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Premix membrane emulsification

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Figure 1. Pressure-driven membrane processes with oil-in-water pre-emulsion: (a) PME without phase inversion ($\Delta P > P_{cap}$, $\theta > 90^{\circ}$) (Suzuki et al 1996). (b) PME with phase inversion ($\Delta P > P_{cap}$, $\theta < 90^{\circ}$) (Suzuki et al 1999). (c) Phase separation ($\Delta P < P_{cap}$, $\theta > 90^{\circ}$) (Koltuniewicz et al 1995). θ is the contact angle at which a dispersed-phase/continuous-phase interface meets the membrane surface.

Premix membrane emulsification (PME) is a homogenization process based on passing coarsely emulsified mixture of two immiscible liquids (pre-emulsion) through a microporous membrane (Suzuki et al 1996) or porous bed of particles (a dynamic membrane) (Yasuda et al 2010). In conventional PME (Fig. 1a), the dispersed phase does not wet the membrane surface ($\theta > 90^\circ$) and thus, hydrophilic and hydrophobic membranes are needed to manufacture oil-in-water (O/W) and water-in-oil (W/O) emulsion, respectively. If the pressure difference is lower than the capillary pressure in a pore (Fig. 1c), the droplets are retained by the membrane, which leads to emulsion separation rather than homogenization (Koltuniewicz et al 1995).

If the membrane surface is wetted by the dispersed phase of the original emulsion ($\theta < 90^{\circ}$) and suitable surfactants are present in both liquid phases, a phase inversion may occur during homogenization (Fig. 1b), leading to the formation of W/O emulsion from an O/W pre-mix or

vice versa (Suzuki et al. 1999). The main advantage of PME with phase inversion is that a fine emulsion with high disperse phase concentration (over 80 vol.%) can be produced from a low-concentration pre-mix. Using a membrane wetted by the middle phase of the multiple emulsion, W/O/W and O/W/O emulsion can be inverted into a W/O or O/W emulsion, respectively. In the case of inversion of W/O/W emulsion (Fig. 2), a lamellar structure is formed inside the pores consisting of surfactant bilayers separated by aqueous films. The aqueous films are ruptured at the pore outlets forming reversed micelles stabilised by mixed surfactants. This W/O emulsion can be redispersed into an aqueous surfactant solution to form a redispersed W/O/W emulsion containing more uniform internal droplets than the original W/O/W emulsion (Hino et al 2000).



Figure 2. Phase inversion of W/O/W emulsion into W/O emulsion using hydrophobic polycarbonate membrane. The original W/O/W emulsion consisted of liquid paraffin (middle phase), Span 80 (a hydrophobic surfactant) and Tween 20 (a hydrophilic surfactant) and a pore size was 3 or 8 µm (Hino et al 2000).

In order to achieve additional droplet size reduction and improve droplet size uniformity, emulsion can repeatedly be passed through the same membrane (Vladisavljević et al 2004). Repeated membrane homogenisation was originally developed for homogenisation of large lipid vesicles using track-etch polycarbonate filters (Olson et al 1979). The advantages of premix over direct membrane emulsification are in smaller droplet sizes and higher droplet throughputs that can be achieved for the given pore size, but at the expense of lower degree of monodispersity.

The droplet size in premix ME is determined by the membrane pore size, transmembrane flux, physical properties of the dispersed and continuous phase and emulsion formulation. Small droplet size in the product emulsion is favoured by small membrane pore sizes, high transmembrane fluxes and low interfacial tensions between the dispersed and continuous phase (Vladisavljević et al 2004; 2006). The membranes used in PME are Shirasu Porous Glass (SPG) membrane (Fig. 3), polymeric microporous membranes (Hino et al 2000) and microsieves (Nazir et al. 2011).



Figure 3. PME using SPG membrane. The droplet size in the product emulsion was 9 μ m and the membrane pore size was 10.7 μ m (Vladisavljević et al. 2004).

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