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Liquid dispersion in premix emulsification within porous membrane structures

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ABSTRACT

Liquid/liquid multiphase dispersion processes are studied within porous membrane structures for emulsification. In membrane emulsification, a liquid premix is dispersed by passing through a porous membrane. The interior membrane structure has a significant impact on the liquid fragmentation as well as on the dispersion process and hence on the resulting droplet size distribution of the emulsified dispersed phase. This contribution investigates the fragmentation of non-miscible oil in water, denoted as o/w, systems using the premix membrane emulsification process with generated droplet sizes of $< 10\ \mu$m. Main aim is to correlate the fluid dispersion and emulsification process to the structural properties of the membranes, as fluid dispersion rates up to 10 where reached. The multiphase fluid dispersion in porous structures is analyzed at different process conditions and under varying the porosity, the pore structure and the pore sizes. Different process performance in dependency on structural features will be described. Membranes generated from non-spherical and spherical shaped particles are employed. A liquid dispersion coefficient is extracted as a function of the relevant structural properties. The structural and hydrodynamic properties of the membranes are gained through computer tomograms and models of sintered sphere packings. This investigation assists the tailored fabrication of structural optimized membranes, which may lead to processing of emulsions with predefined properties.

1. Introduction

Emulsification with structured porous membranes has gained some interest in process industry, as it may provide controlled production of emulsions with droplet sizes in the μm-range. Emulsification processes are used in several industries, like food, cosmetics and health care. Emulsification using micro structured systems, e.g. membranes for premix or crossflow emulsification, obtains high control of the droplet size distribution, as reported by Nazir et al. [1]. Traditional emulsification techniques, like colloid mills, rotor-stator systems, high-pressure homogenizers and ultrasonic emulsification, need at least one order of magnitude higher energy input per unit volume of produced emulsion, while applying shear and extensional stresses that may cause loss of functionality in certain applications [1–3].

Typical crossflow membrane emulsification is limited by relatively low dispersed phase fluxes, whereas for premix emulsification a high dispersed phase fraction up to 0.6 (v/v) can be achieved, with mean droplet sizes independent from the dispersed phase content [4]. Some main parameters influencing the membrane emulsification processes have been identified through experiments as well as multiphase flow simulations [5–9]. The relevant process parameters for the resulting emulsion mean droplet size are characterized e.g. by the capillary number. Droplet formation and droplet size are affected by the transmembrane pressure, dispersed phase flux and crossflow velocity. For premix emulsification processes (Fig. 1), the interior membrane structure has a significant impact on the droplet size, as e.g. the pore size and its distribution are affecting the droplet breakup through changes in Laplace pressure inside the pores. Therefore, the mean emulsion droplet size can precisely be tuned by adjusting the interior structure of the membrane. When decreasing the porosity, an increased risk of coalescence of droplets occurs, accompanied by decrease in disperse phase flux. Fig. 1 shows a schematic of the premix emulsification process for the production of emulsions from an initial, coarser premix emulsion.

The relevant literature on emulsification processes shows a variety of investigated membrane structures for premix emulsification purposes. Several investigations have been performed on

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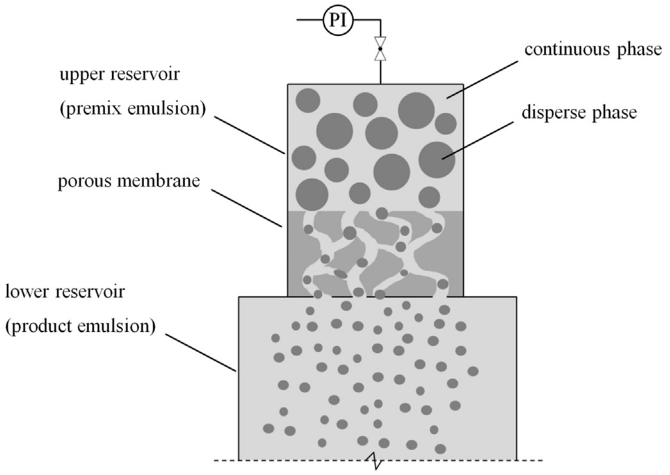

Fig. 1. Scheme of the premix emulsification process.

premix membrane emulsification by porous glass membranes [10]. Here, resulting droplet sizes of approximately twice the mean pore size, depending on transmembrane pressure or flux rate, may be generated at higher emulsifying rates in comparison to crossflow emulsification. Using microporous membranes with a ratio of transmembrane to capillary pressure of less than 5–6, lower span values for o/w emulsions could be produced, as for higher ratios a coalescence due to steric hinderance is occurring [11]. The porosity and number of active pores for emulsification is pointed out as well as the resulting lower wall shear stresses as important features, promoting membrane emulsification processes. Agarose beads have been produced using the premix membrane emulsification process, showing the extent of droplet break-up in premix emulsification processes as affected strongly by the membrane pore size. No significant effect of pore size distribution and shape of pore entry openings on emulsion results was found in [12]. Structural parameters for premix emulsification were investigated by van der Zwan [13] by varying the thickness of membranes made of glass particles by tailoring the membrane structure features through depositing layers of different particles. Furthermore, droplet sizes could be reduced for multiple emulsions by repeated premix emulsification using Shirasu Porous Glass, also referred to as SPG, membranes as shown by Vladisavljević et al. [14]. Tubular membrane structures made of epoxy based polymer materials have been successfully implemented for the production of narrow distributed agarose microspheres [15]. Nakashima et al. investigated SPG membranes structures synthesized from CaO–Al_2O_3–B_2O_3–SiO_2 glass in a wide spectrum of pore sizes $d_{pore}=0.1$ … 20 μm [16]. Porous structures have successfully been surface modified by chemical reactions using organic silanes to control the wetting behaviour [17,18]. To gain membranes with high interior surface areas combined with an advanced product flux, ceramic alumina membranes (α-Al_2O_3) [19], circonium coated alumina membranes [20] as well as polytetrafluorethylene membranes (PTFE) [21] were used. Using nickel membranes with uniform cylindrical pores in a circular disc membrane of distinct pore distances, droplet sizes of less the pore sizes were produced for initial premix droplets of >50 μm [22]. Here, in comparison to disperse phases permeating purely through a membrane, as for direct emulsification, the effect of porosity on mean droplet size was pronounced more for premix membrane emulsification. For premix membrane emulsification, glass microporous membranes are still used most, again pointing out the major effect of pore size and size distribution on resulting droplet sizes [23].

Investigations of premix membrane emulsification using glass particle packings have been performed by Nazir et al. [24]. Hydrophilic glass particles of 55 μm in diameter were used for membrane material. The viscosity ratio between continuous and disperse phase is found to determine the droplet size and flux rate. Droplet sizes of <5 μm were produced up to o/w emulsions of 60% (v/v) disperse phase content. Regarding different sizes of glass beads from 55 to 90 μm combined with a structure supporting sieve, the internal structure of the membranes is described. The droplet to void size ratio is extracted to be dependent on the ratio of height to diameter of the packed bed [25]. The typical disadvantage of membrane fouling in emulsification of organic matter has been overcome by using a cleanable packed bed of hydrophilic glass particles in the range of 53–125 μm, with an average particle diameter $d_{4,3}$ of 75,9 μm [26].

Though several investigations deal with porous membranes for emulsification purposes, no detailed investigations of the internal flow and the interior structural parameters on the resulting emulsion droplet size distribution have been revealed so far. Therefore, this contributions intends to derive the dependency of membrane structure parameters, such as porosity, tortuosity, pore sizes and pore geometry for spherical and non-spherical shaped particulate membranes on fluid dispersion.

2. Experimental facility for premix emulsification

In order to extract the dependency of the structural membrane properties on the resulting droplet size distribution of the dispersed phase of an emulsion, defined coarse premix emulsions have been produced. The batch fabrication of premix emulsions is performed using a rotor-stator device (IKA® T18 basic Ultra-Turrax®), applying varying constant stirring times for a rotation speed of $w=3600\ \text{min}^{-1}$ (Fig. 2). Each premix batch production contains a distinct amount of distilled water, rapeseed oil and emulsifier. The dynamic phase boundary stabilization of newly formed surfaces in the premix emulsification process is affected by the diffusive kinetics of the used emulsifier type. Two emulsifiers are studied, having different molar masses and hence diffusive behaviours. Non-ionic emulsifiers used in food industry as Polysorbat 20 (Tween20®) and Polysorbat 80 (Tween80®) (fabricator: Sigma Aldrich Chemie GmbH, Steinheim, Germany) are used here, as they do not split up into ions involving the presence of an electric charge, are harmless and hence easy disposable. The hydrophilic-lipophilic balance (HLB) is $HLB=16.7$ for Polysorbat 20 (PS20) and $HLB=15$ for Polysorbat 80 (PS80). These emulsifiers are appropriate for the production of o/w emulsions, which require $12<HLB<16$. The emulsifiers have been stirred for two minutes with water at high rotation speed for homogenization, maintaining an emulsifier concentration of three times the emulsifier's individual critical micelle concentration (CMC). Rapeseed oil was added at a constant fraction of 0.5 (v/v) for each premix of 200 ml. After filling the premix into a containment, pressurized air is applied to force the premix through the membrane (Fig. 2).

3. Materials and methods

3.1. Materials

For the premix emulsification experiments, two types of membrane structures are investigated: sintered glass structures made of non-spherical fragmented borosilicate glass 3.3 ($SiO_2+B_2O_3$) [27] and sintered membranes of ceramic spherical microbeads ($Al_2O_3+SiO_2$) [28]. The shape of the investigated structure types illustrate a major difference in their non-spherical (glass) and spherical (ceramic) shape. The spherical ceramic particles are fabricated by ionotropic gelation route. This method