Encapsulation by membrane emulsification

Dragosavac M. M., Vladisavljević G.T., Holdich R.G
Chemical Engineering, Loughborough University, UK (m.dagosavac@lboro.ac.uk)

INTRODUCTION

Membrane emulsification (ME) is a dispersion process to produce a monosized droplets of one liquid phase (e.g. oil) in a second immiscible liquid phase (e.g. water) using low energy per unit volume where the shear stress applied on the membrane surface mainly influences the droplet size (Vladisavljević, 2005). Conventional devices for preparing emulsions (high pressure, ultrasonic homogenisers, colloid mills, rotor–stator systems, microfluidisers) apply more energy than needed for the production of monosized droplets, leading to droplets with a wide size distribution.

It is commonly accepted that the shear on the membrane surface is one of the most important parameter which influences the droplet size. In order to develop a new formulation where tuning of the process parameters (including the shear) is needed Dispersion Cell Fig. 1 represents a valuable tool. In the Dispersion Cell shear is a function of rotation speed and once the formulation and shear needed for production of the drops of certain size are determined process can be scaled up.

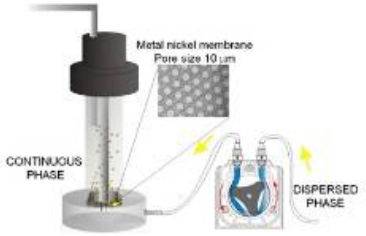


Fig 1. Dispersion Cell (stirred cell) [Dragosavac et al. 2008] with disk membrane (not possible to scale up but good for formulation stage).

Conventional cross-flow membrane emulsification, where the shear is induced by recycled flow of the continuous phase, is not convenient for the production of droplets larger than 20 µm, due to break up in the pump (Vladisavljevic, 2005). New techniques were developed for generating the shear on the membrane surface providing the possibility to generate larger droplets without risk of breakage with possibility for scaling up: pulsating system Fig. 2 (Holdich, 2010) – shear is induced by pulsations of the continuous phase, oscillating system Fig. 3 (Holdich, 2012) – shear is induced by oscillations of the membrane.

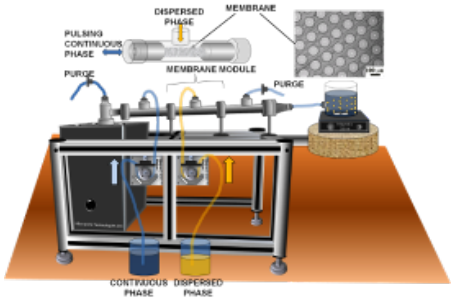


Fig. 2 Pulsating system with tubular membrane [Holdich et al. 2012] (continuous phase pulsates).

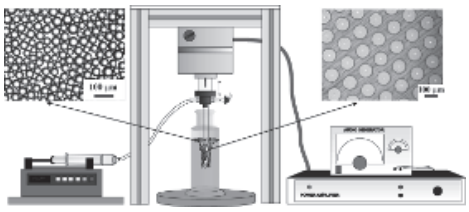


Fig 3. Oscillating system with candle membrane [Holdich et al. 2010] (oscillations of the membrane); same membrane material–nickel.

MODELING OF THE DROP DETACHMENT

To predict the droplet size in a Dispersion Cell a model based on the maximal shear stress (Dragosavac, 2008) can be used. The droplet diameter x is calculated from a force balance of the capillary force (function of interfacial tension and pore size) and the drag force (function of a shear stress and the droplet size) acting on a strongly deformed droplet at a single membrane pore:

$$x = \frac{\sqrt{18\tau^2 r_p^2 + 2\sqrt{81\tau^4 r_p^4 + 4r_p^2\tau^2\gamma^2}}}{3\tau} \quad (1)$$

where r_p is the pore radius, τ is the maximal shear stress, γ is the interfacial tension and x is the formed droplet diameter. The maximal shear over the whole membrane area is given by:

$$\tau = 0.825\eta\omega r_{trans}\frac{1}{\delta} \quad (2)$$

where r_{trans} is the transitional radius (Dragosavac et al, 2008), η is the dynamic viscosity of continuous phase, ρ is the continuous phase density, ω is the angular velocity, and δ is the boundary layer thickness, $\delta = \sqrt{\mu/\omega\rho}$. In the case of continuous membrane emulsification with pulsed flow as well as in the case of oscillation of the membrane if the occurrence of turbulence and bursts near the membrane surface can be neglected, then it may be possible to correlate droplet size with the shear stress at the membrane surface based on the wave equation for shear stress (Holdich et al., 2010):

$$\tau = v_o\left(\frac{\omega_f \mu\rho}{2}\right)^{1/2}\left[\sin(\omega_f t) - \cos(\omega_f t)\right] \quad (3)$$

where ω_f is the angular frequency, determined by:

$$\omega_f = 2\pi f \quad (4)$$

where f is the frequency of the oscillation and v_o is the peak velocity related to both the angular frequency and the amplitude (a) of oscillation by the equation:

$$v_o = \omega_f a \quad (5)$$

A peak shear event occurs when the value of wall shear provided by equation (3) is at a maximum:

$$\tau_{max} = \omega_f^{3/2} a(\mu\rho/2)^{1/2} = 2a(\pi f)^{3/2}(\mu\rho)^{1/2} \quad (6)$$

The maximum shear occurs twice per cycle, and it is the maximum shear that is used in equation (1) to determine droplet size (Fig. 4).

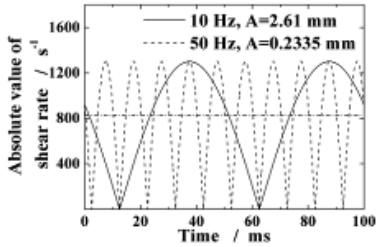


Fig. 4 Shear rate with time where the maximal peak shear for both frequencies was 1.3 Pa, the dashed/dot line represents the average shear rate of 828 s^{-1} which is the same for both frequencies.

RESLTS AND DISCUSSION

There are various parameters that influence the final droplet size (interfacial tension, viscosity, injection rate…) but the shear is one of the most important ones.

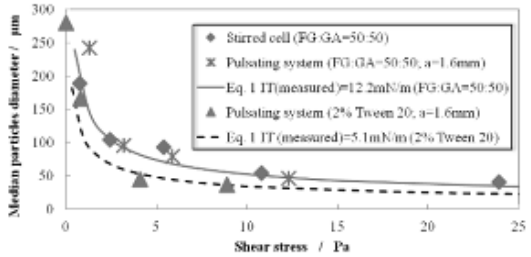
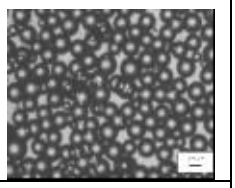
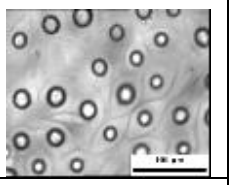
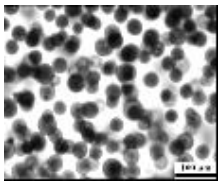
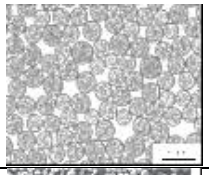
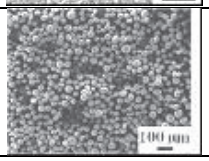


Fig. 5 Median particle diameter vs. shear stress (Pa) using Dispersion Cell and Pulsed Flow continuous phase system. Complex coacervation - Continuous phase fish gelatine and gum arabic; Dispersed phase sunflower oil.

As it can be seen from the Fig. 5 varying only the shear applied on the membrane surface produce droplets between 40 and 250 μm can be produced (used membrane had 20 μm pores). Production of larger droplets of controlled diameter is becoming increasingly popular. Those droplets after additional treatment may be applied in industries such as food and flavour encapsulation, controlled release depots under the skin, medical diagnostic particles, high value fillers, electronic ink capsules, ion exchange resins. Monodispersed droplets and capsules can be used for fundamental studies on controlled release and digestion. Tab. 1 shows some of the experiments conducted using membrane emulsification and it can be seen that highly uniform drops can be produced using membrane emulsification.

Tab. 1 Particles successfully produced up to date using all three membrane emulsification methods

Formulation / possible droplet size for production	Application	Current results – highly uniform particles
Encapsulation of volatile perfume oil by complex coacervation / 30-300 μm	Controlled release [unpublished material]	
Encapsulation of Liquid Crystal Droplets (LCD) by complex coacervation / 10 – 50 μm	Liquid crystal displays [unpublished material]	
Encapsulation of a metal sulphate by complex coacervation and using Pickering emulsions / 30-300 μm	Micro-nutrients for plants [unpublished material]	
Encapsulation of drug for cancer treatment into biodegradable polymer (PLGA) / 10-200 μm	Inhibiting cancer growth [unpublished materal]	
Functional silica particles / 20-100 μm	Sorptiton of heavy metals [Dragosavac et al. 2011]	

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