

## EMULSION TECHNOLOGY – IMPLICATIONS IN PROCESSES AND PRODUCTS

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### 1 Emulsion and emulsification basics

#### 1.1 Emulsions

Emulsions are part of the product range in the chemical or petrol industry, as well as in the pharmaceutical, cosmetic and food industries. An emulsion is a disperse system of at least two immiscible liquids, e.g. water and oil (see Figure 1). One of these phases is finely dispersed and forms droplets in the other one. Depending on the droplet phase, oil-in-water- (o/w-) type and water-in-oil- (w/o-) type emulsions exist. In rare cases, the droplet phase itself is an emulsion. This contribution will concentrate on the simple emulsion type, consisting of two liquids, only.

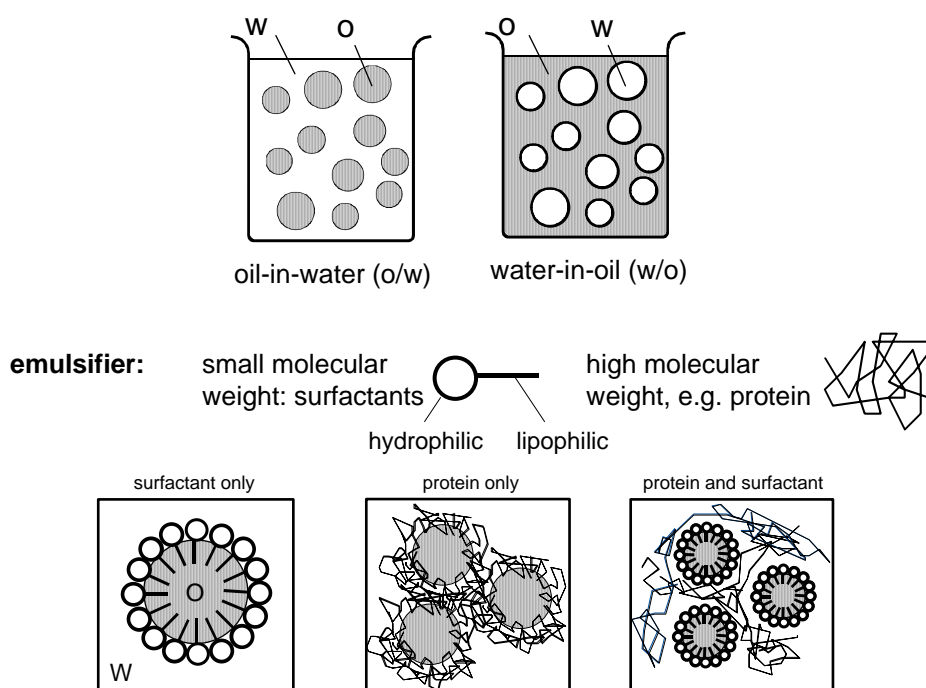


Figure 1 Emulsions: basic structure.

These systems are thermodynamically unstable [1]. If not stabilized, the droplets tend to flocculate and coalesce, or sediment and cream, respectively. Other instabilities, such as Ostwald ripening or phase inversion, are known as well. At worst, an emulsion will break, i.e. the two phases will separate completely. A product becoming unstable will lose its quality within a short period of time and thus, cannot be commercialized.

In industry natural and artificial emulsifiers and thickeners are added. Emulsifiers are amphiphilic molecules that adsorb at the droplets' interfaces (see Figure 1), thus stabilizing them against flocculation and coalescence. Small-molecule surfactants (in food industry e.g. fatty acids or their esters, as e.g. Tweens), as well as high molecular weight emulsifiers (e.g. polymers or proteins) are used. Depending on the molecular structure of an emulsifier, different adsorption mechanisms are found, both depicted in Fig. 1. Besides stabilizing an emulsion, the emulsifier often influences product properties, such as its viscosity.

Thickeners are high-molecular weight molecules that are solved in the continuous phase, thus, enhancing its viscosity. They stabilize emulsions by slowing down droplet mobility. Flocculation, sedimentation or creaming, and coalescence are either slowed down or inhibited at all. Since they increase continuous phase viscosity, they do not only stabilize the emulsion, but also change its properties.

## 1.2 Industrial emulsification

In order to produce emulsions, several processes may be applied. Most often, droplets are formed and disintegrated mechanically. Besides, emulsions may also be formed by e.g. precipitation. However, non-mechanical methods are rarely used in industrial production (see Fig. 2).

**Rotor-stator-machines** consist of a rotating and a fixed machine part. Hundreds of different rotor and stator geometries are available on the market [2]. The simplest rotor-stator-machine is a vessel with a stirrer, which is used to produce emulsions batch-wise or quasi-continuously. A stirred vessel has several advantages in emulsification: In a vessel, different process steps (as e.g. heating, or cooling) can be combined with the emulsification step. Stirred vessels are widely used in industry, although there are some drawbacks. In stirred vessels, the power density is low, and broadly distributed. Therefore, a long residence time and thus, emulsification time is required, often resulting in broad droplet size distributions. Small mean droplet diameters (as e.g.  $< 1 \mu\text{m}$ ) can rarely be produced in stirred vessels. If processes are driven at higher temperatures (e.g. to lower viscosities or to melt ingredients), undesired by-products may be formed.

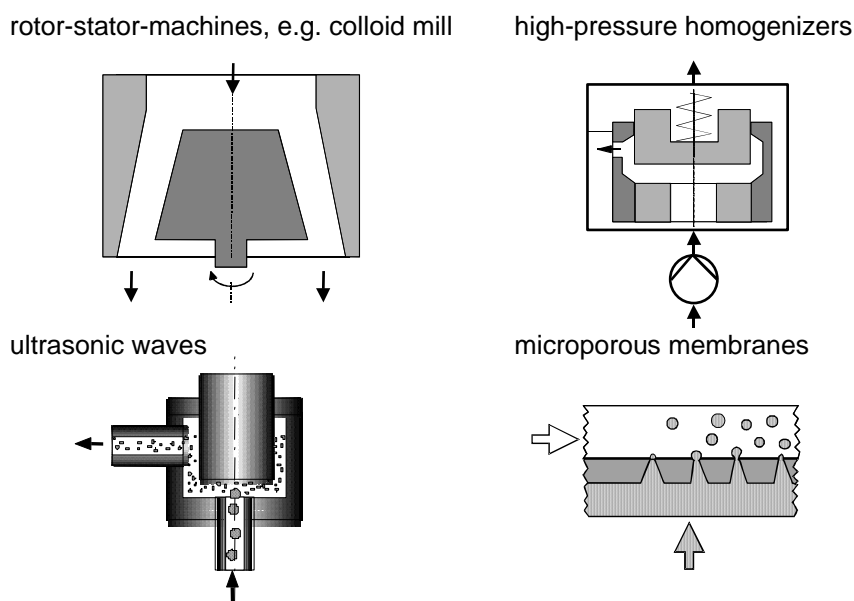


Figure 2 Emulsification machines (mechanical emulsification).

In order to solve these problems, the disruption zone has to be small and well defined, and the power density should be increased. This is realized in continuously working rotor-stator-machines, such as colloid mills, or toothed discs dispersing machines. In a colloid mill, the rotating part is a truncated cone, most often toothed. It rotates within a stator, also toothed. In toothed discs dispersing machines, rotor and stator consist of one or several discs having pins or teeth of different design. Rotor-stator-machines are relatively easy to handle and of low cost. They can be operated at throughputs from about 50 l/hr to several tons per hour. Droplet disruption is mainly due to turbulent flow within the dispersing zone between rotor and stator [2].

**High-pressure homogenizers** are traditionally used in milk industry. These machines are operated continuously at throughputs from 1 to several 1000 l/hr. They consist essentially of a high-pressure pump, and a homogenizing nozzle. The high pressure pump creates the energy, which is then used by the nozzle to disintegrate the droplet phase. The design of the homogenizing nozzle influences the flow pattern of the emulsion in the nozzle and hence the results of droplet disruption [3]. Recent developments in high-pressure homogenizing concentrate therefore on nozzle design. Examples of new homogenizing nozzles are opposing jets (Microfluidizer® [4]), jet disperser [5], and a simple orifice valve [6]. Droplet disruption in high pressure homogenizers predominantly is due to inertial forces in turbulent flow and shear forces in laminar elongational flow [3]; cavitation may also be found [7].

The trend in emulsification is to produce emulsions of very fine droplets ( $< 1 \mu\text{m}$ ) and narrow size distributions at low energy input. Continuous emulsification using ultrasonic waves, microporous membranes, and micro-channel systems are to be mentioned in this context.

In emulsification by means of **ultrasonic waves** (waves of frequency > 18 kHz), droplets are disrupted in zones of locally high turbulence caused by sound-induced cavitation. A batch-wise operation of a small scale is well known for laboratory applications whenever fine droplets are required in low viscous systems [1]. New publications now demonstrate the possibility to produce finely dispersed emulsions by means of ultrasonic waves continuously, as well [8,9]. Continuous applications require a flow chamber of special design into which the ultrasound waves are introduced. Due to the limited power of sound inducers, there are technical limits for very high tonnages (e.g. > 1000 l/hr).

Droplet disintegration usually is done by tensions acting on droplet interfaces via the continuous phase. In order to produce the required flow pattern in the continuous phase, high energy has to be applied. Only a negligible part of the energy (< 1 %) is used for droplet disintegration, while most of the energy is transferred into heat. It is therefore more efficient to produce droplets of the required size directly by a droplet forming process. This could be realized e.g. by pressing the future droplet phase through pores of small diameter and dispersing the droplets into the continuous phase. Industrially, this can be realized by using micro-porous membranes [10,11]. In **membrane emulsification**, the process starts at a disperse phase content of zero. During the process, the disperse phase content is then enhanced to the required value by pressing more disperse phase through the membrane pores. This is realized by recirculation of the emulsion. Recirculation, in turn, decreases energy efficiency. Alternatively, pre-emulsions may be pressed through the membrane pores [12], and phase inversion during membrane emulsification may be induced [13]. Thus, high quantities of emulsions (several tons per m<sup>2</sup> of membrane surface and hour) having a high disperse phase content (e.g. 50-80 %) may be produced by a single pass through the membrane. Membrane emulsification is reported as to produce small droplets (< 3 μm) at a very narrow droplet size distribution and low energy input [10,12]. Investment and manufacturing costs are less than for high-pressure homogenizing [11]. By **micro-channeling** [14], emulsions of extremely narrow droplet size distributions may be produced. However, this process being under development is far from industrialization until now.

### 1.3 Product design in emulsification

By controlling emulsification processes and their process parameters the droplet size of an emulsion can be adjusted to the desired value. This parameter itself offers a good possibility to influence rheological and sensorial quality parameters, such as viscosity, creaminess or mouth-feel, even if the recipe is already given by raw material or legislative restrictions.

In product design, target product properties (as viscosity or creaminess) are defined by e.g. marketing. Product engineers have then to determine the micro-structure (here: mean droplet size) being responsible for these target properties (property function) which in turn has to be realized by an emulsification process. Process engineers will then choose the necessary equipment and design the process according to the process functions.

## 2 Process functions in emulsification

### 2.1 Droplet disruption – Process design based on process functions

Emulsification results are usually given as a mean droplet diameter in dependency of a chosen machine type, and one or more selected process parameters (such as rotor speed), and/or machine parameters (e.g. dispersing zone design) for a selected recipe/formula. Even, if only one product formula has to be produced, hundreds of these diagrams have to be generated before being able to design and optimize the process, and to scale it up.

In order to evaluate the effectivity of droplet disruption independently of machine type and process parameters, the volumetric specific energy  $E_v$  was proposed by Karbstein [2]:

$$E_v = \frac{E}{V} = \frac{P}{\dot{V}} = \Delta p_h = \bar{P}_V \cdot \bar{t}_{res} = \frac{P}{V} \cdot \bar{t}_{res} \quad (1)$$

Herein, E is the energy and P the power applied by the machine, V the emulsion volume,  $\dot{V}$  the volume flow rate of the emulsion,  $\Delta p_h$  the homogenizing pressure (in case a high-pressure homogenizer is used),  $\bar{P}_V$  the mean volume power density of the machine, and  $\bar{t}_{res}$  the mean residence time of the emulsion within the dispersing zone of the machine.

Using the specific energy for continuous processes as well as the power density for batch processes, process functions can be defined for emulsification (eqn (2) to (6)). For each formula, the proportional constants, as well as the exact exponents can then be determined by generating one diagram per formula on lab scale only.

Emulsification mainly due to turbulent flow – continuous processes (rotor-stator-machines, ultrasonic emulsification):

$$\bar{x} \propto E_v^{-0.25 \dots 0.4} \cdot \eta_d^{0 \dots 0.75} \quad (2)$$

Emulsification in laminar flow (mainly lab scale constructions):

$$\bar{x} \propto E_v^{-1} \quad (3)$$

High pressure homogenizing (depending on nozzle design turbulent and laminar flow patterns superposing):

$$\bar{x} \propto E_v^{-0.25 \dots 1} \cdot \eta_d^{0 \dots 0.75} \quad (4)$$

Emulsification in turbulent flow – batch processes (stirred vessel):

$$\bar{x} \propto P_v^{-0.25 \dots -0.4} \cdot f(t_{res}) \cdot \eta_d^{0 \dots 0.75} \quad (5)$$

$$\text{with } f(t_{res}) = k \cdot e^{-bt_{res}} + \bar{x}_{t_{res} \rightarrow \infty} \quad (6)$$

Herein,  $k$  and  $b$  are constants, and  $\bar{x}_{t_{res} \rightarrow \infty}$  is the equilibrium mean droplet diameter which is found for  $t_{res} \rightarrow \infty$ .

Figure 3 gives mean droplet diameters for emulsions of 30 % of rape seed oil in water as a function of specific energy. The emulsions were stabilized using a very fast adsorbing surfactant (a lauryl alcohol, LEO-10), that allows to have a low re-coalescence rate. Thus, disruption governs the process of emulsification. This diagram allows comparing disruption results, depicting areas of application for the different emulsification machines. It thus is the basis for process design.

Using continuous rotor-stator machines or a high-pressure homogenizer with a standard flat nozzle results in relatively large mean droplet diameters. If smaller droplet diameters are required, machines have to be used that induce other flow patterns as well, e.g. laminar elongational flow or cavitation. In commercial emulsification machines, this is realized in high-pressure homogenizers with e.g. the opposing jet nozzle such as Microfluidizer®, or the simple orifice valve, or by sound-induced cavitation (ultrasonic emulsification). In the simple orifice valve, for example, droplets are deformed mainly by laminar elongational flow, destabilized, and thus easy to disrupt by the following turbulent flow conditions [3,15]. This nozzle design is very efficient in droplet disruption, especially if high viscous phases have to be finely dispersed [6]. Similar results are found for the jet disperser [5,6]. Emulsification mainly due to cavitation (continuous ultrasonic emulsification) results in droplet sizes comparable to those of effective high-pressure homogenizers.

In comparison to droplet disrupting machines, membrane emulsification is very efficient, if small droplets ( $x < 3 \mu\text{m}$ ) have to be produced [10]. However, the higher the disperse phase content, the more specific energy has to be applied, since recirculation of the emulsion is required to concentrate the dispersed phase. Using pre-emulsions bypasses these processing problems [12]. Emulsification by membranes results in very steep droplet size distributions, if the membrane surface is not wetting the future continuous phase (small wetting angle). E.g. in order to produce oil droplets the membrane surface material has to be hydrophilic [11,16].

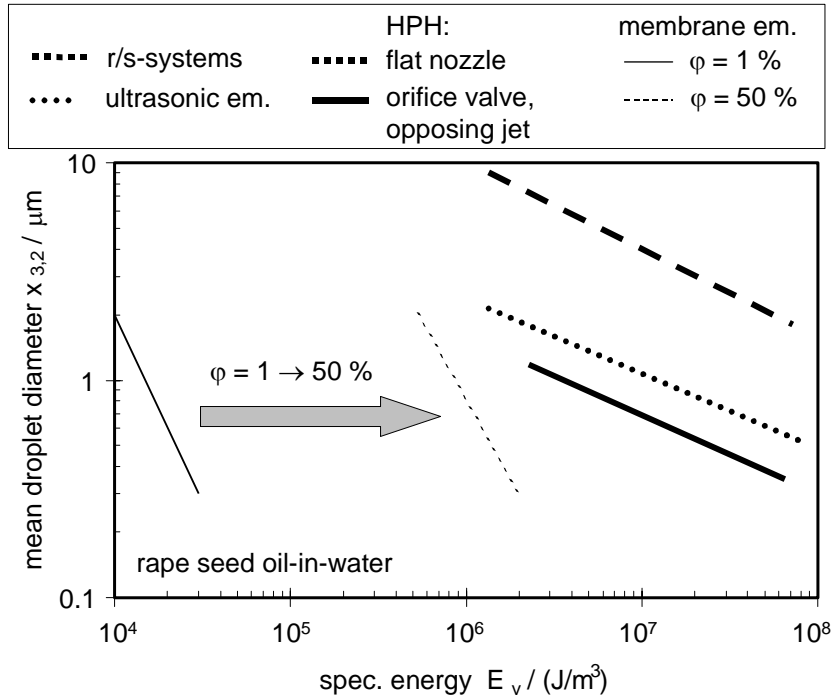


Figure 3 Process functions for droplet disruption by different emulsification processes (values from [2,6,11]).

## 2.2 Coalescence

### 2.2.1 Theory of droplet coalescence

In emulsification, droplets are disrupted. However, they rarely exist for long due to re-coalescence. This takes place within milliseconds after disruption and is found in practically every emulsification process [17,18]. This is due to the fact, that new droplets are not sufficiently stabilized directly after their disruption (either by adsorbing emulsifier molecules or by hydrodynamic effects). Emulsification processes are thus governed by both, droplet disruption and re-coalescence of droplets [2]. Only if the droplet stabilization is very fast, and if the droplet concentration is very low, re-coalescence rates are low enough for droplet disruption to govern the emulsification process.

The effect of re-coalescence is well described in literature [summarized in 17]. A short insight will be given here, only. The number of droplet collisions (collision frequency  $c$ ) depends on several parameters and may be calculated for turbulent flow according to [19]:

$$c = K \cdot u \cdot x^2 \cdot n^2 \quad (7)$$

with

$$K = \sqrt{2\pi/15} \quad (8)$$

$$u = \sqrt{\varepsilon/\nu_d} \cdot x \quad (9)$$

Herein,  $K$  is the collision coefficient,  $u$  the droplet velocity,  $x$  the droplet diameter,  $n$  the number of droplets per volume emulsion,  $\varepsilon$  the mass-specific power density, and  $\nu_d$  the kinematic viscosity of the droplet phase. The coalescence probability of colliding droplets usually is smaller than 1. An easy experimental method based on image analysis allows to determine the coalescence probability  $p_{\text{coal}}$  and the coalescence rate  $\Omega$  for different emulsion formulas [17]:

$$\Omega = p_{\text{coal}} \cdot c \quad (10)$$

Coalescence is found, whenever droplets are disrupted. In rotor-stator-machines, droplets are disrupted at relatively low power densities ( $P_v \approx 10^4 \dots 10^9 \text{ W/m}^3$ ) and long residence times ( $t_{\text{res}} \approx 0,1 \dots 1 \text{ s}$ ). The number of disrupted droplets is relatively low, and time is given to stabilization. Thus, the coalescence probability is relatively low. In high-pressure homogenizers or in continuously working ultrasonic devices, however, the power density is higher ( $P_v \approx 10^8 \dots 10^{12} \text{ W/m}^3$ ), whereas the mean residence time is shorter ( $t_{\text{res}} \approx 0,001 \dots 0,01 \text{ s}$ ). Many small droplets are formed in a time being too short for stabilization. In addition, the forces in droplet collision are higher, leading to a higher coalescence probability. At a constant specific energy, the coalescence rate therefore is higher than in rotor-stator-machines.

### 2.2.2 Experimental determination of droplet coalescence

If the re-coalescence rate is high, the emulsification result in total is changed [2,17]. The mean droplet diameter achievable at a given specific energy increases. The negative slope of the line in the diagram  $x_{3,2} = f(E_v)$  decreases. For high re-coalescence rates, even an increase in mean droplet diameter is found for increasing specific energy.

Coalescence and so the ability of emulsifiers can be determined with the coloring method [17].

Insufficiently stabilized droplets can coalesce in the emulsification zone due to mutual contact. For a design and description of an emulsifying process as well as for the selection of emulsifiers is the determination of coalescence desirable. Often the coalescence is only examined by changes in the particle size distribution of the emulsion.

With the coloring method [17] it is possible to determine the coalescence process during the emulsification step under real conditions. For this new analyzing method two differently dyed premixes were prepared. They are mixed and then the treatment in an homogenizing device starts, s. Fig. 4. If coalescence during emulsification occurs, mixed colored droplets will exist. The amount of mixed-colored droplets is a quantitative indicator for the degree of coalescence in the actual system. The less mixed-colored droplets exist, the better are the stabilizing properties of the emulsifier is.

The coloring method allows a differentiated analysis of the coalescence process separated from the break-up of the droplets.

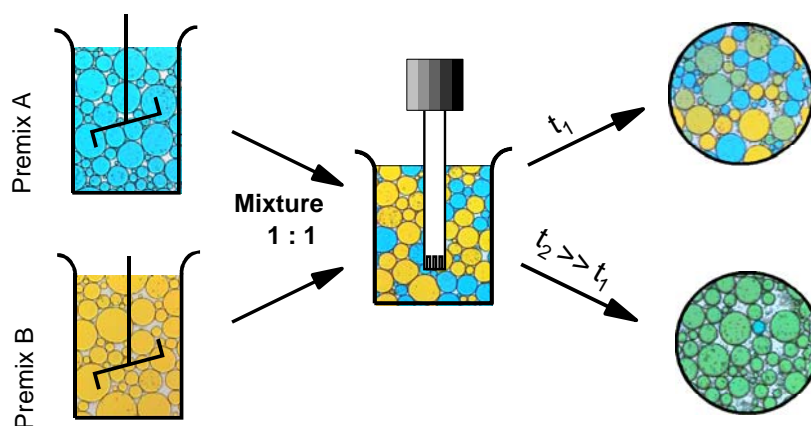


Figure. 4 Coloring method for the determination of coalescence of droplets in emulsions.

Using the coloring method, it is possible to compare the suitability of emulsifiers under real processing conditions. In Fig. 5 two emulsifiers (Tween 80 and salted egg yolk) are compared in regard to their stabilizing properties. It is obvious that Tween 80 stabilizes the droplets better than the egg yolk. With the determination of a coalescence property, a coalescence rate can be determined.

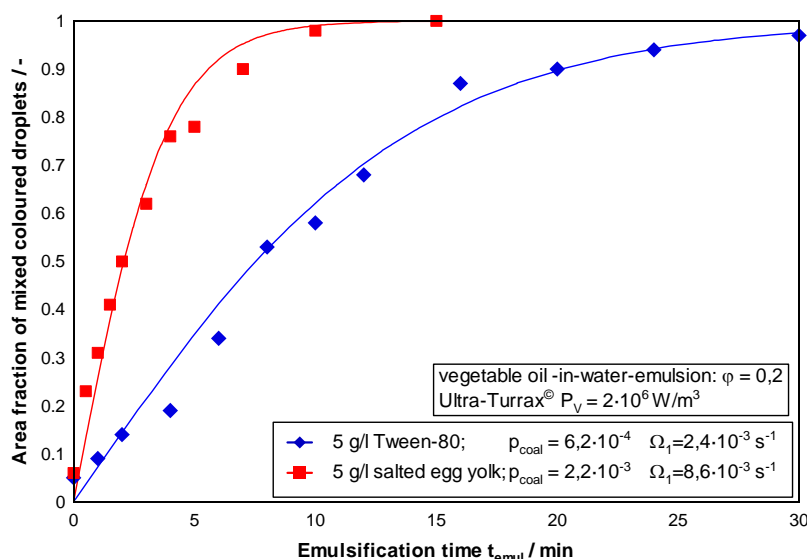


Figure 5 Comparison of the stabilizing properties of different emulsifiers.

### 2.3 Scale up

After having designed and optimized the process, it has to be scaled up for industrialization. The process functions given in chapter 2.1 based on specific energy may also be used for scale up.

For rotor-stator-machines, only one process function per recipe exists. Figure 6 gives an example for the production of a salad cream type emulsion, which is produced in a colloid mill. The process function does not change by going from pilot plant scale to production scale. In order to get the same product quality (i.e. the same mean droplet diameter), the specific energy has to be kept constant. One may even change machine or process parameters, such as teeth design or rotor speed, as long as the specific energy is kept at a constant level.

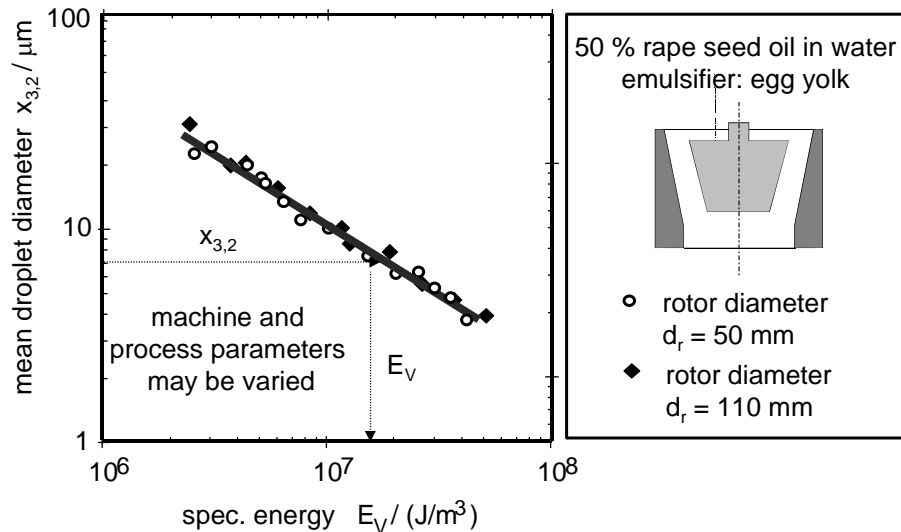


Figure 6 Scale up using the specific energy for an emulsion.

In high-pressure homogenizers, the process function constants are determined by the flow conditions within the nozzle. During scaling up, the flow conditions thus may not be changed. It therefore is recommended to keep the pilot nozzle design and enlarge the number of nozzles according to the throughput. In continuous ultrasonic emulsification, sound inducers of high capacities are rarely found on the market. In addition, the problem of designing a flow chamber will increase with increasing throughput. Thus, it is recommended to work with an increased number of parallel working ultrasonic devices for scale up [8]. In membrane emulsification scale up is done by keeping the membrane material and enlarging the membrane surface according to the required throughput [10]. The specific energy, i.e. the continuous phase wall stress plus the trans-membrane pressure difference have then to be kept constant.

## 3 Applications: Melt Emulsification

### 3.1 Industrial standard in production

Solids, which have to be comminuted to particle sizes in the range of 1  $\mu\text{m}$  are often treated with wet grinding methods (e.g. stirred ball mills). This conventional processing step requires high energy input and long residence times. AS for emulsions, a tailor-made adjustment of the particle size distribution is important since the particle size determines the consistency, rheological properties, storage stability and the color of the dispersion. An alternative to conventional comminuting of fusible, ductile particles is to emulsify them in molten state ('melt emulsification').

### 3.2 Melt Emulsification

#### 3.2.1 Principles

The principle of melt-emulsification is shown in fig. 7. A solid, which has to be comminuted, is heated above its melting point. The liquid melt is emulsified with the continuous phase, in the majority of cases with water. The continuous water phase contains an emulsifier, which is capable of stabilizing the droplets of the melt in the aqueous phase. After adjusting the desired particle size distribution the finely dispersed emulsion is cooled under the melting point of the dispersed phase, obtaining a suspension.

Alternatively, a suspension of solids can be used instead of pure solids. It is heated above the melting point of the solids, then emulsified and again recooled below the melting point.

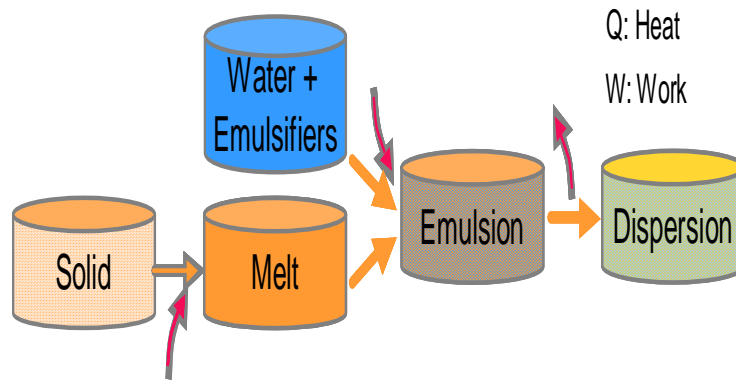


Figure. 7 Principle scheme of melt emulsification.

### 3.3 Properties of melt-emulsification

The melt-emulsification as a formulation step for many industrial applications provides many advantages.

Many different raw materials can be formulated with the melt-emulsification. The materials have to have a softening point or a melting point. At these temperatures the viscosities of the solids decrease either by phase transition or by softening. The dynamic viscosity of the melt should be lower than approx. 10 Pa·s. That means a lot of e.g. polymeric materials can be considered for melt-emulsification.

Substances with viscoelastic behavior, e.g. polymers, which are difficult to comminute to small particles can be formed by melt-emulsification.

Also, the processing from a bulky raw material to a finely dispersed and formulated dispersion can be performed by melt-emulsification in one single step. All additives, like dispersing agents, rheological controllers, etc. can be added either in the continuous or the dispersed phase.

Further on, the interface of the particles is functionalized with the emulsifier. Often, the particles in industrial applications are needed as dispersions. With the melt emulsification the dispersing step, the addition of suitable dispersing agents can be avoided.

The processing times are substantially shorter compared to the wet grinding in a stirred ball mill.

The emulsification of the melt leads necessarily to spherical droplets. In contrast to conventional milling (e.g. with stirred ball mills), beside the particle size distribution the particle shape can also be modified.

On account of the smaller and spherical particles new product properties can be designed.

### 3.4 Droplet break-up

Different emulsification apparatus can be used for the break-up of the melt droplets. The catchiest challenge is the disruption of highly viscous droplets to narrow distributed particle size distributions. The homogenization of highly viscous materials can only be achieved using elongational flow pattern inside the emulsifying device. Specially designed homogenizing devices have to be used to achieve the desired product properties.

The homogenization should take place in one step, rendering unnecessary residence time in the high temperature regime. Therefore, thermal degradation of the products can be avoided. Thus, a lot of engineering know-how is needed to fulfill these requirements. In practice, specially designed rotor/stator-systems as well as modified high-pressure homogenizers are coming into operation.

### 3.5 Stabilization

In the production of emulsions besides the disruption the stabilization of the newly created droplets plays an important role. The interaction between these two processes determines the final particle size and the particle size distribution of the emulsion resp. the dispersion.

For the stabilization detailed knowledge of interfacial phenomena of the products is needed. If an emulsion is produced, using an emulsifier with slow stabilizing properties, the droplets can coalesce immediately after disruption.

In the melt-emulsification unit the processes are even more complex.



## 5 Symbols used

c	collision frequency	$s^{-1} \cdot m^{-3}$
d	droplet diameter	m
E	energy	J
$E_V$	volumetric specific energy	$J \cdot m^{-3}$
K	collision coefficient	-
n	number of droplets per volume	$m^{-3}$
P	power	W
$P_V$	volumetric power density	$W \cdot m^{-3}$
$p_{coal}$	coalescence probability	-
$\Delta p_h$	homogenizing pressure	Pa
u	droplet velocity	$m \cdot s^{-1}$
V	volume	$m^3$
$\dot{V}$	volume flow rate	$m^3 \cdot s^{-1}$
$t_{res}$	residence time	s
x	droplet diameter	m
$x_{3,2}$	mean droplet diameter (Sauter diameter)	m
$\varepsilon$	mass specific power density	$m^2 \cdot s^{-3}$
$\varphi$	disperse phase content	-
$\eta_c$	dynamic viscosity of continuous phase	Pa·s
$\eta_d$	dynamic viscosity of disperse phase	Pa·s
$\eta_e$	dynamic viscosity of the emulsion	Pa·s
$\nu_d$	kinematic droplet viscosity	$m^2 \cdot s^{-1}$
$\Omega$	coalescence rate	$s^{-1} \cdot m^{-3}$

## 6 Literature

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- 1 P. Walstra, in *Encyclopedia of emulsion technology* (Ed: P. Becher), Vol. 1, Marcel Dekker Inc., New York, **1983**, 57-127.
  - 2 H. Karbstein, *Dr.-Ing. Dissertation*, Karlsruhe University **1994**.
  - 3 M. Stang, H.P. Schuchmann, H. Schubert, *Eng. Life. Sci.* **2001**, 1, 151-157.
  - 4 U.S. Patent 4 533 254
  - 5 W. Hovestad, B. Klinksieck, M. Melchior, *Farbe & Lack* **7**, **2000**, 40-44.
  - 6 M. Stang, *Dr.-Ing. Dissertation*, Karlsruhe University **1998**.
  - 7 A. Treiber, *Dr.-Ing. Dissertation*, Karlsruhe University **1979**.
  - 8 O. Behrend, H. Schubert, *Ultrasonics Sonochemistry* **8**, **2001**, 271-276.
  - 9 S. Bechtel, N. Gilbert, H.G. Wagner, part 1, *Chem. Ing. Tech.*, **71**, **1999**, 8, 810-817; part 2: *Chem. Ing. Tech.*, **72**, **2000**, 5, 450-457.
  - 10 T. Nakashima, *Nippon Shokuhin Kogyo Gakkaishi* **41**, **1994** 1, 70-76.
  - 11 V. Schröder, *Dr.-Ing. Dissertation*, Karlsruhe University **1999**.
  - 12 K. Suzuki, I. Fujiki, Y. Hagura, *Food Sci. Technol. Int. Tokyo*, **4**, **1998**, 2, 164-167.
  - 13 K. Suzuki, K. Hayakawa, Y. Hagura, *Food Sci. Technol. Res.* **5**, **1999**, 2, 234-238.
  - 14 T. Kawakatsu, Y. Kikuchi, M. Nakajima, *JAOCs* **74**, **1997**, 3, 317-321.
  - 15 G. Kolb, *Dr.-Ing. Dissertation*, University Halle-Wittenberg **2001**.
  - 16 G.T. Vladisavljevic, S. Brösel, H. Schubert, *Chem. Papers* **54** (6a), **2000**, 282-288.
  - 17 T. Danner, *Dr.-Ing. Dissertation*, Karlsruhe University **2001**.
  - 18 T. Danner, H. Schubert, in *Proc. Int. Congr. Particle Techn. PARTEC 2001*, 06/080, Nuremberg **2001**.
  - 19 A.K. Chesters in *Trans IChemE*, Vol 69, Part A, July **1991**, 259-270.