CONTROLLED EMULSIFICATION USING MICROPOROUS MEMBRANES.

by

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Abstract

Emulsions are a vital part of many products in everyday use, such as foods, cosmetics, and even construction materials. Membrane emulsification is a technique which has been used to produce emulsions in a manner contrary to the traditional methods where droplets are broken and re-broken to make smaller and smaller droplets, and instead each droplet is individually formed at a pore on the surface of the membrane.

This research compared two of the most favoured membrane emulsification techniques; cross-flow and rotating membrane emulsification.

Two systems were built for producing emulsions using tubular microporous membranes, made from shirasu porous glass, polymer, ceramic and stainless steel. One device employed a cross-flow system providing shear to detach the nascent droplets from the membrane pores whilst the other system employed a rotated membrane to produce both shear and potentially centripetal force at the membrane surface. Both systems were used to create emulsions, and the effects of various settings of the systems were investigated.

A direct comparison between cross flow membrane emulsification and rotating membrane emulsification were achieved for the first time, as the same membranes were available for both systems. The modular interchangeable nature of the membranes in the systems also allowed direct comparison between the various different membrane types tested.

The distinct differences in the structure and materials of the membranes tested was compared, and its effects elucidated, as the different membrane types each showed different advantages and disadvantages when producing droplets.

It was shown that the membrane pore size is a major factor on the size of the droplets produced, and the membrane pore size distribution span affects the size distribution span of the droplets. Increasing the emulsifier concentration decreases droplet size, as does increasing the shear force applied to the forming droplets, either by increasing the cross-flow velocity or the rotation rate. Increasing the pressure applied to force the dispersed phase through the membrane increases flux rate, but also increases droplet size slightly. The relative viscosity of the two phases being emulsified has an effect on the droplet size; increasing the continuous phase viscosity decreases droplet size, and increasing dispersed phase viscosity increases droplet size. The systems performed equally well making water in oil, as oil in water emulsions.

Although the rotating membrane system produces lower shear rates than the cross-flow system, similar droplet diameters were produced, implying that detachment is enhanced by the rotation, showing a clear advantage to rotating membrane emulsification.

The systems were also used to produce various more complex particles, including double emulsions and gelled beads, and the level of control over the phases afforded by membrane emulsification was shown to be an advantage in the production of such microstructures.

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Abbreviations and Nomenclature

CFMED – Cross-Flow Membrane Emulsification Device

D_d – Mean diameter of emulsion droplet

D_m – Mean Diameter of a Membrane Pore

HLB – Hydrophile / Lipophile Balance

μ -- The dynamic viscosity of a fluid

P_c – Critical Pressure Required for Droplet Production

P_{dp} – Dispersed Phase Pressure

PGPR – Poly glycerol poly ricinoleate

P_{tm} – Trans-Membrane Pressure

Re – Reynolds Number

ρ -- Density

RMED – Rotating Membrane Emulsification Device

RPM – Rotations per Minute

SDS – Sodium Dodecyl Sulphate

Span – A measure of the size distribution of the droplets in an emulsion given by the difference between the size at 90% and 10% of the population of droplets, divided by the size at 50% of the population.

Ta – Taylor Number

V_{cf} – linear Cross-Flow Velocity

To Helen, Mum, Dad and Tam.

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Chapter 1

Introduction

An emulsion is a type of colloid (two phase system) formed from a mixture of two or more immiscible liquids such as water and oil. One forms the continuous phase of the emulsion within which the other is suspended in small droplets as a dispersed phase. Depending on which forms the dispersed phase and which forms the continuous phase it is possible to have oil in water (o/w) and water in oil (w/o) emulsions. Additionally the emulsion can form the dispersed phase and multiple emulsions can be produced for example water in oil in water emulsions (w/o/w). Emulsions are commonly found in everyday life, and can occur naturally or be man made. Items such as soaps, and cosmetics, foods such as eggs, milk and cheese, and even building materials such as bitumen contain emulsions.

1.1 Properties of Emulsions

The formation of an emulsion requires that a fluid be dispersed as droplets within a second immiscible fluid, requiring an input of energy, coupled with a reduction of the interfacial tension between the two fluids. In a traditional method of emulsion production such as a rotor/stator mixer, the energy is applied to break up the dispersed fluid by the motion of the mixing head creating a shear force within the mixed fluids, and the reduction of the surface tension between the two fluids is achieved by the addition of an emulsifier, usually into the continuous phase fluid, which adsorbs to the interface between the fluids as it is formed during dispersion by the mixer. With each successive breaking and re-breaking of the droplets to make them smaller and smaller, the energy required increases. This increase in energy is because the smaller the droplet, the more it resists deformation because of an increase in the droplets Laplace pressure. The Laplace pressure is defined as the difference in pressure across the surface of a droplet or bubble, (inside pressure - outside pressure). This pressure difference is caused by the surface tension, and can be calculated from the surface tension for a spherical droplet using the equation:

$$\Delta P = \frac{2\gamma}{R} \qquad \text{equation 1.1}$$

Where γ is the interfacial tension, R is the radius of the droplet (assuming a spherical droplet), and ΔP is the change in pressure across the interface (Laplace pressure). As can be seen from the equation, decreasing surface tension will reduce the Laplace pressure of a droplet if the size is constant.

Other factors have an effect on the deformability of droplets and their likelihood of breakup or coalescence, including the type and amount of adsorbed emulsifier at the droplet interface, and the mechanical properties that these impart to the interface, as well as relative viscosities of the phases involved.

Most emulsions are unstable when simply mixed and will separate into their component parts over time (Binks *et al.,* 1998), the least dense phase floating as a separate layer on top of the other liquid. This instability and separation of an emulsion happens due to a combination of four main processes; creaming, coalescence, flocculation and Ostwald ripening.

Creaming or sedimentation is the process by which a difference in density between the dispersed and continuous phase causes the dispersed phase droplets to either rise or sink within the continuous phase under the action of gravity. This forms a concentrated layer of emulsion particles at either the top or bottom of the continuous phase. A cream does not of itself change the size or size distribution span of the emulsion particles, and is completely reversible by gently agitating the emulsion to re-disperse the droplets (Binks *et al.,* 1998).

Coalescence however, is an irreversible process of emulsion degradation, and occurs when two physically adjacent droplets merge to form a single droplet with a larger volume. This occurs when the thin film of continuous phase between the droplets becomes so thin that it breaks, allowing the liquid contained within the two droplets to flow between them, at which point the interfacial layer will change shape to enclose the new volume with the smallest possible surface area (i.e. tend towards spherical). Coalescence combined with or resulting from creaming will eventually lead to breaking of the emulsion, which will manifest itself as a layer of just dispersed phase either on top or below the emulsion, depending on relative densities (Binks *et al.,* 1998).

Flocculation is the process of aggregation of droplets into small groups or ‘flocs’ when the droplets retain their individual size and coalescence does not occur. Flocculation may be reversible or not depending on the strength of attraction between the droplets making up a floc (Binks *et al.,* 1998).

Ostwald ripening is the thermodynamically driven process of parts of smaller droplets diffusing through the continuous phase and becoming included in larger ones because of the larger Laplace pressure inside smaller droplets. Having a smaller number of larger droplets with lower Laplace pressure is more energetically favourable. The overall effect is that the smaller droplets of a population shrink and the larger droplets grow, until the population is essentially all included in one large droplet, having the minimum possible surface area which can contain that volume of liquid, as well as the lowest possible Laplace pressure. This process means that emulsions containing many different sizes of droplet are less stable than more monodisperse emulsions because of the action of Ostwald ripening. The effect also accelerates as more large droplets are formed so the rate of ripening increases (Binks *et al.,* 1998).

The instability of emulsions is detrimental to the shelf life of many products and affects the taste and appearance of foods and the effectiveness and quality of other emulsified products. Even simple creaming whilst not actually changing the product in any way can have a detrimental effect on the perception of the product to the customer, such as changing the look of a liquid in the bottle on a shelf in a supermarket.

Emulsion droplets are considered thermodynamically unstable and require additional substances such as emulsifier or surfactant to protect droplets against these processes (De Luca and Drioli, 2006). An emulsifier or surfactant is any substance capable of slowing or stopping this separation and keeping droplets in suspension, forming a stable emulsion (the terms 'emulsifier' and 'surfactant' are used almost interchangeably, although the food and cosmetics industries tend to use emulsifier, and the petrochemical and detergent industries tend to use surfactant). Commonly used examples include: Dodecyl alcohol -10 - glycol ether (LEO–10), polyoxyethylene (20) sorbitan monolaurate (Tween20) and sodium dodecyl sulphate

(SDS). The latter being a particularly powerful oil in water emulsifier. The more an emulsifier reduces the interfacial tension and the faster this happens, allows the production of smaller droplets. Emulsifiers can also induce electrostatic or steric repulsion between droplets as well as creating a lower interfacial tension, this repulsion reduces coalescence (De Luca and Drioli, 2006).

The application of emulsifiers has many considerations which need to be made when choosing a suitable emulsifier and concentration such as the hydrophile/lipophile balance, or HLB. The HLB is the ratio of molecular weight of the hydrophilic portion of an emulsifier molecule, to the molecular weight of its lipophile region. The HLB gives a rough idea of the practical uses of an emulsifier, higher numbers (typically between 8 and 15 are good oil in water emulsifiers with the higher values giving more powerful emulsifiers, whilst lower numbers (5 or below) are usually good water in oil emulsifiers, the lower being more powerful (Binks *et al.,* 1998).

Emulsions are an expanding area of research as the creation of controlled size and shape particles to achieve specific properties is investigated. The idea that the microstructure of an emulsion can be designed specifically to enhance the designed function of the emulsion has many potential applications. Indeed the properties of double emulsions have already been used in areas such as novel treatments for cancer (Higashi and Setoguchi*,* 2000, and Nakashima *et al.,* 2000). With the interest in creating specifically designed microstructures like double emulsions, gelled beads and core shelled structures; a method of creating emulsion particles in a very controlled manner has become desirable.

1.2 History of Emulsification

Emulsions are found in many places today, both man made and naturally occurring in substances such as plant saps and milk. Historically, these natural emulsions lent themselves as the first step of producing the first man made emulsions as variations on the natural products, as they already contain natural stabilising agents, such as butter churned from milk. Emulsifiers from eggs have been used to make paints by emulsifying water based pigments into oils since the ancient Egyptians, with similar emulsified perfumes and ointments also appearing around the same time. The discovery that other immiscible liquids can be combined into stable emulsions using natural and chemically derived emulsifiers has lead to them becoming very widely used in daily life and many chemical industries, including; cosmetics (moisturisers, lipsticks etc.), food (mayonnaise, cheese, spreads etc.), pharmaceuticals and petrochemicals, and are used to great effect in industries as diverse as high grade plastics manufacturing and fuel oil fire fighting.

Emulsions have been formulated by traditional methods such as whisking and beating (small scale), and machinery such as Silverson mixers or colloid mills (rotor stator systems) and high pressure homogenizers (forcing a coarse premix of the emulsion under high pressure through a small gap causing deformation and breaking of the droplets). These methods work by breaking up droplets mechanically and mixing these into the continuous phase. The smaller the droplets of the dispersed phase the more force is required to break them up further due to an increase in Laplace pressure (Binks *et al.,* 1998).

As an example, the Silverson L4R high shear rotor-stator mixer consists of a high speed 4 vane rotor (the driven mixing part) and a stator (the fixed mixing part). The action of the rotor and stator together generates the shear, turbulence and cavitation which result in the mixing of the liquids involved. The amount of mixing or size reduction depends on the speed of the instrument as well as the viscosity, and the fluid flow characteristics of the substance being mixed. The main characteristics of rotor-stator mixers are high speed, high shear and high power. This equipment is designated as high shear because it generates a higher local energy dissipation and higher shear rate than a conventional mechanically stirred vessel. Typical shear rates can range from 20,000 to 100,000 s^{-1}. Research by the British Hydromechanics Research Group (BHRG) and the High Shear Mixing Research Program at The University of Maryland have determined that rotor-stator mixing shows that:

Only a small amount of the total power input is effective in mixing. The shaft power and power losses increase as the rotor speed increases, the flow rate becomes larger, the viscosity increases or the shear gap becomes smaller. The effect of the width of the shear gap on the power draw is weak.

Some of the substance being mixed may bypass the rotor tip and not be processed (Paul *et al.*, 2004).

The Silverson Machines rotor-stator geometry is a radial discharge impeller. The rotor is a radial impeller which rotates inside a stationary housing and is slotted. The rotor moves the fluid out of the mixer head through the slots or holes in the stator. This radial flow is accompanied by tangential shear flow produced inside the stator.

Several disadvantages arise when producing emulsions using such techniques. Firstly, there is no guarantee that the drop size produced by these machines will be even, and in practice they tend to produce a large range of sizes. This can affect the quality of the final product and make it difficult to control batch to batch reproducibility. Larger ranges of droplet sizes within an emulsion can lead to Ostwald ripening.

Mechanical methods require large inputs of energy (Charcosset *et al.,* 2004, De Luca *et al.,* 2007, Vladisavljevic *et al.,* 2006) and subject the particles in the dispersed phase to much shear and thermal stress (Charcosset *et al.,* 2004, De Luca *et al.,* 2007, Vladisavljevic and Williams*,* 2006, Schadler and Windhab*,* 2006) which may have undesirable effects on sensitive ingredients contained in the emulsion such as proteins and starches (Schroder and Schubert*,* 1999, and Charcosset *et al.,* 2004). Traditional methods of emulsification are also time consuming as many droplet breaking steps are required to produce even a roughly uniform emulsion (Schadler and Windhab*,* 2006).

The idea was suggested that it would be better to produce each droplet already at the desired size, than to try and reduce the size of pre-existing droplets down to the size range required, and that it may be possible to do that by forcing the dispersed phase liquid into the continuous phase through a microporous material, and from this the process of membrane emulsification was derived (Nakashima *et al.*, 2000).

1.3 Membrane Emulsification

Many variations of this idea have been tried and reported, in many different guises, the main ones all fall under the following categories; dead-end membrane emulsification, cross-flow membrane emulsification, sonicated or vibrating membrane emulsification, emulsification using micro-engineered devices (microfluidic devices, microsieves etc.), and rotating membrane emulsification.

Membrane emulsification has been successful in making emulsions in many different areas (Song *et al*., 2003, Katoh *et al*., 1996) and the method of droplet production well explored (Schröder *et al*., 1998 and Joscelyne and Trägårdh, 2000). Droplet detachment of the membrane surface is known to be dependant on four main forces (Schröder *et al*., 1998); shear (induced by continuous phase movement, or membrane movement), interfacial tension between to emulsified fluids, inertia/pressure from the flow through the membrane, and buoyancy (Figure 1.1).

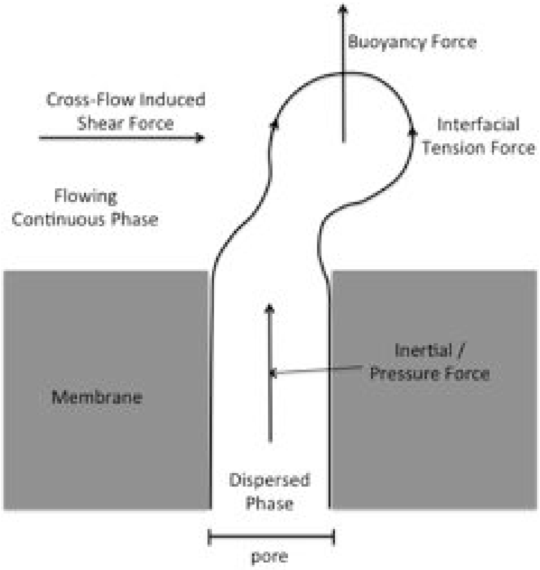


Figure 1.1 The forces acting on the droplets during membrane emulsification.

Due to the tubular shape of the membranes, the buoyancy force is in a different direction relative to the surface at any given point around the circumference of the tube, and so its effects on the overall emulsion will average out, and it is likely to be much smaller in magnitude than the other forces acting on the droplet during detachment (Peng and Williams, 1998). The interfacial tension force is reduced dynamically as emulsifier adsorbs to the interface between the two liquids, and is governed by the rate of this adsorption, and the total reduction in interfacial tension is a function of the specific emulsifier type and concentration (Schröder *et al*., 1998). The applied pressure to the dispersed phase provides the inertial force of the liquid flowing through the pore.

1.3.1 Dead-end membrane emulsification

In its simplest form this method employs applied pressure to force the dispersed phase through a porous membrane into the continuous phase as shown in Figure 1.2. Droplets form at the pore and detach when they reach a specific size relative to the size of the pore. Surfactant is added to the continuous phase to stabilize the newly formed droplets and prevent droplet coalescence. Membrane emulsification ensures not only droplet size homogeneity but depending upon the properties of the membrane chosen it is possible to precisely control droplet size. Droplets are not subjected to shear stress and the energy required to produce membrane emulsions is 10^4 - 10^6 $\mathrm{Jm^{-3}}$ in contrast to 10^6 - 10^8 $\mathrm{Jm^{-3}}$ when using the traditional process (Lambrich and Schubert, 2005).

PTFE membranes are often used for dead end emulsification. With a PTFE membrane of mean pore diameter of 1 µm, it is possible to produce an emulsion with a mean droplet diameter of 2-4 µm (Suzuki *et al.,* 1998).

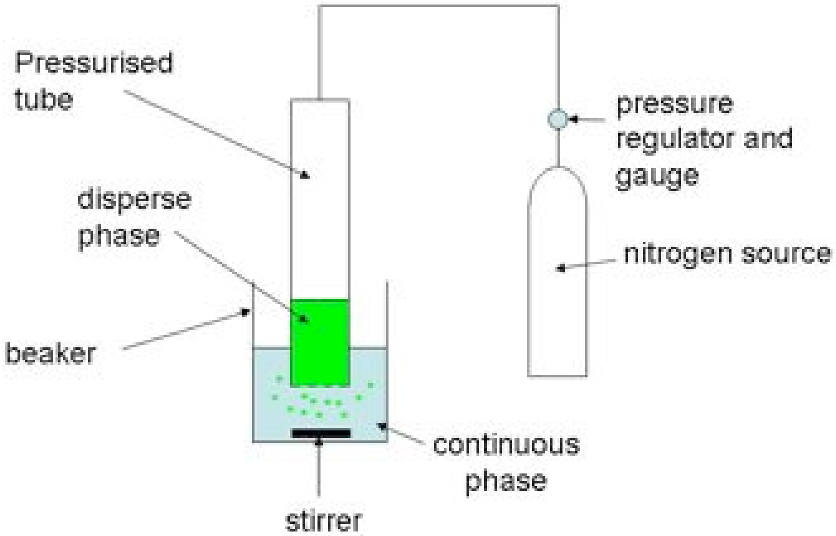


Figure 1.2: Schematic drawing of a dead end membrane emulsification process, adapted from Suzuki *et al.,* 1998.

1.3.2 Cross-Flow Membrane Emulsification

One possible solution to further controlling the droplet detachment event has been suggested using the continuous phase to provide shear by flowing it across the surface of the membrane (cross-flow membrane emulsification) (Nakashima *et al.,* 2000). Figure 1.3 shows a simple crossflow emulsification set up. This has been shown to be a viable method by several groups and has indeed been used as the production method for a ‘low fat spread’ (‘Yes Light’ Moringa Milk Industry) butter substitute in Japan (Nakashima *et al.,* 2000). Cross-flow emulsification has the advantage over dead end emulsification that the droplets are detached before becoming large enough to spontaneously detach and as such are smaller relative to the membrane pore size.

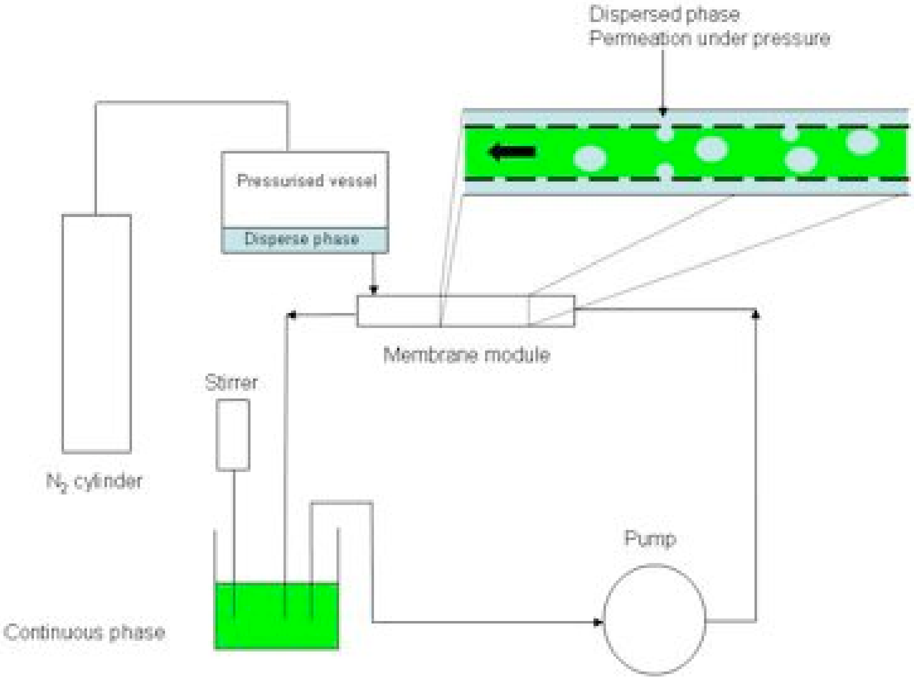


Figure 1.3: A simplified schematic of a cross-flow emulsification system, the enlargement shows the detail of the membrane module. adapted from Charcosset and Fessi, 2005.

1.3.3 Sonicated or Vibrating Membrane Emulsification

Sonicated or vibrating membrane emulsification uses vibration of the membrane (either sub sonic or ultrasonic) to detach droplets from the membrane earlier than they would naturally due to process conditions (Vladisavljević and Williams, 2005). This can be used with most if not all of the other forms of membrane emulsification and may improve the efficiency of emulsification in some circumstances.

1.3.4 Micro-Engineered Devices

Emulsification using specifically designed micro engineered devices is an area of considerable research interest, and consists of two main types of device; the microsieve, and the microfuidic device. Microsieves are essentially membranes, made with specifically shaped and spaced pores, to provide enhanced droplet shape and size control. The design of these devices varies greatly, as does their material construction, some flat sheets of silicon with etched star shaped pores (Figure 1.4), whilst others may be made of materials such as PTFE, with oblong pores (Kobayashi *et al.*, 2002), and terraces to aid droplet detachment (Lambrich and Schubert, 2005).

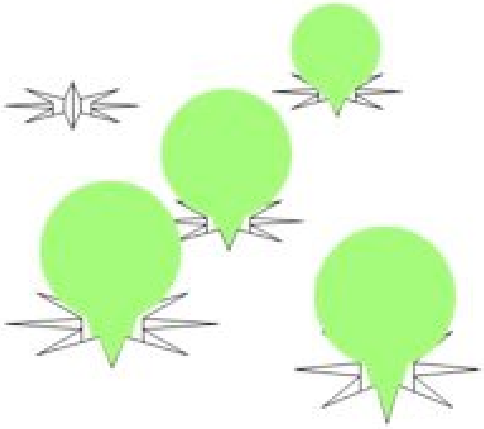


Figure 1.4. Star shaped pores are possible with microsieves, and may aid droplet detachment.

Microfluidics differ from microsieves in that the device itself has only one pore per unit, which makes droplets singly using precise flow of the two (or more) phases down carefully designed converging channels (Figure 1.5). In this way, droplets can be very finely controlled and well defined core/shell and double emulsion systems can be produced in a single step. The main problem facing the industrialisation of microchannels however is scale-up, where the process would need parallelisation to work at a viable production rate.

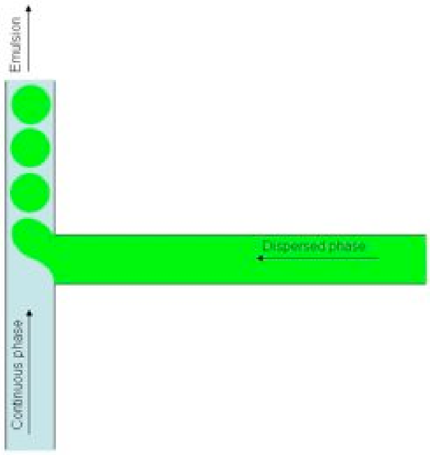


Figure 1.5. A schematic diagram of a simple T channel microfluidic emulsification device.

1.3.5 Rotating Membrane Emulsification

The idea of rotating a tubular membrane to aid droplet detachment has been suggested, and has been experimented with in the production of large droplets (~80 μm) (Vladisavljević and Williams, 2006). The theory proposes that the centrifugal force will work along with the shear at the membrane surface provided by the rotation to detach droplets more quickly than in either simple dead-end or cross-flow emulsification.

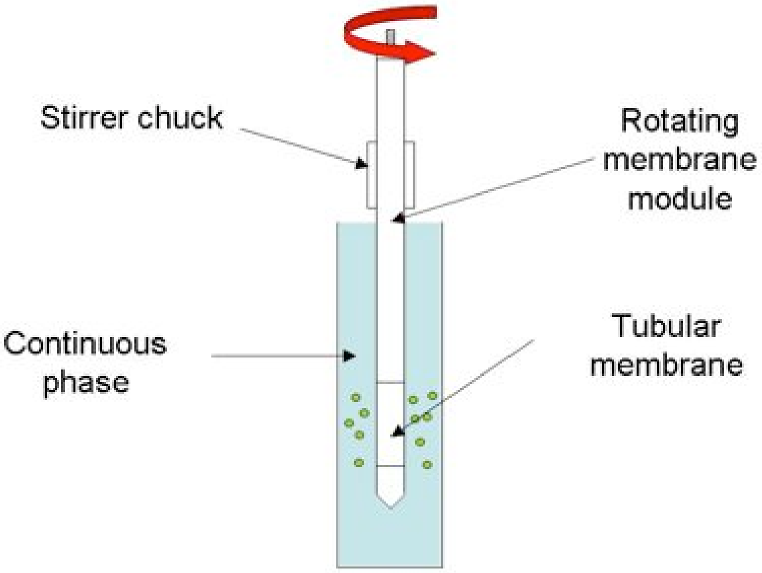


Figure 1.6. The basic principle of rotating membrane emulsification, a tubular emulsification membrane is mounted such that it can be rotated in a vessel containing the continuous phase. Adapted from Vladisavljević and Williams, 2006.

Two distinct variations of rotating membrane emulsification are possible, each with different possible uses and advantages/disadvantages. One approach is to use a small diameter tubular membrane, rotated in a cylindrical vessel 1.5 - 3 times the diameter of the membrane (Figure 1.6) (Aryanti *et al.,* 2006), the other relies on using a larger diameter membrane tube rotated inside a vessel only marginally larger than the membrane itself (Schadler and Windhab, 2006). The first approach seeks to take advantage of the centripetal force provided by the rotation to carry droplets away from the membrane as well as aiding in the detachment of droplets, but without creating a large increase in membrane surface shear, whilst the second approach seeks to create much more shear and relies less on centripetal force to carry droplets from the membrane instead employing a flow of continuous phase out of the vessel to achieve this.

The formation of Taylor vortices in the continuous phase around the membrane is more of a possibility in the smaller diameter membrane scenario, and it has yet to be determined if these would aid or hinder the performance of the process. The Taylor Number is a dimensionless number analogous to the Reynolds Number but in a rotating fluid flow. Above a critical Taylor Number specific to the individual geometry of the equipment, inertial instabilities in the fluid will manifest as Taylor Vortices. The Taylor Number is calculated as follows;

$$Ta = \omega r_1 s \frac{\rho}{\mu}\sqrt{\frac{2s}{r_1 + r_2}} \qquad \text{equation 1.2}$$

Where ω is the angular velocity of the membrane (s^{-1}), r_1 and r_2 are the radii of the membrane and the continuous phase vessel respectively (m), s is the gap size (m), μ is the continuous phase viscosity (Pa•s), and ρ is the continuous phase density (kg•m^3). Using this equation, Schadler and Windhab (2006) reported a decrease in mean droplet diameter above a Taylor number of 41. There is some suggestion that to achieve monodisperse emulsion droplets each droplet should have an equivalent 'droplet history' which would be impossible if the system functioned under a turbulent flow regime, however if the goal is less monodispersity as it is micro-structural control over the forming droplets, then the extra detachment forces produced in turbulent flow may be an advantage (Figure 1.7). In practice, the larger membrane system has a Taylor number only a fifth of that of the smaller system at a similar membrane surface angular velocity, and allows far higher velocities due to its larger circumference. It does of course also impart more shear.

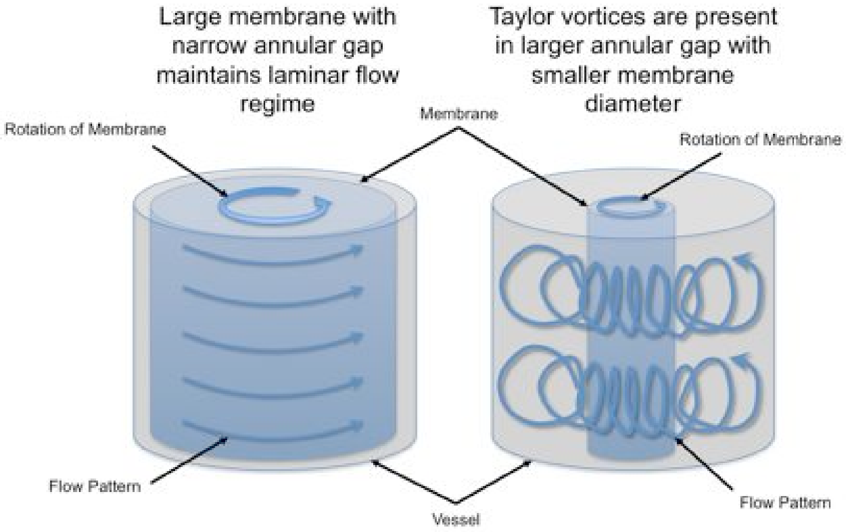


Figure 1.7 The effects of increasing membrane diameter, and decreasing the annular gap between the membrane and the wall of the containing vessel.

The effects of the gap around the membrane through which the continuous phase flows are also dependent on many other factors such as the viscosities of the continuous and dispersed phases, and the resulting viscosity of the emulsion.

With the advances made in emulsification using membrane devices, it is perhaps strange that there have been few applications of the technology up to this point. This may be because the traditional methods used for emulsification are reliable and much investment would be required to change from a working technology to a somewhat unknown new one. This change is unlikely to happen therefore without the new technology offering significant advantages. Whilst membrane emulsification does clearly offer a reduction in the size distribution span of the droplets produced, it is perfectly possible to get low size distribution spans with traditional methods. It may well be that the ultimate advantages of membrane emulsification turn out to be the ability to precisely control 'what goes where' when making microstructures such as double emulsions, along with the decrease in energy requirements (Williams *et al*., 1998).

1.4 Aims of this Research

The aims of this research were to compare rotating and cross-flow membrane emulsification. Systems were designed to use similar membranes in both cross-flow and rotating membrane emulsification. The use of different membranes, their materials and morphologies were investigated, and the effects of these on the production of droplets by the two systems were studied. The resulting emulsification systems would then be used to investigate some structures which can be made, such as gelled beads, and multiple emulsions. The various advantages and disadvantages of membrane emulsification would be explored.

During this study the aim was to try to pull together the various effects of all the factors affecting the membrane emulsification process, to try to make comparisons between the membranes, and the differences in the systems in a way which will be useful to creating systems, particularly in the food and cosmetics industry, that are lower energy and higher control than traditional emulsification methods. The literature reviewed is hard to compare since no two systems used have been similar in their goals or execution, and such a wide range of formulations and methods have been used. It was decided that two systems should be made, utilising cross-flow membrane emulsification in one and a rotating membrane in the other, and that they should as far as possible use the same membranes, and as wide a variety of membrane types as possible, since the only work reported so far involving rotating membrane emulsification was using metal membranes, finding out how other membrane types (such as SPG and ceramic) responded to rotation was important, especially since these offered the possibility on smaller pores (<1 μm). The investigation of the interactions between process parameters such as pressure and shear and the effects these have on the droplets produced was undertaken, and this data used to produce emulsions with controlled microstructures such as gel beads and double emulsions. It was particularly important to try to understand which parameters are the most important in membrane emulsification, to try to better understand and predict what droplet sizes and size ranges a given system will produce, and how a system will react when more complex structures are produced, for example when making a double emulsion will part of the encapsulated inner phase be lost into the bulk phase, and if so how much, and how can that effect be minimised.

The expectation was that the results of this study could be applied to creating emulsions specifically tailored to their intended use, whether that involves reducing the salt content of foods without affecting the taste, or producing bespoke tailored emulsions specific to the customer at point of sale, or simply making current products using lower energy. The information gained should enable the appropriate choice of membrane and system to achieve the required product production.

Chapter 2

Literature Review

2.1 The Beginnings of Membrane Emulsification

Membrane emulsification was first proposed as a technique by Tadao Nakashima in 1988 at a meeting in Japan of the Chemical Engineering Society of Japan (Nakashima *et al.,* 2000). Porous glass had been produced by Corning Glassworks in America since the 1930's (Nakashima *et al.,* 2000), as part of a manufacturing process. Leaching impurities from glass using acid to make it porous and then reheating to remove the voids left behind created a purer silica rich glass similar to quartz glass. Nakashima had recently patented (Nakashima, T. *et al.,* Inventors U.S. Pat. No. 4657875) a method of producing a porous glass with a very narrow pore size distribution span, using a naturally occurring Japanese volcanic ash called shirasu. The glass is made by phase inversion, during a thermal step in the manufacturing process allowing the precise size of the pores diameter to be tightly controlled (Nakashima, T. Inventor U.S. Pat. No. 4657875). This glass is known as Shirasu Porous Glass, or SPG. The idea that membranes made from this glass could be used to make emulsions (or that membranes could be used to make emulsions at all) was presented during the 2nd International Conference on Inorganic Membranes, Montpelier, France in 1991 (Katoh *et al.,* 1996 and Mine *et al.,* 1996). A system for producing emulsions using these micro-porous glass membranes was subsequently patented by Tadao Nakashima in 1994 (Nakashima, T. *et al.,* Inventors

U.S. Pat. No. 5326484). This system was described as being capable of manufacturing droplets ranging from 0.3 - 40 µm in diameter. The system described in the patent uses a tubular SPG membrane, mounted so that the continuous phase is recirculated through the centre of the tube, and the dispersed phase is pressed through the pores of the tube from the outside into the flowing continuous phase in a cross-flow arrangement. This patent claims to produce emulsions which are monodisperse, as defined in the terms of the patent as having a mean droplet diameter of between 0.3 and 40 µm, and having no significant numbers of droplets below 50% of the mean diameter, and with a 'coefficient of particle size dispersion - ε' of less than 0.5 as defined by:

$$\varepsilon = \left({}^{90}D_p - {}^{10}D_p\right)/{}^{50}D_p \qquad \text{equation 2.1}$$

Where ${}^{90}D_p$, ${}^{10}D_p$ and ${}^{50}D_p$ are the droplet diameters when the cumulative frequencies on a particle size distribution curve for the emulsion are 90%, 10% and 50% respectively. The patent also details procedures for producing double emulsions in this way, using a pre existing emulsion as a dispersed phase. The emulsions described in the patent are made using kerosene and water as the immiscible liquids, and with emulsifiers including SDS (Sodium Dodecyl Sulphate), Tween20 (polyoxyethylene (20) sorbitan monolaurate) and PGPR (polyglycerol polyricinoleate).

The patent points out that to achieve emulsion production, a critical pressure must be achieved across the membrane, to force the dispersed phase through the pores. An equation is given for predicting the required critical pressure, P_c (Pa):

$$P_c = 4\gamma_{ow}\cos\theta / D_m \qquad \text{equation 2.2}$$

Where γ_{ow} is the interfacial tension in (Nm^{-1}), θ is the contact angle of the dispersed phase to the membrane surface, and D_m is the mean pore diameter of the membrane. This is essentially the equation for capillary pressure. The patent also specifies that the pressure across the membrane should be 1-10 times the critical pressure (preferably 1-5 times). The pore size distribution span of each of the membranes used in the studies undertaken to support the patent, show that the pore size distribution span of the membrane has a direct correlation with the droplet size distribution span of emulsions it produces under these conditions. They also find that the diameter of the droplets produced are 3-8 times the pore diameter of the membrane used.

The patent also suggests that to make emulsions using membranes, the surface of the membrane should be wettable with the continuous phase, as membranes used for producing water in oil emulsions are described as having been pre-treated by a process of coating in silanes, to make them hydrophobic and therefore wetted by the oil phase.

Membrane emulsification using SPG was further pursued in Japan, where it's potential for making food emulsions was now under investigation. The Morinaga Milk Industry Food Research and Development Laboratory had started to look at using membrane emulsification based on the work of Nakashima *et al*. (1991) to make food emulsions (Katoh *et al.,* 1996). The focus of the research was on increasing a low trans-membrane flux of the dispersed phase, to make the process useful for industrial application. The study found that adding an additional emulsifier to the dispersed phase enabled an increase in trans-membrane flux by up to ten times when making oil in water emulsions. For water in oil however, it was found that pre soaking of a hydrophilic membrane in the oil continuous phase prior to emulsification allowed a 100 fold increase in trans-membrane flux over simply using a hydrophobically treated membrane. Katoh *et al.* (1996) also reported success in producing a low fat (25% wt.) spread made without preservatives. Their results showed that during the production of emulsions the diameter of the droplets produced depended solely on the diameter of the pores of the membrane, and the results shown suggest that even changing the oil from corn oil to kerosene made very little difference to droplet diameter, which was always about five times larger than the pore diameter. In their study, Katoh *et al.* (1996) found that changing the parameters of the process such as the dispersed phase volume were shown to have had little or no effect on the resultant droplet diameter, although since the system used relied on cross-flow the results showed that to make droplets at the minimum diameter and size distribution span for any given membrane there needs to be a minimum flow rate to the cross-flowing continuous phase. Pressure also was shown to have little effect on droplet size, only increasing the droplet size when drastically increased; instead pressure is shown to have had more of an effect on trans-membrane flux, which was shown to increase steadily with increasing pressure.

The finding that the emulsion particle diameter was highly dependant on the membrane pore diameter, and therefore the size distribution span of particles closely followed the size distribution span of the pores in the membrane, was further stated a year later when in 1996 Mine *et al*. published results from an experiment using membranes to make emulsions stabilised by egg yolk phospholipids. Their study however showed a relationship of pore diameter to droplet diameter of 3.18 as found in their results. The results from the experiments reported an increase in stability of emulsions made (both simple and double emulsions) using membrane emulsification, which is attributed to the small size distribution span when compared to traditional droplet breakup techniques for emulsification. Mine *et al*. (1996) also mentioned the need for the membrane to be wetted by the disperse phase as previously stated by Nakashima *et al.* (1991), and suggested that for double emulsions the pore diameter of the membrane used to make the double emulsion should be at least twice the diameter of the dispersed droplets of the primary emulsion, so as to avoid either breaking the droplets as they pass through the membrane or simply filtering them out and making only a simple emulsion.

2.2 Silicon Wafer Membranes

Meanwhile, in the Netherlands, research into silicon wafer membranes had been undertaken. Initially with a goal of increasing filtration and particle separation performance, the silicon microsieve had been developed (Van Rijn and Elwenspoek, 1995). The microsieve was made by micromachining using a combination of Chemical Vapour Deposition (CVD) and reactive ion etching, creating a thin film layer containing the pores, and a stronger support layer with larger openings. At this point, the major applications of this technology were thought to be in blood separation, and other biomedical separation techniques.

The manufacture of silicon microsieves was further refined, and in 1998 results were published (Kuiper *et al.,* 1998) of their manufacture and testing for filtration of yeast from beer. The results shown were promising, offering 40 times higher flux at lower fouling rates than traditional filtration techniques currently in use. There was still no mention in this study for the potential of the sieves for use in membrane emulsification however.

2.3 Increase in Interest

During the final years of the twentieth century, there was an increase in interest in the emerging technique of membrane emulsification. As society continued to move towards a more health conscious more socially responsible lifestyle, trends towards lower fat products, and lower energy production techniques started to become more desirable, and using more natural and less chemical ingredients without compromising perceived taste and quality (and shelf life) became the focus of much research. Membrane emulsification appeared to be a viable solution to achieving some of these goals. In 1998 a paper was published by researchers at the University of Exeter (Peng and Williams, 1998) which started to bring together the ideas and research done so far with membrane emulsification and started to elaborate on the possible mechanisms behind the experimental findings of previous studies.

The study from Exeter was published in two sections, the first concentrating on the way droplets are formed and detached from a single pore, and the second on how membrane emulsification techniques may be applied to industrial manufacture.

The first section of the study, part I, is based on studies via high speed video imaging, of a single pore made from a glass capillary tube, cast in an epoxy resin block. This block is set such that the surface can be overflowed by a continuous phase, whilst a dispersed phase is pressed through the capillary tube into the flow. To test this system, emulsions were produced using an analogue of a cosmetics formulation using water, triethanolamine and preservatives as the continuous phase, and with mineral oil and isosteric acid as the dispersed phase. This section of the study also looks at the forces acting on the droplets as they form, and suggests relationships between the various parameters of the experiments, and the final droplet size, as well as dependent factors such as dispersed phase flux. Peng and Williams (1998) used a similar method of calculating the critical droplet formation pressure as proposed by Nakashima (stated earlier in section 2.1), and goes slightly further when stating the relationship between pore diameter and final droplet diameter, by stating that there is a constant multiplier between the two depending on the process conditions, of somewhere between 2.5 and 8, so the average droplet diameter is 2.5 to 8 times larger than the average pore diameter depending on conditions. Peng and Williams (1998) also state that the size dispersity (size distribution span) of the emulsion droplets depends 'most critically' on that of the pores of the membrane being used.

The results from Peng and Williams (1998) show that the droplets final size is affected by two stages; the growth of the droplet at the pore, and the detachment of the droplet from the pore. The authors suggest how both stages are dependant on the forces applied to the droplet, in a simplified form by examining the four forces thought to be the most critical; drag imposed by the continuous phase cross-flow, interfacial tension between the two phases, buoyancy of the dispersed phase and inertia of the flow of dispersed phase through the pore, as described in figure 1 in the previous chapter. Equations are given relating the forces to the droplet sizes and flow rates, as predictions of the experimental data. The predictions made from these equations are shown to agree with the results, although less agreement is reported as cross-flow is increased. Peng and Williams (1998) reported that pore size and cross-flow velocity were the key factors in determining the droplet size, and that the trans-membrane pressure had a limited effect. Nevertheless, the authors report that the formation of droplets under the conditions tested is predictable and controllable, and that the results show that the design of an industrial process is possible.

The second part of the study, part II (Williams *et al.,* 1998), reports data from an experimental investigation of cross-flow membrane emulsification on a pilot plant scale. For these experiments, the authors used ceramic membranes, made up of a porous ceramic substrate, and one or more thin coatings of a micro porous ceramic. These thin layers are made up of very finely controlled particles of known size, creating consistent gaps (pores) between them when tessellated. The same analogue of a cosmetics formulation was used.

Williams *et al.* (1998) suggest a maximum porosity allowable based on the droplet diameter to pore diameter ratio produced so as to avoid contact between adjacent droplets as they form, based on an equation relating the distance between two adjacent pores and their diameter, this however does assume an ideal membrane with equal pore spacing, and that all pores will be active, in practice these conditions are unlikely to occur.

The findings regarding pressure are that to keep a narrow droplet size range a trans-membrane pressure of between 2 and 10 times higher than the critical pressure is generally considered practical but the highest possible pressure should be used to achieve the highest flux, and this pressure was not possible to predict but could only be found experimentally for each membrane. If the highest usable pressure is exceeded, the dispersed phase will be forced from the pores as a jet, and form much larger droplets of high size distribution span. The major factor affecting droplet diameter was the membrane pore diameter, however it was found that this could be 'tuned' by adjusting the cross-flow velocity of the continuous phase, speeding it up reducing the diameter of the droplets produced slightly.

Williams *et al.* (1998) also reported results from a semi-continuous method of producing a simple emulsion, and showed that using this method the emulsion could be produced without changing the average droplet diameter or the size distribution span. The power requirements of membrane emulsification in this form were compared favourably with those of a typical rotor stator system and with a high pressure homogenisation system. The idea that pre-mixing the emulsion may increase the flux rate of dispersed phase through the membrane was also suggested.

The reproducibility of the membrane emulsification technique was emphasised, along with the control over the product, and it was suggested that scale up should not be a problem for membrane emulsification, because the system could be parallelised, with each parallel module essentially being similar to the pilot scale device described in the experiments.

At a similar time, ceramic membranes were also being tested by researchers at the University of Karlsruhe, in Germany (Schröder *et al.,* 1998). The membranes used in this study were also tubular, but were originally intended as microfiltration membranes, and were made by Membraflow, Germany. A similar cross-flow technique was employed to that of the Exeter researchers, with the dispersed phase being pressed through the membrane into the flowing continuous phase. This study however, used vegetable oil as the dispersed phase, and de-ionised water as the continuous, with a variety of different emulsifiers. This formulation more closely resembled the food type emulsions which had been produced using SPG membranes in previous studies. The results differ from previous studies in that a single membrane was shown to be able to produce a large range of droplet diameters, from the same pore diameter. By changing the emulsifier, a diameter size range of 0.8 to 8 μm was shown from a 0.2 μm pore diameter membrane. The effect of increasing the trans-membrane pressure was also observed as a greater increase in droplet diameter than previously reported, with droplet diameters observed almost doubling due to pressure increases in some cases. Pressure was still shown to have a larger effect on the trans-membrane flux than it did on droplet size; however the increase in droplet size was not insignificant as observed in previous studies. The study also reported that the speed with which emulsifiers reduced the interfacial tension during droplet formation was very important to the membrane emulsification process; the emulsifiers adsorbing quickly to the interface as the droplets were formed allowed the retaining forces to be reduced sooner causing earlier droplet detachment from the membrane surface, and therefore resulting in smaller droplets. Coalescence was found to occur during the formation of most droplets whilst still at the membrane surface, except when extremely fast adsorbing emulsifiers were used. Some interpretations of the forces acting on droplets during formation and detachment from the membrane were given, similar to those proposed from previous studies, essentially with the same four major forces. The study concentrated mainly on the effect of dynamic interfacial tension when different emulsifiers were used. The effects of increasing trans-membrane pressure are shown to be small on the droplet size produced, but increase the trans membrane flux of the dispersed phase according to Darcy's law, with the flux increasing with pressure at a constant slope, but only when the trans-membrane pressure is sufficient to activate all pores. Below this pressure flux increase is not constant as the effective membrane area also increases as pressure is increased and new pores become active. Schröder *et al.* (1998) concluded that the speed with which the emulsifier is adsorbed to the interface is the most important factor in its choice, leading to smaller droplets, and that the trans-membrane pressure has little effect on droplet size so long as the adsorption speed is sufficiently fast that the droplets formation takes longer than adsorption at the surface.

In Sweden, in 1998, research was being undertaken into the production of small droplets of vegetable oil, dispersed into a continuous phase of skimmed milk (Joscelyne and Trägårdh, 1999). The idea that the droplets should be small was simply to reduce instability in the resultant emulsion. To make these emulsions, a tubular ceramic membrane was tested, with various pore sizes, emulsifiers and wall shear stresses, which were related to the cross flow velocity. As with all the previous studies using tubular membranes, the dispersed phase was pressurised into the tube from outside, into the flowing continuous phase. The study concluded that the system could be used to produce small droplets at relatively high flux rates (>100 kg m^{-2} h^{-1}) and the smallest droplets are produced at higher wall shear stresses and emulsifier concentrations.

In Karlsruhe, Schröder and Schubert had looked again at membrane emulsification (Schröder and Schubert, 1999) and this time expanded their conclusions to include the effects of trans-membrane pressure, which they now conclude increases mean droplet size as it is increased, and wall shear stress (as applied by increasing velocity of the continuous phase flow) which reduces droplet size.

By this point the factors affecting the droplet size and size distribution span of emulsions created using membrane emulsification were becoming established, and several different membrane types, shapes and configurations had been tried; however there was still some confusion about the relative importance of the factors, where previously the pore size had been thought to be the only relevant factor (Katoh *et al.,* 1996) the cross flow velocity (Peng and Williams, 1998) and emulsifiers had since proved to be important (Schröder *et al.,* 1998).

Most research agreed that the size of the pores was a very significant factor when it came to the droplets produced (Nakashima *et al.,* 2000, Joscelyne and Trägårdh, 2000), however the results were contradictory, with some studies finding that the droplets produced by a particular sized membrane pore were constant irrespective of changing factors such as the oil used as the dispersed phase (Katoh *et al.,* 1996). Other studies report varying degrees of change when changing other factors (Williams *et al*., 1998). Ultimately the other factors reportedly affecting droplet production are numerous, including; the size, shape and size distribution span of membrane pores, the trans-membrane pressure, the wall shear stress across the membrane surface (as produced by flowing continuous phase, rotation of the membrane etc.), the concentration and type of emulsifiers used, the viscosity of the liquids being emulsified, the phase volume of dispersed and continuous phases etc. Because of this there is no simple way (as yet) to say exactly what size droplets a given membrane and emulsification system will produce without experimental testing.

The idea that narrower pore size distribution spans would produce narrower droplet size distribution spans however, meant that the silicon wafer microsieves being produced in the Netherlands by 2004 (Gijbertsen-Abrahamse *et al.,* 2004) were looking particularly appealing for the production of near monodisperse emulsions. Not only were the pores able to be made to much smaller size tolerances than the glass or ceramic membranes, but also the shape could be individually designed to aid the developing droplets to detach at the correct size, and the optimum separation of pores could be achieved because the placement of the pores on the silicon wafer was by design rather than the random nature of the previous membrane types. The silicon microsieves do have some disadvantages however, they are very expensive to produce, and very fragile, and also much harder to make in large surface areas than the other membrane types previously tested. Nevertheless the silicon membranes were shown to make very narrow size distribution span emulsion droplets. This again makes them more suitable for high value products, rather than for mass produced goods.

Similarly in the quest for monodispersity, silicon had been used to create microchannel devices, along with glass and some other materials (Sugiura *et al.,* 2000). These devices are essentially tiny single pores, with various geometries, and each droplet is produced by the single pore of the microchannel (Lambrich and Schubert, 2005). The simplest geometry used is the 'T' channel microchannel, where the dispersed phase is introduced into a channel of flowing continuous phase via a perpendicular side channel. These devices can be made much more complicated in an effort to further reduce size distribution span of the droplets produced, or to make more complicated emulsions, such as double emulsions or even emulsions containing two different inner dispersed phases (Nisisako and Hatsuzawa, 2010). Microchannels are generally either single pores per module or very small numbers of pores, and so suffer from similar problems to the microsieves, in that they are harder to scale up to industrial levels, whilst exhibiting the best control over the size and size distribution span of any emulsification system they are currently only really useful for creating very small amounts of very high value products, such as spacer beads for liquid crystal display technology, or packing beads for high pressure liquid chromatography columns, where very narrow size distribution span is critical. Scale up of these low production rate techniques would require very precise flow and pressure control and many parallelised modules working in unison, and the relative costs are much higher than using a much simpler membrane emulsification system, so the exact requirements of the application will determine which is more suitable.

2.4 Recent Developments in Membrane Emulsification

The process of membrane emulsification has evolved with the introduction of rotating metal membranes, and the continued increase in the understanding of the factors affecting the size and size distribution span of droplets being produced.

2.5 Factors affecting droplet size

The membrane pore diameter has been shown to be proportional to the diameter of the droplets produced in all studies that investigated the effects of pore size (Katoh *et al*., 1996, Peng and Williams, 1998, Schröder *et al.,* 1998). They do disagree however on the multiplication factor between the two, with values ranging between 2 and 20 depending on the experimental setup. It seems that selecting the correct membrane pore dameter is the first consideration when choosing a membrane for a specific application. Pore size also has effect on the other parameters of membrane emulsification, like the critical pressure for emulsion formation and the flux rate.

The emulsifier choice is also clearly very significant, with most studies showing large variations in droplet size with varying types and concentrations. These choices will also be limited by intended use, for example if the product is required to be food grade. It was shown (Schröder *et al.,* 1998) that the speed with which the emulsifier reduces the interfacial tension, as well as the amount that it is reduced, is very important. The emulsifier also has effects on other parameters, like the critical pressure for emulsification and the flux rate.

Many different formulations have been used to study membrane emulsification, and many different sizes of droplets have been produced from several different membrane types. The range of different experimental setups is one reason that the available literature varies so much, with the droplets produced by different studies from similar membranes varying by large amounts. This implies that there are many other factors affecting the performance of membrane emulsification. The formulation has a profound effect on the emulsion being produced, although the precise effects of factors like viscosity vary between studies (Katoh et al., 1996, Peng and Williams, 1998).

The pressure applied to push the dispersed phase through the pores of the membrane is a factor, although different studies give different significance to the effect of pressure on droplet size, the consensus is that the pressure seems to have a larger effect on the flux of the dispersed phase through the membrane than on anything else. As such several of the studies reported, make the suggestion that the way to optimise performance is to run at the highest feasible pressure below injection regime, to maximise flux (Peng and Williams, 1998, Schröder *et al.,* 1998).

For membrane emulsification systems employing the flow of continuous phase over the membrane surface and the shear force this creates as a method of detaching droplets from the membrane, this flow has a large effect on the size of the droplets produced. All studies having tested this effect report increasing the cross-flow velocity decreases the droplet size, but with varying rates, and within limits. Changing this velocity affects the regime of flow of the continuous phase as it passes over the membrane, as well as changing the shear force applied to the droplets. Increasing the flow of continuous phase will increase the pressure on the continuous side of the membrane, which will in turn require and increase in the pressure applied to the dispersed phase will need to be increased so as to keep the trans membrane pressure constant.

Similarly systems employing other ways of applying shear to the membrane, such as rotating the membrane, cause changes to the droplet sizes and size distribution spans.

The effects of viscosity of the phases has not really been studied to any degree, and studies that have used different viscosities have reported very different effects, from no change in the emulsion at all (Katoh *et al.,* 1996), to small changes in the size of the droplets, and changes in the disperse phase viscosity will obviously change the critical pressure required for emulsification, and will need changes to be made to the applied pressure.

Any emulsion is affected by changes in the relative phase volumes, and membrane emulsification is no different. As the volume of the dispersed phase increases studies generally found an increase in the average droplet size and a corresponding increase in the droplets size distribution span. Higher phase volumes will eventually lead to phase inversion as the emulsion becomes more thermodynamically stable with the original dispersed phase as continuous, which is unavoidable. Several suggestions are made for the causes and some possible solutions to minimise this effect. The main cause is generally thought to be coalescence of droplets increasing as phase volume increases, because of the higher chance of collisions between droplets whilst forming. There is also some suggestion that the porosity of the membrane being too high or not evenly distributed across the membrane surface may cause the collision and merging of droplets whilst still at the membrane pores, and that this effect can be minimised either by using faster adsorbing emulsifiers (Schröder *et al.,* 1998) or by using micro-engineered membranes with set pore distances (Gijsbertsen-Abrahamse *et al.,* 2004). The effect of increasing dispersed phase volume does have other effects which must be taken into account, such as the increase in viscosity for instance in an oil in water emulsion.

The research reviewed so far has all been based on direct membrane emulsification, however it is also worth mentioning that the idea of pre-mixed membrane emulsification has also been studied, where instead of passing only the dispersed phase through the membrane the entire pre-mixed (either by previous step of membrane emulsification or by traditional methods) emulsion is passed through a narrow pore sized distribution membrane to effectively even out the droplet sizes further, and there is some evidence that repeated passes further decrease the droplet size distribution span (Vladisavljevic *et al.,* 2004).

2.6 Factors of Experimental Setup

The original concept of membrane emulsification used a cross-flow setup to produce emulsions, and many experiments are still conducted using similar systems.

Cross flow membrane emulsification has been shown to be viable in producing oil in water emulsions, but by modifying the membrane surface to make it wettable by oil, it has been shown that the production of relatively monodisperse water in oil emulsions is also possible (Cheng *et al.,* 2006). The production of double emulsions, solid particles and other particles has been shown to be possible in many studies (Vladisavlevic and Williams, 2005).

The concept of moving the membrane instead of flowing the continuous phase to cause detachment of newly formed droplets from the membrane surface was investigated by two separate research groups, one in Zurich, Switzerland, at the ETH Zentrum Laboratory of Food Process Engineering, lead by Professor Erich Windhab, and the other from Leeds, at the Institute of Particle Science and Engineering at the University of Leeds, lead by Professor Richard Williams. The two systems have similarities; they both use micro-engineered metal membranes, of tubular form rotated in continuous phase. This differs from the cross-flow studies reported previously, in that the dispersed phase is pressed from the outside in, in the cross-flow studies, and from the inside out for rotating membrane emulsification. The two groups have used vastly different sizes of tube and rotational speeds, resulting in very different shear rates. The metal used and its construction is also very different, along with the pore size, with Professor Windhab’s group using a 100 mm diameter membrane tube with pore diameters between 1 and 5 µm (Schadler and Windhab, 2006) and Professor Williams’ group using 10mm diameter membrane tube, with 100-150 µm pore diameter (Aryanti *et al.,* 2006).

The goal of the research of Professor Williams’ group was to create droplets of around 80 µm diameter, having low polydispersity, using low shear production and high repeatability. The membrane itself was made of stainless steel tube, with holes laser drilled through the tube in a skewed grid pattern. This membrane emulsification device was shown to produce relatively monodisperse emulsions in the target size range, and was patented (UK patent number WO0145830, 2001). The skewed grid pattern was so that adjacent pores would not produce droplets at the same height up the membrane surface, which would therefore decrease the likelihood of collisions and so coalescence. The smaller tube reduced the surface velocity at any given rpm over that of a larger diameter tube, and so reduced shear.

The larger membrane of Professor Windhab's group was made in the Netherlands using a new bespoke technique, by Stork Veco B.V. The aim of the research with the larger membrane was to produce small monodisperse droplets, by ensuring that the 'droplet history' of each droplet was as close to the same as possible. The membrane used was an etched nickel foil sheet, the etching providing equally spaced round pores of around 5 μm in diameter, which could be further reduced in diameter as required to around 1 μm using Plasma Enhanced Chemical Vapour Deposition (PECVD), a process similar to the one used to gold coat samples for electron microscopy. Again this study reports success in producing monodisperse droplets. The larger diameter membrane rotated at high speed in a narrow annular gap was designed specifically to create a high shear rate at the membrane surface, whilst keeping the shear rate even and equal at each pore. The narrow annular gap decreases the formation of Taylor vortex flow regime around the rotating cylinder, and instead keeps the flow regime fully laminar. With an even smaller gap of just 0.5 mm the flow regime stays laminar up to (above if the equipment would allow) 8000 rpm. The larger annular gap of 1 mm allowed the transition to Taylor vortex flow at around 4500 rpm (at a critical Taylor number of ~41), which was observed as a decrease in produced droplet size.

Some discussion is made in the literature about the effects of flow regimes on membrane emulsification (Williams *et al*., 1998). With cross-flow membrane emulsification, the flow of the continuous phase along the wall of the membrane is used to detach the forming droplets of dispersed phase from the membrane surface, as a shear force. The shear rate applied by this flow depends on the regime of the flow, and is different if the flow is turbulent or laminar. In a laminar flow regime the force applied at the membrane surface would be constant and similar across the entire surface of the membrane, whereas in a turbulent flow regime the shear rate would be changeable and different across the surface at different times and at different points. This will no doubt affect the size and size distribution span of the droplets being detached. Whilst there is no direct investigation of these effects there is general consensus that the existence of turbulent flow during membrane emulsification will detract from the production of monodisperse droplets, and tend to broaden the size distribution span, although the increased shear will tend to decrease the mean droplet size (Yuan *et al.,* 2009).

The regime of flow of the dispersed phase through the pores has also been mentioned, in terms of the method of droplet detachment or breakup. Under low pressure and shear, the droplets may simply grow to the maximum size supported by the pore, and detach under the effects of buoyancy and surface tension. With an increase in shear they break off sooner, and are therefore smaller. Increasing pressure causes droplets to break off under the influence of the inertia of the liquid flowing from the pore, and in extreme circumstances the pressure can cause a stream to issue from each pore which then breaks up due to Raleigh instability. These different methods of droplet detachment all lead to changes in the droplet size and size distribution span.

Since the use of micro-engineered membranes, the effects of varying the pore geometry away from random or round have been understood to cause a reduction of the shear force required to detach the forming droplet from the pores (Kobayashi *et al.,* 2002, Kobayashi and Nakajima *et al.*, 2002) Various other shapes have been used in dead end, cross-flow and vibrating membrane emulsification devices showing that the detachment force is less. Under certain circumstances, the geometry itself aids detachment. Rectangular pores were shown to cause detachment of the forming droplets at a specific size and therefore aid in the production of more monodisperse emulsions (Kobayashi and Nakajima *et al.*, 2002). This idea has recently been tested using a square or slotted pore shape on a rotating membrane emulsification system (Yuan *et al.,* 2009). Whilst the droplets produced by the rectangular and square pores are more monodisperse than the equivalent round pores, the droplets produced are considerably larger, and so the pores must be made much smaller to compensate. The results show an increase in trans-membrane flux with the slotted or square pores with rotating membrane emulsification; however this may be negligible when the pores are made smaller to compensate for the increased droplet sizes produced.

It seems that the idea of membrane emulsification has many ways in which it can be utilised with different systems and products having been tested, and the most effective way clearly depends on the application to which it is being put.

This study aims to advance the current knowledge of membrane emulsification by comparing the morphologies and materials of several different membranes, and how the geometry of the membrane emulsification system affects the performance and droplet production.

Chapter 3

Materials and Methods

3.1 Chemical Components

All chemicals were obtained from Sigma Aldrich Company Ltd, Dorset, UK, with the exception of the PGPR which was supplied by Danisco A/S, Denmark and the Sunflower Oil which was obtained from a local supermarket. The same brand and type of oil was used for all tests.

3.1.1 Emulsions

All emulsions were prepared using Milli Q water and Sunflower Oil.

3.1.2 Emulsifiers

Emulsifiers used in this study fall into two main categories, those used for oil in water (o/w) emulsions, and those used for water in oil emulsions (w/o).

3.1.2.1 Oil in Water (O/W) Emulsifiers

3.1.2.1.1 Tween20 (Polyoxyethylene (20) sorbitan monolaurate)

Tween20 (Polyoxyethylene (20) sorbitan monolaurate) (E432) is a non ionic emulsifier with the molecular formula $C_{58}H_{114}O_{26}$ and a molecular mass of 1227.54 $gmol^{-1}$. It is a clear yellow viscous liquid with a density of 1100 kgm^{-3}. Tween20 is regarded as having a high level of stability and a low level of toxicity and as such is widely used in the preparation of emulsions and as a detergent. The HLB of Tween20 is 16.9.

Concentrations of Tween20 were used of between 0.01 and 2 % by weight in the dispersed phase.

3.1.2.1.2 Tween80 (Polyoxyethylene (20) sorbitan monooleate)

Tween80 (Polyoxyethylene (80) sorbitan monooleate) (E433) is a non ionic emulsifier with the molecular formula $C_{64}H_{124}O_{26}$ and a molecular mass of 1310 $gmol^{-1}$. It is a clear yellow viscous liquid with a density of 1060 – 1090 kgm^{-3}. Tween80 is regarded as having a high level of stability and a low level of toxicity and as such is widely used in the preparation of emulsions for medicinal and food uses, often being an ingredient in ice creams. The HLB of Tween80 is 14.9

Concentrations of Tween80 were used between 0.01 and 2 % by weight in the dispersed phase.

3.1.2.1.3 SDS (Sodium Dodecyl Sulphate)

SDS (Sodium dodecyl sulphate) is an anionic emulsifier with the molecular formula $NaC_{12}H_{25}SO_4$, a molecular mass of 288.38 $gmol^{-1}$ and a density of 1010 kgm^{-3}. SDS was used at concentrations of 0.01 to 2 % by weight in the dispersed phase. SDS has an HLB value of 40.

3.1.2.1.4 Soy Lecithin

Soy lecithin has been classified as non toxic and is widely used in the preparation of foods. Soy lecithin was used at concentrations of up to 8 % by weight in the dispersed phase. The soy lecithin used had a HLB of 8.

3.1.2.1.5 Sodium Caseinate

Sodium caseinate is a naturally occurring type of protein extracted from milk. Sodium caseinate is widely in the food industry for thickening, stabilisation, gelling and emulsification. Supplied as a powder, sodium caseinate was used in concentrations up to 2 % by weight in the dispersed phase. The HLB of the sodium caseinate used was around 14.

3.1.2.1.6 WPI (Whey Protein Isolate)

WPI (whey protein isolate) is a combination of globular proteins isolated from the whey that is formed during the manufacture of cheese from cow's milk. The main proteins found in the whey include beta-lactoglobulin, alpha-lactalbumin, bovine serum albumin and immunoglobulins. Whey protein isolate was used in concentrations of up to 2 % by weight in the dispersed phase. Whey protein isolate has a HLB of between 13 and 18.

3.1.2.2 Water in Oil (W/O) Emulsifiers

3.1.2.2.1 Span 80 (sorbitan (Z)-mono-9-octadecenoate)

Span 80 (sorbitan (Z)-mono-9-octadecenoate) is a non ionic emulsifier with the molecular formula $C_{24}H_{44}O_6$, a molecular mass of 428.61 $gmol^{-1}$ and a density of 986 kgm^{-3}. Span 80 was used in concentrations of up to 10 % by weight in the dispersed phase. Span80 has an HLB value of 4.3.

3.1.2.2.2 PGPR (polyglycerol polyricinoleate)

PGPR (polyglycerol polyricinoleate) is a lipophilic emulsifier made from soybeans and castor beans. PGPR was used in concentrations of up to 10 % by weight in the dispersed phase. The PGPR used had a HLB of 2.8.

3.2 Equipment

3.2.1 Rotor Stator High Shear Mixer; the Silverson L4R Mixer

Emulsions were produced by high shear rotor-stator mixing using a Silverson L4R mixer (Silverson Machines Ltd, Buckinghamshire, UK). Mixing speeds of up to

6000 rpm are achievable and the emulsions were prepared in volumes ranging from 50 ml to 5 l. Emulsions were prepared using the standard emulsifying screen with round perforations and a 4 vane rotor (Silverson Machines Ltd, Buckinghamshire, UK).

3.2.2 Laser Diffraction Particle Size Analysis; the Malvern Mastersizer

The Malvern Mastersizer model 2000 with a Hydro SM manual small volume sample dispersion unit (Malvern Instruments Ltd, Worcestershire, UK) was used as the primary method of measuring the drop size and drop size distribution produced from the emulsification devices. For all samples the Malvern Mastersizer was switched on for 1 hour before use to allow the laser to equilibriate at a constant temperature and to reach at least 75% of full power. The dispersion unit was cleaned at least three times using ultra pre water at a stirring speed of 3000 rpm and until the Mastersizer reading was in the green range (≥80% laser light transmitted to the detector). The machine was also cleaned in this way between samples and after using the equipment. For measuring droplets of water in oil emulsions the Mastersizer was switched to run with sunflower oil as the continuous phase through the detection cell and the dispersion unit. For sunflower oil a refractive index of 1.47 was used and for water a refractive index of 1.33 was used at 25 °C. Three measurements were obtained for each sample tested. The results of the Mastersizer are in volume weighted mean diameter, (i.e. the equivalent diameter of a spherical particle containing the same volume as the particle measured) or $D_{[4,3]}$. The size of each particle measured is recorded and the size distribution and the mean particle size are calculated for each of the three measurements. The Mastersizer also produces a measure of size distribution from the droplet size distribution called span, which is the equivalent of the coefficient of particle size dispersion as used by Nakashima (US Pat. No. 5326484, 1994).

The Malvern Mastersizer is able to determine the size of the droplets in an emulsion by using laser diffraction (Malvern Mastersizer 2000 Documentation, Malvern Instruments). Laser diffraction relies on the principle that particles passing through a laser beam will scatter light at an angle that is directly related to their size. Large particles scatter light at smaller angles and small particles scatter light at larger angles. The light scattered by larger particles is also at higher intensity than light scattered by smaller particles. The laser diffraction is accurately described by the Fraunhofer Approximation and Mie Theory. Mie Theory assumes that the sample is homogenous, that the particles being measured are spherical, the suspension is dilute to ensure that the light that is scattered is measured before it is re-scattered by any other particles, the optical properties of the particles and the suspending medium is known. Mie Theory predicts the light scattering from the surface of the particle and the intensity of the light scattering from the difference in the refractive index between the particle and the dispersion medium. It also predicts how light absorbed by a particle can affect any secondary scattering signals generated if light is refracted inside the particle. Secondary internal light scattering becomes relevant for particles of 50 µm or less and if the particle is transparent. The Fraunhofer Approximation also assumes that the particles being measured are opaque discs, the light scatter occurs at narrow angles, all sizes of particle scatter light equally effectively and that the difference in the refractive index between the particle and surrounding medium is infinite. These approximations are accurate for large particle sizes (above 50 microns in size) but become increasingly less accurate for small particle sizes. Particles ranging in size from 50 nm to 100 µm can be detected using Mastersizer technology. Samples are mostly prepared with water, but other solvents can also be used (ethanol, isopropanol, or octane). It is possible to carry out the measurement on dry powders by adapting the Mastersizer equipment. The Malvern Mastersizer is an attractive technology because only a few minutes are required for the sample analysis enabling real time measurements of a sample to be determined. Several ml of sample are required for analysis making it a suitable method for analysis of systems where limited sample is available. However, care must be taken when assuming that a small sample is representative of a large system or that removing a sample from a system doesn’t compromise the remaining stock. Other limitations of this method appear for small sizes, for non-spherical particles, and for materials with a low refractive index with respect to the dispersive medium. The Malvern Mastersizer 2000 contains a laser, to provide a source of coherent, intense light of fixed wavelength, A sample presentation system to ensure that the material under test passes through the laser beam as a homogeneous stream of particles in a known, reproducible state of dispersion and a series of detectors which are used to measure the light pattern produced over a wide range of angles (Malvern Mastersizer 2000 Documentation, Malvern Instruments).

3.2.3 Microscopy

Samples of the prepared emulsions were made into microscope slides and viewed using a Reichert Polyvar Met Optical Microscope. Samples of double emulsions were visualised using a Leica confocal laser microscope and suitable dyes such as Nile blue.

Chapter 4

Development of Membrane Systems

Several new pieces of equipment were designed and built specifically for the research presented here. The design, construction and development of this equipment and its components were as follows.

4.1 Cross Flow Membrane Emulsification Device

The cross flow membrane emulsification device (CFMED) used in this study was designed using some commercially available parts, and several made ‘in house’ by the workshop in the School of Chemical Engineering at the University of Birmingham. The specification required that a membrane could be mounted in the device such that a continuous phase liquid could be flowed across one surface, whilst a second liquid is pressurised through the membrane from the other side.

The first decision was to choose the shape of the membranes used. Since for simplicity commercially obtainable membranes were more desirable, the shapes were limited to those available. These included sheets, discs and tubes. The tubes seemed most practical, as their shape gave a natural resistance to pressure, although several studies have been undertaken successfully with other shapes (Vladisavljevic and Williams, 2005). Most commercially available tubular membranes are 10 mm O.D., and so the membrane module was chosen to be able to accept this size, in 250 mm lengths.

TAMI industries (Nyons, France) make a housing designed for desktop microfiltration, which houses this size of membrane, and separates the inside and outside surfaces. This membrane module provides hose fittings to flow fluid across the inside and the outside of the membrane tube. To circulate the continuous phase the corresponding hose fittings of the membrane module were connected to a tank (a sidearm conical flask), and a pump.

The pump was initially configured using a 200 rpm Electrolab peristaltic pump, after the membrane module, so as to create a low pressure in the membrane module. It was initially thought that this would act as an additional detachment force for the droplets. This did indeed prove to be the case, but the effect was found to be identical to increasing the trans-membrane pressure, and so to simplify the arrangements the pump was moved to before the membrane module. This meant that the trans-membrane pressure would never be negative, which was possible with the previous setup. The pump itself was causing a problem with pulsing pressure in the membrane module, and as such was thought to be the cause of higher than necessary droplet size distribution in the resulting emulsions. A gear pump with precision drive, and set displacement per revolution of 1.0 ml was purchased (Cole-Parmer 5000 rpm console drive with 'A mount' 1 mlrev^{-1} gear pump head consisting of PTFE gears and seals), this allowed for an increase in the cross-flow velocity across the membrane due to the higher flow rate than was possible with the peristaltic pump.

The pressurisation of the dispersed phase through the membrane from the inside was more of a problem. There was no suitable commercially available system for applying pressure to a liquid, and so a tank was designed to hold the dispersed phase liquid, and use air from the laboratory compressed air supply to apply a constant pressure. The tank was built by the department workshop from Perspex tube and sheet, and bonded together (Figure 4.1). The tank's endplates were also made of Perspex, into which a groove was machined to accept a neoprene 'O' ring seal. These were mounted to the tank at either end using 6 M6 stainless steel bolts and wing nuts, with suitable stainless steel washers. In the endplates, tapped holes were used to mount an inlet and outlet, and also a gauge and safety pressure blow off valve, and a filling port. The working capacity of the tank was 600 ml of dispersed phase, and the maximum working pressure was set at 300 kPa.

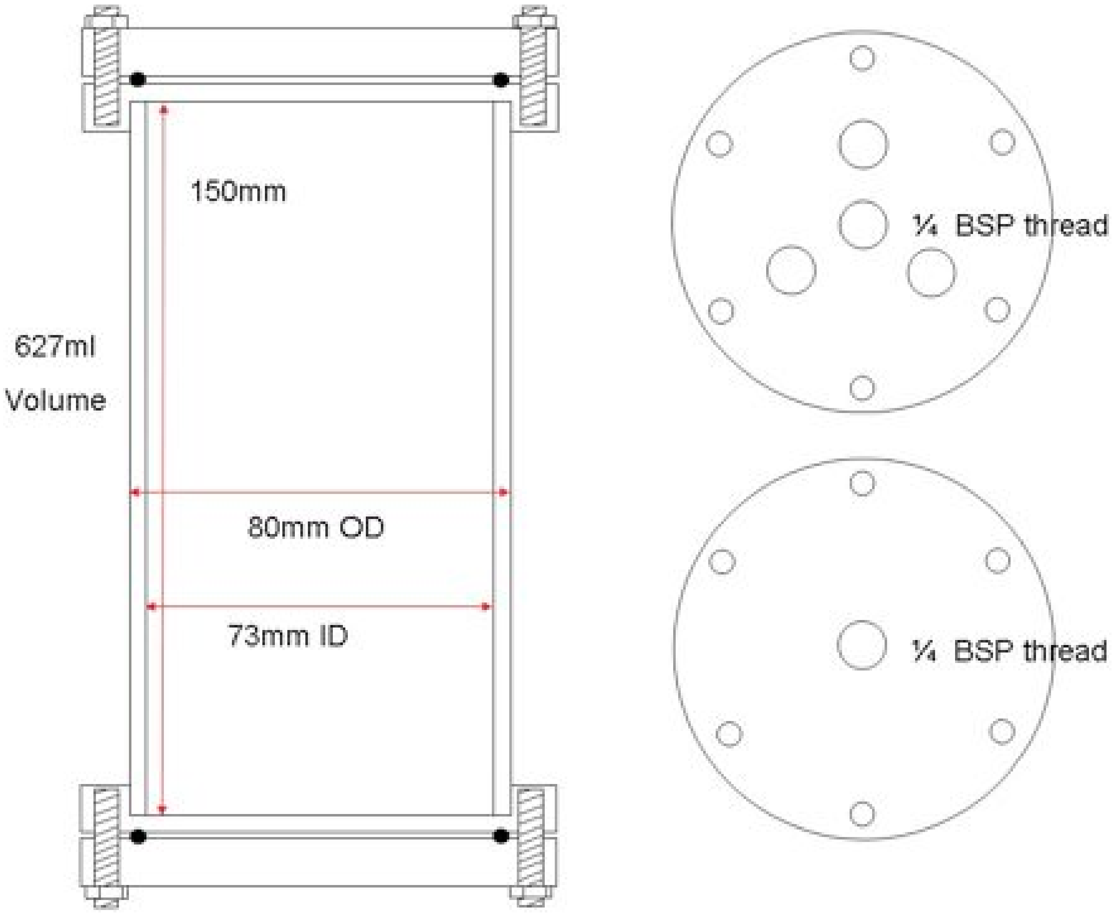


Figure 4.1. The design for the pressure tank used for pressurising the dispersed phase liquid.

The dispersed phase flowed from the tank through a fibre reinforced hose to the membrane module, and was prevented from flowing straight out of the other side by a bleed tap, which could be opened to let air bleed out of the system.

Various gauges were added at several points in the system to determine the actual pressures across the membrane (Figure 4.2).

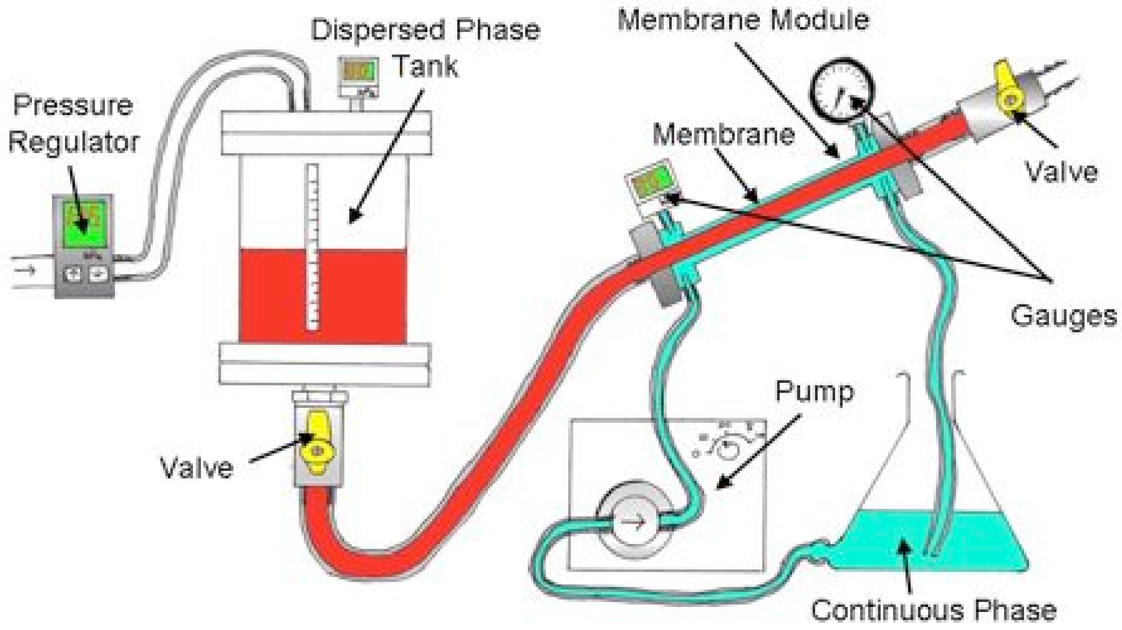
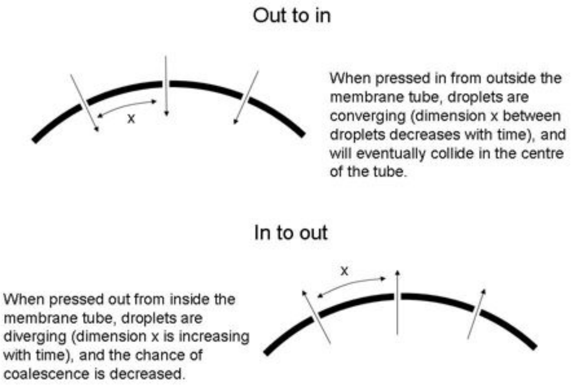


Figure 4.2. Normal layout of the CFMED.

Digital and analogue gauges were used depending on the position of the measurement within the system, and the expected pressures being measured. Where rapid changes, pulses or fluctuations were expected an analogue gauge was used. Where accurate stable pressure measurements were required a digital gauge was used. The gauges were purchased from RS Components, and were zeroed at atmospheric pressure before each experimental run. The precise layout of the CFMED was flexible, and could be set up to run in many different configurations for different products. For these tests the system was primarily run in a re-circulating continuous phase mode; however the system could have been run as a continuous process by using longer membranes to achieve higher dispersed phase volumes instead of needing to re-circulate. The direction of flow across the membrane is not fixed, i.e. the system can be run with the dispersed phase pumped out of the tube through the membrane or into it, and the flow of the continuous phase is therefore across the surface of the tubular membrane, or through the middle respectively. For the majority of the tests, it was decided to run the continuous phase along the outer surface of the tubular membrane and pressurise the dispersed phase through from inside the tube, this meant that the chance of collisions would be marginally decreased as the trajectory of the detaching droplets would be away from other droplets instead of into the path of other droplets as in the case of pushing the dispersed phase through from the outside in (Figure 4.3). In practice this was thought to have little effect because of considerations of scale.


Out to in

When pressed in from outside the membrane tube, droplets are converging (dimension x between droplets decreases with time), and will eventually collide in the centre of the tube.

In to out

When pressed out from inside the membrane tube, droplets are diverging (dimension x is increasing with time), and the chance of coalescence is decreased.

Figure 4.3. The rationale behind pressing the dispersed phase out from inside the membrane tube.

The hydraulic shape of the inside of the membrane module was defined schematically so as to enable the calculation of shear rates and velocities of the fluids within the module around the membrane surface, and also to allow an approximation of the state of the flow with respect to turbulence.

The module channel was of 14 mm inside diameter, and the membrane used (in the case of SPG, ceramic and stainless steel membranes) was 10 mm in outside diameter. The geometry is represented in Figure 4.4.

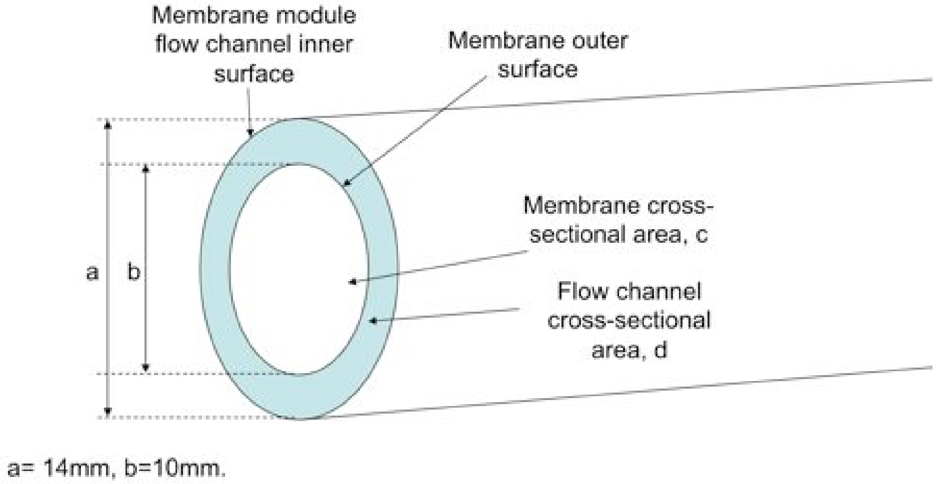


Figure 4.4. A schematic representation of the continuous phase flow channel around the membrane through the membrane module in the cross-flow membrane emulsification system.

The cross sectional area of the flow channel was calculated as 75.4 mm^2, with the pump giving a flow of just over 5 litres per minute at maximum, this works out at a linear cross-flow velocity of just over 1.1 ms^{-1}. The Reynolds number was then calculated by using the equation;

$$\mathrm{Re} = \frac{\rho V_{cf} D_H}{\mu} \qquad \text{equation 4.1}$$

Where Re is the Reynolds number, ρ is the density of the fluid (kgm^{-3}), V_{cf} is the velocity of the fluid (ms^{-1}), μ is the dynamic viscosity of the fluid (Pa•s) and D_H is the hydraulic diameter of the channel (m). The hydraulic diameter being defined as 4 times the cross sectional area, divided by the wetted perimeter, which with the annular gap geometry used can be thought of as the channel diameter minus the membrane diameter. At 1.1 ms^{-1} flow rate, with a 1% wt. Tween20 in water continuous phase of viscosity 0.001 Pa•s, and a density of 1000 kgm^{-3}, and the calculated hydraulic diameter of the channel 0.004 m, the Re is 4400, in this case indicating a turbulent flow within the module. For slower speeds with the same continuous phase however, the results are different. At 0.1 ms^{-1} flow rate (~10% pump speed) the Re is only 400, indicating a laminar flow regime. This is in contrast to the flow given along the inside channel of the membrane if the continuous phase were to be flowed along the inside and the dispersed phase flowed from outside the tube into the continuous phase, which would give a Reynolds number twice as large assuming an 8 mm channel diameter.

As the system was tested the pressurisation of the dispersed phase became a problem. It became obvious that the control of the pressure was very inaccurate using the regulator on the laboratory air supply. The system would creep up and down so that keeping the pressure constant during an experiment became impossible, and the tiny adjustments required to the regulator knob meant that over shooting the desired pressure when making pressure corrections was inevitable. This fluctuation in pressure caused an very large size distribution of droplets to be produced during the experiments, with droplets ranging in size by 50 μm. The addition of a second regulator in line with the first improved the pressure control, but did not solve the problem completely. Manual pressure regulators are not designed for this type of fine pressure control, and work by keeping the applied pressure within limits, rather than at a set pressure. For this reason a different pressure control system needed to be found.

To solve the problem a digital pressure regulator manufactured by SunX was purchased from RS Components, and included in the line between the standard regulator and the tank. This allowed the upper and lower limits of the tank pressure to be set, and the tank pressure was then accurately controlled throughout the experiment to a tolerance of +- 0.5 kPa. The digital control resulted in an immediate drop in the size distribution of droplets on subsequent tests.

4.1.1 CFMED Standard Operating Procedure (SOP)

In testing, a standard operating procedure was developed to run the CFMED, and all subsequent tests were run with this procedure for the results in the following chapters unless otherwise specified.

Firstly the equipment was dismantled and cleaned if not already in a dismantled state, the cleaning was with standard detergent and water, and the membrane to be used was cleaned depending on the specific cleaning instructions for its type (see the 'membranes' section, chapter 4.3).

The equipment was then assembled according to the method of operation required, normal operation was considered to be a recirculating loop for the continuous phase, flowing around the outside of the membrane tube, with the dispersed phase pressurised through the membrane tube from inside. Although other arrangements were tried as documented in the relevant results sections, the vast majority of experiments with the CFMED were carried out with this arrangement (Figure 4.4).

The membrane was then pre-soaked in the continuous phase of the emulsion being prepared for at least 1 hour to ensure full saturation of the continuous phase over the membrane and through the pores. With more viscous continuous phases the membrane was soaked for much longer, and sonication was used where necessary to aid the liquid to penetrate each pore fully.

Whilst the membrane was soaking, the pipe work for the rest of the system was assembled, and the electronic gauges zeroed at atmospheric pressure. With all the valves shut the dispersed phase was be filled into the tank. The membrane was then carefully but quickly assembled into the membrane module, thus separating hydrodynamically the inside and outside surfaces of the membrane. The speed with which this was done was important as the membrane should not have a chance to dry out as that may be detrimental to the process performance. Once the membrane was safely mounted into the module, the module was fitted to the rest of the pipe work, and the system was ready for bleeding.

To bleed the system the components were all powered up, and the dispersed phase tank was connected to the quick release outlet of the laboratory air supply. The digital pressure regulator was initially set at 0 kPa, and the continuous phase was filled into the continuous phase tank. The continuous phase was then recirculated slowly (0.1 ms^{-1} V_{cf}) for 5 minutes, to allow any bubbles to disperse. The continuous phase pump was then turned off and the dispersed phase tank was pressurised slightly (1 kPa) and the valve allowing the dispersed phase into the membrane module was opened gently. The bleed valve was then opened to allow air out of the membrane module, which slowly allowed the dispersed phase to fill the membrane module. Depending on the viscosity of the dispersed phase more pressure may be needed to force the dispersed phase into the membrane module, and if necessary the pressure could be slowly increased as required when bleeding the system.

Once the system had been bled and was free of any air, the continuous phase pump was set at the speed required for the experiment being undertaken, and run for a further 5 minutes. This allowed a consistent measurement of the starting pressure in the membrane module due to the recirculation of the continuous phase. The gauges before and after the membrane module in the system constantly monitor the pressure, and the difference between them could be taken as the membrane module pressure. The trans-membrane pressure (P_{tm}) is the difference between the membrane module pressure and the pressure being applied to the dispersed phase via the pressure tank. Once the tank was correctly pressurised and the continuous phase was recirculating, the emulsification process was started simply by opening the valve allowing the dispersed phase from the tank to the membrane module. The experiment was then run either until the correct amount of time had passed or the desired amount of dispersed phase had been emulsified, depending on the experiment being run. Through out the experiment the pressure gauges were checked to ensure the P_{tm} remained constant, and the pressure regulator was adjusted as necessary to account for continuous phase pressure changes due to factors such as increasing viscosity. To finish the experiment the valve allowing dispersed phase into the membrane module was simply shut, the pressure regulator set to zero, which released the pressure in the tank, and the continuous phase could then be drained into sample containers for analysis. The system was then stripped down for cleaning, unless it was required to continue with similar dispersed and continuous phases, in which case the system's continuous phase loop could be rinsed through with successive amounts of continuous phase, until it was clean (at least 5 rinses, more after making more viscous emulsions), and another run could be made. Once the equipment was stripped the components were washed individually, in hot water and detergent, and if necessary soaked or sonicated in diluted detergent to remove any residues of either phase. The pump was cleaned by running through with detergent and then water, if necessary the pump was left re-circulating diluted detergent until clean and then rinsed with water.

4.2 Rotating Membrane Emulsification Device

The rotating membrane emulsification device (RMED) was designed over several evolutions or stages, using a commercially available IKA Eurostar Digital overhead stirrer to provide the rotating motion. Because one of the projected advantages of using a membrane emulsification system was that the use of shear sensitive ingredients would be more viable, the interior of the rotated section of the device was designed to impart as little shear force to the dispersed phase as possible. This meant that the interior should have as few projections as possible. The initial design was that a hollow tube of 10 mm outside diameter would run through the stirrer, and onto the end a central shaft would hold the membrane against a sealing ring by means of a threaded section of the shaft and a nut with corresponding seal.

The shaft would be smaller in diameter than the internal diameter of the tube, so that the dispersed phase could flow down the inside of the tube into the interior of the membrane. The central shaft would be held at the top of the tube by the top plate of a suitable rotating fluid coupler through which the dispersed phase could be introduced under pressure from a pressure vessel similar to the one already successfully employed in the CFMED. This idea however, presented too many construction problems and had to be simplified in several ways. The membrane mounting system caused many issues, and so it was decided to sacrifice some of the versatility of the mount and use a system of stainless steel ferrules which simply contained a female M10 thread which corresponded to a male thread on the main 10 mm outside diameter tubular shaft as driven by the stirrer motor. This meant the central threaded shaft was no longer needed, which also helped to simplify the rotating joint at the top of the tube. This did however require that each membrane to be used had to be bonded to a ferrule at one end, and the other end to a suitable cap to form a tight seal. The adhesive used to bond the membranes (particularly the SPG membranes, which need cleaning with acetone) was another problem as the solvents used to clean the system often meant that the bond was broken down and this was a regular cause of failed tests, until a resistant epoxy resin was used. The top of the main tubular shaft above the stirrer was coupled via a rotating seal and ball bearing, to the outlet from a pressure tank, so as to introduce dispersed phase into the system under pressure (Figure 4.5).

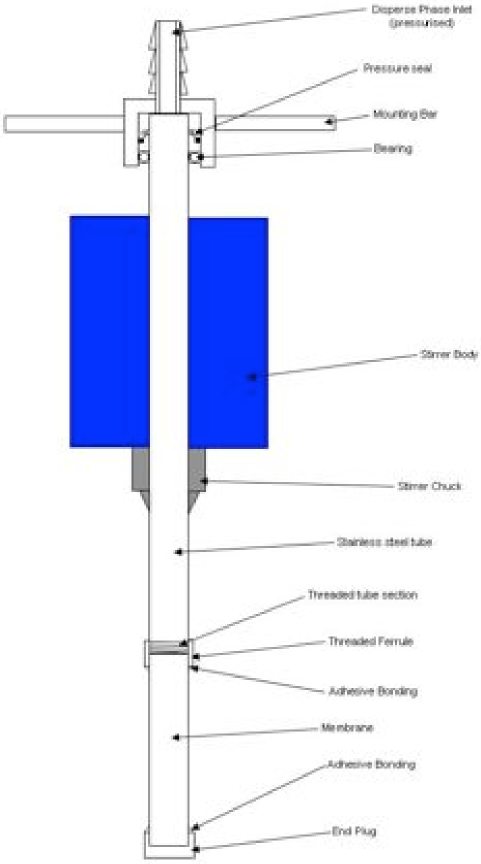


Figure 4.5. The final design diagram for the Rotating Membrane Emulsification Device, with the detail of the rotating fluid coupling.

The vessel used to hold the continuous phase in which the membrane is rotated was not built as part of the system, but instead could be changed to provide different volumes and gaps between the rotating membrane and the vessel walls. Calculations were made of the Taylor number for the rotating membrane system, at different rotation rates, continuous phase viscosities and for different gaps using the following equation (Schadler and Windhab, 2006);

$$Ta = \omega r_1 s \frac{\rho}{\mu}\sqrt{\frac{2s}{r_1 + r_2}} \qquad \text{equation 4.2}$$

Where ω is the angular velocity of the membrane (s^{-1}), r_1 and r_2 are the radii of the membrane and the continuous phase vessel respectively (m), s is the gap size (m), μ is the continuous phase viscosity (Pa•s), and ρ is the continuous phase density (kgm^3). With water as the continuous phase and a 30mm diameter vessel the Taylor number at 200 rpm is 166, and at 2000 rpm (the stirrer maximum) it is 1666. These high Taylor numbers suggest that Taylor vortices will be present in the continuous phase even at low rotational speeds, as Schadler and Windhab (2006) found the critical Taylor number above which vortices formed to be 41.

4.2.1 RMED Standard Operating Procedure

To run the rotating membrane emulsification device, a standard operating procedure was developed to ensure consistency of the results gathered. Similar to that of the CFMED, the specifics of the experiment meant some adaptation was required, but the overall procedure was the one predominantly used in the following chapters, and any deviation from this is noted with the relevant results.

As with the CFMED, the membranes were fully cleaned depending on the type being used, and then soaked for at least 1 hour in the continuous phase being used to ensure full saturation of the continuous phase over the membrane and through the pores. With more viscous continuous phases the membrane was soaked for much longer, and sonication was used to aid the liquid to penetrate each pore fully as it was for the CFMED in such circumstances.

Once the membrane had been prepared, the system was assembled, with the membrane still soaking. The dispersed phase was filled into the pressure tank, and the power turned on to all the components. A visual check of the seal of the rotating coupling was made and the depth of the rotating shaft inserted into the coupling was also checked to ensure a tight seal.

The continuous phase was filled into the vessel (tank) in which emulsification was to take place, (frequently a beaker or measuring cylinder of the diameter required in the particular test being undertaken) and when this was ready, the membrane was screwed in place on the end of the rotating tubular shaft. This was then immediately immersed in the continuous phase tank, so that the surface of the liquid just covered the top of the metal ferrule. The stirrer was then run, first slowly (50 rpm) and then if there were no vibrations or other problems the speed was slowly increased all the way to maximum, checking for vibrations. If the system vibrated at any point, the machine was stopped and the shaft rotated slightly in the chuck and re-tightened, and the checks run again. This invariably removed any noticeable vibration from the system.

Once the membrane was mounted and the rotation checked, the dispersed phase could be introduced in a very similar way to the CFMED, except that the rotating system did not need bleeding, instead any air within the rotating tube simply flowed upwards into the dispersed phase tank, and out of the system. The valve allowing dispersed phase out of the bottom of the tank was opened, and the vent valve on top of the tank was also opened, at which point the dispersed phase would fill the rotating shaft and the membrane. Both valves were then closed, and the tank was pressurised to the value for that particular test. Since the continuous phase was at atmospheric pressure, the regulator pressure was also the trans-membrane pressure (minus negligible losses due to the pipe work).

The stirrer was then set to the required speed for the experiment, which was started when the pressure tank bottom valve was opened.

The experiment was then allowed to run for the required time, or until the required amount of dispersed phase had been emulsified. Stopping the experiment simply involved shutting the dispersed phase valve, setting the regulator to zero (which also vented the tank) and stopping the stirrer.

The continuous phase tank was removed, and the emulsion it now contains was decanted into suitable containers for analysis and storage. The equipment was then stripped down and cleaned, or if similar emulsions were to be made, the membrane was rinsed with distilled water (or oil if the emulsion being made was oil continuous) and immersed in a fresh tank of continuous phase. The dispersed phase tank was topped up as necessary, and subsequent runs could be undertaken.

4.3 Membranes

The membranes tested were selected from the available types of commercial filtration membranes, specifically designed emulsification membranes, or constructed to order. Several different membrane materials were tested.

4.3.1 Ceramic

Ceramic membranes make up the bulk of the commercially available water filtration membranes. The ceramic membranes chosen for testing were made by TAMI industries (France), and are made up of a coarse titanium or aluminium oxide support tube, 10 mm in diameter with 3mm thick walls (Figure 4.6), the inside surface of which has a thin finer coating of similar material which is the actual filter membrane. Because the membrane is coated on the inside surface of the support material, the droplets formed during emulsification using these membranes will form within the support material rather than on the membrane surface as with the other membranes used.

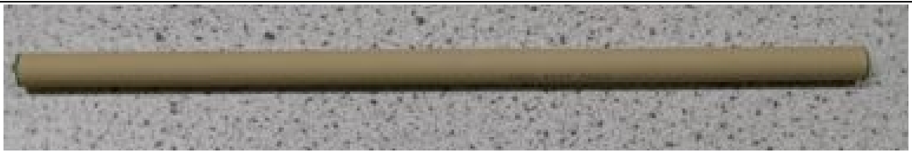


Figure 4.6. the ceramic membranes as used in both the cross-flow and rotating membrane systems

These were available from TAMI industries in several filter cut-off sizes (i.e. they are sold by the size of the smallest particles that will be filtered by the membrane) This does not necessarily correspond to the pore size, and on closer inspection the term ‘pore’ is less applicable, as the filter is made up of tiny particles, and the holes left where these don’t tessellate form the tortuous path taken by any fluid traversing the membrane, more a series of interconnected voids than an actual pore, and there are no well defined circular openings on the membrane surface as suggested by the term (Figure 4.7).

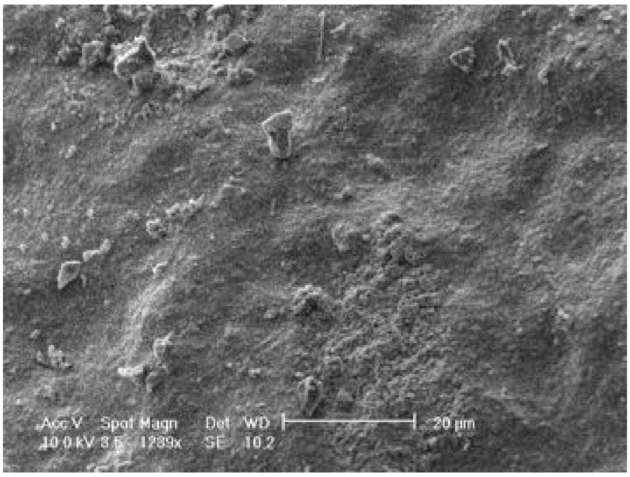


Figure 4.7: An electron micrograph of the surface of a 1 µm cut off ceramic membrane from TAMI industries, France. The particles making up the membrane surface can be seen, but distinct 1 µm pores cannot.

The ceramic membranes are very resilient to heat, pressure and solvents and as such very thorough cleaning can be done using an autoclave, followed by soaking in acetone, followed by ethanol, and finally overnight soaking in water. Normal cleaning between runs can be done with diluted detergent and water, and thorough cleaning should be done when emulsification performance is impaired. Sonication of these membranes is not recommended as on several occasions this was found to cause de-lamination of the membrane from the support.

8 ceramic membranes in total were used ranging in cut off filtration sizes from 0.2 μm to 10 μm. Those purchased were 250 mm in length, and the ends were glazed so as to form a seal with the inside and outside surfaces at each end.

4.3.2 SPG

The Shirasu Porous Glass (SPG) membranes are produced using volcanic ash in Japan, specifically for producing emulsions. The pores through the membrane are made by thermal phase inversion of two phases within the glass, which forms particles of $CaO{\bullet}B_2O_3$ within the glass of very narrow size distribution. These particles are leached from the glass using hydrochloric acid leaving tortuous voids through the remaining $Al_2O_3{\bullet}SiO_2$ glass with the similar narrow size distribution (Nakashima, US Patent No. 4657875). By careful management of the length of time and temperature of the phase inversion step, the particle size and therefore the size of the voids left and ultimately the pores on the surface of the membrane can be controlled very accurately. The membranes are thinner than the ceramic membranes at just 1 mm thick, and are made of the same material all the way through. Their pore sizes are of a narrower size distribution than the ceramic membranes, however the term ‘pore’ is still not entirely accurate. The paths that liquid takes through the membrane are made up of channels of a very narrow cross-sectional diameter, they are however, still far from straight paths, they twist and turn through the membrane, and as they emerge on the surface to form pores they are at many different angles, and so the pores are of many different sizes and shapes depending on the exposed channels shape. The thinner nature of the SPG membranes, and their brittle material, presents different challenges to those of the ceramic membranes.

4.3.3 Polymer

The polymer membrane provided a greater range of construction possibilities than any of the other membrane materials, because of the range of types of polymer available and the different ways that they could be used to construct a membrane suitable for membrane emulsification. Because the membrane had to fit into the same emulsification devices as the other membrane types, a membrane readily available as a tube the correct size and shape was sourced, this was a poly-propylene membrane called Accurel, developed by Akzo AG and made by Microdyn-Nadir, which is usually used for water filtration. The pores are formed by thermal phase inversion and as such are highly uniform, making the surface of the membrane look very much like that of a sponge. This membrane is tubular with an inner channel diameter of 5.5 mm and an outer diameter of 8 mm (Figure 4.8). This being slightly smaller than the other membranes means a slight modification in the mounting was necessary. This membrane is flexible which presented some unique challenges to its use in membrane emulsification. The membrane had to be stretched in place by hand whilst the seals were tightened, so as to ensure an even gap around it in the membrane module. The material flexibility was however to flexible for use in the rotating membrane system, and the membrane bent as soon as the system was rotated.

Figure 4.8. The polymer membrane used in this research as it came off the roll. The flexibility of the material posed unique challenges to mounting in the membrane module.

4.3.4 Stainless Steel

Stainless steel membranes have been used before for membrane emulsification, at the time of writing however, stainless steel had only previously been used to produce large emulsion droplets (Vladisavljevic and Williams, 2005) using a membrane with laser drilled pores in the region of 100-150 μm. Since then, the improvement of laser technology has allowed the production specifically for this research, of a tubular stainless steel membrane with a uniform pore size of 15 μm, made by Laser Micromachining Limited, Denbighshire, UK (Figure 4.9).

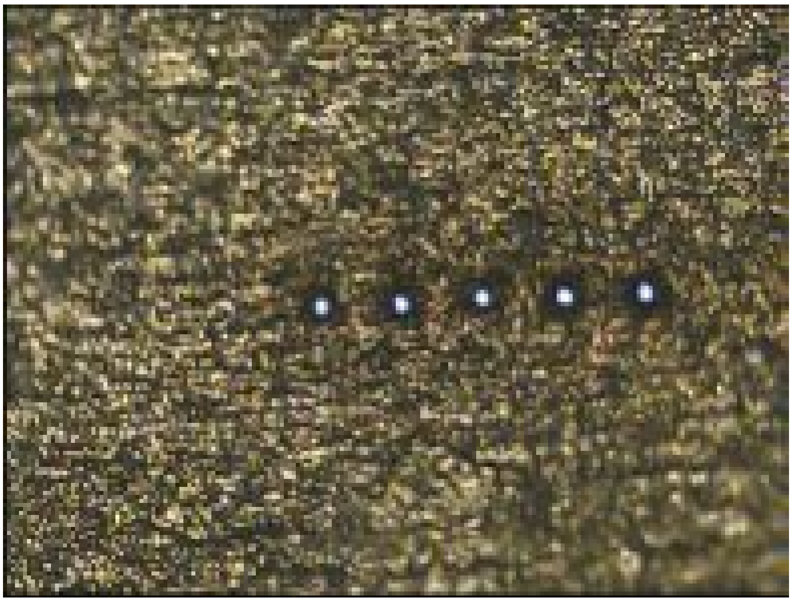


Figure 4.9. Test drillings for the metal membrane, the distance between the hole centres is 1 mm.

The pores are uniformly spaced in a helical pattern around the tube (Figure 4.10) so as to minimise the coalescence of droplets due to collisions as they detach and flow away from the pores i.e. pores do not line up with adjacent pores in the direction of the flow or rotation. The pores in the stainless steel membrane are straight and perpendicular to the membrane surface. These membranes have a much lower porosity to the other types of membrane tested.

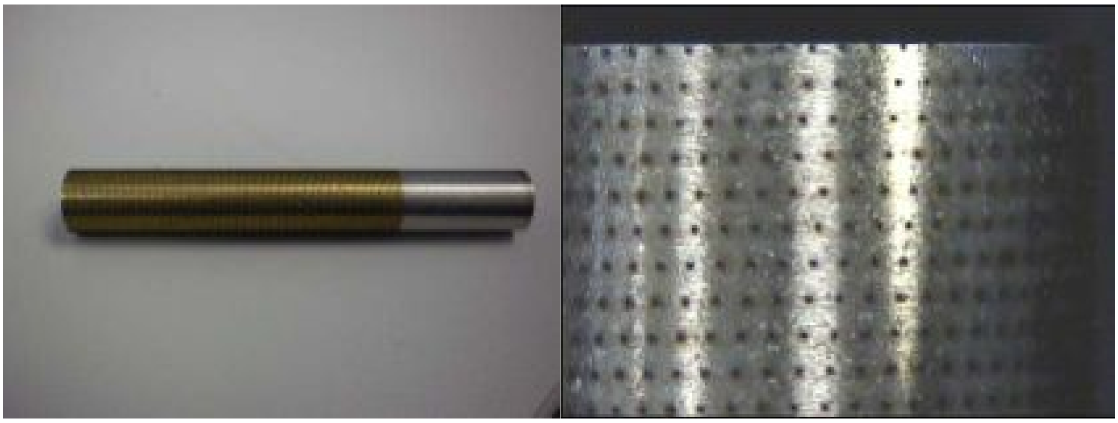


Figure 4.10. The stainless steel membrane and a close up showing the staggered hole pattern.

The metal membrane mounted as all the others into the cross-flow module, but for the rotating module a special ferrule was heated to fit the membrane, and when cooled the ferrule sealed and gripped the membrane, so no extra bonding was needed, essentially removing the bonding and cleaning issues seen with the SPG and ceramic membrane used with the rotating system.

Chapter 5

Cross Flow Membrane Emulsification

The aim of the work in this chapter was to determine the capabilities and effectiveness of the Cross-Flow Membrane Emulsification Device (CFMED) as described in the proceeding chapter. After the initial testing several refinements were made to the system as detailed in chapter 4. The CFMED was then ready for testing. Whilst the effects of pore size are thought to be the major factor in the size of droplets produced through membrane emulsification (Katoh *et al.,* 1996), before the size of the pores could be effectively tested, the effects on droplets size of the formulation of the emulsion and the morphology of the membranes must first be found. The experiments continue to determine the effects of changing pressure across the membrane, the effects of changing the shear applied by the cross-flow of continuous phase, the effects of changing viscosity of the continuous phase, and of changing the dispersed phase volume.

5.1 Effect of Emulsifier

Since the formulation of an emulsion has a profound effect on the droplets it contains, the effects of the emulsifier needed to be considered first, so as to eliminate these from the effects of changing the parameters of the system itself. Since the research here was primarily concerned with making food and cosmetics type formulations for potential use within those industries, the emulsifiers chosen were all commonly found in use within those areas. The CFMED was tested to see the effects of changing the emulsifier type and concentration on the resultant emulsion droplets. The emulsifier type and concentration have been previously shown to have an effect on both the size and size range of the droplets produced using membrane emulsification (Schröder *et al.,* 1998). The effects of the different membrane types were also investigated with respect to the different emulsifiers. This was achieved by running a series of tests using each type of membrane; the exact membranes used were chosen to give a rough equivalence to each other with respect to pore size where possible.

5.1.1 SPG Membrane

The membrane module was set up with an SPG membrane, with average pore size of 1 µm (a mid range pore size from those available). The dispersed phase tank was filled with sunflower oil, and the continuous phase tank was filled with the dispersed phase for the first test, in this case it was a 0.5 % wt. Tween20 in Milli-Q filtered distilled water solution. The continuous phase pump was started and run at a calibrated 0.6 ms^{-1} (the middle of the range the equipment is capable of). This produced a membrane module pressure of 28 kPa and so the continuous phase tank was pressurised to 38 kPa i.e. a trans-membrane pressure of 10 kPa (the lower end of the range but known to produce droplets from the initial testing). The time taken to flow the amount of oil to achieve a 1% phase volume of oil in water was recorded (to try to reduce any effects seen caused by phase volume based coalescence). The experiment was repeated with several different concentrations of emulsifier (0.01, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 % wt.), and then again with several different emulsifiers at the same concentrations (Tween20 and Tween80, SDS, whey protein isolate, Sodium caseinate, and lecithin). The applied pressure was kept constant, meaning that there were slight changes in the trans-membrane pressure with fluctuations in the pressure of the continuous phase through the membrane module, although these were generally very small. Each test was itself repeated in triplicate to give a measure of reproducibility, and the droplet sizes given are an average of three Mastersizer measurements each of the three repeats, with error bars indicating 1 standard deviation above and below the mean. The results of the tests of the emulsifiers with the 1 µm SPG membrane are shown in Figures 5.1 and 5.2.

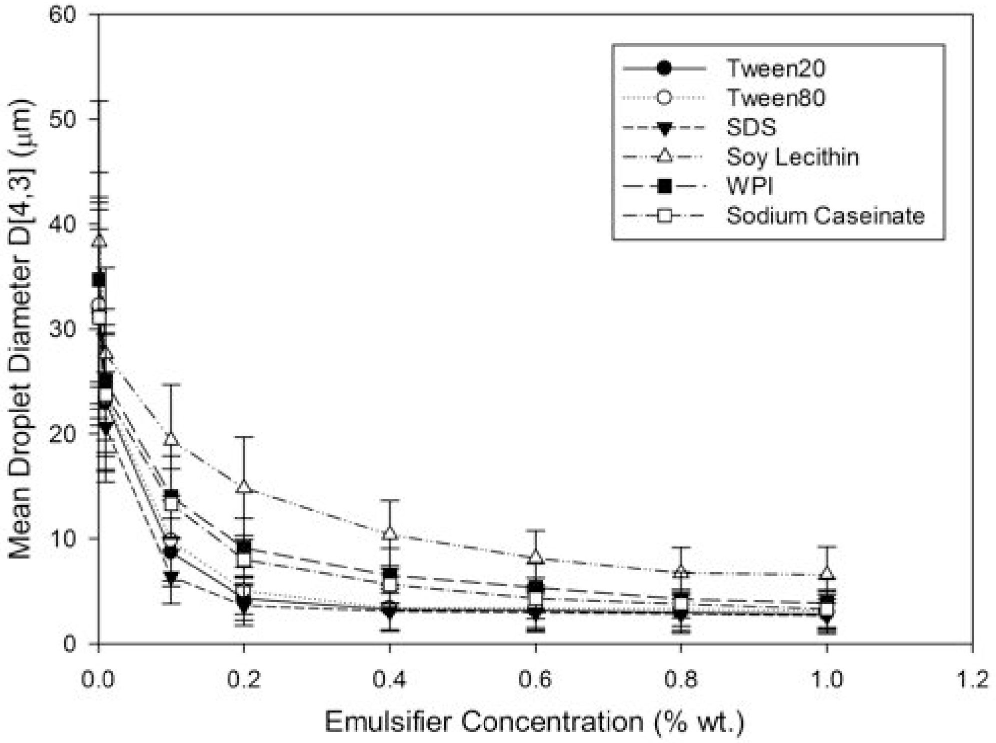


Figure 5.1. The effects of emulsifier concentration on the sunflower oil droplet size in water at a dispersed phase volume of 1%, produced by a 1 µm pore size SPG membrane, at a pressure of 10 kPa and a cross-flow velocity of 0.6 ms^{-1}.

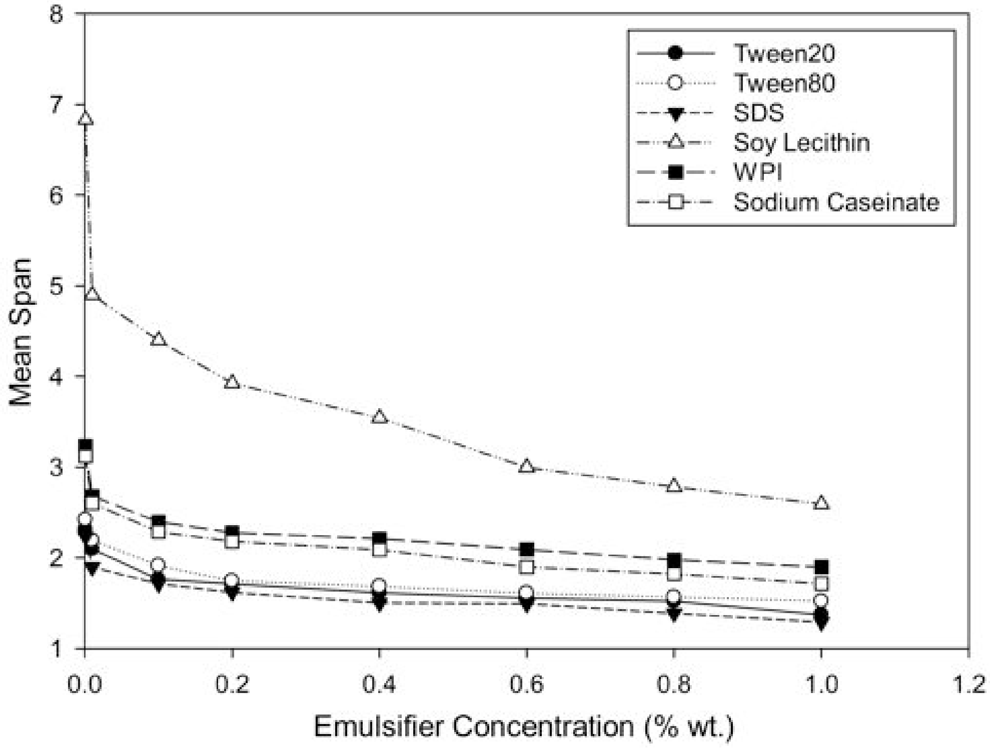


Figure 5.2. The effects of emulsifier concentration on the size distribution span of the droplets produced in the emulsions made for Figure 5.1

The emulsifiers tested in this experiment were Tween20 and Tween80, Sodium dodecyl sulphate (SDS), Lecithin (from soy beans), whey protein isolate (WPI), and Sodium caseinate. These were chosen as they are widely used emulsifiers, and several have potential for, or are already used in food or cosmetics type products.

The results show a decrease in droplet size as emulsifier concentration increases. There is also a decrease in the size distribution span of the droplets as emulsifier concentration increases. The action of the emulsifier reduces the surface tension of the droplets, allowing a greater interface curvature (smaller radius of curvature) i.e. a more curved surface, and meaning smaller droplets remain stable. If, hypothetically, the droplets produced at the membrane surface are of constant size irrespective of the concentration of emulsifier, then the difference in droplet size when the concentration of emulsifier is changed is because of the stabilising effect the emulsifier has on the droplets after they are formed. Less emulsifier allows more coalescence of the droplets and this may explain the increase in size and size distribution. It is more probable that the increasing concentration of emulsifier has an effect on the size of forming droplets, allowing them to detach from the membrane surface before they grow as large as with lower concentrations, in practice both of these effects of increased emulsifier concentration are likely to occur, and cumulatively produced the observed reduction in droplet diameter and diameter distribution span. This effect agrees with results from the literature on emulsifiers in membrane emulsification (Schröder *et al.,* 1998).

The higher the hydrophile/lipophile balance (HLB) of the emulsifier (listed in chapter 3), the quicker the droplet size decreases with concentration and the lower the droplet size gets overall. This effect is because the HLB is essentially a measure of the strength of an emulsifier, the higher the HLB, the better able to stabilise an oil in water emulsion an emulsifier is (Binks *et al*., 1998). The droplet size is not directly related to the HLB however, probably due to differences in the way the emulsifiers work. In this work several different emulsifier types were chosen to give a range of results; the SDS is an anionic surfactant, the tween20 and tween80 are both non-ionic, the Sodium caseinate and whey protein isolate are proteins, and the lecithin is a zwitterionic phospholipid. The lowest droplet diameters are produced using the SDS, which whilst having a high HLB also induces an ionic repulsion mechanism between stabilised droplets minimising coalescence after formation. The tween20 and tween80 have high HLB's but don't induce a repulsive force making them the next smallest. Whilst the protein emulsifiers still effectively reduce the interfacial tension of the droplets, they adsorb much slower than the SDS or tweens, and therefore allow the droplets to grow larger before detachment than the smaller molecular weight emulsifiers.

It can be seen from the results that the emulsifier lecithin seems to produce particularly large droplets, perhaps because of its specific surface chemistry which allows the interface to grow in an elastic fashion (Dimitrov *et al.,* 1978), perhaps resulting in non-spherical droplets (this may also account for the particularly wide size distribution of droplets produced as the mastersizer only detects the size in the plane of the laser and so depends on droplet orientation). It may also be caused by lecithin forming vesicles in solution, meaning that at any given time the effective free concentration in the bulk solution is lower, because these vesicles must dissociate before the lecithin can adsorb to the droplet interface - effectively increasing the adsorption time significantly and therefore resulting in the formation of larger droplets. The larger the vesicles formed the larger the increase in adsorption time.

The final droplet size is limited by the limits of the membrane used, so the final droplet sizes of the higher HLB emulsifiers are very similar, and would be lower if a smaller pore sized membrane or a faster cross-flow velocity (leading to increased surface shear) were used, for example. This effect is confirmed in results later in this chapter (section 5.3).

The droplet size distribution was wider at lower emulsifier concentrations (figure 5.3), this effect was expected and is consistent with other emulsification processes and also with the results reported in the literature (Schröder and Schubert, 1999); the droplets are less thermodynamically stable and are therefore more likely to coalesce leading to the likelihood of many different sizes of droplet being present in the emulsion, particularly larger sizes resulting from the coalescence of several smaller droplets. Some of the typical droplet size distributions are shown in Figure 5.3.

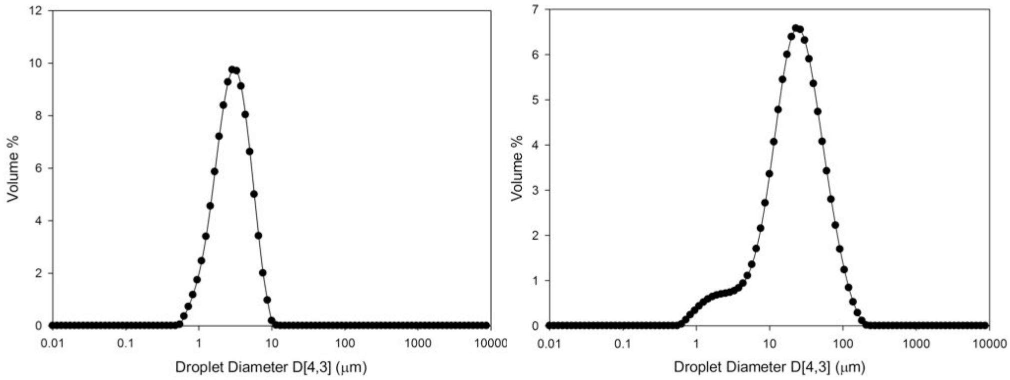


Figure 5.3. Size distributions of droplets produced during the test of emulsifiers using the SPG membranes. The left distribution was produced using Tween20 at 1 %wt. and has an average droplet diameter of 2.843 μm and a span of 1.423, whilst the right distribution was produced using Tween20 in the continuous phase at only 0.01 %wt. producing an average droplet size of 23.732 μm with a span of 2.473.

The preliminary testing of the SPG membranes showed that the membrane emulsification system was working well and the system was easy to control and use. The time taken to produce emulsions was between 2 and 5 minutes to produce a 1% dispersed phase emulsion at 500 ml total. The higher emulsifier concentrations did give a noticeable increase in flux (as will be discussed in the section regarding flux later). The emulsions were stable for a period of six weeks stored in the laboratory fridge (excepting the very low emulsifier concentration samples, which separated quickly), and although they all creamed, once re-dispersed there was no significant change in the droplet size distribution over this time.

5.1.2 Ceramic Membrane

A similar set of tests were run using similar parameters except for the membrane which was changed for a 1 μm ceramic (titanium oxide) membrane. The emulsifiers and concentrations used were the same as for the SPG membrane, to allow a direct comparison. The parameters of the experiments can only really be thought of as equivalent to the SPG tests, as the different porosity and physical characteristics of the ceramic membrane mean that the droplets are formed in a slightly different way. Droplets forming at the membrane surface are not necessarily subject to the same forces with the ceramic membrane as with the SPG. The membrane module was setup similar to the experiments run with the SPG membranes, with 0.6 ms^{-1} cross flow velocity and 10 kPa trans-membrane pressure. Once again the system was run until the emulsion had a phase volume of 1%.

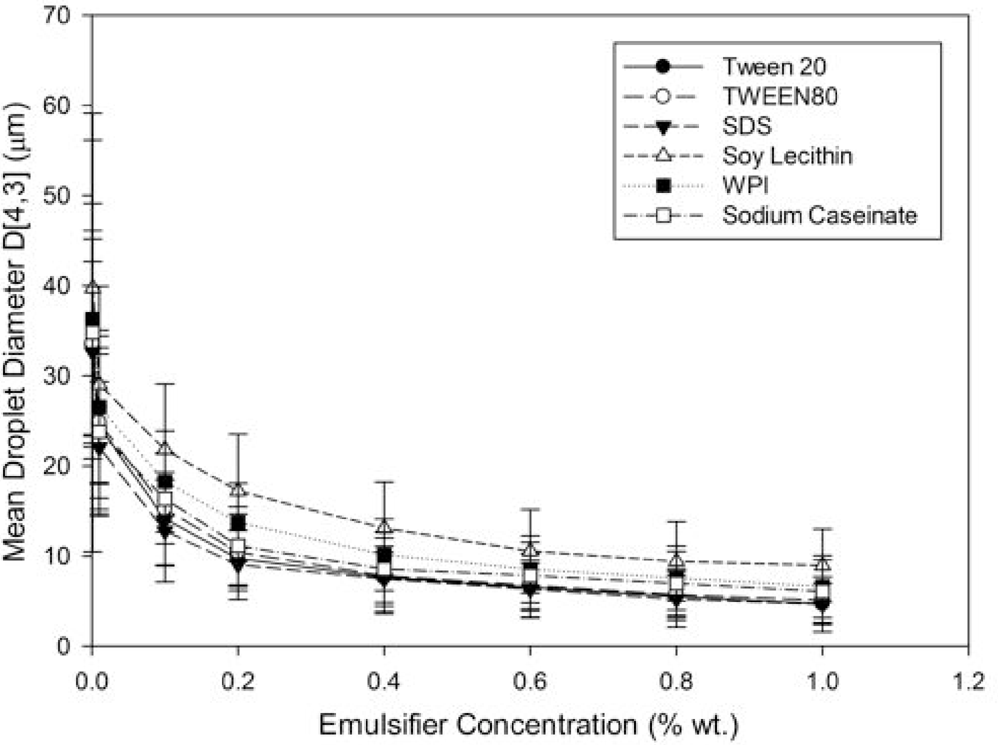


Figure 5.4. The effects of emulsifier concentration on the sunflower oil droplet size in water at a dispersed phase volume of 1%, produced by a 1 μm pore size ceramic membrane, at a pressure of 10 kPa and a cross-flow velocity of 0.6 ms^{-1}.

As can be seen from the graph (Figure 5.4), the emulsifiers still reduce the mean droplet size produced with increasing concentration, although the droplet size does not reach such a well defined minimum as it did using the SPG membrane; that is to say the droplet size continues to reduce with increasing emulsifier concentrations unlike the SPG membrane which reached a minimum droplet size at a lower emulsion concentration. The droplet size distribution span follows the sam trend as it did with the SPG membrane.

The localised decreasing in concentration of emulsifier within the ceramic support material as the emulsifier is used up as droplets form may also account for some of this effect. The morphology of the ceramic membrane is such that the surface of the membrane itself is shielded from the cross flow by the support material, and forming droplets are therefore subjected to a lower shear force than if they were being formed on the surface exposed to the flow of continuous phase. This effect is discussed further in the section regarding cross-flow velocity (section 4.3). The membrane itself is coated onto the inside of the ceramic support material tube, as described in chapter 4. Because the cross-flow system is set up to pressurise the dispersed phase out from inside the tube (although it could easily be setup to run the outside to inside, for these tests it was decided to run inside to outside as explained in chapter 4), the dispersed phase is therefore pushed through the membrane first followed by the support, the droplets forming as the dispersed phase emerges from the membrane layer into the support layers. The support will have larger voids filled with continuous phase, however these will become locally depleted of emulsifier as droplets are formed, using up emulsifier from the continuous phase trapped within the support material. This emulsifier will be replenished from the bulk by diffusion, which will happen more quickly at higher emulsifier concentrations, which may well explain how the droplet size continues to decrease at higher concentrations where the SPG membrane does not. This effect may not happen when the ceramic membranes are used with the dispersed phase pressed in from outside the tube, as the dispersed phase will pass through the support material first and then through the membrane, emerging as droplets directly into the bulk continuous phase.

Except for this phenomenon the results are quite similar to those of the SPG membrane, with the emulsifiers with higher HLB producing smaller droplets overall, and decreasing the droplet size faster with increasing concentration.

The ceramic membranes, as the SPG ones, produce emulsions easily with the CFMED setup used. The ceramic membranes are easier to handle than the SPG, as they are far more robust, and are much easier to install into the membrane module. The ceramic membrane showed a slightly higher flux than the SPG membranes (1.5 to 2 times the flux of the SPG in this case), with the 500 ml of emulsion at 1% dispersed phase being made in between 1 and 3 minutes at the pressure and cross-flow velocity used in these tests. It should be noted that the flux rate of oil through the membrane is not controlled during these experiments, rather the pressure applied to force the oil through the membrane. Although the flux through the ceramic membranes is slightly higher than that of the SPG the flux rate itself is a dependant variable and a larger flux will not in of itself give rise to larger droplets, simply the experimental setup resulting in the higher flux (higher pressure, higher porosity etc.) is also the cause of the larger droplet diameters seen. An increase in flux due to higher emulsifier concentration for example, results in smaller droplets at the same time. The stability of the emulsions produced was similar to the SPG emulsions.

5.1.3 Polymer Membrane

The 1 µm polymer membrane was used to perform similar experiments to see the effects of changing emulsifier concentration. The polymer membranes are different again from the previous two membrane types, since they possess a thicker wall, and being less easily wetted by water (the continuous phase). The same tests were run, at 0.6 ms^{-1} cross flow velocity and 10 kPa trans-membrane pressure. The dispersed phase was allowed to flow through the membrane until 1% dispersed phase volume was reached, as in the previous tests. The polymer membrane is much cheaper than the other membranes used, and comes on a roll, so the membrane itself is consumable, and thrown away after 1 day or when the dispersed phase is changed. The results from the tests using different emulsifiers with the polymer membranes were as shown in Figure 5.5.

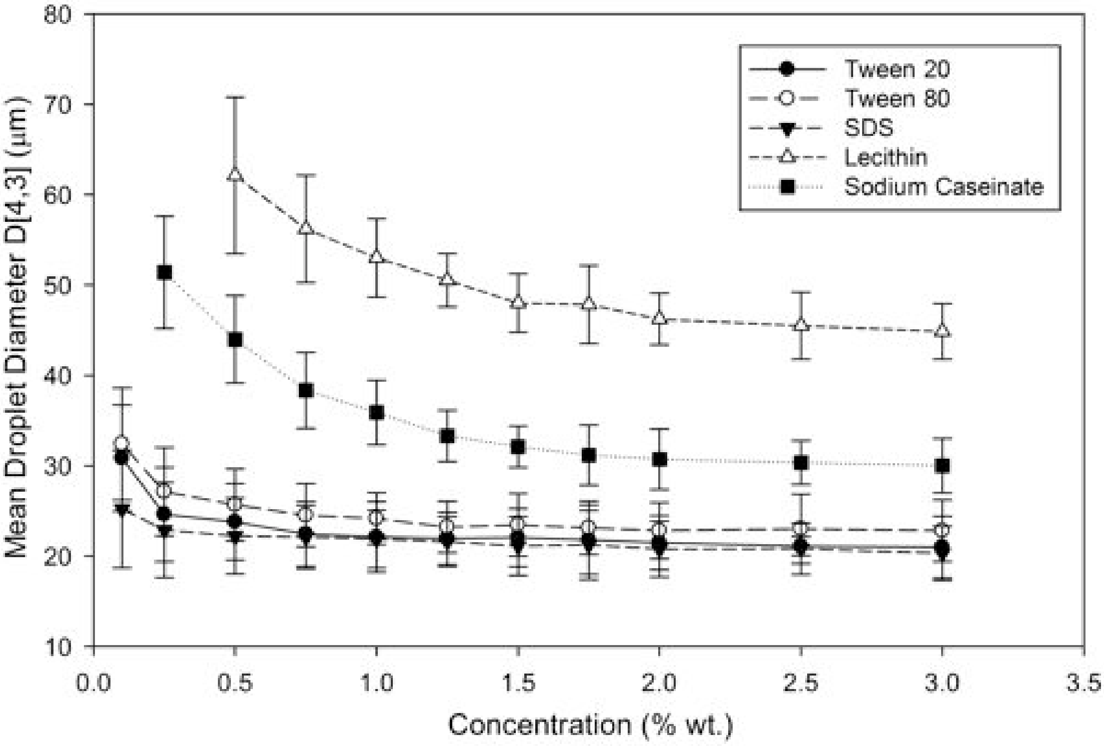


Figure 5.5. The effects of emulsifier concentration on the sunflower oil droplet size in water at a dispersed phase volume of 1%, produced by a 1 μm pore size polymer membrane, at a pressure of 10 kPa and a cross-flow velocity of 0.6 ms^{-1}.

Although the pore size used was the same as for the SPG and ceramic membranes, the droplets produced were larger and had a wider size distribution than either of them at similar emulsifier concentrations. Some example size distributions for the emulsions produced are shown in Figure 5.6.

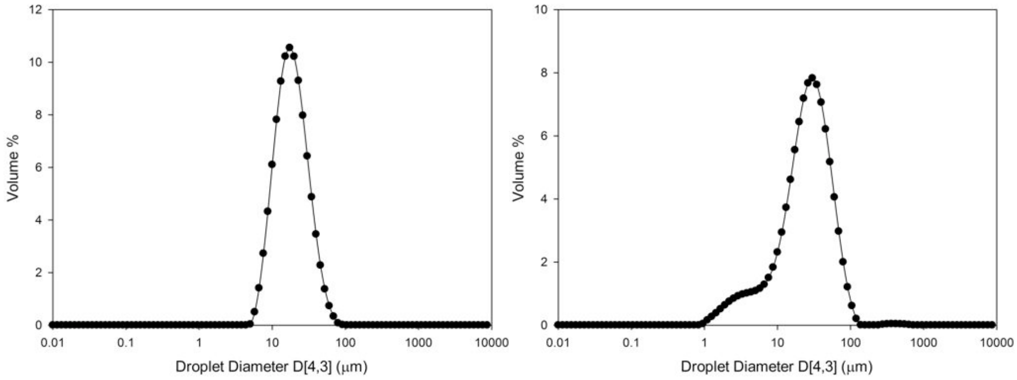


Figure 5.6. the size distributions produced using the polymer membrane. The left distribution was produced using 1 % wt. Tween20 as the emulsifier having an average droplet size of 22.072 μm and a span of 1.497, the right graph shows the distribution of droplets produced using only 0.01 % wt. of Tween20, and has an average size of 32.910 μm and a span of 2.018

The polymer membrane seems to produce a larger diameter droplet than a similar pore sized SPG, polymer or stainless steel membrane under any circumstances, and for this reason the emulsifier concentration was increased further than the other membranes to see if the size decreased eventually with high concentrations (which it didn't). This effect is probably due to the higher porosity of the polymer membrane, meaning that droplets are actually formed from several adjacent pores instead of each one at a single pore, as suggested in the literature (Lepercq-Bost *et al.,* 2010).

Although the droplet size still decreases with increases in emulsifier concentration, it never reduces to the small sizes of the previous two membrane types.

The polymer membrane has a very thick wall, and this has been shown to increase the levels of coalescence in other membrane types (Gijsbertsen-Abrahamse *et al.,* 2004), this effect is because the thicker membrane decreases the effect of local reduction of pressure around an active pore, which usually stops adjacent pores from becoming active with thinner membranes, but this effect does not happen as much with thicker membranes.

The wetability of the polymer with continuous phase is less than for the other two membrane types, although this is not true of all polymer membranes. The pore structure itself is quite similar to that of the SPG membrane, indeed the pores are formed by phase inversion in a very similar way to those of the SPG membranes. The surface of the membrane looks very much like a sponge under the light microscope. Because of this similar structure it is probable that the cause of the larger droplets and droplet distributions is the increased porosity, factors due to the increased membrane thickness, or the material surface properties, or a combination of all three. The stability of the emulsions was slightly less with the polymer membranes than the previous two with a slight increase in mean droplet size and a widening of size distribution over the six week period. The membranes themselves were easy enough to handle but fitting them to the membrane module was sometimes problematic because of the flexibility of the material. The flux through the membrane was comparable to the ceramic membrane, taking between 1 and 3 minutes to produce the 500 ml of emulsion made in each of the tests for this experiment.

5.1.4 Stainless Steel Membrane

The stainless steel membrane is totally different from all the other membranes tested in that the pores are of a specific size and shape. Rather than being random, convoluted paths, the pores are as they were drilled; straight through the tube perpendicular to the surface, round, and 15 μm in diameter (as described in chapter 4). The tests with the metal membrane were carried out in the same manner as the previous tests, using various different emulsifiers, but keeping the 0.6 ms^{-1} cross-flow velocity, and the 10 kPa trans-membrane pressure. The results of the tests with the stainless steel membrane in the CFMED are shown in Figure 5.7.

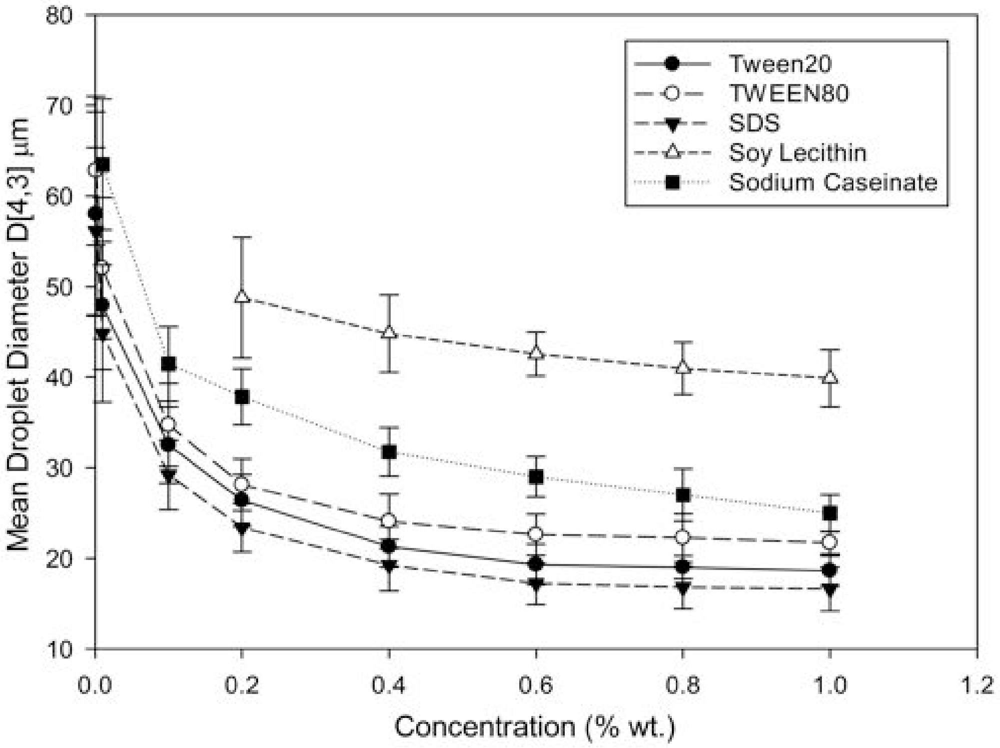


Figure 5.7. The effects of emulsifier concentration on the sunflower oil droplet diameter in water at a dispersed phase volume of 1%, produced by a 15 μm pore diameter stainless steel membrane, at a pressure of 10 kPa and a cross-flow velocity of 0.6 ms^{-1}.

Once again, the stainless steel membrane shows similar results to the SPG membrane when the similar tests are run. The larger pore size of the stainless steel membrane means the overall droplet sizes will be larger than with the other membranes. The increase in concentration of emulsifier causes a corresponding decrease in the size of the droplets, and also a decrease in the range of sizes being produced.

The exact results of the emulsifier tests are not directly comparable as the stainless steel membranes have a pore diameter around 15 μm, and therefore droplets much smaller than this will not be produced.

The larger droplets require larger concentrations of emulsifier as they are less thermodynamically stable, so the decreases in droplet size are at higher emulsifier concentrations when compared to the SPG membrane (and the other membrane types previously tested).

Larger concentrations of emulsifier will be required to stabilise the larger droplets, although the total surface area of interface to be stabilised will be less for the same dispersed phase volume. Once again the system was run to make 500 mls of emulsion at a dispersed phase volume of 1%. The stainless steel membrane is of a smaller surface area than the other membranes, with only a 50 mm length of the 250 mm stainless steel tube being drilled (the centre section). The porosity of the membrane is also much lower than the other membranes, but the pores themselves are much larger decreasing the pressure required to produce emulsions. For this reason the stainless steel membrane had a similar flux rate to the other membranes with the emulsions made in between 2 and 3 minutes each. Whilst the droplets themselves were larger than the other membranes the size distribution spans were smaller than those seen using the polymer membranes, an example is given is Figure 5.8.

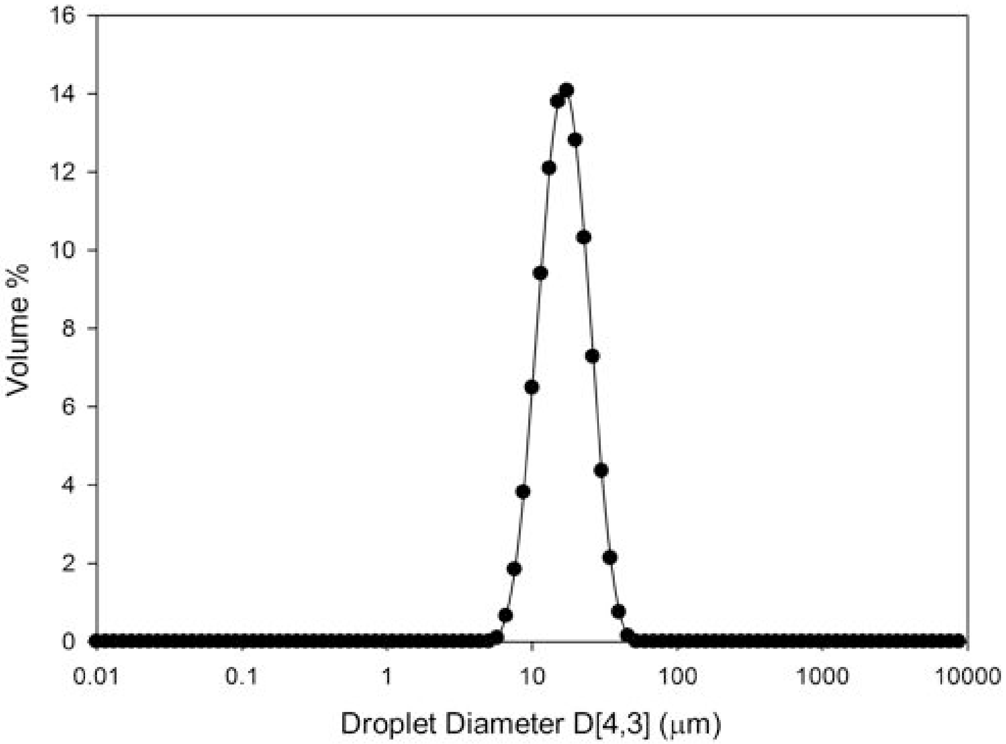


Figure 5.8. A typical droplet size distribution produced from the stainless steel membrane. The emulsion was made using 1% wt. Tween20, to emulsify sunflower oil into water at 1% phase volume, and 10 kPa trans membrane pressure. The average droplet size is 18.885 μm, and the span is 0.998.

Also the droplet size was much less than twice the pore size, making the droplets produced the lowest droplet size to pore size ratio of all the membranes tested. The stainless steel membrane was the easiest to use us it is both robust, and easy to clean between runs. The larger droplets meant that the emulsions were not as stable, with the lower concentration lecithin emulsions not being stable enough to get a meaningful measurement from the mastersizer.

5.2 Effect of Pressure

The pressure applied to the dispersed phase to force it through the membrane pores causes changes of the droplets which are formed as the liquid is forced out of the membrane into the continuous phase. One of the forces involved in the detachment of droplets from the membrane surface from the literature (Schröder et al., 1998) is inertia of the dispersed phase as it travels through the pores, and into the forming droplet. The pressure applied to the dispersed phase to force it through the pores governs the rate at which the dispersed phase flows through the pores and therefore the inertia applied to the forming droplet. Another effect from the literature of the applied pressure is the activation of the pores (Gijsbertsen-Abrahamse *et al.,* 2004); the higher the pressure the more pores are activated until the dispersed phase is flowing through all possible pores. The applied pressure also has to exceed the pressure on the other side of the membrane in the continuous phase, and so the relevant pressure is actually the difference between the pressures on either side of the membrane, or the trans-membrane pressure (P_{tm}). The minimum pressure required to force dispersed phase through the membrane and form droplets can be estimated according to the literature (Nakashima, US Patent 5326484, 1994) using the equation for capillary pressure (as detailed in the literature review, chapter 2.1) and it can be seen from this that the minimum pressure required is inversely proportional to the pore size, i.e. a halving of the pore size will double the minimum pressure required before droplets are formed. In practice the minimum pressure is not easily estimated from the capillary pressure equation (also as reported in the literature) for all the different membrane types because of the complexity of the structure of the pores (the equation assumes an ideal pore) and the different membrane types, and so the minimum pressure was always found experimentally by incrementally increasing the pressure until droplets were formed.

Each membrane type was tested by using the cross-flow system to produce droplets at several different pressures, whilst keeping all other factors of the system constant. The pressure is generally thought to have the most effect on the flux of the dispersed phase rather than droplet size, but this effect is dealt with later in this section. The first tests in this experiment were performed using the ceramic and SPG membranes, as they were available earlier than the others. The CFMED was used to make 500 ml of emulsion for each test, consisting of 1% Tween20 in the continuous water phase, and sunflower oil as the dispersed phase, at a phase volume of 1%. The system was run at a continuous phase velocity of 0.6 ms^{-1}. The effects of changing pressure on the droplets produced by both the SPG and ceramic membranes at 1 µm pore size are shown in Figure 5.9.

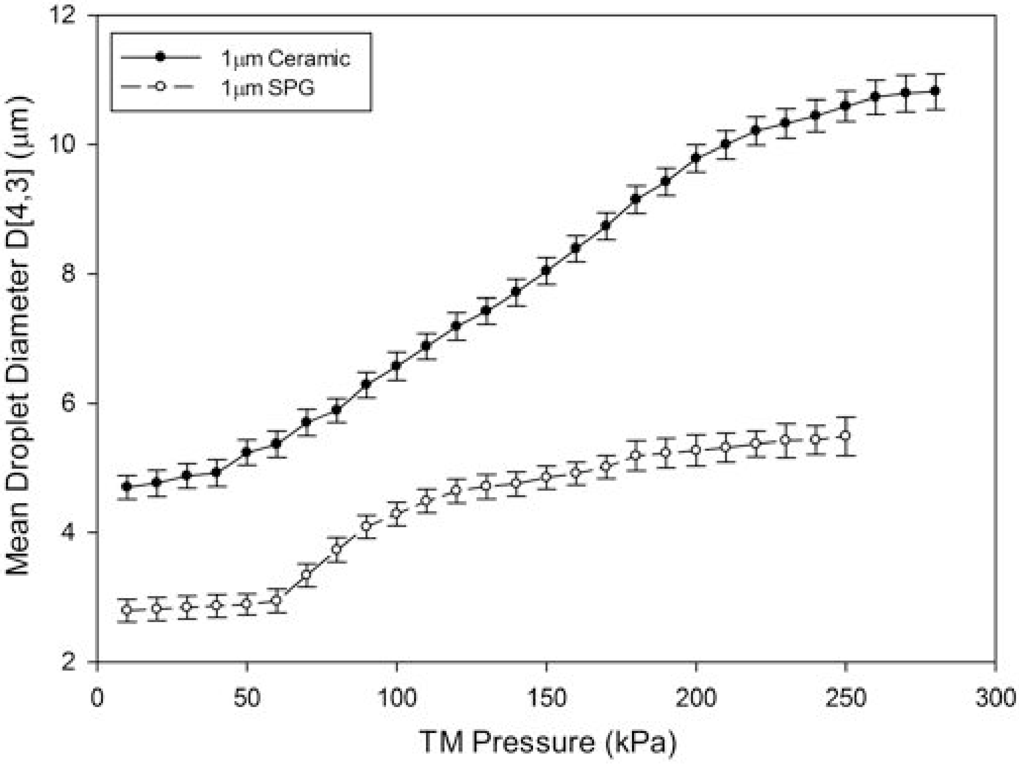


Figure 5.9. The effects of changing pressure on the droplet size produced of sunflower oil dispersed into water containing 1% Tween20, at 0.6 ms^{-1} cross-flow velocity.

The results show that increasing pressure increases droplet size. This is in general agreement with the literature (Williams *et al*., 1998), however the magnitude of the increase is perhaps surprising, with the size of the droplets more than doubling with the ceramic membranes. The SPG membrane shows less of an increase.

Perhaps more interesting is the way in which the size increases, which is not linear, increasing slowly at first from the critical pressure, then the increase in droplet size becomes faster, until it starts to level off towards the end of the curve. The effect is more pronounced with the SPG membrane, but the increase is larger overall for the ceramic.

Pressure is intrinsically linked with cross-flow velocity, increasing the cross-flow velocity changes the results from increasing the pressure. The increase in pressure causes the growth of droplets at the pores to occur faster, and the higher pressure of the fluid inside the growing droplets allows their shape to be held better, and so they become larger before detachment. This is countered however by increasing the cross-flow velocity and hence the shear force applied, to break the droplet from the pore sooner. Figure 5.10 shows what happens when tests are run using an SPG membrane varying the pressure applied to the dispersed phase at several different cross-flow velocities. Once again the membrane is a 1 μm pore size, and the formulation is sunflower oil in water with 1% wt. Tween20 as the emulsifier. The tests were run to 1% dispersed phase volume.

Because of the increase in membrane module pressure due to increasing the cross-flow velocity, the actual applied pressure was also increased to keep the required trans-membrane pressure.

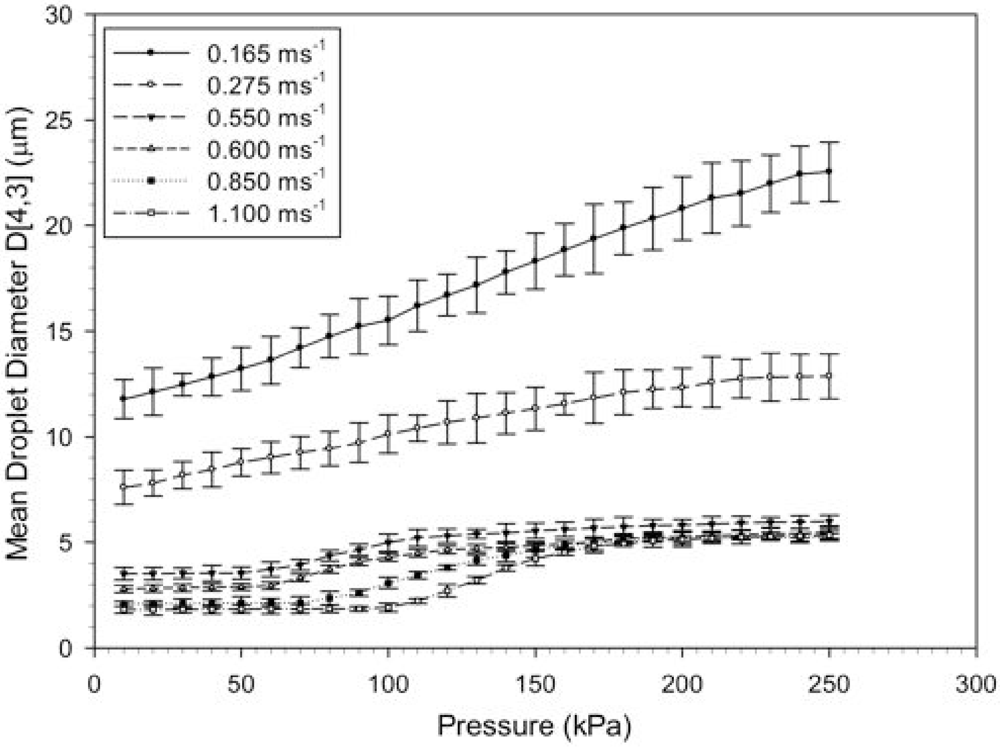


Figure 5.10. The effects of changing cross flow velocity on the droplet size change produced by changing the trans-membrane pressure, using a 1 µm pore size SPG membrane, to make 1% phase volume sunflower oil in water emulsions at 1% phase volume with 1 % wt. Tween20 as the emulsifier.

As can be seen from the graphs, in general, increasing the pressure increases the mean droplet size. In the time between a droplet beginning to form and the time at which it detaches from the membrane, more liquid is forced into the droplet at higher trans-membrane pressures. Whilst this effect is nearly linear when the cross-flow velocity is low, as the cross-flow velocity is increased this effect becomes more and more sigmoidal and at high cross-flow velocities the effect of increasing pressure has three distinct regimes depending on which factor is the prevalent one causing the detachment of forming droplets from the membrane.

Under these higher cross-flow velocity conditions, the first stage at lower pressures corresponds to the droplet detachment regime in which the shear created by the cross-flow velocity is the factor controlling the size at which the droplets detach. The droplets are broken off before they have a chance to grow to their natural detachment size and are the lowest size droplets which can be produced at this cross-flow velocity.

The second stage, when the pressure has been increased, is a stage in which neither the pressure nor the cross-flow shear is the dominant force in droplet detachment, the droplets grow to the maximum natural size at a pore before detaching due to surface tension and buoyancy effects. The higher the dispersed phase flow through the pores (due to the pressure) the faster the growth of each droplet, the greater the droplet size at detachment. During this stage increasing the pressure increases droplet size more quickly than the other two stages.

Continuing to increase the trans-membrane pressure causes the instigation of the third stage of droplet detachment, which is that of an injection regime, the pressure is sufficient to force a constant stream of dispersed phase through each pore, which then breaks up due to Raleigh instabilities in the stream. This produces the largest droplets possible at the specific cross-flow velocity, and entering this regime causes a further increase in droplet size distribution span (as shown in Figure 5.11), as many different primary and satellite droplet sizes are produced. Some typical size distributions are given in figure 5.12. Increasing the pressure further past this point seems to have little real effect; the mean droplet diameter seems to plateau at this point for the specific membrane and cross-flow velocity conditions (the equipment also limits the further investigation of higher pressures as the dispersed phase tank is only designed for 300 kPa maximum). If the droplets were still being formed by detachment rather than streaming, the droplet size would continue to increase until the oil simply poured through the membrane and pooled around it;

since that does not happen at any pressure the streaming regime must be the final droplet breakup regime.

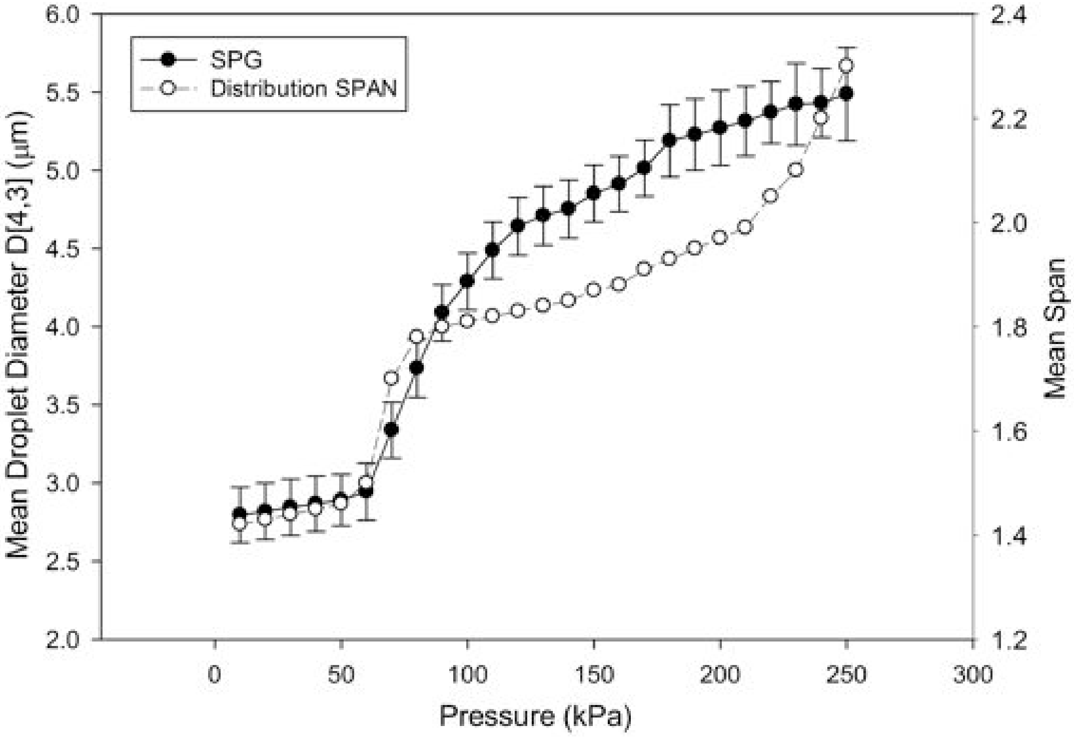


Figure 5.11. The effects of pressure increases on the size distribution span of droplets produced during the SPG pressure experiments.

Also, as the rate of droplet formation increases with increasing pressure, the rate of interface formation increases, but the rate of adsorption of emulsifier remains the same, and so interfacial tension is reduced more slowly relative to the formation rate. This effect cannot be significant as if it were increasing cross-flow velocity would not decrease droplet size, as a greater surface area of interface would need to be formed faster to cover the smaller droplets produced at the same flux rate.

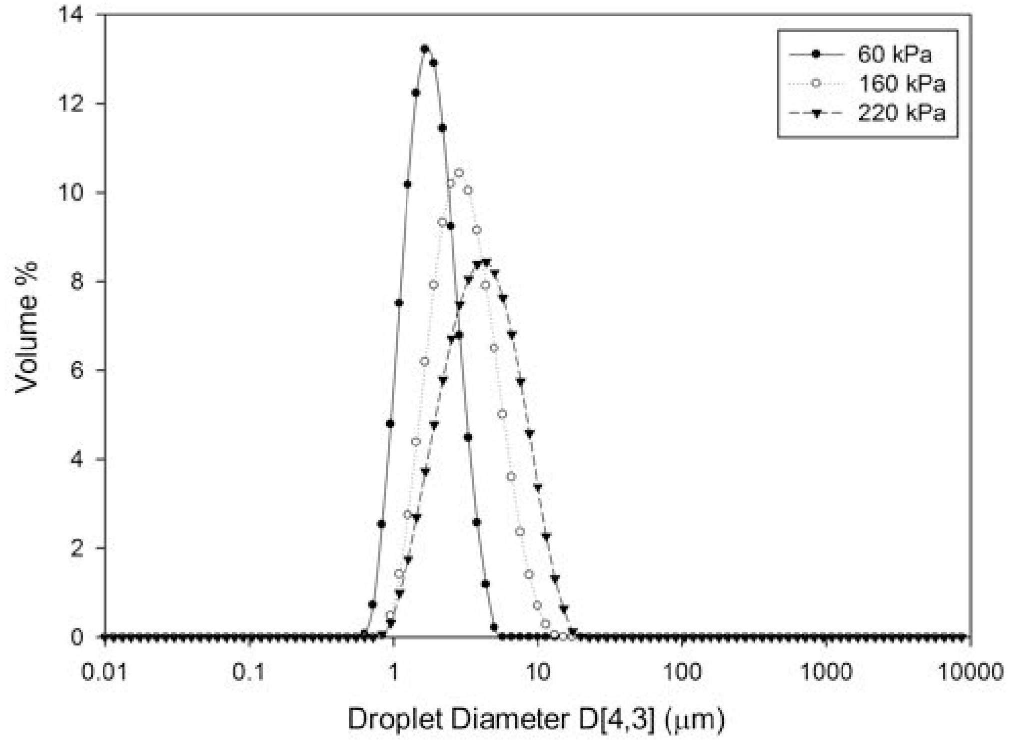


Figure 5.12. shows some typical size distributions from the same 1 μm pore size SPG membrane run at different pressures. This illustrates not only how the average droplet size increases with pressure, but also the width of the size distribution.

At low cross-flow velocities, the increase in droplet size is linear, with no obvious changes in the way that droplets are detached from the membrane. This shows that the effects of the cross-flow induced shear are lower than the effects of pressure at all the pressures tested, and so the droplets are detaching under the effects of inertia of the dispersed phase, and surface tension. The droplets at these low cross-flow velocities are much larger, some over twenty times the pore size, suggesting that they are resident at the pore for much longer in these lower shear conditions, it is clear that the shear across the membrane surface has a larger effect on droplet size than pressure. At higher pressures and low cross-flow velocities it is likely that the droplets are either still transitioning to an injection regime, and the difference in droplet size this produces is negligible compared to the large droplets produced in the low shear conditions, or that the larger droplets forming at the pores simply absorb the increased flow through the pores until they detach, and so stopping the transition to an injection regime until even higher pressures.

The different membrane types each react slightly differently to changes in the trans-membrane pressure. This difference in pressure profile can be related to the structural and surface chemistry differences between the membranes. The results for the polymer and stainless steel membranes are shown in Figure 5.13.

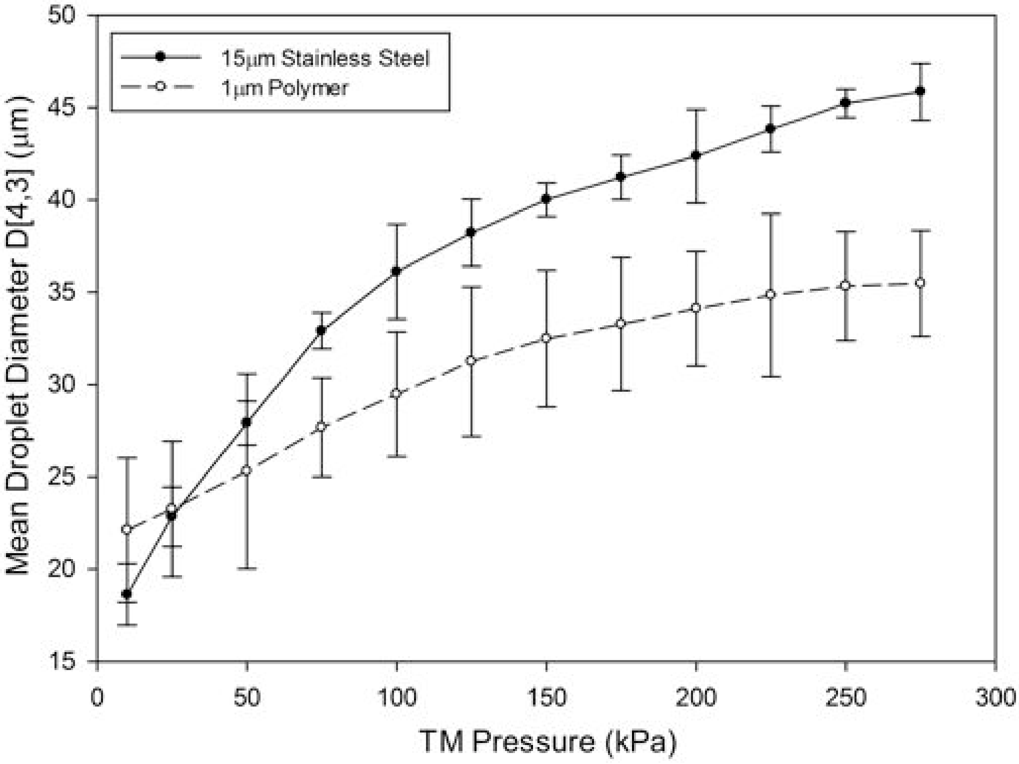


Figure 5.13. The results of producing emulsions at different pressures with the stainless steel and polymer membranes in the CFMED.

The large pores of the stainless steel membrane mean that the critical pressure for emulsion formation is lower, and the droplets produced by the membrane increase in size quickly with pressure. The increase is beginning to plateau toward the high end of the applied pressures. The large pores provide much less resistance to the dispersed phase. The polymer membrane droplets increase in size much more slowly with increases in pressure, since each droplet is likely to be formed at several pores, and with a high resistance due to the thick membrane wall, it is quite likely that the flow through the pores does not form a consistent stream, instead just produces droplets over larger groups of pores more rapidly.

The literature showed an increase in pressure causing an increase in droplet size (Williams *et al.,* 1998), which is consistent with the results shown here. The pressure also has an effect on how the droplets are formed in membrane emulsification which means that the pressure a system runs at should be carefully chosen depending on the required output; small narrow size distribution droplets are produced at low to mid pressures, with the smallest just above the critical pressure for droplet formation. At higher pressures flux is greatly increased, which is an advantage if particularly narrow size distribution is not important.

Pressure also affects the trans-membrane flux of dispersed phase. The flux rate of dispersed phase through the membranes is of vital importance to the possibility of any kind of industrial use of membrane emulsification. Making perfectly identical droplets is useless if it takes several seconds to make each one. To achieve a sensible level of flux the membrane choice will again be important, but so will the operating pressure, along with many of the other factors discussed during this study. To give an idea of the flux rates achievable, the amount of dispersed phase which crosses a given area of membrane in a given time was investigated for each of the membrane types and at several pressures. The results are not really like for like given the different droplet sizes produced by the different membranes, but do give a rough idea of the flux rates which are possible with each membrane. The results are shown in Table 5.1.

Membrane type	Trans-membrane pressure (kPa)	Measured flux rate (mlm^{-2}s^{-1})
SPG 1 µm pore size	10	5.21
	20	15.5
	40	37.1
	100	83.1
	250	238
Ceramic 1 µm pore size	10	10.3
	20	27.8
	40	63.7
	100	162
	250	440
Polymer 1 µm pore size	50	74.1
	250	435
Stainless Steel 15 µm pore size	10	27.9
	50	139
	250	726

Table 5.1. The data from the flux rate calculations for the different membrane types at different pressures. The results were produced by making emulsions at 1% dispersed phase volume and measuring the time taken to flow the 5 ml of dispersed phase. The emulsions were made at a cross-flow velocity of 0.6 ms^{-1}, and using 1% wt. Tween20 as the emulsifier.

From the results it can be seen that the stainless steel membrane has the highest flux rate of the membranes, this can't be taken as a fair comparison however, as the pore size is much larger than the other membranes tested. From the other three membrane types, the ceramic had the highest flux rate, followed closely by the polymer membrane (which took longer to flow the dispersed phase than the ceramic, but because of the smaller diameter and therefore surface area had a very similar flux rate). The SPG membrane had the lowest flux rate of the three. As was shown in previous studies (Schröder *et al.*, 1998), the flux rate is roughly proportional to the pressure, so long as all the pores are active, i.e. not necessarily at lower pressures close to the critical pressure.

5.3 Effect of Cross Flow Velocity

The speed with which the continuous phase is pumped across the surface of the membrane is measured as the cross-flow velocity. This is in fact the linear fluid velocity of the continuous phase in the channel around the membrane in the membrane module. In practice the actual speed of the fluid will be near zero at the membrane surface, and will increase up to a maximum before the mid point of the channel, and decrease to near zero again at the wall of the membrane module. The pump was calibrated by measuring the volume of fluid pumped in a given time, at each pump setting, and this translated into a linear cross-flow velocity using the surface area of a section of the membrane channel.

Changing the cross flow velocity of the continuous phase across the surface of the membrane changes the forces applied to the forming droplets of dispersed phase as has already been shown as part of the pressure results (section 4.2). The shear rate applied by the continuous phase can be estimated from the formula;

$$\dot{\gamma} = \frac{8V_{cf}}{D_H} \qquad \text{equation 5.1}$$

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. The viscosity of the fluid is not considered in the shear rate (only in shear stress), and so the shear rate is directly proportional to cross-flow velocity. Some shear rates are given in Table 5.2.

Cross-Flow Velocity (ms^{-1})	Shear rate $\dot{\gamma}$ (s^{-1})
0.1	200
0.3	600
0.5	1000
0.8	1600
1.1	2200

Table 5.2. Some shear rates through the membrane module at different linear cross-flow velocities.

In practice the shear rate will be higher in a turbulent flow, and so the Reynolds number of the flow at different velocities and with different viscosities of continuous phase was calculated using;

$$\mathrm{Re} = \frac{\rho V_{cf} D_H}{\mu} \qquad \text{equation 5.2}$$

Where Re is the Reynolds number, ρ is the density of the fluid (kgm^{-3}), V_{cf} is the velocity of the fluid (ms^{-1}), μ is the dynamic viscosity of the fluid (Pa•s) and D_H is the hydraulic diameter of the channel (m). The hydraulic diameter being defined as 4 times the cross sectional area, divided by the wetted perimeter, which with the annular gap geometry used can be thought of as the channel diameter minus the membrane diameter. Some Reynolds numbers for the system are given in Table 5.3.

Cross-Flow Velocity (ms^{-1})	Reynolds Number
0.1	400
0.3	1200
0.5	2000
0.8	3200
1.1	4400

Table 5.3. Some example Reynolds numbers assuming a water continuous phase, at different linear cross-flow velocities.

The Reynolds numbers show that assuming a water continuous phase, the flow will begin to transition to turbulent at around 0.5 ms^{-1} (Re 2000), and becomes fully turbulent at around 1 ms^{-1} (Re 4000). It is interesting to note that the Reynolds number would be twice as high at the same cross-flow velocity if the continuous phase were flowed along the centre of the membrane tube.

To test the effects of varying the cross-flow velocity on the CFMED, the system was used to make sunflower oil in water emulsions at several different cross-flow velocities. The emulsions were made using 1% Tween20 as the emulsifier, initially with the 1 µm SPG and ceramic membranes. The trans-membrane pressure used was membrane specific, and was chosen to correspond to equivalent points on the pressure curves of the membranes used. The applied pressure was varied to keep the trans-membrane pressure correct, as the membrane module pressure varies with changes in the cross-flow velocity. The results of the cross-flow velocity tests are shown in Figure 5.14.

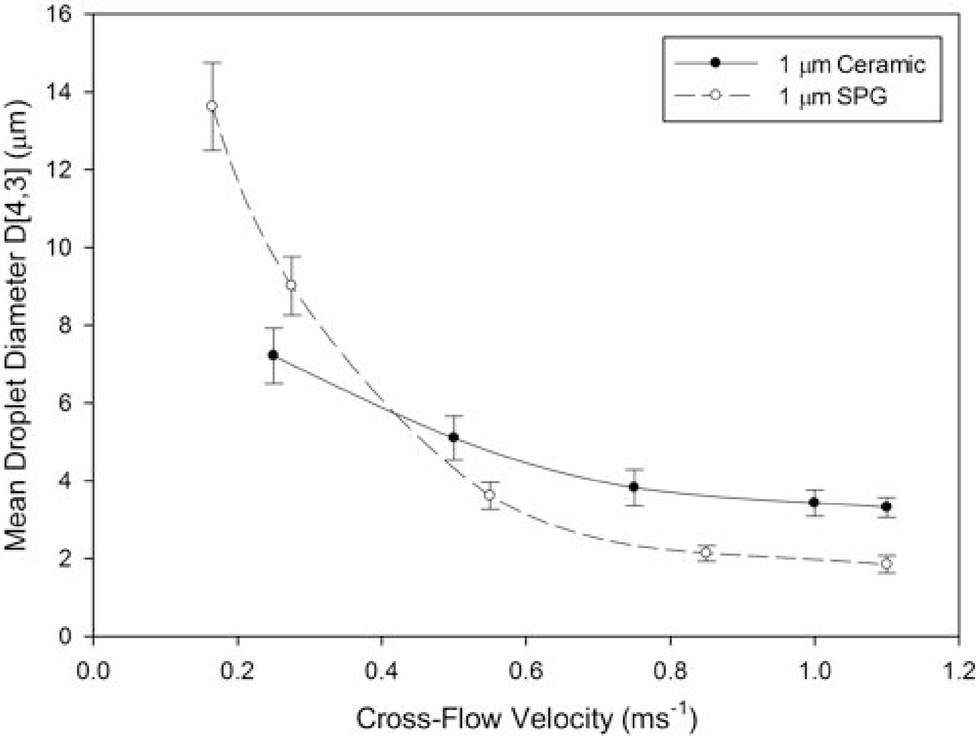


Figure 5.14. The changes in droplet size due to increasing cross-flow velocity, and therefore shear rate at the membrane surface. The tests were run using a 1 μm ceramic and a 1 μm SPG membrane. The effect of increase in cross-flow velocity has a greater effect on droplets produced using the SPG membrane.

To test the effects of different trans-membrane pressures on the effects of changing the cross-flow velocity, the tests were repeated at several different pressures for the SPG membranes, and the results are shown in Figure 5.15.

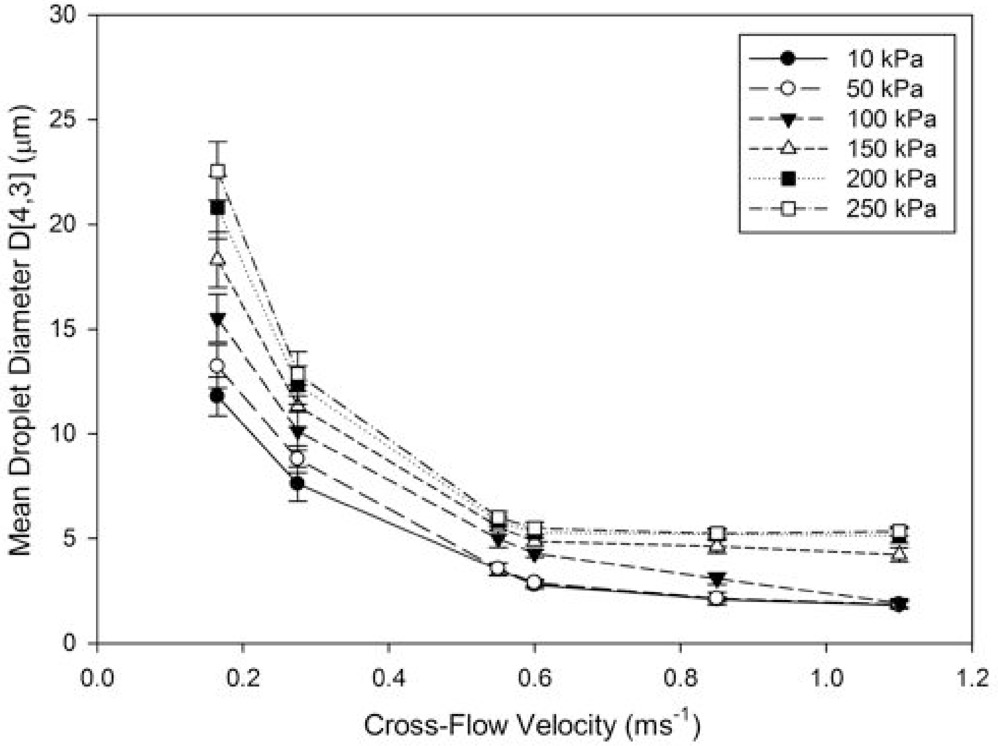


Figure 5.15. The effect of changing the cross-flow velocity at different trans-membrane pressures on the droplet sizes produced, using a 1 μm SPG membrane to produce sunflower oil droplets in water, using 1% wt. Tween20 as the emulsifier.

Increasing the cross flow velocity raises the shear rate at the membrane surface; this in turn reduces the average droplet size of the emulsion droplets produced. The effect of cross-flow velocity is the most important and powerful factor governing cross-flow emulsification.

The action of the shear on the detachment of droplets from the membrane surface can cause the produced droplets to be smaller than the pore size. A schematic representation of the probable mechanism for this is shown in Figure 5.16.

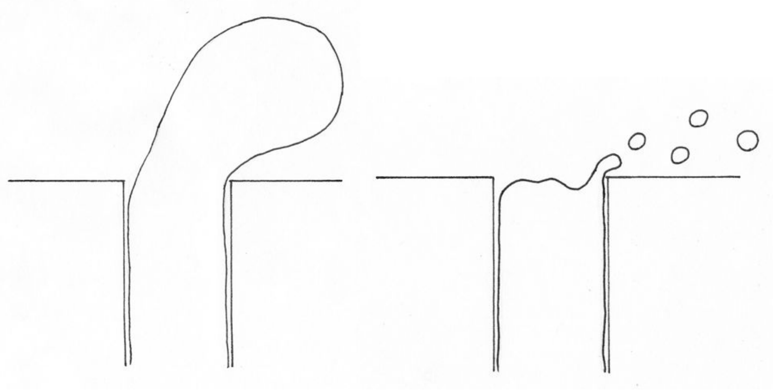


Figure 5.16. Schematic diagram to illustrate the change in the mechanism of droplet formation at low (left) and high (right) shear rates.

The ceramic membrane has a support material covering the outside of the membrane tube, this partially shields the membrane itself from the effects of the shear caused by the cross flow of the continuous phase. Increasing the cross flow velocity still has an effect on the droplet size produced by the membrane. The support material may act to aid the droplet formation in some way, and perhaps the action of the cross-flow velocity is similar to that of a suction pump, pulling the droplets through the membrane and out through the larger channels of the support material. Figure 5.17 shows the difference in the formation of droplets using a ceramic membrane from either direction, i.e. membrane first or support material first.

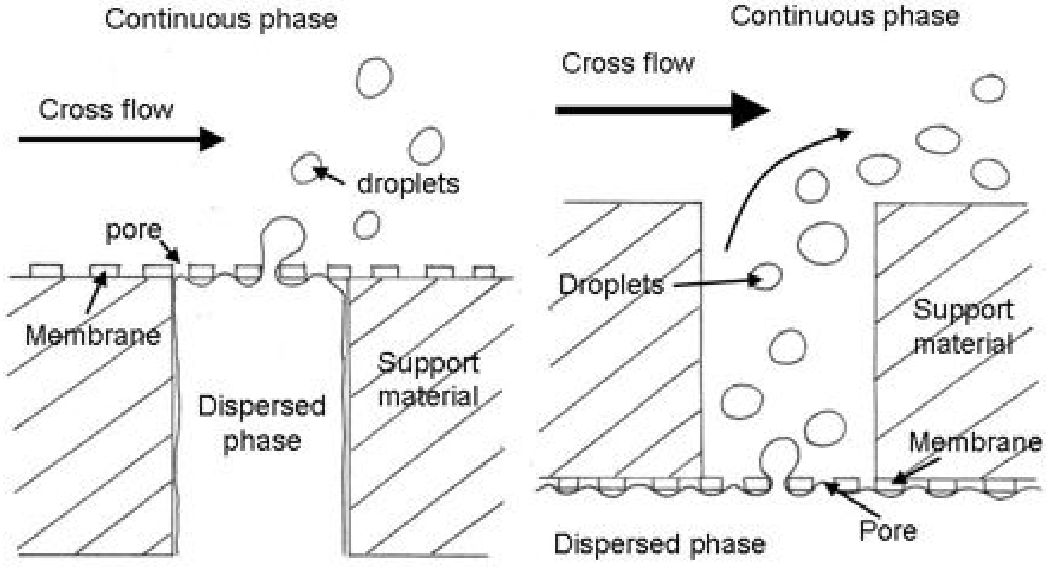


Figure 5.17. Schematic diagrams for when the dispersed phase passes through the support material before or after the membrane. In the case that the dispersed phase passes through the support material first (left diagram), it emerges from the membrane directly into the cross-flow of the continuous phase and is subject to the full shear force. In the case that the dispersed phase passes through the membrane and then the support material (right diagram), the newly formed droplets are not subject to shear, but may be pulled through the support material by the action of the flowing continuous phase in the same manner as a suction pump.

The effect of changing the cross-flow velocities at several different pressures was investigated using a 1 μm ceramic membrane to see how the shielding effect of the support material changed with pressure, the results of which are shown in figure 5.18.

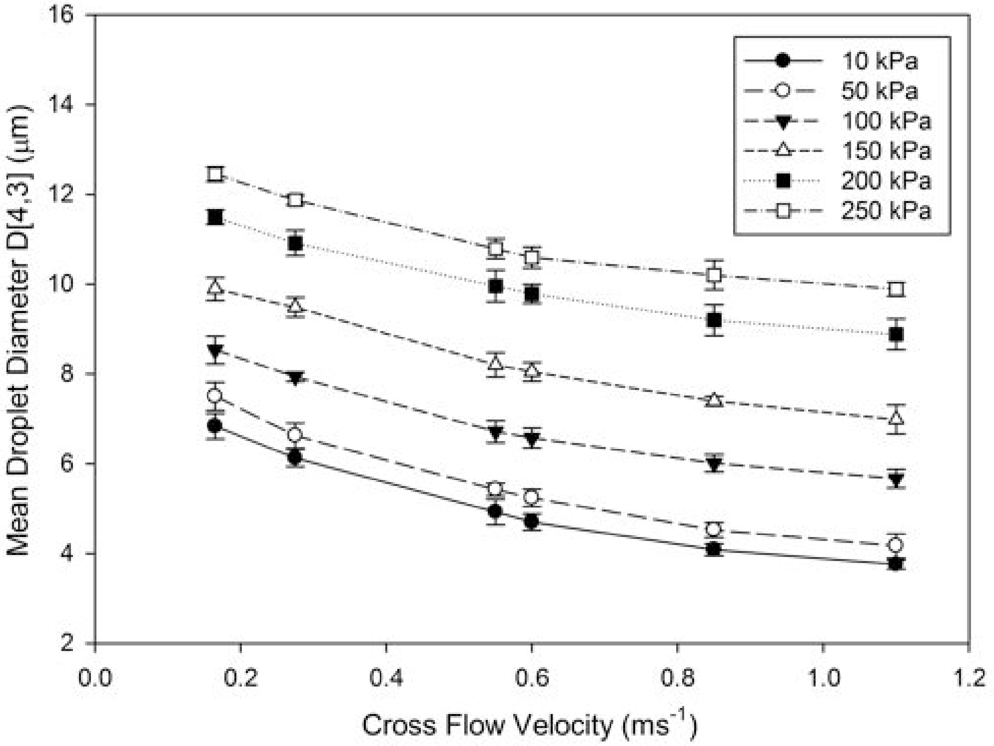


Figure 5.18. The effects of changing the cross-flow velocity when making emulsions using a 1 μm ceramic membrane to make emulsions at several different pressures.

Changing the cross-flow velocity has a similar effect irrespective of pressure when using the ceramic membranes. This is consistent with what is expected with the support material stopping the full effects of the shear increase from being applied to the forming droplets.

The stainless steel and polymer membranes were tested with respect to the cross-flow velocity in a similar way to the SPG and ceramic membranes. Both membranes were run in a series of tests at 10 kPa and several different cross-flow velocities making sunflower oil in water emulsions using 1% wt. Tween20 as the emulsifier. The results are shown in figure 5.19.

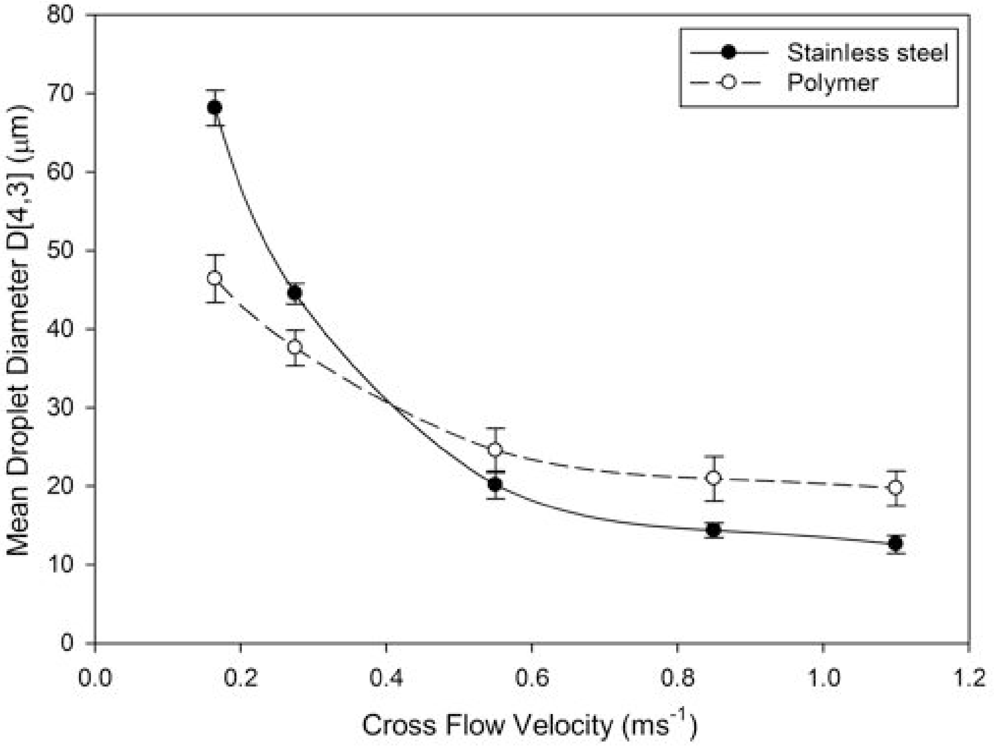


Figure 5.19. The results of changing the cross-flow velocity when making emulsions using the 15 μm stainless steel and 1 μm polymer membranes. The emulsions were made at 10 kPa trans-membrane pressure, with 1 % Tween20 emulsifier.

The larger pore size of the stainless steel membrane makes very large droplets at low cross-flow velocities. The droplet size decreases to less than the pore size at higher cross flow velocities.

The polymer membrane acts as if it has a much larger pore size than it actually does. To be effective as a filter medium it has a high porosity, but for use in membrane emulsification it is probable that the emulsion droplets are being produced from several adjacent pores rather than at each single pore. The thickness of the wall of the membrane tube may well increase this effect. At higher cross-flow velocities the droplet size does decrease significantly (in line with the results from the SPG and stainless steel membranes), however it never decreases to the small droplet sizes seen in the other membranes with similar pore sizes.

5.4 Effect of Pore Size

The pore size of the membrane used to make emulsions with the CFMED is an important factor. The literature suggests that pore size may be the most important factor in membrane emulsification. To test this, the CFMED system was used to make emulsions using similar membranes with different pore sizes. The only membranes available with several different pore sizes were the SPG and ceramic membranes. The emulsions were made using sunflower oil as the dispersed phase, water as the continuous phase with 1% wt. Tween20 as the emulsifier, and at 0.6 ms^{-1} cross-flow velocity. The results of these tests are shown in Figure 5.20.

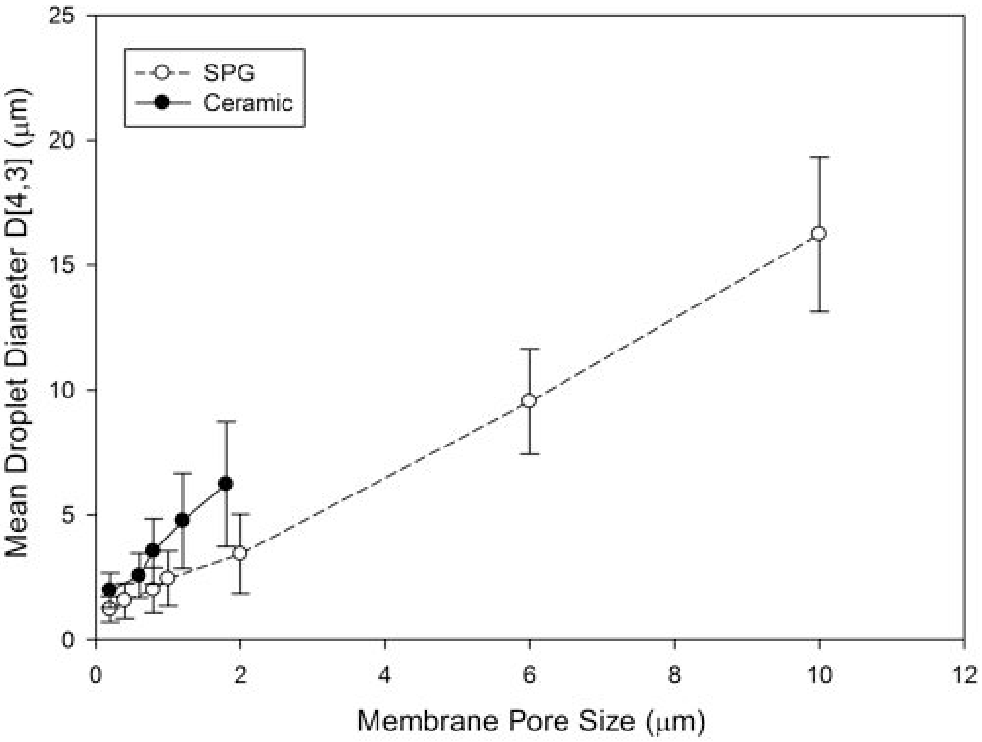


Figure 5.20. The change in droplet size with different membrane pore size. The pore size of the membrane remains one of the most important factors to consider when choosing a membrane for making a specific size of emulsion droplet. 1% phase volume emulsions were made using 1% tween20 as the emulsifier at 0.6 ms^{-1} cross flow velocity.

The droplet size increases proportionally to the increase in pore size. This increase has a multiplication factor specific to the geometry and surface properties of the membrane, i.e. it is fixed for SPG in the same geometry system, but different between SPG and ceramic, for example. This shows that pore size alone is not responsible for the resultant droplet size, but pore shape and structure, and probably the wider membrane structure also have an effect. Some typical size distributions for the different pore sizes are given in Figure 5.21.

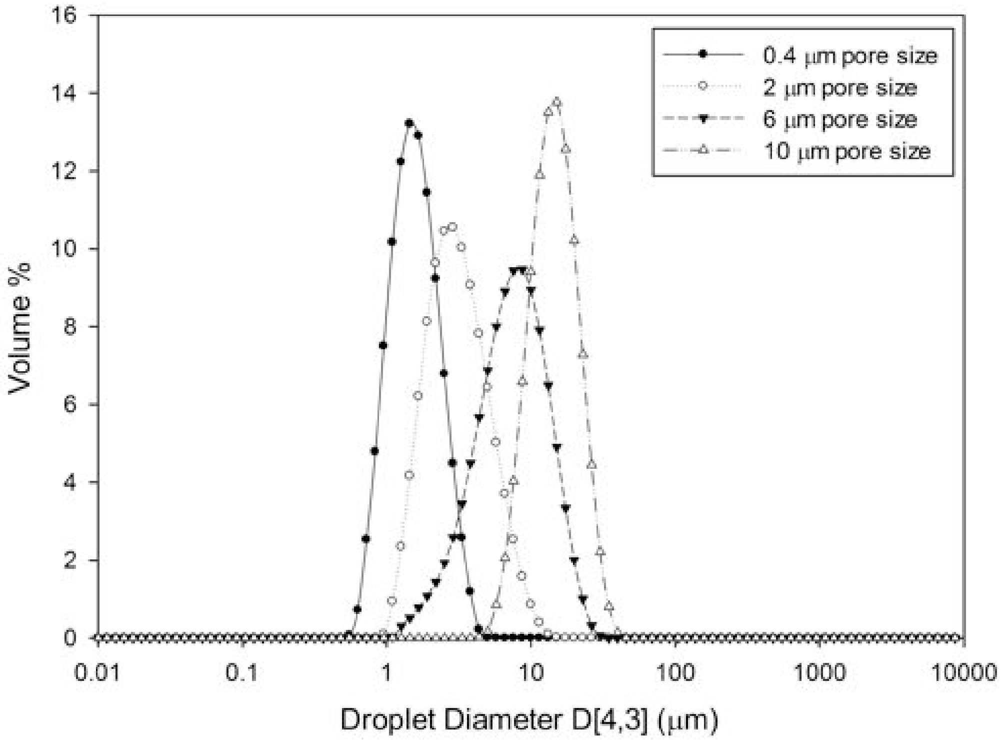


Figure 5.21. Some example size distributions produced making the same emulsion using different pore size SPG membranes.

The pore size distributions show different distributions widths and shapes for the different membranes, in practice each different membrane has a slightly different pore size distribution, and this results in the slightly different shapes of the distribution curves, even between two membranes of the same pore size.

The pore size and the size distribution should be carefully considered when commissioning a membrane emulsification depending on the size and type of droplets to be produced.

The tests were performed using SPG membranes of differing pore sizes whilst keeping other factors as constant as possible.

There are intrinsic problems with the comparison, as changing the pore size also changes the pore size distribution, and the total pore area of the membrane. The pressure drop across the membrane is different and also the trans-membrane flux. This means that setting up the trans-membrane pressure to be ‘equal’ is not relevant, and instead an effort was made to keep the trans-membrane pressure ‘equivalent’.

In general, a larger pore size means a larger produced droplet. Whilst the droplet size distribution increases with increasing pore size, the size distribution as a fraction of the droplet size decreases.

Larger pore size generally increases trans-membrane flux, and decreases the pressure required to flow the dispersed phase through the membrane according to the capillary pressure equation.

Increasing the pore size does also increase the minimum droplet size achievable with the membrane however. To achieve small droplets a small membrane pore size is required. It is possible however, to produce droplets from a membrane which are smaller than the pore size, by running at low pressures and high cross-flow velocities, droplets are detached before becoming fully formed at the pores (see cross-flow velocity, section 4.3).

The decrease in the pressure required to produce droplets using larger pore sized membranes is partly due to the decrease in Laplace pressure of the larger droplets produced, and the lower capillary pressure of the larger membrane pores.

5.5 Effect of Continuous Phase Viscosity

The viscosity of the two phases in membrane emulsification has not been investigated thoroughly in the literature. The effect of changing the viscosities of the two fluids in effect changes the forces applied to droplets forming at the membrane surface, and as such is likely to have an effect on the size and size distribution of the droplets formed. To test this the 1 µm pore size SPG membrane was used to perform a series of tests making emulsions with sunflower oil and water, using 1% wt. Tween20 as the emulsifier in the water phase. The viscosity of the water phase was manipulated by adding glucose until the required viscosity was achieved. The results of the experiment are shown in figure 5.22.

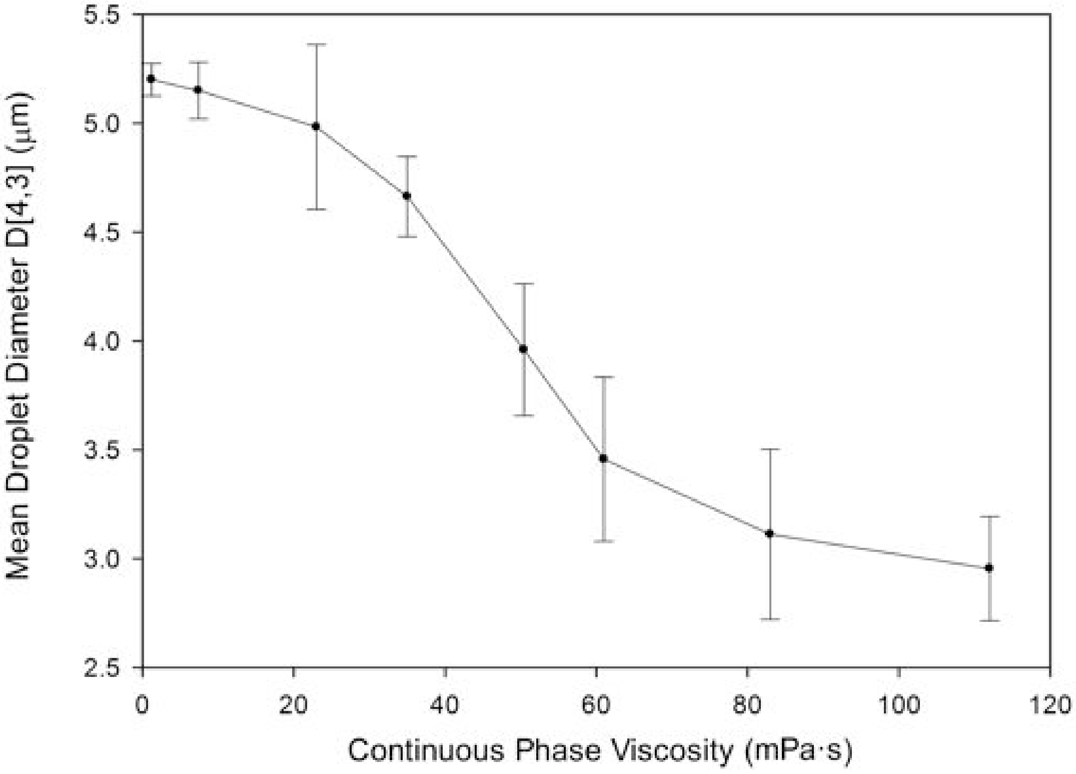


Figure 5.22. The viscosity of the continuous phase has an effect on the droplets produced using a 1 µm pore size SPG membrane making sunflower oil in water emulsions with a 1% wt. Tween20 emulsifier and 0.2 ms^{-1} cross-flow velocity

The results show that the droplet size is larger at lower continuous phase viscosities and lower at higher viscosities, with an unexpected sigmoidal curve to the graph. Interestingly the point at which droplet size changes most dramatically is the point at which the viscosity of the continuous and dispersed phases is roughly equal. The results can be explained by considering the changes in forces applied to the dispersed phase droplets as they form; in the case of higher dispersed phase viscosity than that of the continuous phase, the droplets of dispersed phase are better able to resist deformation by the less viscous continuous phase and so grow larger at the pores before detachment. In the other case, when the continuous phase is more viscous the dispersed phase has more trouble pushing into the viscous continuous phase and is subjected to higher shear stress as a result of the viscosity increase.

Droplet size distribution span is much lower when viscosities are similar, when there are large discrepancies between the viscosities of the two phases, larger size distribution spans are apparent. this effect is due to the droplets either growing for longer than they should at the pores (in the case of lower continuous phase viscosity) and the pore size no longer being the overriding factor in droplet formation, or the droplets being broken from the pore before being fully formed, as is the case for higher continuous phase viscosity, again resulting in the pore size no longer being the dominant factor in final droplet formation. It should be noted that in order to produce mono-dispersity from a uniform pore sized membrane the pore size should always be kept as the dominant factor in determining the size of the forming droplets. If the dominant factor is something other than the pore size, it is unlikely that a uniform droplet size will be achieved. Therefore the process parameters should be set such that the pore size determines droplet size (i.e. minimum pressure to achieve desired flux (as close to the critical trans-membrane pressure as possible), low cross flow velocity etc.).

For efficiency the viscosity of the dispersed phase is best kept as low as possible so as to decrease the power requirements and increase trans-membrane flux, as should the continuous phase to reduce the pump power required. If processing of higher viscosity components is required, heating the components during emulsification would be an advantage, so as to reduce the apparent viscosities.

To summarise, increasing continuous phase viscosity increases shear at the membrane surface, making droplets detach sooner, and therefore smaller, increasing the dispersed phase viscosity increases the resistance of the forming droplets to the effects of shear, making droplets larger before they detach. Logically then the smallest droplets are produced with a viscous continuous phase and a low viscosity dispersed phase, and the opposite produces the largest droplets.

5.6 Effect of Dispersed Phase Volume

The dispersed phase volume is an important factor for emulsions, being able to make the required formulation for the product is a necessity for any emulsification system. The ability of membrane emulsification to make higher phase volume emulsions has so far not been tested as part of these experiments, instead the phase volume has been kept low to minimise any effects it may have on emulsion droplet size. These effects however, must be investigated, and so the SPG membrane was used to make emulsions up to 50% dispersed phase volume. The results of increasing the dispersed phase volume are shown in Figure 5.23.

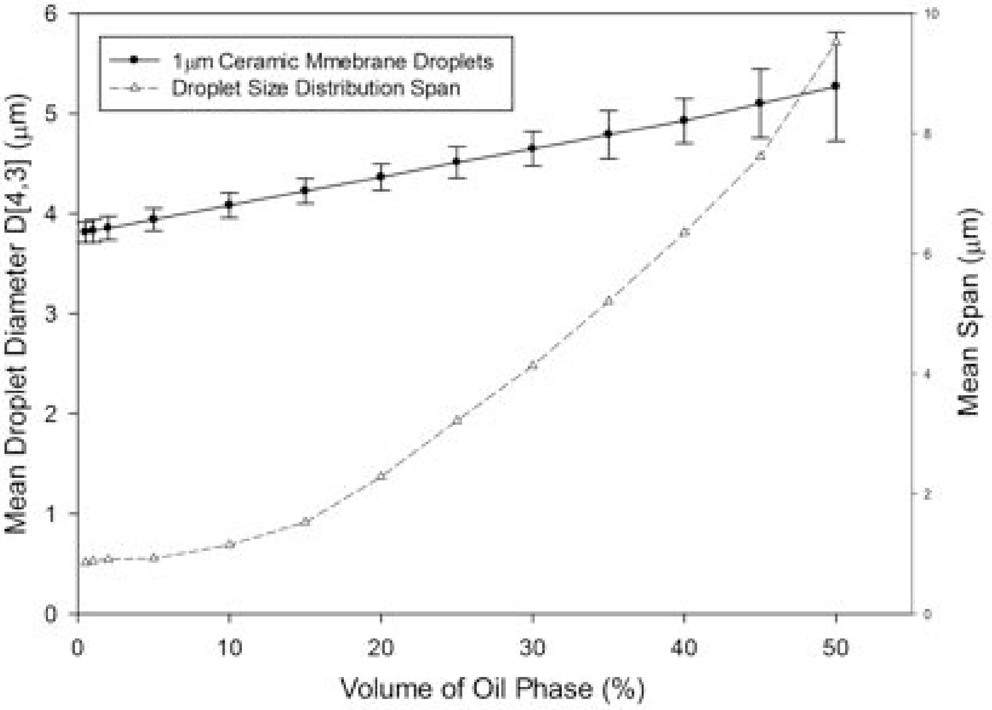


Figure 5.23. The changes in droplet sizes produced using membrane emulsification using a 1 µm ceramic membrane.

The phase volume of the produced emulsions was changed whilst keeping all other factors similar, using sunflower oil as the dispersed phase and water containing 1% wt. Tween20 as the emulsifier. The system was run at 0.6 ms^{-1} cross-flow velocity, and 40 kPa trans-membrane pressure.

The dispersed phase volume relative to the total volume increases the longer the system is run whilst the dispersed phase is pressurised through the membrane (assuming the system is being run in re-circulating mode).

Increasing the phase volume leads to some small increases in the average droplet size, as the chances of coalescence and contact with other droplets as they are forming also increases.

The increase in viscosity as the phase volume increases will tend to decrease the droplet size, but coalescence at the higher phase volumes increasing means that the droplet size distribution effectively gets larger with out major changes to the droplet size, as the effects counteract each other to some extent.

5.8 Summary

The work carried out in this chapter shows that the CFMED created for this work is highly capable of making a wide range of emulsions very simply and efficiently.

The effect of emulsifier is similar to that when using droplet breakup systems to create emulsions, with the possible advantages that the emulsifier concentration required may be smaller, as interface isn't being created at the same rate, and so as large an excess of emulsifier is not required. Since the minimum size of the droplets produced is governed by the pore size of the membrane, continuing to increase emulsifier concentration past a given point no longer produces a reduction in droplet size as it does with droplet breakup techniques.

Increasing pressure across the membrane increases flux rate, but also increases droplet size slightly.

The cross-flow velocity allows some tuning of the system, as noted by Williams *et al*. (1998). Increasing the cross-flow velocity increases shear, which causes droplets to detach sooner, and therefore means they are smaller. This effect is less prevalent using a membrane with a support material if the continuous phase flow is across the support material rather than the membrane itself.

The size distribution is narrowest when the pore size of the membrane dictates the droplet size, if there is too high a pressure, or to high or low a cross-flow velocity, they become the dominant factor over droplet size, and the size distribution is larger.

The smallest size distributions are produced therefore at moderate cross-flow velocities and at pressures not much higher than the critical pressure.

The viscosity of both phases changes the forces applied to the droplets, and so has an effect on droplet formation. The size distribution produced is lowest when the viscosities of the two phases are close, the droplet size is smallest however when the continuous phase viscosity is higher.

When the pressure is relatively high the flux is proportional to the pressure, and so increasing the pressure increases flux, which is important for industrialisation of membrane emulsification, where high flux rates need to be achieved to realise rapid production rates.

Chapter 6

Rotating Membrane Emulsification

The aim of the work described in this chapter was to determine the capabilities of the Rotating Membrane Emulsification Device (RMED) as described in the systems development section (chapter 4.2), and to compare and contrast them with those of the CFMED results of the previous chapter.

The effects of different settings and parameters of producing emulsions using the rotating membrane emulsification device were investigated, and the advantages and disadvantages of rotating the membrane were examined.

The idea behind creating a membrane emulsification device in which the membrane is rotated was to provide an additional force (centrifugal force) to detach the droplets from the membrane, to determine if this would increase throughput and decrease the size of the droplets produced by detaching them from the membrane sooner. It was also thought that the droplets produced by this method may be of a more consistent size because of more similar droplet histories, and therefore the produced emulsions would have a lower droplet size distribution.

As with the CFMED, the results in this chapter deal only with the production of oil in water emulsions, the production of water in oil emulsions is dealt with in a subsequent chapter (chapter 7.1).

The RMED was setup as described in chapter 4.2.

6.1 Effect of Choice of Emulsifier

Before determining the effects of the differences in the system parameters between the RMED and CFMED, the effects of emulsifier on emulsions created with the RMED were tested to ensure that the results were comparable to the CFMED, and that the system was running as expected.

6.1.1 SPG Membrane

The RMED was used to make emulsions with an SPG membrane fitted. Similarly to the CFMED tests, the emulsifier used and its concentration were varied to establish the effects on the resultant droplets. This effect can then be compared to the CFMED results. The RMED does have some differences from the CFMED experiments used to determine the effects of the emulsifier. The most important difference to note is the trans-membrane pressure. Where in the CFMED the trans-membrane pressure was calculated from the average pressure within the continuous phase side of the membrane module and the pressure applied to the dispersed phase in the dispersed phase tank. In the RMED however, the pressure across the membrane is simply the gauge pressure of the dispersed phase tank, as the continuous phase is at atmospheric pressure. The middle of the possible range of rpm was chosen, so the tests were run at 1000 rpm, and a low pressure known to produce emulsion droplets from the initial testing was chosen, in this case 10 kPa. Emulsions were made at 1% phase volume to keep coalescence to a minimum, and the emulsifiers were varied. The results of these tests are shown in Figure 6.1.

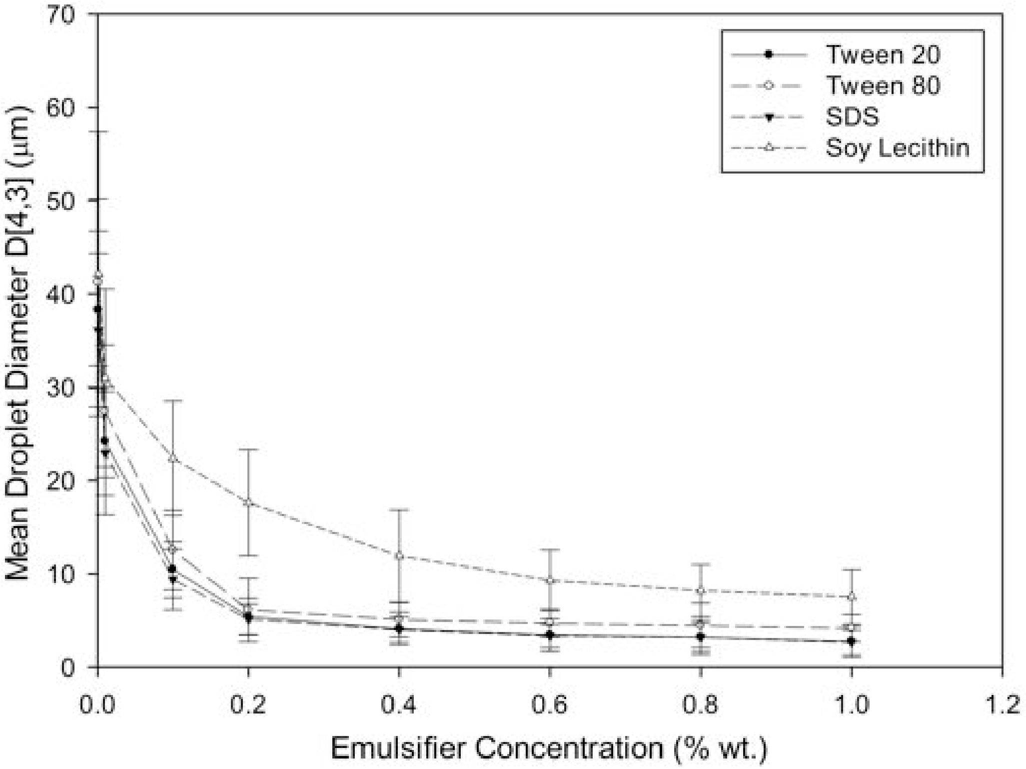


Figure 6.1. The effects of changing emulsifier type and concentration on the droplet size of emulsions made using the RMED. The emulsions produced were 1% phase volume oil in water emulsions, at 10 kPa trans-membrane pressure, and 1000 rpm.

The results from the RMED were similar for the SPG membrane to the CFMED results; with the increasing emulsifier concentration decreasing droplet sizes were produced. Also similar to the CFMED, the droplet size seems to reach a minimum, where increasing emulsifier concentration further sees no real further decrease in droplet size. The resultant droplets were slightly smaller using the RMED for an equivalent pressure. The pressure effects are different using the RMED than the CFMED, as pressure is linked to the rotation rate of the membrane. There could be many reasons why the droplet size is slightly smaller than the equivalent, the most likely is that the trans-membrane pressure is slightly lower than in the CFMED because of the way the pressure is measured in the CFMED (because of the averaging of the pressure between the inlet and outlet of the CFMED membrane module). Essentially the same membrane is producing a similar emulsion between the two systems, since this is the first time that an SPG membrane has been used on a rotating membrane emulsification system there was no previous data on how the membrane would perform, but the performance seems comparable to the cross-flow system from the initial results.

6.1.2 Ceramic Membrane

The ceramic membrane was not particularly suited to use in the RMED, as the membrane filter itself is coated on the inside of a tube made of more coarse ceramic material. This means that the membrane surface is not itself directly exposed to the continuous phase and therefore the shear that helps detach droplets from the surface of the other membranes. It does however work to produce emulsions, although they are less uniform and contain larger droplets than the SPG or stainless steel membranes.

As with the CFMED, the support material acts to shield the membrane from the shear; however the centrifugal force still acts on the liquid inside the membrane tube, as well as the applied pressure to force the dispersed phase through the membrane into the continuous phase as droplets.

To test the effects of emulsifier concentration the 1 µm ceramic membrane was used with the RMED to make emulsions using varying concentrations of Tween20 as the emulsifier. 1% phase volume sunflower oil in water emulsions were produced using 10 kPa trans-membrane pressure, and 1000 rpm. There was no need to run the tests using the other emulsifiers, as the effects of varying type of emulsifier have been clearly shown by previous tests. The results are shown in Figure 6.2.

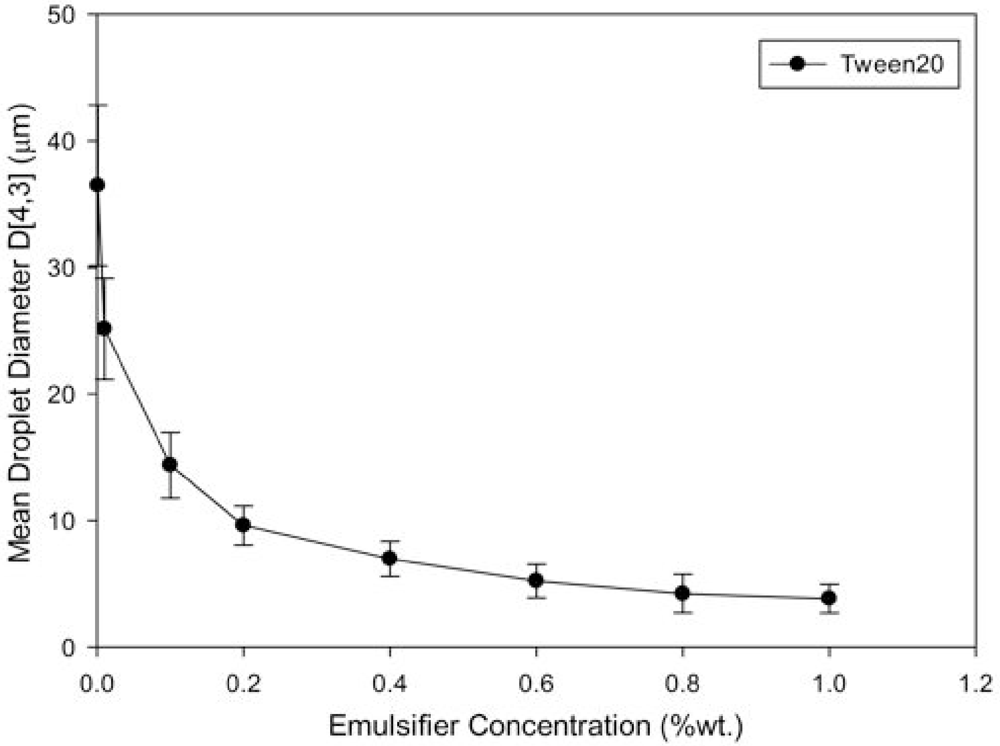


Figure 6.2. The results of changing emulsifier type and concentration on emulsion droplets produced using the RMED with a 1μm ceramic membrane fitted. The emulsions were made using sunflower oil in water at 1% phase volume. The system was run at 10 kPa trans-membrane pressure, and 1000 rpm.

The results show that the RMED produces similar droplet sizes at similar pressures to the CFMED using ceramic membranes. Once again the droplets produced by the RMED are slightly smaller than their equivalent CFMED droplets. The ceramic membrane shows a continued decrease in droplet size with increasing emulsifier concentration as it did using the CFMED; again it is probable that the localised decrease in emulsifier concentration within the ceramic support material is the cause of this effect. It would be interesting to compare the performance of the ceramic membranes in both systems if bespoke membranes were manufactured with the membrane coated onto the outside of the tube rather than the inside.

Since ceramic membranes have never been used for rotating membrane emulsification before there is no data to compare the results with, but the production of droplets similar to the same membrane used in the CFMED shows the system is working.

6.1.3 Polymer Membrane

In many ways the polymer membranes would be ideally suited to the RMED (high porosity, narrow pore size distribution and inexpensive), in one however the polymer membranes used in the CFMED study are impossible to use in the RMED: they are too flexible.

The polymer membrane was mounted for the RMED, however when spun the membrane vibrated and eventually bent to one side. The polymer membrane used in this research was simply not rigid enough to test in the RMED.

It may be possible to use an internal support to reinforce the membranes structural integrity, this was however, beyond the scope of these experiments, but is well worth investigating further. Other types of polymer membranes may be more rigid, and therefore more suitable for rotating membrane emulsification.

6.1.4 Stainless Steel Membrane

A 15 μm stainless steel membrane of the same type made to fit the CFMED was mounted to fit the RMED, and experiments were performed to find the effects of emulsifier concentration as with the other membranes and systems. Once again there was little point including all the emulsifiers, as they clearly follow the same trend, and so Tween20 was used. The membrane was installed in the system, and used to make 1% phase volume sunflower oil in water emulsions at a trans-membrane pressure of 10 kPa, and 1000 rpm. The results of the tests are shown in Figure 6.3.

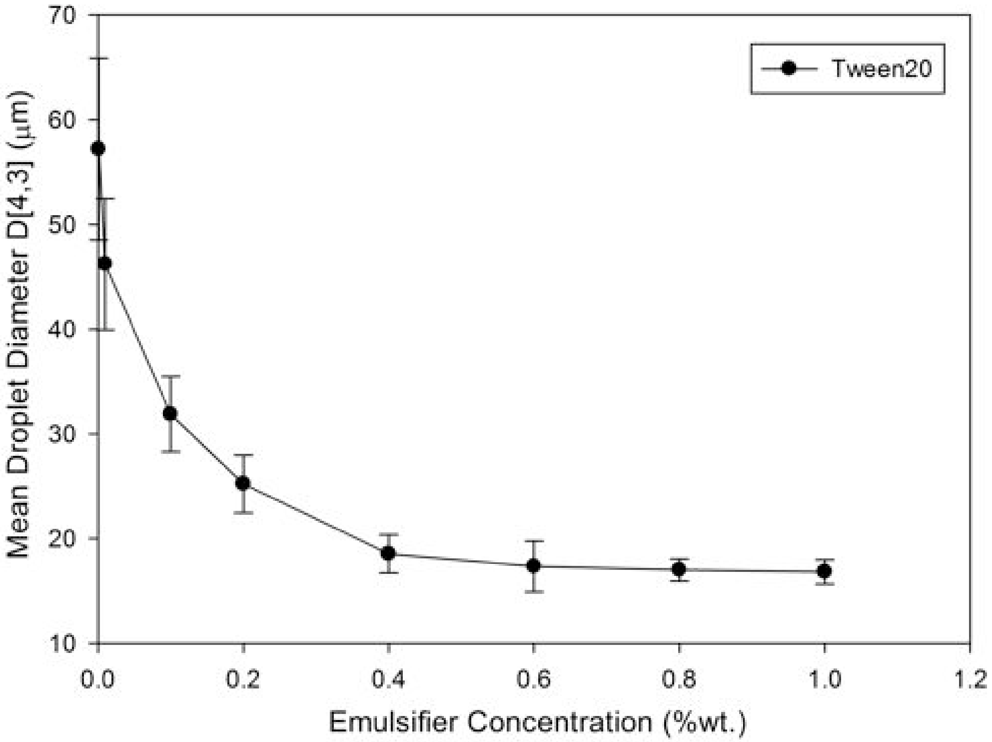


Figure 6.3. The results of making emulsions with a stainless steel membrane and different concentrations of Tween20. The system was run at 10 kPa trans-membrane pressure, and 1000 rpm.

The results show the larger pores of the laser drilled stainless steel membranes produce larger droplets, as was also seen in the results from the CFMED, and therefore a higher emulsifier concentration is required to make them stable. Even so the stainless steel membrane produced droplets not much larger than the pore size of the membrane. It would seem from these initial results that the straight through pores of the stainless membrane are particularly suited to rotating membrane emulsification. Since the only previous work with rotating stainless steel membrane emulsification was with much larger pore sizes (Vladisavljević and Williams, 2006), the results shown here are not really comparable.

The effects of emulsifier were still quite similar to those of the stainless steel membrane used in the CFMED.

6.2 Effect of Pressure

The effects of varying pressure across the membrane are likely to be just as important using rotating membrane emulsification as they were found to be using the CFMED.

6.2.1 SPG Membrane

The effects of varying the pressure whilst keeping all other factors equal were investigated in the RMED. The effects of pressure in CFMED were shown to cause a small increase in droplet size as pressure was increased, but the main effect was shown to be on the flux of dispersed phase across the membrane. As with the CFMED results the flux rate is dealt with in a subsequent section (6.8) and this section deals instead with the increase in droplet size with increase in pressure. The pressure was changed whilst making emulsions at 1% phase volume of sunflower oil in water, with 1% wt. Tween20 as the emulsifier. The system was run at 1000 rpm for all the tests in this section. The results of these tests are shown in Figure 6.4.

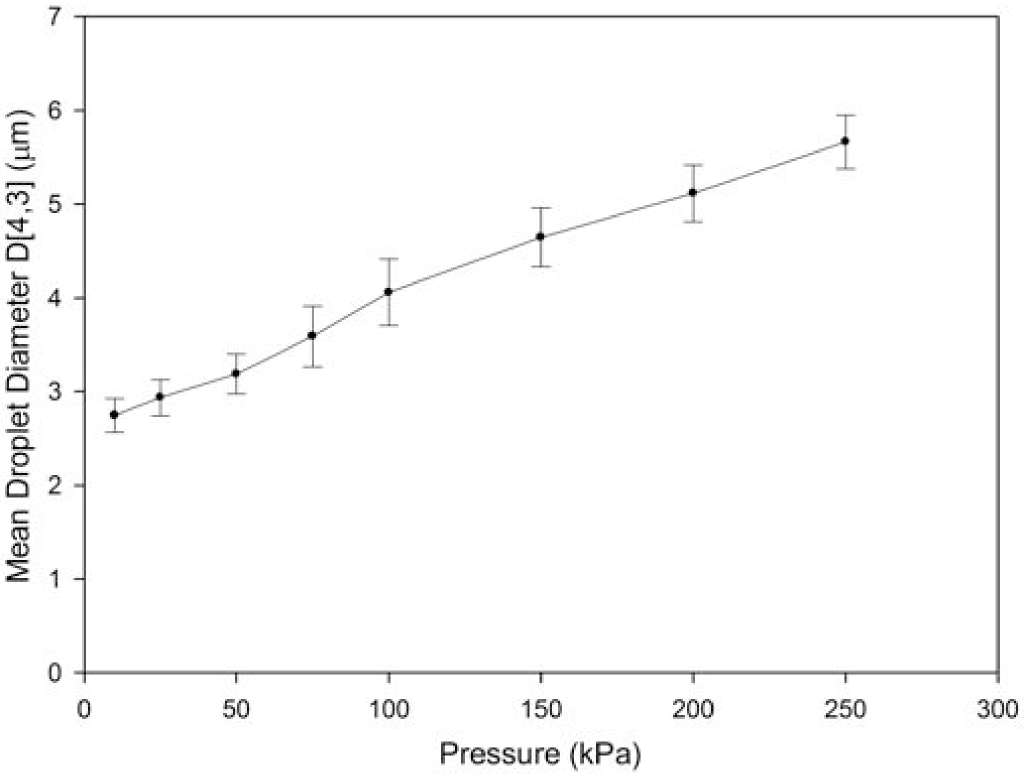


Figure 6.4. The effects of changing the trans-membrane pressure on the droplet sizes produced by the RMED with a 1 μm pore size SPG membrane. The emulsions were sunflower oil in water with 1% wt. Tween20 as the emulsifier at 1000 rpm.

The results of the pressure tests were similar to the pressure results from the CFMED as run at low cross-flow velocity, with the increase in pressure causing a slight increase in droplet size. There is no sign of the sigmoid curve as seen with the CFMED pressure curves at higher cross-flow velocities, suggesting that the rotation rate used in these tests more closely correlates with a droplet detachment equivalent to that present at lower cross-flow velocities in the CFMED. The shear rate of 26.18 s^{-1} was much lower than the CFMED and yet still produced small droplets, much smaller than would be produced using a similar shear rate in the CFMED. The implication is therefore that the rotating membrane system produces smaller droplets at lower shear rates, perhaps due to the extra centrifugal detachment force suggested in the literature (Aryanti et al., 2006, Schadler and Windhab, 2006). This will be discussed further in the section dealing with rotation rates (chapter 6.3) The membrane surface velocity of 0.524 ms^{-1} is however very close to the linear cross-flow velocity of the CFMED when it produces comparable droplet sizes at comparable pressures (as shown in chapter 5.2).

Whilst running the tests for pressure, another factor which may detract from the production of very narrow size distribution emulsions using membrane emulsification was noticed. The dispersed phase was seen to be emerging preferentially from the top part of the rotating membrane. At higher pressures it became obvious that more and more of the membrane was becoming active towards the lower part. It seems to be that the pressure drop through the membrane (caused by the outflow of dispersed phase through the pores) leads to the pores closest to the pressure source being activated first. Because pressure is shown to have an effect on droplet size, this effect will cause the pressure to vary in different parts of the membrane tube (lower the further away from the dispersed phase inlet) the droplet sizes produced will also vary along the length of the tube, increasing droplet size distribution. It is likely that this effect also occurs when using the CFMED although the membrane surface is not visible in the specific experimental setup used here. This effect could be minimised by design - by introducing dispersed phase under pressure at both ends of the membrane module perhaps, although it is probable that it will still exist when any length of membrane tube is used, and may have implications for scale up where size distribution is important.

6.2.2 Ceramic Membrane

The pressure tests were also run in a similar fashion for the 1 μm ceramic membrane on the RMED. The system was used to make emulsions of 1% phase volume sunflower oil in water, with 1% wt. Tween20 as the emulsifier. The system was run at 1000 rpm, with only the pressure varied. The results of these tests are shown in Figure 6.5.

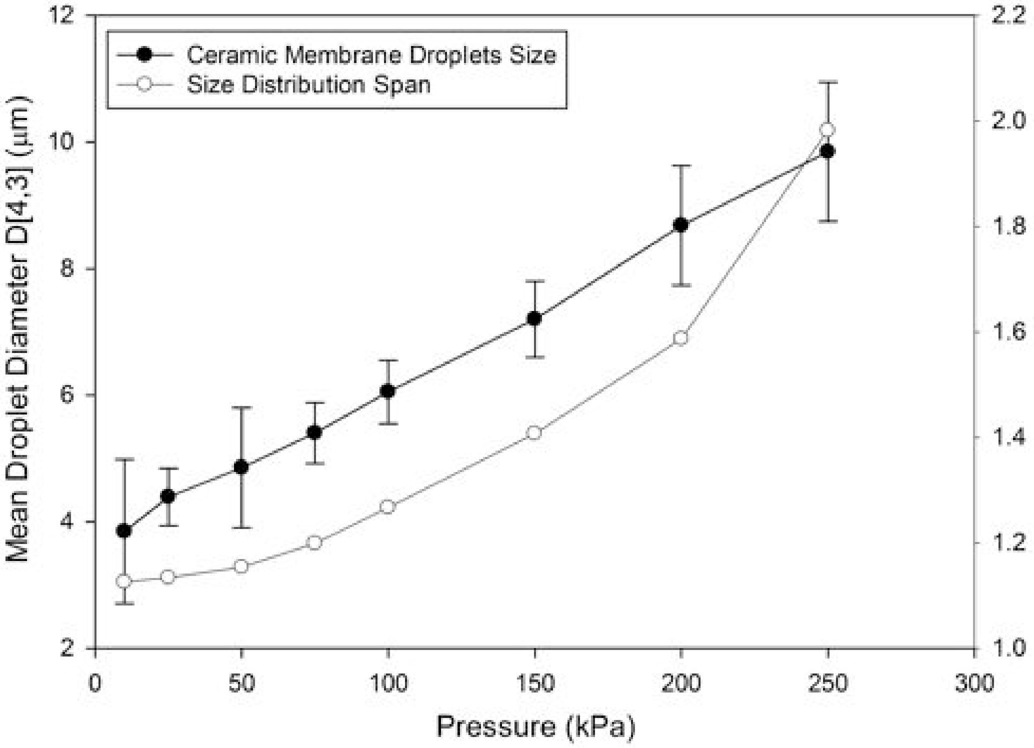


Figure 6.5 The results of changing the trans-membrane pressure on droplets made using a 1 μm ceramic membrane on the RMED. The emulsions produced were sunflower oil in water, with 1% wt. Tween20 as the emulsifier, at 1000 rpm.

The results from the ceramic membrane were similar to the same membrane run at low CFV on the CFMED. Again as with the SPG membrane there is no sign of the sigmoid curve, and it is likely that the system is in the regime where the droplets are detaching due to reaching the maximum size that is retainable at the pore. It is possible that the droplets are detaching due to the injection regime at the higher pressures as the droplet size distribution has started to increase (Figure 6.6).

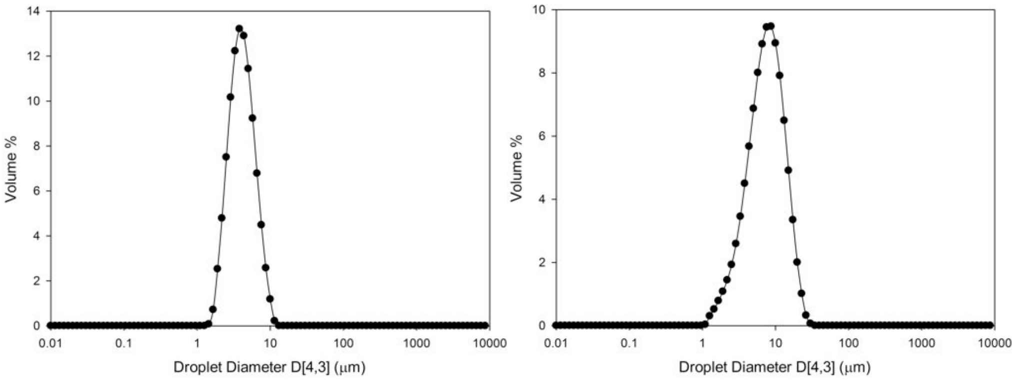


Figure 6.6. The droplet size distributions for two emulsions made using a 1 μm pore size ceramic membrane on the RMED. The emulsions were both 1% phase volume sunflower oil in water, with 1% wt. Tween20 as the emulsifier. The RMED was run at 1000 rpm. The left distribution is from an emulsion made at 10 kPa trans-membrane pressure, and the right hand distribution was made at 200 kPa.

6.2.3 Stainless Steel Membrane

The effects of changes in the trans-membrane pressure were also investigated using the stainless steel membrane on the RMED. The RMED was used to create emulsions consisting of 1% phase volume of sunflower oil in water, using 1% Tween20 dissolved in the continuous phase as the emulsifier. The system was run at a rotation rate of 1000 rpm for the tests. The results are shown in Figure 6.7

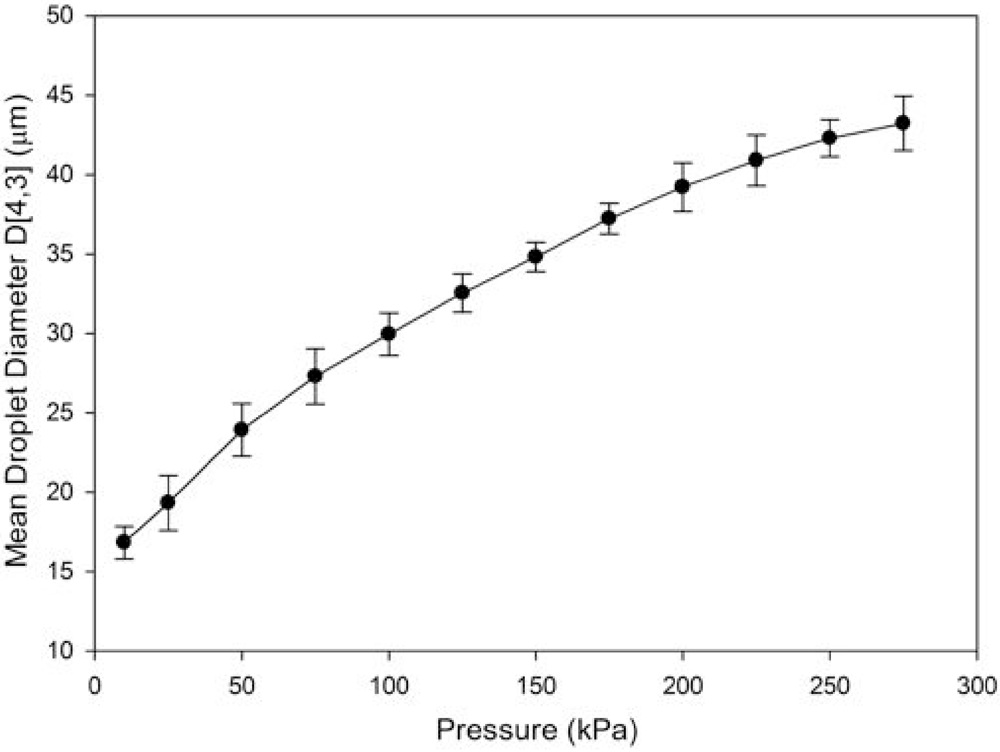


Figure 6.7. The results of varying the trans-membrane pressure when making emulsions using the 15 μm pore size stainless steel membrane on the RMED. The emulsions were made at 1% phase volume of sunflower oil in water using 1% Tween20 as the emulsifier.

The stainless steel membrane needs far less pressure to form droplets than the other membranes tested because of the large pore size of 15 μm. Because of this the effects of pressure are different, and instead of the droplet size being proportional to the pressure, the increase in droplet size starts to tail off at higher pressures, the maximum droplet size for this pore size is being reached, and the droplets are being formed in an injection regime.

6.3 Effect of Rotation Rate

The rotation rate of the rotating membrane emulsification device is the equivalent of the cross-flow velocity variable on the CFMED. Changing the rate of rotation changes the shear applied at the membrane surface caused by the resistance to rotation of the continuous phase around the membrane. The magnitude of the shear is proportional to the rate of rotation, but the rotation also causes a centrifugal force which acts on the dispersed phase within the membrane, perpendicular to the membrane surface, forcing the dispersed phase through the membrane into the continuous phase in the same way as the pressure applied to the dispersed phase.

This extra centrifugal force also increases with rotation rate, and is the equivalent of also increasing the pressure.

During cross-flow emulsification, pressure is used to force the dispersed phase through the pores in the membrane, however in rotating membrane emulsification the pressure used to move the dispersed phase across the membrane is partially replaced by the centrifugal force generated by the rotation of the membrane itself. This causes a problem when the route through the membrane from inside to outside consists of a tortuous path, as any sections of the path requiring the liquid to double back on itself will be subjected to a negative force, and will result in the critical pressure for emulsification being increased.

This will only affect some pores, not all, which will lead to an overall increase in size distribution at higher pressures and a decrease in porosity at lower pressures for membranes made up of tortuous paths when used in rotating membrane emulsification.

The shear rate applied by rotating the membrane can be calculated by using the same method as used by Vladisavljević and Williams, (2006) with the following equation:

$$\dot{\gamma} = \frac{\pi R_1{}^2 n_1}{15(R_2{}^2 - R_1{}^2)} \qquad \text{equation 6.1}$$

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.

The shear rates for several different speeds with the 30 mm vessel diameter are given in Table 6.1.

RPM	Shear rate, $\dot{\gamma}$ (s^{-1})
100	2.62
250	6.55
750	19.6
1000	26.2
1500	39.3
2000	52.4

Table 6.1. The shear rates at different rotation rates in the RMED using a 10 mm outer diameter membrane and a 30 mm inner diameter vessel.

It should be noted that the shear rates are far lower than are possible in the CFMED used in this study, however cross-flow devices used in previous studies have all used the inside of the membrane tube (where a tubular membrane was used), and the channel diameter has therefore generally been around 8 mm, whereas the cross-flow membrane device used for this research had only a 2 mm gap around the membrane, substantially increasing the shear rate applied at the same cross-flow velocity. The shear rates applicable to the RMED are similar to those produced by the rotating membrane device used by Vladisavljević and Williams (2006), as the geometries are largely similar. The other rotating membrane device as used by Schadler and Windhab (2006), produces much higher shear rates with a maximum according to the same equation of around 167000 s^{-1}. This large shear rate is the result of the larger diameter membrane, in a much smaller annular gap, at 4 times the maximum rotation rate (8000 rpm).

6.3.1 SPG Membrane

The effects of increasing the rate of rotation were investigated using the different membrane types, starting with the SPG membrane. As with the CFMED, the 1 µm SPG membrane was used to make emulsions using sunflower oil dispersed in water at 1% phase volume using 1% wt. Tween20 as the emulsifier. The applied dispersed phase pressure was set at 10 kPa, and the system was run with varied rotation rates. The results are given in Figure 6.8.

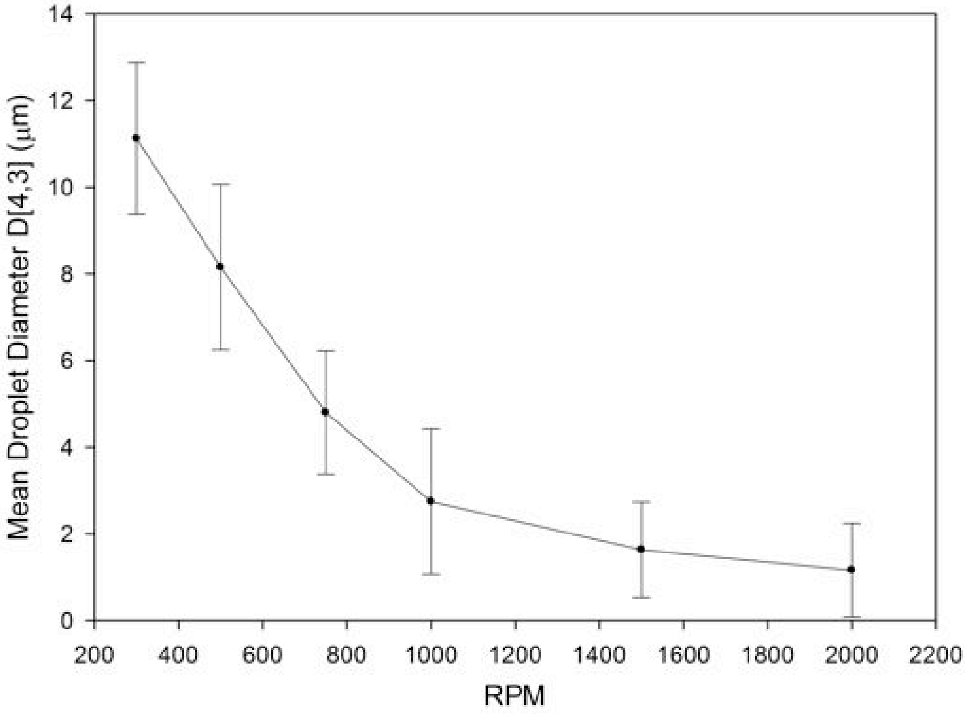


Figure 6.8. The results of varying the rpm with the RMED and a 1 µm SPG membrane. The emulsions made were 1% phase volume sunflower oil in water with 1% Tween20 as the emulsifier, and at 10 kPa trans-membrane pressure.

The graph shows that the increase in rpm and therefore the increase in shear at the membrane surface is not proportional to the decrease in droplet size it causes. The corresponding increase in pressure through the membrane caused by the increase in centrifugal force tends to increase droplet size, and the shear increase alone also doesn't cause a proportional decrease in droplet size as there is a minimum size limit to the droplets that can be produced using a given pore size membrane (as can be seen from the CFMED CFV results). This means as the droplets size tends towards this limit, the droplet size decrease due to increases in the shear is lessened. The limit of droplet size is however very close to the membrane pore size, and since the shear rate is lower than that of the CFMED, the droplet size should likely be larger than it is. This suggests that there is some other effect either increasing the average droplet size for the CFMED or decreasing the droplet size produced using the RMED. The results from the RMED are comparable with those from the CFMED, as shown in Figure 6.9.

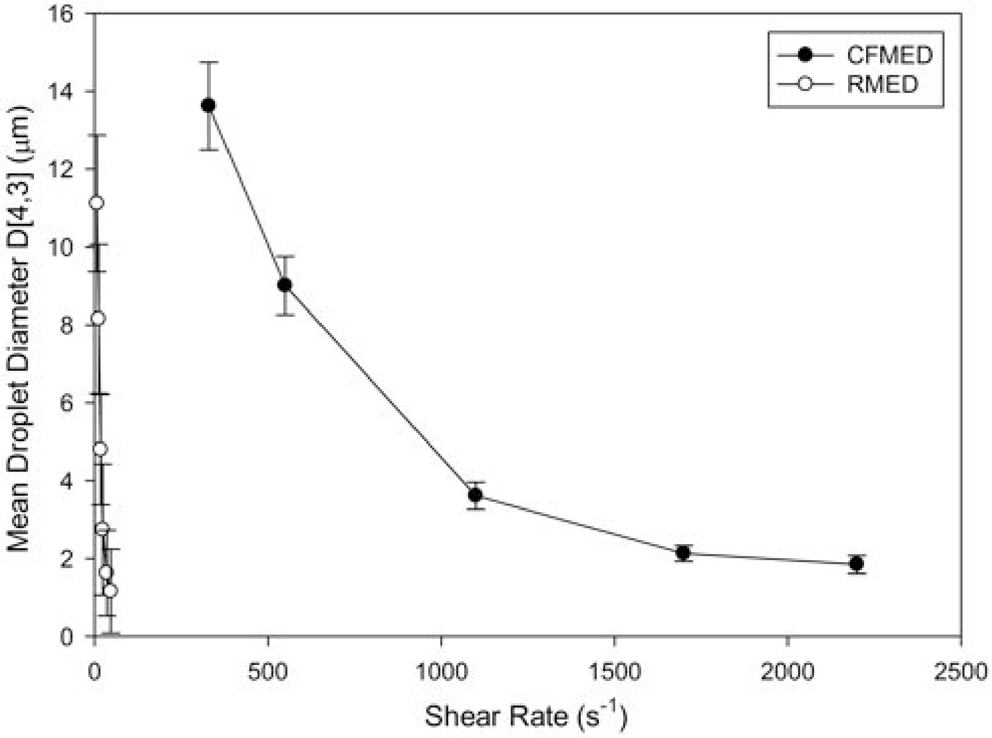


Figure 6.9. A comparison of the same emulsion (1% wt. tween20 with 1% phase volume oil in water made at various cross flow velocities on the CFMED and various rotation rates on the RMED. The results are plotted by shear rate. The RMED shear rates are significantly lower for similar droplet diameters, showing that other factors effect droplet detachment in the RMED system.

The droplet size limits of the membrane used are the same. The shear rate of the RMED shear rate was much lower when producing a similar droplet size to the CFMED however; this can be explained by the addition of the centrifugal force. It is also possible that some other factors of the RMED contribute to this effect, such as vibration of the membrane under rotation aiding droplet detachment etc.

The difference between the CFMED and RMED is in the way in which the continuous phase flows around the membrane, and so not only how the droplets are formed is different, but their path away from the membrane surface after detachment. In the cross-flow system, the flow of the continuous phase is axial to the tubular membrane, and the formed droplets once detached flow along parallel to the surface of the membrane, because of shear force from the continuous phase, and so stand a chance of hitting other newly formed or still forming droplets on that surface. The RMED however, causes detached droplets to initially follow a path tangential to the circumference of the rotating tube under inertial force, away from the membrane into the bulk emulsion. It is this effect which causes the droplets made by rotating membrane emulsification to have a slightly lower average size than those made using a cross-flow system. The density difference between the two phases may also play a part here, in the same way as during centrifugation, although this effect is likely very small in this case as the densities of the dispersed and continuous phases are not very different. Since the buoyancy of the dispersed phase under centrifugal force would cause the water continuous phase to tend towards the vessel wall, and the oil droplets to tend towards the membrane wall, the oil droplets 'floating' on the more dense water. This effect was never observed, probably because of the turbulent nature of the bulk emulsion during processing, which keeps the two phases well mixed.

6.3.2 Ceramic Membrane

The ceramic membranes were tested to see the effect of increasing the rotation rate of the membrane on the sizes of the droplets produced by the RMED. Since the results from the CFMED show that the ceramic membranes are not so affected by the shear, because the membrane is shielded from the effects by the support material, the ceramic membranes were expected to behave similarly to the increase in rotation rate as they did to the cross-flow velocity increases in the CFMED.

To test this the 1 μm ceramic membrane was installed in the RMED, and emulsions were produced using 1% phase volume sunflower oil as the dispersed phase, into water continuous phase containing 1% wt. Tween20 emulsifier. The system was run using the same 30 mm continuous phase vessel, with a trans-membrane pressure of 10 kPa. The results of these tests are given in Figure 6.10.

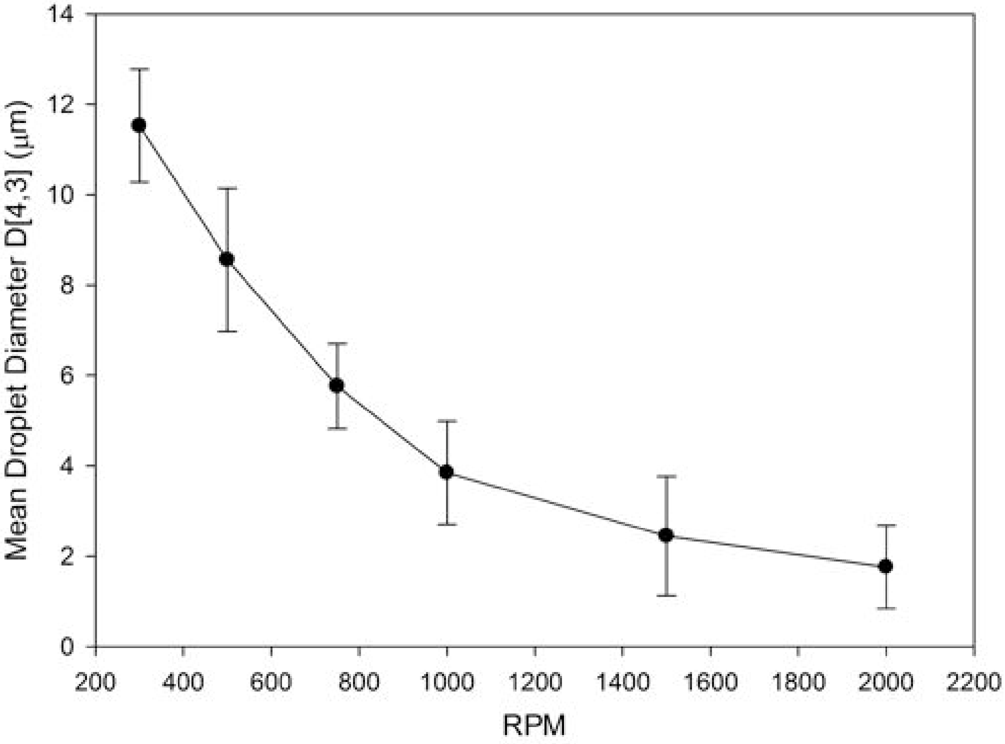


Figure 6.10. The effect of varying rpm an the size of emulsion droplets produced using the RMED and a 1 μm ceramic membrane. The emulsions are 1% phase volume sunflower oil in water, with 1% wt. Tween20 as the emulsifier, and at 10 kPa trans-membrane pressure.

The rpm results for ceramic membrane produce a slower decrease in droplet size with increases in rpm than occurs with the SPG membrane. The decrease is however, faster than was seen when increasing the cross-flow velocity in the CFMED tests. The centrifugal force acts through the support material as well as the membrane, whilst the pressure drop across the membrane means that the effects of pressure alone do not continue into the support material. The effects of buoyancy may play a part here; the support material being pre-soaked in continuous phase will contain both oil and water, so the oil droplets may congregate within the support material until they push each other out into the bulk emulsion. It is probable that this effect is minimal given the small difference in densities in this case, and the relatively slow rotation rates, the centrifugal and inertial forces will be much higher, as is the case using CFMED. This means that the droplets are not held within the support material so long with the RMED, and so the chances of coalescence are smaller, decreasing the average droplet size as rpm is increased. Combined with the formed droplets taking a tangential path away from the membrane surface rather than flowing along it as in the CFMED (the same effect as mentioned in the results for the SPG membranes) the droplets produced from the RMED with ceramic membranes are smaller on average than from the CFMED even though the shear is less.

6.3.3 Stainless Steel Membrane

The stainless steel membrane was tested to find the effects of varying the rotation rate on the average size of the droplets it produced. The membrane was used to create emulsions containing 1% phase volume of sunflower oil in water with 1% wt. Tween20 as the emulsifier, at 10 kPa trans-membrane pressure. The results of the tests are given in Figure 6.11.

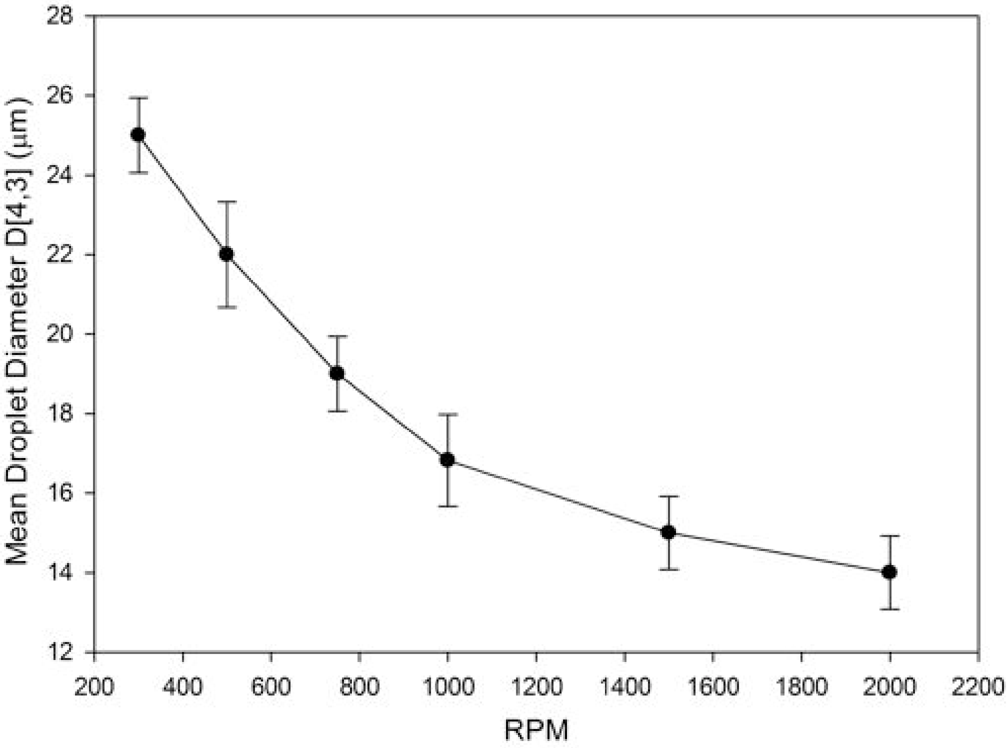


Figure 6.11. The effect of varying rpm on emulsions made using the RMED and a 15 μm pore size stainless steel membrane. The emulsions are sunflower oil in water, at 1% phase volume, and using 1% wt. Tween20 as the emulsifier. 10 kPa trans-membrane pressure was used.

The stainless steel membrane used here was purpose built to be used with the rotating membrane system; the membrane was attached to the threaded ferrule by heat shrinking the metal over the membrane, as was the membrane end plug. The straight pores of the metal membrane are particularly suited to the RMED, with the extra centrifugal force applied acting directly all the way through each pore, and this can be seen in the rpm data. At this pore size (15 μm) the rotation of the membrane is enough to provide sufficient pressure to flow the dispersed phase through the pores even without any applied pressure. The large pore size means that the droplets are automatically going to be much larger than those produced from the other membranes tested here, which means that the droplets produced will be subject to greater drag force, and will be more affected by increase in shear (by increasing the rotation rate than the droplets produced by the other membrane types.

Interestingly the droplets produced by the stainless steel membrane in this test are smaller than the pore size at higher rpm.

6.4 Effects of Pore Size

The effects of different membrane pore size are likely to be important with rotating membrane emulsification in the same way that they were with the cross-flow system tested in the preceding chapter. The rotating membrane systems reported in the literature so far have been of a single pore size, and so there have been no discussions on the effects of pore size. Given the profound effects reported for the cross-flow system however, the pore size is expected to have a similar strong effect on the droplet size produced using the RMED.

The full range of pore sizes of SPG membranes were mounted for use in the RMED, and tests were performed to see the effects of these different sizes on the droplets produced when making emulsions. Each membrane was used to produce an emulsion of 1% phase volume sunflower oil in water, with 1% wt. Tween20 as the emulsifier. The system was run at 1000 rpm and 10 kPa trans-membrane pressure for all the tests. The results are given in Figure 6.12.

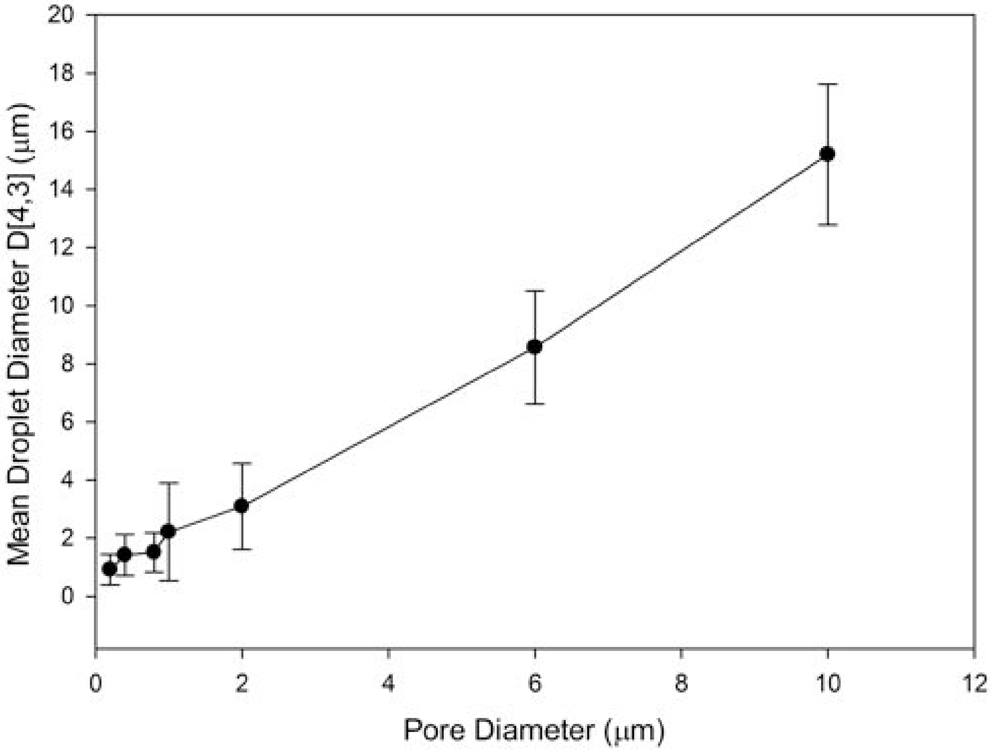


Figure 6.12. The size of droplets changes with changes in pore size. The emulsions were made by at dispersing 1% phase volume of sunflower oil in water, with 1% wt. Tween20 as the emulsifier. The RMED was run at 1000 rpm and 10 kPa trans-membrane pressure.

The results show that, as expected, the pore size has a large effect on the average size of the droplets produced using rotating membrane emulsification. The pore size is still one of if not the most important factors in rotating membrane emulsification as it was shown to be in cross-flow membrane emulsification.

6.5 Effects of Continuous Phase Viscosity

The viscosity of the continuous phase changes the shear forces applied to forming droplets in the same way as with the CFMED. To see the effects this had on the droplet sizes produced using the RMED, a series of tests were run with the same viscosity continuous phases as were tested in the CFMED.

The tests were run at 500 rpm since viscosity was expected to decrease droplet size this change will be larger if the size is further from the pore size already (i.e. not close to the pore size where further changes will be small). The continuous phase used was water with 1% wt. Tween20 as the emulsifier, and glucose added to increase the viscosity. Sunflower oil was dispersed into the continuous phase using the RMED at 10 kPa trans-membrane pressure. The results of the tests are shown in Figure 6.13.

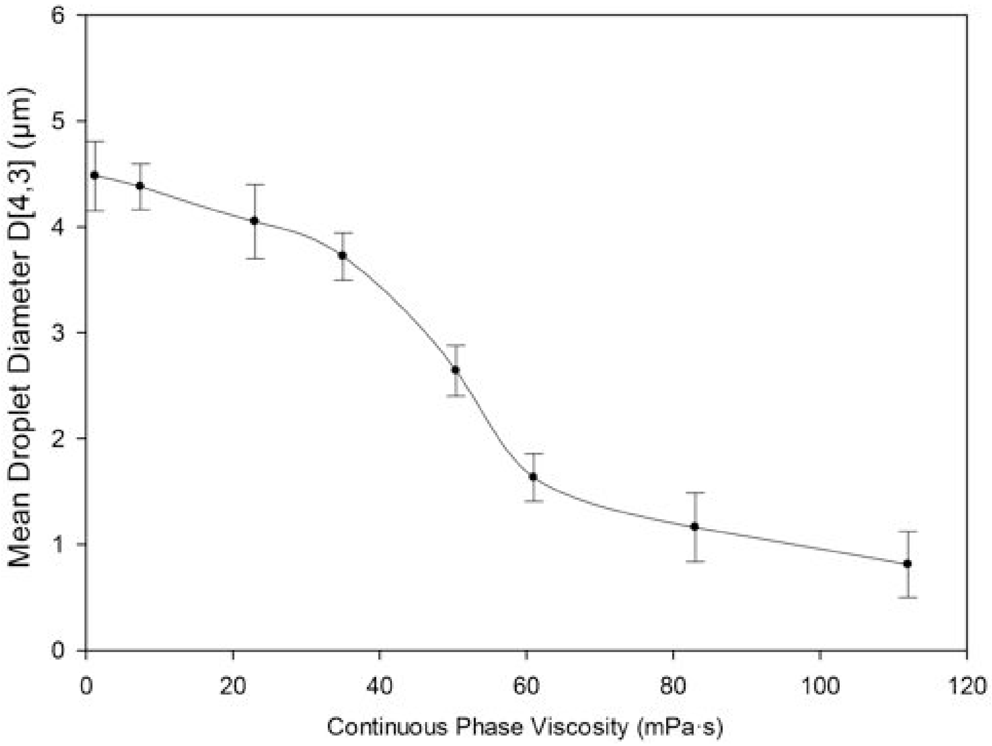


Figure 6.13. The results of creating emulsions using the RMED with different viscosity continuous phases. The emulsions were 1% phase volume sunflower oil in water containing 1% wt. Tween20, and glucose to change the viscosity.

As with the CFMED, the viscosity of the continuous phase changes the average size of the droplets produced. Increasing the viscosity decreases the droplet size, because the shear applied to the forming droplets is increased.

The rate of change of the droplet size is greatest around the point where the viscosities of the two phases are nearly equal, which was also observed for the CFMED.

6.6 Effects of Annular Gap Size

An interesting factor peculiar to the RMED was the ability to change the vessel in which the membrane was rotated. The annular gap changes the shear rate of in the continuous phase flowing around the membrane as it rotates. From the shear rate equation used in the rotation rate section (6.3) it can bee seen that reducing the size of the gap will increase the shear rate ($\dot{\gamma}$), whilst increasing is will reduce it. The shear rate when using some of the different vessel sizes is shown in Table 6.2.

Annular gap size (mm)	Shear rate, $\dot{\gamma}$ (s^{-1})
5	69.8
10	26.2
18	10.4
24	6.42

Table 6.2. The annular gap used effects the shear rate in the continuous phase around the membrane, the shear rates above are for a 10 mm diameter membrane rotated at 1000 rpm.

This factor although feasible was not investigated on the CFMED as the annular gap around the membrane was determined by the fixed inner diameter of the membrane housing module, and was not easily changeable.

To test the effect of changing the gap size tests were run using the RMED with several different vessel diameters, when using a 1 μm pore size SPG membrane, rotated at 1000 rpm, and producing 1% phase volume sunflower oil in water emulsions with 1% wt. Tween20 as the emulsifier. The results of these tests are given in Figure 6.14.

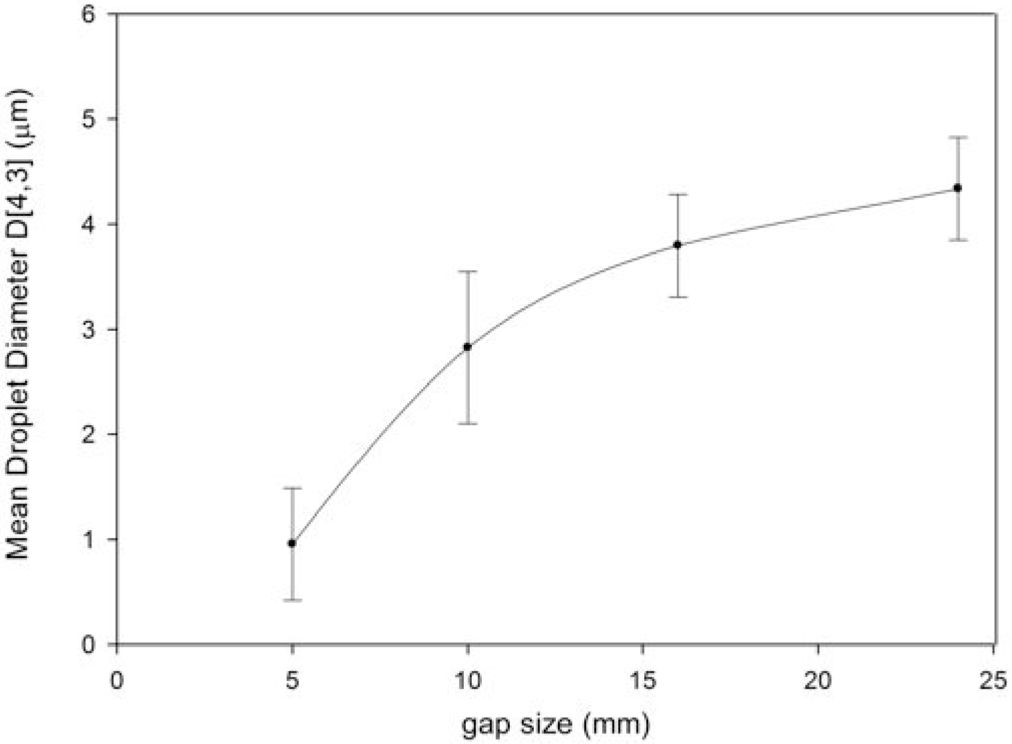


Figure 6.14. The results of changing the annular gap size when using the RMED to make emulsions with a 1 μm pore size SPG membrane at 10 kPa trans-membrane pressure and 1000 rpm.

The result of changing the annular gap around the rotating membrane was that the droplet size decreased when the gap decreased and increased with larger gap sizes. This was expected, and is similar to the effects of changing the shear in other ways like increasing rpm.

6.7 Flux rates

The trans-membrane flux changes with both pressure (as it did with the CFMED) and the rate of rotation of the membrane (as the centrifugal force is increased proportionally with rpm). In practice the increase with the centrifugal force over the ranges of rpm available in the system tested here is negligible compared to the increase in flux due to pressure. Once again the flux was measured by timing the duration of the run to flow a fixed amount of dispersed phase across the membrane into the continuous phase. The flux is given in ml per second per square metre of membrane surface, and is shown in Table 6.3. The emulsions were made using sunflower oil in water, with 1% wt. Tween20 as the emulsifier, at 1000 rpm.

Membrane type	Trans-membrane pressure (kPa)	Measured flux rate (mlm^{-2}s^{-1})
SPG 1 µm pore size	10	5.84
	100	86.4
	250	252
Ceramic 1 µm pore size	10	9.01
	100	166
	250	446
Stainless Steel 15 µm pore size	10	31.6
	50	147
	250	745

Table 6.3. The trans-membrane flux of some membranes as run on the RMED at several different pressures, at 1000 rpm

The results of flux rate are particularly similar to those produced by the membranes when run in the CFMED. This is entirely expected, as the membranes are the same, the resistance to the flow of dispersed phase is similar, and so the change in flux rates with changing pressure are nearly identical. Because the change in flux with increase in rotation rate is so low as to be not measurable, and the applied pressure is clearly the dominant factor in determining flux rate the increase in pressure due to increasing rotation rate is likely to also be very small. This is probably because the pressure applied to the system is controlled and so any pressure caused by rotation will reduce the applied pressure automatically by the action of the pressure regulator.

6.8 Summary

The RMED is capable of making emulsions similar to those the CFMED made in the last chapter. The droplets produce are detached from the membrane due to the same forces as the CFMED, with the addition of a centrifugal force, and under certain circumstances there are advantages to the rotating membrane system, with lower coalescence, and the control over the droplet formation parameters is finer, and in some respects the system itself is simpler, with less pipe work and much easier setup and cleaning than the cross-flow system. Because the rotating membrane device does not of itself create as much shear as the CFMED in the configurations used here, the system is best suited to the production of emulsions where the system shear is not as important, for example the larger droplets produced using the stainless steel membrane which have more drag and therefore need less shear to detach, or with more viscous continuous phases, where the viscosity increases the shear force applied. The system can easily be modified to produce more shear by decreasing the size of the annular gap around the membrane. Both the SPG and ceramic membrane types are just as suited to rotating membrane emulsification as the stainless steel membrane, as both have been shown to produce emulsions with controllable size ranges, they are also more porous than the metal membranes, with smaller pore sizes available than with stainless steel, meaning the production of small droplets is a possibility. The extra detachment force produced by rotating the membrane allows smaller droplet sizes to be produced from rotating membrane emulsification than from cross-flow at similar shear rates.

Pore size still has the greatest effect on the size and size distribution of droplets produced, with the rotation rate having the next largest effect along with the continuous phase viscosity and annular gap size. The pressure increases flux more than it affects droplet size, but increases droplet size distribution if it is too high.

Chapter 7

Applications for Making Complex Microstructures

The aim of the work in this chapter was to determine the abilities of the CFMED and the RMED for making structures other than the simple oil in water emulsions made so far, whilst highlighting any advantages and drawbacks to either system in comparison with each other and also more traditional methods of membrane emulsification.

Some possible applications of membrane emulsification have been investigated, with particular emphasis on areas which may be of use in food production, specifically in more healthy food preparation such as lower salt or fat foods.

7.1 W/O Emulsions

The possibility to make emulsions with the oil phase as the continuous phase was investigated. Water in oil emulsions are common in the food industry, being the major component of butters and spreads amongst other things.

From the literature (Mine *et al*, 1996), the surface chemistry of the membrane has been shown to make a difference to the ability to make emulsions; the better the membrane is wetted by the continuous phase, the better the emulsion production. For this reason, SPG membranes are manufactured in both hydrophilic (for oil in water production) and hydrophobic (for water in oil production).

To test the ability of the systems to make water in oil emulsions several tests were performed with the systems making them, using two different emulsifiers, and distilled MilliQ filtered water and sunflower oil as the dispersed and continuous phases respectively.

7.1.1 Cross Flow Emulsifier Results (water in oil)

As with the results shown for the oil in water emulsions, the CFMED was first used to produce emulsions with varying concentrations of each of the two emulsifiers. Each membrane type was tested and the results of these tests follow. The results from the systems whilst producing water in oil emulsions must be taken with two things in mind, the first is that the viscosities of the continuous and dispersed phases are swapped, and this has been shown in previous results to have an effect on the size of the droplets produced (the higher the continuous phase viscosity the smaller the droplets). The second thing to note is that the viscosity of water in oil emulsions does increase considerably over the continuous phase alone as the phase volume increases. Hence the viscosity effects will increase steadily as the emulsion is created, and this is likely to increase the size distribution of the droplets produced.

7.1.1.1 SPG Membrane (hydrophobic)

To test the effects of emulsifier when using membrane emulsification the CFMED was used to make water in oil emulsions. The trans-membrane pressure used was 10 kPa, and the cross-flow velocity was 0.6 ms^{-1}. The emulsifiers used were PGPR (polyglycerol polyricinoleate) and Span80 (Sorbitan monooleate). The experiments were run with different concentrations of each emulsifier, and the results are shown in Figure 7.1.

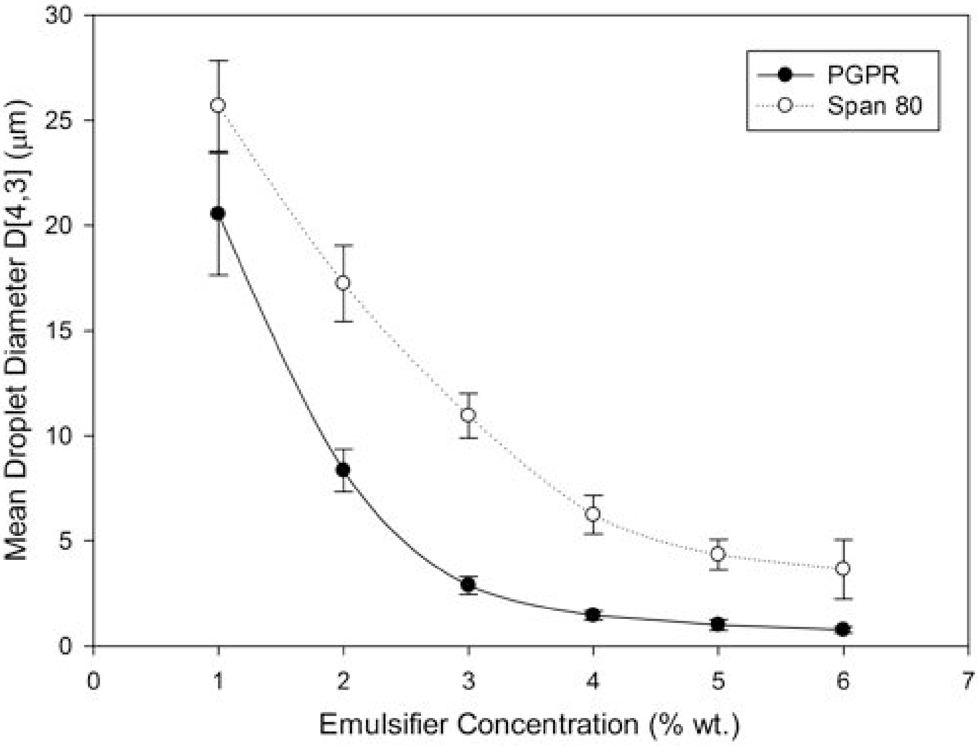


Figure 7.1. The results from making water in oil emulsions using the CFMED and a 1 µm hydrophobic SPG membrane. The emulsion was water in sunflower oil at 1% dispersed phase volume, with various emulsifier concentrations, made at 10 kPa trans-membrane pressure, and 0.6 ms^{-1} cross-flow velocity.

The results of the emulsifier tests making water in oil emulsions using the hydrophobic SPG membranes are quite similar to the oil in water results. The first interesting note is that the emulsifier content of the oil phase needs to be higher than the equivalent when making oil in water emulsions. The second notable result is how small the PGPR stabilised emulsion droplets are, at slightly smaller than the pore size. This is partly because at high concentrations PGPR has been shown to be a very effective water in oil emulsifier (Mine *et al.*, 1996), and partly because the continuous phase is more viscous than the dispersed phase, and so the shear stress applied to the forming droplets is higher than when producing the equivalent oil in water emulsion. The droplet size still reaches a minimum value and does not decrease further with increasing concentration of PGPR, and the droplet size with Span80 is beginning to level out at 6 % wt. as well.

7.1.1.2 Polymer Membrane

The polymer membrane was used to make water in oil emulsions with the same system parameters as with the hydrophobic SPG membranes. The polymer membranes are not purpose made for making emulsions in the same way that the SPG membranes are, and the polymer membranes are not surface treated to make them especially hydrophobic for producing water in oil emulsions. The results of making water in oil emulsions with the polymer membrane in the CFMED are shown in Figure 7.2.

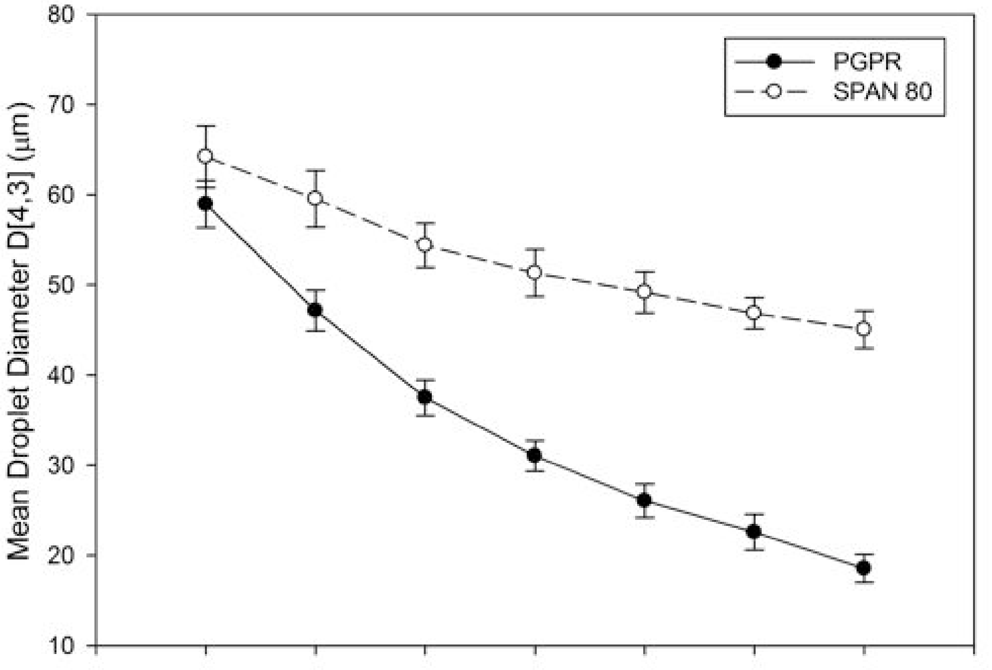


Figure 7.2. The results from making water in sunflower oil emulsions using the 1 μm pore size polymer membrane in the CFMED. The emulsions were made at 0.6 ms^{-1} cross-flow velocity, 10 kPa trans-membrane pressure and with varying emulsifier concentrations.

The results using the 1 μm pore size polymer membrane to make water in oil emulsions are again quite similar to the results for oil in water emulsions; the polymer membrane again makes much larger droplets than expected. The naturally hydrophobic polymer was expected to perform better with water in oil emulsions; however it is likely that the porosity of the polymer membrane is the cause of the larger than expected droplets, as it was when making oil in water emulsions. The polymer membrane probably produces the droplets from several pores rather than each droplet from one pore, as the produced droplets are at least double what was expected from the pore size, although visualisation of the membrane surface during emulsification would be necessary to verify this.

7.1.1.3 Stainless Steel Membrane

The effects of producing water in oil emulsions using the 15 µm stainless steel membrane was examined using the CFMED. The stainless steel membranes are neither hydrophilic nor hydrophobic, and are easily wetted by either phase. The CFMED was used to make water in oil emulsions, at 0.6 ms^{-1} cross-flow velocity, and 10 kPa, with varying concentrations of the two emulsifiers. The results of the experiments are shown in Figure 7.3.

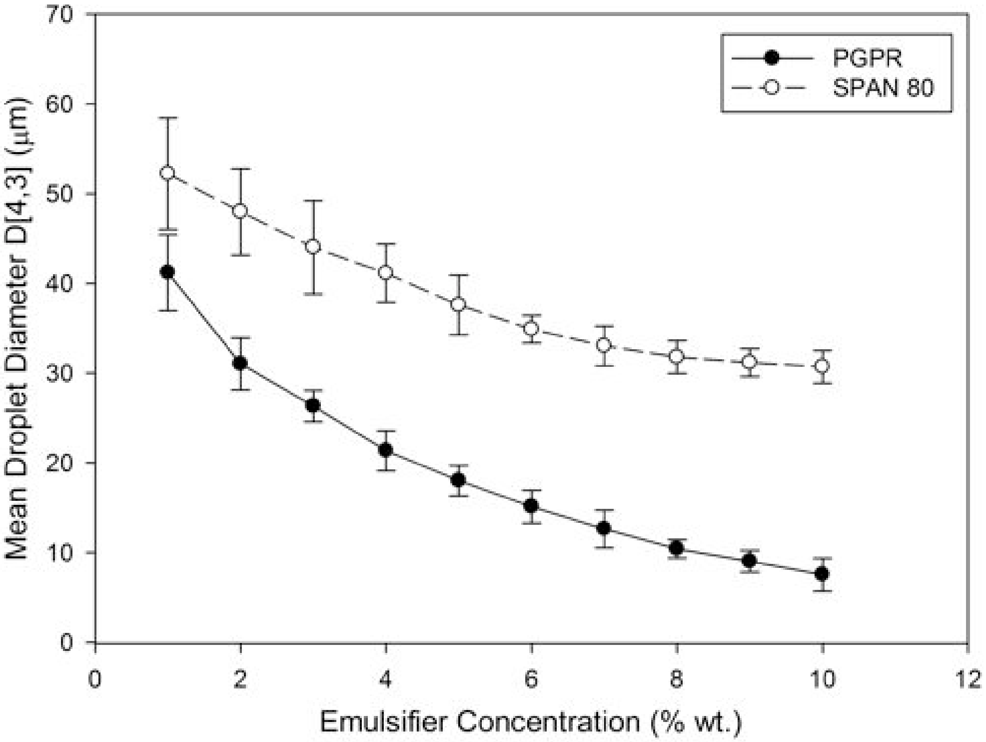


Figure 7.3. The results of making water in oil emulsions using the 15 μm stainless steel membrane in the CFMED. The emulsions were 1% phase volume water in sunflower oil with varying concentrations of emulsifier. The system was run at 0.6 ms^{-1} cross-flow velocity and 10 kPa trans-membrane pressure.

The stainless steel membranes have a far larger pore size than the other membranes tested, and this accounts for the result that the system produced droplets below the pore size at higher concentrations of PGPR. The larger surface area of the larger droplets means they are subjected to greater force in the same shear than the smaller droplets produced by the smaller pore sized membranes, and so the droplet size to pore size ratio can be lower. The droplets produced are still larger than those made by the other membranes. The droplets produced by the stainless steel membrane with the Span80 emulsifier are much larger however, suggesting that the powerful PGPR emulsifier is partly responsible for this effect, along with the increased drag of the larger droplets.

7.1.1.4 Ceramic Membrane

The 1 μm ceramic membranes were also used to make water in oil emulsions. The same water in sunflower oil at 1% phase volume was made using different concentrations of the same two emulsifiers as in the previous tests. The CFMED was used at 0.6 ms^{-1} cross-flow velocity and 10 kPa trans-membrane pressure. The results are shown in Figure 7.4.

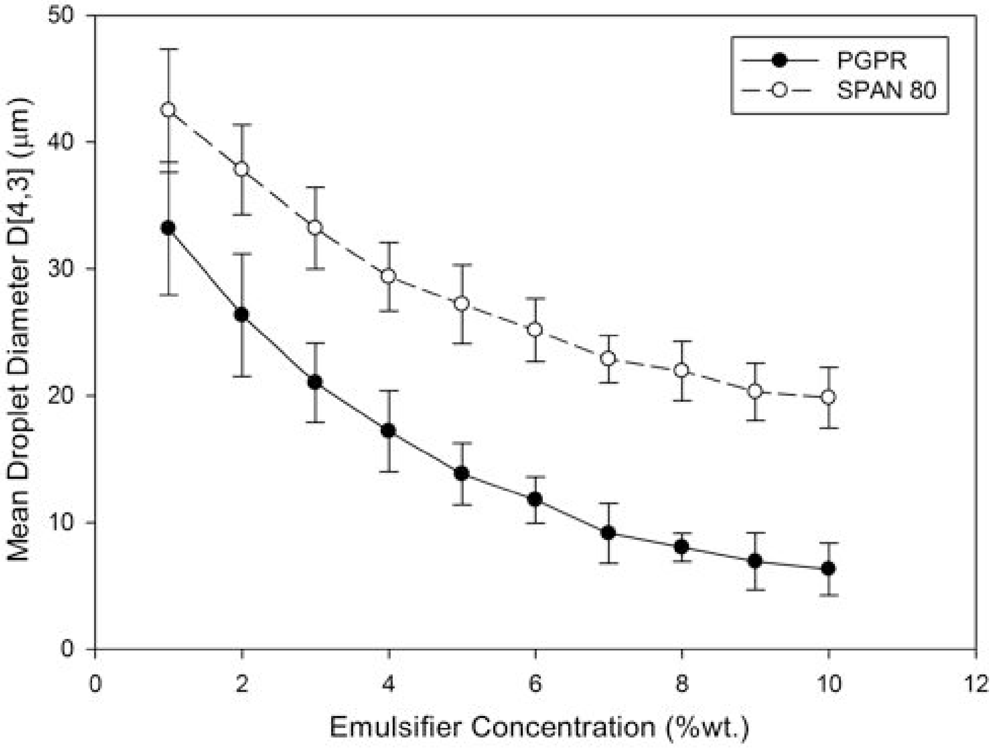


Figure 7.4. The results of producing 1% phase volume water in sunflower oil emulsions using the 1 μm ceramic membrane in the CFMED. The system was run at 0.6 ms^{-1} cross-flow velocity, and 10 kPa trans-membrane pressure, with varying concentrations of emulsifier.

Once again how easily the membrane is wetted by the continuous phase is an issue, and the ceramic membrane did not perform as well as it did when producing oil in water emulsions. The general trend is similar, decreasing droplet size with increasing emulsifier concentration, and as with the oil in water emulsions, there is no sign of the droplets reaching a minimum size at higher concentrations. Whilst the performance is not as good as for oil in water, the ceramic membranes are by no means incapable of producing water in oil emulsions, and may well be even better if the membrane were coated on the outside of the membrane (or the dispersed phase was flowed into the tube rather than out).

7.1.2 Rotating System Emulsifier Results (w/o)

The Rotating membrane emulsification device was also used to make water in oil emulsions with the SPG, ceramic and stainless steel membranes.

7.1.2.1 SPG Membrane

The 1 μm pore size hydrophobic SPG membrane was used to make water in sunflower oil emulsions at 1% phase volume, with a 10 kPa trans-membrane pressure, and 1000 rpm. The emulsifier concentrations were varied, and the results are shown in Figure 7.5.

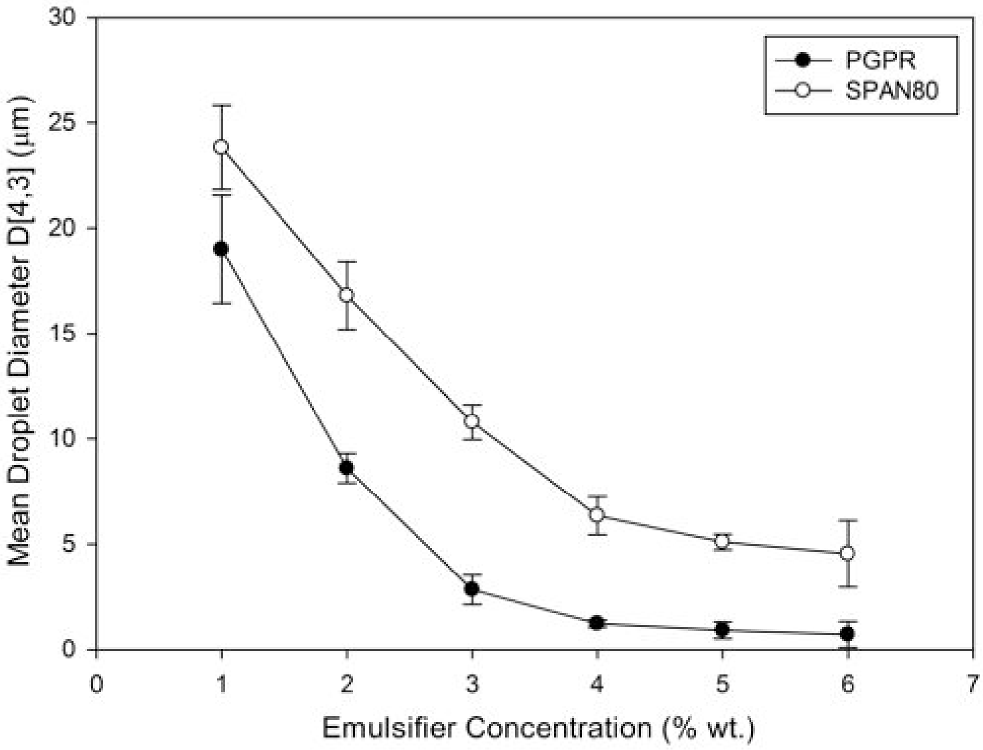


Figure 7.5. The results of using the RMED to make 1% phase volume water in sunflower oil emulsions. The emulsifier concentration was varied, and the system was run at 10 kPa trans-membrane pressure and 1000 rpm with the 1 μm SPG membrane.

The results show very similar droplets are produced using the RMED as were produced with the CFMED and the hydrophobic SPG membrane. The droplet sizes are if anything slightly lower. The centrifugal force created by the rotation of the membrane more than compensates for the lower shear rate of the RMED.

7.1.2.2 Ceramic Membrane

The ceramic membrane was tested on the rotating membrane system making water in oil emulsions with the same 1% phase volume water in sunflower oil emulsions, at 1000 rpm and 10 kPa trans-membrane pressure, with varied concentrations of emulsifier. The results are given in Figure 7.6.

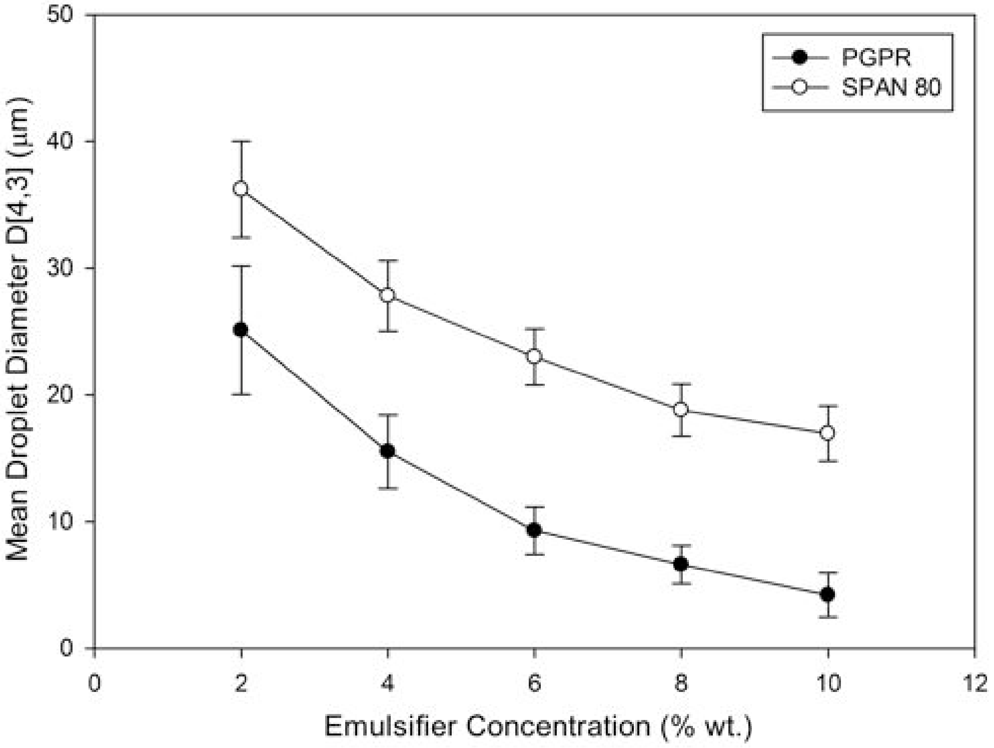


Figure 7.6. The results of making water in sunflower oil emulsions at 1% phase volume sing the RMED with a 1 µm ceramic membrane. The emulsifier concentration was varied, and the system was run at 10 kPa trans-membrane pressure, and 1000 rpm

The ceramic membrane, as in the CFMED made water in oil emulsions, however the average droplet size was larger than was seen when making oil in water emulsions, because the ceramic membrane was not as wettable with continuous phase as with the dispersed phase. The droplets produced with the ceramic membrane on the RMED are again slightly smaller than those produced with the CFMED.

7.1.2.3 Stainless Steel Membrane

The 15 µm stainless steel membrane was used on the RMED to create water in oil emulsions at 1% phase volume, with varying concentrations of emulsifier. The system was run at 1000 rpm, and 10 kPa trans-membrane pressure. The results are shown in Figure 7.7.

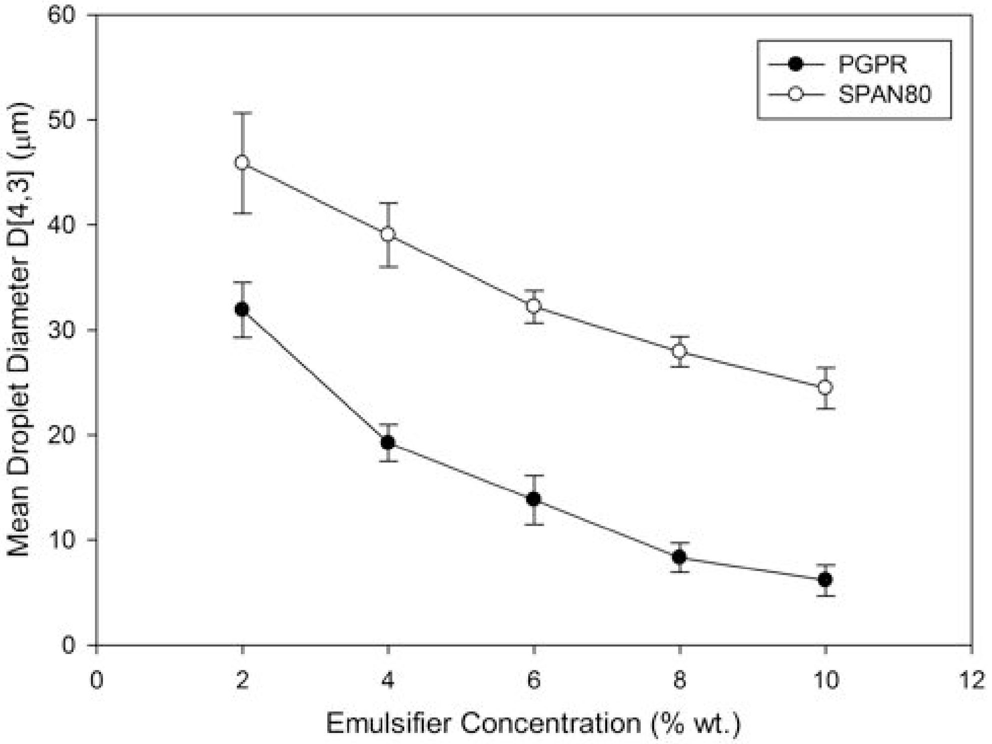


Figure 7.7. The results of using the 15 μm stainless steel membrane with the RMED to make water in oil emulsions at 1% phase volume. The system was run at 10 kPa trans-membrane pressure, and 1000 rpm.

The result are as expected, similar to the same membrane run on the CFMED making the same emulsions. The droplets are slightly smaller than those made with the CFMED, again showing that the centrifugal force detaching the droplets wore than compensates for the lower shear rate of the rotating membrane emulsification device. The droplets are much larger than those produced with the SPG or ceramic membranes, as the pores are much larger.

7.2 Nano emulsions

The CFMED was used with the smaller membrane pore sizes, to make emulsions with sub-micron droplets. The most effective membrane was the 0.2 μm SPG membrane which at high cross-flow velocity (1.1 ms^{-1}) and 150 kPa trans-membrane pressure consistently made droplets in the 150 nm size range, as shown in the droplet size distribution graph in Figure 7.8.

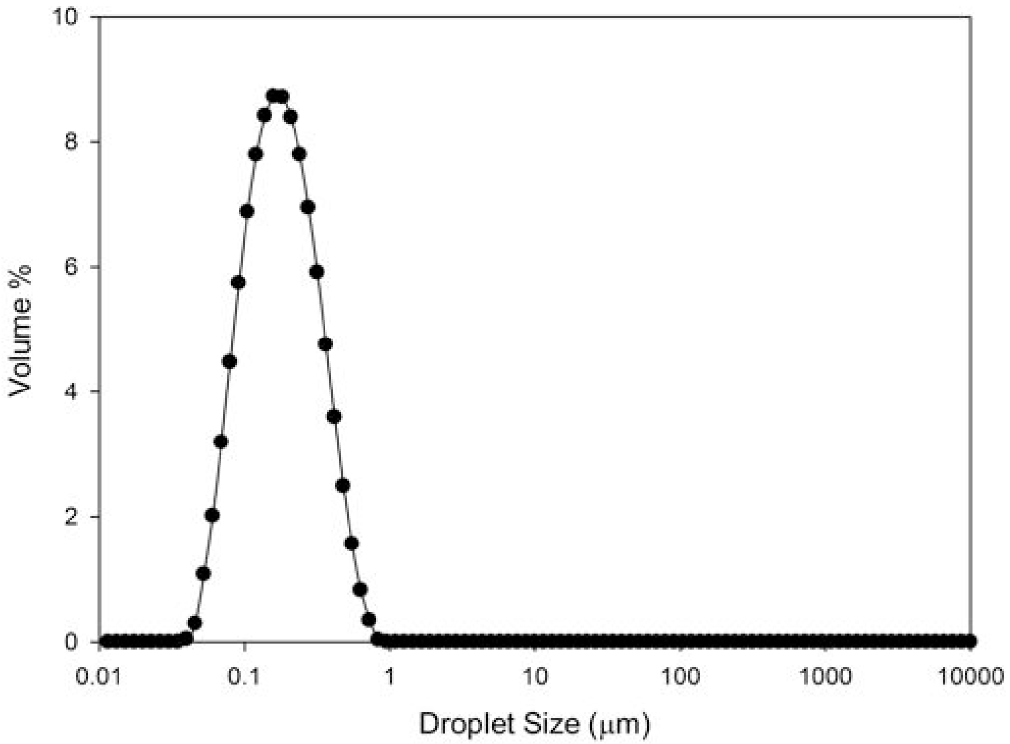


Figure 7.8. The 0.2 μm SPG membrane makes droplets around 150 nm. The distribution shown has an average droplet size of 162 nm and a span value of 0.68.

There are some small problems with the creation of nano sized emulsion droplets using membrane emulsification however, the small membrane pore size has a higher critical pressure, so the system has to run at higher pressure, and even then the flux rates are lower. To get 10% phase volume (10 ml oil volume flowed) of the droplets mentioned above, took over an hour.

7.3 Double Emulsions (w/o/w) (o/w/o)

One of the major advantages of membrane emulsification lends itself to the making of double emulsions, and the uses of such emulsions are a focus of much research interest at the moment, not least because of the possible uses for tasks such as fat and salt reduction of foods, and delayed or controlled release of substances contained within the inner phase, or for hiding substances within the inner phase which are desirable but may affect flavour for instance.

To make double emulsions in a droplet breakup system the primary emulsion must be reprocessed through the system to emulsify it into the second continuous phase, and inevitably the inner droplets are re-broken and some of them will end up in the bulk phase, their contents released into the rest of the emulsion, as well as bulk continuous phase often being included as part of the internal droplets (Figure 7.9). This simply doesn’t happen when making double emulsions with membrane systems, where the droplets of the primary emulsion stay within the droplets of dispersed phase in the secondary (assuming the formulation will allow), as long as the membrane pore size of the membrane making the double emulsion is greater than around double the size of the primary emulsion droplets.

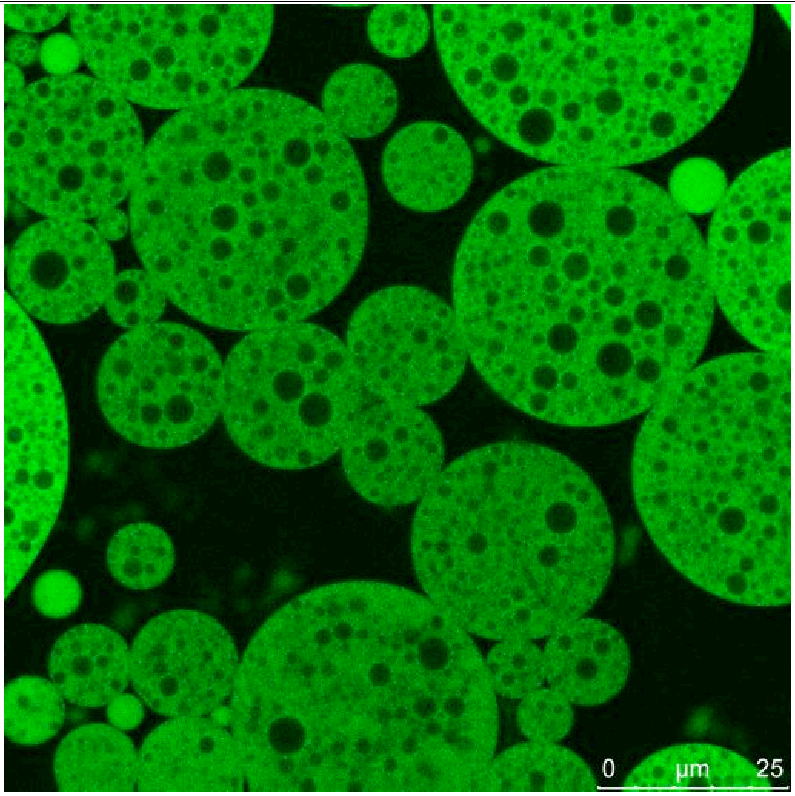


Figure 7.9. A confocal micrograph of a double (W/O/W) emulsion made using a Silverson L4R mixer. The inner water phase was dyed using Nile blue dye, emitting light at 674 nm when excited at 635 nm in water, the inside of the large oil droplets appears bright because of the small water droplets containing the dye. the dark patches within the large droplets are the second water phase which has been included within the primary emulsion when the primary was mixed into the second (water) continuous phase to create the double. It is also likely that the main continuous phase also contains some of the internal water phase, but the dye is so dilute it isn't detected. If the Nile blue dye were to have partitioned into the oil phase it would no longer be seen, as the absorption and emission of Nile blue is at much shorter wavelength in an oil solvent.

The formulation is very important when making double emulsions, if there are too high a concentration of emulsifiers in any of the phases (or too low) the balance of the double emulsion is upset and the inner phase will be lost. The concentrations of substances such as salts dissolved in the inner dispersed phase are also important, if the concentration is higher than in the bulk emulsion for example, diffusion will try to equalise the concentration, pulling continuous phase into the inner droplets swelling them, which may also break the emulsion.

As a proof of concept, the CFMED was used to make several ‘simple’ water in oil in water double emulsions, using PGPR and Tween20 as the emulsifiers, and containing nothing else other than sunflower oil and water. A primary emulsion was made using the hydrophobic SPG membrane to emulsify water at 50% phase volume in to sunflower oil containing 4% wt. PGPR. This emulsion was then itself emulsified through the 2 μm hydrophilic SPG membrane into a water phase containing just 0.25% wt. Tween20. The resultant emulsion can be seen in the light micrograph in Figure 7.10.

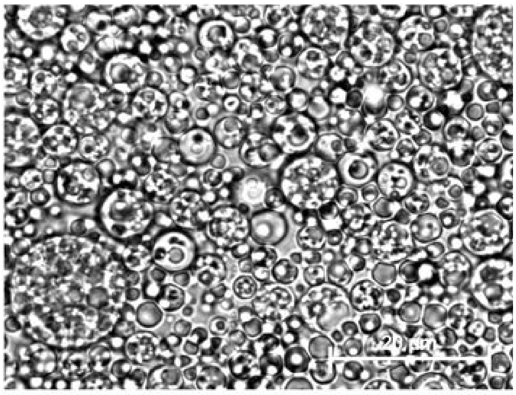


Figure 7.10. A micrograph of a double (water in oil in water) emulsion made using the CFMED. The emulsion has a primary emulsion with 50% phase volume water in oil containing 4% wt. PGPR, which is then emulsified as the dispersed phase into water containing 0.25% wt. Tween20 to a phase volume of 50%.

Double emulsions have many possible uses, and so the ability to quickly create controlled double emulsions with completely separate internal and external water phases for example, is of interest and will have industrial significance.

The possibility that the double emulsion systems could be used to create lower salt but similar taste and feel for foodstuffs has started to be investigated. There are several ways that have been suggested to reduce either salt content or fat content of foods using controlled microstructures. Bulking of an oil phase with an internal water phase without salt (or with a less palatable but more healthy salt such as potassium chloride to balance the osmotic pressure) and thus retaining the salt concentration of the external water phase (and therefore the taste) but with a lower overall salt amount has been suggested. This approach may however increase viscosity and change the overall feel of the product as the apparent phase volume ratios will have changed, even if the actual quantities are kept the same.

The encapsulation of a salt containing phase causing a release in mouth and therefore a local increase in perceived saltiness has also been put forward, and the possibility of this was tested.

The CFMED was used to make double water in oil in water emulsions, with the inner water phase containing a beetroot dye. The dye was not seen in the external bulk phase but was seen strongly in the primary water phase under the microscope, suggesting that there was little or no leakage into the bulk phase of the internal water droplets. The same emulsion made using a Silverson L4R high shear mixer however showed a pronounced pink in the continuous water phase.

The CFMED can therefore make double emulsions losing much less if any of the primary dispersed liquid into the continuous liquid.

7.4 Gel Beads

As a proof of concept alginate gel beads have been made using the crossflow membrane emulsification device. Sodium alginate was dissolved into milliQ water, and then passed through the membrane (requiring very small TMP) into a continuous phase containing Calcium chloride. The resultant alginate beads are shown in Figure 7.11.

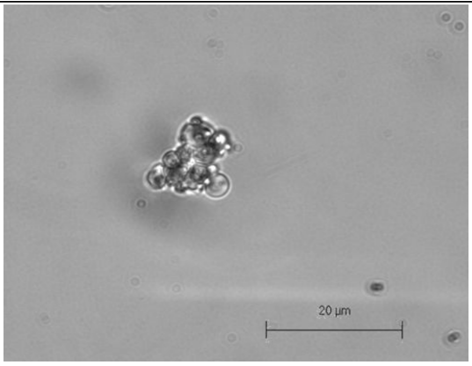


Figure 7.11. A micrograph showing alginate beads made using the CFMED.

The concentration of alginate and calcium chloride in the solutions is critical. The beads shown in the micrograph were made using a 5% wt. sodium alginate solution and a 0.25% wt calcium chloride solution. If the concentration of calcium chloride is too high the solution diffuses back through the membrane too quickly causing the solidification of the dispersed phase before passing through the membrane, resulting in the gelling of the contents of the membrane module. This also happens if the continuous phase pressure ever exceeds the dispersed phase pressure in the membrane module, so the standard operating procedure needs to be modified slightly. Once the procedure was worked out however, the beads were produced reliably. The beads do end to clump together as seen in the micrograph; they can be separated by agitation or sonication if needed.

7.5 Comparison with a high shear mixer

To compare the membrane emulsification process with a traditional method of emulsification, emulsions were made using various concentrations of emulsifier in both the CFMED and a high shear rotor stator mixer, the Silverson L4R. Emulsifier concentration has less effect on final droplet size with membrane emulsification than in droplet breakup systems as long as there is sufficient to stabilise droplets as they form, it was shown that further increases have little effect on the size of the droplets produced. This can be seen in the results from tests comparing the Silverson L4R mixer with the membrane emulsification device (Figure 7.12). Similar emulsions were made at 50% phase volume (to pronounce the effect of the emulsifier by increasing the likelihood of collisions and coalescence) of sunflower oil in water using varying concentrations of Tween20 as the emulsifier. The membrane device was set up with a 1 μm SPG membrane at 60 kPa trans-membrane pressure, and a cross-flow velocity of 0.6 ms^{-1} (similar to earlier tests and representative of the systems capabilities). One litre of the emulsion was produced using each device. The Silverson was run for 15 minutes at 6000 rpm, whilst the membrane system took 10 minutes to flow the 0.5 litres of sunflower oil required. The increasing concentrations of Tween20 have a gradual effect on mean droplet size on the emulsions made using the Silverson, and increasing concentrations above 1% still causes further size decreases. However, the membrane device has reached a smaller mean droplet size at 0.4% wt. Tween20, and the size remains relatively unchanged past this concentration. The Silverson never produces a mean droplet size quite as low as that produced by the membrane system at 0.4% Tween20.

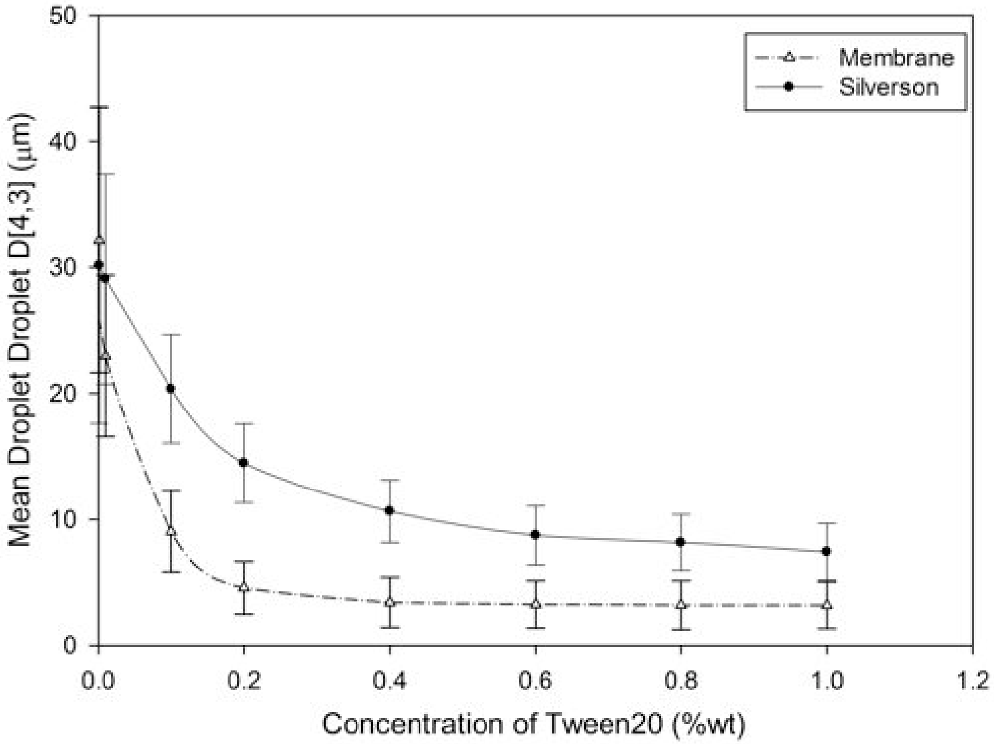


Figure 7.12. The comparison of emulsifier usage in membrane emulsification and a high shear mixer. The membrane system is able to achieve lower mean droplet size using less emulsifier.

It was also observed that the Silverson increased the heat of the emulsion by around 30º C during the runs, whilst the membrane emulsification system causes an increase of less than 5º C on average, this implies that membrane emulsification could allow the use of more heat sensitive ingredients if required. Previous studies (Williams *et al.*, 1998) have found that membrane emulsification is also far more power efficient than the rotor stator systems. At higher shears (ie. higher rotation speeds the Silverson will produce smaller droplets in shorter times, and at higher cross-flow velocities the CFMED will also produce smaller droplets in shorter times. The evaluation of the two systems is meant to highlight the advantages and disadvantages rather than provide an exhaustive comparison. The advantage of being able to produce similar droplets at much lower shear rates is clearly shown when using the CFMED, and further increasing the shear applied by the Silverson was not necessary, rather a typical median example of each was chosen.

Similarly a high pressure homogeniser can produce much smaller droplets at much greater throughputs, however the advantage of membrane emulsification is its low applied shear and energy. An exhaustive comparison of various alternative emulsification systems would perhaps be useful future research.

7.6. Summary

The CFMED and RMED are simple and useful systems capable of making varied emulsions and other particles. The production of water in oil emulsions is as simple and controllable as oil in water, only requiring the careful selection of the correct membrane type and settings to produce the correct size and size distribution of droplets. The membrane emulsification systems can also be used effectively to produce gelled beads, and nano sized emulsion droplets at higher shear rates and pressures. The potential for many other microstructured particles and emulsions provides a promising area for future research.

Chapter 8

Conclusions

Increasing the shear force applied to the membrane surface decreases the droplet size, but won’t reduce it as quickly below the pore size of the membrane. It is possible to produce droplets smaller than the membrane pore size at high shear, but the size distribution span increases as the droplet size is no longer determined by the pore size.

Droplets produced by membrane emulsification are formed under different flow regimes depending on the process conditions; the droplets are either sheared off before being fully formed, detached under the effects if inertia and interfacial tension, on injected into the continuous phase as a stream which breaks up under Raleigh instability. The regime by which the droplets are produced is determined by the combination of shear, trans-membrane pressure, relative phase viscosities and pore size.

The larger the droplets being produced, the less shear is required to detach them from the pores, because of the higher drag that they incur. Inversely smaller droplets require increasingly higher shear to detach.

Making low size distribution emulsions requires keeping the size of the formed droplets determined by the pore size of the membrane. This means keeping the pressure below the point at which the regime changes to injection, and the cross-flow velocity below the point at which the droplet size becomes lower than the pore size.

If the size distribution is less important than the flux the pressure can be increased without any other adverse effects other than slightly higher size distribution. Flux rates are largely determined by the flow resistance of the membrane and the trans-membrane pressure, being similar between the two devices when using the same membrane.

The relative viscosity of the two phases being emulsified has an effect on the size and size distribution of the emulsion droplets produced. Increasing the viscosity of the continuous phase decreases droplet size, whilst increasing the dispersed phase viscosity increases droplet size. There is a greater change in droplet size when the two phases viscosities are similar. The size distribution of the droplets is lowest when the viscosities of the two phases are similar.

Membranes with too high a porosity may produce droplets from more than one pore, meaning the droplets are larger and have higher size distribution, such as with the polymer membrane used in these tests.

The specific morphology of each membrane type tested gives specific advantages and disadvantages to each membrane.

The ceramic membranes have a support material, which changes the way the droplet size reacts to changes in the shear applied when the dispersed phase passes through the membrane first, and then the support material. The forming droplets are shielded from the shear and so grow larger before detaching.

The stainless steel membrane is the most versatile, being equally good at making oil in water and water in oil emulsions, the large size of the pores being the limiting factor. With improvements in laser manufacturing processes, it is possible that smaller pore stainless steel membranes will be available in the future for production of smaller droplets.

Rotating the membrane is an improved method of imparting shear to the forming droplets to cause detachment, the extra centrifugal force this provides makes similar droplet sizes with at much lower shear rates.

The relative densities of the dispersed and continuous phases have an effect on the performance of the rotating membrane system, as the least dense phase tends to float and collect near to the membrane. This is an advantage with a more dense dispersed phase, and a disadvantage with a more dense continuous phase.

The rotating membrane device works equally well when making emulsions with SPG or ceramic membranes as it does with the stainless steel, the higher porosity and irregular pores of these membranes having little real effect on the droplets produced, which are similar to the droplets produced using the same membrane with cross-flow membrane emulsification.

Hydrophobically modified SPG membranes make good water in oil emulsions, the ceramic membranes however do not perform as well when making water in oil emulsions, because they are more easily wetted by the water dispersed phase.

One of the major advantages of membrane emulsification is the ability to control microstructure by specifically choosing where the phases end up; the dispersed phase of a primary emulsion stays within the primary emulsion when that emulsion is dispersed as a double emulsion for example. The low shear imparted to the dispersed phase means that the primary emulsion is not disrupted when re-emulsified into the duplex emulsion

This ability will enable membrane emulsification to make many other microstructured particles like beads, and core-shell structures at higher production rates than the equivalent microfluidic devices.

The formulation of the product is important in membrane emulsification, the membrane is easily clogged, and whilst products like gel beads can be created in a single step, the formulation must be carefully considered to avoid membrane fouling.

Nano sized droplets are produced easily from membranes with a small pore size, at higher pressures and shear rates, although this does increase the energy input required.

Chapter 9

Further Studies

Currently, membrane emulsification has not been successfully scaled up, there are several problems with membrane emulsification; fouling of the membrane, and cleaning, scale up problems because of pressure drop along the membrane. The system used in this study was of relatively low pressure, and low pump and rotation speeds, and as such could only produce low viscosity emulsions.

Continuing the development of membrane emulsification eventually will lead to the production of an emulsion product using membrane emulsification. The next step will be to try to produce usable quantities of a real formulation, perhaps for food use. The scale up to pilot plant work (in a food grade environment) is a major step in the path toward using membranes for industrial emulsification processes.

The effects of chemically treating the ceramic membranes to make them hydrophobic, on the water in oil emulsions that they produce would be interesting to investigate, as would the effects of testing a ceramic tube with the membrane coated on the outside of the support tube. Although previous studies have used ceramic tubes with the continuous phase flowing along the centre of the tube adjacent to the membrane coating the effects of running the system with the continuous phase flowing through the smaller annular gap would be interesting. The membrane being coated onto the outside of the support tube would also allow the membrane to be adjacent to the continuous phase when used on the rotating membrane emulsification device. It is possible that this would combine the low droplet/pore size ratio of the SPG membranes with the resilience and higher flux rates of the ceramic, which would improve the technique

The ability of the membrane emulsification system to make gelled beads has been shown, but investigating the possibilities for making more complex structures such as polymerised core-shell structures and other microstructures, perhaps as part of a continuous production process would be a good continuation of the study.

Investigation of the ability to make nano sized emulsion particles at higher production rates would require the creation of a higher pressure system, but would be another interesting line of research with membrane emulsification.

The effects of using different emulsifiers such as fat crystals, and Pickering stabilising particles such as silica particles with membrane emulsification would be another interesting area of research.

The rotating membrane emulsification device would benefit from being able to run at higher pressures (currently limited by the dispersed phase tank and the rotating coupling) and faster rotation rates (currently limited by the stirrer to 2000 rpm). At faster speeds and higher pressures, it would be possible to run the smaller pore sized SPG membranes and make nano sized emulsion particles. Several other upgrades would make the rotating membrane system more accurate, including a system for centring and holding the continuous phase vessel (and possible flowing continuous phase through the vessel to make the process continuous rather than batch), and possibly including a bearing to hold the lower end of the membrane itself centred, and eliminate vibrations, which would improve the control over droplet size.

The CFMED also could be adapted to run as a continuous process, and possible a second one could run in serial with it to make double emulsions as a continuous process.

The ability of membrane emulsification has possibilities to make semi-solid emulsions, with adaptations it would be very interesting to set up and test the CFMED with higher pressure equipment particularly on the continuous phase loop, where a high pressure pump (probably a piston pump or screw type extrusion pump) and higher pressure pipe work would be required.

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