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Processing effects during rotating membrane emulsification

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In this study, a rotating membrane emulsification setup incorporating a 6.1 μm pore diameter SPG membrane was used to produce O/W emulsions of average droplet sizes between 23.4 and 216.6 μm. All emulsions consisted of 10 vol% of sunflower oil or silicone oil stabilised by 1 wt% Tween 20. The transmembrane pressure (0.1–1.8 bar), rotational speeds (100–2000 RPM) annular gap width (5–45 mm), dispersed and continuous phase viscosity were all investigated as to their effect on emulsion droplet size and dispersed phase flux. Modification of the dispersed phase flow properties alters the droplet size with four regions being suggested; a decrease in size (as droplet coalescence is minimised), a plateau (size-stable zone), a gradual increase in size (due to transfer of mass via droplet neck) and then a rapid increase (due to jetting). The importance of Taylor vortices development was seen with larger droplets formed in their absence; typically at low rotational speeds, narrow vessel diameters and more viscous continuous phases. It was concluded that the flow behaviour of each phase requires careful consideration to understand the likely formation mechanism(s) during operation. Across the pressure and viscosity ranges investigated, the dispersed phase flux ranged between 50 and 12,500 $\mathrm{Lm^{-2}\,h^{-1}}$ and pore activity was within the range of 0.5–2.7%.

1. Introduction

Emulsions are defined as dispersed systems of at least two immiscible liquid phases, typically an organic and an aqueous phase. One of these phases is dispersed in the form of droplets within a continuous 'bulk' phase. Such systems are encompassed within many food, cosmetic, agrochemical and pharmaceutical formulations and therefore there is great interest in the control of their microstructure. Industrially, emulsions are manufactured using well established processes such as high pressure homogenisers and rotor-stator mixers in which the two phases or pre-emulsion are subjected to high shear forces in the region of 20,000–100,000 $\mathrm{s^{-1}}$ [1]. Droplets are broken down into smaller droplets within turbulent eddies – a phenomenon which is not homogeneous throughout the multi-phase system or over the processing time. As a consequence, the droplet size and size distribution of the resultant emulsion can vary significantly with each batch, which in turn may potentially have an adverse effect on desired functional properties related to structure, as well as stability. Furthermore, these processes require high amounts of mechanical energy which is delivered inefficiently to the system. The rate by which the interface is created far exceeds the rate of which the stabilising molecules (known as surfactants) can adsorb at the newly created interfaces hence formed droplets can quickly coalesce through a 'back-reaction' that increases emulsion droplet size. This is obviously counter-productive if the intention is to reduce droplet size to a desired value as the energy required to increase interfacial area is essentially wasted. The emulsion may also experience significant thermal stresses within areas of high localised energy dissipation. Ingredients or microstructures which could be susceptible to damage due to high shear and thermal stresses are therefore unsuitable for processing using these conventional emulsification techniques. The disadvantages associated with such processes eliminate to an extent the use of many proteins and starches within formulations, as well as hinder production of specifically designed microstructures such as double emulsions.

However, there is a different approach to emulsification where droplets are created individually and then dispersed into the continuous phase over time. One such method is membrane emulsification. Since its introduction as a novel process to formulate emulsions by Nakashima in the early 1990s [2], membrane emulsification has been a subject of increasing interest to researchers due to the numerous potential advantages it offers [3,4]. The energy input to produce a specific volume of emulsion of identical droplet size is of at least two orders of magnitude lower when compared to traditional formulation processes [5]. With a more gradual increase in interfacial area, formulations no longer require heavy loading of surfactant to stabilise small droplets [6]. The shear forces required to produce droplets are also much lower

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since they are intended to detach rather than break up forming droplets. Membrane emulsification is therefore a more environmentally sustainable process for producing emulsions. Such benefits also offer greater compatibility with fragile ingredients and microstructures (e.g. double emulsions, nano-emulsions) lending itself towards formulating 'smarter' products in future.

At the most fundamental level, the process entails passing dispersed phase through the pores of a membrane into the continuous phase. This is commonly achieved via the application of pressure. Droplets detach from the membrane surface through the generation of a shear force. However, the method by which shear is applied to the system has led to the development of a subset of membrane emulsification processes. The most widely used membrane emulsification process is that of cross-flow membrane emulsification, in which the continuous phase is re-circulated (through a pump) to flow parallel and across the surface of the membrane. Alternatively, the process of dead end membrane emulsification can be used which relies on spontaneous detachment of droplets and therefore no applied shear at all. More recently, rotating membrane emulsification has emerged as a promising process [7–9]. The membrane undergoes rotational motion to generate a shear force on forming droplets, acting tangential to the membrane surface. Additional detachment forces induced by rotation and milder fluid hydrodynamics serve as further optimisation towards producing more intricate microstructures.

At present, one of the limitations of membrane emulsification is the relatively low emulsion production rate as determined by the dispersed phase flux [10]. The flux largely depends on properties related to the membrane as well as the pressure applied and dispersed phase viscosity. However, some of these can be chosen by the operator and thus the process can be optimised depending on whether droplet size or throughput is the main priority [11]. Understanding of the interplay between processing and formulation parameters remains a topic of much deliberation within the literature. Furthermore, there is overall limited research available on rotating membrane emulsification despite its potential advantages. The aim of this study is to gain insight into how O/W emulsion droplet size and production rate are affected by the flow behaviour of the dispersed phase (flow through the membrane) and continuous phase (flow within the processing vessel). The discussion considers a wide range of phenomena relevant to emulsification using SPG membranes, focussing towards higher throughput processing in order to make the process more industrially viable. In addition, this study is designed to further current understanding of the droplet formation mechanisms involved within this process, which in turn should allow for the development of approaches to precisely formulate specific emulsion microstructures.

2. Materials and methods

2.1. Materials

Oil-in-water emulsions containing 10 vol% of dispersed phase were produced in all cases. The oil phase was either commercially available sunflower oil or silicone oil (Sigma Aldrich, United Kingdom) with density values shown in Table 1. The aqueous phase was passed through a reverse osmosis unit and then a milli-Q water system. The emulsions were stabilised by Tween 20 (polysorbate 20, Sigma Aldrich, United Kingdom) dissolved in the continuous phase using at a concentration of 1 wt% of the whole emulsion system. The continuous phase viscosity was modified using varying quantities of Glycerol (Sigma Aldrich, United Kingdom) between 1 and 87.5 wt%. All materials were used with no further purification or modification of their properties.

Table 1
Dispersed phase density values used to convert mass flow rates into dispersed phase fluxes.

Dispersed phase	Density (kg m^{-3})
Sunflower oil	919
Silicone oil (0.012 Pa s)	930
Silicone oil (0.023 Pa s)	950
Silicone oil (0.085 Pa s)	960

2.2. Experimental setup and procedure

The experiments were performed using a tubular, hydrophilic SPG membrane of 6.1 μm mean pore size (SPG Technology Co. Ltd., Miyazaki, Japan). The membrane dimensions were 10 mm outer diameter and 45 mm length, corresponding to an effective membrane surface area of 14.1 cm^2. The wall thickness of the membrane was approximately 1 mm. The membrane was mounted on an IKA Eurostar digital overhead stirrer and positioned in the processing vessel. This vessel was interchangeable allowing for different diameter vessels to be used. This altered the amount of continuous phase within the vessel since the membrane had to be submerged during process operation. Emulsion batch sizes between 20 and 360 g were produced. The membrane rotational speed in each experiment was kept constant between 100 and 2000 RPM. The transmembrane pressure was also held at a fixed value ranging from 0.1 to 1.8 bar (gauge). Since the outer vessel was open to atmosphere, the continuous phase was considered to be at atmospheric pressure throughout the whole fluid since the hydrostatic pressure exerted was negligible.

The schematic of the equipment setup is shown in Fig. 1. The oil phase was introduced to the inside of the membrane tube at the beginning of the experiment with the opening of the dispersed phase valve. Pressurisation of the dispersed phase storage tank with compressed air enabled the oil to permeate through the membrane to the outer continuous phase. Once the required mass of oil was added, the experiment was stopped by closing the dispersed phase valve and venting the storage tank.

2.3. Droplet size measurements

Droplet size distribution of all emulsion samples were measured using a Malvern Mastersizer (United Kingdom) with a hydro 2000 small volume sample dispersion unit. Droplet sizes given here was expressed as volume weighted mean diameter ($d_{4,3}$).

2.4. Interfacial tension measurements

Interfacial tension (IFT) values were measured using a goniometer Easydrop from Kruss (Germany). The pendant drop method was used to determine the interfacial tension at 20 °C between a droplet of dispersed (oil) phase formed from a 1.8 mm diameter needle within a cuvette containing the continuous (aqueous) phase. These measurements were taken over a period of 1800s at 30 s intervals to acquire both initial and equilibrium interfacial tension values. Due to the nature of the measurements, there is an inherent time delay (of 3.5 s) between the point when the two phases first encounter one another and the point at which the instrument starts measuring. As such, it is not possible to measure interfacial tension phenomena that occur over the extremely small timescales when the two phases are first introduced. In order to be able to obtain a relatively accurate estimate of interfacial tension values over these timescales, the follow approach was taken. Interfacial tension measurements were undertaken over a duration of 60 s at much shorter time intervals (≈ 0.2 s) in order to obtain a logarithmic function representing the