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Geometric parameters influencing production of O/W emulsions using flat metallic membranes and scale-up

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ABSTRACT

The influence of geometric parameters (e.g., tank dimensions, diameter and position of impeller, continuous phase height-to-tank diameter ratio and impeller-to-tank diameter ratio) on the droplet size of emulsions produced by membrane emulsification has been studied. Two flat metallic membranes with pore sizes of 5 μm and 50 μm were used to prepare oil-in-water (O/W) emulsions in stirred tanks. Results show that the influence of geometric parameters depends on the rotational speed of the impeller. Under optimal geometric conditions, it was possible to obtain emulsions with minimum droplet sizes of 45 μm and 105 μm and span values of 0.60 and 0.53 using membranes with pore sizes of 5 μm and 50 μm, respectively. Scale-up experiments were carried out with different tanks and impellers, while maintaining geometric similarity. Emulsions with the same droplet size distributions were obtained using the impeller tip speed as the scale-up criterion.

1. Introduction

Emulsions are widely used in the food, pharmaceutical, cosmetic and coating industries. In some specific applications, such as drug delivery, a very narrow droplet size distribution is required to ensure proper activity. Conventional methods for preparing emulsions (e.g., rotor–stator systems, colloid mills) generate polydisperse droplet size distributions. Since its introduction in the 1990s [1–5], membrane emulsification is considered suitable for preparing monodisperse emulsions. One phase (the dispersed phase) is forced by a pressure gradient (transmembrane pressure) to flow through the pores of a membrane into a second phase (the continuous phase). Droplets formed on the membrane surface are detached and dispersed into the continuous phase by applying a low shear stress. Membranes used for emulsification may have different geometries (flat or tubular) and are available in several materials: ceramic [3,5–7], metal [8–11], microporous glass [1,2] and organic polymers [12,13]. Metallic membranes have been used in crossflow [14–16] systems and commercial stirred tank modules [8–11] and also in rotating and oscillating devices [17–19]. The main advantage of metallic membranes is their mechanical strength, compared to the more fragile ceramic and microporous membranes. In addition metallic membranes produce a narrower droplet size distribution.

Control of the droplet size coupled with an associated narrow size distribution is a critical factor in membrane emulsification. Several parameters (see Table 1), influence both factors: emulsion composition, membrane type, equipment characteristics and operating parameters [20–22]. The influence of membrane type [3,23,24] and operating parameters [20,23,25–27] has been studied for several membrane emulsification systems and composition parameters [5,27,28]. However, the composition parameters are determined by the formulation of the emulsion, which often is imposed by the final application of the emulsion, so changes are not always possible. Furthermore, equipment parameters, which are important for scaling-up membrane emulsification processes have not been studied as thoroughly because of the limitations of the laboratory equipment used.

Several studies on membrane emulsification in tubular crossflow systems at pilot plant scale have been reported [5,29–32]. In addition, some experimental parallel flow designs have been proposed for microengineered devices in order to increase their throughput [33].

The objective of this work was to study the influence of equipment and operating parameters on droplet size distribution for pilot plant scale membrane emulsification with flat membranes in stirred tanks. An appropriate combination of these parameters might help to make the emulsification system more versatile and to retain a constant droplet size distribution when larger tanks and impellers are used.

2. Experimental

2.1. Materials

Emulsions were prepared with a food-grade extra virgin olive oil (μ_d=51 mPa s, ρ_d=886 kg/m^3, and n=1.4677, at 25 °C; acid value lower than 0.8) as the dispersed phase. Emulsions were

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Table 1
Parameters influencing membrane emulsification.

Process variables	Degrees of freedom	Properties and design parameters
Composition	Continuous phase (CP) Dispersed phase (DP) Surfactant concentration Concentration of DP Concentration of co-stabilizers	Interfacial tension Viscosities of DP and CP Densities of DP and CP Stability behaviour (coalescence, creaming)
Membrane	Membrane material Membrane shape Pore size and shape	Pore distance Contact angle of DP and CP Porosity Pore tortuosity Membrane area Membrane thickness Emulsification system
Equipment	Emulsification system	Emulsion volume CP pump DP feed system Pipes, circuit Impeller (size and design) Tank dimensions Stirred tank geometric ratios
Operating conditions	CP flow rate Transmembrane pressure DP flux Rotational speed of the impeller	Shear stress Droplet growth time Droplet detachment time

stabilized using a non-ionic surfactant added to the continuous aqueous phase, namely Tween 20® at 2 wt%, along with a viscosity modifier, medium viscosity sodium carboxymethylcellulose with a degree of polymerization 1100 (CMCNa), at 0.01 wt% (both supplied by Sigma Aldrich).

2.2. Methods

Emulsification was achieved using a flat membrane module of special design (Fig. 1), which has been described previously [34]. The device has a behaviour similar to that of commercial units operating with small volumes of continuous phase. The module can be used with tanks of different diameters, geometry and material. In addition, it is possible to use impellers of different design and size if other shear rates or flow patterns are desired.

Two tailor-made flat membranes fabricated from nickel and stainless steel were used for the experiments. They had a regular array of pores and an active diameter of 3.15 cm. The nickel membrane, supplied by Micropore Ltd. (Derbyshire, United Kingdom), had a 5 μm pore size, with a distance between pores of 200 μm, and a thickness of 200 μm. The stainless steel membrane, supplied by Pantur S.L. (Barcelona, Spain), had a 50 μm pore size, with a distance of 500 μm between pores, and a thickness of 50 μm.

Membranes were cleaned with a dishwashing detergent and deionised water in an ultrasound bath for 10 min, followed by rinsing for 10 min with acetone in an ultrasound bath. Finally, they were dried using compressed air and soaked in the continuous phase.

The shear stress for droplet detachment was provided by three impellers moved by a Heidolph 2102 RZR motor with rotational speed control. The two paddle impellers were 0.06 m and 0.09 m long and 0.015 m and 0.03 m high, respectively. These impellers were selected because they generate a radial flow pattern [35], suitable for droplet detachment. The third impeller was a marine propeller with three blades, 0.06 m diameter and a pitch of 1.7. The distance between each impeller and the membrane surface was 5 mm.

The dispersed phase was gently fed into the cell using a Masterflex peristaltic pump (Cole Parmer Instrumental Co., Chicago). All the membrane pores were active under the operating conditions and dispersed phase flux was in the range of 17–34 L/m^2 h (0.2–0.4 g/min) so that oil concentrations of ca. 1.5 wt% were achieved. All emulsification experiments were conducted at room temperature, and replicated three times. The standard deviation of the droplet size was less than 5 μm, with a coefficient of variation in the range 3–12%. The droplet size distribution was measured using laser diffraction with a Malvern Mastersizer S (Malvern Instruments Ltd, UK). Droplet diameter (D_d) relates to the mean volume diameter ($D_{[4,3]}$).

2.3. Selection of geometric parameters

The droplet size has been considered the control criterion for experiments in which geometric parameters are changed. It is commonly assumed that the smaller the droplet size, the better the performance of the emulsification process. The width of droplet size distribution, given by the span value $[(D_{90}-D_{10})/D_{50}]$, has also been considered as an additional criterion to control the emulsification process.

Paddle impellers have often been used [8–10] because in stirred tanks they provide a radial flow pattern [35] suitable for droplet detachment. In this work, the performance characteristics of two impellers providing radial flow (paddle impellers) and one providing axial flow (a marine propeller) were compared. The influence of impeller diameter was also studied for paddle impellers.

Shear stress has been reported to be a key parameter affecting the droplet size of emulsions prepared in stirred tanks. Models for commercial cells [8], which are based on general stirred tank hydrodynamics [36], do not include geometric parameters because they are based on impeller-to-tank ratios [36,37]. The shear stress (τ) for Newtonian liquids in the turbulent regime can be determined from the volumetric power input (P/V), Eq. (1). This expression of the shear stress includes geometric parameters [34,38,39].

$$\tau = \sqrt{\mu_c \frac{P}{V}} \tag{1}$$

μ_c and V are the continuous phase viscosity and volume, respectively. P/V can be estimated from dimensionless correlations plots [35,40] for different impellers and operating conditions,