.; Henzler, H.-J. Continuous Mixing of Fluids. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2012.
34. Kraume, M. (Ed.) *Mischen und Rühren. Grundlagen und Moderne Verfahren*; Wiley-VCH: Weinheim, Germany, 2005.
35. Pravinata, L.; Akhtar, M.; Bentley, P.J.; Mahatnirunkul, T.; Murray, B.S. Preparation of alginate microgels in a simple one step process via the Leeds Jet Homogenizer. *Food Hydrocoll.* **2016**, *61*, 77–84. [[CrossRef](#)]
36. Burgaud, I.; Dickinson, E.; Nelson, P.V. An Improved High-Pressure Homogenizer for Making Fine Emulsions on a Small-Scale. *Int. J. Food Sci. Technol.* **1990**, *25*, 39–46. [[CrossRef](#)]
37. Vladisavljevic, G. Emulgieren mit mikrostrukturierten Systemen. In *Emulgiertechnik*; Köhler, K., Schuchmann, H.P., Eds.; Behrs Verlag: Hamburg, Germany, 2012; pp. 253–290.
38. Bai, L.; McClements, D. Extending Emulsion Functionality: Post-Homogenization Modification of Droplet Properties. *Processes* **2016**, *4*, 17. [[CrossRef](#)]
39. Floury, J.; Bellettre, J.; Legrand, J.; Desrumaux, A. Analysis of a new type of high pressure homogeniser: A study of the flow pattern. *Chem. Eng. Sci.* **2004**, *59*, 843–853. [[CrossRef](#)]
40. Aguilar, F.A.; Freudig, B.; Schuchmann, H.P. Herstellen von Emulsionen in Hochdruckhomogenisatoren mit modifizierten Lochblenden. *Chem. Ing. Technik* **2004**, *76*, 396–399. [[CrossRef](#)]
41. Muschiolik, G.; Roeder, R.-T.; Lengfeld, K. Druckhomogenisator. Patent DE19530247 A1, 20 February 1997.
42. Forschungskreis der Ernährungsindustrie e. V. *Energiesparende und Schonende Homogenisierung von Milch und Auswirkungen auf die Textur von Milchprodukten*; AiF FV 14073 N; FEI: Bonn, Germany, 2008.
43. Forschungskreis der Ernährungsindustrie e. V. *Entwicklung einer Verbesserten Düse zum Hochdruckhomogenisieren und -Emulgieren*; AiF FV 12405 N; FEI: Bonn, Germany, 2002.
44. Winkelmann, M.; Schuler, T.; Uzunogullari, P.; Winkler, C.A.; Gerlinger, W.; Sachweh, B.; Schuchmann, H.P. Influence of mixing on the precipitation of zinc oxide nanoparticles with the miniemulsion technique. *Chem. Eng. Sci.* **2012**, *81*, 209–219. [[CrossRef](#)]
45. Freudig, B.; Tesch, S.; Schubert, H. Herstellen von Emulsionen in Hochdruckhomogenisatoren—Teil 2: Bedeutung der Kavitation für die Tropfenzerkleinerung. *Chem. Ing. Technik* **2002**, *74*, 880–884. [[CrossRef](#)]
46. Schlender, M.; Minke, K.; Spiegel, B.; Schuchmann, H.P. High-pressure double stage homogenization processes: Influences of plant setup on oil droplet size. *Chem. Eng. Sci.* **2015**, *131*, 162–171. [[CrossRef](#)]
47. Kurzhals, H.A.; Reuter, H. Untersuchungen über die physikalisch-technischen Vorgänge beim Homogenisieren von Milch in Hochdruck-Homogenisiermaschinen. *Chem. Ing. Technik* **1979**, *51*, 325. [[CrossRef](#)]
48. Jahnke, S. The theory of high-pressure homogenization. In *Emulsions and Nanosuspensions for the Formulation of Poorly Soluble Drugs*; Benita, S., Bohm, B., Eds.; CRC Press: Boca Raton, FL, USA, 1998.

49. Freudig, B.; Tesch, S.; Schubert, H. Production of emulsions in high-pressure homogenizers—Part II: Influence of Cavitation on Droplet Breakup. *Eng. Life Sci.* **2003**, *6*, 266–270. [[CrossRef](#)]
50. Finke, J.H.; Niemann, S.; Richter, C.; Gothsch, T.; Kwade, A.; Büttgenbach, S.; Müller-Goymann, C.C. Multiple orifices in customized microsystem high-pressure emulsification: The impact of design and counter pressure on homogenization efficiency. *Chem. Eng. J.* **2014**, *248*, 107–121. [[CrossRef](#)]
51. Kessler, H.G. *Food and Bio Process Engineering: Dairy Technology; 109 Tables*, 5th ed.; A. Kessler: München, Germany, 2002.
52. Kolb, G.E. *Zur Emulsionsherstellung in Blendensystemen*; Universität Bremen: Bremen, Germany, 2001.
53. Karasch, S.; Kulozik, U. Hochdruckhomogenisierung von Milch mit modifizierten Lochblenden im Vergleich zu konventionellen Flachventilen. *Chem. Ing. Technik* **2008**, *80*, 1117–1124. [[CrossRef](#)]
54. Kempa, L.; Schuchmann, H.P.; Schubert, H. Drip-reducing and drip coalescence in mechanical emulsifying with high pressure homogenisers. *Chem. Ing. Technik* **2006**, *78*, 765–768. [[CrossRef](#)]
55. Hecht, L.L.; Merkel, T.; Schoth, A.; Köhler, K.; Wagner, C.; Muñoz-Espí, R.; Landfester, K.; Schuchmann, H.P. Emulsification of particle loaded droplets with regard to miniemulsion polymerization. *Chem. Eng. J.* **2013**, *229*, 206–216. [[CrossRef](#)]
56. Köhler, K.; Aguilar, F.A.; Hensel, A.; Schubert, H.; Schuchmann, H.P. Design of a Micro-Structured System for the Homogenization of Dairy Products at High Fat Content—Part III: Influence of Geometric Parameters. *Chem. Eng. Technol.* **2009**, *32*, 1120–1126. [[CrossRef](#)]
57. Köhler, K.; Aguilar, F.A.; Hensel, A.; Schubert, K.; Schubert, H.; Schuchmann, H.P. Design of a Microstructured System for the Homogenization of Dairy Products at High Fat Content Part II: Influence of Process Parameters. *Chem. Eng. Technol.* **2008**, *31*, 1863–1868. [[CrossRef](#)]
58. Köhler, K.; Santana, A.S.; Braisch, B.; Preis, R.; Schuchmann, H.P. High pressure emulsification with nano-particles as stabilizing agents. *Chem. Eng. Sci.* **2010**, *65*, 2957–2964. [[CrossRef](#)]
59. Schlender, M.; Schuchmann, H.P. Fortschritte bei der Milchloromogenisation. *Food Lab* **2014**, *2014*, 40–43.
60. Tiarks, F.; Landfester, K.; Anonietti, M. Encapsulation of carbon black by miniemulsion polymerization. *Macromol. Chem. Phys.* **2001**, *202*, 51–60. [[CrossRef](#)]
61. Steiert, N.; Landfester, K. Encapsulation of organic pigment particles via miniemulsion polymerization. *Macromol. Mater. Eng.* **2007**, *292*, 1111–1125. [[CrossRef](#)]
62. Lelu, S.; Novat, C.; Graillat, C.; Guyot, A.; Bourgeat-Lami, E. Encapsulation of an organic phthalocyanine blue pigment into polystyrene latex particles using a miniemulsion polymerization. *Polym. Int.* **2003**, *52*, 542–547. [[CrossRef](#)]
63. Mitzi, D.B. Thin-Film Deposition of Organic-Inorganic Hybrid Materials. *Chem. Mater.* **2001**, *13*, 3283–3298. [[CrossRef](#)]
64. Vossmeier, T.; Guse, B.; Besnard, I.; Bauer, R.E.; Mullen, K.; Yasuda, A. Gold nanoparticle/polyphenylene dendrimer composite films: Preparation and vapor-sensing properties. *Adv. Mater.* **2002**, *14*, 238–242. [[CrossRef](#)]
65. Gong, T.; Yang, D.; Hu, J.H.; Yang, W.L.; Wang, C.C.; Lu, J.Q. Preparation of monodispersed hybrid nanospheres with high magnetite content from uniform Fe<sub>3</sub>O<sub>4</sub> clusters. *Colloids Surf. A Physicochem. Eng. Asp.* **2009**, *339*, 232–239. [[CrossRef](#)]
66. Soppimath, K.S.; Aminabhavi, T.M.; Kulkarni, A.R.; Rudzinski, W.E. Biodegradable polymeric nanoparticles as drug delivery devices. *J. Control. Release* **2001**, *70*, 1–20. [[CrossRef](#)]
67. Kawashita, M.; Tanaka, M.; Kokubo, T.; Inoue, Y.; Yao, T.; Hamada, S.; Shinjo, T. Preparation of ferrimagnetic magnetite microspheres for in situ hyperthermic treatment of cancer. *Biomaterials* **2005**, *26*, 2231–2238. [[CrossRef](#)] [[PubMed](#)]
68. Bechthold, N.; Tiarks, F.; Willert, M.; Landfester, K.; Antonietti, M. Miniemulsion polymerization: Applications and new materials. *Macromol. Symp.* **2000**, *151*, 549–555. [[CrossRef](#)]
69. Zhang, S.W.; Zhou, S.X.; Weng, Y.M.; Wu, L.M. Synthesis of SiO<sub>2</sub>/polystyrene nanocomposite particles via miniemulsion polymerization. *Langmuir* **2005**, *21*, 2124–2128. [[CrossRef](#)] [[PubMed](#)]
70. Charoenmark, L.; Polpanich, D.; Thiramanas, R.; Tangboriboonrat, P. Preparation of superparamagnetic polystyrene-based nanoparticles functionalized by acrylic acid. *Macromol. Res.* **2012**, *20*, 590–596. [[CrossRef](#)]
71. Bourgeat-Lami, E.; Farzi, G.A.; David, L.; Putaux, J.L.; McKenna, T.F.L. Silica Encapsulation by Miniemulsion Polymerization: Distribution and Localization of the Silica Particles in Droplets and Latex Particles. *Langmuir* **2012**, *28*, 6021–6031. [[CrossRef](#)] [[PubMed](#)]

72. Diaconu, G.; Paulis, M.; Leiza, J.R. High solids content waterborne acrylic/montmorillonite nanocomposites by miniemulsion polymerization. *Macromol. React. Eng.* **2008**, *2*, 80–89. [[CrossRef](#)]
73. Luo, Y.D.; Dai, C.A.; Chiu, W.Y. Nucleation Mechanism and Morphology of Polystyrene/Fe<sub>3</sub>O<sub>4</sub> Latex Particles via Miniemulsion Polymerization Using AIBN as Initiator. *J. Appl. Polym. Sci.* **2009**, *112*, 975–984. [[CrossRef](#)]
74. Pickering, S.U. Emulsions. *J. Chem. Soc. Faraday Trans.* **1907**, *91*, 2001–2021. [[CrossRef](#)]
75. Ramsden, W. Separation of solids in the surface-layers of solutions and ‘suspensions’ (observations on surface-membranes, bubbles, emulsions, and mechanical coagulation). *Proc. R. Soc. Lond. (1854–1905)* **1903**, *72*, 156–164. [[CrossRef](#)]
76. Aveyard, R.; Binks, B.P.; Clint, J.H. Emulsions stabilised solely by colloidal particles. *Adv. Colloid Interface Sci.* **2003**, *100*, 503–546. [[CrossRef](#)]
77. Braisch, B.; Köhler, K.; Schuchmann, H.P.; Wolf, B. Preparation and Flow Behaviour of Oil-In-Water Emulsions Stabilised by Hydrophilic Silica Particles. *Chem. Eng. Technol.* **2009**, *32*, 1107–1112. [[CrossRef](#)]
78. Walstra, P.; Geurts, T.J.; Noomen, A.; Jellema, A.; van Boekel, A.J.S. *Dairy Technology: Principles of Milk Properties and Processes*; CRC Press: Boca Raton, FL, USA, 1999.
79. Schlender, M.; Köhler, K.; Schuchmann, H.P. Neue Technologie ermöglicht Energieeinsparungen beim Hochdruckhomogenisieren. *Rundsch. Fleischhygiene Lebensmittelüberwachung* **2014**, *66*, 10–12.
80. Abramov, S.; Ruppik, P.; Schuchmann, H. Crystallization in Emulsions: A Thermo-Optical Method to Determine Single Crystallization Events in Droplet Clusters. *Processes* **2016**, *4*, 25. [[CrossRef](#)]
81. Schuchmann, H.P.; Köhler, K. Verfahren zur Herstellung einer Dispersion und Vorrichtung Hierzu. Patent DE102009009060 B3, 12 May 2010.
82. Runde, M. Oral correspondence: Mixolutions engineering, Frankfurt, **2016**.



© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).