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Controlled production of oil-in-water emulsions containing unrefined pumpkin seed oil using stirred cell membrane emulsification

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ABSTRACT

Membrane emulsification of unrefined pumpkin seed oil was performed using microengineered flat disc membranes on top of which a paddle blade stirrer was operated to induce surface shear. The membranes used were fabricated by galvanic deposition of nickel onto a photolithographic template and contained hexagonal arrays of uniform cylindrical pores with a diameter of 19 or 40 μm and a pore spacing of 140 μm. The uniformly sized pumpkin seed oil drops with span values less than 0.4 were obtained at oil fluxes up to 640 L m^{-2} h^{-1} using 2 wt.% Tween 20 (polyoxyethylene sorbitan monolaurate) or 2–10 wt.% Pluronic F-68 (polyoxyethylene–polyoxypropylen copolymer) as an aqueous surfactant solution. Pumpkin seed oil is rich in surface active ingredients that can be adsorbed on the membrane surface, such as free fatty acids, phospholipids, and chlorophyll. The adsorption of these components on the membrane surface gradually led to membrane wetting by the oil phase and the formation of uniform drops was achieved only for dispersed phase contents less than 10 vol.%. At high oil fluxes, Pluronic F-68 molecules present at a concentration of 2 wt.% could not adsorb fast enough, on the newly formed oil drops, to stabilise the expanding interface.

1. Introduction

Membrane emulsification is a relatively new method of producing micron-sized emulsion droplets of a predefined size, based on the extrusion of the dispersed phase into the continuous phase liquid through a microporous membrane [1,2]. In addition to the direct process, in which a pure dispersed phase is forced through the membrane, other modes of operation have also been developed, such as premix membrane emulsification, or membrane homogenisation, in which a coarse emulsion is homogenised by passing through the membrane in a single pass or several consecutive passes [3–5]. Another interesting novel approach in membrane emulsification is the formation of drops through fragmentation of the dispersed phase in the lumen of hollow fibre membranes due to permeation of pure continuous phase through the membrane [6]. The main application areas of membrane emulsification are production of double emulsions [4,5,7,8], creation of drops for biphasic enzymatic reactions [9], and production of solid microparticles [10], such as solid lipid microcapsules [11], polymeric microspheres [12], silica particles [13], and gel microbeads [14].

In order to detach droplets from the membrane surface and allow better control over the droplet size distribution, the shear stress is usually controlled at the surface of the membrane. The surface shear can be created by recirculating the continuous phase in cross flow (Fig. 1(a)) [1,2], by vibrating [15,16] or rotating the membrane (Fig. 1(b) and (d)) [17–19], by vibrating an element (e.g. a wire or plate) in the continuous phase at a short distance from the membrane (Fig. 1(c)) [20,21] or by stirring the continuous phase using a stirring bar (Fig. 1(f)) [22,23] or a paddle stirrer (Fig. 1(e)) [24–26]. Table 1 lists potential advantages and disadvantages of the various techniques used for generation of surface shear in membrane emulsification. Cross flow is the most conventional way to control shear force in direct membrane emulsification [2]. If the surfactant has sufficient time to stabilise the interface so that the drops do not coalescence, a regular droplet detachment from the membrane surface and formation of uniform drops can be achieved even without any surface shear, providing that the drops are strongly deformed from their preferred spherical shape before detachment. It may happen if there is a large number of drops at the membrane surface and the drop diameter is bigger than the distance between the pores, so that

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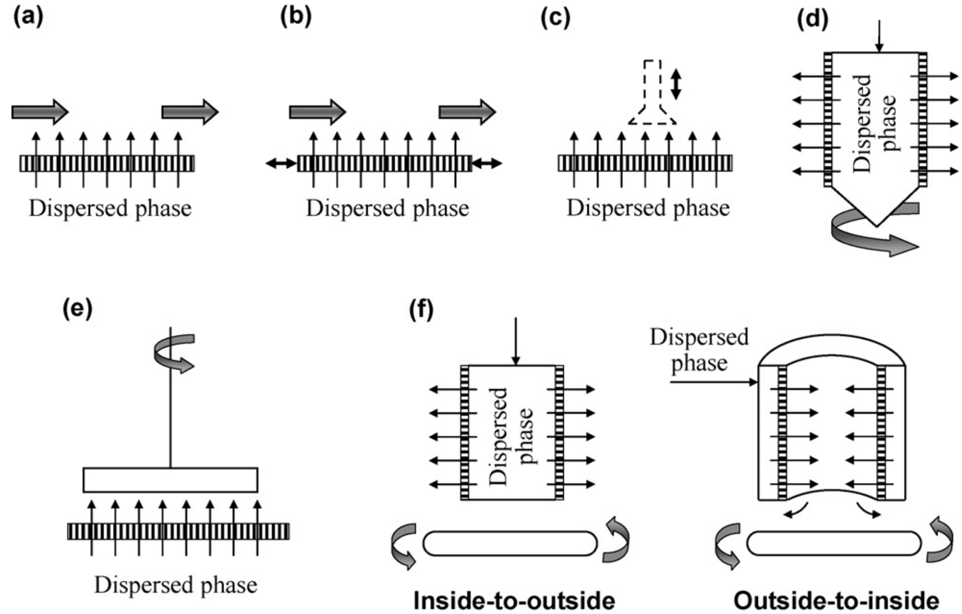

Fig. 1. Formation of surface shear in membrane emulsification. (a) Cross flow, (b) cross flow + membrane vibration, (c) vibration in continuous phase, (d) rotating membrane, (e) stirred cell, flat sheet membrane, and (f) stirred cell, tubular membrane.

the drops push each other at the membrane surface [27]. The drops can also be deformed from their spherical shape if they are generated at the pores or channels with a distinct non-spherical shape such as rectangular channels with a high aspect ratio [28] and asymmetric microchannels [29] or if the droplets are squeezed between a microstructured substrate and a cover glass before detachment [30]. However, it is widely accepted that the shear stress at the membrane surface does have to be applied to obtain uniform drops at relatively high drop productivity. As a rule, the higher the injection rate of the dispersed phase, the greater the surface shear stress that has to be applied to enhance the monodisperse nature of the particle size distribution [31].

In this work membrane emulsification was performed using microengineered flat disc membranes on top of which a paddle blade stirrer was operated to induce surface shear (Fig. 1(e)). A stirred cell is an unusual device for membrane emulsification, because it is commonly believed that a uniform shear field at the membrane surface is required for the generation of uniformly sized drops. However, in the previous studies [24,25], it was found that a stirred cell with a varying radial shear field at the surface of the flat disc membrane could produce uniformly sized drops of paraffin wax and refined sunflower oil. In this work the same stirred cell was used to produce emulsions of unrefined pumpkin seed oil. This system presents a significant challenge because unrefined pumpkin seed oil contains a broad range of components that not only have beneficial health effects, but may also be adsorbed on the membrane surface and hinder the emulsification process. Unrefined pumpkin seed oil is particularly rich in omega-3 fatty acids [32], ranking second only to flax seed and should be emulsified under low shear conditions to avoid heating and lipid oxidation. Therefore, membrane emulsification seems to be a very convenient technique for production of emulsions of unrefined pumpkin seed oil of high biological value and desired organoleptic properties.

2. Experimental

2.1. Materials

The oil phase in O/W emulsions was unrefined pumpkin seed oil with a density of 913 kg m^{-3} and viscosity of 55 mPa s at 298 K, kindly donated by GEA Tovarna Olja (Slovenia). The continuous phase was 2 wt.% Tween® 20 (polyoxyethylene sor-

Table 1
Comparison of different techniques for creation of shear stress at the membrane surface in membrane emulsification

	Potential advantages	Potential disadvantages	References
Cross flow	Easy scale-up, constant shear stress at the membrane surface, modules widely available	Droplets can be damaged during recirculation in pipes and pumps, long operation times for concentrated emulsions	[1,2]
Cross flow + membrane vibration	Additional control over droplet detachment, decrease in mean droplet size as compared with a simple cross flow	Complicated design, no evidence that drop size monodispersity is improved	[15,16]
Vibration in continuous phase	Simple set-up	Poor control of shear stress, suitable only for small scale applications	[20,21]
Rotating membrane	Suitable for creation of fragile particles and viscous emulsions	Complicated and expensive design, high power consumption	[17–19]
Stirring, tubular SPG membrane	Volume of continuous phase liquid can be as low as several mililitres	Maximum transmembrane pressure restricted to several bars, non-uniform shear stress at the membrane surface	[22,23]
Stirring, flat microengineered membrane	High injection rates of dispersed phase through the membrane	Mean droplet size in product emulsions above 20 μm, batch operation	[24–26]