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The Effects of Membrane Composition and Morphology on the Rotating Membrane Emulsification Technique for Food Grade Emulsions

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Abstract

The effects of using different membrane materials and morphologies in the membrane emulsification process were observed using similar operating parameters and system geometry, allowing a direct comparison of not only the membranes themselves but also between both a stationary cross-flow membrane emulsification device and a rotated membrane emulsification device. Each membrane type tested had distinct characteristics, and the droplet sizes produced responded differently to changes in operating conditions.

The rotating membrane produced similar droplet sizes to the cross flow membrane system, but at a much lower shear rate. This suggests that the detachment of the droplets occurs sooner due to the additional centrifugal force and system vibration. The Shirasu porous glass (SPG) membrane produced the smallest droplet sizes (<1µm from a 1µm membrane), however the stainless steel membrane produced the lowest droplet size to pore size ratio (~0.5:1) due to its cylindrical pore geometry as opposed to the tortuous geometries of the other membranes used. The droplet sizes produced at different pressures are similar between rotated and cross-flow membrane emulsification, with increases in pressure increasing droplet size and size distribution. The viscosity of the continuous phase has an effect on the droplet size; increasing the viscosity decreases the droplet size by increasing the applied shear, allowing fine tailoring of the size produced, with a more viscous continuous phase reducing the droplet size from ~4µm to ~1µm with an increase in viscosity of 100 mPa•s.

Rotating membrane emulsification has properties with potential to produce shear sensitive emulsion microstructures with small droplet sizes. Emulsion microstructures such as duplex emulsions, core/shell structures beads etc. can be used in the production of novel food structures.

Keywords:

Rotating Membrane; Emulsification; Shear; Cross-Flow; Morphology.

Highlights:

- We examine materials used as membranes in rotating membrane emulsification
- We compare similar membranes between rotating and cross-flow membrane emulsification
- Rotating membranes produce equivalent droplets at lower shear than cross-flow systems
- Rotating membrane emulsification has potential for producing shear sensitive microstructures

1. Introduction

The manufacture of emulsions is an important part of many processes across many industry sectors; however, the emulsification process often still relies on traditional droplet break-up systems during which droplets are produced by repeatedly breaking large droplets into smaller ones until the desired size range is reached [1]. The last few decades have brought many advances in producing droplets with very tightly controlled size distribution spans, which find uses in high value products such as spacers for liquid crystal displays[2] and packing beads for chromatography columns[3]. These droplets are produced by more careful emulsification techniques, producing the droplets at the size that is required rather than breaking them up from pre-existing larger droplets[4, 5]. One such technique is that of membrane emulsification, and this has been explored with the aim of producing near mono-disperse droplets[6, 7].

Membrane emulsification does allow a degree of control over the size distribution of the droplets produced, however there are other made to measure droplet production techniques capable of far better monodisperse droplet production, such as micro and nanochannel devices,[8, 9] edge emulsification[10, 11] and micro-sieve emulsification[12]. The ability to control the microstructure of the droplets is perhaps a more appealing possibility of this technique, as well as minimising the amount of shear applied to droplets as they form[13]. It also has the advantage of easier scaling (whilst not without challenges) than the slower microchannel devices, which require complicated parallelisation to scale production[8].

The idea of applying shear to break forming droplets from the surface of the membrane has been previously explored, using both a flow of continuous phase along the membrane surface[14-16] and by rotating a tubular membrane[6, 17] as well as vibrating/sonicated[18] membrane devices. The forces that result in the eventual detachment of a droplet as it grows at a pore have been identified as shear, pressure/inertia of the dispersed phase, interfacial tension, and buoyancy[19]. Since buoyancy is usually several orders lower than the others it is usually disregarded[20]. The interfacial tension is dependant on the emulsifier present, and the initial interfacial tension between the two immiscible liquids making up the two phases. The pressure of the dispersed phase through a pore, and the resultant inertia is a factor of the trans-membrane pressure applied. The shear

force is provided by flowing the continuous phase across the surface of the membrane, or by rotating the membrane in a vessel of the continuous phase [6, 21].

The application of a perpendicular flowing (rather than static) continuous phase was shown to reduce the droplet size[22] with greater shear (faster flow) producing greater reduction in average droplet size[23]. Changes to the pores size and morphology has been varied and shown to have a great effect on the detachment of droplets[24, 25], with faster, more consistent detachment from structured uniform pores (varying slightly with shape[26]) and slower more uneven detachment from unstructured pores such as porous glass membranes[22].

Vibration of the membrane was studied[18] and found to detach droplets from pores sooner, producing smaller droplets, but only at low vibrational frequencies <100Hz. In this study, Zhu and Barrow (2005) also suggest a detachment mechanism in membranes of low pore separation due to steric hindrance between forming droplets, where droplets are 'pushed' from the membrane surface by those beginning to form behind them.

Rotation of the membrane has been studied with metal membranes and shown to enhance membrane detachment, with large droplets produced at low shear rates[6] and very small droplets produced in a high shear system [17]. Both of these studies used metal membranes, which were not studied in a comparison cross flow system.

The aim of this study was to investigate rotating membrane emulsification with different membrane types and morphologies, and to directly compare the same membrane size and type in the two hydrodynamic configurations of the cross-flow and rotating membrane techniques for the preparation of food grade emulsions.

2. Experimental

2.1 Membrane Emulsification Systems

For this research two membrane emulsification systems were used, both accepting the same diameter membrane tube, one capable of rotating the membrane whilst dispersed phase is pressurised through it from inside (Figure 1), and the other capable of allowing cross-flowing continuous phase to flow over the membrane whilst dispersed phase is pressurised through from inside (Figure 2).

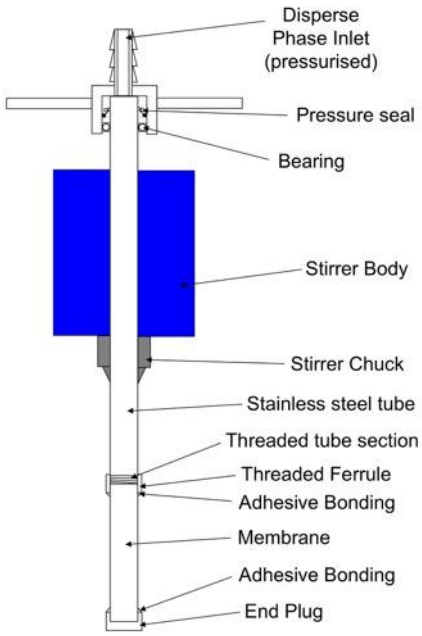

Figure 1. The rotating membrane emulsification system employed a rotating fluid coupling to allow pressurised fluid to flow into the shaft and on into the rotating tubular membrane. The continuous phase was housed in a suitable vessel in which the membrane was submerged.

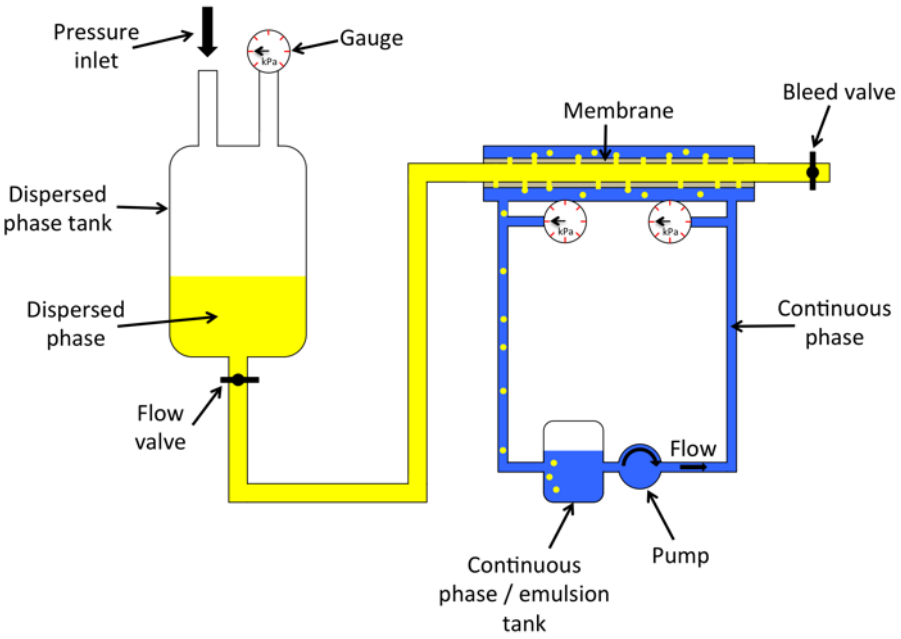

Figure 2. The cross-flow membrane emulsification system used in this study was setup as shown. The membrane module houses the interchangeable membranes such that they separate the dispersed and continuous phases, with the continuous phase flowing along the outside of the membrane tube.

The membrane tubes used had an outside diameter of 10mm, and in the rotating system the vessel used to house the continuous phase in which the membrane was rotated had a inside diameter of 30mm, giving a gap to the membrane of 10mm.

2.2 Materials

Emulsions produced were made with commercial sunflower oil (it was important that no special oil was used to give an accurate representation of what would normally be used in food production), and deionised filtered (milliQ reverse osmosis) water. Several different emulsifiers were used (Tween®20 (polyoxyethylene 20 sorbitan monolaurate), Tween®80 (polyoxyethylene 80 sorbitan monolaurate), SDS (Sodium Dodecyl Sulphate), Soya Lecithin (phosphatidylcholine), sodium caseinate) and were all purchased from Sigma Aldrich, UK.

2.3 Emulsion analysis

The resultant emulsion droplets were analysed using a Malvern Mastersizer 2000 with an attached hydro 2000 small volume sample dispersion unit. Droplet diameters are given in $D_{[4,3]}$ (volume weighted mean) and size distributions are given in % by volume. Relative span is calculated by $D_{0.9} – D_{0.1}/D_{0.5}$ where D is the diameter in microns, below which the subscript proportion of the population resides.

Error bars show 1 standard deviation above and below the mean value of three repeated measurements each of three separate experiments.

2.4 Emulsification membranes

The membranes tested were of three types; the original Shirasu Porous Glass (SPG) made by SPG Techno. Ltd., Japan, ceramic (titanium oxide) desktop microfiltration membranes made by TAMI industries, France, and a laser drilled stainless steel membrane manufactured by Laser Micro Machining Limited, UK. A polymer membrane was also considered, but proved too flexible for use in a rotating membrane system without further support.

A range of pore sizes was used of each membrane type. The SPG membranes are made by leeching particles of volcanic ash from the glass to leave voids, which form tortuous pathways through the glass emerging from the surface as pores of similar size to the removed particles. These pores are non-uniform, and make up a high proportion of the membrane surface, leading to a rough surface and random pore shape[27]. The SPG membranes are available in both their natural hydrophilic state, and silane treated to produce a hydrophobic variant, used in the production of water in oil emulsions.

The ceramic membranes (TAMI Industries, France) used have a thin coating of fine ceramic, which is the membrane, on a much more coarse porous ceramic support material with voids around 50μm. The membrane coating is on the inside of the tube of support material. Because the systems used flowed the continuous phase along the outside of the tube surface, the

shear produced does not act directly on the droplets as they form at the membrane, but instead through the coarse support material.

The stainless steel membrane (Laser Micro Machining Limited, UK) was commissioned for this study, and was created by laser drilling circular holes through a stainless steel tube perpendicular to the surface. The holes were drilled in a skewed grid pattern of 1mm pitch and offset so that pores were not in direct line with adjacent pores along the length or around the circumference of the tube to minimise collisions of nascent droplets. This results in a membrane with larger pores but a much lower porosity than the other membranes studied, thereby keeping the pressure drop and therefore the pore activity along the length of the membrane similar to the more porous SPG and ceramic membranes.

3. Results and Discussion

3.1 Emulsifier effects

The rotating membrane system was used with an SPG membrane of pore diameter 1 μm to make emulsions with a range of emulsifiers at different concentrations. Oil in water emulsions were produced at 1% dispersed phase volume (in order to minimise any coalescence), at a rotation rate of 1000 rpm and a trans-membrane pressure of 10 kPa. The results are shown in figure 3.

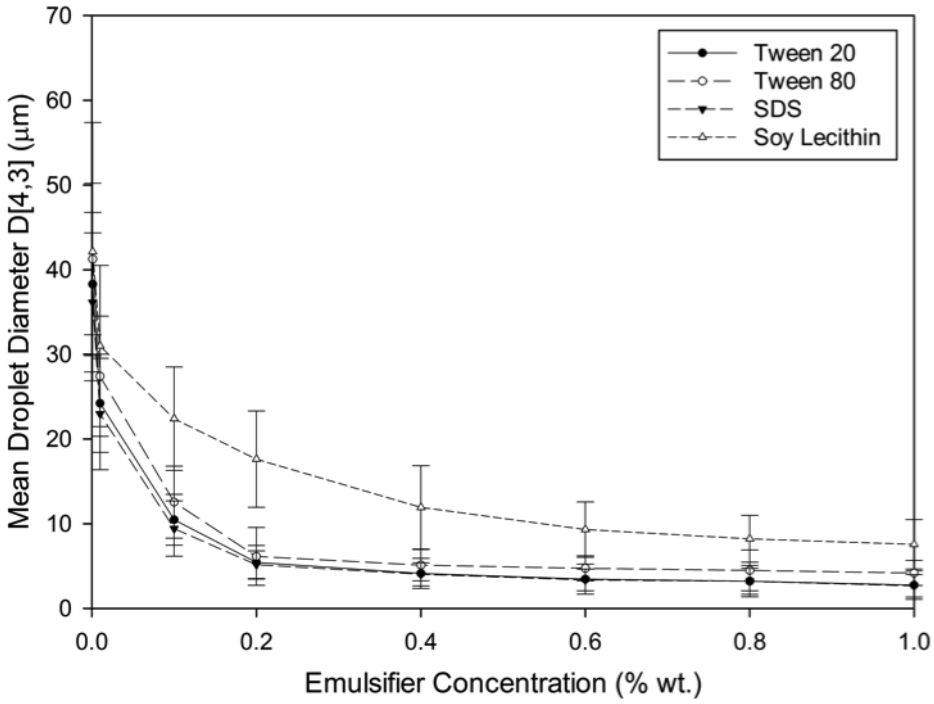

Figure 3. The effects of the concentration of different emulsifiers on the droplet size produced at 10 kPa and 1000 rpm with a rotating membrane emulsification system.

The droplet diameters produced decrease with increasing emulsifier concentration, until a minimum droplet diameter is reached. These results are comparable across the membrane types, with similar trends, but with different

minimum droplet diameters. The droplet sizes produced and the trends with changing emulsifier concentration are similar to those found with the cross-flow membrane emulsification device[16], which was shown to produce smaller droplets at a given emulsifier concentration than those produced at high shear in a droplet break-up emulsification system (a Silverson high shear mixer)[28]. The timescale for emulsifier to be adsorbed to the surface of newly formed interface is much longer in membrane emulsification. Therefore a high concentration of emulsifier is not required to achieve fast coverage[29].

A comparison of the droplets produced from the various membrane types with the emulsifier Tween20 and the rotating system is shown in figure 4.

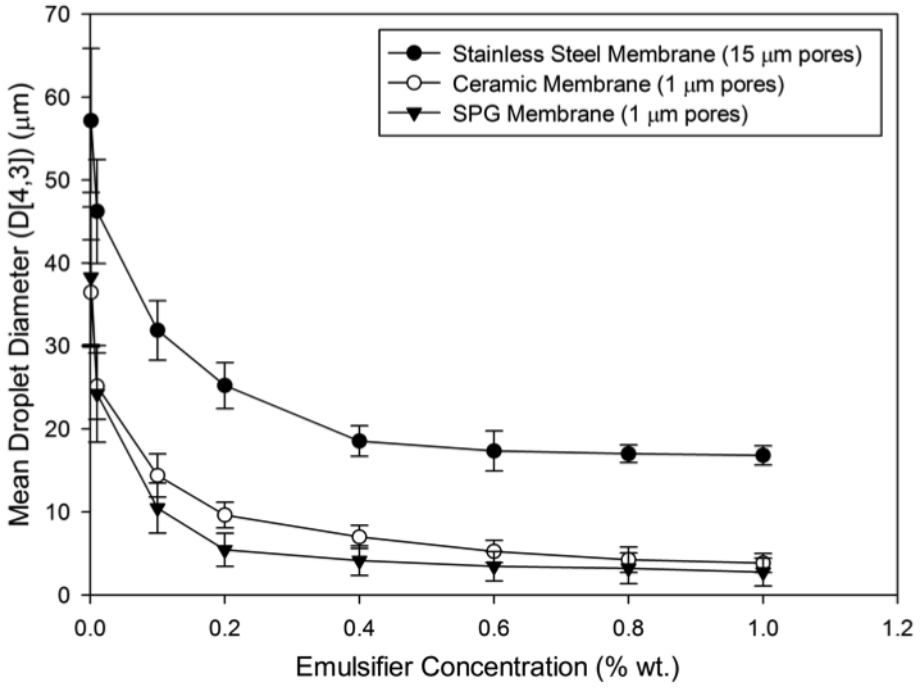

Figure 4. The effects of different concentrations of Tween20 on the droplet sizes produced from the three different rotating membranes at 10 kPa and 1000 rpm.

Irrespective of the minimum size corresponding to the reduction in interfacial tension provided by the emulsifier, the membrane pore size and membrane type also have an effect on the minimum droplet diameter. Larger pores give a larger minimum droplet diameter, and the two membranes with similar pore size but different structures also produce droplets that differ slightly in the produced droplet size. These results are comparable to other results from cross flow membrane emulsification studies [16]. The membrane pore size is the most important factor, although the ratio of pore diameter to droplet diameter is lowest with the laser drilled circular pores, with exits perpendicular to the tube surface. The ceramic membrane having a coarse ceramic support material has the highest ratio of pore diameter to droplet diameter, with the support material shielding the detaching droplets from some of the shear at the tube surface, although this effect is less than was reported for the cross-flow membrane systems [16]. The droplets produced by the ceramic membrane are much smaller than the pores in the support

material (around 50 μm) and so it is unlikely that the droplets are being produced at the interface between the support and the continuous phase.

As was found by Mine et al. (1996), the droplet size distribution is directly related to the membrane pore size distribution,[30] and whilst the emulsifiers have an effect on particle size, the distribution stays very similar. All the membranes produce unimodal distributions of droplets, with the SPG membrane having a relative span of approximately 1.2, the ceramic 1.3 and the stainless steel the lowest at approximately 1. This is in line with expectations as the stainless steel has the cleanest pore geometry and the narrowest pore size distribution.

3.2 Shear effects

The shear rates of the two systems were calculated using:

$$\dot{\gamma} = \frac{8V_{cf}}{D_H} \qquad \text{equation 1}$$

For the cross flow device, where V_{cf} is the linear cross flow velocity in ms^{-1}, D_H is the hydraulic diameter of the flow channel through the membrane module in metres, and $\dot{\gamma}$ is the shear rate in s^{-1}. This assumes a Newtonian continuous phase fluid[29].

$$\dot{\gamma} = \frac{\pi R_1^{\,2} n_1}{15(R_2^{\,2} - R_1^{\,2})} \qquad \text{equation 2}$$

Equation 2 was used to calculate the shear rate for the rotating membrane device, where $\dot{\gamma}$ is the shear rate in reciprocal seconds, R_1 is the outer radius of the membrane in metres, R_2 is the inner radius of the vessel in metres, and n_1 is the rotation rate in rpm, as derived by Vladisavljević and Williams (2006) for a similar geometry[6].

The calculated shear rates were then used to create a graph of shear rate and mean droplet diameter when using the 1 μm pore diameter SPG membrane on both systems, and 1% tween 20 as an emulsifier until 1% phase volume of oil had been achieved. These results are shown in Figure 5.

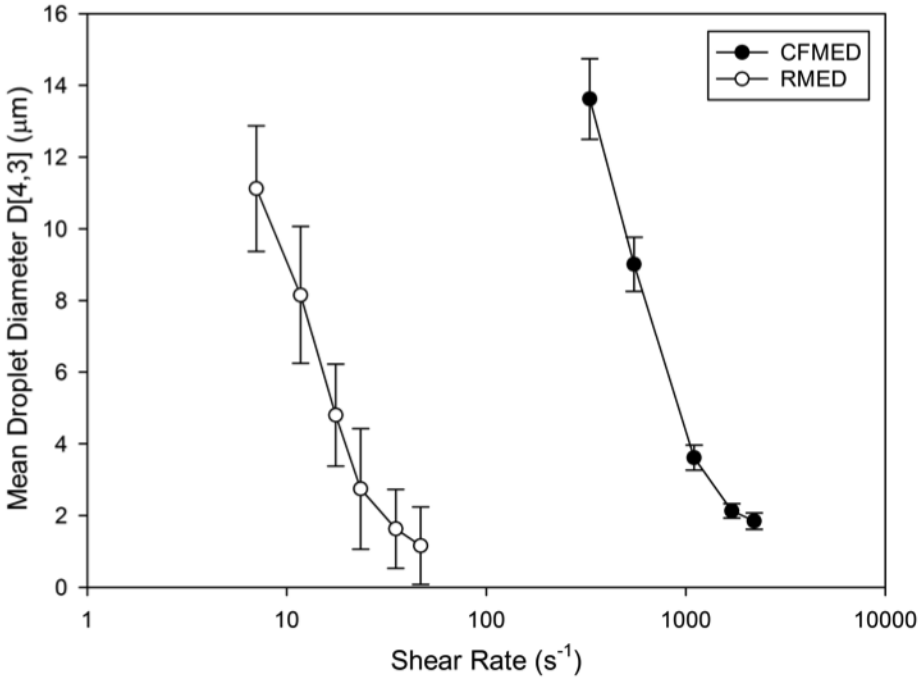

Figure 5. The effects of shear rate on the droplet sizes produced via cross-flow membrane emulsification device (CFMED) and rotating membrane emulsification device (RMED). The membranes are similar 1µm SPG, with 1% tween20 and 1% oil phase volume.

As can be seen from the graph, the rotating membrane emulsification device creates similar sized droplets to the cross-flow device using the same membrane, but at far lower shear. The cross-flow system does, however give more repeatable results. The extra detachment forces provided by the rotating membrane system (potentially a combination of centrifugal force and the vibrations caused by any roughness or eccentricity of the movement of the membrane tube) causes the nascent droplets to detach from the membrane surface sooner, creating droplets of smaller size. The droplet size range is greater however, and this is likely to be caused by an increase in coalescence at the membrane surface with the rotating system.

The effects of shear in the rotating membrane system show slight differences depending on the morphology of the membrane used as can be seen from Figure 6.

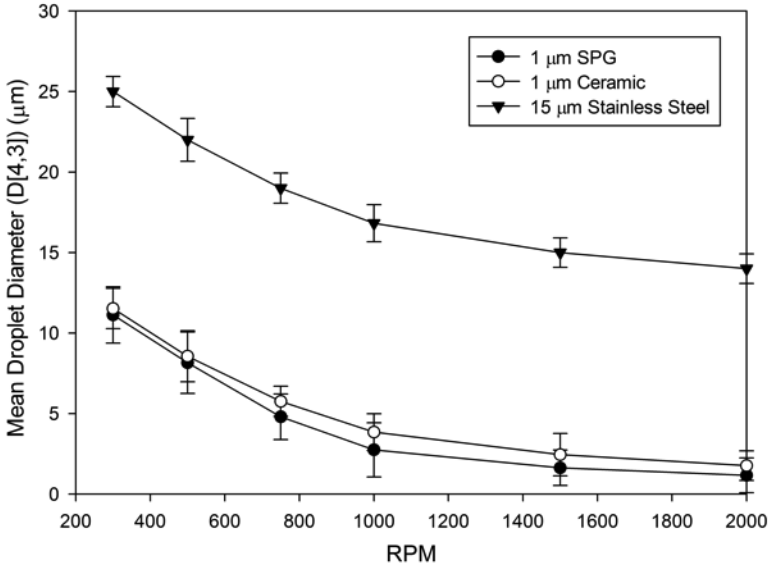

Figure 6. The effects on droplet size of changes in rotation rate (and therefore shear rate) with different membrane morphologies. 1% tween 20 was used to produce emulsions at 1% oil phase volume.

The stainless steel membrane has large pores that run perpendicular to the surface of the membrane in a straight line. Although the pores are larger than the other membranes, the reduction in droplet diameter with increasing shear is more pronounced. The detachment of droplets from the pores of this membrane is highly influenced by shear, with the resulting droplets at higher rpm (and therefore shear rate) having a diameter comparable to that of the pores. The reduction in droplet diameter as shear is increased is lower for the other two membranes tested; the SPG membrane shows a steady decrease until the droplet diameter approaches twice the pore diameter, and the ceramic membrane shows the smallest droplet diameter change with shear with the smallest droplets produced at about 2.5 times the pore diameter.

The stainless steel membrane has pores that exit the surface perpendicular to it, which means that the nascent droplets are forming directly in the flow of continuous phase fluid and subject to the full force of shear at the surface. The SPG membrane has tortuous pores, and a much rougher surface morphology, and so some proportion of the forming droplet is likely to be shielded from the flow of continuous phase past it by protuberances in the surface, leading to a lower effect of increasing shear. The Ceramic membrane has a thick support material made up of large ceramic particles on top of the membrane, this acts as a shield and the forming droplets are likely to see less of the shear as they form, leading to a lower shear effect. This effect is less however, than with similar membranes in cross-flow membrane emulsification

[16], and in fact the difference between the two is small enough that it is within error bounds. This similarity in size of the droplets produced by the SPG and ceramic membranes shows that the shear force is not the only detachment mechanism that is increased with increasing rpm in rotating membrane emulsification, otherwise the difference would be greater.

It should be noted that the effect of the difference in densities of the dispersed and continuous phases is of greater consequence in the rotating membrane system. The buoyancy force of the oil dispersed phase is of little significance in the cross flow device, as the continuous phase shear force is so much larger, and the droplets are carried away into the bulk emulsion quickly once formed. In the rotating system however, a density gradient is set up by the rotation of the system, such that the more dense (in this case water) phase is thrown to the outside of the cylindrical vessel, and the least dense (in this case oil) phase remains close to the membrane. In circumstances such as this where the least dense phase is the dispersed phase, this effect is detrimental, concentrating the already formed droplets near to droplets that are still forming at the membrane. This effect, whilst not easily quantifiable, can be clearly observed during the process. This effect is lower when the flow regime is producing Taylor vortices as the mixing more evenly distributes the droplets within the mixed volume. It is, however pronounced when the flow regime is laminar. It is likely that in the highly mixed Taylor vortex regime the actual effect on droplet size in all but the most extreme density differences are negligible, as was shown with gravity effects in cross-flow emulsification at all but the lowest flow velocities[20].

3.3 Pressure effects

The effects of increasing the pressure across the membrane were investigated with respect to droplet diameter and diameter span. Emulsions were produced using 1% Tween 20 at 1% dispersed phase volume, with each membrane, at several different trans-membrane pressures. The emulsions were made using a rotation rate of 1000 rpm, and the results are shown in Figure 7.

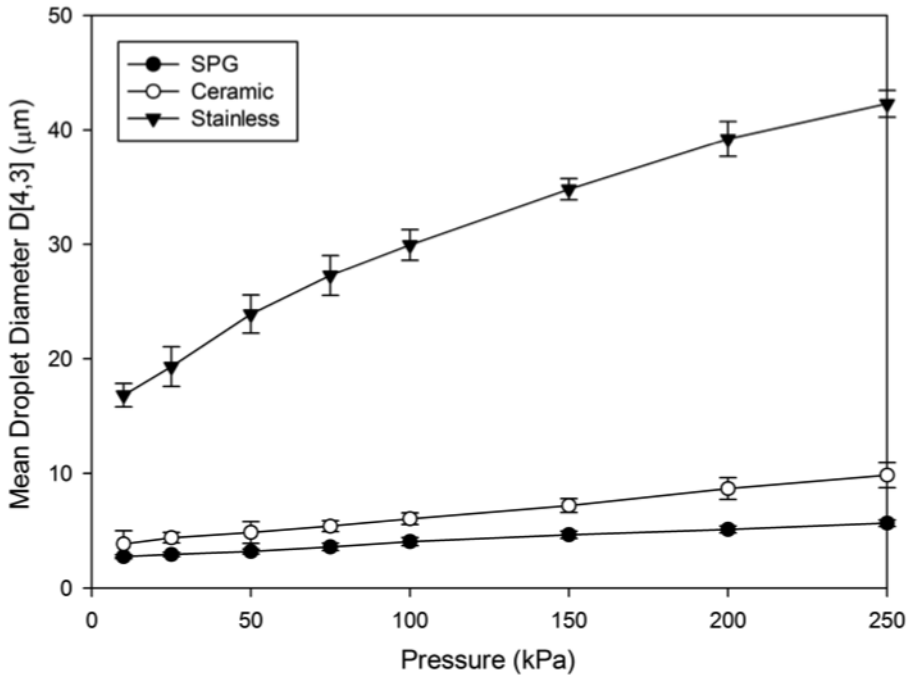

Figure 7. The effects of changing trans-membrane pressure on the droplet size of emulsions produced using the rotating membrane system at 1000 rpm, 1% tween 20 at 1% oil phase volume.

It can be seen from Figure 7 that the droplet diameter of the emulsions increases linearly with increases in pressure for the ceramic and SPG membranes. The droplet sizes produced using the stainless steel membrane initially increase quickly as pressure is increased. At higher pressures the increase in pressure causes less of an increase in droplet size. Because of the large pores of the stainless steel membrane, the critical pressure to force the dispersed phase through the pores is much less than for the other membranes, and the pressure required to force the dispersed phase through each pore as a jet is also much lower. As the pressure increases towards the jetting pressure the droplet size increases less, as droplet sizes at these pressures will be due to breakup of the jet of dispersed phase exiting the pore due to Raleigh instability, rather than detachment of a formed droplet directly from the pore.

The effects of pressure with the SPG and ceramic membrane types are comparable to those seen in cross-flow membrane emulsification[16], the sigmoidal change in droplet size with increasing pressure, which was present in the cross-flow system at high shear rates is not seen. This was not present in the cross flow system at lower shear rates, corresponding to the low shear rate at which the rotating membrane system operates.

This suggests that the dominant droplet detachment forces are pressure and interfacial tension, rather than shear.

Pressure and interfacial tension as the droplet detachment regime is supported by the size distribution, as pressure has the largest effect on the droplet size distribution, as shown in figures 8a and 8b.

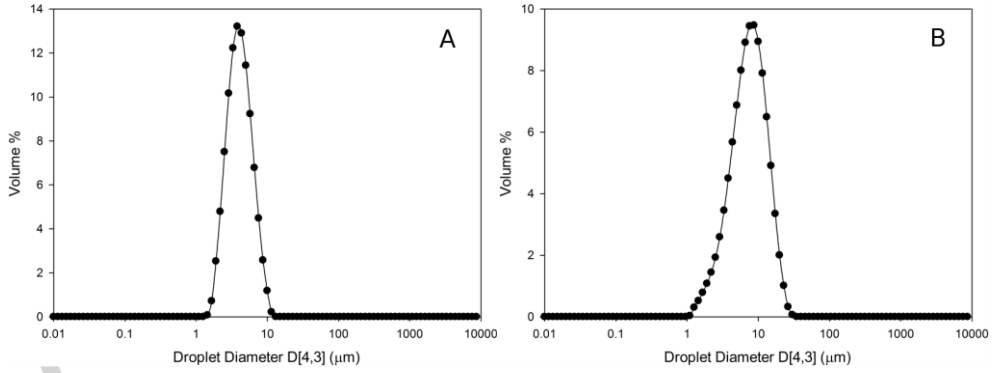

Figure 8a and 8b. A shows the droplet size distribution at 10 kPa 1000 rpm with 1% oil phase volume and 1% Tween 20 as the emulsifier with a 1μm ceramic membrane, and b shows the same emulsion produced at 200 kPa. The relative span of a is 1.13 and of b is 1.54.

As the droplet detachment regime begins to become a stream or jet regime with increased pressure, the pore size distribution becomes less important, and the breakup of the stream (due to Raleigh instabilities) determines the droplet size distribution, explaining why the relative span increases at higher pressures.

Another effect of note, which is peculiar to the rotated membrane system, is that of centrifugal force. This force due to the rotation of the fluid

inside the membrane tube adds an extra force to propel the fluid through the pores, this can be thought of as equivalent to the addition of extra trans membrane pressure. Although this effect continues through the continuous phase outside the rotating tube, the pressure drop across the membrane effectively separates the two regions, allowing the apparent increase of pressure against the inner wall of the membrane to act to force the fluid through the pores.

3.4 Phase volume effects

Increase in phase volume has little effect on droplet size, an increase from 1% wt. oil to 50% wt. oil using tween20 as the emulsifier showed an increase in droplet size from around 3µm to around 5µm when using a 1µm pore size SPG membrane. The Span of the droplet size distribution increased slightly with phase volume, probably because of the increased likelihood of collisions between droplets causing coalescence.

3.5 Viscosity effects

The relative viscosity of the two phases has an effect on rotating membrane emulsification. The viscosity of the continuous phase was changed using glucose as a viscosity modifier. As the viscosity of the continuous phase is increased, the droplet sizes produced by the system decreases. As can be seen from the graph shown in figure 9, this change is not linear, but instead the droplet size decreases more rapidly as the viscosity of the continuous phase increases past that of the dispersed phase, creating a sigmoidal trend.

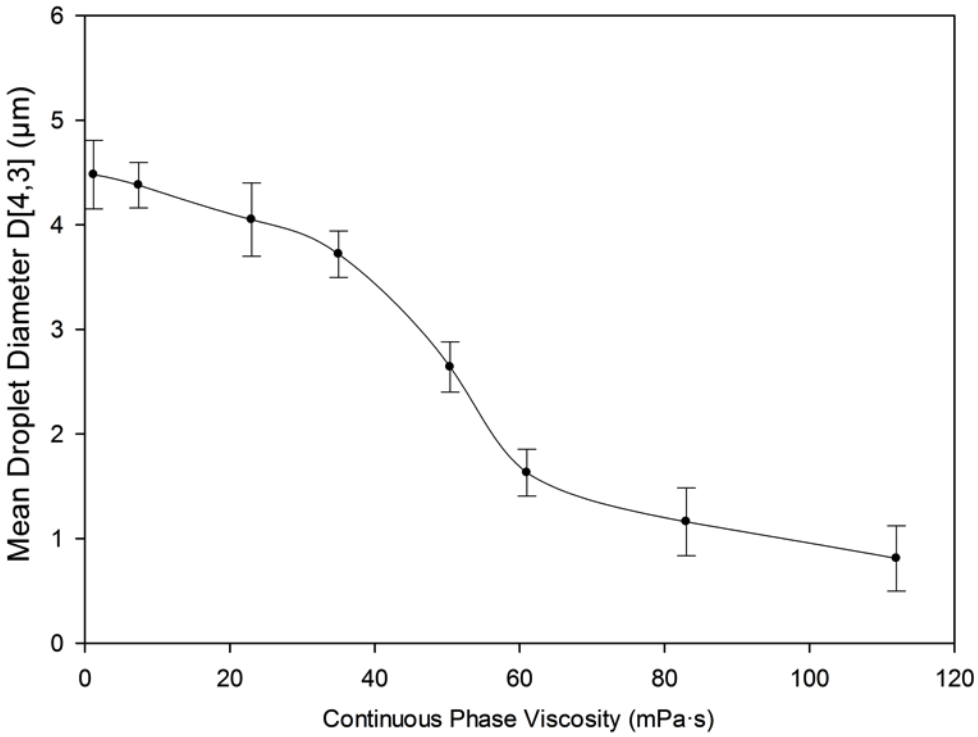

Figure 9. The effects of continuous phase viscosity changes on droplet size. The droplets were produced using a 1µm SPG membrane at 10 kPa trans-membrane pressure and 1000 rpm, at 1% dispersed phase volume and 1% tween 20 emulsifier.

This trend suggests that the dispersed phase forms larger droplets when the resistance to flow is larger than that of the continuous phase, as a less viscous continuous phase will flow around a forming droplet, whereas a continuous phase with greater viscosity than the forming droplet is more likely to break the droplet from the pore rather than flow around it. This phenomenon suggests that the potential for tailoring small changes in droplet size changes is possible in membrane emulsification, using continuous phase viscosity modifiers.

3.6 Water in oil and other emulsion types

In order to make water in oil emulsions using membrane techniques it is generally understood that the membrane should be preferentially wetted by the continuous phase[30]. The SPG membranes are available specially treated using silane surface modification for this purpose, and these have been previously shown to produce water in oil emulsions. The ceramic and stainless steel membranes are not pre-treated in this way, and for this study were used without surface treatment. Figure 10 shows the results of producing 1% water in oil emulsions with these membranes with varying concentrations of the water in oil emulsifier PGPR.

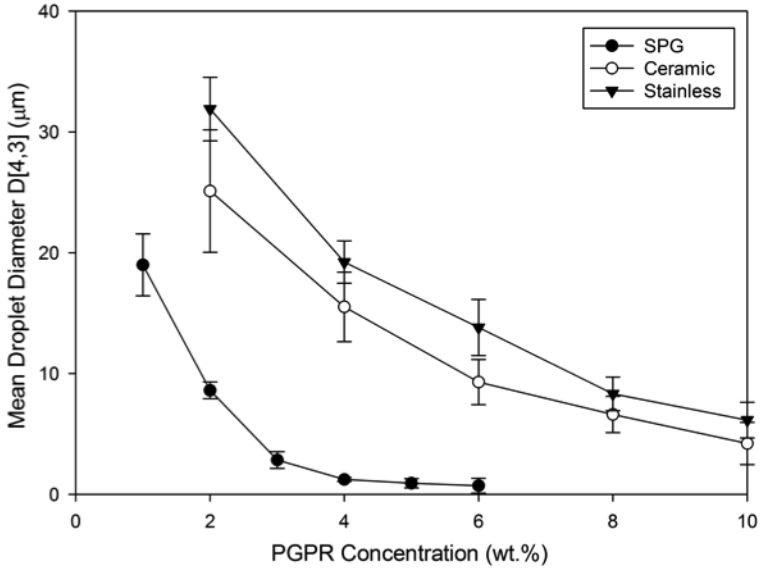

Figure 10. The effect of emulsifier concentration on the size of water in oil droplets produced using rotating membrane emulsification. The emulsions were made to 1% phase volume at 10 kPa and 1000 rpm.

As can be seen from figure 9, the SPG membrane produces droplets comparable to the oil in water emulsions, although a higher concentration of emulsifier is required to reach the smallest droplets. The untreated metal and ceramic membranes do not perform as well when producing water in oil emulsions, with the ceramic membrane producing much larger droplets than those produced for oil in water emulsions. The stainless steel membrane does produce small droplets at very high emulsifier concentrations however, achieving a minimum droplet size lower than the pore size. The small droplet size produced by the stainless steel membrane at high emulsifier concentration is due to the more efficient pore shape allowing the surface

shear to have maximum droplet detaching effect, and the wettability of the steel by the continuous oil phase. The SPG membrane is still more suitable for water in oil production since it produces much smaller droplets when hydrophobic after silane treatment.

Because of the ability to make both water in oil and oil in water emulsions at low shear rates, the rotating membrane device is capable of making double emulsions effectively, as was previously shown[31]. It is likely that rotating membrane emulsification will be able to make bead and shell structures at lower shears than cross-flow membrane emulsification as well.

4. Conclusions

Rotating membrane emulsification compares favourably in many respects to cross-flow membrane emulsification. It produces similar droplet mean diameters at much lower shear rates than the comparable cross-flow system, although at the expense of having larger droplet size distribution spans. This makes it suitable for possible applications in the food industry, where mono-disperse droplet size is less important than production rate and minimising the exposure of sensitive structures to shear (for example in flavour masking of neutraceuticals) is more relevant.

Lower droplet sizes are achieved with membrane emulsification at lower emulsifier concentrations than traditional emulsification techniques like high shear mixers, as a result of the ‘made to measure’ production of droplets rather than droplet break up. The move industrially toward ‘clean labelling’ of food products can aided by this as the amounts of added emulsifier required can be reduced or removed.

Membrane morphology has a similar effect on the emulsification process between cross-flow and rotating membrane emulsification, with the straight accurate laser drilled pores having the lowest pore size to droplet size ratio. The advantages of the straight through pores are lower backpressure and lower shear of the dispersed phase through the pore for the same resultant droplet size, however they are currently restricted to larger pores and therefore a larger minimum droplet size by manufacturing limitations.

The potential of rotating membrane emulsification to make small droplets at low shears has possibilities for producing shear sensitive structures such as double emulsions and encapsulated products. These shear sensitive products have applications in the food industry, such as reduced calorie or salt foods, without adversely affecting flavour.

6. Acknowledgements

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