



# Emulsification with microfiltration ceramic membranes: A different approach to droplet formation mechanism



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## ABSTRACT

Oil-in-water (O/W) emulsions were prepared by membrane emulsification (ME) in a large scale stirred tank with a submerged cell using flat membranes, and in a cross-flow tubular unit. Results obtained with flat and tubular membranes devices were compared. Common ceramic microfiltration (MF) membranes ( $ZrO_2$  supported on  $TiO_2$ ) were used in both cases. The main advantage of these membranes is their low cost compared to others frequently used in ME (SPG membranes), which implies a reduction up to 60%. The effect of operation parameters on droplet size distributions was studied to understand the droplet formation mechanism that takes place in both devices.

Monodisperse O/W emulsions were obtained using flat membranes with a droplet-to-pore diameter ratio ( $D_d/D_p$ ) in the range 2.1–2.9. Span values of 0.58, 0.66 and 0.81 corresponded to membrane pore diameters of 0.45, 0.80, and 1.4  $\mu m$ , respectively, being the active pores fraction in the range of 27–36%. The cross-flow tubular unit allowed for production of monodisperse O/W emulsions but with larger droplet sizes, having droplet-to-pore diameter ratios ( $D_d/D_p$ ) in the range 3.9–4.7. It was observed a major influence of pore activation by dispersed phase pressure on droplet size distribution.

Shear stress had little influence on the droplet size, with both flat and tubular membranes. This suggested that droplet formation mechanism was not shear stress-based. A spontaneous emulsification mechanism was proposed.

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## 1. Introduction

Producing emulsions by dispersion of a liquid into another immiscible liquid is an area of interest in pharmaceutical, chemical, cosmetic and food industries. Current industrial emulsification processes, such as high pressure homogenizers, rotor stator devices (e.g., colloid mills), and static mixers techniques, can produce small droplets but with a high strain on the liquids, causing activity loss in compounds. Furthermore, droplet size is difficult to control and, therefore, usually polydisperse emulsions are obtained. In membrane emulsification (ME) the strain on the liquid phases is reduced, and droplet size can be narrowly distributed with less shear stress and energy consumption [1–6]. Although ME is technically simpler and needs less surfactant, the production of highly monodisperse emulsions requires the use of membranes with well-controlled pore size distribution [7].

Techniques for ME may be classified into two groups [8,9]: (1) Direct ME: The dispersed phase is injected through the membrane into the continuous phase; (2) Premix ME: A coarse emulsion is pressed through the membrane to reduce the droplet size.

Membranes frequently used in ME processes have been manufactured specifically for this purpose, such as, Shirasu Porous

Glass (SPG) membranes, which have a narrow pore size distribution [10–12]. The most common processes involve cross-flow systems where the shear stress required for the droplet detachment is induced by the continuous phase flow, although rotating devices can also be used [13].

There have been several studies using tubular, microporous membranes made of SPG,  $\alpha-Al_2O_3$  or  $ZrO_2$  [2,3,14–21]. Some of them used asymmetric, tubular-ME membranes [2,3,14,19–21], which are more cost-effective and easier available than the SPG membranes. In these studies, the performance of ME was investigated with changes in the operation and composition parameters [2,3,14–21]. Several studies about the potential ME applications in producing high-value products were also performed [22–28].

Flat ceramic membranes have been used for ME with cross-flow systems [29–31]. In commercial cells with flat-disc metallic membranes, the shear stress required for the droplet detachment was provided by a simple paddle-impeller that was rotating over the membrane [1,32–35].

The effect of ME process parameters on droplet formation has been evaluated by relating them to the forces acting on the system [6,16,32,36,37]. Several mathematical models have been developed to explain ME performance. The simplest ones were based either on a force balance [6,14,16,20,32,38] or a torque balance [16,36,37]. More complex models were also developed by using the Navier–Stokes equation and computational fluid dynamics [38–40], while others were based on dynamic diffusion [41,42].

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In this work, we investigated the performance of commercially available microfiltration (MF) flat-disc ceramic membranes in a tailor-made emulsification cell. Several membrane pore diameters were selected for batch emulsification in a high-capacity stirred tank.

The effect of operation parameters such as impeller rotational speed, transmembrane pressure, continuous phase viscosity and geometric parameters on droplet size distribution was studied to determine the optimal operation conditions. The stability of the emulsions obtained by the ME and conventional agitation was monitored and compared.

Experimental results were compared with predicted values by a droplet size estimation model and with the force balance, to understand the emulsification performance and droplet formation mechanism. Experiments were also carried out using a cross-flow emulsification equipment with the MF tubular ceramic membranes at the same pore diameter, to understand the actual mechanism of the droplet formation in the process.

One advantage of MF membranes for ME is their low cost compared to SPG membranes. The cost of these membranes is around 0.17 €/cm<sup>2</sup> while the estimated cost for conventional MF membranes is around 0.07 €/cm<sup>2</sup>, roughly a reduction of 60%.

## 2. Theoretical background

### 2.1. Pressure and dispersed phase flux

In order to produce droplets, the pressure on the dispersed phase should overcome the interfacial tension to permeate through the membrane pores [43]. The minimum value required is the critical pressure ( $P_c$ ) and may be expressed by

$$P_c = \frac{4\gamma \cos \theta}{D_p} \quad (1)$$

where  $\gamma$  is the interfacial tension,  $\theta$  is the contact angle between the dispersed phase and the membrane surface and  $D_p$  is the nominal membrane pore diameter. The driving force for dispersed phase flow through the pores is the transmembrane pressure ( $\Delta P$ ):

$$\Delta P = P_d - P_0 \quad (2)$$

where  $P_d$  and  $P_0$  are the pressures at the dispersed phase side and at the continuous phase side, respectively. For a flat membrane module  $P_0$  is the pressure on the membrane surface.

It is desirable to have a higher flux rate of dispersed phase for the industrial-scale emulsion production using membranes [15,44]. The dispersed phase flux ( $J_d$ ) increases as the mean pore diameter and/or the transmembrane pressure ( $\Delta P$ ) increases [2,3,12]. The flux,  $J_d$ , is given as a function of  $\Delta P$  by Darcy's law [14]:

$$J_d = \frac{\Delta P}{\mu_d R_m} \quad (3)$$

where  $\mu_d$  is the viscosity of the dispersed phase (Pa s) and  $R_m$  is the intrinsic membrane resistance (m<sup>-1</sup>). It may be experimentally determined by measuring pure water flux at different  $\Delta P$  values since the resistance depends only on membrane characteristics, such as pore size, porosity and tortuosity.

### 2.2. Fraction of membrane active pores

Droplets are produced by only a fraction of membrane pores in the emulsification process using ceramic and SPG membranes. The fraction of active pores determines the flow in every pore and thus the dispersed phase velocity.

There have been several mathematical models for estimating the fraction of active pores ( $K$ ), most of them based on dispersed phase flux data. Vladisavljevic and Schubert developed a simple model

correlating the fraction of active pores ( $K$ ) with the membrane hydraulic resistance ( $R_m$ ) and the dispersed phase flux ( $J_d$ ):

$$K = \frac{J_d \mu_d R_m}{\Delta P} \quad (4)$$

where  $\mu_d$  is the viscosity of the dispersed phase [18].

A similar model was proposed by Lepercq et al. [21] in their study of the droplet coalescence on ceramic membranes. Flow through the membrane is explained in terms of flow through a packed bed using the Carman–Kozeny equation [21]. This model, however, uses a theoretical parameter that does not take into account certain membrane characteristics (e.g., tortuosity) that are related to the hydraulic resistance.

Coalescence of droplets is an undesirable phenomenon in the emulsion process. It takes place on the surface of a ceramic membrane when two droplets are formed very close to each other. The fraction of active pores should be kept below a maximum value to avoid coalescence. Vladisavljevic and Schubert proposed an equation to estimate this maximum fraction [18]. Assuming that the active pores were in a square-array on the membrane surface and that there is no coalescence at the membrane pore openings, the maximum fraction value ( $K_{max}$ ) can be expressed as

$$K_{max} = \left( \frac{\pi}{4\varepsilon} \right) \left( \frac{D_d}{D_p} \right)^{-2} \quad (5)$$

where  $D_d$  is the droplet diameter,  $D_p$  is the pore diameter and  $\varepsilon$  is the membrane porosity.

Droplet formation time ( $t_f$ ) can be calculated with the ratio of the droplet volume ( $V_d$ ) and the volumetric flow rate through a single pore ( $Q_{dp}$ ). This can then be rearranged as shown in the following equation:

$$t_f = \frac{V_d}{Q_{dp}} = \frac{\frac{\pi}{6} D_d^3}{\frac{\pi}{4} D_p^2 \frac{J_d}{\varepsilon K}} = \frac{2\varepsilon K D_d^3}{3 D_p^2 J_d} \quad (6)$$

where  $K$  is the fraction of active pores. The droplet formation time is also affected by the dynamic interfacial tension, and therefore, the type of the emulsifier [14,43].

### 2.3. Shear stress

For an emulsification cell in a stirred tank, droplet detachment is caused by the shear stress. The phenomenon can be modelled well by conventional hydrodynamics [1,32–35]. A liquid moving in a stirred tank may be in a regime of either free or forced vortex [45]. The free vortex regime is influenced by the tank walls. Shear stress decreases in proximity to the wall. The forced vortex regime develops around the rotation axis and, there, the liquid moves as a rigid body. The distance of the boundary between the two regions from the axis is called the *critical radius* ( $r_c$ ). The shear stress expression for the each region can be expressed by Eqs. (7) and (8), in the forced and free vortex regions, respectively [32]:

$$\tau = 0.825(2\pi)^{1.5} \rho_c^{0.5} \mu_c^{0.5} N^{1.5} r \quad (7)$$

$$\tau = 0.825(2\pi)^{1.5} \rho_c^{0.5} \mu_c^{0.5} N^{1.5} r_c^{1.6} r^{0.6} \quad (8)$$

where  $\rho_c$  and  $\mu_c$  are the density and viscosity of the continuous phase, respectively,  $N$  is the impeller rotational speed and  $r$  the distance to the rotation axis. These equations may be applied if droplet diameter is smaller than the boundary layer thickness. It is a modification of Nagata's model [45] using a correction factor of 0.825 based on experimental data obtained with an impeller-to-tank diameter ratio of 0.8 [46].

These expressions for the shear stress differ from the one for tubular membranes ( $\tau$ ), which is based on the pressure drop due to

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