Premix Emulsification Systems

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This research was conducted under the auspices of the Graduate School VLAG (Advanced studies in Food Technology, Agrobiotechnology, Nutrition and Health Sciences).
Premix Emulsification Systems

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Thesis
submitted in fulfilment of the requirements for the degree of doctor
at Wageningen University
by the authority of the Rector Magnificus
Prof. dr. M.J. Kropff,
in the presence of the
Thesis Committee appointed by the Academic Board
to be defended in public
on Monday 18 March 2013
at 4 p.m. in the Aula.
Akmal Nazir
Premix Emulsification Systems
151 pages

## Contents

**Chapter 1**  
Introduction  

**Chapter 2**  
Premix emulsification: a review  

**Chapter 3**  
High-throughput premix membrane emulsification using nickel sieves having straight-through pores  

**Chapter 4**  
The effect of pore geometry on premix membrane emulsification using nickel sieves having uniform pores  

**Chapter 5**  
Droplet break-up mechanism in premix emulsification using packed beds  

**Chapter 6**  
Influence of the emulsion formulation in premix emulsification using packed beds  

**Chapter 7**  
Discussion and future prospects  

**Summary**  

**Notation**  

**Acknowledgement**  

**About the author**  

**List of publications**  

**Training activities**
CHAPTER 1

Introduction
A B S T R A C T

This chapter provides an introduction on emulsion formation together with an overview of various emulsification techniques and their underlying mechanisms. The aim and outline of this thesis are presented at the end of this chapter.
1.1. Emulsions

An emulsion is a dispersion of two (or more) immiscible liquids, such as oil and water. One liquid is present in the form of droplets (dispersed phase) into another liquid (continuous phase). Emulsions are widely used in various industries including food, cosmetics, pharmaceuticals, paints, agrochemicals, bitumen, etc [1]. The oil-in-water (O/W) emulsion is the most common form of emulsions and is also the subject of the current thesis.

As the liquids forming the emulsions are immiscible, an external energy is needed for creating droplets. The formation of droplets leads to an increase in the overall energy of the system, which is proportional to the interfacial area created:

\[ \Delta G = \int_0^A \sigma \, dA, \quad (1.1) \]

where \( \Delta G \) is the Gibbs energy needed to create the interfacial area \( A \) and \( \sigma \) is the interfacial tension. The energy required per m\(^2\) of interfacial area is the interfacial energy or interfacial tension, having units of N m\(^{-1}\) or J m\(^{-2}\). The interfacial tension of the interface of a droplet results in an inward force, which is dependent on the radius of curvature, \( R_d \), of a (spherical) droplet and is called the droplet Laplace pressure, \( \Delta P_{\text{Laplace}} \):

\[ \Delta P_{\text{Laplace}} = \frac{2\sigma}{R_d}, \quad (1.2) \]

Owing to a positive interfacial tension, most emulsions are thermodynamically unstable (with the exception of so-called micro-emulsions which are outside the scope of this thesis). In general, emulsion droplets have the tendency to coalesce to form bigger droplets. In the absence of stabilising components the density difference between both phases ultimately leads to phase separation, also known as demulsification.

For droplet stabilization, the presence of an energy barrier is of prime importance in an emulsification process. This is usually accomplished by the presence of surface-active molecules, known as emulsifiers or surfactants. These are amphiphilic molecules that adsorb at the interface, where they reduce the interfacial tension and also give rise to electrostatic or steric repulsion between
the droplets. Apart from promoting emulsion stability, the surfactants also facilitate the emulsification process by reducing the amount of energy needed for droplet disruption. Various components can be used for this ranging from low-molecular weight molecules (such as Tweens that are also used in this research) to naturally occurring emulsifiers such as proteins, or even particles in so-called Pickering emulsions.

1.2. Emulsification devices

A small droplet size can be achieved with some of the conventional emulsification devices. For example, in high-pressure homogenizers a droplet size of less than 0.2 μm can be realised [2], although, the resulting emulsions are rather polydispersed [3]. These machines exert high stress that is released as heat, and might cause cavitation after the homogenising valve, potentially damaging shear and heat sensitive constituents. To prevent these problems, microstructure-based systems could be more suitable as they are known for low energy input and better monodispersity. Below, first some characteristics of conventional emulsification systems are described, followed with those of microstructure-based systems (Fig. 1.1).

1.2.1. Conventional systems

For large scale production of emulsions, various emulsification devices are used, e.g., rotor-stator systems and high-pressure homogenizers. A stirred vessel is the simplest form of a rotor-stator system, operating at low energy input per unit volume, and only suitable for making coarse emulsions. A colloidal mill is an example of a continuous high energy input rotor-stator system where droplet break-up takes place in a conical gap between rotor and stator that are available in various designs [2]. The effective droplet disruption is carried out mainly by shear and inertial forces in turbulent flow. High-pressure homogenizers, consisting of a high-pressure pump and a homogenizing nozzle, are the most important (continuously operated) emulsifying devices used in industry to produce finely dispersed emulsions [4]. Various designs are possible, e.g., standard nozzle, Microfluidizer, jet disperser, and orifice valve, etc., each having a specific droplet break-up mechanism [4].
Fig. 1.1 Schematic representation of some emulsification devices: (a) stirred vessel, (b) rotor-stator system, (c) high-pressure homogenizer, (d) ultrasonic homogenizer, (e) cross-flow membrane emulsification, (f) premix membrane emulsification, (g) T-junction and (h) microchannel emulsification.

A static mixer consists of a series of specially designed stationary elements placed transversely in a tube forming crossed channels that promote the distribution and longitudinal recombination of the liquid over different channels [5]. Static mixers
have been employed for the production of dispersions in laminar to turbulent flow. Besides, also ultrasonic systems have been used for making emulsions where sound energy causes cavitation and turbulence locally, however, this technology is only suitable for smaller scale production of emulsions.

1.2.2. Microstructured systems

During the last two decades extensive research has been carried out on microstructured emulsification systems. These systems exert much less stress on the product, and are very energy efficient, e.g., membrane [6], microchannel [7] and various microfluidic [8] emulsification systems. In a typical membrane emulsification process the to-be-dispersed phase is pushed through the membrane pores, which results in droplet formation on the other side of the membrane in contact with the cross-flowing [9] or stirred continuous phase [10]. Various microfluidic devices also use shear forces to produce droplets, e.g., T-[11, 12], Y-[13] and cross junctions [14], co-flow [15] and flow focussing devices [16, 17]. In spontaneous emulsification devices such as grooved [18] and straight-through [19] microchannels, the droplets detach spontaneously due to Laplace pressure differences. Mostly, a single droplet is formed from a single droplet forming unit, however, in edge-based droplet generation (EDGE) devices multiple droplets are generated simultaneously from a single droplet forming unit [20]. More information on emulsification with microstructured systems is available in a comprehensive review recently carried out by Vladisavljevic et al. [21]. In general, microstructured systems ensure a high droplet monodispersity; typical coefficients of variation are less than 5% [22, 23]. However, up-scaling is still a major challenge towards commercialization of these systems.

In premix membrane emulsification, a coarse emulsion (premix) is passed under mild pressure through a membrane to get a fine emulsion, hence, the process can also be regarded as low-pressure homogenization. The droplet disruption results from shear and (or) inertial forces; the relative magnitude of each force may vary in different systems. Although the droplets are not as monodispersed as produced by the more sophisticated microstructured systems discussed above, the production rates are orders of magnitude higher, which makes the technique much
more suited for industrial production of emulsions with reasonable monodispersity.

The major problem in premix membrane emulsification is that the whole emulsion has to pass the membrane and this makes the membrane more or less susceptible to depth fouling, depending on the components that are used. This is especially a problem when proteins, polysaccharides, lecithin or other more complex emulsifiers are used. In tandem with this, the inaccessibility of the membrane pores to cleaning agents adds to this problem. Better defined membranes will certainly help to reduce this problem, while the use of membranes that are accessible for cleaning would allow better flux regeneration of the membrane.

A few years ago Van der Zwan et al. proposed an adapted system, in which the emulsification is realised in a layer of small particles deposited on a carrier [24]. The interstitial voids between the particles act as the pores in a membrane. As soon as these pores become clogged, the layer of particles can be removed, and the particle suspension can be cleaned or replaced before re-depositing it on the carrier. Although various aspects have been investigated for this system, it is not yet clear what the limiting aspects are. For example, it is not clear what the influence is of the carrier membrane used for depositing the particle layer.

1.3. Thesis aim and scope

While premix membrane emulsification is a promising process, given its high throughputs, it is clear that internal fouling is the most important drawback. Thus, this thesis aims to better understand the fundamental limitations in this process, and to find a solution to this, by either reducing fouling by using well-defined membranes, or by making use of a dynamic membrane in the form of packed bed.

For the first option, custom-made metal membranes with various pore geometries were used. Given the well-defined geometry, without tortuous and branching pores, it was expected that these would be less sensitive to fouling. The second option employed a layer of glass beads on top of a well-defined metal membrane (carrier).
1.4. Thesis outline

Premix membrane emulsification is discussed in detail in Chapter 2. Its energy efficiency and required membrane area are compared with other emulsification techniques. The droplet break-up and effect of different process parameters are discussed. Finally, the application of premix emulsification in different areas is described.

In Chapter 3, premix membrane emulsification is discussed using nickel sieves having long rectangular straight-through pores. The influence of the pressure drop on the droplet size (and distribution) and flux is investigated, and scaling relations are proposed to relate the droplet size to the amount of required energy input.

Various nickel sieves having rectangular or squared pores are compared in Chapter 4, with special emphasis on the effect of the pore geometry on the droplet generation. The effects are characterised with dimensionless numbers.

The packed bed system for the production of emulsions is discussed in Chapter 5. The process parameters especially related to the internal structure of the porous media are investigated, and the droplet break-up as a result of changing porous structure is described.

In Chapter 6, the influence of a number of formulation parameters such as the dispersed phase fraction, the viscosities of dispersed and continuous phases, and the type and concentration of surfactant or stabiliser, is reported for the packed bed system. Scaling relations are established to relate process and product properties to the droplet size produced.

Chapter 7 summarizes the conclusions of the chapters in the thesis and provides a general discussion. The status of premix emulsification among other emulsification systems is reviewed with special emphasis to the findings of the current research. To make the technique more practical, a modified system named inline premix emulsification is proposed which was experimentally tested for the preparation of emulsions and foams using food ingredients.
References


Premix emulsification: a review

ABSTRACT

Membrane emulsification is known to be a mild technique that renders narrowly dispersed emulsions at energy inputs that are orders of magnitude lower than in traditional emulsification techniques. Cross-flow membrane emulsification is the most investigated and is known for the monodispersity of the emulsions produced; however, this can only be obtained at relatively low dispersed phase fraction. For emulsions with higher dispersed phase fraction, premix membrane emulsification is an interesting alternative that is in our opinion on the verge of breaking through.

Principally, in this mild process, a coarse premix is pushed through a porous membrane leading to a fine emulsion having smaller and uniform droplets, at the expense of relatively low energy input. The mean emulsion droplet size can precisely be tuned by adjusting the pore size, transmembrane pressure and the number of cycles. The process can be used for a range of applications, including shear sensitive products such as double emulsions. The present manuscript provides an overview covering the state of the art, including insights in break-up mechanisms and the preparation of various products, and an outlook on further improvement of the process.
2.1. Introduction

An emulsion is a mixture of two immiscible liquids, e.g., oil and water. Emulsions have applications in many industries like food, pharmaceutical, cosmetic, agriculture, petrochemical and other chemical industries [1]. An emulsion may be single, e.g., oil-in-water (O/W) and water-in-oil (W/O) emulsions, or it may be an emulsion of an emulsion, e.g., water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O) emulsions, also termed as double or multiple emulsions.

Many different methods for emulsification have been developed, mostly depending upon the product (and economical) requirements. Conventionally, the emulsions are prepared by mechanical disruption of the droplets of the dispersed phase into the continuous phase. Colloid mills, rotor-stator systems, high-pressure homogenizers and ultrasonic homogenizers are popular types of equipments due to their high throughput [2]. However, owing to high energy inputs, these systems apply shear and extensional stresses to the product that may cause loss of functional properties of heat and shear sensitive components [3]. In addition, they show poor control over droplet size and distribution [4, 5].

To overcome these problems, new methods for emulsification using microstructured systems like cross-flow membrane emulsification [6] and premix membrane emulsification [7] have received much attention. For simplicity reasons we will call these techniques cross-flow and premix emulsification from now on. Besides these two shear-based methods, also spontaneous emulsification devices have been reported, such as microchannel emulsification [8-10] and edge-based droplet generation (EDGE) emulsification [11], however, these technologies are still in the development phase and will not be discussed further in this review.

In cross-flow (or direct) emulsification, the emulsion is formed by pushing the to-be-dispersed phase through a membrane into the cross-flowing continuous phase. Ideally, droplet size can be controlled primarily by the choice of the membrane, the cross-flow velocity and the transmembrane pressure; typically, a factor of 2–5 is found between pore size and droplet size. Cross-flow emulsification has advantages such as low shear stresses, low energy requirement, uniform droplet size (which allow use of less surfactant) and ease of design and scale-out [12]. The
most commonly used membranes for oil-in-water emulsions are hydrophilic Shirasu porous glass (SPG) membranes [6], ceramic aluminium oxide ($\alpha$-Al$_2$O$_3$) membranes [13], $\alpha$-alumina- and zirconia-coated membranes [14], macroporous silica glass membranes [15], and micro fabricated metal membranes [16, 17]. Further, work has been done on silicon and silicon nitride microsieves [18-21]. For water-in-oil emulsions, polytetrafluoroethylene (PTFE) membranes [22-25], hydrophobized SPG membranes [22-25], hydrophobized micro fabricated metal membranes [16] and hydrophobized silicon nitride microsieves [26] have been used. A limitation in case of cross-flow emulsification is the low dispersed phase flux through the conventional membranes (like SPG or ceramic membranes which have a relatively high resistance), and therefore recirculation is often required to increase the amount of dispersed phase. In that case, interactions of forming droplets with droplets in the emulsion lead to a considerable polydispersity as was visualized by Abrahamse et al. for microsieves [18]. Further, the required membrane area is rather large, and this makes the technology too expensive for large-scale application. For ‘diluted’ specialty products that need to meet high quality standards, cross-flow emulsification is however an interesting technique to consider. Some of the cross-flow emulsification studies using SPG membranes are reviewed in Table 2.A.1 in Appendix 2.A of this chapter, showing emulsion characteristics under different operating conditions.

Contrary to cross-flow emulsification, premix emulsification can be used to produce emulsions with high dispersed phase fraction, albeit that the size of the droplets is not as monodisperse as for cross-flow emulsification. In its appearance, premix emulsification is a modified form of the classic emulsification systems, such as high-pressure homogenization. These also start with a coarse premix that is refined upon passage through the emulsification machine, while in premix emulsification, as introduced by Suzuki et al. [23], the premix emulsion is passed through a microporous membrane. In most cases, a membrane is used that is wetted by the continuous phase of the premix and the emulsion is broken up into smaller droplets. Sometimes the membrane is wetted by the dispersed phase, and in that case phase inversion can take place, leading to very high dispersed phase
volume fractions (Fig. 2.1). It has to be mentioned that phase inversion was found to be possible only for a limited number of products.

The energy costs for premix emulsification are relatively low, since no cross-flow is needed. The energy needed can be one order of magnitude lower than for cross-flow emulsification [27] for highly concentrated products. However, in general the desired emulsion cannot be produced in a single passage. Further homogenization by repetitive cycles, commonly termed as repeated or multi-stage premix emulsification, yields better control of droplet size and distribution [3], but at a corresponding increase of overall energy input. The drawback of premix emulsification is membrane fouling that may become serious depending on the formulation components [28], and related to that their interaction with the membrane and their ease of removal.

Fig. 2.1. Schematic representation of batch premix emulsification systems: (a) emulsion without phase inversion, (b) emulsion with phase inversion and (c) double emulsion.

When comparing various emulsification methods, the energy density, usually defined as energy input per unit volume of emulsion, is a useful parameter that enables comparison of emulsification efficiencies. In Fig. 2.2, the energy efficiency of premix emulsification using metal sieves having rectangular pores (pore dimension $10 \times 405 \, \mu m$, porosity 4%) [28] is compared with cross-flow emulsification using ceramic membranes (pore size 0.2 and 0.8 $\mu m$) and different conventional emulsification systems [4]. We can see that for cross-flow or premix emulsification less energy is required to produce small droplets compared to the
classic methods. In cross-flow emulsification, the energy is applied more efficiently than in premix emulsification, but it should be noted that the pore size of metal sieves is far from optimal for production of small droplets through premix emulsification, and it is expected that considerable improvement is possible here.

![Graph showing Sauter mean droplet diameter, $d_{32}$, as a function of energy density, $E_V$, for various emulsification devices.](image)

**Fig. 2.2.** Sauter mean droplet diameter, $d_{32}$, as a function of energy density, $E_V$, for various emulsification devices: (○) 1, (●) 5, (□) 10, (■) 20 and (◊) 50% cross-flow emulsification [4]; (×) 5% premix emulsification [28]; and (♦) orifice valve, (▲) flat valve homogenizer and (▲) Microfluidizer (all 30%) conventional systems [4].

Besides the energy efficiency, also the required membrane area is of great importance for membrane emulsification techniques. Fig. 2.3 shows a comparison between premix and cross-flow emulsification for the required membrane area as a function of transmembrane pressure, given a production of 20 m$^3$ hr$^{-1}$ of a 30% O/W emulsion. Please keep in mind that these are calculated values, based on the numbers shown in Table 2.1. In case of cross-flow emulsification, microsieves, although having a low porosity, show the lowest membrane area required [20]. This is due to the extremely low resistance of these sieves compared to other membranes. The low porosity of the microsieves was chosen to prevent any hindrance among the growing droplets that can result in a polydispersed emulsion.
The experiments for cross-flow and premix emulsification are not from the same study. There are essential differences mainly in the membrane pore size, which is in one case considerably higher and in one case comparable to that of the membranes used for cross-flow emulsification. Although this restricts the validity, we would like to stress the importance of trends that are observed in Fig. 2.3. In both premix studies, the required area is much more strongly related to the applied pressure than for cross-flow emulsification, and this could result in lower required areas when pressures are used that are comparable to those applied in cross-flow emulsification. For commercial production, of course, the cost and life span of the membranes and the cost of modules and additional equipment should be considered together with the required area, but these details are not readily available, and therefore we find the area an indicative starting point for any comparison.

Fig. 2.3. Membrane area, $A$, required to produce a 30% O/W emulsion at the rate of 20 m$^3$ hr$^{-1}$ as a function of transmembrane pressure, $\Delta P$: a comparison of cross-flow and premix emulsification (see Table 2.1 for further details used in the calculations).
Table 2.1

Data used for the calculations in Fig. 2.3.

<table>
<thead>
<tr>
<th>Code in Fig. 2.3</th>
<th>Emulsification process</th>
<th>Membrane</th>
<th>(d_p^a) (µm)</th>
<th>S.D. (b^c) (µm)</th>
<th>(\epsilon^c)</th>
<th>O/W emulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPG Premix</td>
<td>Premix [7]</td>
<td>SPG</td>
<td>2.4</td>
<td>-</td>
<td>0.5(d^d)</td>
<td>25% corn oil</td>
</tr>
<tr>
<td>PES</td>
<td>Premix [29]</td>
<td>Polyethersulfone</td>
<td>0.8</td>
<td>-</td>
<td>0.5(d^d)</td>
<td>30% sunflower oil</td>
</tr>
<tr>
<td>SPG CF</td>
<td>Cross-flow [20]</td>
<td>SPG</td>
<td>0.2</td>
<td>0</td>
<td>0.6</td>
<td>30% milk fat</td>
</tr>
<tr>
<td>Al₁</td>
<td>Cross-flow [20]</td>
<td>(\alpha)-Al₂O₃</td>
<td>0.2</td>
<td>0</td>
<td>0.35</td>
<td>30% milk fat</td>
</tr>
<tr>
<td>Al₂</td>
<td>Cross-flow [20]</td>
<td>(\alpha)-Al₂O₃</td>
<td>0.2</td>
<td>0.1</td>
<td>0.35</td>
<td>30% milk fat</td>
</tr>
<tr>
<td>Al₃</td>
<td>Cross-flow [20]</td>
<td>(\alpha)-Al₂O₃</td>
<td>0.2</td>
<td>0.25</td>
<td>0.35</td>
<td>30% milk fat</td>
</tr>
<tr>
<td>M₁</td>
<td>Cross-flow [20]</td>
<td>Microsieve</td>
<td>0.2</td>
<td>0</td>
<td>0.01(e^e)</td>
<td>30% milk fat</td>
</tr>
<tr>
<td>M₂</td>
<td>Cross-flow [20]</td>
<td>Microsieve</td>
<td>0.2</td>
<td>0</td>
<td>0.01(e^e)</td>
<td>30% milk fat</td>
</tr>
</tbody>
</table>

\(^a\) membrane pore diameter; \(^b\) standard deviation of the log-normal pore size distribution; \(^c\) membrane porosity; \(^d\) assumed; \(^e\) \(\epsilon = 0.25\pi(d_p/d_d)^2 = 8\times10^{-3} = 1\times10^{-2}\) assuming a square array of pores, where \(d_d\) = droplet diameter.

As is clear from Figs. 2.2 and 2.3, membrane emulsification holds a number of advantages over conventional emulsification technology. The simplicity of premix emulsification makes it an interesting option for large scale production of emulsions, although many aspects are still not (well) understood. Since its introduction, several investigations have been carried out concerning principles, process parameters, and application of premix membrane emulsification. The aim of the present chapter is to provide a review that covers all these explorations, and which provides an outlook on future prospects.

2.2. Emulsion characterization

As mentioned, premix emulsification begins with a coarse emulsion, which is then extruded/homogenized through a membrane under pressure to obtain a fine emulsion. The resulting emulsion is mostly characterized by the Sauter mean droplet diameter and the droplet size distribution (represented by droplet span), while, the productivity is related to the transmembrane flux.

The droplet size distributions are usually measured with laser light diffraction. The Sauter mean diameter, \(d_{32}\), is defined as the diameter of a spherical droplet having
the same area per unit volume, $S_V$, as that of the total collection of droplets in the emulsion:

$$d_{32} = \frac{6}{S_V} = \left( \sum_{i=1}^{k_s} \frac{V_i}{d_i} \right)^{-1},$$

(2.1)

where $V_i$ is the volume fraction of droplets in the $i^{th}$ range of sizes having mean diameter of $d_i$, and $k_s$ is the number of size ranges. The size distribution data can be used to calculate the droplet span, $\delta$, to indicate the width of size distribution:

$$\delta = \frac{d_{90} - d_{10}}{d_{50}},$$

(2.2)

where $d_x$ is the droplet diameter corresponding to $x\%$ volume on a cumulative droplet volume curve. If the droplet span is less than 0.4, the droplets can be considered to be monodispersed [30].

The transmembrane flux, $J$, is defined as:

$$J = \frac{\phi_V}{A},$$

(2.3)

where $\phi_V$ is the volumetric flow rate, and $A$ is the cross sectional area of the membrane. The actual velocity in the pores, which is related to local shear forces responsible for droplet break-up [31], is a function of the flux and the porosity of the membrane. The average wall shear stress, $\tau_w$, inside the membrane pores [27] can be defined as:

$$\tau_w = \frac{8\eta_c J \xi}{\varepsilon d_p},$$

(2.4)

where $\eta_c$ is the continuous phase viscosity and $\xi$, $\varepsilon$ and $d_p$ are the membrane tortuosity, porosity and pore diameter, respectively.

### 2.3. Break-up mechanisms

In general, it is assumed that shear forces are responsible for droplet break-up; however, it is far from clear how these forces operate, and how they can be related to design of a process. One may expect that more mechanisms operate simultaneously [27]. For example, Van der Zwan et al. [32] microscopically
visualized the droplet break-up mechanism in O/W premix emulsification using microfluidic devices and found three factors responsible for break-up.

### 2.3.1. Localized shear forces

Break-up due to the shear forces exerted on a droplet coming close to the tip of a channel branching, or due to divergent flow in both legs of a branching, e.g., Y- or T-shaped branching. Link et al. [33] also studied the droplet break-up in T-junctions, albeit for W/O emulsions, and found an expression for critical capillary number, $\text{Ca}_{cr}$, for breaking a drop in the T-junction:

$$\text{Ca}_{cr} = \psi \varepsilon_o \left( \frac{1}{\varepsilon_o^{2/3}} - 1 \right)^2,$$

(2.5)

where $\psi$ is a dimensionless constant (a function of the viscosity contrast of the two fluids and the geometry of the channel) and $\varepsilon_o$ is the droplet initial extension before entering into the T-junction (defined as the ratio of droplet length to its circumference).

### 2.3.2. Interfacial tension effects

Break-up due to deformation inside a channel, because of the channel geometry, is comparable to the mechanism of microchannel emulsification. When a droplet is squeezed through a constriction in the channel, the dumbbell-shape of the droplet gives rise to a difference in Laplace pressure between the dispersed phase inside the constraint, $\Delta P_o$, and the dispersed phase before, $\Delta P_{d1}$, and after $\Delta P_{d2}$ the constriction [34]. In a three-dimensional, cylindrical pore, Van der Zwan et al. [32] estimated that the snap-off can take place when:

$$\Delta P_c > \Delta P_{d1} \Rightarrow \frac{\sigma}{R_{c1}} - \frac{\sigma}{R_{c2}} > \frac{2\sigma}{R_1},$$

$$\Delta P_c > \Delta P_{d2} \Rightarrow \frac{\sigma}{R_{c1}} - \frac{\sigma}{R_{c2}} > \frac{2\sigma}{R_2},$$

(2.6)

where $R_{c1}$ and $R_{c2}$ are the constriction radii as shown in Fig. 2.4, and $\sigma$ is the interfacial tension. Further, $R_1$ and $R_2$ are the droplet radii before and after the constriction. If $R_{c2} >> R_{c1}$, snap-off is induced when $2R_{c1} < R_1$ and $2R_{c2} < R_2$. Although, shear forces may act simultaneously on the droplet, the lower value of...
the critical capillary number (around $3 \times 10^{-3}$) in this case, indicates that the deformation of the droplet inside the constriction already destabilizes the droplets, along the lines of the interfacial tension-induced snap-off mechanism.

Fig. 2.4. Schematic representation of the dumbbell-shaped droplet in a 3D constriction [32].

In addition to above mentioned Laplace instabilities, Rayleigh instabilities may operate in case of higher continuous phase flow [35]. The droplets after having left the constriction remain elongated, which then may lead to break-up into polydisperse droplets.

2.3.3. Steric hindrance between droplets

The dispersed phase droplets start accumulating before the membrane and inside the channels. These accumulating droplets can influence each other and thus induce break-up. Break-up in this case is strongly dependent on the interfacial properties: a stable emulsion will resist coalescence, and yield net steric break-up; a less stable emulsion may well coalesce.

In cross-flow emulsification, the forces acting on the forming droplet are mainly the interfacial tension force (that keeps the droplet connected to the pore) and the shear force (due the continuous phase flow that tries to remove the droplet). However, in case of big droplets (> 10 μm), also the buoyant and inertia forces need to be considered. The point at which the oil will start to have a pressure gradient from pore to droplet is:
\[ \Delta P_p \geq \Delta P_d \Rightarrow \frac{\sigma}{R_p} \geq \frac{2\sigma}{R_d} \Rightarrow R_d \geq 2R_p , \quad (2.7) \]

where \(\Delta P_p\) and \(\Delta P_d\) are the Laplace pressure difference in the pore and of emerging droplet having radius of \(R_p\) and \(R_d\), respectively. So, once the droplet radius is about twice as large as the pore radius, there is a possibility of spontaneous snap-off. Nevertheless, at higher transmembrane pressure, pores may generate a liquid jet instead of single spherical droplets. And if the shear forces are strong enough, this effect can be used to produce droplets from a liquid jet emerging from the membrane pore due to Raleigh instabilities, like premix emulsification. So, in this way, certain similarities may exist between droplet break-up in premix and cross-flow emulsification depending upon the operating parameters.

In the next section, the most relevant process parameters are discussed, together with some examples from various literature sources.

### 2.4. Process parameters

Various parameters influence the droplet size, such as the membrane properties (pore size, pore size distribution, etc.), transmembrane pressure, dispersed phase fraction and stabilization, continuous phase viscosity and number of homogenizing cycles, which are discussed here.

#### 2.4.1. Membrane properties

SPG membranes are the most extensively studied membranes for premix emulsification (Table 2.A.2), which were reported to have various advantages like i) interconnected micropores, ii) a wide spectrum of available mean pore sizes (0.05–30 \(\mu m\)) with narrow size distribution, iii) a high porosity (50–60%) and besides, iv) the surface can be hydrophobized by reaction with organic silanes [3]. However, the effect of these properties is not simple. For example, the porosity of the membranes as such may be high, but the percentage of active pores is often very low; usually below 10% as demonstrated by Vladislavljevic et al. [36] for cross-flow emulsification.

The membrane pore size correlates with the droplet size and the size distribution (and the flux of the emulsion). Zhou et al. [37] studied the size and uniformity of
agarose beads prepared by premix emulsification using SPG and polyethylene (PE) membranes, and they found a linear relationship between the number average diameter of agarose beads and membranes pores size. Besides, it was noted that the pore size distribution and the shape of the openings of the pores do not affect the emulsification results within a wide range. Probably, the largest pores carry most of the liquid, and the droplet formation inside these pores decides the droplet size of the resulting emulsion. This is different from cross-flow emulsification where droplet formation takes place on the surface of the membrane, rather than inside the membrane, as is the case for premix emulsification. With premix membrane emulsification, thicker membranes gave more uniform emulsions, again pointing to multiple break-up inside the membrane. Most important for premix emulsification is that the contact angle between the continuous phase and the membrane surface must be low enough for complete wetting in order to obtain uniformly sized particles. Membranes that are incompletely wetted by the continuous phase often lead to polydispersity and larger average droplet sizes. As mentioned previously, a membrane that is wetted by the dispersed phase may result in phase inversion. Depending on the formulation, this inversion either leads to demulsification or in a limited number of cases to phase inversion.

Vladisavljevic et al. [31] prepared W/O/W emulsions by extruding a coarse W/O/W emulsion through SPG membranes and found that the mean outer droplet size increased with increasing pore size, as was the case for the gel beads mentioned in the previous section. The ratio between droplet and pore size decreased with increasing pore size and number of passes, and was 1.25–0.68 after five passes. While for cross-flow emulsification it was 3.46, which is relatively high and also independent on the pore size.

2.4.2. Transmembrane pressure

The premix emulsification process involves using a transmembrane pressure to push the coarse emulsion through the membrane. Increasing the transmembrane pressure increases the permeating flux, \( J \) [7, 23, 38], according to Darcy’s law, if the emulsion can flow through the membrane as if it were only the continuous phase:
where $\Delta P$ is the transmembrane pressure, $R_m$ is the membrane resistance and $\eta_e$ is the emulsion viscosity inside the pores. In (repeated) premix emulsification, the transmembrane pressure is utilized to overcome flow resistances inside the pores, $\Delta P_{\text{flow}}$, and for droplet disruption, $\Delta P_{\text{disr}}$, i.e., to overcome interfacial tension forces [27]. This is summarized as:

$$\Delta P = \frac{\eta_e R_m J_i}{\Delta P_{\text{flow}}} + C \varphi_d \sigma (d_i - 1/d_{i-1}),$$

where $J_i$ is the transmembrane flux corresponding to $i^{th}$ cycle, $C$ is a constant, $\varphi_d$ is the volume fraction of dispersed phase in the emulsion and $d_i$ is the resulting mean droplet diameter corresponding to $i^{th}$ cycle. If fouling occurs, an additional resistance could be added to account for this.

The pressure that needs to be applied for premix emulsification is co-determined by various factors. First, the continuous phase of the premix should be able to intrude the pores, and for a non-wetting liquid a minimum pressure needs to be applied corresponding to the Laplace pressure (assuming cylindrical pores):

$$\Delta P_{\text{cr}} = \frac{4 \sigma \cos \theta}{d_p},$$

where $\Delta P_{\text{cr}}$ is the critical pressure and $\theta$ is the contact angle. The final droplet diameter, $d_2$, may be larger or smaller than the pore diameter, $d_p$, depending on the shear stresses inside the pores.

Further, the local transmembrane pressure acting across the droplet needs to be higher than the Laplace pressure of the droplets in order to deform them, and as mentioned needs to be higher than a critical pressure to allow intrusion in a pore. If the initial droplet diameter, $d_i$, is not much larger than the membrane pore diameter, $d_p$, in other words, the ratio $d_i/d_p$ is close to 1 (but larger), the critical pressure is given by [39]:

$$\Delta P_{\text{cr}} = \frac{2 \sigma \left[2 + 2d^6/\sqrt{d^6 - 1} \times \arccos(1/d^3) - 4d^2 \right]}{d_p (d + \sqrt{d^2 - 1})},$$

(2.11)
where $d$ is the ratio $d_1/d_p$. For larger values of $d$ ($d_1 \gg d_p$), the critical pressure becomes equal to the capillary pressure given in Eq. 2.10.

### 2.4.3. Dispersed phase fraction and stabilization

Another promising feature of premix emulsification is that at given operating conditions, the mean droplet size is independent of the dispersed phase content over a wide range (1–60% vol.); although it should be noted that the transmembrane flux significantly decreases with increasing dispersed phase content due to an increase in viscosity [27]. The droplets coming out of the membrane pores may be readily stabilized by surfactants while passing through the membrane, which ultimately leads to negligible coalescence.

Moreover, the droplet size and uniformity of the coarse emulsion do not affect the emulsification results; the mean droplet size is primarily dependent on the mean pore size and wall shear stress inside the pores [40, 41]. In case of, e.g., high-pressure homogenizers, at constant operating conditions the droplet size is strongly dependent on the dispersed phase percentage [42]. This is because the surface area that is created during passage in such devices cannot be covered in time by the surfactants, leading to instability of the produced emulsion, and a need for repeated processing. To some extent, this could also be the case for premix emulsification, but here the process allows more time for coverage of produced surface area.

### 2.4.4. Continuous phase viscosity

The influence of the continuous phase viscosity on the premix emulsification process is complex. Primarily, the permeate flux is inversely proportional to the emulsion viscosity as indicated in Eq. 2.8. The emulsion viscosity will be close to the viscosity of the continuous phase viscosity at low dispersed phase volume fraction, but can become considerably higher at higher dispersed phase fraction. Further, the continuous phase viscosity influences the wall shear stress as indicated in Eq. 2.4, which will be higher for viscous liquids, resulting in smaller droplets [31].
2.4.5. Number of homogenization cycles

In repeated or multi-stage premix emulsification, in addition to improving monodispersity, the permeate flux also increases with increasing number of passes, \( N \) \([27, 41, 43]\), most probably as a result of the decreased viscosity related to droplet size reduction. Besides, as mentioned earlier, if the droplet size is similar to the pore size, it is expected to pass unhindered, and less pressure is needed. Under non-fouling conditions, the largest increase in flux takes place in the second pass as the largest droplet size reduction occurs in the first pass. The increase in flux can be explained by a decrease in \( \Delta P_{\text{disr}} \) and an increase in \( \Delta P_{\text{flow}} \) (Eq. 2.9) and ultimately transmembrane pressure becoming equal to \( \Delta P_{\text{flow}} \) after few passes, usually 3–5 depending upon the nature of the coarse emulsion.

Components in the premix emulsion may have negative side effects when they foul the membrane. Surh et al. \([44]\) studied the preparation of lecithin-stabilized O/W emulsions by repeated premix emulsification using SPG membranes. They found that as the number of passes through the same membrane increased from 1 to 5, the transmembrane flux decreased from 30 to 1 m\(^3\) m\(^{-2}\) hr\(^{-1}\) because of membrane fouling due to lecithin.

2.5. Applications

2.5.1. Single emulsions

Single emulsions play an important role in the formulation of various products such as foods; examples of O/W emulsions are dressings, artificial milks, cream liqueurs etc., and examples of W/O emulsions are margarines and low fat spreads. In addition, there are numerous non-food emulsions like pharmaceutical products, cosmetics, pesticides, bitumen (for road application), water-based paints, photographic films, paper coatings, lubricants, etc. The method used for the preparation of emulsions has a great influence on the physicochemical properties of the final product. The droplet size and size distribution are among the most important properties that have to be considered while preparing a certain type of emulsion. Moreover, application of high shear and extensional stresses during the process may cause loss of functional properties of shear and heat sensitive
components. In regard of droplet size, droplet size distribution and low shear stress, premix emulsification is a good candidate for the preparation of single emulsions, as obvious from literature on the production of single emulsions carrying food ingredients like corn oil, soybean oil etc. [7, 27, 44].

### 2.5.2. Multiple emulsions

Recently, several premix emulsification studies have been carried out for the production of multiple emulsions that have potential applications for controlled release of a substance from the inner phase. Vladisavljevic et al. [27] prepared W/O/W emulsions with a narrow droplet size distribution (span = 0.28) at high production rates (transmembrane flux = 1.8–37 m$^3$ m$^{-2}$ hr$^{-1}$) by repeated premix emulsification using SPG membranes. In another study, Vladisavljevic and coworkers [31] found that the mean size of the outer drops was unaffected by the volume fraction of inner droplets in the range of 0.3–0.5, and the encapsulation efficiency of a hydrophilic marker (CaNa$_2$-EDTA) was virtually independent of the number of passes.

Also Shima et al. [45] reported on repeated premix emulsification for the production of W/O/W emulsions prepared as a carrier system for the daily uptake of a bioactive substance. They passed the premix through a cellulose acetate membrane to produce a fine emulsion with a mean oil droplet diameter of < 1 μm with an encapsulation efficiency of > 90%. During preparation of the premix in a rotor-stator system, inclusion of the outer water phase solution into the oil phase was observed; however, the included water phase disappeared during membrane emulsification, most probably because it wetted the membrane wall, and was captured in this way. Unlike the internal phase, the external water phase is not stabilized with a surfactant suitable for stabilization of W/O emulsion, and therefore, when captured it will re-coalesce with the external phase inside the membrane.

Surh et al. [46] studied the preparation of W/O and W/O/W emulsions containing gelled internal water droplets. They compared emulsification methods and observed that with a high-pressure valve homogenizer smaller droplets were obtained compared to premix emulsification, but the membrane produced a
narrower droplet size distribution at high encapsulation efficiency of the internal phase (> 95%).

Kukizaki [47] prepared hydrophilic drug-encapsulating solid lipid microcapsules (SLMCs) for drug delivery with a narrow particle size distribution via solid-in-oil-in-water (S/O/W) dispersions by premix emulsification using SPG membrane with a mean pore diameter of 14.8 µm. Subsequent solidification of the oil phase in the S/O/W dispersion resulted in SLMCs with a mean particle diameter of 15.4 µm and a high encapsulation efficiency up to 93.5%.

2.5.3. Gel microbeads

Monodispersed beads (e.g., of agarose) are important for a variety of chromatographic applications such as gel filtration [48], ion-exchange chromatography [49], hydrophobic interaction chromatography [50] and affinity chromatography [51]. Investigations have been carried out to produce agarose beads using premix emulsification. Conventional methods like suspension gelation [52] or spraying gelation [53] are not efficient enough for producing uniform-sized beads. Zhou et al. [54] were the first who reported the production of uniform agarose beads by premix emulsification and prepared beads with diameters ranging from 15–60 µm using membranes with different pore size. Later on, they reported the production of uniform-sized agarose beads with smaller diameter (less than 10 µm) and high agarose content (more than 14%); which was not possible by regular cross-flow emulsification [37].

2.5.4. Polymer microspheres

For drug-loaded microspheres, the solvent evaporation method involving high-speed homogenization, mechanical stirring or ultrasonication have been studied extensively [55-59]. Various biodegradable polymers were considered (such as polylactide, poly(glycolide), poly(ɛ-caprolactone), poly(saccharides), or albumin), however, the size of the particles prepared by these methods is difficult to control and also the size distribution is very broad. Sawalha et al. [60] prepared narrowly-dispersed polylactide (PLA) hollow microcapsules with sizes 0.35–5 µm by premix emulsification and found that particles of defined size and size distribution can be
produced. Wei et al. [61] prepared uniform-sized poly(lactide-co-ethylene glycol) (PELA) microspheres with high encapsulation efficiency of antigen by premix emulsification. Under optimum conditions, they obtained a particle size of about 1 µm and reported that the polymer properties and solidification rate are two effective strategies to yield high encapsulation. Even a few studies targeted biodegradable nanoparticles, e.g., Wei et al. [62] prepared uniform-sized PLA nanoparticles by combining premix emulsification and solvent removal, starting from larger droplets that were subsequently reduced in size due to solvent removal. They obtained mean sizes of about 321–669 nm depending upon the volume ratio of the phases in the emulsion, and mentioned that this method has high productivity and is suitable for easy scale-up.

In a recent investigation, Kooiman et al. [63] studied the synthesis and characterization of novel polymeric microcapsules for ultrasound-triggered delivery of lipophilic drugs. Microcapsules (having mean number-weighted diameter in the range of 1.22–1.31 µm) with a shell of fluorinated end-capped poly(L-lactic acid) were prepared through premix emulsification and contained, apart from a gaseous phase, different amounts of hexadecane oil as a drug-carrier reservoir. The partially oil-filled microcapsules with high drug loads and well defined acoustic activation thresholds were reported to have a great potential for ultrasound-triggered local delivery of lipophilic drugs under ultrasound image guidance.

2.6. Outlook

Although the knowledge base for premix emulsification does not seem to be as wide as for other emulsification methods, various effects that occur, e.g., in cross flow emulsification are also of relevance for premix emulsification and can be used to design processes. It should be mentioned that the interaction of droplets and its influence on the actual size of the obtained droplets is still uncharted territory. It is obvious from the available data, that it is an interesting technique for the controlled production of emulsions and all kinds of related products having small sized droplets. Various aspects such as narrow droplet size distribution, high productivity and robustness make premix emulsification not only suited for shear
sensitive emulsions and related products, but also for emulsions in general as long as the membrane is not fouled during operation. If this is the case, an alternative system could be used consisting of a packed bed of glass beads instead of a membrane [28]. Such type of ‘dynamic’ membrane, having morphology very similar to the conventional premix emulsification membranes, has the advantage that the system can be easily cleaned after emulsification, and therefore, such a system could be interesting for emulsions having ingredients that cause (depth) fouling of conventional membranes.
### Appendix 2.A

Tables 2.A.1 and 2.A.2

#### Table 2.A.1

Cross-flow emulsification studies using SPG membranes.

<table>
<thead>
<tr>
<th>Membrane characteristics</th>
<th>Emulsion characteristics (1 = continuous phase, 2 = dispersed phase)</th>
<th>Droplet characteristics ($d_o$ = droplet diameter, $d_p$ = pore diameter, $\delta$ = span, $CV$ = coefficient of variation)</th>
<th>Pressure, $\Delta P$ (kPa)</th>
<th>Flux, $J$ ($m^3 \cdot m^{-2} \cdot hr^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat SPG membrane disks (3.01 and 9.83 μm)</td>
<td>O/W: (1) water + Tween-20 or SDS + polyethylene glycol, (2) decane + liquid paraffin</td>
<td>With 9.83μm membrane using 2% SDS: $d_o = 29.98 \mu m$, $d_o/d_p = 3.05$, $\delta = 0.53$</td>
<td>$J \approx 14 \times 10^{-5}$</td>
<td>$\Delta P = 3.5–17.4$</td>
<td>[64]</td>
</tr>
<tr>
<td>Tubular SPG membrane (4.8 μm)</td>
<td>O/W: (1) commercial skimmed milk, (2) soy/rapeseed oil</td>
<td>Using soy oil: $d_o = 12.4 \mu m$</td>
<td>$J = 0.05$</td>
<td>$\Delta P = 90$</td>
<td>[65]</td>
</tr>
<tr>
<td>Tubular SPG membranes (0.2 and 0.4 μm hydrophilic; 0.4 and 1 μm hydrophobic)</td>
<td>O/W, solid lipid particles: (1) water + Tween-20 or Pluronic F68, (2) Gelucire or Compritol</td>
<td>$d_o = 50–750 \text{ nm}$</td>
<td>$J = 0.008–0.84$</td>
<td>$\Delta P = 400$ or 600</td>
<td>[66]</td>
</tr>
<tr>
<td>Tubular SPG membrane (7.0 μm)</td>
<td>O/W: (1) water + Tween-60 or Tween-20, (2) sunflower oil (20%)</td>
<td>$d_o \approx 32 \mu m$ at 30 °C</td>
<td>$\Delta P = 3.3–4.8$</td>
<td>[67]</td>
<td></td>
</tr>
<tr>
<td>Asymmetric tubular SPG membrane, consisting of an inner skin layer (0.67 μm) and a support layer (4.7 μm)</td>
<td>O/W: (1) water + SDS (0.3% w/v), (2) Soybean oil</td>
<td>$d_o = 2.18–2.22 \mu m$</td>
<td>$J = 0.011–0.039$</td>
<td>$\Delta P = 35–120$</td>
<td>[68]</td>
</tr>
<tr>
<td>Hydrophobic modified SPG membranes (1.8, 2.0, 2.5, 4.8 and 11.1 μm)</td>
<td>W/O: (1) kerosene oil (0.1–5.0% wt.) + PGPR 90, (2) water + NaCl (0.017–0.855 mol L$^{-1}$)</td>
<td>$d_o/d_p = 3.11 \pm 0.13$, $\delta \approx 0.28$</td>
<td>$\Delta P = 0.5–16.5$</td>
<td>[30]</td>
<td></td>
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</table>
Table 2.A.1 (continued)

<table>
<thead>
<tr>
<th>Membrane characteristic and system design</th>
<th>Emulsion characteristics (1 = continuous phase, 2 = dispersed phase)</th>
<th>Droplet characteristics ($d_{\text{d}}$ = droplet diameter, $d_{\text{p}}$ = pore diameter, $\delta$ = span, $CV$ = coefficient of variation)</th>
<th>Pressure, $\Delta P$ (kPa)</th>
<th>Flux, $J$ (m$^3$ m$^{-2}$ h$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tubular SPG membrane (0.4–6.6 µm)</td>
<td>O/W: (1) demineralized water + Tween-80 (2%, w/w), (2) rapeseed oil</td>
<td>$d_{\text{d}}/d_{\text{p}} = 3.5$, $\delta = 0.26–0.45$</td>
<td>With 4.8 µm membrane: $J = 0.08$ at $\Delta P = 40$</td>
<td>[40]</td>
<td></td>
</tr>
<tr>
<td>SPG membrane (15 µm)</td>
<td>O/W: (1) water + SDS (0.3% wt.), (2) soybean oil</td>
<td>$d_{\text{d}} = 30 \mu$m</td>
<td>$J = 0.58 \times 10^{-6} – 5.8 \times 10^{-6}$</td>
<td>[69]</td>
<td></td>
</tr>
<tr>
<td>Cylindrical SPG membrane (1, 2.94 µm)</td>
<td>O/W: (1) water + polyvinyl alcohol + sodium lauryl sulfate, (2) styrene + divinyl benzene + hexadecane</td>
<td>$d_{\text{d}}/d_{\text{p}} = 6.6$</td>
<td>$J = 3.24 \times 10^{-6} – 2.52 \times 10^{-5}$ m$^3$ hr$^{-1}$</td>
<td>[70-72]</td>
<td></td>
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</table>

| Ref. | ΔP = 12.8–68.7 |

Table 2.A.2

Premix emulsification studies.

<table>
<thead>
<tr>
<th>Membrane characteristic and system design</th>
<th>Emulsion characteristics (1 = continuous phase, 2 = dispersed phase)</th>
<th>Droplet characteristics ($d_{\text{d}}$ = droplet diameter, $d_{\text{p}}$ = pore diameter, $\delta$ = span, $CV$ = coefficient of variation)</th>
<th>Pressure, $\Delta P$ (kPa)</th>
<th>Flux, $J$ (m$^3$ m$^{-2}$ h$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tubular SPG (2.7 and 4.2 µm), cross flow</td>
<td>O/W: (1) water, (2) corn oil, PGPR and PGFE as emulsifiers for oil and water phase, respectively</td>
<td>$d_{\text{d}}/d_{\text{p}} = 1.4–2.1$, $\delta = 0.4–0.62$</td>
<td>$\Delta P = 10–100$, $J = 0.03–3.5$</td>
<td>[7]</td>
<td></td>
</tr>
<tr>
<td>Flat PTFE (1.0 µm), dead end</td>
<td>O/W and W/O</td>
<td>$d_{\text{d}}/d_{\text{p}} = 2–4.1$</td>
<td>$J = \text{up to 9}$</td>
<td>[23]</td>
<td></td>
</tr>
<tr>
<td>Flat PTFE (1.0 µm), dead end, phase inversion</td>
<td>O/W and W/O: (1) water, (2) corn oil, PGPR and PGFE as emulsifiers for oil and water phase, respectively</td>
<td>$d_{\text{d}}/d_{\text{p}} = 2.8–4.0$</td>
<td>$\Delta P = 100–800$, $J = 1–5$</td>
<td>[24]</td>
<td></td>
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</table>
### Table 2.A.2 (continued)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Emulsion Type</th>
<th>Details</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat polycarbonate (0.33, 0.38, 0.47, 0.6 and 1.0 µm), dead end, multi-stage ($N = 1–18$)</td>
<td>O/W: (1) water + SDS (0.2% wt.), (2) kerosene oil</td>
<td>$d_ω/d_p ≤ 1.6$ (for $N &gt; 12$)</td>
<td>$\Delta P = 100$, $J = 0.2–0.6$ [39]</td>
</tr>
<tr>
<td>Flat PTFE (1.0 µm), dead end, multi-stage ($N = 1–3$)</td>
<td>O/W</td>
<td>$d_ω/d_p = 1.2–2.6$, $\delta = 0.55–0.9$</td>
<td>$J = 2–18$ [73]</td>
</tr>
<tr>
<td>Tubular SPG (1.1 µm), dead end, multi-stage ($N = 3$)</td>
<td>S/O/W: (1) water + surfactant L-1695 (1% wt.) + sodium cholate (1% wt.) + D-glucose (1% wt.), (2) surfactant-coated insulin dispersed in soybean oil to form S/O</td>
<td>$d_ω/d_p = 1.0$</td>
<td>$J = 1.6$ [74]</td>
</tr>
<tr>
<td>Flat cellulose acetate (0.2, 0.45, 0.8 and 3.0 µm), dead end</td>
<td>W/O/W: (1) Hank’s solution, (2) $10^{-4}$ mol L$^{-1}$ PTSA sol. + C8TG containing hexaglyceryl condensed ricinoleate (1–10% w/v) to form W/O emulsion</td>
<td>$d_ω/d_p = 1.0–3.5$</td>
<td>$\Delta P = 300–440$ [45]</td>
</tr>
<tr>
<td>Tubular SPG (10.7 µm), dead end, multi-stage ($N = 1–5$)</td>
<td>W/O/W: (1) water + Tween-80 (0.5% wt.) + D-glucose (5% wt.) + sod. alginate (1% wt.), (2) 5% wt. D-glucose aqueous sol. dispersed in soybean oil having 5% wt. PGPR</td>
<td>$d_ω/d_p = 0.41–1.2$, $\delta = 0.28–0.6$</td>
<td>$\Delta P = 20–300$, $J = 1.8–37$ [27]</td>
</tr>
<tr>
<td>Tubular α-alumina (1.5 µm), stirring</td>
<td>O/W: (1) water + SDS (2% wt.), (2) toluene</td>
<td>$d_ω/d_p = 1.5–1.8$, $\delta = 1–1.2$</td>
<td>$\Delta P = 200$, $J = 0.42–0.62$ [75]</td>
</tr>
<tr>
<td>Tubular SPG (5.4–20.3 µm), dead end, multi-stage ($N = 1–5$)</td>
<td>W/O/W: (1) water + Tween-80 (0.5% wt.) + glucose (5% wt.) + sod. alginate (1% wt.), (2) aqueous sol having glucose (5% wt.) and CaNa$_2$-EDTA (5% wt.) dispersed in soybean oil containing 5% wt. PGPR</td>
<td>$d_ω/d_p = 0.37–1.2$, $\delta = 0.28–0.93$</td>
<td>$\Delta P = 70–150$, $J = 2–240$ [31]</td>
</tr>
<tr>
<td>Tubular SPG (8.0 µm), dead end, multi-stage ($N = 1–5$)</td>
<td>O/W: (1) water + emulsifier (a combination of both SDS and Tween-20), (2) corn oil</td>
<td>$d_ω/d_p = 0.5–1.4$, $\delta = 0.33–0.77$ ($N = 7$)</td>
<td>$\Delta P = 100$, $J = 3–60$ [76]</td>
</tr>
<tr>
<td>Table 2.A.2 (continued)</td>
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<tr>
<td><strong>Flat polycarbonate, dead end, multi-stage (N = 5)</strong></td>
<td>W/O/W: (1) water + SDS (1 cmc) + NaCl (0.1 M), (2) aqueous sol. having NaCl (0.1 M) and dextran ($9 \times 10^{-5} $M) dispersed in dodecane having Arlacel P135 as surfactant</td>
<td>$d_{w} = 0.7–2.5 \mu m$</td>
<td>$J = 3.7–14.7$</td>
</tr>
<tr>
<td><strong>Tubular SPG (8.0 µm), dead end, multi-stage (N = 5)</strong></td>
<td>W/O/W: (1) water + Tween-20 (0.5% wt.) + phosphate buffer, pH 7 (5 mM) + NaCl (100 mM) + NaN$_3$ (0.02% wt.), (2) water with or without WPI dispersed in corn oil having 8% wt. PGPR</td>
<td>$d_{w}/d_p = 0.20–0.29$</td>
<td>$\Delta P = 100, J = 70$ (N = 5)</td>
</tr>
<tr>
<td><strong>Glass filter (1.0 µm), dead end, multi-stage (N = 11)</strong></td>
<td>Polymer (PLA) microspheres</td>
<td>$d_{w} = 1.0 \mu m$, $\delta = 0.7$</td>
<td>–</td>
</tr>
<tr>
<td><strong>Glass filter (1.0 µm), dead end, multi-stage (N = 1–15)</strong></td>
<td>Polymer (PLA) microspheres</td>
<td>$d_{w} = 0.35–5.0 \mu m$</td>
<td>–</td>
</tr>
<tr>
<td><strong>SPG (5 µm), continuous membrane module run for 100 minutes</strong></td>
<td>O/W: (1) water + SDS + phosphate buffer, pH 7 + PVA, (2) Isooctane + racemic naproxen methyl ester</td>
<td>$d_{w} = 1.32 \mu m$</td>
<td>$\Delta P = 120$</td>
</tr>
<tr>
<td><strong>SPG (8 µm), dead end, multi-stage (N = 1–5)</strong></td>
<td>O/W: (1) aqueous sol (pH 3) containing 100mM acetic acid, 0.02% wt. NaN$_3$ and 1.6 or 1.8% wt. lecithin, (2) corn oil up to 10 or 20% of emulsion</td>
<td>$d_{22} = \text{upto} 5 \mu m$</td>
<td>$\Delta P = 100–150, J = 30–1$</td>
</tr>
<tr>
<td><strong>SPG (5.2 µm), dead end</strong></td>
<td>Polymer (PELA) microspheres</td>
<td>$d_{w} = 1.0 \mu m$</td>
<td>$\Delta P = 300$</td>
</tr>
<tr>
<td><strong>SPG (1.4 µm), dead end</strong></td>
<td>Polymer (PLA) nanoparticles</td>
<td>$d_{w} = 321–669 \text{ nm}$</td>
<td>$\Delta P = 1000$</td>
</tr>
<tr>
<td>Table 2.A.2 (continued)</td>
<td>Medium</td>
<td>Dispersed phase</td>
<td>Coarse phase</td>
</tr>
<tr>
<td>--------------------------</td>
<td>--------</td>
<td>----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>SPG (10.2 µm), dead end, multi-stage (N = 3)</td>
<td>W/O, agarose beads: (1) liquid paraffin/petroleum ether (7:5 v/v) + hexaglycerin penta ester (4% wt), (2) 10% wt. agarose sol. + 0.9% wt. NaCl</td>
<td>d_w = 10 µm</td>
<td>∆P = 98</td>
</tr>
<tr>
<td>Glass beads (mass mean bead diameter = 75.9 µm and span=0.68), dead end, multi-stage (N = 6)</td>
<td>0/W: (1) water + Tween-20 (0.5% v/w), (2) n-hexadecane upto 5% of emulsion</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SPG (10.2 µm) and PE (11.8 and 25.6 µm), dead end, multi-stage (N = 3)</td>
<td>W/O, agarose beads: (1) liquid paraffin/petroleum ether (7:5 v/v) + hexaglycerin penta ester (4% wt), (2) 10% wt. agarose sol.</td>
<td>d_w = 3.06–9.02 µm</td>
<td>∆P = 98</td>
</tr>
<tr>
<td>Polycarbonate (1.0 µm), nylon (0.8 µm), Polyethersulfone (0.8 µm) and nitrocellulose mixed ester (0.8 µm), dead end, multi-stage (N = 1–7)</td>
<td>O/W: (1) water + Tween-20 (2% w/w) or BSA (1–2% w/w), (2) sunflower oil</td>
<td>d_S = 1–12 µm</td>
<td>∆P = 100–900, J = up to 46</td>
</tr>
<tr>
<td>Tubular SPG membrane (5.4, 7.6, 9.9 and 14.8 µm), dead end</td>
<td>S/O/W: (1) water + Tween-40 (1% wt), (2) vitamin B12 (0.2–1.1% wt) dispersed in glycerol trimyristate containing 5% wt. PGPR</td>
<td>d_w (S/O) = 15.5 µm</td>
<td>∆P = 25–200, J = 11.8–114.2</td>
</tr>
<tr>
<td>Glass filter (1.0 µm), dead end, multi-stage (N = 10)</td>
<td>Polymer (pLA-pFO) microcapsules</td>
<td>d_{10} = 1.22–1.31 µm</td>
<td>–</td>
</tr>
</tbody>
</table>
References


High-throughput premix membrane emulsification using nickel sieves having straight-through pores

ABSTRACT

We report on the use of nickel sieves, having a uniform pore size (typically $10 \times 300 \ \mu m$), for oil-in-water premix emulsification at relatively low transmembrane pressures. The droplet break-up was found to be based on elongation and recompression of droplets typical of high-pressure homogenization. The dependence on the transmembrane pressure indicated at least partial turbulent conditions. In line with this, the transmembrane fluxes were very high, while a reasonable span (around 1) of the droplet size was found. There was no indication of fouling in the process, even after 5 passes, which indicates that the process is tolerant to product and conditions. A master curve was found for the droplet Weber number as function of the transmembrane pressure normalized on the Laplace pressure of the emulsion before emulsification, which is helpful in further scale-up of this process.
3.1. Introduction

Emulsions are of great significance in our daily life, as they are the basis of many products from, e.g., food, pharmaceutical, cosmetics and chemical industries. For stable emulsions, the droplet size needs to be small and ideally uniform. Traditional emulsification techniques are known to be rather energy consuming; in some cases only 1% of the applied energy is used to form emulsion droplets, and the rest is dissipated as heat leading to temperature increase of the product, which may influence the ingredients negatively [1].

A lot of research has been carried out to make the emulsification process more efficient. In the last decades, a number of new emulsification techniques have become available which are based on microstructured systems, such as membranes and microfluidic devices. With these systems, emulsion droplets may be formed directly by extrusion through pores, or larger droplets from a coarse premix may be broken up into smaller ones. Some of these techniques are compared in Chapter 2. As introduced by Suzuki et al. [2], premix membrane emulsification, along with other latest emulsification techniques, has established itself as a promising technique for the production of small sized and relatively monodispersed emulsions at relatively low energy inputs as compared to traditional emulsification techniques. As the name implies, the process starts with a coarse emulsion (premix) which is then pushed under pressure through a membrane. This results in a (more or less) homogenized emulsion. The emulsion may be passed through the membrane repeatedly depending on the desired level of homogenization [3]. The simplicity of the process and the fact that a higher dispersed phase fraction can be made possible in premix emulsification makes it an attractive technique for large-scale production of dispersions [4]. On the other hand, cross-flow membrane emulsification and straight-through emulsification with microfluidic devices result in relatively more monodispersed emulsions, even though the process is only feasible for relatively low dispersed phase fractions.

In this chapter, we focus on premix emulsification. From the work of Vladisavljevic et al. [5] it is known that the membrane type has a great influence on the emulsion droplets. Shirasu porous glass (SPG) membrane is the most popular membrane of
choice, not just for premix emulsification but also for cross-flow emulsification. Various membrane related factors have been reported in literature that influence droplet size and monodispersity, such as pore size, porosity, thickness, tortuosity and membrane surface properties. A hydrophilic surface is normally required to produce oil-in-water (O/W) emulsions whereas for water-in-oil (W/O) emulsions the surface should be hydrophobic. Alternatively, phase inversion can be induced in premix emulsification to get high dispersed phase fraction [6]. For example, by using a hydrophilic membrane with a W/O premix emulsion, the resulting emulsion would become O/W with high dispersed phase fraction. It should be noted that phase inversion can only be applied with specific systems.

In premix emulsification, besides the membrane properties, the transmembrane pressure and also the properties of the various ingredients, e.g., the viscosity ratio of the phases (as is the case in traditional emulsification driven by elongation or local shear), surfactant, temperature (related also to viscosity and adsorption rate) and pH (in case charged components are present) influence the resulting emulsion. These aspects have already been considered in literature [3, 7-14], but simultaneous optimization of all these factors is far from trivial. Ideally, scaling relations are used for this, as are available for a number of microfluidic devices. However, due to different droplet break-up mechanisms that occur simultaneously, as described by Van der Zwan et al. [15], the scaling relations are not readily available for premix emulsification.

Compared to other novel production methods like cross-flow membrane emulsification and microchannel emulsification, premix emulsification is an attractive technique because of its high production rate per m$^2$ membrane area [Chapter 2]. However, its sensitivity to depth fouling of the membrane is a major obstacle in its commercialization with systems containing, e.g., proteins [16]. A potential solution is the use of membranes that are very thin and do not have long, narrow interconnected pores.

We report here on the use of metal (nickel) sieves, which have relatively short, straight-through pores and are available with different pore sizes and shapes. The effects of operating conditions like transmembrane pressure and number of
homogenization cycles were evaluated in terms of their influence on emulsion properties and transmembrane flux. Besides, all data points were compiled into a single master curve based on dimensionless numbers. Finally, the energy usage and fouling tendency were quantified and compared to more traditional techniques.

3.2. Theory

The average wall shear stress, $\tau_w$, inside the membrane pores can be defined as [8]:

$$\tau_w = \frac{8\eta_c J \xi}{\epsilon d_p},$$

(3.1)

where $\eta_c$ is the continuous phase viscosity, $J$ is the transmembrane flux, $\xi$ is the membrane tortuosity ($\approx 1$ for straight through pores), $\epsilon$ is the membrane porosity and $d_p$ is characteristic pore dimension (pore width in this case). The pore Reynolds number, $Re_p$, is given by:

$$Re_p = \frac{\rho_e v_p d_h}{\eta_e},$$

(3.2)

where $\eta_e$ and $\rho_e$ are the emulsion viscosity and density, respectively, $v_p$ is the emulsion velocity inside the pore ($v_p = J/\epsilon$) and $d_h$ is the pore hydraulic diameter, defined for rectangular pores as:

$$d_h = \frac{2l_p w_p}{l_p + w_p},$$

(3.3)

where $l_p$ and $w_p$ are the pore length and width, respectively.

The process of droplet break-up in the turbulent regime has been described in literature by using the dimensionless Weber number, which is a ratio between the inertial forces (as a result of local pressure fluctuations) and interfacial tension forces [17]. For our emulsification setup, we defined droplet Weber number, $We_d$, as:

$$We_d = \frac{d_{32,o} \rho_e v_p^2}{2\sigma},$$

(3.4)

where $d_{32,o}$ is the Sauter mean diameter of droplet produced and $\sigma$ is the interfacial tension.
The friction coefficient, $f$, inside the pore can be calculated by the following expression:

$$f = \frac{\Delta P \ w_p}{z \rho v^2 \ h_p}, \quad (3.5)$$

where $\Delta P$ is the pressure drop across the sieve and $h_p$ is the depth of the pore. Vankova et al. [18] used a similar relation to calculate $f$ for a narrow-gap homogenizer.

Following the approach of Van der Zwan et al. [16], the pressure drop across the sieve was estimated with the following second order polynomial equation:

$$\Delta P = aJ^2 + bJ, \quad (3.6)$$

where $a$ and $b$ are the fit parameters. For the first pass through the sieve, the pressure drop can be used instead of energy density, $E_V$:

$$E_V = \frac{P}{\phi V} = \frac{\Delta P \phi V}{\phi V} = \Delta P, \quad (3.7)$$

where $P$ is the power input and $\phi V$ is the volume flow rate. For more than one pass, the energy densities of all the passes are cumulative.

The dimensionless pressure, $\hat{P}$, indicative of the minimum amount of energy needed to deform the droplet relative to the applied energy, can be defined as a ratio of the transmembrane pressure and the droplet Laplace pressure:

$$\hat{P} = \frac{d_{32,i} \Delta P}{\sigma}, \quad (3.8)$$

where $d_{32,i}$ is the ingoing Sauter mean droplet diameter. Karbstein and Schubert [19] derived an expression for the Sauter mean droplet diameter, $d_{32}$, of a homogenized emulsion and the energy density for continuous mechanical emulsification processes (avoiding re-coalescence) where the residence time of droplets in the dispersing zone lies in the order of milliseconds to tenths of a second:

$$d_{32} = \alpha E_V^{-\beta}, \quad (3.9)$$
here $\alpha$ and $\beta$ are constants. $\alpha$ depends on the efficiency of droplet disruption and is effected by dispersed phase viscosity, whereas, $\beta$ is affected by the flow conditions. In case of multiple passes, Eq. 3.9 can be extended to incorporate the number of cycles, $N$, with $\gamma$ as another fit parameter [16]:

$$d_{32} = \alpha E_{\nu}^{-\beta} N^{\gamma}.$$

(3.10)

The droplet span (an indicator of droplet uniformity), $\delta$, is calculated as:

$$\delta = \frac{d_{90} - d_{10}}{d_{50}}$$

(3.11)

where $d_x$ is the droplet diameter corresponding to $x\%$ vol. on a cumulative droplet volume curve.

### 3.3. Experimental

#### 3.3.1. O/W premix preparation

An O/W premix consisting of 5% n-hexadecane (99% for synthesis, MERCK) in Milli-Q water having 0.5% vol. Tween-20 (for synthesis, MERCK) as a surfactant, was prepared with an ultra-turrax homogenizer (IKA® T-18 basic) operated at 3500 rpm for 10 minutes (unless otherwise mentioned). This led to reproducible starting emulsions for our experiments having droplet size typically around 27 µm with a span of 0.9.

#### 3.3.2. Nickel sieves used for emulsification

The different nickel sieves (Stork Veco BV, Eerbeek, The Netherlands) used in this study have long rectangular pores as shown in Table 3.1. Around the pores, the sieves may have raised supporting structures, either on one side or on both sides. The overall thickness of the sieves (including the supporting structures) was 80, 200, 350 and 400 µm, and the pore width (determined by SEM imaging) was 13.2, 12.8, 11.6 and 10.6 µm, respectively. The pore depth (without supporting structures) was around 80 µm for all the sieves. The SEM images were obtained without coating in a field emission scanning electron microscope (Magellan 400, FEI, Eindhoven, The Netherlands). The samples were fitted on SEM sample holders.
Table 3.1.
SEM images of the nickel sieves used in this study along with their specifications.

<table>
<thead>
<tr>
<th>Sieve specifications</th>
<th>Front view</th>
<th>Back view</th>
</tr>
</thead>
</table>
| Pore size: **10.6 × 330.2 μm**  
Thickness: 400 μm  
Porosity: 3.62%  
Supporting structure on both sides | ![SEM image](image1.png) | ![SEM image](image2.png) |
| Pore size: **11.6 × 331.1 μm**  
Thickness: 350 μm  
Porosity: 3.95%  
Supporting structure on back side | ![SEM image](image3.png) | ![SEM image](image4.png) |
| Pore size: **12.8 × 329.3 μm**  
Thickness: 200 μm  
Porosity: 4.37%  
Supporting structure on back side | ![SEM image](image5.png) | ![SEM image](image6.png) |
| Pore size: **13.2 × 336.9 μm**  
Thickness: 80 μm  
Porosity: 4.79%  
Flat surface on both sides | ![SEM image](image7.png) | ![SEM image](image8.png) |
by carbon adhesive tabs (EMS Washington, USA) and subsequently analysed at 2 KV at room temperature, and the images were digitally recorded.

3.3.3. Emulsification setup

The emulsification setup is shown in Fig. 3.1. The pressure vessel containing the premix emulsion was connected to the module (a Plexiglas column) having a metal sieve at the bottom with an effective surface area of 1.43 cm$^2$. The sieve was held in place by two rubber o-rings (above and below) at the bottom junction of the column. The experiment was started by pressurizing the emulsion vessel (containing about 500 mL of emulsion) with air, keeping the valve opened and connected to the column.

![Fig. 3.1. Schematic representation of the experimental setup.](image)

The emulsification was started by opening the outlet valve of the column and collecting the homogenized emulsion in a flask placed on a balance for recording the flux. The cycle was repeated up to five times; no significant differences in droplet size were observed when more cycles were used. The coarse emulsion and all the homogenized emulsion samples were analysed for droplet size and size distribution with light scattering (Mastersizer 2000, Malvern Instruments Ltd.,
Three readings were taken, and the average droplet diameter and span were determined.

The results were compared and fitted to the relations presented in the theory section. All fits were conducted using solver function of MS Excel 2010, and the correlation coefficients and 95% confidence intervals were determined.

### 3.3.4. Interfacial tension measurement

The equilibrium interfacial tension at the hexadecane and surfactant-solution interface was measured using a drop profile analysis tensiometer PAT-1 (SINTERFACE Technologies, Germany) at a controlled temperature of 23 °C. A surfactant-solution droplet was formed at the tip of a capillary immersed in hexadecane. The measurements were started soon after the droplet formation and continued till a constant (equilibrium) interfacial tension was obtained. The equilibrium interfacial tension at the hexadecane water (0.5% vol. Tween-20) interface was found to be 5.8 mN m⁻¹, and was used in calculations.

### 3.4. Results and discussion

At Reynolds numbers larger than 50, the friction coefficient remained nearly constant ($f = 1$), which was around 7 times higher than the constant value obtained with a narrow-gap homogenizer [18], and around 2.4 times higher than obtained with a static mixer [20]. A higher friction coefficient in case of these nickel sieves suggests that in spite of relatively low Reynolds numbers ($Re_p \leq 220$), the emulsification regime is turbulent because of the specific pore geometry, possibly leading to droplet break-up after passage of the pore [21].

As indicated in the theory, various factors are expected to influence the resulting droplet size after premix emulsification. Here we start by discussing the effect of pressure drop on droplet size (distribution) and flux, and relate the results to various dimensionless numbers introduced in the theory section.

#### 3.4.1 Effect of transmembrane pressure

Emulsions containing 5% n-hexadecane were repeatedly passed through a 13.2 μm sieve at different pressures. Higher transmembrane pressure resulted in much
smaller droplets (Fig. 3.2), as could be expected since the actual shear stress on the 
droplets increased (Eq. 3.1). The final droplet diameter at 200 kPa was around 6 
μm after the fifth pass through the sieve which was much lower than the pore 
width of the sieve (13.2 μm, as indicated by the dotted line). All sieves showed 
similar droplet size behaviour as a function of pressure and number of passes; here 
we limit the discussion to only this sieve in this section.

![Fig. 3.2. Effect of transmembrane pressure, ΔP, on droplet diameter, d_{32}: (◊) 1st, (□) 3rd and (▲) 5th pass through 13.2 μm sieve.](image)

The size reduction during the first pass was maximum, and in general after the 3rd 
pass, the droplet size did not essentially decrease anymore, indicating that the 
limit of the system is reached. The droplet size to pore width ratio of emulsions 
prepared with cross-flow membrane emulsification are typically between 3 and 
10. The droplet size of the coarse premix emulsion (prior to emulsification) was 
around 2.2–2.3 times the pore width, and after the fifth pass, the droplet size was 
around 0.4 times the pore width.

The droplet Weber number (Eq. 3.4) was used to compare the results. The We_d 
number is based on the size of the droplets that are produced, where it is also 
expected that the droplet size of the feed emulsion (premix) will have a decisive 
role in the droplet size reduction. Therefore, in Fig. 3.3, we used droplet Weber 
number against Ṕ (the applied pressure over the minimum pressure required to 
deform droplets of certain size) calculated using Eq. 3.8. A high Ṕ value
corresponds to a surplus of applied energy. Smaller droplets have a high Laplace pressure, and on the other hand due to a decrease in the effective surface area, smaller droplets experience less disruptive forces, i.e., a decrease in numerator of \( \text{Eq. 3.4} \). This results in a decrease in Weber number as a result of different passes through the sieve.

All data collapsed into one master curve that can be used to link premix size and applied pressure to the actual droplet size that can be obtained under specified experimental conditions. Please keep in mind that in all experiments, the \( \dot{\mathbf{P}} \) values were high, indicating that the amount of energy used largely surpasses the minimum amount of energy needed to deform feed droplets (which is not equal to the energy needed to make them).

![Diagram](image)

**Fig. 3.3.** Droplet Weber number, \( \text{We}_d \), as a function of dimensionless pressure, \( \dot{\mathbf{P}} \): (\( \bigcirc \)) 1\(^{\text{st}} \), (\( \bullet \)) 2\(^{\text{nd}} \), (\( \triangle \)) 3\(^{\text{rd}} \), (\( \blacktriangle \)) 4\(^{\text{th}} \) and (\( \square \)) 5\(^{\text{th}} \) pass through 13.2 µm sieve.

From Fig. 3.3, also information on different break-up mechanisms was obtained, especially at very low Weber number, where it is expected that the droplet is deformed by the pore, and may or may not snap off depending on the local conditions. A droplet breaks spontaneously due to Laplace pressure differences if the Weber number exceeds a certain value, the so-called critical Weber number, \( \text{We}_{\text{cr}} \), and most probably, we are very close to this critical value at \( \text{We}_d = 5 \), below which there was hardly any reduction in droplet size. This type of droplet break-up has also been reported for microchannel emulsification [22].
The flux was not completely linearly dependent on the transmembrane pressure, as shown in Fig. 3.4. The convex curve is probably an indication on the development of (more) turbulent flow conditions at higher pressures. Alternatively, this could also be an indication that pressure losses occurred between our pressure vessel and the module, and that this effect was larger at higher applied pressures, although we expect the pressure losses in the sieve to be far greater.

![Graph showing dependence of flux on transmembrane pressure](image)

**Fig. 3.4.** Dependence of the flux, $J$, on the transmembrane pressure, $\Delta P$: (●) water flux, (●) 1st and (□) 5th pass through 13.2 µm sieve.

Despite their low porosity (0.05), the emulsification fluxes using nickel sieves were more than 100 times higher compared to premix emulsification studies by Surh et al. [10]. There was no significant difference between pure water flux and emulsion fluxes of first and last cycles. This implies that droplet break-up did not contribute significantly to the friction loss in the sieve, and that there was no appreciable membrane fouling throughout the experiments.

The droplet uniformity, expressed as the span of the distribution (Eq. 3.11), was typically in the order of 1.0–1.4 for all emulsions, which increased somewhat at higher transmembrane pressure (Fig. 3.5). At higher pressure ($v_p = 8–10$ m s$^{-1}$ at 200 kPa), droplet break down is expected to be accelerated, but re-coalescence is more probable due to insufficient stabilization by surfactant.
Fig. 3.5. Effect of transmembrane pressure, $\Delta P$, on droplet span, $\delta$: (◊) 1st, (□) 3rd and (▲) 5th pass through 13.2 µm sieve.

3.4.2. Membrane characterization based on energy density

The experimental data was fitted to Eq. 3.10 extended to take in the influence of homogenization cycles. In Fig. 3.6, the experimental Sauter mean droplet diameter is plotted against the fitted results of Eq. 3.10 for all the sieves. It is clear that the suggested equations gave reasonable descriptions, although a slight curved behaviour is visible, which could be related to a change in droplet break-up mechanism.

Table 3.2
Values and standard deviations of fit parameters of Eq. 3.10.

<table>
<thead>
<tr>
<th></th>
<th>10.6 µm</th>
<th>11.6 µm</th>
<th>12.8 µm</th>
<th>13.2 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$17.39 \pm 0.76$</td>
<td>$19.18 \pm 1.03$</td>
<td>$17.32 \pm 0.66$</td>
<td>$16.59 \pm 0.55$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$0.66 \pm 0.05$</td>
<td>$0.66 \pm 0.07$</td>
<td>$0.66 \pm 0.05$</td>
<td>$0.67 \pm 0.04$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$0.35 \pm 0.07$</td>
<td>$0.43 \pm 0.09$</td>
<td>$0.37 \pm 0.06$</td>
<td>$0.40 \pm 0.05$</td>
</tr>
</tbody>
</table>

The estimated values of fit parameters $\alpha$, $\beta$ and $\gamma$ using Eq. 3.10 are shown in Table 3.2 along with their standard deviations. The values of $\alpha$ decreased somewhat with increasing pore size; the others were more or less constant, except for the 10.6 µm sieve. This may be because of the different morphology of the membrane (Table 3.1).
Fig. 3.6. Experimental values of Sauter mean droplet diameter, $d_{32}$, plotted against estimated values using Eq. 3.10.

The value of $\beta$ contains information about the droplet disruption mechanism. For high-pressure homogenizers, values are found between 0.35 (turbulent inertial forces) and 1 (laminar shear or elongational flow) [23], whereas, for membrane emulsification it may be greater than one [24]. As for our experiments, $\beta$ was in the range of homogenisation, with at least partly turbulent flow. As mentioned before, we expect that the droplets may pass the constriction, but will break-up after passing the pore, as was described by Harvie et al. [21] for microfluidic circuits in which turbulence after a constriction was identified as the reason for droplet break-up. This could also contribute to the retention of the high fluxes upon repeated passage of the membrane since droplet break-up does not require contact between droplet and membrane. The correlation coefficients between the
three fit parameters of Eq. 3.10 are shown in Table 3.3, which shows that they are not correlated.

Table 3.3

<table>
<thead>
<tr>
<th></th>
<th>10.6 μm</th>
<th>11.6 μm</th>
<th>12.8 μm</th>
<th>13.2 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>-</td>
<td>-0.313</td>
<td>-0.705</td>
<td>-0.30</td>
</tr>
<tr>
<td>β</td>
<td>0.313</td>
<td>-</td>
<td>0.776</td>
<td>-0.70</td>
</tr>
<tr>
<td>γ</td>
<td>0.705</td>
<td>0.776</td>
<td>-0.66</td>
<td>0.77</td>
</tr>
</tbody>
</table>

3.4.3. Effect of dispersed phase fraction, including a comparison with SPG membrane

Premix emulsification allows the preparation of more concentrated emulsions; also this aspect was evaluated through experiments carried out at 25 and 50% vol. dispersed phase (100 kPa transmembrane drop and 0.5% Tween-20 concentration). In both cases, similar trends were obtained as for 5% of dispersed phase, but the residual droplet size was considerably larger. The closest available comparison for our results can be found in the work of Vladisavljievic et al. [9], who used a SPG membrane (8.5 μm pore diameter, 0.8 mm wall thickness compared to our sieve 12.8 μm pore width and 0.08 mm wall thickness), to produce a 40% vol. corn oil in water emulsion.

The emulsification conditions in the work of Vladisavljievic were similar to our study, and it is clear that the SPG membrane is eventually more effective in reducing the droplet size as shown in Fig. 3.7. The internal structure of the SPG membrane, which has long interconnected pores, is expected to lead to different droplet break-up mechanisms compared to our sieves which only have one constriction point, i.e., the pore. The sieves operate in similar fashion as a high pressure homogenizer (fluxes are much higher than for SPG), where inside an SPG membrane, the droplets may break-up due to Laplace instabilities that are expected at lower fluxes. In case of nickel sieves, the major droplet reduction took place after the first pass and after that, the reduction was quite gradual; while in case of SPG membrane, the reduction may continue up to the third pass.
It is clear that membrane emulsification with metal sieves shows distinctive behaviour, which makes it a valuable addition to the range of emulsification techniques that are currently available. Especially for the preparation of large amounts of emulsions with droplet sizes of around 5–10 µm that don’t need to be perfectly monodispersed the technique presented here could be of interest. When technological developments lead to production of sieves with smaller pores, also smaller emulsion droplet sizes come within reach.
3.5. Conclusions

Premix membrane emulsification with nickel microsieves was found to be based on elongation and recompression of droplets, and thereby it is comparable to high-pressure homogenization. The transmembrane fluxes were very large, while a reasonable span of the droplet size was found; the dependence on the transmembrane pressure indicated at least partial turbulent conditions. There was no indication of fouling in the process, even after five passes, which indicates that the process is tolerant to product and conditions.

A master curve was derived for the droplet Weber number as a function of the transmembrane pressure normalized on the Laplace pressure of the emulsion before emulsification. This curve comprises all process parameters and allows estimation of the emulsion droplet size.

References


High-throughput premix emulsification using nickel sieves


The effect of pore geometry on premix membrane emulsification using nickel sieves having uniform pores

ABSTRACT

Oil-in-water premix membrane emulsification was successfully carried out using various nickel sieves having rectangular (width << length) or squared pores. The emulsification process was characterized using droplet Reynolds number (Re_d), droplet Weber number (We_d) and dimensionless pressure (\(\hat{P}\)). The inertial forces were found to be more important for sieves having rectangular pores that allow more chances for liquid-liquid interactions. Whereas, in case of sieves having squared pores spontaneous droplet break-up due to Laplace pressure differences may be more important. The curve between We_d and \(\hat{P}\) represents a change in the droplet break-up mechanism from spontaneous to shear based (extension) for each sieve (depending on ingoing droplet size) and between different sieves (in terms of efficient energy usage). Stacking sieves either on top of each other or at some distance was found to have no additional effect on droplet break-up compared to two separate passes. This illustrates the importance of matching the residence time between two passes with the interfacial dynamics of the surfactant system used.
4.1. Introduction

Premix membrane emulsification is an interesting technique for the controlled production of small sized emulsions and all kinds of related products [Chapter 2]. In this process, a coarse emulsion (premix) is first prepared which is then passed under mild pressure through a (microporous) membrane. The membrane is usually wetted with the continuous phase, however, if phase inversion is required, the membrane is wetted with the dispersed phase of the premix. The large droplets in the premix are broken-up into finer droplets at relatively low energy inputs [1]. In this respect, the process can also be regarded as low-pressure homogenization. If the desired droplet size and uniformity is not achieved in a single step, further homogenization by repeated or multi-stage premix membrane emulsification may be achieved [1, 2], but with a corresponding increase of overall energy input.

Premix emulsification is quite simple in its design, and can be used to produce emulsions at reasonable monodispersity, though the droplet size is not as monodispersed as for other microstructure-based emulsification techniques such as cross-flow membrane emulsification [3, 4], microchannels [5, 6], T- [7-9] and Y-junctions [10], flow focusing devices [11, 12], and edge-based droplet generation (EDGE) devices [13, 14]. However, contrary to these techniques, very high production rates and high dispersed phase fractions are possible using premix membrane emulsification, hence, making this technique attractive; that is if the membrane is not susceptible to fouling. The technique is very suited for fast product prototyping and even for bulk production of emulsions provided that the design of the systems can be made reliable, e.g., by using good scaling relations for the process.

Van der Zwan et al. [15] microscopically visualized the droplet break-up mechanisms in oil-in-water premix emulsification using microfluidic devices and found following three factors responsible for droplet break-up:

- snap-off due to localized shear forces
- break-up due to interfacial tension effects (Rayleigh and Laplace instabilities)
• break-up due to steric hindrance between droplets

In premix emulsification, the droplet break-up is directly affected by membrane properties (e.g., pore size, thickness, tortuosity and porosity) and transmembrane pressure. Other factors include emulsion viscosity (as is the case in traditional flow based emulsification), dispersed phase volume fraction, surfactant (type and concentration), temperature (also related to emulsion viscosity and surfactant adsorption rate), and pH (in case charged components are present, or charged membrane surfaces) [16-20]. As there are a number of factors involved, the derivation of scaling relations for premix emulsification is not so straightforward. Therefore, we will focus mostly on the effect of pore design on the obtained droplet size, and link this to the local conditions in the pore such as shear rate, and the properties of oil-water interfaces as reflected in the interfacial tension.

Since its introduction [21] various membranes have been investigated for premix emulsification, with Shirasu porous glass (SPG) membrane as the most popular membrane of choice [18, 21, 22]. These membranes are known for their interconnected micron-sized pores, a wide spectrum of available pore sizes (0.05–30 μm) with narrow size distribution and high porosity (50–60%) while their surface can be hydrophobized by reaction with organic silanes [23] to make them suitable for both oil-in-water and water-in-oil emulsification. Further, different polymeric membranes (e.g., polytetrafluoroethylene [1, 2, 24], polycarbonate [25-27], nylon [27], polyethersulfone [27], nitrocellulose mixed ester [27, 28], polyethylene [17], and cellulose acetate [29]), ceramic membranes (e.g., α-alumina [30]) and glass filters [31-33] have been reported in literature. Although all these membranes have been used (to some extent) successfully in the preparation of emulsions and related products, there is no single model or description available that covers the overall behaviour of these systems.

In addition to affecting the droplet break-up, the membrane type also determines the overall production rate of a process through its permeability, which may gradually decline due to fouling of the membrane with ingredients (e.g., proteins) from the premix. For membranes with interconnected pores, it might be difficult to clean fouled areas because of inaccessibility for the cleaning agents. In that respect,
straight-through pores are preferred, as discussed in Chapter 3. We used rectangular and uniformly sized pores, and thin active layers, which allowed us to operate at relatively low transmembrane pressure and at higher productivity than reported for other membranes. In previous work we focused on the effect of various process conditions and found that the droplet Weber number could be used to describe the expected droplet size. In this paper, we compare different pore (and sieve) designs and evaluate how this affects the droplet size.

4.2. Theory

The flux, $J$, across the sieve was calculated from the mass flow rate, $\phi_m$, using the following equation:

$$J = \frac{\phi_m}{\rho_e A},$$

(4.1)

where $\rho_e$ is the emulsion density and $A$ is the surface area of the sieve. The flux is related to average liquid velocity inside the pore, $v_p$, by:

$$J = v_p \epsilon,$$

(4.2)

where $\epsilon$ is the sieve porosity. The hydraulic Reynolds number inside the pore, $Re_p$, is defined as:

$$Re_p = \frac{\rho_e v_p d_h}{\eta_e},$$

(4.3)

where $d_h$ is the pore hydraulic diameter and $\eta_e$ is the emulsion viscosity. The pore hydraulic diameter is defined as:

$$d_h = \frac{2l_p w_p}{l_p + w_p},$$

(4.4)

where $l_p$ and $w_p$ are the pore length and width, respectively. The droplet Reynolds number, $Re_d$, is defined using the pore Reynolds number as [34]:

$$Re_d = Re_p \left(\frac{d_3}{d_h}\right)^2,$$

(4.5)
where \( d_{32,i} \) is the ingoing Sauter mean droplet diameter. The droplet Weber number, \( \text{We}_d \), which is a ratio between the inertial forces (as a result of local pressure fluctuations) and interfacial tension forces on a droplet, is defined as:

\[
\text{We}_d = \frac{d_{32,o} \rho_e \nu^2}{2\sigma},
\]

(4.6)

where \( d_{32,o} \) is the Sauter mean diameter of the droplet produced and \( \sigma \) is the droplet interfacial tension. The dimensionless pressure, \( \hat{\rho} \), which relates the applied energy to the minimum amount of energy needed to deform the droplet, was defined as a ratio of the transmembrane pressure to the droplet Laplace pressure [Chapter 3]:

\[
\hat{\rho} = \frac{d_{32,i} \Delta P}{\sigma}.
\]

(4.7)

### 4.3. Experimental

#### 4.3.1. Premix preparation

A coarse oil-in-water premix consisting of 5% n-hexadecane (99% for synthesis, MERCK) in Milli-Q water having 0.5% vol. Tween-20 (for synthesis, MERCK) as a surfactant was prepared with an ultra-turrax homogenizer (IKA® T-18 basic) operated at 3500 rpm for 10 minutes. This led to reproducible starting emulsions for our experiments. The droplet size was typically around 27 μm with a span of 0.9.

#### 4.3.2. Nickel sieves used for emulsification

Contrary to Chapter 3 in which we used the energy density to describe the droplet size, in this chapter we are interested in different sieves and how they influence droplet break-up. For this we used six different nickel sieves (Stork Veco BV, Eerbeek, The Netherlands); five sieves having rectangular pores (width \( << \) length) of width between 7.1–13.2 μm and one sieve having very small squared pores (4 × 4 μm). The SEM images were obtained using scanning electron microscope (Magellan 400, FEI, Eindhoven, The Netherlands) as described in Chapter 3, and are shown in Table 4.1.
Table 4.1. SEM images of the nickel sieves used in this study along with their specifications.

<table>
<thead>
<tr>
<th>Sieve specifications</th>
<th>Front view</th>
<th>Back view</th>
</tr>
</thead>
</table>
| **Pore size:** 4 × 4 μm  
**Thickness:** 60 μm  
**Porosity:** 2.65%  
**Supporting mesh on back side** | ![SEM Image](image1.png) | ![SEM Image](image2.png) |
| **Pore size:** 7.1 × 413.2 μm  
**Thickness:** 200 μm  
**Porosity:** 1.53%  
**Supporting structure on back side** | ![SEM Image](image3.png) | ![SEM Image](image4.png) |
| **Pore size:** 10.6 × 330.2 μm  
**Thickness:** 400 μm  
**Porosity:** 3.62%  
**Supporting structure on both sides** | ![SEM Image](image5.png) | ![SEM Image](image6.png) |
| **Pore size:** 11.6 × 331.1 μm  
**Thickness:** 350 μm  
**Porosity:** 3.95%  
**Supporting structure on back side** | ![SEM Image](image7.png) | ![SEM Image](image8.png) |
### 4.3.3. Emulsification setup

The emulsification setup consisted of a pressure vessel containing the premix emulsion and a module (a Plexiglas column) having a sieve at the bottom with an effective surface area of 1.43 cm$^2$ (Fig. 4.1). The sieve was held in place by two rubber o-rings (above and below) at the column’s bottom junction. The vessel containing 300–500 mL emulsion was pressurized with air or nitrogen while keeping the entrance valve connected to the module opened. The emulsification was started by opening the outlet valve of the module. The homogenized emulsion was collected in a flask placed on an electrical balance while the increase in mass per second was digitally recorded. Emulsification was continued for up to five repeated cycles and samples for droplet size measurement were collected after every pass.

### 4.3.4. Characterization of the emulsion samples

The emulsion samples were analysed for droplet size (distribution) with light scattering (Mastersizer 2000, Malvern Instruments Ltd., UK). The size distribution

---

**Table 4.1 (Continued)**

<table>
<thead>
<tr>
<th>Pore size: 12.8 × 329.3 μm</th>
<th>Thickness: 200 μm</th>
<th>Porosity: 4.37%</th>
<th>Supporting structure on back side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size: 13.2 × 336.9 μm</td>
<td>Thickness: 80 μm</td>
<td>Porosity: 4.79%</td>
<td>Flat surface on both sides</td>
</tr>
</tbody>
</table>
was given as the volume frequency as a function of drop size. Three readings were taken, and average values of Sauter mean droplet diameter, $d_{32}$, and droplet span, $\delta$, were determined and used in the analysis.

Fig. 4.1. Schematic representation of the experimental setup.

4.4. Results and discussion

4.4.1. Effect of the sieve support structure on emulsification

For the nickel sieves used here having long slits instead of interconnected pores, it was expected that the pore width determines the emulsion droplet size. For the sake of simplicity, we use the pore width to indicate the sieve under discussion, as shown in bold in Table 4.1. The sieve with a pore width of 13.2 µm has a flat surface on both sides, whereas, some of the sieves, i.e., 7.1, 11.6 and 12.8 µm sieves, have a somewhat raised surface on the backside to reinforce the sieve. Only 10.6 µm sieve has this supportive structure on both sides. The actual pore depth (the narrowest layer) for all these sieves was on average around 80 µm.

It was expected that the presence of supportive structures, before or after the pores, may have an added effect on the droplet break-up. The sieves having pore width of 7.1 and 11.6 µm with different supportive structures are presented here. The total sieve thickness, including supportive structure, was 200 and 350 µm,
respectively, however, the pore depth was the same for both sieves. Experiments were performed at different pressures from the front and back sides. These results are shown in Fig. 4.2.

![Fig. 4.2. Sauter mean droplet diameter, $d_{32}$, reduction with increasing number of passes, $N$, at different operating pressures using (a) 7.1 µm (200 µm thickness) and (b) 11.6 µm (350 µm thickness) sieves from front (empty mark) and back (filled mark) sides: (○) 50, (∗) 100 and (∆) 200 kPa.](image)

The droplet size decreases with the number of passes, and the reduction was faster at higher pressures, as expected. For both membranes, the supportive structures did not significantly affect the droplet size as there is hardly any difference between passage from the front or the back side. Hence, it is only the specific pore geometry that may have effect on droplet size, and this was investigated further.

Here, we would like to mention that the standard deviation of each experiment was quite small as evident from Fig. 4.2. We also repeated experiments and found them very reproducible. Therefore, we preferred to do experiments that cover a larger parameter space and focus on the general trends.

### 4.4.2. Effect of pore geometry on droplet break-up

The experiments were performed using different sieves having rectangular or squared pores at an applied pressure of 50–200 kPa. The mean droplet size obtained after the final pass through the sieve is shown in Table 4.2 together with the hydraulic diameter of the pore that was used in the calculations of the dimensionless numbers. Remarkably, the droplets obtained with rectangular pores were typically 2 times smaller than the smallest dimension of the pore (i.e., width),
while for squared pores the droplets were twice as large as the smallest dimension of the pore, at the maximum applied pressure (200 kPa). It is also clear from the literature that in premix membrane emulsification [19, 24] the ratio between droplet and pore size greatly depends on the pore size and the applied pressure.

### Table 4.2

Sauter mean diameter and span obtained after fifth pass through different pores at different applied pressures.

<table>
<thead>
<tr>
<th>Pore dimension [µm]</th>
<th>Pore hydraulic diameter [µm]</th>
<th>Applied pressure [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d_{32})</td>
</tr>
<tr>
<td>4 × 4</td>
<td>4</td>
<td>13.4</td>
</tr>
<tr>
<td>7.1 × 413.2</td>
<td>14.0</td>
<td>13.3</td>
</tr>
<tr>
<td>10.6 × 330.2</td>
<td>20.5</td>
<td>14.1</td>
</tr>
<tr>
<td>11.6 × 331.1</td>
<td>22.4</td>
<td>19.4</td>
</tr>
<tr>
<td>12.8 × 329.3</td>
<td>24.6</td>
<td>18.2</td>
</tr>
<tr>
<td>13.2 × 336.9</td>
<td>25.4</td>
<td>17.1</td>
</tr>
</tbody>
</table>

In case of rectangular pores, although the pore length was an order of magnitude larger than the pore width, a smaller droplet size was obtained at higher pressures compared to much smaller squared pores. However, the squared pores were efficient at low pressures in reducing the emulsion droplet size. This shows a clear effect of pore geometry on the mean droplet size. A different droplet break-up mechanism might operate as a function of changing pore geometry. In case of long rectangular pores, the flow through the pores was not well developed and partial turbulent conditions may have existed after the pores therewith contributing to droplet break-up [Chapter 3]. Depending on the porosity and pore geometry these effects might be more or less pronounced, and we used various dimensionless numbers to characterize the droplet break-up.

As the major droplet size reduction took place after the first pass through the sieve (Fig. 4.2), initially the results using different pore geometries were compared at different flow velocities for the first pass only. In Fig. 4.3, the droplet Weber number (Eq. 4.6) is plotted against the droplet based Reynolds number calculated
from the pore based Reynolds number using Eq. 4.5. The equilibrium interfacial
tension at the interface between the hexadecane and surfactant solution was 5.8
mNm$^{-1}$ as reported earlier [Chapter 3], and was used in the calculations. The sieves
having rectangular pores all behave similarly, but differently from the sieves with
squared pores. At both extreme ends, sieves with rectangular pores have about five
times higher droplet Weber number. Thus, the flow is more constrained in the
squared pores. The inertial forces seem to be more important for sieves having
rectangular pores that allow more chances for liquid-liquid interactions, and are
facilitated at higher droplet Reynolds number. Whereas, in case of sieves having
squared pores spontaneous droplet break-up due to Laplace pressure differences
may be more important, especially, at a lower droplet Reynolds number.

![Graph](image)

**Fig. 4.3.** Droplet Weber number, $\text{We}_d$, versus droplet Reynolds number, $\text{Re}_d$: (□) 4, (■) 7.1,
(○) 10.6, (●) 11.6, (△) 12.8 and (▲) 13.2 μm sieves.

To compare droplet break-up among different sieves while keeping all the
operating conditions constant, droplet Weber number was used as a function of
the pressure relative to the Laplace pressure of the premix emulsion droplets, $\hat{P}$
(Fig. 4.4), as suggested in previous work [Chapter 3]. A high $\hat{P}$ value indicates a
surplus of applied energy compared to the Laplace pressure of the droplet. Here,
the results of all the passes were incorporated to see the effect of different premix
(ingoing) droplet sizes on droplet break-up mechanism and energy usage. The
curve obtained in this way relates ingoing droplet size and pressure drop to the actual droplet size that can be obtained under specified experimental conditions. For high $W_{e_d}$ and $\hat{P}$ (large premix droplets), the slope of the curve is different from low $W_{e_d}$ and $\hat{P}$ (small premix droplets) where the curve is almost linear. This change in slope may be related to a change in droplet break-up mechanism, the droplet size becoming more dependent on the pressure drop for small premix droplets.

Fig. 4.4. Droplet Weber number, $W_{e_d}$, as a function of dimensionless pressure, $\hat{P}$: (□) 4, (◊) 7.1, (○) 10.6, (Δ) 11.6, (×) 12.8, and (+) 13.2 μm sieves.

The relation is different for each sieve, indicating an effect of the precise pore geometry. For larger ingoing droplets the sieve having rectangular pores with the smallest pore width (7.1 μm) exerts more inertia. These inertial effects decrease with increasing pore width and finally becoming comparable to squared pores (4 μm) for the higher pore width (13.2 μm). On the other hand, with decreasing ingoing droplet size the inertial effects decrease more rapidly for the smaller pore width and less rapidly for the bigger pore width. All the curves for the rectangular sieves ultimately coincide with each other at a certain point where the interfacial tension of the droplets becomes quite high compared to the external disruptive forces. Here, the pore width will be no longer effective in further reducing the droplet size indicating that we are already at or at least close to the system limit.
However, the squared pores behaved differently for smaller ingoing droplets and still showed droplet break-up at a very low We$_a$ confirming the constriction effects taking place.

The droplet uniformity, as expressed by the span values in Table 4.2, was typically around 1.0-1.5 depending upon the pressure applied. In all the cases a monomodal distribution of volume fraction to droplet size was obtained. There was not a well ordered difference between different pore geometries for the span values, but they did increase with increasing applied pressure, however, there was a limit to this effect. For an experiment performed at pressure up to 500 kPa using 11.6 µm sieve (results not shown in Table 4.2) no further increase in span was observed while droplet reduction was still taking place ($d_{32} = 3 \mu m$ and $\delta = 1.4$ at 500 kPa).

4.4.3. Effect of stacking sieves

In premix membrane emulsification repeated passes are often needed for a uniform and small droplet size. Here, we present the effect of combining membranes on droplet size and uniformity. Two 11.6 µm sieves were used in two different combinations: either put together or separated by a gap as shown in Fig. 4.5. The results were compared with that of a single 11.6 µm sieve that is repeatedly used for emulsification.

**Fig. 4.5.** (a) Schematic representation of the module used for holding the sieves, and (b) different arrangements of the sieves: (i) two sieves (top and bottom) separated by the length of the column, (ii) two sieves together at bottom, and (iii) single sieve at bottom.
The droplet size and droplet span obtained by using different combinations of the sieves are shown in Fig. 4.6. It is obvious from the results that at both pressures, using two sieves separated by a gap (length of the column) did not significantly affect the droplet size and uniformity. This is possibly due to a high emulsion velocity inside the column (Table 4.3). The average residence time for the droplets inside the pores is extremely short, (i.e., 8 µs at 100 kPa), whereas, the residence time in the dispersing zone of a high-pressure homogenizer is around 1–10 ms [35].

After passing through the first sieve, the droplets follow their path through the column to approach the second sieve. The average relaxation time for the droplets inside the column was around 0.3–0.5 seconds depending upon the pressure applied. This time may have been rather short for surfactant molecules to immediately stabilize the newly created interface. The newly formed droplets would then not be stabilized enough and might coalesce with each other while entering the second sieve. However, the time needed for diffusion of surfactant molecules to oil-water interface in high-pressure homogenizers is reported to be shorter (1 µs) [36], indicating that if our system would operate in similar fashion the calculated time should be enough for the surface to be covered completely. Still we think that the second constriction (sieve), where the droplets are subjected to, may enforce coalescence to take place as also illustrated in the work of Van der Zwan et al. [15] who visualized droplet passage through constrictions. In that
respect, the situation is not comparable to that in a high pressure homogenizer where the liquid velocities are much higher.

Table 4.3

Average emulsion velocity inside column and pore, and corresponding relaxation/residence time for different sieve combinations along with symbols used in Fig. 4.6.

<table>
<thead>
<tr>
<th>Sieve combinations</th>
<th>Applied pressure [kPa]</th>
<th>Avg. emulsion velocity inside column [m s(^{-1})]</th>
<th>Avg. emulsion velocity inside pore [m s(^{-1})]</th>
<th>Relaxation time inside column [s]</th>
<th>Residence time inside pore [µs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single sieve</td>
<td>100 (◊)</td>
<td>0.26</td>
<td>6.20</td>
<td>0.35</td>
<td>12.90</td>
</tr>
<tr>
<td></td>
<td>200 (♦)</td>
<td>0.38</td>
<td>9.48</td>
<td>0.24</td>
<td>8.44</td>
</tr>
<tr>
<td>Two sieves together</td>
<td>100 (Δ)</td>
<td>0.20</td>
<td>5.05</td>
<td>0.45</td>
<td>31.67</td>
</tr>
<tr>
<td></td>
<td>200 (▲)</td>
<td>0.36</td>
<td>9.18</td>
<td>0.25</td>
<td>17.44</td>
</tr>
<tr>
<td>Two sieves apart</td>
<td>100 (□)</td>
<td>0.17</td>
<td>4.24</td>
<td>0.54</td>
<td>15.83</td>
</tr>
<tr>
<td></td>
<td>200 (■)</td>
<td>0.36</td>
<td>9.10</td>
<td>0.25</td>
<td>8.72</td>
</tr>
</tbody>
</table>

In case of two sieves put together, we can see a slight decrease in droplet size (at 200 kPa) and a slight increase in droplet uniformity (at 100 kPa). These differences are rather small compared to those obtained when using an additional pass. These measurements confirmed that droplet stabilisation after break-up is crucial in emulsification, especially, when the residence time in the dispersing zone is too short. At low pressures (100 kPa), the span of the resulting emulsions is more or less constant, while at higher pressures (200 kPa), the span first increases and then levels off, while the droplet sizes are consistently below those obtained at 100 kPa. Even after the fifth pass the average droplet size still decreases but comparatively at a reduced rate.

The current investigation on premix emulsification, where the droplet break-up is actually favoured by injection normal to the membrane, is different from the conventional membrane emulsification where the shear is also applied parallel to the membrane surface. Because of a different droplet break-up mechanism taking place, the produced emulsions were not as monodispersed as reported for conventional membrane emulsification and other sophisticated emulsification techniques (mentioned in the introduction section). However, these sieves might be of interest for applications where higher production rates are desired [Chapter 3], and sieves with rectangular pores would be a better choice then.
4.5. Conclusions

Various nickel sieves having rectangular or squared pores were analysed for oil-in-water premix emulsification at different transmembrane pressures. A plot of droplet Weber number and droplet Reynolds number shows that the inertial forces are more important for sieves having rectangular pores and allow more chances for liquid-liquid interactions, whereas, in case of sieves having squared pores spontaneous droplet break-up due to Laplace pressure differences may be more important, especially, at a lower droplet Reynolds number. The curve between $\text{We}_d$ and $\dot{\mathcal{P}}$ represents a change in the droplet break-up mechanism from spontaneous to shear based (extension) for each sieve (depending on ingoing droplet size) and between different sieves (in terms of efficient energy usage). Using multiple sieves instead of a single sieve did not affect the obtained mean droplet size. This illustrates the importance of droplet stabilization, and matching the time between two passes to the interfacial dynamics of the surfactant system.

References


Effect of pore geometry in nickel sieves


Droplet break-up mechanism in premix emulsification using packed beds

ABSTRACT

Some emulsification techniques based on microstructures are known for the monodispersity of produced droplets, however, they lack in scalability. The techniques that are able to produce emulsions in larger amounts do not usually produce monodispersed droplets. We here report on a specific technique that has the potential to combine the best of both worlds: premix emulsification using a packed bed of differently sized glass beads (55, 65, 78 and 90 µm) supported by a metal sieve. The production of oil-in-water emulsions was targeted, and the process conditions especially related to internal structure of the porous medium like pore size and bed height were investigated.

The pore Reynolds number, \( Re_p \), was used to characterize the flow inside the packed bed consisting of asymmetric pores following a tortuous path inside the porous media. The pore size and the flow velocity determined the droplet break-up. Two droplet break-up mechanisms were identified: either dominated by constriction (\( Re_p < 40 \)) or inertia (\( Re_p > 40 \)). Droplets below 5 µm (droplet to pore size ratio \( \approx 0.2 \)) could easily be produced, having relatively narrow droplet size distribution (droplet span \( \approx 0.75 \)). The measured fluxes were comparable to the highest reported flux values for premix membrane emulsification studies. Statistically significant scaling relations were established for the studied process conditions.
5.1. Introduction

Emulsions are a part of many aspects of daily life and have gained a lot of interest especially related to their desired droplet size (distribution). Food, chemical, cosmetics and pharmaceutical industries are among the main sectors in which emulsions have found numerous applications [1]. Smaller droplet sizes and appreciable droplet uniformity is generally required for a good structural stability of a product. To further prolong the shelf-life it is also possible to adjust physical properties, like viscosity and density, of the dispersed and the continuous phases that will prevent or at least delay (the onset of) creaming, sedimentation or coalescence over time.

In the last decades, several microstructured emulsification systems have been proposed with the intent of having better control on the droplet size and droplet size distribution, compared to the conventional energy intensive equipment. Among them, membrane emulsification is prominent, either in cross-flow [2] or dead-end (premix) mode [3]. In cross-flow emulsification, the dispersed phase is pushed through the membrane pores into the flowing continuous phase on the other side of the membrane. This technique is known to yield high droplet monodispersity at low dispersed phase fractions. To produce emulsions at higher dispersed phase fraction, premix membrane emulsification in which a coarse emulsion is pushed through the membrane to get a fine emulsion, is an interesting alternative given its low energy input. In addition, a number of microfluidic devices have been proposed, such as microchannels [4], T- [5] and Y-junctions [6], flow focusing devices [7], and edge-based droplet generation (EDGE) devices [8]. Each technique has its own pros and cons, but up- or out-scaling of these devices is still a major challenge.

To evaluate the potential of an emulsification process, in addition to droplet size (distribution), other factors have to be considered like production rate, energy efficiency, ease of design, etc. Several publications report on premix emulsification using different membranes and under different operating conditions. The production rate is quite high in premix emulsification, and the emulsions obtained are relatively monodispersed [9-11]. The mean droplet diameter can be tuned
through the membrane pore size and the operating parameters, especially the transmembrane pressure. However, its sensitivity to depth fouling of the membrane, and in tandem with this, the inaccessibility of the membrane pores to cleaning agents is regarded as the largest disadvantage of premix emulsification, which in many cases is decisive.

Application of a packed bed of small glass beads (supported by a metal sieve) results in a ‘dynamic’ membrane that is morphologically similar to the conventional membranes [12]. The system has a great advantage that the particles can be easily cleaned by disintegrating the bed, and then the bed can be formed anew. Van der Zwan et al. [12] compared their results with this system to those of Vladisavljevic et al. [13] with membranes, and found that the results were in good agreement with a low dispersed phase volume fraction of hexadecane in an aqueous phase. Hence, this system can be used as a model for premix membrane emulsification.

In this investigation, we took the packed bed system much further and investigated glass beads of different sizes focusing on the internal structure of the bed. The droplet break-up mechanism was explained in terms of a change in flow behaviour inside the porous media, and existing scaling relations were successfully modified to relate all operating conditions to the droplet size produced.

5.2. Experimental

5.2.1. O/W premix preparation

An O/W premix emulsion consisting of 5% n-hexadecane (99% for synthesis, MERCK) in Milli-Q water having 0.5% v/v Tween-20 (for synthesis, MERCK) was used. For each experiment, 300 mL of coarse premix was prepared with an ultra-turrax homogenizer (IKA® T-18 basic) operated at 3500 rpm for 6 ± 1 minutes. This led to reproducible starting emulsions for our experiments having Sauter mean droplet diameter, \( d_{32} \), typically around 30 μm and a droplet span, \( \delta \), of 0.9.

5.2.2. Emulsification setup

The emulsification setup is shown in Fig. 5.1. The pressure vessel containing the premix was connected to a module (a Plexiglas column) having a packed bed of
glass beads on top of a support sieve (described below) with an effective surface area of 1.43 cm$^2$. The support sieve was held in place by two rubber o-rings (above and below) at the bottom junction of the column. To properly wet the system with the continuous phase, a small amount of continuous phase was introduced inside the module. Then it was turned upside down for few times and placed vertically to let the glass beads settle down in the form of a bed. The emulsion vessel (containing the premix) was pressurized with nitrogen keeping the valve connected to the column opened.

The emulsification was started by opening the outlet valve of the module and homogenized emulsion was collected in a beaker placed on an electrical balance for digitally recording the increase in mass every second. The flux, $J$, across the packed bed was calculated from the mass flow, $\phi_m$, using the following equation:

$$J = \frac{\phi_m}{\rho_e A},$$

(5.1)
where $\rho_e$ is the emulsion density and $A$ is the effective surface area of the packed bed. The emulsification process was repeated up to five cycles.

The premix emulsion and the all homogenized emulsion samples were analysed for droplet size (distribution) with a laser diffraction particle size analyser (Mastersizer 2000, Malvern Instruments Ltd., UK). The machine takes three readings, and the average values of droplet size and droplet size distribution (span) were determined and used in the analysis.

5.2.3. Support sieve

Nickel sieves (Stork Veco BV, The Netherlands) having straight-through rectangular pores were used as a support for the glass beads. A sieve having an average pore size of $11.6 \times 331 \ \mu m$ was used that was thick enough (350 $\mu m$) to provide a good support to the bed and withstand the applied pressure. The SEM images of top and bottom view of the sieve are shown in Fig. 5.2.

![SEM image of the support sieve used in this study: (left) top view, plane surface and (right) bottom view, structured surface.](image)

5.2.4. Packed bed

Hydrophilic glass beads (100HFL, Pneumix SMG-AF) having diameters between 30–200 $\mu m$ were used in this study. Three metal test sieves of pore sizes 63, 75 and 90 $\mu m$ were put on top of each other on an electrical shaker (JEL Engelsmann AG, Ludwigshafen, Germany) with the sieve having the largest pore size at the top and the one with the smallest pore size at the bottom. Four different size fractions of the glass beads were obtained after sieving the stock beads. The particle size
(distribution) of the fractions obtained was also analysed with a laser diffraction particle size analyser (Mastersizer 2000, Malvern Instruments Ltd., UK). Fig. 5.3 shows the particle size distribution of each fraction. The span of the distributions in all the cases was around 0.65 ± 0.01.

![Particle size distribution of different fractions of glass beads](image)

**Fig. 5.3.** Particle size distribution of different fractions of glass beads: (○) 55, (∆) 65, (□) 78 and (◊) 90 µm.

The particle, \( \rho_p \), and bulk, \( \rho_b \), densities of each fraction were measured in water and in air, respectively, and subsequently the porosity, \( \epsilon = 1 - \rho_b/\rho_p \), was calculated. For all the fractions the porosity was around 0.4.

The capillary model for fixed beds proposed by Comiti and Renaud [14] was used to determine the structural properties of the porous media like pore diameter and tortuosity. This model assumes the packed beds to consist of a bundle of identical cylindrical tortuous pores, and this concept has been adopted by various researchers [15-17] to characterize the emulsification process in static mixers.

The pore diameter, \( d_p \), was defined as:

\[
d_p = \frac{4\epsilon}{A_{vd}(1-\epsilon)},
\]

where \( A_{vd} \) is the dynamic specific surface area that is a ratio of wetted surface area to volume of solid. It is related to the bead diameter, \( d_b \), by:
\[ A_{vd} = \frac{6}{d_b} . \]  

(5.3)

The bed tortuosity, \( \xi \), was calculated as:

\[ \xi = 1 + q \ln(1/\epsilon) , \]  

(5.4)

where \( q = 0.41 \) for tightly packed spheres. The average pore velocity, \( v_p \), was defined as:

\[ v_p = \frac{v_o \xi}{\epsilon} , \]  

(5.5)

where \( v_o \) is the superficial velocity equal to \( J/\epsilon \). The flow inside the packed bed was characterized using the pore Reynolds number, \( Re_p \), which is a ratio of the inertial to the viscous forces defined as:

\[ Re_p = \frac{\rho_e v_p d_p}{\eta_e} , \]  

(5.6)

where \( \eta_e \) is the emulsion viscosity. The energy density, \( E_V \), for a single pass defined as energy input per unit volume of emulsion is related to pressure drop, \( \Delta P \), through:

\[ E_V = \frac{P}{\phi_V} = \frac{\Delta P \phi_V}{\phi_V} = \Delta P , \]  

(5.7)

where \( P \) is the power input and \( \phi_V \) is the volume flow rate. For more than one pass the energy densities of all the passes are cumulative.

Even though droplet break-up also occurs when no glass beads are used and only the metal sieve is present; this is only true for very high pore velocities [Chapter 3 and 4] which were not attained in this investigation. Thus, break-up by the sieve can be safely disregarded. The droplet break-up is expected to occur only due to the packed bed. Contrary to Van der Zwan et al. [12] who also considered the metal sieve, we here took only the pressure drop over the bed for droplet size analysis, as we previously established that the pressure drop over the membrane we use is extremely small. The pressure drop over a bed of glass beads of diameter \( d_b \) at a bed height of \( H \) was calculated using the Ergun equation:

90
\[ \Delta P = \frac{150(1-\epsilon)^2 \eta_e v_0 H}{e^3 d_b^2 \rho_e v_0^2 H} + \frac{1.75(1-\epsilon) \rho_e v_0^2 H}{e^3 d_b} \]  

(5.8)

5.3. Results and discussion

5.3.1. Effect of bead size and bed height

The bead size and bead packing arrangement are directly related to the size of the interstitial voids between the beads. These interstitial voids can be seen as interconnected asymmetric capillaries that follow an irregular path through the packed bed, somewhat comparable to pores in conventional membranes; especially to those in ceramic membranes which are prepared by sintering a packed bed of individual ceramic particles similar to those used in our packed bed. The size of the beads constituting the bed, thus, is an important parameter to be considered for understanding the emulsification process using a packed bed.

The experiments were carried out using glass beads of different average diameters, i.e., 55, 65, 78 and 90 μm at a fixed bed height of 2.5 mm with an applied pressure of 200 kPa. The droplet diameter obtained using different glass beads was made dimensionless by dividing the droplet diameter by the respective pore diameter (Eq. 5.2). These values are plotted in Fig. 5.4 against the pore size. A small droplet to pore size ratio was obtained for 55 μm glass beads, which then increased for 65 μm glass beads. A further increase in pore size again resulted in a smaller ratio.

Fig. 5.4. Effect of pore size, \(d_p\), on dimensionless droplet diameter, \(d_{32}/d_p\), and droplet span, \(\delta\): (□) 1st (△) 3rd and (◊) 5th pass.
It is remarkable that the droplet size is considerably smaller than the pore size irrespective of the applied transmembrane pressure; the droplet to pore size ratio is as low as 0.2. In various premix emulsification studies, droplet to pore size ratios over a range from 0.2 to 4.1 have been reported [Table 2.A.2 in Chapter 2]; thus in this work we are at the low end of this spectrum. In cross-flow membrane emulsification the droplet size is typically 3 to 10 times the pore size [18-21], and narrower pores are needed to produce the same droplet size.

The largest droplet size reduction took place till the third pass, and after this pass there was only minor decrease in the droplet size. The span values depended strongly on the pore size, and decreased with smaller pore sizes. The span decreased with repeated passes through the bed, especially in case of smaller pore size. However, for larger pore sizes a small increase in span was observed which means that given the size of the droplets, this particle size is no longer effective in breaking up these droplets, while smaller particles are still effective in doing so. This was investigated further by varying the bed height for one particle size.

![Fig. 5.5. Effect of bed height, \(H\), on dimensionless droplet diameter, \(d_{32}/d_p\), and droplet span, \(\delta\): (□) 1\(^{st}\), (∆) 3\(^{rd}\) and (◊) 5\(^{th}\) pass.](image)

Emulsification was carried out with 78 µm beads using different bed heights from 1–20 mm at an applied pressure of 200 kPa. In Fig. 5.5, the dimensionless droplet diameter and droplet span are plotted against the bed height used. The results show an increase in the droplet size with the bed height. The increase in droplet size is attributed to a decrease in pore velocity with increasing bed height, resulting in less shear force on the droplets, as was also demonstrated by Van der
Zwan et al. [22] who used microfluidic systems to vary the ‘bed height’. Moreover, the chances that droplets meet inside the packed bed increase with increasing bed height, possibly leading to coalescence.

The span values decreased strongly with the increasing bed height up to a certain limit, after which it remained almost constant. Also here the span seemed to increase very slightly with increasing number of passes, but this effect is small. The observed effects are most probably a combination of break-up and coalescence that ultimately cancel out upon reaching an average droplet size.

We further investigated the effect of the flow velocity inside the porous medium on the final droplet size and uniformity using the pore Reynolds number that characterizes the flow inside the porous media. We here show two series of experiments, one in which the bed height was varied (yielding different hydrodynamic resistances and therefore yielding different velocities and pore Reynolds numbers) and one in which different sized beads were used in the bed. The final droplet to pore size ratio and the span obtained after the fifth pass of each experiment are plotted against the respective pore Reynolds number (Fig. 5.6).

![Graph](image_url)

**Fig. 5.6.** Dimensionless droplet diameter, $d_{32}/d_p$ and droplet span, $\delta$, as a function of pore Reynolds number, $Re_p$: (Δ) pore size varied, $d_p$ and (○) bed height varied, $H$.

Both data series start off separately at relatively low pore Reynolds number but then merge at pore Reynolds number above 40. At low pore Reynolds numbers, the pore size has a greater influence on the droplet size than the velocity, indicating that the constriction needed for spontaneous droplet snap-off is here
dominant in the size reduction; this is corroborated by the reduction of the span. With increasing pore Reynolds number both curves are the same, which indicates that the break-up mechanism becomes similar (a decreasing bed height or an increasing pore size) and this is due to dominance of inertial effects (i.e., droplet break-up due to local shear forces). This inertial droplet break-up region is characterized by a decrease in droplet uniformity.

This establishes that the internal structure of a packed bed is important in determining the droplet size and uniformity. With small pores, the constrictions mainly determine the droplet snap-off, which is the mechanism found in microchannel devices. However, contrary to microchannel devices the shear stress could also be relevant to droplet disruption to some extent depending upon the flow velocity inside the pores. With larger pore sizes and sufficient flow, the local shear forces are so large, that these determine the break-up of the droplets. This is similar to the mechanisms found in T- and Y-junctions, and in flow focusing and co-flow microdevices.

As more uniform droplets were produced in spontaneous droplet forming region at low Re_p, further experiments were carried out using 55 µm glass beads at different flow velocities. The subsequent droplet size (distribution) is discussed in the next section.

5.3.2. Droplet break-up in spontaneous droplet formation dominated region

The droplet size and the corresponding flux obtained after different passes through the bed using different applied pressures are shown in Table 5.1. The droplet size decreases with increasing applied pressure as would be expected at increased shear on the droplets inside the pores as a result of higher flow velocities and also due to an increased number of active pores.

At all applied pressures and especially at elevated pressures, the droplet size reduction was highest after the first pass. Significant further reduction was found up till the third pass after which only minor reduction was found. The flux values are reasonably high and of course have direct dependency on the pressure applied. The obtained fluxes are comparable to the highest reported flux values for premix
Table 5.1

Droplet size and flux obtained after different passes through the 55 µm glass beads at different applied pressures.

<table>
<thead>
<tr>
<th>Applied pressure [kPa]</th>
<th>Pass through the packed bed</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>3</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{32}$ [µm]</td>
<td>$J$ [m²·m⁻²·hr⁻¹]</td>
<td>$d_{32}$ [µm]</td>
<td>$J$ [m²·m⁻²·hr⁻¹]</td>
</tr>
<tr>
<td>50</td>
<td>14.1</td>
<td>30.0</td>
<td>8.0</td>
<td>34.9</td>
</tr>
<tr>
<td>100</td>
<td>11.0</td>
<td>157.9</td>
<td>5.9</td>
<td>99.5</td>
</tr>
<tr>
<td>150</td>
<td>8.9</td>
<td>247.4</td>
<td>5.6</td>
<td>241.9</td>
</tr>
<tr>
<td>200</td>
<td>8.2</td>
<td>279.8</td>
<td>5.3</td>
<td>291.9</td>
</tr>
<tr>
<td>250</td>
<td>8.1</td>
<td>388.5</td>
<td>5.2</td>
<td>303.2</td>
</tr>
<tr>
<td>300</td>
<td>7.3</td>
<td>433.6</td>
<td>4.8</td>
<td>456.6</td>
</tr>
<tr>
<td>400</td>
<td>7.5</td>
<td>505.3</td>
<td>4.7</td>
<td>585.8</td>
</tr>
<tr>
<td>500</td>
<td>5.6</td>
<td>636.8</td>
<td>4.3</td>
<td>763.4</td>
</tr>
</tbody>
</table>

membrane emulsification (while the size distribution remains much narrower as discussed in the next section) and around 100–1000 higher than those with cross-flow membrane emulsification [Chapter 2]. There is no clear trend of the flux over the different passes, which we think is due to the inherent variability in the internal structure of a packed bed that may exist even among repeated emulsification passes in a single experiment.

Fig. 5.7. Droplet size distribution as a function of applied pressure: (□) 50, (+) 100, (Δ) 200, (×) 300, (○) 400 and (○) 500 kPa.
The droplet size distributions after the final pass through the bed are shown in Fig. 5.7. The distribution is wide at lower pressures (≤ 100 kPa) and becomes narrower (a span value typically around 0.75) with a moderate increase in pressure. A further increase in pressure (> 400 kPa) resulted again in a wider distribution and in the formation of a small second peak with droplets < 1 µm. These might be regarded as satellite droplets produced as a result of increased pore velocity at higher pressures (Rayleigh instability), and are in agreement with droplet break-up by flow (either shear or extensional).

### 5.3.3. Scaling relations

The droplet disruption in a continuous emulsification method can be correlated to the energy density, which is the amount of energy applied per unit volume of emulsion in the dispersing zone of an emulsification device [23]. In case of emulsification using a packed bed of glass beads, the energy density is related to the pressure drop across the bed through the relation given in Eq. 5.7, and is cumulative over all the passes. For the relation of the energy density, $E_V$ (bar) to the Sauter mean droplet size, $d_{32}$ (µm), the following equation is proposed:

$$\frac{d_{32}}{d_p} = \alpha E_V^{-\beta} \left(\frac{H}{D}\right)^\gamma$$  \hspace{1cm} (5.9)

where $\alpha$, $\beta$ and $\gamma$ are fit parameters. This is a modified form of the equation that was originally derived by Van der Zwan et al. [12] for packed beds. As energy density is cumulative over all the passes, it also covers the effect of the number of passes. Further, to characterize the emulsification process using differently sized glass beads, the droplet to pore size ratio, $d_{32}/d_p$, is used here. The $d_p$ is the calculated pore diameter based on the glass bead size, $d_b$, as discussed in the theory section. The $H/D$ is the height to diameter ratio of the packed bed.

The droplet size was fitted to the energy density and other process related parameters like pore size and bed height for each pass through the bed. In Table 5.2, the calculated values of the fit parameters are shown along with their standard deviations. One should bear in mind that the particle sizes, bed heights and pressures are all incorporated in the data shown in Fig. 5.8. The experimental and modelled data show reasonable agreement, especially given the large variations in
process conditions that were explored. As a result of internal structure of the porous media the process is comparable regarding energy usage, irrespective of the specific break-up mechanism, and can be described by Eq. 5.9. As shown in Table 5.2, the standard deviations of the fit parameters are less than 10% and they are not correlated with each other.

Table 5.2
Values, standard deviations and correlation coefficients of fit parameters of Eq. 5.9.

<table>
<thead>
<tr>
<th>Fit parameters</th>
<th>Values and standard deviations</th>
<th>Correlation coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>α</td>
</tr>
<tr>
<td>α</td>
<td>0.693 ± 0.034</td>
<td>-</td>
</tr>
<tr>
<td>β</td>
<td>0.172 ± 0.017</td>
<td>0.88</td>
</tr>
<tr>
<td>γ</td>
<td>0.351 ± 0.020</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Fig. 5.8. Experimental values of Sauter mean diameter, \( d_{32} \), plotted against the result of Eq. 5.9 using fit parameters given in Table 5.2. See Table 5.3 for explanation of the symbols.

The Sauter mean diameter of the droplet produced using glass beads and the corresponding energy input is plotted in Fig. 5.9, and compared with various microstructured and conventional emulsification devices from literature. Obviously, each device has its own energy requirement principally depending upon the specific droplet break-up mechanism taking place. Compared to emulsification techniques such as Y-junction and flat valve homogenizers, the
energy requirement of the packed bed system is less. Apart from the energy density comparison relative to the droplet size produced, this plot also yields information on the range of droplet sizes that a technique may give. This is especially true in case of microfluidic devices (e.g., microchannel an EDGE emulsification) where there is a narrow working region for stable droplet formation. Although it is useful to know the specific energy requirement of a certain process, we should keep in mind that we cannot rank different processes by only looking at their energy efficiencies. In addition, for example, droplet size (distribution), production rate, system behaviour under different product properties, etc., are very important.

The results discussed in this chapter show that the emulsification using a packed bed of glass beads is a technique with potential for the controlled production of emulsions. The system offers more flexibility (in terms of desired droplet size and production rate) as the internal structure of the packed bed can be easily regulated using differently sized particles. In that respect the packed bed (a dynamic membrane) outperforms the classical membranes. Compared to microstructured emulsification systems, the up-scaling is much easier as the packed bed area can be
increased using larger support sieves or by constructing several modules in parallel. The sieves that we used can be standardly produced in sizes of > 1 m²; dispersing glass beads over the sieve is not such a big issue since they can be deposited onto the sieve by filtering a dispersion, and re-dispersion can be achieved by back pulsing the column. As the research will progress in this area, we expect that the production of even smaller droplet size using smaller glass beads or other materials will become realistic.

5.4. Conclusions

Oil-in-water emulsions were prepared by premix emulsification using a packed bed of differently sized glass beads supported by a metal sieve. The process conditions especially related to internal structure of the porous medium like pore size and bed height were investigated, and both were found responsible for droplet break-up. Two different droplet break-up mechanisms were identified: either dominated by constriction \( \text{Re}_p < 40 \) or inertia \( \text{Re}_p > 40 \). Droplets below 5 µm
(droplet to pore size ratio ≈ 0.2) could easily be produced using pore sizes that were considerably larger, and the measured fluxes were comparable to the highest reported flux values for premix emulsification studies. An appreciable droplet size distribution (droplet span ≈ 0.75) was obtained over a pressure range of 200–400 kPa. Scaling relations were established based on the studied process conditions, and a reasonably good agreement was observed between the experimental and modelled data, making these relations suitable for design studies.

References


Influence of the emulsion formulation in premix emulsification using packed beds

**ABSTRACT**

Premix emulsification was investigated using packed beds consisting of micron-sized glass beads; a system that avoids fouling issues, unlike traditional premix membrane emulsification. The effects of the formulation were investigated; most notably the viscosity and the concentration and type of surfactant. The droplet size was reduced by increased shear stress in the emulsion. This was stronger at low viscosity ratios than at high ratios. The flux was proportional to the overall emulsion viscosity. Emulsions with small droplet size (Sauter mean droplet diameter < 5 μm) could still be produced at up to 60% of dispersed phase provided that sufficient surfactant was available. More uniform emulsions (span ≈ 0.75) were produced with Tween-20 (nonionic) and SDS (anionic) as surfactants than with CTAB (a cationic surfactant), possibly due to a combination of a low equilibrium interfacial tension and electrostatic attractions with the glass surface. Scaling relations were proposed taking into account all investigated product properties.
6.1. Introduction

Premix membrane emulsification gains attention for the production of various types of dispersions [1-3]. The simplicity of its design, the high production rates, the ease of scale-up and the possibility to produce concentrated emulsions are advantages reported for this technique [Chapter 2]. In premix membrane emulsification, a coarse emulsion (premix) is first prepared, which is then extruded under relatively mild pressure through a microporous membrane to get a homogenized emulsion. Unlike other microstructure-based emulsification techniques, where the to-be-dispersed and the continuous phases flow separately [4], in premix emulsification the coarse premix passes as a whole through the membrane pores. While this simplifies the process operation as only one flow has to be controlled, it increases the risk of fouling of the pores by the emulsion components, which in turn may compromise the stability of the process in time.

The interaction of the emulsion ingredients with the membrane surface is of prime importance. For example, proteins are often used as stabilisers, but their amphiphilic nature also makes them prone to aggregate and adsorb irreversibly on the surface of the membrane pores. Since this often leads to multilayer adsorption, the pores may become blocked [5]. Cleaning of fouling inside pores is very difficult, as flow through the pores is impeded. In addition, protein aggregates may block membrane pores, or alternatively emulsion droplets may get trapped due to interaction between the proteins on the droplet surface and the membrane surface. The membrane type, surface properties and pore size in relation to a specific product ingredient are therefore important aspects in premix membrane emulsification. Once fouled, the membranes are not easy to clean and often the original flux may not be restored even after extensive cleaning, since internal fouling is not accessible to the cleaning agent [6].

When using metal sieves having straight-through pores, we found recently that high production rates could be achieved (flux ≈ 1000 m³ m⁻² hr⁻¹ at 100 kPa) without any noticeable fouling [Chapter 3]. Also, a packed bed system consisting of micron-sized glass beads was found to be an interesting alternative to typical membranes to avoid fouling problems [7]. This system is easy to clean as the glass
beads can be re-suspended and washed or replaced subsequently. The packed bed works very similar to conventional membranes (e.g., ceramic membranes that are basically a sintered bed of individual particles) and droplets with appreciable uniformity (droplet span ≈ 0.75) could be produced, which is better than the typical span values found for the metal sieves with straight-through pores (droplet span typically around 1.0–1.4). For the packed beds, two different droplet break-up mechanisms were identified: (i) dominated by constriction and (ii) dominated by inertia. The constriction effect, characterized by a low pore Reynolds number, provides better droplet uniformity [Chapter 5].

Apart from the process conditions that were covered in previous chapter, droplet disruption is also affected by several formulation parameters, like viscosities of the dispersed and continuous phases, and interfacial tension effects [8]. The viscosities of the dispersed and the continuous phases affect the droplet size (distribution) differently in various emulsification techniques. For example, in cross-flow membrane emulsification, the droplet size is said to be determined by the ratio of the shear stress (related to the viscosity of the continuous phase) and the interfacial tension [9]. However, the overall dependence is hard to predict since high shear stresses lead to high expansion rates of the surface and related to that high interfacial tensions if the adsorption rate of the surfactant is slower than the expansion rate.

To our knowledge, there is only one study on premix emulsification using Shirasu porous glass (SPG) membrane for the production of W/O/W double emulsions focussing on the effect of continuous phase viscosity [10]. A smaller outer droplet diameter was obtained with increasing continuous phase viscosity, owing to the higher shear stress exerted by the continuous phase in the pores. In addition to this, these authors noted that the surfactant type and concentration played a vital role in the droplet break-up process and the stability of newly created interface afterwards, although these effects were not studied in detail.

The aim of the study reported here is to gain more insight into the effects of product properties such as viscosities of dispersed and continuous phases and surfactant (type and concentration) on droplet break-up, and to check the
possibility to produce concentrated emulsions by premix emulsification using packed beds. The obtained results were used to construct a window of operation for this process through relevant scaling relations.

6.2. Experimental

6.2.1. Premix preparation

An O/W premix consisting of n-hexadecane (99% for synthesis, MERCK) in Milli-Q water was used as the continuous phase. The experiments concerning viscosity and surfactant effects were carried out using a 5% vol. emulsion. The premix emulsions were prepared with an ultra-turrax homogenizer (IKA® T-18 basic) operated at 3500–4500 rpm for 5–10 min. To ensure similar starting emulsions for our experiments, the premix droplet size was checked at regular intervals. The ultra-turrax was stopped when the Sauter mean droplet diameter was around 30 µm, and it was checked whether these emulsions remained stable.

| Table 6.1 |
| Dispersed and continuous phases used to investigate viscosity effects in this study. |
| Blends | Relative fractions | Viscosity [mPa s] | Density [kg m⁻³] | Eq. interfacial tension* [mN m⁻¹] | Refractive index |
| Dispersed phases | Hexadecane | Paraffin |
| O₃ | 1 | 0 | 3.3 | 770 | 4.9 | 1.435 |
| O₁₀ | 0.54 | 0.46 | 9.8 | 810 | 4.6 | 1.450 |
| O₂₃ | 0.30 | 0.70 | 22.8 | 830 | 5.0 | 1.460 |
| O₃₂ | 0.22 | 0.78 | 31.9 | 840 | 4.8 | 1.463 |
| O₄₅ | 0.18 | 0.82 | 44.5 | 850 | 4.6 | 1.466 |
| O₁₀₁ | 0 | 1 | 100.6 | 860 | 6.2 | 1.473 |
| Continuous phases | Water | PEG |
| W₁ | 1 | 0 | 1 | 1000 | - | 1.333 |
| W₃ | 0.74 | 0.26 | 3.2 | 1034 | 5.0 | 1.369 |
| W₁₀ | 0.52 | 0.48 | 10.1 | 1062 | 2.0 | 1.404 |
| W₂₁ | 0.40 | 0.60 | 20.5 | 1078 | 2.0 | 1.418 |
| W₃₂ | 0.33 | 0.67 | 32.1 | 1087 | 2.0 | 1.428 |
| W₄₂ | 0.28 | 0.72 | 42.4 | 1094 | 2.0 | 1.434 |

*equilibrium interfacial tension of the interface between oil and water containing 0.55% w/v Tween-20
prior to emulsification. For the experiments with concentrated premixes (up to 60% vol.) we prepared the premixes by mixing with a magnetic stirrer at 700 rpm for half an hour.

Viscous paraffin (MERCK) and polyethylene glycol (PEG 400 for synthesis, MERCK) were used to increase the viscosity of the oil and water phases, respectively. The oil and water blends with different viscosities were prepared as shown in Table 6.1 along with some of their physical properties. To stabilize the newly formed droplets, different surfactants were used at concentrations shown in Table 6.2, which also gives information on the equilibrium interfacial tension.

**Table 6.2**

Surfactant types and concentrations used in this study.

<table>
<thead>
<tr>
<th>Surfactant type</th>
<th>Charge</th>
<th>HLB&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CMC&lt;sup&gt;b&lt;/sup&gt; [% w/v]</th>
<th>Conc. used [% w/v]</th>
<th>Equilibrium interfacial tension&lt;sup&gt;c&lt;/sup&gt; [mN m&lt;sup&gt;-1&lt;/sup&gt;]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyoxyethylene (20) sorbitan monolaurate (Tween-20)</td>
<td>Nonionic</td>
<td>16.7</td>
<td>0.0072</td>
<td>0.011</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.11</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.55</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.1</td>
<td>4.7</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>Anionic</td>
<td>40</td>
<td>0.23</td>
<td>0.55</td>
<td>6.8</td>
</tr>
<tr>
<td>Cetyltrimethylammonium bromide (CTAB)</td>
<td>Cationic</td>
<td>10</td>
<td>0.04</td>
<td>0.55</td>
<td>2.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> hydrophilic-lipophilic balance; <sup>b</sup> critical micelle concentration; <sup>c</sup> equilibrium interfacial tension of the interface between n-hexadecane and surfactant solution

**6.2.2. Emulsification setup**

The emulsification setup is shown in Fig. 6.1. The pressure vessel containing the premix was connected to a module (a Plexiglas column) having a packed bed of glass beads pre-deposited on top of a support sieve (described below) with an effective surface area of 1.43 cm<sup>2</sup>. The support sieve was held in place by two rubber o-rings (above and below) at the bottom junction of the column. The emulsion vessel (containing about 300 ml of premix) was pressurized with nitrogen keeping the valve connected to the column opened. The emulsification was started by opening the outlet valve of the module and homogenized emulsion
was collected in a beaker placed on an electrical balance for digitally recording the increase in mass every second. The volume flux, $J$, across the packed bed was calculated from the mass flow rate, $\phi_m$, using the equation:

$$J = \frac{\phi_m}{\rho_e A},$$

(6.1)

where $\rho_e$ is the emulsion density and $A$ is the effective surface area of the packed bed. The process was repeated up to five cycles. The premix and all homogenized emulsion samples were analysed for droplet size (distribution) with a laser diffraction particle size analyser (Mastersizer 2000, Malvern Instruments Ltd., UK). The machine takes three readings and the average values of droplet size and droplet span were used in analysis.

**6.2.3. Support sieve**

Nickel sieves (Stork, Eerbeek, the Netherlands) having straight-through rectangular pores were used as a support for the glass particles. A sieve having an
average pore size of $11.6 \times 331 \, \mu m$ was used that was thick enough (350 \, \mu m) to provide good support to the bed and to withstand the applied pressure. The SEM images of top and bottom view of the sieve are shown in Fig. 6.2.

![SEM images of top and bottom view of the sieve](image)

**Fig. 6.2.** SEM image of the support sieve used in this study: (left) top view, plane surface and (right) bottom view, structured surface [Chapter 5].

### 6.2.4. Packed bed

Hydrophilic glass beads (100HFL, Pneumix SMG-AF) were used in the form of a packed bed on top of the support sieve. The characteristics of the glass beads and the resulting packed bed are shown in Table 6.3. Before starting an experiment, a small amount of the continuous phase was introduced inside the column to properly wet the packed bed and support sieve with the continuous phase. The column was then turned upside down for few times and placed vertically to let the glass beads settle down under the influence of gravity.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass beads</td>
<td></td>
</tr>
<tr>
<td>Sauter mean diameter [\mu m]</td>
<td>55</td>
</tr>
<tr>
<td>Span [-]</td>
<td>0.65</td>
</tr>
<tr>
<td>Packed bed</td>
<td></td>
</tr>
<tr>
<td>Height [mm]</td>
<td>2.5</td>
</tr>
<tr>
<td>Pore size* [\mu m]</td>
<td>23.4</td>
</tr>
<tr>
<td>Porosity* [-]</td>
<td>0.4</td>
</tr>
</tbody>
</table>

* pore size and porosity were calculated as described in Chapter 5.
6.2.5. Physical properties of blends

The densities of the blends were calculated using the densities of pure chemicals based on their fractions. Similarly, the density of resulting emulsion was calculated using the relation:

$$\rho_e = \varphi_d \rho_d + (1 - \varphi_d) \rho_c,$$  \hspace{1cm} (6.2)

where $\varphi_d$ is the dispersed phase volume fraction, $\rho_d$ and $\rho_c$ are the dispersed and continuous phase densities, respectively.

The viscosities of the blends were measured with a rheometer (MCR 301, Anton Paar) with Couette geometry (DG 26.7, Anton Paar). Shear rate sweeps were performed at a controlled temperature of 23 °C between 1 and 1000 s\(^{-1}\) to exclude non-Newtonian behaviour. Each of the 29 shear rates was applied for five seconds; measurement of the shear stress was done halfway each period. The emulsion viscosity, $\eta_e$, was calculated as [11]:

$$\eta_e = \eta_c \left[ 1 + 2.5 \varphi_d \left( \frac{\eta_d + \frac{2}{5} \eta_c}{\eta_d + \eta_c} \right) \right],$$  \hspace{1cm} (6.3)

where $\eta_d$ and $\eta_c$ are the dispersed and continuous phase viscosities.

The equilibrium interfacial tension at the oil and water (without PEG) interface was measured through drop profile analysis using a drop tensiometer PAT-1 (SINTERFACE Technologies, Germany) at a controlled temperature of 23 °C. A surfactant-solution droplet was formed at the tip of a capillary immersed in oil. The measurements were started soon after droplet formation and continued for 30 minutes. Based on diffusion-controlled adsorption of a surfactant, described in general by Ward and Tordai [12], the equilibrium interfacial tension, $\sigma_{eq}$, was derived from a plot of the interfacial tension, $\sigma$, against the inverse square root of time, $\frac{1}{\sqrt{t}}$. A linear relation was fitted to the initial part of the plot, and $\sigma_{eq}$ was then found as the intercept with the y-axis.

The equilibrium interfacial tension at the interface of hexadecane and water (with PEG) having 0.55% w/v Tween-20 was measured using a spinning drop tensiometer. A dense PEG blend was put into a thin tube and a drop of less dense
hexadecane was placed in it. The tube was then horizontally rotated to elongate the droplet, and from its equilibrium dimensions that were reached after one hour the equilibrium interfacial tension was calculated according to the Vonnegut theory [13], which states that:

\[
\sigma_{eq} = \frac{1}{4} \Delta \rho \omega^2 R_d^3, \quad \text{if } L_d/2R_d > 4, \tag{6.4}
\]

where \( \Delta \rho \) is the density difference between the liquids, \( \omega \) is the angular velocity in radians, \( R_d \) is the radius of the elongated droplet and \( L_d \) is the length of the elongated droplet. The measured radius of the elongated droplet needs an optical correction:

\[
R_{d(\text{true})} = R_{d(\text{meas})} \frac{R_{I_{\text{air}}}}{R_{I_{\text{sol}}}}, \tag{6.5}
\]

where \( R_{d(\text{true})} \) is the actual radius of the elongated droplet, \( R_{d(\text{meas})} \) is the measured radius of the elongated droplet, \( R_{I_{\text{air}}} \) is the refractive index of air and \( R_{I_{\text{sol}}} \) that of the solvent.

The refractive indices of the mixtures were measured with an Abbe refractometer (Zeiss-Opton, Germany).

6.3. Results and discussion

The experiments described below were carried out with 55 \( \mu \)m glass beads at a bed height of 2.5 mm and an applied pressure of 300 kPa unless specified differently. The conditions that were systematically varied are the viscosities of dispersed and continuous phases, the dispersed phase volume fraction, and the surfactant type and concentration in the continuous phase. The results are presented as droplet size and droplet size distribution. Ultimately, all factors are summarized in scaling relations.

6.3.1. Effect of dispersed and continuous phase viscosities

The viscosities of both phases were varied systematically (Table 6.1); the dispersed phase viscosity was increased while keeping the continuous phase viscosity constant, and vice versa. In Fig. 6.3, the dimensionless droplet diameter \( (d_{32}/d_p) \) obtained after different number of passes through the bed is plotted.
The droplet size was small at low viscosity ratio because the droplets can be effectively elongated by the highly viscous continuous phase, after which the liquid threads will break into small droplets during recompression inside the pore labyrinth in the network. The flux increases till a viscosity ratio of 3 due to the lower overall emulsion viscosity, which also results in flow conditions that are less effective for droplet break-up, because the exerted shear on the dispersed phase will decrease. At a viscosity ratio of 3, the flux reaches its maximum after which it decreases again, most probably because of the emulsion droplets that now have to
be broken up by a different mechanism, as they cannot be easily elongated by the continuous phase. Interaction with the pore walls (glass beads) now becomes important. At a low viscosity ratio, it is expected that droplet break-up will take place upon exit of the bed, as was also found for metal sieves [Chapter 3]. At higher viscosity ratio, the dispersed phase will still be able to intrude into the porous bed, but break-up will mainly take place due to constriction inside the bed, leading to a constant droplet size, as the droplet size now is determined by the average pore size in the packed bed. This is also reflected in the slightly lower fluxes at high viscosity ratio, indicating that the dispersed phase inside the packed bed impedes the flow. This conclusion is strengthened by the observation that the flux increases systematically, albeit slightly, at higher number of passes corresponding to smaller droplets.

Please note that all droplet sizes were much smaller than the pore size. The droplet to pore size ratio was as low as 0.1, which is the lowest ratio already reported for premix membrane emulsification [Chapter 2], whereas, in cross flow membrane emulsification the droplet size is typically 3 to 10 times the pore size [14]. This also indicates that pore sizes need to be much smaller for cross flow emulsification to produce droplets of the same size, which is also reflected in the typical fluxes in cross-flow membrane emulsification that are orders of magnitude lower than the fluxes observed in this study.

The narrowest droplet size distribution was obtained around a viscosity ratio of 3, however, in general, the droplet size distributions were narrower for higher viscosity ratios (Fig. 6.4 left images for various passes) compared to those obtained at low viscosity ratios (Fig. 6.4 right images). It is expected that the droplet-droplet interactions are reduced at high viscosity ratio, resulting in a lower chance of coalescence, and thus a narrower size distribution. At viscosity ratio $\geq 10$, a second small peak was formed after few passes and which stayed after the fifth pass. This may be due to formation of satellite droplets during the break-up process, and indicates droplet breakup through elongation. The presence of the small peak does not substantially influence the Sauter mean diameters that were reported previously.
Fig. 6.4. Effect of increasing dispersed phase viscosities (left: $\eta_d/\eta_c = (\Box) 3.3$, (○) 9.8, (Δ) 22.8, (+) 31.9, (◊) 44.5 and (×) 100.6) and continuous phase viscosities (right: $\eta_d/\eta_c = (\Box) 3.3$, (○) 1.03, (Δ) 0.33, (+) 0.16, (◊) 0.10 and (×) 0.08) on droplet size distribution.

One of the effects that we expect to play an important role in the overall droplet size distribution is the interaction between droplets, either in the packed bed or after passing it. In the next sections, we vary the dispersed phase fraction and the surfactant concentration to investigate this.
6.3.2. Effect of dispersed phase fraction

Experiments were carried out using different volume fractions of n-hexadecane in surfactant solution (Milli-Q water + Tween-20) resulting in a constant viscosity ratio \( \approx 3 \). A pressure of 300 kPa was applied (as used for experiments with different viscosity ratios, section 6.3.1) for emulsions with up to 30% vol. of dispersed phase, however, at or above 45% of dispersed phase, this pressure was insufficient and therefore the pressure had to be increased to 500 kPa. As shown in Table 6.4, the droplet size was reduced with the number of passes for all conditions that were investigated. Droplets with a Sauter mean diameter less than 5 \( \mu \text{m} \) could be produced even at 60% of dispersed phase as long as sufficient surfactant was present.

The fluxes were lower for concentrated emulsions, but still high compared to those reported for premix membrane emulsification. The decrease in flux might be due to an increased viscosity inside the pores as a result of multiple droplets passing simultaneously and interacting with each other and with the pore walls. At the highest dispersed phase fraction, an increased amount of surfactant resulted in a droplet size reduction as expected. However, the flux was also reduced, which might be due to congestion of small droplets inside the pores between the glass beads, therewith effectively increasing the local viscosity.

After repeated passes, the size distributions as represented by span values in Table 6.4 became wider at higher dispersed phase fraction when using the same pressure and surfactant concentration. Most probably the higher collision frequency of droplets and the lower local availability of surfactant cause these effects. One should bear in mind that at high dispersed phase fraction, the amount of available surfactant plays an important role in establishing the droplet size, as obvious from the change in Tween-20 concentration from 0.55% to 1.1% (last two entries in Table 6.4) that reduces the droplet size and its distribution considerably. This indicates that droplets are broken up inside the packed bed but cannot be stabilised fast enough to prevent re-coalescence. Alternatively, a lower interfacial
Table 6.4
Droplet size, span and flux obtained using different dispersed phase fractions.

<table>
<thead>
<tr>
<th>Dispersed phase fraction [% v/v]</th>
<th>Applied pressure [kPa]</th>
<th>Surfactant concentration [% w/v]</th>
<th>Pass through the bed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$d_{32}$ [µm]</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>0.55</td>
<td>8.2</td>
</tr>
<tr>
<td>15</td>
<td>300</td>
<td>0.55</td>
<td>8.5</td>
</tr>
<tr>
<td>30</td>
<td>300</td>
<td>0.55</td>
<td>7.2</td>
</tr>
<tr>
<td>45</td>
<td>500</td>
<td>0.55</td>
<td>7.7</td>
</tr>
<tr>
<td>60</td>
<td>500</td>
<td>0.55</td>
<td>9.3</td>
</tr>
<tr>
<td>60</td>
<td>500</td>
<td>1.10</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$d_{32}$ [µm]</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>0.55</td>
<td>4.3</td>
</tr>
<tr>
<td>15</td>
<td>300</td>
<td>0.55</td>
<td>4.3</td>
</tr>
<tr>
<td>30</td>
<td>300</td>
<td>0.55</td>
<td>3.9</td>
</tr>
<tr>
<td>45</td>
<td>500</td>
<td>0.55</td>
<td>3.6</td>
</tr>
<tr>
<td>60</td>
<td>500</td>
<td>0.55</td>
<td>5.9</td>
</tr>
<tr>
<td>60</td>
<td>500</td>
<td>1.10</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$d_{32}$ [µm]</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>0.55</td>
<td>3.9</td>
</tr>
<tr>
<td>15</td>
<td>300</td>
<td>0.55</td>
<td>4.1</td>
</tr>
<tr>
<td>30</td>
<td>300</td>
<td>0.55</td>
<td>3.2</td>
</tr>
<tr>
<td>45</td>
<td>500</td>
<td>0.55</td>
<td>3.1</td>
</tr>
<tr>
<td>60</td>
<td>500</td>
<td>0.55</td>
<td>5.3</td>
</tr>
<tr>
<td>60</td>
<td>500</td>
<td>1.10</td>
<td>2.8</td>
</tr>
</tbody>
</table>
tension at higher surfactant concentration could have similar influence; dynamic interfacial tension effects leading to low surfactant coverage may cause effects related to coalescence. Clearly, the surfactant concentration is a parameter that may influence various aspects of droplet formation, therefore it was investigated further in the next section.

6.3.3. Effect of surfactant type and concentration

The Tween-20 concentration was varied from 0.011–1.1% w/v using 5% volume fraction of the dispersed phase at an applied pressure of 300 kPa. The effect on the droplet size and span is shown in Fig. 6.5. The mass mean droplet diameter, $d_{43}$, is used here to focus on the presence of larger droplets. Initially, a decrease in the droplet size and span is evident with increasing Tween-20 concentration that levels off at a concentration of 0.11%, which is around 15 times the critical micelle concentration (CMC). This concentration is expected to be sufficient to cover the created interface. In that case the (equilibrium) interfacial tension becomes constant, and both droplet size and span will not be influenced at higher surfactant concentration as is reported in Fig. 6.5.

![Fig. 6.5. Droplet size, $d_{43}$, and span, $\delta$, obtained at different surfactant (Tween-20) concentrations, $c_s$, after different passes: (◊) 1st, (□) 3rd and (Δ) 5th pass.](image-url)

SDS (anionic surfactant) and CTAB (cationic surfactant) at a concentration of 0.55% (far above CMC of each surfactant) were used for comparison with Tween-20 (nonionic surfactant). Similar droplet size distributions were obtained with Tween-20 and SDS, while the distribution with CTAB was wider, most probably caused by the interfacial tension which is significantly lower compared to that of
The emulsions prepared using different surfactant types and concentrations were kept in quiescent storage for a period of four weeks (airtight container at room temperature, ≈ 23 °C in a dark place) and the samples were analysed at regular intervals. Over the entire storage period, all the emulsions were quite stable except for the one having 0.011% of Tween-20 (Fig. 6.7). For this specific sample, there was a rapid increase in droplet size and span during storage, leading to a visible oil phase after two days of storage. The droplet sizes of all other emulsions were stable during the four weeks experiment, which is indicative of the suitability of the preparation method.

### 6.3.4. Scaling relations

As discussed above, various product related properties influence the resulting droplet size. In Chapter 5, we considered the process parameters related to the
Fig. 6.7. Droplet size, \(d_{43}\), and span, \(\delta\), during storage using different surfactant types and concentrations: (◊) 0.011%, (□) 0.11%, (∆) 0.55% and (○) 1.1% Tween-20; (+) 0.55% SDS; (×) 0.55% CTAB.

internal structure of the porous media that influence the Sauter mean droplet diameter, \(d_{32}\) (μm), via the relation:

\[
\frac{d_{32}}{d_p} = 0.69 \times \left(\frac{E}{V}\right)^{-0.17} \left(\frac{H}{D}\right)^{0.35},
\]

(6.6)

where \(d_p\) (μm) is the packed bed pore size, \(E/V\) (bar) is the energy density per unit volume of emulsion and \(H/D\) is the height to diameter ratio of the packed bed. To extend this relation to incorporate the parameters studied in the current chapter, we obtained:

\[
\frac{d_{32}}{d_p} = \alpha \times E^{\gamma} \left(\frac{H}{D}\right)^{\beta} \left(\frac{\eta_d}{\eta_c}\right)^{\zeta}.
\]

(6.7)

As the viscosity ratio affects the droplet size differently below or above a ratio of 3 (section 6.3.1), we used a value of \(\zeta = 0\) for viscosity ratios above 3, and calculated its value for lower viscosity ratios. As discussed in section 6.3.3, the concentration of surfactant needs to be above a certain level for successful emulsification, and since we only consider stable emulsions here, we did not include this as an extra parameter.

The data obtained from 55 experiments was fitted to Eq. 6.7 using the MinErr function in Mathcad 15.0, and the standard deviations and the correlation coefficients of the fit parameters were determined accordingly, as shown in Table 6.5. In Fig. 6.8, the fitted values are plotted as function of the measured data. A
good agreement of fit was obtained and reliable estimates were obtained for the parameters.

**Table 6.5**

Values, standard deviations and correlation coefficients of fit parameters of Eq. 6.7.

<table>
<thead>
<tr>
<th>Fit parameters</th>
<th>Values and standard deviations</th>
<th>Correlation coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\alpha$</td>
</tr>
<tr>
<td>$\eta_d/\eta_c &gt; 3$</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$0.73 \pm 0.031$</td>
<td>-</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$0.31 \pm 0.024$</td>
<td>0.92</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$\eta_d/\eta_c &lt; 3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$0.57 \pm 0.050$</td>
<td>-</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$0.50 \pm 0.061$</td>
<td>0.80</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>$0.16 \pm 0.037$</td>
<td>0.29</td>
</tr>
</tbody>
</table>

As $H/D$ was not varied, $\gamma$ was taken as equal to the previously established relation (Eq. 6.6).

From Table 6.5 it is clear that parameters $\beta$ and $\zeta$ are not heavily correlated. A higher value of $\beta$ in case of $\eta_d/\eta_c < 3$ corresponds to a more effective utilization of available energy for droplet disruption leading to a smaller droplet size at lower viscosity ratios. We can conclude that Eq. 6.7 can be used to describe the premix emulsification process using packed beds.

**Fig. 6.8.** Experimental values of Sauter mean droplet diameter, $d_{32}$, plotted against the result of Eq. 6.7 using fit parameters given in Table 6.5: (□) $\eta_d/\eta_c < 3$, (○) $\eta_d/\eta_c > 3$. 
6.4. Conclusions

The resulting droplet size obtained with the emulsification system based on packed beds of micron-sized glass beads is strongly influenced by the viscosity ratio between continuous and dispersed phase. At low viscosity ratio, the droplet size is strongly correlated to this parameter that directly relates to the shear applied on the droplets, while at values > 3 the droplet size becomes constant due to a change in break-up mechanism that is now related to constriction in the bed. The flux through the emulsification system is directly linked to the viscosity of the emulsion. The emulsions with substantially small droplet size (Sauter mean droplet diameter < 5 μm) could be produced even at 60% dispersed phase, as long as sufficient surfactant is present. Based on the obtained results scaling relations were found that takes the viscosity ratio into account and can describe the droplet size successfully.

References


CHAPTER 7

Discussion and future prospects
ABSTRACT

The main factors that are important in droplet disruption during premix emulsification are discussed in the first section of this chapter, with special emphasis on the results presented in this thesis. Next, the status of premix emulsification compared to other conventional and microstructured emulsification systems is provided. Further, the use of the investigated systems is extended to the production of food dispersions and foams in the last section of this chapter, which is also supported by first experimental results.
7.1. Main findings and conclusions of the current research

In Chapter 2, literature on premix membrane emulsification was reviewed. It was concluded that membrane properties such as pore size, thickness, tortuosity and porosity are of prime importance in determining the emulsion droplet size. In addition, the membrane type also determines the overall droplet production rate, which may gradually decline due to fouling of the membrane by the ingredients (e.g., proteins) from the premix. It is expected that membranes with a deep network of interconnected pores are difficult to clean; in that respect, membranes with straight-through pores as used in Chapters 3 and 4 are preferred. Interconnected pores may be provided with a packed bed of glass beads [Chapters 5 and 6] that can be deposited on a carrier membrane. The packed bed can be cleaned efficiently by re-suspending the beads.

Metal sieves having long, rectangular straight-through pores (width << length), were used in Chapter 3. These membranes allowed us to operate at relatively low transmembrane pressure and at higher productivity than reported for other membranes. Typical fluxes were 1500 m$^3$ m$^{-2}$ hr$^{-1}$ at 200 kPa, resulting in a droplet diameter around 5 μm with a span of 1.4. The droplet break-up in these metal sieves is based on elongation and recompression of droplets. There was no indication of fouling, even after repeated passes, which indicates that the process is tolerant to the product formulation and the operational conditions. The pore geometry plays a key role in the droplet break-up, as demonstrated in Chapter 4. The inertial forces are important in emulsification with sieves having rectangular pores that allow more chances for liquid-liquid interactions, whereas for sieves with squared pores, spontaneous droplet break-up due to Laplace pressure differences is more important.

The premix emulsification system using a packed bed of micron-sized glass beads [Chapters 5 and 6] is easy to clean as the glass beads can be re-suspended and cleaned or replaced. The packed beds work very similar to conventional membranes, and small droplets (< 5 μm, droplet to pore size ratio ≈ 0.2) with an appreciable uniformity (span ≈ 0.75) could be produced. The pore Reynolds number, $Re_p$, can be used to characterize the flow inside the packed bed. The pore
size and the flow velocity determine the droplet break-up, either by constriction ($\text{Re}_p < 40$) or inertia ($\text{Re}_p > 40$) at fluxes comparable to the highest reported flux values for other premix membrane emulsification studies [Chapter 2].

In Chapter 6, the effects of various product properties were investigated. The droplet size is affected strongly by the viscosity ratio between the dispersed and the continuous phases at values below 3, but is unaffected at higher values. This is related to a change in the droplet break-up mechanism. Further, some effects of the choice of surfactant and its concentration were noted, but in general, stable emulsions can be created using the packed bed system, as long as sufficient surfactant or stabiliser is present.

7.2. Premix emulsification versus other emulsification systems

Various microstructured emulsification systems are able to produce monodispersed emulsions at energy inputs that are orders of magnitude lower compared to conventional emulsification techniques [1, 2]. Cross-flow membrane emulsification is investigated most and is known for the monodispersity of the emulsions produced [3], albeit at low throughputs and only for emulsions with relatively low dispersed phase fraction. For emulsions with higher dispersed phase fractions, premix emulsification is an interesting alternative that can be used for the controlled production of small and uniform sized droplets at high production rates. A general comparison is made in Table 7.1 between conventional, microstructured and various premix emulsification systems.

Table 7.1
A comparison of conventional and microstructured emulsification systems with premix emulsification.

<table>
<thead>
<tr>
<th>Characteristic features</th>
<th>Conventional emulsification</th>
<th>Microstructured emulsification</th>
<th>Premix emulsification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Membrane</td>
</tr>
<tr>
<td>Droplet size</td>
<td>++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Droplet uniformity</td>
<td>–</td>
<td>+ ++</td>
<td>++</td>
</tr>
<tr>
<td>Energy efficiency</td>
<td>– –</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Productivity</td>
<td>+ +</td>
<td>– –</td>
<td>+</td>
</tr>
<tr>
<td>Risk of fouling</td>
<td>+</td>
<td>++</td>
<td>– –</td>
</tr>
</tbody>
</table>
With premix membrane emulsification, the droplet size (distribution) may be tuned by adjusting especially the membrane pore size and the transmembrane pressure. The narrow droplet size distribution obtained, the high production rates and the robustness of the process make premix emulsification an attractive process as long as the membrane is not fouled during operation. If this is the case, alternative strategies have to be employed such as straight-through pores and packed beds of glass beads as discussed in Chapters 3-6.

As an example, the droplet size distribution obtained using a packed bed consisting of 55 μm glass beads [Chapter 5] is compared with those obtained using other emulsification techniques from literature in Fig. 7.1. The dispersed phase fraction was ≤ 5% in all the cases. The obtained sizes are dependent on the methods and conditions used, here we only focus on the width of the droplet size distribution. The Microfluidizer, a typical high-pressure homogenizer, results in a wide droplet size distribution. The edge-based droplet generation (EDGE) system is an example of a microstructured emulsification system that produces very narrow droplet size

![Droplet size distributions obtained using different emulsification systems](image)

**Fig. 7.1.** Droplet size distributions obtained using different emulsification systems: (□) Microfluidizer, 1100 bar, N=2 [4]; (×) Microfluidizer, 50 bar, N=1 [4]; (△) cross-flow membrane emulsification, \(d_p=0.4 \, \mu m\), 3.3 bar [4]; (●) packed bed system, \(d_p=23 \, \mu m\), 2 bar, N=5 [Chapter 5]; (◊) EDGE system, 1.2 μm [5]; (+) Microchannel, 16 μm [4].
distributions. Cross-flow membrane emulsification then follows with a distribution that is somewhat less narrow. The packed bed system results in a fairly good distribution, and bearing the low energy inputs and the high throughputs in mind, the system is an interesting alternative for the controlled production of emulsions and all kinds of related products.

7.3. Future prospects

For practical application of the tested systems in food production, the process needs to be continuous, and the effects of food ingredients on the emulsification performance need to be evaluated. Preliminary results are shown here, including some related to foam formation, which is akin to but not the same as emulsification.

**Fig. 7.2.** Schematic representation of the inline premix emulsification.

7.3.1. Batch versus continuous operation

For large scale production of emulsions, the coarse premix is ideally made inline to prevent creaming or sedimentation in storage tanks, which would lead to nonhomogeneous supply of feed emulsion and non-constant emulsion quality. The
Discussion and future prospects

Premix can be formed inline through injection of to-be-dispersed phase, with the added benefit that the dispersed phase fraction can be controlled by the rate of injection. The droplet size distribution was the same as for the system with off-line preparation of the premix [Chapters 5 and 6] while keeping the same process and formulation parameters.

7.3.2. Food emulsions

Food grade oil-in-water emulsions were prepared using sunflower oil and whey protein isolate (WPI) through inline premix emulsification. The results after the fifth pass of the experiments performed at 5 bar pressure using 1% w/v WPI with even smaller glass beads (i.e., 30 μm) than discussed in Chapter 5 and 6 are shown in Table 7.2. Emulsions with a Sauter mean droplet diameter < 5 μm could be produced, however, the span values were rather high compared to emulsification with 65 μm glass beads due to a bimodal droplet size distribution as shown in Fig. 7.3.

Table 7.2

<table>
<thead>
<tr>
<th>Glass bead diameter [μm]</th>
<th>Bed pore diameter [μm]</th>
<th>Bed height [mm]</th>
<th>Sunflower oil fraction [%]</th>
<th>Sauter mean droplet diameter [μm]</th>
<th>Droplet span [-]</th>
<th>Flux [m³/m²·hr⁻¹]</th>
</tr>
</thead>
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<tr>
<td>30 (◊)</td>
<td>12.8</td>
<td>2.5</td>
<td>2.6</td>
<td>3.7</td>
<td>1.3</td>
<td>53.3</td>
</tr>
<tr>
<td>30</td>
<td>12.8</td>
<td>1.5</td>
<td>2.8</td>
<td>3.3</td>
<td>1.5</td>
<td>289.8</td>
</tr>
<tr>
<td>30*</td>
<td>12.8</td>
<td>1.5</td>
<td>5.5</td>
<td>3.5</td>
<td>1.5</td>
<td>207.7</td>
</tr>
<tr>
<td>65 (○)</td>
<td>23.4</td>
<td>2.5</td>
<td>6.5</td>
<td>10.1</td>
<td>1.0</td>
<td>798.3</td>
</tr>
</tbody>
</table>

* oil was added during first two passes

This might be due the flow velocities that are greatly reduced with decreasing pore size. Constriction may still play its role (as evident from the presence of the second peak comprising of very small droplets) but due to low pore velocities the effective wall shear stress might be insufficient and some of the droplets may escape whole. Using even higher flow velocities for smaller glass beads could result in a narrower size distribution with smaller mean droplet size. Moreover, as the proteins have much lower interfacial adsorption rate, the possibility of coalescence cannot be
ignored. Increase of the amount of protein in the formulation may result in better emulsions.

![Droplet size distribution graph](image)

**Fig. 7.3.** The droplet size distribution of sunflower oil-in-water emulsion stabilized by whey protein isolates using 2.5 mm thick packed beds of (◊) 30 and (○) 65 μm glass beads at 5 bar pressure.

### 7.3.3. Foams

The technologies presented in this thesis are also suited to create foams, which are important in the food industry, e.g., in the preparation of meringues, soufflés, angel-food cakes, dessert toppings, cappuccino coffee and more [6, 7]. Foams are conventionally produced by steam injection, turbulent mixing and rotor-stator mixing, which are rather energy inefficient techniques and give wide size distributions [8] resulting in foams that are not very stable due to disproportionation (Ostwald ripening).

Foaming by membranes and other microstructured systems like EDGE are examples of methods for cold aeration that produce small and uniform bubbles, but at low production rates. Interestingly, the packed bed system can successfully be used to produce stable foams at high production rates. The proposed system is actually a modified form of inline premix emulsification as shown in Fig. 7.4. The process starts with simultaneous injection of continuous and dispersed phases forming a spray of the continuous phase that uniformly wets the glass beads. The air is entrapped by thin films of the continuous phase inside the packed bed and air
bubbles are generated on the other side of the packed bed. The flow of injecting liquid should be tuned to allow adequate spray formation. Experiments were performed using 10% w/v WPI solution as continuous phase with 65 μm glass beads at 1–5 bar pressure, and the results are shown in Figs. 7.5 and 7.6.

The bubble size decreased significantly when the pressure increased from 1 bar to 2 bar, and at 3 bar the bubble uniformity seems to increase slightly. At pressures > 2 bar, many bubbles were ≤ 100 μm. The large bubbles may be due to rapid bubble coalescence while transferring the sample for microscopic observation. No further decrease in bubble size was observed till 5 bar (not quantified further). The volumetric foam production rate increased linearly with the applied pressure (Fig. 7.6c), as expected, but was low compared to the flux during emulsification. The overrun (the difference between the density of the original liquid and that of the foam, divided by the density of the foam), which is a criterion for the gas holding capacity of the foam, was reasonably high as shown in Fig. 7.6a. The overrun decreased with increasing applied pressure, which is related to the much smaller bubbles that are formed, and that are more stable than the large droplets formed at low pressures (Fig. 7.6b).
Fig. 7.5. Packed bed foaming using 65 μm glass beads at different applied pressures: (▬) is equal to 500 μm.

Instead of further decreasing the bubble size, various strategies can be employed to make stable foams by reducing the drainage of the aqueous film between bubbles. This can be achieved by using stabilizers like polysaccharides, or by thermal denaturation of the whey proteins making them better stabilisers [9, 10].

While these were initial experiments conducted with packed beds, the obtained results look promising. Further improvements in the process are obviously possible through optimising the air and liquid flow rates to form a more uniform spray, and using even smaller glass beads. The supply of the continuous phase can be made more homogeneous by using relatively polydispersed glass beads that will reduce the interstitial voids of the packed beds holding the liquid, therewith effectively reducing the porosity and thus the flow rates inside the pore labyrinth.
Discussion and future prospects

135

Fig. 7.6. The bubble overrun, drainage (after 30 min) and flux as a function of applied pressure.

7.4. Concluding remarks

Premix emulsification as presented in this thesis has much potential: it combines the positive aspects of typical conventional and microstructured emulsification systems. Avoiding the fouling problems that are associated with the use of conventional (e.g., polymeric or ceramic) membranes is a critical step towards practical application of this technique. The results obtained show the suitability of packed beds over conventional membranes for the production of different kinds of emulsions (and foams).

References


Summary

Emulsions are dispersions of two (or more) immiscible liquids (e.g., oil and water), and are widely used in various industries including food, cosmetics, pharmaceutics, paints, agrochemicals, bitumen, etc. The droplet size (distribution) of an emulsion has a great influence on appearance, consistency, rheology and stability of the emulsions. A small droplet size can be achieved with some of the conventional emulsification devices (e.g., rotor-stator systems and high-pressure homogenizers), however, the emulsions are rather polydispersed. Additionally, these machines exert high stress that is released as heat, potentially damaging shear and heat sensitive constituents. To limit these issues, various microstructured systems have been suggested (e.g., membrane, microchannel and various microfluidic emulsification systems) that are known for low energy input and better monodispersity. However, it should be mentioned that the up-scaling is yet a major challenge towards commercialization of these systems.

Premix membrane emulsification gains attention for the production of various types of dispersions. The simplicity of its design, the high production rates, the ease of scale-up and the possibility to produce concentrated emulsions are advantages reported for this technique [Chapter 2]. In this process, a coarse emulsion (premix) is first prepared which is then extruded through a (microporous) membrane to get a fine emulsion; the process can be regarded as low-pressure homogenization.

In Chapter 2, literature on premix membrane emulsification was reviewed, and it was concluded that along with the transmembrane pressure, the membrane properties (such as pore size, thickness, tortuosity and porosity) are of prime importance in determining the emulsion droplet size (distribution). Additionally, the membrane type determines the overall droplet production rate. Unlike other microstructured emulsification techniques, where the to-be-dispersed and the continuous phases flow separately, there is a risk of membrane fouling by the emulsion components, which in turn may compromise the productivity. For membranes having interconnected pores the situation may even be worse because of inaccessibility of the pores to the cleaning agents.
The research in this thesis was mainly focused on alternatives for typical membranes for premix emulsification in order to avoid fouling problems. Two different systems were used: metal sieves having straight-through pores and packed beds consisting of micron-sized glass beads. Metal sieves having long rectangular straight-through pores (width << length) were used, which allowed us to operate at relatively low transmembrane pressure and at higher productivity than reported for other membranes [Chapter 3]. Typical fluxes were 1500 $\text{m}^3\text{m}^{-2}\text{hr}^{-1}$ at 200 kPa, resulting in a droplet diameter around 5 $\mu$m with a span of 1.4. The droplet break-up in these metal sieves is based on elongation and recompression of droplets. There was no indication of fouling, even after repeated passes, which indicates that the process is tolerant to the product formulation and the operational conditions. The pore geometry plays a key role in determining the droplet break-up, as demonstrated in Chapter 4. The inertial forces are important in emulsification with sieves having rectangular pores that allow more chances for liquid-liquid interactions, whereas for sieves with squared pores spontaneous droplet break-up due to Laplace pressure differences is more important.

The premix emulsification system using a packed bed of micron-sized glass beads [Chapters 5 and 6] is easy to clean as the glass beads can be re-suspended and cleaned or replaced. The packed beds work very similar to conventional membranes and small droplets (< 5 $\mu$m, droplet to pore size ratio $\approx 0.2$) with an appreciable uniformity (span $\approx 0.75$) could be produced. The pore Reynolds number, $\text{Re}_p$, can be used to characterize the flow inside the packed bed. The pore size and the flow velocity determine the droplet break-up, that could be either by constriction ($\text{Re}_p < 40$) or inertia ($\text{Re}_p > 40$) at fluxes comparable to the highest reported flux values for premix membrane emulsification studies [Chapters 2 and 5]. In Chapter 6, the effects of various product properties were investigated. The droplet size is affected strongly by the viscosity ratio between the dispersed and the continuous phases at values below 3, but is unaffected at higher values. This is related to a change in the droplet break-up mechanism. Further, some effects of the choice of surfactant and its concentration were noted, but in general, stable emulsions can be created using the packed bed system, as long as sufficient surfactant or stabiliser is present.
It is obvious from the research presented in this thesis that premix emulsification is an interesting technique for the production of emulsions. In Chapter 7 this is taken even one step further, and new designs for continuous operation for emulsification and foam formation are presented, together with the first obtained results, which look promising. Avoiding fouling problems as suggested in this thesis is the key element that is expected to help the proposed technologies towards their industrial application.
Notation

List of symbols used in this thesis, along with their SI units.

\( a \) and \( b \)  
fit parameters of Eq. 3.6 [-]

\( A \)  
area \([\text{m}^2]\)

\( A_{vd} \)  
dynamic specific surface area \([\text{m}^2 \text{ m}^{-3}]\)

\( C \)  
constant in Eq. 2.9 [-]

\( C_{cr} \)  
critical capillary number [-]

\( c_s \)  
surfactant concentration [%]

\( CV \)  
coefficient of variation [-]

\( D \)  
packed bed diameter \([\text{m}]\)

\( d \)  
ratio of droplet size to pore size [-]

\( d_1 \)  
initial droplet diameter \([\text{m}]\)

\( d_2 \)  
final droplet diameter \([\text{m}]\)

\( d_{32} \)  
Sauter mean droplet diameter \([\text{m}]\)

\( d_{32,i} \)  
ingoing Sauter mean droplet diameter \([\text{m}]\)

\( d_{32,o} \)  
Sauter mean diameter of the droplet produced \([\text{m}]\)

\( d_{k3} \)  
mass mean droplet diameter \([\text{m}]\)

\( d_b \)  
bead diameter \([\text{m}]\)

\( d_{dr} \)  
droplet diameter \([\text{m}]\)

\( d_h \)  
pore hydraulic diameter \([\text{m}]\)

\( d_i \)  
mean droplet diameter in the \( i^{th} \) cycle/range of sizes \([\text{m}]\)

\( d_p \)  
pore diameter \([\text{m}]\)

\( d_x \)  
droplet diameter corresponding to \( x\% \) vol. on a cumulative droplet volume curve \([\text{m}]\)

\( E_V \)  
energy density \([\text{J m}^{-3}]\)

\( f \)  
friction coefficient [-]

\( H \)  
packed bed height \([\text{m}]\)
<table>
<thead>
<tr>
<th>Notation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_p$</td>
<td>pore depth [m]</td>
</tr>
<tr>
<td>$J$</td>
<td>flux [m$^3$ m$^{-2}$ s$^{-1}$]</td>
</tr>
<tr>
<td>$J_i$</td>
<td>flux corresponding to $i^{\text{th}}$ cycle [m$^3$ m$^{-2}$ s$^{-1}$]</td>
</tr>
<tr>
<td>$k_s$</td>
<td>number of size ranges [-]</td>
</tr>
<tr>
<td>$L_d$</td>
<td>length of the elongated droplet [m]</td>
</tr>
<tr>
<td>$l_p$</td>
<td>pore length [m]</td>
</tr>
<tr>
<td>$N$</td>
<td>number of passes [-]</td>
</tr>
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<td>$\hat{P}$</td>
<td>dimensionless pressure [-]</td>
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<td>power input [W]</td>
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<td>constant for tightly packed spheres ($\approx 0.41$) in Eq. 5.4 [-]</td>
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<td>droplet radius before and after constriction, respectively [m]</td>
</tr>
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<td>$R_{c1}$ and $R_{c2}$</td>
<td>constriction radii [m]</td>
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<tr>
<td>$R_d^{\text{(true)}}$</td>
<td>actual radius of the elongated droplet [m]</td>
</tr>
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<tr>
<td>$Re_p$</td>
<td>pore Reynolds number [-]</td>
</tr>
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<td>$RI_{\text{air}}$</td>
<td>refractive index of air [-]</td>
</tr>
<tr>
<td>$RI_{\text{sol}}$</td>
<td>refractive index of solvent [-]</td>
</tr>
<tr>
<td>$R_m$</td>
<td>membrane resistance [m$^{-1}$]</td>
</tr>
<tr>
<td>$R_p$</td>
<td>pore radius [m]</td>
</tr>
<tr>
<td>$S_v$</td>
<td>area per unit volume [m$^{-1}$]</td>
</tr>
<tr>
<td>$t$</td>
<td>time [s]</td>
</tr>
<tr>
<td>$V_i$</td>
<td>volume fraction of droplets in the $i^{\text{th}}$ cycle/range of sizes [m$^3$]</td>
</tr>
<tr>
<td>$v_p$</td>
<td>emulsion velocity inside the pore [m s$^{-1}$]</td>
</tr>
<tr>
<td>$We_d$</td>
<td>droplet Weber number [-]</td>
</tr>
<tr>
<td>$w_p$</td>
<td>pore width [m]</td>
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Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<td>$\alpha$, $\beta$, $\gamma$ and $\zeta$</td>
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</tr>
<tr>
<td>$\delta$</td>
<td>droplet span [-]</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs energy [J m^{-2}]</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>transmembrane pressure [Pa]</td>
</tr>
<tr>
<td>$\Delta P_c$</td>
<td>Laplace pressure of dispersed phase inside the constriction [Pa]</td>
</tr>
<tr>
<td>$\Delta P_{cr}$</td>
<td>critical pressure [Pa]</td>
</tr>
<tr>
<td>$\Delta P_d$</td>
<td>Laplace pressure of emerging droplet [Pa]</td>
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<td>$\Delta P_{d1}$ and $\Delta P_{d2}$</td>
<td>Laplace pressure of dispersed phase before and after the constriction, respectively [Pa]</td>
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<td>$\Delta P_{disr}$</td>
<td>transmembrane pressure utilized for droplet disruption [Pa]</td>
</tr>
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<td>$\Delta P_{flow}$</td>
<td>transmembrane pressure utilized to overcome flow resistances inside the pores [Pa]</td>
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<td>$\Delta P_{Laplace}$</td>
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<td>$\Delta P_p$</td>
<td>Laplace pressure of dispersed phase inside the pore [Pa]</td>
</tr>
<tr>
<td>$\Delta \rho$</td>
<td>density difference between the liquids [kg m^{-3}]</td>
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<tr>
<td>$\epsilon$</td>
<td>porosity [-]</td>
</tr>
<tr>
<td>$\epsilon_o$</td>
<td>droplet initial extension, ratio of droplet length to its circumference [-]</td>
</tr>
<tr>
<td>$\eta$</td>
<td>viscosity [Pa s]</td>
</tr>
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<tr>
<td>$\eta_e$</td>
<td>emulsion viscosity [Pa s]</td>
</tr>
<tr>
<td>$\theta$</td>
<td>contact angle [°]</td>
</tr>
<tr>
<td>$\xi$</td>
<td>tortuosity [-]</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>bulk density [kg m^{-3}]</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>continuous phase density [kg m^{-3}]</td>
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### Notation

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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tr>
<td>$\rho_d$</td>
<td>dispersed phase density</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>emulsion density</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>particle density</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>interfacial tension</td>
<td>N m(^{-1})</td>
</tr>
<tr>
<td>$\sigma_{eq}$</td>
<td>equilibrium interfacial tension</td>
<td>N m(^{-1})</td>
</tr>
<tr>
<td>$\tau_w$</td>
<td>wall shear stress</td>
<td>Pa</td>
</tr>
<tr>
<td>$v_o$</td>
<td>superficial velocity</td>
<td>m s(^{-1})</td>
</tr>
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<td>$v_p$</td>
<td>pore velocity</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>$\phi_d$</td>
<td>dispersed phase volume fraction</td>
<td>-</td>
</tr>
<tr>
<td>$\phi_m$</td>
<td>mass flow rate</td>
<td>g s(^{-1})</td>
</tr>
<tr>
<td>$\phi_V$</td>
<td>volume flow rate</td>
<td>m(^3) s(^{-1})</td>
</tr>
<tr>
<td>$\psi$</td>
<td>constant in Eq. 2.5</td>
<td>-</td>
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<tr>
<td>$\omega$</td>
<td>angular velocity</td>
<td>radian</td>
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Acknowledgements

There are a number of people without whom this thesis might not have been written, and to whom I am greatly indebted.

To start with, I am thankful to Higher Education Commission (HEC) of Pakistan for their financial support for this research. Also thanks to Nuffic, which acted as a bridge between the HEC and my host university.

I am extremely grateful to my mother and father whose endless efforts sustained me at all stages of my life and whose hands always remained raised in prayer for my success. I am also obliged to my sisters (Amina, Asima and Asifa) and brothers (Ajmal and Muzammal) for their best wishes for me. It wasn’t so easy to be away from you; I missed you a lot. I want to extend my deepest gratitude to my grandparents, aunts and uncles for their prayers.

I want to express my indebtedness to my wife, Rabia. Although, you joined me during the last year of my PhD, you are a major contributor to this success. Thanks for your encouragement and moral support. You tried your best to let me concentrate only on my PhD while handling our newly born son, Raheesh. I know, it wasn’t so easy for you. Dear Raheesh, your entry at the very last stage of my PhD was a precious gift that I will always remember in connection with my PhD. Here, I can’t ignore my wife’s family, especially my mother-in-law for her prayers.

I want to express my sincere gratitude to my honourable promoters, Karin and Remko, for their support during the whole project. Dear Karin, no acknowledgements could ever adequately express my obligation for all what you have done for me during my stay in the Netherlands. Dear Remko, I am very thankful to you for helping me out with interpretation of my experimental results. I am also thankful to all FPE staff members, especially Anja, Joyce, Marjan, Jos, Martin, Maurice and Gerrit, for their support. I am thankful to my colleagues, Sami, Anna, Marta, Rianne, Solomon, Francisco, Thomas, Nicolas, Jimmy, Nirmal, Anja, Martijn, Yvette, Lena, Laura, Katarzyna, Jacqueline, Pascalle, Jorien and Ekaraj, for their assistance. I am thankful to my MSc student, Eral, for his contribution.
Outside the FPE group, I am thankful to Miranda, Fred, Harry, Hans, Adriaan, Surender, Dmitry and Huanhuan for their help.

I am highly obliged to all the teachers who ever taught me. I can never forget my kind and hardworking college teachers Sir Javaid and Sir Naseer. I am much thankful to my home university professor, Dr. Masood Butt. I learnt a lot under your kind supervision.

I am profoundly grateful to my friends Abid and Kashif for their earnest support. I really enjoyed working with you for the last nine years. Apart from work, we also had a very good time. Thanks to Kashif for joining me for various sport activities, and thanks to Abid for updating me about on-going political scenario. I want to express my sincerest gratitude to my friend Liyakat for his assistance and moral support. I will always remember the last month before thesis submission that I spent with you. You really helped me focussing on my work. I am indeed thankful to my Pakistani friends in Wageningen, especially Imtiaz, Mustafa, Masood, Abbas\textsuperscript{2}, Zeshan, Hamid, Sultan, Jamil, Ali, Sajid, Farrakh, Nadeem, Munawar, Imran, Shafqat, Noorullah, Mazhar\textsuperscript{3}, Sabaz, Nazir and Asad. I am much grateful to Tahir Butt for his support regarding my residence, and for providing a platform to play cricket in the Netherlands. I really enjoyed playing with Cricket Club Arnhem (CCA) fellows, especially with Umer, Anwar, Rizwan, Arfan, Zohaib, Aamir and Hamid. I feel so lucky to meet very nice people in Wageningen from various nations: Mustafa (Morocco), Hassan (Palestine), Shahrul (Malaysia) and Wesaam (Syria). I am much thankful to all of you. Back home, I always remembered my friends, especially Kamran, Tahir, Tauseef, Nasir, Sarfraz, Moazzam and Shafique\textsuperscript{2}. Finally, thanks to all those who have been helpful to me in my studies.
About the author

Akmal Nazir was born in Sheikhupura (Pakistan) on 7th September 1984. He completed his secondary and higher secondary education from his home town in 2001. Afterwards he went to University of Agriculture, Faisalabad (Pakistan) from where he was graduated in 2005 with Food Technology as major subject. In 2007 he completed his MSc (Hons.) in Food Technology with thesis entitled ‘Extraction and Application of Natural Antioxidants from Various Plant Sources’. During his master's study he was appointed as Research Officer in a one year research project entitled ‘Utilization of Rice Industrial Wastes for Oil Extraction and Value Added Products’ in Institute of Food Science and Technology. In 2008, he got a scholarship from Higher Education Commission of Pakistan to carry his PhD from any reputed university of Europe. He chose Wageningen University of the Netherlands and started his PhD in Food Process Engineering Group. His doctorate thesis is about ‘Premix Emulsification Systems’. The results of this research are presented in this thesis. Akmal can be reached through akmal.nazir@yahoo.com.
List of publications

Peer-review journals


Conference proceedings


Overview of completed training activities

Discipline specific activities

Courses
Reaction kinetics in food science, 2009
Computational fluid dynamics for chemical engineers, 2009
Thermodynamics for the process technology, 2009
Sustainability analysis in food production, 2011
Rheology and structure of food, 2012

Conferences/symposia/congresses
Delivery of functionality in complex food systems: Third international symposium, Wageningen, 2009
European PhD conference in food science and technology, Berlin, 2010
5th world congress on emulsions, Lyon, 2010
Netherlands process technology symposium, Veldhoven, 2010
11th international congress on engineering and food, Athens, 2011
The 6th international symposium on food rheology and structure, Zurich, 2012

General courses
Information literacy, including introduction EndNote, 2009
PhD week, 2010
PhD competence assessment, 2010
Project and time management, 2010
Adobe InDesign, 2011
Scientific writing, 2012
Techniques for writing and presenting a scientific paper, 2012
Presentation skills, 2012

Optionals
PhD research proposal, 2009
PhD excursion to USA, 2010
PhD excursion to Finland, 2012
FPE annual internal Symposia, 2009-2012
FPE weekly meetings, 2009-2013
The research described in this thesis was partially financed by the Higher Education Commission of Pakistan.