

Separation of oil drops from produced water using a slotted pore membrane

By

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Dedicated to my parents, brothers and sister

Abstract

Microfiltration is one of the most important processes in membrane sciences that can be used for separating drops/particles above 1 μ m. Depth microfiltration membranes retain drops/particles inside the surface of the membrane, the process is expensive and membranes quickly become fouled. On the other hand, surface microfiltration membranes stop drops/particles on the surface of the membrane and the process is less fouling. Higher permeate flux and lower trans-membrane pressure is obtained with a shear enhanced microfiltration technique.

Production of specific size of drops and stability of the drops are very important in testing the microfiltration of crude oil drops/water emulsions. Oil drops from 1-15 µm were produced with a food blender, operated at its highest speed for the duration of 12 mins. In addition, vegetable oil drops were stabilised with 1% polyvinyl alcohol (PVA), Tween 20 and gum Arabic, stability was assessed on the basis of consistency in the size distribution and number of drops in each sample analysed at 30 mins interval.

A slotted pore Nickel membrane with the slot width and slot length of 4 and 400 μ m respectively has been used in the filtration experiments. The slot width to the slot length ratio (aspect ratio) of the used membrane is 100. Vibrating the membrane at various frequencies created shear rates of different intensities on the surface of the membrane. Membrane with a tubular configuration is preferred over the flat sheet because it is easy to control in-case of membrane oscillations both at lab and industrial scale. Besides this, a tubular membrane configuration provides a smaller footprint as compared to the flat sheet.

The influence of applied shear rate on slots/pore blocking has been studied. Applying shear rate to the membrane reduced the blocking of the slots of the membrane; and reduction of slots blocking is a function of the applied shear rate. At higher shear rate, lower blocking of the slots of the membrane was verified by obtaining lower trans-membrane pressure for constant rate filtration. The experiments are in reasonable agreement with the theoretical

blocking model. Divergence of the experimental data from the theory may be due to involvement of deforming drops in the process.

During microfiltration of oil drops, the drops deform when passing through the slots or pores of the membrane. Different surfactants provided different interfacial tensions between the oil and water interface. The influence of interfacial tension on deformation of drops through the slots was studied. The higher the interfacial tension then the lower would be the deformation of drops through the slots. A mathematical model was developed based on static and drag forces acting on the drops while passing the membrane. The model predicts 100% cut-off of drops through the membrane. Satisfactory agreement of the model with the experiments shows that the concept of static and drag force can be successfully applied to the filtration of deformable drops through the slotted pore membranes.

Due to the applied shear rate, inertial lift migration velocities of the drops away from the surface of the membrane were created. Inertial lift velocities are linear functions of the applied shear rate. A mathematical model was modified based on inertial lift migration velocities. The critical radius of the drops is the one above which drops cannot pass through the surface of the membrane into the permeate due to the applied shear rate and back transport. The model is used as a starting point and is an acceptable agreement with the experiment.

The model can be used to predict the 100% cut-off value for oil drops filtration and a 'linear fit' between this value and the origin on a graph of grade (or rejection) efficiency and drop size to slot width ratio was used to predict the total concentration of dispersed oil left after filtration. Hence, it is shown how it is possible to predict oil discharge concentrations when using slotted filters.

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Nomenclature

- *a* oscillation amplitude
- c concentration of oil in the permeate (kg m⁻³)
- d^{**} diameter of pore/slot at the start of the process when it is assumed to be completely

open (m)

- D particle diameter (m)
- D_{max} maximum particle diameter (m)
- D_{sp_h} spherical drop diameter (m)
- D' diffusion coefficient (m² s⁻¹)
- *E* hydrocyclone efficiency
- E_{ca} capillary energy (N m)
- $f_p(D)$ probability distribution function of particle diameter
- f function
- *F* oscillation Frequency (Hz)
- F' force required in pulling out the ring from one phase into in other (N)
- F_c static force (N)

- F_d drag force (N)
- g_i volume fraction of oil in the feed of hydrocyclone
- g_u volume fraction of oil in the underflow of hydrocyclone
- *h* half width of the slot (m)
- J permeate flux rate $(1 \text{ m}^{-2} \text{ hr}^{-1})$
- *k* Boltzmann constant (J K⁻¹)
- k_i number of drops in an increment
- k_o initial permeability (m²)
- k_w drag force correction factor
- *m* mass of oil (kg)
- *n* empirical correlation
- ΔP pressure difference across membrane (Pa)
- Q_i hydrocyclone feed volumetric flow rate (m³ s⁻¹)
- Q_o hydrocyclone overflow volumetric flow rate (m³ s⁻¹)
- *R* radius of the ring (m)
- *R'* hydrocyclone flow split

- R_{ell} radius of ellipsoid (m)
- R_{eo} oscillatory Reynolds number
- R_{sp} radius of spherical drop (m)
- S_{ell} surface area of ellipsoid (m²)
- S_{sp} surface area of sphere (m²)
- *t* filtration time (s)
- *T* absolute temperature (K)
- U in-pore velocity (m s⁻¹)
- v kinematic viscosity (m² s⁻¹)
- v_{if} inertial lift migration velocity (m s⁻¹)

$$v_o$$
 velocity amplitude (m s⁻¹)

- v' convection velocity of drops towards membrane surface with shear rate applied (m s⁻¹)
- v'_o convection velocity of drops towards membrane surface without shear rate applied (m s⁻¹)
- x_i mid-size of an increment (m)

y' blocking constant (m²)

Greek letters

- α angle at which slot converges towards inside (°)
- ω angular frequency (s⁻¹)
- $\dot{\gamma}_{cr}$ critical shear rate (s⁻¹)
- ρ_f density of the fluid (kg m⁻³)
- σ interfacial tension (N m⁻¹)
- β parameter to characterize membrane pore influence
- β' correction factor
- $\dot{\gamma}$ shear rate (s⁻¹)
- \sum summation
- η viscosity of the fluid (Pa s)

$$\lambda \qquad \frac{h}{R_{sp}}$$

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Chapter 1

Introduction

1.1 Background

Produced water is the biggest liquid waste obtained during oil and gas production. In the US alone, annual production of produced water is 33 billion barrels. It contains dispersed crude oil drops of various sizes [Arscott, 1989]. Due to the high concentration of crude oil in produced water, it cannot be discharged into the sea or reinjected into the oil wells. The composition of crude oil in produced water ranges from 50-1000 ppm [Taylor et al., 1991]. Oil in water is a threat for life within the water and also harmful for the environment. Concentration of crude oil in produced water used for rejecting into oil wells or discharging into the sea should be 10, and 30 ppm respectively [Bevis, 1992].

Separating oil drops from dilute oil/water emulsions and meeting the allowed oil concentration in the permeate is still a challenge for researchers [Rautenbach and Albrecht, 1989]. Initially, conventional treatment technologies like gravity separators and coalescer plates were used, but the purity requirements were not meet [Mueller et al., 1997]. Problems with the conventional separators were the requirements of chemicals, expensive process and production of large sludge volumes [Cheryan and Rajagopalan, 1998]. Hydrocyclones were found ineffective with drops below 10 μ m and its efficiency increases with increasing drops size [Cumming et al., 2000]. To handle oil drops less than 10 μ m membrane separation technology was tested. Membrane technology provides a better separation of materials, a high permeate quality and consumes a lower energy as compared to conventional methods like gravity separators and hydrocyclones. Therefore, membrane technology is preferred over conventional separation techniques.

Permeate flux rate around 150 l m⁻² hr⁻¹ was obtained with ultrafiltration. The flux rate obtained with ultrafiltration was too low and the process was expensive [Lia et al., 2006]. The idea of microfiltration was investigated by a number of researchers [Mueller et al., 1997; Koltuniewicz et al., 1995; Ohya et al., 1998; Kim et al., 1997]. Flux rate with microfiltration (150 l m⁻² hr⁻¹) was not much higher than ultrafiltration; the membranes used had complex tortuous internal structures that became highly fouled and the process was referred to as a depth filtration. It was found that the permeate flux rate was strongly dependent on oil drop size.

In the last decade, instead of depth, surface filtration attracted research in which suspended particles and dispersed drops are retained on the surface of the membrane [Holdich et al., 1998; Cumming et al., 1999]. Surface filtration is effective due to low fouling of the membrane and the process is more economical as compared to depth filtration [Holdich et al., 1998]. The other advantage of surface filtration was the low trans-membrane pressure and high permeate flux rate [Holdich et al., 1998; Chandler and Zydney, 2006]. Surface filtration increased the separation efficiency of the membranes used for oil/water emulsions [Cumming et al., 2000].

To control the fouling further, and to enhance membrane efficiency, filtration operations with various shapes of pores were investigated [Bromley et al., 2002; Kuiper et al., 1998; Ho and Zydney, 1999]. Slotted pore membranes provide more open area to dispersed drops and suspended particles as compared to circular pore membranes (for details see figure 2.1) [Chandler and Zydney, 2006]. Circular pore membranes foul quickly and a layer of materials forms on the membrane surface that offers resistance to flow of fluid through the membrane [Bromley et al., 2002]. On the other hand, slotted pore membranes fouled less compared to circular pore membranes found le

Permeate flux rate enhancement has been a prime focus for scientists and researchers in the last few years. Shear rate is applied to the surface of the membrane by oscillating/rotating the membrane with various frequencies and this type of filtration is referred to as shear enhancement dynamic filtration [Jaffrin, 2008]. Shear enhanced dynamic filtration is an alternative to cross-flow filtration. In cross-flow filtration, shear is created due to a high flow rate of the fluid that requires an extensive consumption of electricity [Postlethwaite et al., 2004]. Permeate flux rate increased with oscillating the membrane above 25 Hz [Gomaa and Rao, 2011]. Blocking of membrane slots was considerably decreased with oscillating the membrane pressure was found as a function of the applied shear rate [Gomaa and Rao, 2011].

1.2 Aims and objectives

The overall aim of this research was to develop the most effective technique to separate crude oil drops from produced water using slotted pore membrane microfiltration. The following objectives were identified to achieve the set goals.

• In membrane separation, production of specific size drops is a prime factor. Production of oil drops from 0-10 μ m was considered as a starting point for the research. Producing a significant number of drops with-in the range of the measuring equipment was also a challenge.

• Drops coalesce making larger drops: to avoid coalescence of drops, various surfactants were tested and selecting the one providing efficient results was considered necessary for the research.

• In the literature membrane oscillation is found to be very effective in the production of monosized drops during emulsification [Holdich et al., 2013]. To investigate how membrane oscillation affects trans-membrane pressure and comparison of experiments with a blocking model was one of the aims in the study.

• To study how changes in interfacial tension between oil/water, influence deformation, passage, and separation efficiency of oil drops through a slotted pore membrane. Comparison of experimental data with the drops deformation model through the slots was considered important.

• Studying membrane oscillation and its influence on rejection of oil drops through the membrane. Also, to develop a mathematical model taking into account the inertial lift migrations produced during oscillating the membrane.

• The developed model is used to predict size distribution of drops in the permeate in order to investigate the permeate concentration is within the standard and validated with genuine size distribution data coming from oil rigs.

1.3 Main contribution of this work

Summary of the main contributions of the study are explained as follows,

• Oil drops from 1-15 μ m were produced and stabilised, analysed using the Coulter Multisier and a technique was developed for assessing the number of drops with-in the range of the Coulter.

• Oil drops were stabilised using water soluble surfactants polyvinyl alcohol, gum Arabic and Tween 20 on the basis of consistency in size distributions and number of drops when samples were analysed at the interval of 30 mins. Crude oil drops did not require any surfactants.

• The membrane was oscillated at various frequencies that created a shear rate on the surface of the membrane which affected the trans-membrane pressure considerably. Reduction in trans-membrane pressure was found as a function of the applied shear rate. The Starov blocking model was used to study the influence of the applied shear rate on blocking the slots of the membrane. A satisfactory agreement of the experimental data with the theory showed that the model can be efficiently applied for filtering oil drops with a slotted pore membrane with, and with-out, shear rate applied.

• Different surfactants gave rise to different interfacial tensions between the oil and water interface. It is investigated how the interfacial tension influenced deformation of oil drops through the slots of the membrane without shear rate applied. A theory is developed taking into account the difference in energy required for deformation of a spherical drop into a spheroid drop. The model is applied to the experiments and good agreement is obtained. A concept of 'linear fit' is introduced that can be used for drops below 100% cut-off of oil drops through the membrane.

• Membrane oscillation influenced rejection of oil drops through the membrane. With the oscillation of the membrane a lift migration velocities away from the membrane were created. A mathematical model is used as a starting point, taking into account inertial lift migration velocities for fast laminar flow away from the membrane. Rejection of oil drops through the surface of the membrane increased with increasing the applied shear rate and the number of

drops in the permeate reduced. It is found that shear-induced and inertial lift migration velocities were functions of the applied shear rate. The developed theory is found reasonably consistent with the experimental data.

• The idea of 'linear fit' is extended for predicting the rejection and, therefore, the size distribution of drops in the permeate. Predicted permeate size distribution can be obtained by multiplying the size distributions of a feed to the fraction of drops passed through the membrane for a given size of drops, and the overall permeate dispersed oil content can be computed from the predicted 100% cut-off and 'linear fit'. Hence, it is possible to predict what slot size filter is required for any given oil dispersion and permeate flux rate, in order to meet the overall rejection requirements of, for example, 30 ppm oil in water, suitable for discharge of produced water containing crude oil into the sea under current international agreements.

1.4 Thesis structure

A brief description of each chapter is as follows,

Chapter 1: Introduction: The chapter explains a brief introduction of the thesis.

Chapter 2: Literature review: This chapter is divided into four main parts. The first part contains a description of produced water: the origin and composition of produced water; effects of produced water on the environment and type of technologies used for separation of crude oil drops from produced water are explained. Membrane separation technology is preferred over other technologies with reasons given and literature is provided. In the second part, literature about emulsion stability and various factors effecting stability of emulsions are explained. The third part contains detailed descriptions about critical and sustainable flux rates. It is explained how operating conditions influence critical/sustainable filtration conditions. In the last part, shear enhanced filtration is explained. Vibrating the membrane at various frequencies and its influence on flux rates and trans-membrane pressure is provided.

Chapter 3: Emulsion preparation and drop stability: This chapter explains the technique developed for preparation of oil/water emulsion with stable drop size from 1-15 μ m. Different surfactants and the technique used for drops stabilisation are explained.

Chapter 4: Membrane oscillation and sustainable flux rates: This chapter contains a detailed description of the oscillating membrane system with various frequencies that provided shear rate of different intensities to the surface of the membrane and its influence on the trans-membrane pressure. A blocking model is used for the theoretical prediction of the trans-membrane pressure. It is explained that deviation of experimental data from the theory is due to the applied shear rate, and deformable drops that squeeze through the slots not blocking the slots completely.

Chapter 5: Interfacial tension and a model for deformation of oil drops without membrane oscillation: A detailed description about interfacial tension and its influence over the deformation of oil drops passing through slotted pore membranes without shear rate applied to the surface of the membrane is provided in this chapter. It is explained that increase in interfacial tension between oil/water decreases deformation, and passage, of oil drops through the slots of the membrane used. A mathematical model is developed on the basis of drag force and static force on a drop passing through a slot of the membrane. The model was successfully applied to the experimental data for 100% cut-off showing that the developed model can be applied for filtering deformable oil drops through a slotted pore membrane. The concept of 'linear fit' is provided, which is an efficient idea to predict theoretical rejection of oil drops below 100%.

Chapter 6: Membrane oscillation and rejection of drops through the membrane: This chapter explains that due to oscillation of the membrane rejection of oil drops increased and it is found experimentally that number of oil drops in the permeate decreased with the applied shear rate. A theory is used (used as a starting point) on the basis of inertial lift migration velocities for fast laminar flow away from the surface of the membrane and drag and static forces. A theoretical description is provided for critical size of the drops that would not pass the membrane surface into permeate of the membrane due to applying certain intensity of shear rate.

Chapter 7: Prediction of size distribution of crude oil drops in the permeate: The 'linear fit' approach can be used for predicting rejection of drops below 100% cut-off. 'Linear fit' can be obtained by extrapolating theoretical 100% cut-off to the origin of the rejection graph. For a given size of drops, fraction of drops rejected and passed through the membrane can be

obtained from the 'linear fit'. Multiplying the fraction of drops passed through the membrane to the size distribution of feed for a given drops size; permeate size distribution and overall dispersed phase oil drop rejection can be predicted.

Chapter 8: Conclusions and future work: This chapter provides a brief summary of the work done during the research experimentally and theoretically. The main conclusions and proposals for future work are provided.

Chapter 2

Literature review

2.1 Produced water

Produced water represents the largest volume waste liquid produced during oil and gas production on most offshore platforms [Alkhudhiri et al., 2013; Lee and Neff, 2011]. Water in produced water either comes from sea water or fresh water trapped for millions of years with oil and gas reservoirs [Collins, 1975]. Also, water is used for oil production and comes to the surface along with crude oil [Ahmadun et al., 2009]. Produced water represents 80% of all the residuals produced during oil/gas production operations [McCormack et al., 2001]. The ratio of produced water to oil or gas production varies from well to well. Normally, for one barrel of oil, eight barrel of produced water is generated [Alkhudhiri et al., 2013]. In most cases the ratio of produced water to gas is higher than produced water to oil [Lee and Neff, 2011]. The volume of produced water increases with age of the well and when oil and gas production decreases [Henderson et al., 1999].

Produced water can be either used for oil produced or discharge into the sea [Ahmadun et al., 2009]. The quantities of produced water discharged into the sea ranges between 860 and 2700 m³ day⁻¹ [Ahmadun et al., 2009; Hargreaves and Silvester, 1990]. Produced water poses a threat to aquatic life and due to this reason the amount of oil in produced water discharged into the sea is limited to 30 mg l⁻¹ [Kosvintsev et al., 2007]. Water scarcity is one of the serious problems the globe faces these days. One third of the world population lives in water stressed countries in recent years, and it is predicted that by 2025 this ratio can jump up around two third. Mostly third world and developing countries are hugely facing this problem but situation in the developed world is also alarming in the near future if measurable steps are not taken. Statistics shows that 1.2 billion people are lacking in having access to fresh water, millions of people die annually and 3,900 children die a day because to using contaminated water [Shannon et al., 2008]. Population growth, industrialization, poverty, climate change and contaminated water sources further complicated providing fresh and clean water to people around the globe. Discharging produced water into the sea further worsen the situation. Therefore, removal of crude oil from produced water needs a voluminous research to be made in order to identify a robust and novel technology that minimize both cost and energy remands as well as addresses environmental issues.

2.1.1 Chemical composition of produced water

Produced water contains dissolved and particulate solids, organic and inorganic materials [Lee and Neff, 2011]. Physical and chemical properties of produced water vary from well to well and location to location. Properties of produced water also depend upon well age, well depth and method of production [Ray and Engelhardt, 1993]. Normally, produced water contains inorganic salts, organic acids, metals, production chemicals as well as petroleum hydrocarbons.

2.1.1.1 Salts

Concentration of salts in produced water various from place to place. Salt concentration in produced water ranging from a few ppm to 3000000 ppm [Zhang et al., 2013; Rittenhouse et al., 1969]. Sea water contains 3.2-3.6% dissolved solids, so, most produced water contains higher amount of salts than sea water. Due to higher concentration of the salts in the produced water, it represents a danger to the sea water life [Collins, 1975]. Salinity of produced water varies from field to field. The Hibernia field produced water contains 4.6- 20% salts [Ayers and Parker 2001]. Sodium salts are the most abundant form of salts present in produced water. Other forms of salts present in produced water are calcium, potassium and magnesium etc [Pillard et al., 1996]. Sulphate and sulphide are present in insoluble forms and their concentration is very low [Witter and Jones, 1999].

2.1.1.2 Organic acids

Organic acids in produced water are normally present in the form of mono- and di-carboxylic acids, aliphatic and aromatic hydrocarbons [Somerville et al., 1987]. Formic or acetic acid are the most abundant form of organic acid present in produced water, their concentration decreases with increase in molecular weight of organic acid [Stromgren et al., 1995]. Organic acids are also produced by the microbial degradation of hydrocarbons [Tomczyk et al., 2001].

2.1.1.3 Metals and radioactive materials

Metals are present in produced water in dissolved or microparticulate forms. Concentration and type of metals depends upon the age, geology and type of oil and gas [Collins, 1975].

Type and composition of injected water into oilfield also effects concentration of metals. Normally barium, iron, manganese, mercury and zinc present are in produced water [Neff et al., 1987]. Injecting anoxic water in oilfield produces high concentration of iron and manganese in produced water [Lee et al., 2005]. High concentration of iron and manganese results in precipitate of iron and manganese oxyhydroxides [Azetsu-Scott et al., 2007]. Radioactive materials are usually present in the form of ions. The most abundant radioactive material present in produced water is Radium (²²⁶Ra and ²²⁸Ra) [Ahmadun et al., 2009]. The other radioactive material is Barium (Ba) that is present in the form of isotopes [Ahmadun et al., 2009].

2.1.1.4 Produced chemicals

Different chemicals are used for various purposes during oil production: protection of equipment from corrosions, facilitate separation of oil and gas etc [Stephenson, 1992]. Some of the used chemicals in produced water are toxic, like corrosion inhibiters, and needs treatment before discharging into sea [Karmen and Reerink, 1996]. Besides, a large number of charged molecules like linear alkylbenzen sulfonate, 2-alkyl-1-ethylamine-2-imidazolines etc, are present in produced water and their presence are dangerous for life in the sea waters [Mccormack et al., 2001].

2.1.1.5 Petroleum hydrocarbons

Hydrocarbons are the most important compounds present in produced water, and of great environmental concern. Petroleum hydrocarbons are classified into (1) saturated hydrocarbons (2) aromatic hydrocarbons [Lee and Neff, 2011]. Solubility of hydrocarbons decreases with increase in molecular weight. Normally, saturated hydrocarbons are more soluble than aromatic hydrocarbons [Lee and Neff, 2011]. Hydrocarbons appear in dissolved and dispersed oil drops [Nicolaisen, 2003, Ekins et al., 2007]. Dispersed oil drops are high molecular weight, while dissolved oil is low molecular weight hydrocarbons [Faksness et al., 2004].
Table 2.1 shows composition/characteristics of produced water obtained at different locations around the world [Ahmadun et al., 2009]:

Parameter	Values	Heavy metals	Values (mg/l)
Density (kg/m ³)	1014-1140	Calcium	13-25800
Surface Tension (dynes/cm)	43-78	Sodium	132-97000
TOC (mg/L)	0-1500	Potassium	24-4300
COD (mg/L)	1220	Magnesium	8-6000
TSS (mg/L)	1.2-1000	Iron	< 0.1-100
pH	4.3-10	Aluminum	310-410
Total oil (IR; mg/L)	2-565	Boron	5–95
Volatile (BTX; mg/L)	0.39–35	Barium	1.3-650
Base/neutrals (mg/L)	<140	Cadmium ^a	< 0.005-0.2
(Total non-volatile oil and grease by GLC/MS) base (g/L)	275	Chromium	0.02-1.1
Chloride (mg/L)	80-200,000	Copper	<0.002-1.5
Bicarbonate (mg/L)	77–3990	Lithium	3–50
Sulfate (mg/L)	<2–1650	Manganese	< 0.004-175
Ammoniacal nitrogen (mg/L)	10-300	Lead ^a	0.002-8.8
Sulfite (mg/L)	10	Strontium	0.02-1000
Total polar (mg/L)	9.7-600	Titanium	<0.01-0.7
Higher acids (mg/L)	<1-63	Zinc ^a	0.01-35
Phenols (mg/L)	0.009–23	Arsenic ^a	< 0.005-0.3
VFA's (volatile fatty acids) (mg/L)	2-4900	Mercury	< 0.001-0.002
		Silver ^{a,b}	< 0.001-0.15
		Beryllium	< 0.001-0.004

2.1.2 Environmental effects of produced water

Due to the higher density of produced water than oil/gas, it is either injected into the oil/gas reservoirs for oil/gas production or discharge into the sea [Neff et al., 2006]. Produced water is a mixture of different hydrocarbon and toxic chemicals that are very harmful to the marine environment [Ekins et al., 2006]. Due to high and rapid dilution by the ocean water it is expected that produced water would not influence marine life greatly [Neff, 2002]. But the case is different when high concentration of toxic chemicals and hydrocarbons greatly influence life in the ocean. The presence of alkylated phenols in produced water causes the endocrine disruptors that greatly influence animals inside water [Thomas et al., 2004, Boitsov et al., 2007, Sundt et al., 2009]. The presence of nitrates, phosphates, ammonia and organic acids in produced water are harmful for micro-organism's growth [Rivkin et al., 2000]. Metals and hydrocarbons accumulate near produced water discharge, influence benthic communities greatly [Neff et al., 1989]. Dissolved iron in produced water badly effects metabolism of fish and other marine animals [Neff, 2002].

Due to the lower density of oil dispersed oil drops in produced water, they float on the surface of oceanic water and increase biochemical oxygen demand (BOD) [Stephenson, 1992]. Non-

polar organic compounds in oil are extremely toxic [Samlalsingh and Agard, 2003]. Chronic toxicity is the adverse toxicity of produced water caused by the long-term presence of hydrocarbons in produced water [Hansen and Davies, 1994].

2.1.3 Technologies used for oil/produced water separation

Oil can be removed either by physical processes or by chemical treatment from produced water depending on the nature and concentration of oil. Selection of treatment technology for oil removal is strongly dependent on size of dispersed oil drops [Ahmadun et al., 2009]. The following physical technologies are used for the removal of oil from produced water.

2.1.3.1 API gravity separator and corrugated plates

The API gravity separator is mainly used as a primary separator and works efficiently when oil drops are 150 μ m and above. The performance of an API separator depends mainly on the design of the tank, operation conditions, oil properties and retention time [Brunsmann et al., 1962]. Oil/water is kept in a rectangular tank for a period of 2-3 hours; due to lower density oil, it comes to the surface and is collected through pipes [Wang et al., 2005]. On the other hand, corrugated plates can be used to separate upto 40 μ m and above oil drops. It consists of two plates installed at 45° angle to each other that reduces the required occupying space of the equipment. Water flow through the plates and oil coalesces on the inner side of the plates, and is then collected [Wang et al., 2005].

2.1.3.2 Hydrocyclones

Initially, hydrocylones were used for alternative separations [Young et al., 1994]. Hydrocylones became popular in 1980s for oil/water separation. Hydrocyclones separate mixtures of immiscible liquids on the basis of density difference and the addition of enhanced gravitational forces increase its separation efficiency. They can be used for separating drops above 15 μ m; and their efficiency increases from 50-80% by increasing drop size [Grini et al, 2002]. Fluid enters tangentially to the hydrocyclone where it divides into two parts [Belaidi and Thew, 2003]. Oil comes to the centre and is collected in the overflow, while, water is forced towards the walls due to spinning motion within the hydrocyclone and goes to the underflow [Husveg et al., 2007]. Inside a hydrocyclone two forces act on the oil: centrifugal

force created by the hydrocyclone geometry and drag floatation force by the liquid [Zhao et al., 2005].

The term 'flow split' is referred to as the ratio of volume flow of the overflow to the feed and as given as:

$$R' = 100 \left(\frac{Q_o}{Q_i}\right) \tag{2.1}$$

Where R' is the flow split, Q_o is volumetric flow rate of overflow and Q_i is volumetric flow rate of the feed [Bai et al., 2011]. A better efficiency of a hydrocyclone means lower the concentration of oil in the underflow, and can be expressed as:

$$E = 100 \left(1 - \frac{g_u}{g_i} \right)$$
(2.2)

E is hydrocyclone efficiency, g_u and g_i are volume fraction of oil in the underflow and feed [Bai et al., 2011]. Increase in feed flow of the hydrocyclone reduces the pressure drop ratio and due to it the efficiency of the hydrocyclone decreases [Husvag et al., 2007]. Air bubbles have been injected inside hydrocyclones and separation efficiency for oil/water increased from 72%-85% [Bai et al., 2011].

2.1.3.3 Membrane technology

Membrane technology has been successfully applied and attracted researchers in recent years for oil/water separation [Shu et al., 2006]. Membrane technology is preferred over other conventional methods because of the following reasons [Alkhudhiri et al., 2013]:

- a. Low space requirement for the equipment installation
- b. The process is physical and no chemical additives are required
- c. The process is environmentally friendly
- d. Low energy cost

e. High permeate quality

Membrane processes are pressure driven processes in which drops/particles are retained on one side of the membrane and on other side some amount of fluid flow is obtained [Ahmadun at, al., 2009; Wakeman and Tarleton, 2005]. Mainly, there are four processes: microfiltration, ultrafiltration nanofiltration and reverse osmosis used for produced water treatment. The selectivity of the process depends upon drop size and concentration of oil. Microfiltration is used for separation of drops/particles ranging from 0.1-10 µm; ultrafiltration is used to separate macromolecules, suspended solids from 0.1 µm-5 nm; nanofiltration separates dissolved solids, low molecular weight molecules ranging from 5-1 nm; and reverse osmosis is effective for ions and low molecular weight molecules separation below 1 nm [Ahmadun at, al., 2009; Ruston et al., 2008; Alkhudhiri et al., 2013]. Ultrafiltration is useful with low oil content, but has permeate flux rates lower than 100 l m⁻² hr⁻¹ which is too low to be commercially attractive offshore [Lin and Lan, 1998; Lipp et al., 1988]. Trans-membrane pressure in reverse osmosis is higher than microfiltration and ultrafiltration [Sharif et al., 2009; Lin and Lan, 1998]. Higher flux rates (above 100 1 m⁻² hr⁻¹) may be achieved and permeate flux rates in microfiltration depend on droplet size and type of membrane used. Particles/droplets can be retained inside the membrane in depth microfilters [Holdich et al., 1998; Bromley et al., 2002].

Recently, developments in membrane pore size and geometry have attracted great interest. Membranes with circular pores are often investigated [Cumming et al., 2000]. Using the same trans-membrane pressure, a membrane with smaller pore size $(2 \ \mu m)$ has higher efficiency for separating oil droplets up to 10 μm compared to a 5 μm membrane [Cumming et al., 2000]. Even better separation of oil droplets was achieved with slotted pore-filters under lower transmembrane pressure [Bromley et al., 2002]. Different mechanisms govern the droplet passing through the membrane when circular, or slotted pores are used. When using circular pores, it is the trans-membrane pressure that governs whether the droplets pass through the membrane into the permeate, while in the case of the slotted pores it is the drag force around the droplets induced by the motion of the fluid that is responsible for the droplets passing through the membrane see Figure 1.1 [Kosvintsev et al., 2007].



Figure 2.1: (a) A drop is approaching to a circular pore, the size of the drop is equal pore diameter. The drop would completely block the pore. (b) A drop is approaching to a slot, the size of the drop is equal to the slot width. The drop will partially block the slot and fluid could flow around the drop in the open available space.

Clearly, membrane-particle interaction is highly important and it is desirable to maintain the particles on the surface of the membrane; not allowing them to penetrate the membrane structure and foul the membrane internally, or if the particles can pass through the pore openings on the surface of the membrane then it is desirable to have them pass through the entire membrane pores and into the permeate, provided that this does not adversely influence the permeate properties. Such membrane filters that provide this behaviour are the 'surface microfilters', for example the track-etched and sieve-like types [Holdich et al., 2006].

The membrane surface is of great importance for researchers these days [Hilal, 2012]. Surface of filters used for separation of oil/water may be hydrophilic or hydrophobic, including multi-walled carbon nanotubes on stainless steel mesh. One of the special features of the hydrophobic filters is higher flux rates with low trans-membrane pressure along with better separation [Kochkodan et al., 2014; Lee and Baik, 2010]. The effectiveness of these filters depends upon initial droplets being filtered. Higher permeation of oil is reported by the super-hydrophobic and super-oleophilic nature of carbon nanotubes [Lee et al., 2011]. Ceramic

membranes are used extensively for separation of organic material such as oil, but can be fouled easily. ZrO₂ membranes were modified [Gao et al., 2011] with a self-assembled monolayer of hexadecyltrimethoxysilane (HDTMS). With these modified membranes high permeation of fluid was obtained with effective separation. Separation of material using membrane technology strongly depends on surface properties of membranes used. Nanoparticles (25 nm) were used for coating and surface roughness modification of membranes and materials were separated effectively [Bansal et al., 2011]. Surfaces of Al₂O₃ membranes have been modified with nanoparticles ZrO₂ and steady flux maintained at 88% while separation efficiency increased to 98% [Zhou et al., 2011] are reported. One of the major features in hydrophilic membranes is resistance to fouling, and it makes these superior than hydrophobic membranes for filtering wastewater [Maximous et al., 2009]. A highly hydrophilic membrane surface was achieved with alumoxane nanoparticles, and it was found that with this membrane rejection was not affected by trans-membrane pressure [Boyle and Barron, 2011].

Dynamic or shear enhanced filtration is the one in which shear rate is applied to the membrane by rotating or vibrating the membrane, and it attracted a large focus of research in recent years [Jaffrin, 2008]. In cross-flow filtration, shear rate over the membrane is applied by flow of fluid with a high velocity [Postlethwaite et al., 2004]. While, in shear enhanced filtration, shear rate is created with a low velocity of fluid and only vibrating the membrane [Akoum et al., 2002]. Higher permeate flux rate was achieved by controlling the fouling of the membrane with the vibration of the membrane during filtration of yeast suspension [Beier et al., 2011]. Permeate flux rate was found as a function of vibrational frequency, and amplitude at which membrane was vibrated [Gomaa and Rao, 2011].

2.2 Emulsion stability

An emulsion is the combination of two or more immiscible liquids, and can be obtained by mixing the liquids and shaking. After shaking the mixture, one of the liquids will consist of drops which is referred to as the dispersed phase, while, the other liquid phase is called the continuous phase. The dispersed phase is also referred to as internal and the continuous phase is known as external phase. Emulsions have a great importance in food, cosmetics, pharmaceutical and oil industries [Spasic and Hsu, 2006]. In the oil industry, when oil is the

dispersed phase and water is the continuous phase it is written as oil-in-water (O/W) emulsions. On the other hand, when water is the dispersed phase and oil is the continuous phase it is expressed as water-in-oil (W/O) [Garti and Bisperink, 1988]. Drop size plays in important role in the stability of an emulsion, larger drops make an emulsion unstable and that is the reason the smaller drops emulsions are more stable than larger drops emulsions [Spasic and Hsu, 2006]. Drops are considered stable when they are stable against creaming, aggregation and coalescence processes [Rosen, 2004; Boyd et al., 1972]. Drops coalesce due to various reasons explained as follows:

2.2.1 Physical nature of interfacial film

Dispersed drops in a liquid are always in motion causing frequent collisions between the drops. Due to drop collision, the surrounding film between the drops may rupture and smaller drops will form larger drops. It is a continuous process and eventually the dispersed phase will not remain as a dispersed phase but form a second continuous phase, so, for the stability of dispersed drops mechanical strength of interfacial film is a prime factor [Rosen, 2004]. The strength of a surrounding film around oil drops can be increased by adding lauryl alcohol and NaCl that decreases electrostatic ruptures of the drops [Saito et al., 1990]. Strength of interfacial film of the dispersed oil phase was increased with Tween which is soluble in oil and water phase and was found very interactive with the interfacial film [Boyd et al., 1972]. Liquid crystal formation helps stabilising dispersed drops that surrounds the drops, decreasing van der Waals forces does not allow the drops to coalesce [Friberg et al., 1976].

Solid condensed type of film surrounding drops can make the dispersed phase stable because this kind of film is rigid and very resistant to breakage [Schulman and Cockbain, 1940; Ford and Furmidge, 1966].

2.2.2 Existence of an electric charge

The presence of a charge in the dispersed phase plays an important role in the coalescence of the drops [Bowen and Sharif, 1998]. It is believed that the presence of charge in oil dispersed drops is due to the adsorption of surfactants in a layer. Surface active components present in the crude oil greatly influence the stability of oil/water emulsions [Hannisdal et al. 2007]. Emulsions stabilised with ionic surfactants provide a polar charge on the dispersed oil drops

[Rosen, 2004]. The influence of charge on the surface of drops was decreased by adding metal oleates which are insoluble in both oil and water phases [Albers and Overbeek, 1959]. Hydrophilic solids particles were used for oil/water emulsion stability that effected the concentration of the charge on the dispersed oil drops [Rosen, 2004]. The presence of silica and clay particles play an important role countering the presence of charge on oil drops [Dudasova et al., 2008; Kotlyar et al., 1999]. Inorganic particles can be used to enhance the stability of crude oil/water emulsions [Sztukowski and Yarranton, 2005]. Addition of β - lactoglobulin made coating over the oil drops, reduced the influence of charge on drops and increased emulsion stability [Mao and McClements, 2012].

2.2.3 Viscosity of continuous phase

Increase in viscosity of the continuous phase decreases the diffusion coefficient (D') of the drops, and D' can be expressed in the Stokes-Einstein equation [Rosen, 2004]:

$$D' = \frac{kT}{6\pi\eta R_{sp}} \tag{2.3}$$

Where k is the Boltzmann constant, T is the absolute temperature and R_{sp} is the radius of the drop.

Coalescence of drops can be reduced by reducing the diffusion constant. The viscosity of the external phase increases with increase in number of drops in the dispersion [Rosen, 2004]. Viscosity of external phase can also be increased with the addition of agents called "thickening" agents [Friberg et al., 1969].

2.2.4 Size of dispersed drops

Stability and size of dispersed drops are interrelated. The bigger the size of the drops, the higher would be the rate of coalescence [Rosen, 2004]. Bigger drops attract each other with higher force than smaller drops [Abismail et al., 1999]. Bigger drops have less interfacial surface per unit volume than smaller drops, and emulsion with smaller drops are more thermodynamically stable than the bigger drops [Rosen, 2004]. Similarly, bigger drops break more easily than smaller drops which make the emulsion unstable [Azizi and Taweel, 2011].

2.2.5 Temperature

Solubility of surfactants, viscosity of external and dispersed phases, nature of interfacial film and interfacial tension between continuous and dispersed phase are dependent on temperature; and all above mentioned parameters play an important role in emulsions stability [Rosen, 2004]. Therefore, a slight change in temperature of the system completely changes emulsions stability. Increase in temperature decreases the strength of interfacial film and that's why the stability of emulsion decreases [Davies and Rideal, 1963]. Increase in temperature, increases the rate of coalescence of drops and due to it, the stability of emulsions decreases [Gullapalli and Sheth, 1999].

2.3 Critical and sustainable flux rates in microfiltration

A variety of modelling approaches have been adopted to account for membrane fouling in microfiltration, normally considering the shear at the membrane surface to reduce the influence in terms of flux decline for constant pressure filtration, but there is an additional complication when the particles being filtered can deform and be sucked through the membrane; such as when filtering oil drops. The permeate flux obtained from clean water tests is called the water flux [Dickenson, 1992] and it is desirable to obtain filtration flux as close to this as possible. Critical flux has been defined in two ways: when trans-membrane pressure (TMP) deviation, as a function of permeate rate, starts from the pure water line; or when permeate flux is always below the clean water line [Bacchin et al., 2006]. Strong critical flux is the former: when deviation of TMP starts from pure water line [Field et al., 1995; Field and Pearce, 2011]. In weak critical flux the TMP line rapidly deviates from pure water line due to almost instant, but limited, fouling of the membrane [Metsamuuronen et al., 2002]. The flux rate below which no fouling of the membrane occurs is referred to as sub-critical flux and can be used to control fouling of the membrane [Howell, 1995]. A flux rate between high fouling and low fouling conditions is now called sustainable flux [Hughes and Field, 2006; Field and Pearce, 2011].

Critical, or sustainable, flux can be a function of ionic strength and pH of colloidal suspensions. An increase in ionic strength of a TiO_2 suspension was observed to increase the permeate flux due to a decreased fouling influence [Zhao et al., 2005]. While in the case of silica suspension permeate flux decreased with increase in ionic strength of suspension. Silica

suspensions were more stable at low ionic concentration due to the higher repulsion of the particles [Elzo et al., 1998]. Clearly, these results depend on the type of particles used and their state of mutual attraction and aggregation during the filtration tests.

The concentration of the suspension influences the permeate flux, and the critical conditions of operation are affected. The flux rate of latex suspensions linearly decreased with increasing suspension concentration up to 3 g l^{-1} [Guiziou et al., 2002]. A higher membrane resistance was observed by increasing concentration from 10-50 mg l^{-1} , and therefore, permeate flux decreased [Tian et al., 2013].In another study, only a slight decrease was observed in critical flux of bacteria suspensions by increasing concentration [Persson et al., 2001].

Like suspension concentration, size of particles also affects critical conditions of operation. Keeping operation conditions constant (pore size of membrane, cross-flow velocity, ionic strength and temperature) the influence of different sizes of suspended particles on critical flux was studied [Kwon et al., 2000; Wakeman and Tarleton, 1991]. A decrease in transmembrane pressure (TMP) was observed by increasing particle size from 0.1-0.46 μ m filtering on a 0.2 μ m pore size membrane [Harmant and Aimar, 1998]. In another study higher membrane resistance was observed with particles of large diameter as compared to small ones [Kwon and Vigneswaran, 1998].

When performing tests of one immiscible liquid dispersed in another, it is necessary to stabilise the liquid drops. This can be done by creating an emulsion and using a surfactant to attach to the interface between the two liquid phases. When the drops are stabilised they may be filtered in a similar fashion to solid particles. However, it will always be possible to deform a liquid drop in a way that a solid particle does not normally allow. Hence, it may be possible to deform the drop such that it can pass through the membrane pore [Cumming et al., 2000]. Surfactant type and concentration can influence critical conditions of microfiltration. An increase in concentration of surfactants can lead to an increase in deposition of particles on the membrane surface and a critical flux decrease [Guiziou et al., 2002; Peuchot and Ranisio, 1997].

Membranes made from different materials, but similar nominal pore sizes, give different flux rates under the same operation conditions. Higher flux was obtained with micro porous silica

membranes as compared to Zeolites and PVA PERVAP 2510 membranes under similar operation conditions [Lizon et al., 2002]. Higher critical flux was obtained with α - alumina membrane as compared to zirconia and titanium membranes using the same operational conditions [Huisman et al., 1999]. Hydrophobic membranes gave higher critical flux as compared to hydrophilic membranes, attributed in the reported paper to the hydrophobic membrane having higher pore porosity which favours higher flux rates [Metsamuuronen et al., 2002], but this could also be due to surface interactions with the suspended materials. Changing the electrostatic properties of a membrane surface changes the ability of the membrane to adsorb and it has been shown to have a direct impact on the permeate flux of a membrane [Schwarz et al., 1994].

The pore size of a membrane plays an important role in the critical flux condition of a membrane. Higher flux rates with various TMP were achieved by increasing the pore size of membrane operating with clean water and an oil/water emulsion [Cumming et al., 2000]. Membranes with different pore sizes from 0.1-0.65 µm were also tested with latex suspension. Small pore size membranes offered higher membrane resistance as compared to membranes having relatively larger pore size. The influence of pore size on critical flux was not significant due to the reason that drag force was nearly the same at different points on the membrane surface. As the drag force deposition of particles on the membrane pores at different points was the same, the fouling was also similar [Kwon et al., 2000]. In another study higher TMP was obtained with membranes of large pore size under the same operational conditions [Field et al., 1994]. Increase in critical flux was observed increasing with pore size of the membrane [Chiu et al., 2006], but it has also been observed that with an increase in cut-off of a membrane the critical flux declined [Wu et al., 1999]. The influence of geometry of a membrane has been shown to have a significant impact on flux rates of membranes. Higher flux rates were obtained with slotted pore membranes as compared to circular pore membranes when both were subjected to same suspension under similar operational conditions. Particles deposited at higher rates on pores of circular membranes and, because of that the fouling rate of circular membranes was higher than slotted pore membranes [Bromley et al., 2002]. An overall higher porosity of a circular pore membrane helped to minimise the fouling of a membrane [Kuiper et al., 2000].

A commonly observed result is due to the feed velocity pattern, or surface shear condition, on the critical flux rate of a membrane. An increase in critical flux was found with an increase in cross-flow velocity of fluid over the membrane surface [Chiu et al., 2006]. However, increasing the cross-flow velocity of operation can lead to segregation of the fouling material, leading to a higher fouling rate from the finer end of the particle size distribution [Madaeni et al., 1999]. In general, higher fluxes of permeate are obtained with increasing cross-flow velocity [Manttari and Nystrom, 2000]. Providing the particle-membrane interaction does not reduce this effect. In another study, shear rate was applied to the membrane surface by oscillating the membrane applying various frequencies and it was found that reduction in trans-membrane pressure was a function of applied shear rate [Gomaa et al., 2011].

Filters used for separation of oil/water may be hydrophilic or hydrophobic, including multiwalled carbon nanotubes on stainless steel mesh. One of the special features of the hydrophobic filters is higher flux rates with low trans-membrane pressure along with better separation [Lee and Baik, 2010]. Effectiveness of these filters depends upon initial droplets size being filtered. Higher permeation of oil is reported by the super-hydrophobic and superoleophilic nature of carbon nanotubes [Lee et al., 2011]. Ceramic membranes are used extensively for separation of organic material such as oil, but they can be fouled easily. ZrO_2 membranes were modified [Gao et al., 2011] with a self-assembled monolayer of hexadecyltrimethoxysilane (HDTMS). With these modified membranes high permeation of fluid was obtained with effective separation. Separation of material using membrane technology strongly depends on surface properties of the membranes used. Nanoparticles (25 nm) were used for coating and surface roughness modification of membranes have been modified with nanoparticles ZrO_2 and steady flux maintained at 88% while separation efficiency increased to 98% [Zhou et al., 2010].

2.4 Shear enhanced dynamic microfiltration

Dynamic or shear enhanced filtration is the one in which shear rate is applied to the membrane surface by rotating or vibrating the membrane, and is a prime focus of research in recent years [Jaffrin, 2008]. In cross-flow filtration, shear rate over the membrane is applied by flow of fluid with a high velocity [Postlethwaite et al., 2004]. While, in shear enhanced

filtration, shear rate is created with rotating/vibrating the membrane [Akoum et al., 2002]. The concept of dynamic microfiltration was first used in 1970s, where, shear rate was applied to the membrane by rotating the membrane [Margaritis, 1976]. Initially, rotating the membrane was used for removing living organisms [Tobler, 1982; Kroner and Nissinen, 1988; Rushton and Zhang, 1988; Murase et al., 1991; Park et al., 1994; Choi et al., 1999].

In another form of dynamic microfiltration, shear rate is applied by vibrating the membrane and called Vibratory Shear-Enhanced Processing system (VSEP). This Shear-Enhanced Vibrating system was first reported by [Culkin and Armando, 1992]. In the VSEP process the membrane is oscillated at various frequencies and shear is applied due to oscillation of the membrane. It is an economical process as compared to cross-flow filtration because lots of energy in cross-flow filtration is consumed by pumping the fluid again and again into the system and that provides a low permeate flux rate [Sarrade et al., 2001]. In cross-flow filtration the membrane fouls easily and higher trans-membrane pressure is created due to uneven distribution of fouling, while in the case of VSEP systems, membrane fouling is lower and due to it a lower trans-membrane pressure produced [Culkin and Armando, 1992]. VSEP and cross-flow comparison is illustrated in Figure 1.2 [Ahmadun et al., 2009].



Figure 2.2: A lower membrane fouling is observed in-case of VSEP as compared to a cross-flow system [Ahmadun et al., 2009].

In the VSEP, nearly 99% of the total energy consumed converted into shear rate applied, while, on the other hand, in cross-flow filtration only 10% of the total energy converted into shear rate applied [Culkin and Armando, 1992]. Applications of VSEP for NF/RO [Frappart

et al., 2008; Zouboulis and Petala, 2008], while for UF [Culkin and Armando, 1992; Takata et al., 1998; Akoum et al., 2002i, ii, iii,; Jaffrin et al., 2004; Petala and Zouboulis, 2006; Shi and Benjamin, 2008; Zouboulis and Petala, 2008] are reported. A wide range of VSEP applications have been presented in microfiltration [Culkin and Armando, 1992; Akoum et al., 2002i, ii, iii,; Jaffrin et al., 2004; Postlethwaite et al., 2004; Petala and Zouboulis, 2006; Zouboulis and Petala, 2008]. For the removal of humic substances from the river water, VSEP system was found more effective than conventional filtration system and yielded a high permeate flux rate with a good water quality [Takata et al., 1998]. Better separation of yeast cells was observed when VSEP was used with a higher permeate flux rate [Postlethwaite et al., 2004].

Creation of shear rate at the surface of the membrane is the main factor of VSEP filtration system that makes it distinguishable from conventional filtration systems. Shear rate is a function of oscillation amplitude (a), vibrational frequency (F) and kinematic viscosity of the feed (v) and can be expressed as [Jaffrin et al., 2004],

$$\dot{\gamma} = f(a, F^{3/2}, v^{-1/2}) \tag{2.4}$$

An empirical correlation for flux rate and applied shear rate is found in literature as follows,

$$J = f(\dot{\gamma}^n) \tag{2.5}$$

The value of n varies with type of material being filtered and type process of process [Jaffrin, 2011].

With the oscillation of the membrane, shear rate is created that caused an increase in permeate flux rate [Gomaa and Rao, 2011]. Using a combination of turbulence promoters and membrane oscillation, permeate flux rate increased by 4 times as compared to only oscillation of the membrane without turbulence promoters [Gomaa et al., 2011].

Chapter 3

Emulsion preparation and drop stability

3.1 Introduction

In this chapter, the method, equipment, procedures and operating conditions used in the preparation of oil/water emulsions and oil droplets stability testing are described. Emulsification is a process in which one fluid is dispersed into another fluid [Calderon et al., 2007]. The preparation of oil/water emulsions with oil droplets in the range 1-15 μ m is the prime focus of this chapter. For that purpose, a magnetic stirrer and a food blender were tested, that were operated at various speeds and durations. The required oil/water emulsions with oil droplets in the range 1-15 μ m drops were obtained with a food blender operated at the highest speed for 12 mins. The number of droplets counted by the Coulter was out of range for the 100 μ m aperture with the analyses of 1 ml emulsion sample. In order to obtain the number of droplets within the range of the aperture, the volume of analysing sample was therefore reduced to 0.4 ml, which was added to 180 ml contained in the Coulter beaker.

Stability of emulsions is important because due to attractive forces between the oil droplets, the droplets produced flocculate forming larger aggregates then coalescence [Friberg et al., 1976]. Attractive forces between the oil droplets can be reduced using surfactants [Hodgson and Lee, 1968]. In order to stabilise oil droplets various surfactants were tested. The stability of the droplets was determined based on the size distribution and number of droplets present in the samples analysed at the 30 mins time intervals during experiments.

3.2 Material

The initial oil phase in O/W emulsions was Co-operative vegetable oil (EU Rapeseed for Cooperative group Ltd, UK). Tween 20 (polyoxyethylene sorbitan monolaurate from Fluka, UK), gum Arabic and PVA (polyvinyl alcohol) from (Sigma Aldrich, UK) were used in the experiments. A magnetic stirrer (SM1 Stuart Scientific UK) was used with various speeds and operated for different durations of time for producing oil droplets with the droplet size in the described range 1-15 μ m. Finally, oil droplets in the required size range 1-15 μ m were produced by a food blender (Kenwood manufacturing co Ltd Havant Hants, England). A stopwatch was used for measurements of time duration. A Coulter Multisizer II (Coulter Counter, Coulter Electronics Ltd) was used to measure the number of dispersed droplets and size distribution, enabling a material balance to be performed on the known amount of oil added to the system, and that determined from the Coulter count and size distribution.

3.3 Experimental setup

3.3.1 Coulter Multisizer II

A Coulter Multisizer II was used for number and size distribution measurement of suspended droplets/particles as shown in Figure 3.1. A glass tube contains electrolyte, which is normally 1% saline solution, and two electrodes are immersed into the solution. A small aperture containing a tube is dipped into the electrolyte. Droplets are suspended in the electrolyte solution and can be detected by passing a specific volume of the sample through the aperture opening. When a droplet passes through the aperture sucked by a vacuum pump, it displaces a volume of electrolyte and the latter changes the resistance between the electrodes and a series of voltage pulses are produced. Droplets/particles from 0.4-800 μ m can be measured, depending upon the size of the aperture used. The amplitude of each pulse is directly proportional to the size of the droplet measured. The number of droplets can be obtained from the number of pulses produced. The aperture consists of a number of channels and the size of the droplet is obtained from the size of channel through which the droplet is recorded. A 100 μ m aperture was used in the experiments that can measure a maximum 20000 droplets per 2 ml. The size range detected for the aperture used is from 2-60 μ m.

Before using the saline solution in the Coulter, it is passed through a $0.45 \,\mu\text{m}$ filter to stop any kind of background particles in the solution. A good background sample would be the one having a very low number of suspended particles. To measure the number of dispersed particles, the saline solution is analysed first in the Coulter, and the reading is referred to as a background reading. When the emulsion sample is analysed the background reading is subtracted to measure the actual number of dispersed drops.

The data can be transferred into computer software by choosing "Acquire" and then "New Sample" followed by "Acquire from Multisizer" in the Multisizer AccuComp software's menu. When the data is received by the software pressing "Print" saves it in the computer memory. For the actual dispersed drops measurement, selecting the option "Analyse", "Subtract from background" was used.



Figure 3.1 Schematic diagram of Coulter Multisizer II.

3.3.2 Method

For vegetable oil droplet stability, three surfactants (1 wt % gum Arabic, 1 wt % PVA and 1 wt % Tween 20) were used. The used surfactants provided a wide range of interfacial tensions and main purpose was to investigate how interfacial tension influence drop passage and deformation. Tween 20 easily dissolves in cold water by stirring it for a few mins. Gum Arabic and PVA cannot be dissolved easily in cold water, so water was heated up to 50 and 100 °C for dissolving gum Arabic and PVA, respectively. Water was stirred after heating and gum Arabic or PVA were slowly added. A food blender operated at highest speed for 12 mins was used for the production of oil droplets in the range 1-15 µm. For droplet stability samples were analysed using the Coulter at 30 mins intervals and based on the size distribution and number of droplets in each sample, stability of the droplets was established.

3.4 Results and discussion

3.4.1 Emulsion preparation

The main objective of these experiments was to recover at least 75% of the entered mass (feed) by material balance using the Coulter. Mass entered and recovered mass by the Coulter was obtained using the following equations:

$$m = \frac{\pi}{6} (no \ of \ droplets) (mid \ size \ of \ droplets \ dia)^3 (density \ of \ the \ droplets)$$

$$m = \frac{\pi}{6} \rho_f \sum k_i x_i^3$$
(3.1)

Where k_i is the number of drops in an increment and x_i is the mid-size of the increment.

Initially, a magnetic stirrer operated with highest speed for 10 mins was used to produce oil droplets. However, Figure 3.2 (a) shows that a large portion of the oil droplets by mass was above 20 μ m; i.e. too large droplets were produced. Figure 3.2 (b) also demonstrates that only 20% and 60% of all mass that was recovered by the Coulter was below 20 μ m and 40 μ m, respectively. Hence, the operational time for magnetic stirrer was increased from 10-15 mins. However, the latter did not show any considerable influence on the produced oil droplets as illustrated in Figure 3.3 (a) and Figure 3.3 (b).



Figure 3.2 (a) Size distribution (by mass) of oil droplets produced with magnetic stirrer operated for 10 mins at highest speed.



Figure 3.2 (b) Size distribution (mass undersized %) of oil droplets produced with magnetic stirrer operated for 10 mins at highest speed.



Figure 3.3 (a) Size distribution (by mass) of oil droplets produced with magnetic stirrer operated for 15 mins at highest speed.



Figure 3.3 (b) Size distribution (mass undersized %) of oil droplets produced with magnetic stirrer operated for 15 mins at highest speed.

A food blender was tested to produce smaller droplets as compared with droplets produced using the magnetic stirrer. Initially, the food blender was operated at its lowest speed for 10 mins and droplets obtained are shown in Figure 3.4 (a) and Figure (b). Figure 3.4 (b) shows that 40% and 80% droplets are below 20 and 30 μ m, respectively, which was quite encouraging but still not sufficient. A number of experiments were done with the food blender to achieve the required size of drops and number of drops within the range of the used aperture. Some illustrations are provided in this chapter. A full description of all the experiments performed along with mass balance calculations are provided in the Appendix A.



Figure 3.4 (a) Size distribution (by mass) of oil droplets produced with food blender operated for 10 mins at lowest speed.



Figure 3.4 (b) Size distribution (mass undersized %) of oil droplets produced with food blender operated for 10 mins at lowest speed.

In order to produce smaller droplets the food blender was operated at the highest speed for 12 mins. Figures 3.5 (a) and (b) show that all droplets produced are below 15 μ m in size. Initially, a 1 ml sample of emulsion was analysed using the Coulter but the number of droplets counted were above (more than 20000 droplets) the aperture range. So the volume of the sample was reduced gradually, and finally the number of droplets counted was within the range of the Coulter when 0.4 ml sample was analysed when added to the Coulter beaker containing 180 ml of saline solution. The dashed lines in the following figures shows the portion of oil drops below the range of the used aperture (2 μ m) and was not measured by the Coulter. It is assumed that the size distribution can be extrapolated to the origin from this size, and that the shape of this extrapolated curve is the classic 'S' shape distribution curve.



Figure 3.5 (a) Size distribution (by mass) of oil droplets produced with food blender operated for 12 mins at highest speed.



Figure 3.5 (b) Size distribution (mass undersized %) of oil droplets produced with food blender operated for 12 mins at highest speed; note that below 2 µm, the curve is extrapolated to the origin.

3.4.2 Drop stability

The surfactants Tween 20, PVA and gum Arabic were used to stabilise oil droplets. Samples were analysed at intervals of 30 mins. The stability of droplets was studied based on size distribution and number of droplets in each sample. After the droplets were produced the emulsion was gently stirred to prevent coalescence of the droplets. Figure 3.6 (a) and Figure 3.6 (b) show that nearly the same size distribution was obtained with the samples analysed at the intervals of 30 mins stabilised with 1 wt % PVA. A total 44707 of droplets per ml were counted by the Coulter when a sample was analysed after 1 mins after preparation of the emulsion (see Table 3.1). When samples of the same emulsion were analysed after 30 and 60 mins then 43789 and 42714 droplets were counted, respectively. The number of droplets in the samples analysed after each 30 mins remained nearly the same. This observation demonstrates that the oil/water emulsion was stable, which was confirmed by both size distribution and number of droplets using 1 wt % PVA.



Figure 3.6 (a) Size distributions (by mass) of samples analysed at the interval of 30 mins stabilised with 1 wt % PVA.



Figure 3.6 (b) Size distributions (mass undersized %) of samples analysed at the interval of 30 mins stabilised with 1 wt % PVA; with extrapolated curves below 2 μ m.

It can be seen from Figures 3.7 (a) and Figure 3.7 (b) that oil/water emulsion was also efficiently stabilised with 1 wt % gum Arabic based on the analysis of the size distribution. Nearly, the same number of droplets was observed when samples were analysed at intervals of 30 mins as illustrated in Table 3.1. Similarly, Figures 3.8 (a) and 3.8 (b) shows that the size distributions of emulsion samples was stabilised using 1 wt % Tween 20, and those figures demonstrate that all three samples have nearly the same size distributions. Studying the number of droplets (Table 3.1) taken from samples stabilised with Tween 20 shows that each sample contained nearly the same number of droplets. So it can be concluded that oil/water emulsions were efficiently stabilised with the surfactants (PVA, gum Arabic and Tween 20).



Figure 3.7 (a) Size distributions (by mass) of samples analysed at the interval of 30 mins stabilised with 1 wt % gum Arabic.



Figure 3.7 (b) Size distributions (mass undersized %) of samples analysed at the interval of 30 mins stabilised with 1 wt % gum Arabic; with extrapolated curve below 2 μ m.



Figure 3.8 (a) Size distributions (by mass) of samples analysed at the interval of 30 mins stabilised with 1 wt % Tween 20.



Figure 3.8 (b) Size distributions (mass undersized %) of samples analysed at the interval of 30 mins stabilised with 1 wt % Tween 20; with extrapolated distribution below 2 μ m.

Table 3.1	Number	of	droplets	in	emulsions	obtained	using	various	surfactants.	Samples	analysed	at
intervals o	f 30 mins											

Surfactant	Time (mins)	No of droplets per 1 ml sample
1 wt % Gum Arabic	1	34280
1 wt /0 Guill / Huble	30	33193
	60	34151
1 wt % PV A	1	44709
1 Wt /01 VA	30	43789
	60	42710
1 wt % Tween 20	1	54650
1 we /0 1 ween 20	30	53897
	60	51511

3.4.3 Crude oil/water emulsion

The main purpose for using vegetable oil was to develop a technique for crude oil/water emulsion formation with drop size 1-15 μ m and to provide a system to test the developed mathematical modelling approach described in the coming chapter (Chapter 5). Crude oil drops of 22, 27, and 31 °API were created with a food blender, operated at its highest speed for 12 mins. Due to the presence of various solid particles and chemicals in crude oil, there was no need to use any surfactant to ensure crude oil drop stability. As can be seen in Figures 3.9 (a) and (b), nearly the same size distributions for all crude oil (22, 27, and 31 °API) were obtained when drops are produced under the same operating conditions used for the vegetable oil (with a food blender operated at its highest speed for 12 mins). Thus, it is possible to test the modelling approach with a variety of different oils and systems displaying a wide variety of drop sizes and interfacial tensions.



Figure 3.9 (a) Size distributions (by mass) of various crude oil drops.



Figure 3.9 (b) Size distributions (mass undersized %) of various crude oil drops; with extrapolated distribution below 2 µm.

3.5 Conclusions

A magnetic stirrer and a food blender operated at different speeds and various duration of time were used to produce oil droplets in the range 1-15 μ m. The required droplet size results were achieved with the food blender operated at the highest speed for 12 mins. The number of droplets within the range of the aperture was achieved by reducing the volume of sample from 1- 0.4 ml added to the Coulter beaker containing 180 ml of saline solution.

Tween 20 can easily be dissolved in cold water by stirring for few mins. While gum Arabic and PVA cannot be dissolved in cold water and the water was heated upto 50 °C for dissolving gum Arabic and 100 °C for PVA. The heated water was kept under stirring and the required amount of PVA or gum Arabic was added. After emulsion preparation and to avoid coalescence the prepared emulsions were continuously stirred gently. Vegetable oil droplets were efficiently stabilised with all surfactants tested (PVA, Tween 20 and gum Arabic). The stability was demonstrated by analysing both size distribution and number of droplets in each sample at intervals of 30 mins in the Coulter. The Coulter using an orifice diameter of 100 μ m could not measure drops below 2 μ m, hence, it was assumed the drop size distribution curve could be extrapolated to the origin below this lower limit of size. A material balance was

performed to check on the apparent 'recorded' mass of oil based on the drop size distribution and the number of drops measured, compared with the known mass of oil added. The results are shown in Appendix A with a more comprehensive discussion on the validation of the operating conditions, and it is demonstrated that when using the preferred technique (0.4 ml sample) the recorded oil is 80-85% of the added oil. This is consistent with the remaining 15-20% of the oil being present in the drops less than 2 μ m, which were not used in the material balance check.

Chapter 4

Membrane oscillations and sustainable flux rates

This Chapter is based on

1. **A. Ullah,** V.M. Starov, M. Naeem, R.G. Holdich, "Microfiltration of deforming oil droplets on a slotted pore membrane and sustainable flux rates", Journal of Membrane Science 382 (2011) 271-277.

2. **A. Ullah,** M. Naeem, R.G. Holdich, V.M. Starov, S. Semenov, "Microfiltration of deforming droplets", Progress in Colloids and Polymers Science 139 (2012) 107-110.

4.1 Introduction

One of the major problems associated with membrane processes is the reduction of flux rate and increase in trans-membrane pressure due to the fouling of the membrane. The fouling of the membrane may be due to deposition of particles/droplets. Particles/droplets deposition forms a layer on the surface of the membrane that partially or completely blocks off the pores/slots of the membrane [Field et al., 1995]. The layer of particles/droplets can be reduced with a cross-flow, in which shear is applied by the flow of fluid over the surface of the membrane [Baker, 2004; Wakeman and Tarleton, 2005]. A high amount of energy is consumed in cross-flow filtration due to the pumping of fluid continuously around the system [Proctor, 2010]. Shear can also be applied by the oscillation of the membrane which can be energy efficient, because shear is only applied to the membrane surface.

Control of permeate flux is important in microfiltration processes as it influences transmembrane pressure and fouling of a membrane. Particles of vegetable oil ranging from 1-15 μ m were filtered on a 4 μ m slotted pore membrane at various flux rates. Various intensities of shear were applied parallel to the membrane by vibrating the membrane at different frequencies. At the lowest permeate flux rate (200 l m⁻² h⁻¹) the membrane fouled because the drag force was too low to squeeze the deformable oil droplets through the membrane or reject them from the membrane surface. At higher flux rates the drag force over the oil droplets increased and deformation, and passage, of oil droplets into the permeate was possible. Without any applied shear the highest trans-membrane pressure was observed due to fouling, which could be modelled by a pore blocking model. A positive displacement pump was used in the experiments which maintained nearly constant flow of permeate. Flux rates varied from 200-1200 l m⁻² h⁻¹, and the highest shear rate used was 8000 s⁻¹. The experimental system provided a simple technique for assessing the behaviour of the microfilter during the filtration of these deforming particles.



Figure 4.1 Drop "a" would pass through the membrane into the permeate due to lower size than slot size of the membrane. Drop "b" is bigger than the membrane slot size; it could deform and pass through the membrane, or stay on the membrane surface or be sheared off from the membrane surface.

4.2 Theory

A mathematical model for a dead-end microfiltration of dilute suspension was suggested [Filippov et al., 1994]. The model was based on sieve mechanism and during the process pore blocking of the membrane was taken into account [Filippov et al., 1994]. This model can be used to predict trans-membrane pressure during surface microfiltration processes. Final expression of permeate flux rate was deduced in [Filippov et al., 1994].

$$J = k_o \Delta P (1 + k_o y' c t \Delta P)^{-1}$$
(4.1)

Where J is the permeate flux through the membrane, k_o is the initial permeability of membrane, ΔP is the pressure difference across the membrane, c is the concentration of dispersion (number of drops per m³), y' is the blocking constant and t is filtration time [Filippov et al., 1994].

Equation (4.1) can be rearranged as follows:

$$J = \frac{k_o \Delta P}{(1 + k_o y' ct \Delta P)}$$
$$J + Jk_o y' ct \Delta P = k_o \Delta P$$
$$k_o \Delta P - Jk_o y' ct \Delta P = J$$
$$k_o \Delta P(1 - Jy' ct) = J$$

Hence, the filtration pressure is related to the flux and time by:

$$\Delta P = \frac{J}{k_o \left(1 - cy'Jt\right)} \tag{4.2}$$

The blocking constant y' can be related to the physical properties of the membrane and the particles being filtered [Filippov et al., 1994]:

$$y' = (\pi \beta d^{**2} / 4) \int_{d^{**}}^{D \max} f_p(D) dD$$
(4.3)

Where $f_p(D)$ is probability distribution function of particle diameter, D_{max} is maximum particle diameter and β is assumed the hydrodynamic specific surface force of interaction between the surface of the membrane pores/slots and the particles. β is referred as parameter to characterize membrane pore influence [Filippov et al., 1994]. The constant d^{**} is assumed to be the diameter of pore/slot at the start of the process when it is assumed to be completely open, D is the diameter of particles/droplets that will cause fouling (between d^{**} and the maximum dispersed phase size). Hence, y' is the blocking constant and independent of time for any given set of filtration conditions. The model presented in equation (4.2) can be applied to circular and slotted pore membranes with filtration of non-deforming particles. It may be valid up to a point when filtering deforming oil drops; i.e. where the passing of deformed drops through the membrane may result in higher flux rates, or lower operating pressures, than would otherwise be obtained when filtering solid (non-deforming) particles. In addition, the model is one that applies the full concentration of the dispersed phase (c) and blocking constant (y') to the analysis. During conditions of microfiltration applying shear at the membrane surface, rather than dead-end filtration, then it could be argued that either (or both) of these constants may be altered compared to those obtained in the absence of shear.

4.3 Experimental setup

4.3.1 Materials

Most of the materials used are already explained in Chapter 3. Permeate flux was sucked through the membrane by a peristaltic pump (RS 440-515, UK). To measure trans-membrane pressure a sensitive pressure transducer (HCX001A60, Farnell, UK) was used. Shear rates were applied on the surface of membrane and membrane frequency was controlled through a voltage controller (Delta eteckronika, 1464).

4.3.2 Emulsion preparation

1% gum Arabic was dissolved in 1000 ml water using a magnetic stirrer operated at its highest speed so that particles of gum Arabic did not cluster in water. Silica (SiO₂) was dispersed in vegetable oil using the magnetic stirrer. 1 ml of the dispersion of silica/vegetable oil was added into 500 ml water gum Arabic solution. 1-15 μ m vegetable oil particles were produced with a food blender operated using its highest speed for 12 mins, a typical size distribution is illustrated in Figure 4.2.


Figure 4.2 Typical size distribution (Cumulative mass undersized "m" VS droplet diameter "d") of the oil droplets produced.

4.3.3 Filtration

All filtration experiments were carried out using a 4 μ m slotted pore membrane attached to a vibrating arm activated by an electromechanical oscillator see Figure 4.3. A replaceable membrane was attached to the vibrating head using a hollow steel rod that provided both structural support as well as the permeate flow tube. Frequency and amplitude of membrane oscillation were controlled and were adjusted between 0-100 Hz and 0-10 mm respectively. Vibration is produced in the vertical direction that creates shear on the outer surface of the membrane. Emulsion feed was contained outside of the membrane and permeate was sucked, by a peristaltic pump (a positive displacement type of pump enabling almost constant flow rate conditions), and periodically collected in a measuring cylinder, trans-membrane pressure was recorded and the permeate returned to the feed tank. Trans-membrane pressure is defined here as the difference in pressures between the inside of the membrane and atmospheric pressure.

Filtration of vegetable/water oil emulsion was carried out with, and without, vibration of the membrane using various frequencies and flux rates. The membrane was vibrated vertically with various frequencies and, due to it, different intensities of shear rates were applied to the membrane. The influence of different intensities shear rates were studied at different flux rates.



Figure 4.3 Schematic view of vibrating microfiltration rig.

Shear rate is a function of velocity at the membrane surface [Beier et al., 2006], angular frequency ω ($\omega = 2\pi F$) and velocity amplitude. Shear rate ($\dot{\gamma}$) at any instance of time can be calculated as follows:

$$\dot{\gamma} = v_0 \sqrt{\frac{\omega}{2\nu}} \left[\sin(\omega t) - \cos(\omega t) \right]$$
(4.4)

where v is kinematic viscosity of water. The variation in shear rate with respect to time is illustrated in Figure 4.4, and it is believed that the peak shear rate is the value that dictates the filtration performance. In further discussion, it is the peak shear rate that will be used to characterise the experiments and results.



Figure 4.4 Illustration of shear rate against time applied to a membrane vibrated with 6, 12 and 21 Hz frequencies.

4.4 Results and discussion

Figures 4.5 and 4.6 illustrate how the pressures and flux rates varied during filtration whilst using the different rates of shear at the surface of the membrane. In all the tests the flux rates reduced slightly from the original set-point and then stabilised. The reduction from the original flux rate was approximately 20% at all the different shear rates. The reasonably fast establishment of a constant flux rate, in all the tests, means that the filtration can be viewed as a 'constant rate filtration'; whereby an increase in filtration pressure is required to compensate for any membrane fouling. In none of the experiments did the filtration flux diminish to negligible amounts, this is a consequence of using a permeate pump that approximates to a 'positive displacement' type of pump. Hence, the trans-membrane pressure increased to compensate for fouling.



Figure 4.5 (a) Experimental measurements of flux rates with time during the oscillating filtration experiments at 0 s⁻¹ shear rate.



Figure 4.5 (b) Experimental measurements of flux rates with time during the oscillating filtration experiments at 1200 s⁻¹ shear rate.



Figure 4.5 (c) Experimental measurements of flux rates with time during the oscillating filtration experiments at 3200 s⁻¹ shear rate.



Figure 4.5 (d) Experimental measurements of flux rates with time during the oscillating filtration experiments at 8100 s⁻¹ shear rate.

At zero shear rate, Figures 4.5 (a) and 4.6 (a), there is no contribution towards membrane cleaning by shear parallel to the membrane surface and membrane blocking should be at its worst. The pressure required to suck permeate through the membrane, under minimal fouling, can be deduced from the intercept on the pressure axis. The pressures varied from 1-14 kPa, which are low values of trans-membrane pressure, but this is a consequence of the slotted pore membrane structure [Holdich et al., 2006; Bromley et al., 2002].



Figure 4.6 (a) Experimental measurements and theoretical predictions (using equation 4.2) of pressure drop with time during the oscillating filtration experiments using the blocking model at 0 s^{-1} shear rate.

When filtering with applied shear, Figures 4.6 (b), (c) and (d), the measured blockage is reduced: the pressure only rises to less than 4 kPa for filtration at 1200 l m⁻² h⁻¹ at 8100 s⁻¹ shear rate. Looking at the lower flux rates, 400 and 200 l m⁻² h⁻¹, at low shear rates the pressure increases, Figures 4.6 (b) and (c), but remains constant when filtering at a shear rate of 8100 s⁻¹, Figure 4.6 (d).



Figure 4.6 (b) Experimental measurements and theoretical predictions (using equation 4.2) of pressure drop with time during the oscillating filtration experiments using the blocking model at 1200 s^{-1} shear rate.

Sustainable flux conditions are apparent on Figure 4.6 (d), for all the flux rates, but finite time is required before these conditions are achieved. For example, in the case of the 1200 l m⁻² h⁻¹ filtration 200 seconds is required before the trans-membrane pressure and the permeate flux rate (Figure 4.6 (d)) becomes stable. Again, it is likely that membrane blockage is occurring until a balance between the approach velocity of the permeate liquid and the ability of the drops to remain seated on the membrane is reached: a further reduction in membrane open pore area would increase the drag force to deform and pass the drops through the membrane.



Figure 4.6 (c) Experimental measurements and theoretical predictions (using equation 4.2) of pressure drop with time during the oscillating filtration experiments using the blocking model at 3200 s^{-1} shear rate.



Figure 4.6 (d) Experimental measurements and theoretical predictions (using equation 4.2) of pressure drop with time during the oscillating filtration experiments using the blocking model at 8100 s^{-1} shear rate.

Figure 4.6 also illustrates the blocking model applied to the data, in terms of predicted transmembrane pressure with respect to filtration time. In all cases, the blocking constant 'y'' is used as a fitting parameter to the experimental data. Permeate flux is a component of Equation (4.2), and in a completely predictive model a constant flux would be used, equal to the initial flux rate. However, as the intention here is to investigate the blocking model with respect to microfiltration with both applied shear at the membrane surface as well as particles that may deform and pass through the membrane, the measured value of flux rate at any instance in time was used in Equation (4.2) to predict the trans-membrane pressure drop. Figure 4.6 (a) is the microfiltration in the absence of any surface shear; i.e. a dead-end filtration which should follow the blocking model the closest, in the absence of drops deforming and passing in to the permeate.

Blocking of the pores is apparent as filtration progresses, indicated by the pressure rise, and can be seen in all figures (4.6(a)-4.6(d)). However, after 200 seconds the measured pressure curve goes through a point of inflection (Figures 4.6 (c) and (d)), which is not predicted by the blocking model (experimental data forms a 'S' shaped curve), and it is believed that this is due to oil drops deforming and being sucked through the membrane pores. This occurs as membrane blockage reduces the pore area available for liquid flow, hence the liquid velocity within the remaining open pores will increase, causing increasing drag on the oil drops and encouraging them to deform and pass through the membrane [Kosvintsev, et al., 2007]. A similar influence is just visible for the filtrations at lower flux rates: 900 and 400 1 m⁻² h⁻¹. Apart from these deviations, the simple blocking model does appear to predict the filtration data very well: suggesting a single blocking constant for each filtration. However, a different blocking constant is required for each permeate flux rate: it is expected that the blockage rate at the highest permeate flux rate is greater than that at the lowest flux rate [Madaeni et al., 1999] but due to the involvement of deforming drops, it passes through the membrane rather than blocking the membrane pores at higher flux rate. At first sight, this is not obvious from equations (4.2) and (4.3) where a universally applicable blocking constant may be expected, for the same concentration of dispersed phase and size distribution. However, the 'hydrodynamic interaction coefficient' within the definition of equation (4.3) should vary with flux rate: as a higher flux rate may lead to a greater region of influence above the membrane pore contributing towards the fouling at the pore. Higher flux rate increases deformation of oil drops and it may be possible that at higher flux rates drops would not seat on the surface of the membrane and would deform and pass through the membrane into the permeate.

It is apparent in Figure 4.6 (a) that there is an influence due to droplet deformation in terms of divergence (experimental data formed 'S' shaped curve) from a membrane blocking model, and the establishment of a sustainable flux. The influence of surface shear on the establishment of a sustainable flux, and the divergence from a blocking model, is illustrated in Figures 4.6 (b)-(d). Clearly, the divergence from the blocking model becomes more pronounced as the surface shear increases. Another observation is that the blocking constant also changes with the surface shear rate: at the highest surface shear, Figure 4.6 (d), the starting trans-membrane pressure for 1200 l m⁻² h⁻¹ (and hence the blocking constant) gives rise to a pressure of 2.5 kPa, whereas at zero surface shear the starting trans-membrane pressure is 4 kPa. There is a consistent reduction in the blocking constant as the shear rate increases for all the different flux rates studied. However, a single value of blocking constant can be attributed to each of the experiments and the subsequent fouling performance of the filtration with respect to time appears to be adequately modelled until a point where experimental data diverge from the theory.

As it is explained that divergence of the experimental data from the theory (that can be seen in figures 4.6(a)-(d)) may be due to the involvement of deforming oil drops that deform and pass through the membrane. Increase in flux rate increased drag and deformation of drops through the slots [Kosvintsev et al., 2007] and that is the reason that at higher flux rate divergence from the theory occurred quickly as compared to lower flux rates with and without shear rate applied. Similarly, shear rate increased linearly divergence of the experimental data from the theory due to the reason of reduction in fouling with the applied shear rate [Gomaa and Rao, 2011; Koltuniewicz et al., 1995].

Flux rate (l m ⁻² hr ⁻¹)	Shear rate (s ⁻¹) Blocking constant, y' (m ²)			
200	0	5.5E-10		
400	0	4.4E-10		
900	0	3.2E-10		
1200	0	2.7E-10		
200	1200	5E-10		
400	1200	4E-10		
900	1200	2.9E-10		
1200	1200	2.21E-10		
200	3200	3.5E-10		
400	3200	2.2E-10		
900	3200	1.6E-10		
1200	3200	1.3E-10		
200	8000	1E-10		
400	8000	9E-11		
900	8000	8E-11		
1200	8000	7.5E-11		

Table 4.1 Blocking constant (y') at various shear rates and flux rates

Blocking constant is a function of shear rate and permeate flux: y' = f(shear, permeate flux). Blocking constant against shear rate and permeate flux are provided in Figure 4.7 (a) and (b). Experimental points are fitted with polynomial trendlines and line equations are provided.



Figure 4.7 (a) Blocking constant (y) against shear at various permeate flux.



Figure 4.7 (b) Blocking constant (y) against permeate flux at various shear rates.

4.5 Conclusions

Sustainable flux can be rationalised by the approach of a simple blocking model for microfiltration. The model assumes uniform blockage of the pores as a function of time: where the degree of blockage can be correlated to the volume of permeate passed and the concentration of the dispersed phase causing a formation of blocking deposit on the membrane surface. During filtration of oil drops the simple blocking model is not followed (experimental data formed 'S' shaped curve). There are two reasons which are the cause: (i) the deforming nature of the oil drops. Because of that the droplet may pass into the permeate rather than contribute towards the blockage of the membrane surface, and (ii) the application of surface shear. Clearly, the stronger surface shear applied the less surface blockage would be expected. Both of the above mentioned reasons will contribute towards the reduction in blockage and the formation of a steady state flux. A universally predictive model should take into account both the above reasons. The most important parameters that contributes towards the blocking model are the hydrodynamic and specific surface forces of interaction between

the surface of the membrane pores/slots and the particles, or interaction coefficient, which is clearly a function of the shear conditions.

The filtration of a stabilised oil emulsion by a microfilter with long narrow slots with a minimum 4 micron slot width followed the developed blocking model under most of the applied operating conditions. Whilst blocking occurs the filtration cannot be described as 'sustainable', or under critical flux. However, when the blocking model is no longer followed the filtration may be sustainable. These conditions could be induced for all the measured permeate flow rates: easily for the lowest flow of $200 \ 1 \ m^{-2} \ h^{-1}$ and even possible at the highest permeate flow rate of $1200 \ 1 \ m^{-2} \ h^{-1}$, but only after a short period of filtration that did follow the blocking model first. Further work is required to establish the membrane/particle interaction coefficient and to investigate practical mixtures, which are multi-component systems. In this case complex interacting relations between the mixtures of suspended materials will be involved. However, such mixtures are present at the filtration of produced water in the oil industry and cutting fluids.

Chapter 5

Interfacial tension and a model for deformation of oil drops without membrane oscillation

This Chapter is based on

A. Ullah, R.G. Holdich, M. Naeem, V.M. Starov, "Stability and deformation of oil droplets during microfiltration on a slotted pore membrane", Journal of Membrane Science 401-402 (2012) 118-124.

5.1 Introduction

The influence of interfacial tension between two fluids, on the passage and rejection of oil droplets through slotted pore membranes is reported. A mathematical model is developed in order to predict conditions for 100% cut-off of oil droplets through the membrane as a function of permeate flux rate. Good agreement of theoretical predictions with experimental data shows that the model can be applied to the filtration of deformable droplets through slotted pore membranes. At high interfacial tension (47 mN m⁻¹) with lower flux (2000 l m⁻² hr⁻¹) droplets of crude oil (22 °API) were 100% rejected at droplet diameter 4.05 μ m using a 4 μ m slotted pore membrane. At lower interfacial tension (5 mN m⁻¹), with the same flux rate, 100% rejection occurred at 5.2 μ m droplet diameter using the same membrane. It was also found that the droplet rejection efficiency below the 100% cut-off was roughly linear with drop size, down to zero rejection at zero drop diameter. Hence, the model, coupled with this approximate linear correlation, can be used to predict dispersed oil drop concentration from any known feed drop size distribution.

5.2 Theory

The relevant theory was introduced earlier in [Kosvintsev et al., 2007], where the derivation was not provided, and the final equation given contained an error and requires modification for the current case. Equations are obtained by the energy balance approach on a droplet using the static force (F_c) and force of deformation that can also be referred to as drag force (F_d) see Figure 5.1. F_{cx} is the x coordinate of the static force F_c . This model can be applied for the theoretical prediction of 100% rejection of oil drops in the slot of the membrane under various flux rates. It is assumed when a spherical droplet having radius (R_{sp}) passes through the slot with a half width h, if the size of droplet is bigger than the slot half width it will deform into an ellipsoid with a bigger radius (R_{ell}) . The slot converges with an inside angle of α . Value of α is 34° [Kosvintsev et al., 2007].



Figure 5.1 Schematic view of deforming droplet at equilibrium position.

The excess capillary energy E_{ca} required to squeeze a droplet from a sphere to ellipsoid is the difference in surface area of ellipsoid (S_{ell}) and sphere (S_{sp}) multiplied by interfacial tension (σ) .

$$E_{ca} = \sigma(S_{ell} - S_{sp}) \tag{5.1}$$

The surface area of a sphere is

$$S_{sp} = 4\pi R^2_{sp} \tag{5.2}$$

A prolate spheroid has surface area

$$S_{ell} = \left(h^2 + \frac{hR_{ell}\beta}{\sin\beta}\right)$$
(5.3)

where, $\beta = \arccos \frac{h}{R_{ell}}$,

A prolate (elongated) spheroid can be formed by rotating an ellipse around its major axis.

In the case of a sphere

$$V = \frac{4}{3} \pi R_{sp}^{3}$$
(5.4)

In the case of a spheroid

$$V = \frac{4}{3}\pi h^2 R_{ell}$$
(5.5)

For the same drop because of volume conservation we conclude from equations (5.4), (5.5):

$$\frac{4}{3}\pi R_{sp}^{3} = \frac{4}{3}\pi h^{2}R_{ell} \text{ or } R_{ell} = \frac{R_{sp}^{3}}{h^{2}}$$
(5.6)

Hence,

$$S_{ell} = 2\pi \left(h^2 + \frac{hR_{ell} \arccos \frac{h}{R_{ell}}}{\sqrt{1 - \left(\frac{h}{R_{ell}}\right)^2}} \right)$$
(5.7)

Substitution equation (5.6) into equation (5.7) results in

$$S_{ell} = 2\pi \left(h^2 + \frac{\frac{R_{sp}^3}{h} \arccos\left(\frac{h}{R_{sp}^3}\right)^3}{\sqrt{1 - \left(\frac{h}{R_{sp}}\right)^6}} \right) = 2\pi R_{sp}^2 \left(\left(\frac{h}{R_{sp}}\right)^2 + \frac{\arccos\left(\frac{h}{R_{sp}}\right)^3}{\frac{h}{R_{sp}}\sqrt{1 - \left(\frac{h}{R_{sp}}\right)^6}} \right)$$
(5.8)

Put eqn (5.2) and (5.8) in (5.1) gives:

$$E_{ca} = \sigma \left(2\pi R_{sp}^{2} \left(\left(\frac{h}{R_{sp}} \right)^{2} + \frac{\arccos\left(\frac{h}{R_{sp}}\right)^{3}}{\frac{h}{R_{sp}} \sqrt{1 - \left(\frac{h}{R_{sp}}\right)^{6}}} \right) - 4\pi R_{sp}^{2} \right)$$

$$E_{ca} = 2\pi R_{sp}^{2} \sigma \left(\left(\left(\frac{h}{R_{sp}} \right)^{2} + \frac{\arccos\left(\frac{h}{R_{sp}}\right)^{3}}{\frac{h}{R_{sp}} \sqrt{1 - \left(\frac{h}{R_{sp}}\right)^{6}}} \right) - 2 \right)$$
(5.9)

According to [Kosvintsev et al., 2007]:

$$F_{cx} = \left(\frac{\partial E_{ca}}{\partial I}\right)_{I=R_{sp}-h} \sin\frac{\alpha}{2} = -\left(\frac{\partial E_{ca}}{\partial h}\right) \sin\frac{\alpha}{2}$$

$$\Rightarrow \frac{\partial E_{ca}}{\partial h} = \frac{\partial}{\partial h} \left(2\pi R_{sp}^{2} \sigma \left(\left(\frac{h}{R_{sp}}\right)^{2} + \frac{\arccos\left(\frac{h}{R_{sp}}\right)^{3}}{\frac{h}{R_{sp}}\sqrt{1 - \left(\frac{h}{R_{sp}}\right)^{6}}\right) - 2\right)\right)$$
(5.10)

$$\frac{\partial E_{ca}}{\partial h} = 2\pi R_{sp}^{2} \sigma \left(\left(\frac{\partial}{\partial h} \left(\frac{h}{R_{sp}} \right)^{2} + \frac{\partial}{\partial h} \left(\frac{\arccos\left(\frac{h}{R_{sp}} \right)^{3}}{\frac{h}{R_{sp}} \sqrt{1 - \left(\frac{h}{R_{sp}} \right)^{6}}} \right) \right) \right)$$

$$=2\pi R_{sp}^{2}\sigma\left(\left(\frac{2h}{R_{sp}^{2}}\right)+\left(\frac{\frac{h}{R_{sp}}\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}}{\frac{\partial}{\partial h}\arccos\left(\frac{h}{R_{sp}}\right)^{3}-\arccos\left(\frac{h}{R_{sp}}\right)^{3}}\frac{\partial}{\partial h}\left(\frac{h}{R_{sp}}\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}\right)}{\left(\frac{h}{R_{sp}}\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}\right)^{2}}\right)\right)\right)$$

$$=2\pi R_{sp}^{2} \sigma \left(\left(\frac{2h}{R_{sp}^{2}} + \frac{1}{\left(\frac{h}{R_{sp}}\sqrt{1 - \left(\frac{h}{R_{sp}}\right)^{6}}\right)^{2}} + \frac{1}{\left(\frac{h}{R_{sp}}\sqrt{1 - \left(\frac{h}{R_{sp}}\right)^{6}}\right)^{2}} - \arccos\left(\frac{h}{R_{sp}}\right)^{3} \left(\frac{h}{R_{sp}} + \frac{1}{2\sqrt{1 - \left(\frac{h}{R_{sp}}\right)^{6}}} + \frac{1}{R_{sp}}\sqrt{1 - \left(\frac{h}{R_{sp}}\right)^{6}}\right) + \frac{1}{R_{sp}}\sqrt{1 - \left(\frac{h}{R_{sp}}\right)^{6}}\right) \right) \right) \right)$$

$$=2\pi R_{sp}^{2}\sigma\left(\left(\frac{2h}{R_{sp}^{2}}\right)+\frac{1}{\left(\frac{h}{R_{sp}}\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}\right)^{2}}\left(\frac{h}{R_{sp}}\left(\frac{-3h^{2}}{R_{sp}^{3}}\right)-\arccos\left(\frac{h}{R_{sp}}\right)^{3}\left(\frac{h}{R_{sp}}\frac{1}{2\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}}\left(\frac{-6h^{5}}{R_{sp}^{6}}\right)+\frac{1}{R_{sp}}\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}\right)\right)\right)\right)$$

$$=2\pi R_{sp}^{2}\sigma\left(\left(\frac{2h}{R_{sp}^{2}}\right)+\left(\frac{\frac{h}{R_{sp}}\left(\frac{-3h^{2}}{Rs_{p}^{3}}\right)-\arccos\left(\frac{h}{R_{sp}}\right)^{3}\frac{1}{2\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}}\left(\frac{1}{R_{sp}}\left(\frac{-6h^{6}}{R_{sp}^{6}}\right)+\frac{1}{R_{sp}}\left(2-2\left(\frac{h}{R_{sp}}\right)^{6}\right)\right)\right)\right)\right)\right)$$
$$\left(\frac{h}{R_{sp}}\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}\right)^{2}$$

$$=2\pi R_{sp}\sigma\left(\left(\frac{2h}{R_{sp}}\right)+\left(\frac{-3\left(\frac{h}{R_{sp}}\right)^{3}-\arccos\left(\frac{h}{R_{sp}}\right)^{3}\frac{1}{2\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}}\left(-6\left(\frac{h}{R_{sp}}\right)^{6}+\left(2-2\left(\frac{h}{R_{sp}}\right)^{6}\right)\right)\right)}{\left(\frac{h}{R_{sp}}\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}\right)^{2}}\right)\right)$$

$$\frac{\partial E_{ca}}{\partial h} = 2\pi R_{sp} \sigma \left[\left(\frac{2h}{R_{sp}} \right)^{4} + \left(\frac{-3\left(\frac{h}{R_{sp}}\right)^{3} - \arccos\left(\frac{h}{R_{sp}}\right)^{3} \frac{1}{2\sqrt{1 - \left(\frac{h}{R_{sp}}\right)^{6}}} \left(-8\left(\frac{h}{R_{sp}}\right)^{6} + 2\right) \right) \right] \right]$$
(5.11)
$$\left(\frac{h}{R_{sp}} \sqrt{1 - \left(\frac{h}{R_{sp}}\right)^{6}} \right)^{2}$$

Put $\frac{\partial E_{ca}}{\partial h}$ in equation (5.10) gives:

$$F_{cx} = -\left(2\pi R_{sp}\sigma\left(\left(\frac{2h}{R_{sp}}\right) + \left(\frac{-3\left(\frac{h}{R_{sp}}\right)^{3} - \arccos\left(\frac{h}{R_{sp}}\right)^{3}\frac{1}{2\sqrt{1-\left(\frac{h}{R_{sp}}\right)^{6}}}\left(-8\left(\frac{h}{R_{sp}}\right)^{6}+2\right)\right)}\right)\right)\right)\sin\frac{\alpha}{2}$$

$$(5.12)$$

Equation (5.12) is different from the flowing equation derived by [Kosvintsev et al., 2007] for the final expression of the static force. It was assumed that a drop deforms from spherical to oblate spheroid while passing through a converging slot. The deformation of spherical drop to oblate spheroid is only possible when drop is passing through a non-converging slot. So, the developed equation was not valid for a drop deformation through a converging slot.

$$F_{cx} = \frac{\pi\sigma}{2} \left(\frac{\left(8D_{sph}h^4 - 8D^4_{sph}h + 6D^5_{sph} - 3D^2_{sph}h^3\right)}{h\left(D^3_{sph} - h^3\right)} + \frac{\sqrt[3]{D_{sph}}h^5 \arcsin\left(\sqrt{h^3 - D^3_{sph}} / \sqrt{h^3}\right)}{\sqrt{\left(h^3 - D^3_{sph}\right)^3}} \right) \sin\left(\frac{\alpha}{2}\right)$$

The drag force exerted on a sphere moving between parallel plates is given as in [Kosvintsev et al., 2007] $F_d = k_w F_o$ where k_w is a wall correction factor and F_o is the drag force and can be obtained using Stokes drag expression [Genkin et al., 2006; Soubiran and Sherwood, 2000; Kosvintsev et al., 2007]. For a similar system k_w value 4.3 is used [Kosvintsev et al., 2007]. Here η is viscosity of the fluid, R_{sp} is the radius of the droplet and U is the velocity of the fluid.

$$F_d = k_w 12\pi\eta R_{sp} U \tag{5.13}$$

The droplet will be under steady state conditions when F_{cx} becomes equal to F_d and will stay on the surface of the membrane. The droplet will deform and will pass through the membrane when $F_d > F_{cx}$ and it will be rejected by the membrane in the case of $F_{cx} > F_d$. The point at which $F_{cx} = F_d$ is assumed as 100% cut-off or 100% rejection point.

The theory predicts the drag and the static forces over a single drop inside the slot and multi body interactions has not been considered. A lower drag would be experience when multi drops passing through the slot as compared to a single drop. Also, electro static electrostatic interactions are not considered in the development of the theory. Electrostatic forces act dominantly outside the membrane surface, while the deformation and passage inside the membrane slot is taken into account.

5.3 Experimental setup

5.3.1 Material

Some of the materials used are described in Chapter 3. Crude oil was supplied by North Sea operating companies. Silica (SiO₂) (Degussa AG, Germany) was used to enhance oil droplet stability by decreasing the deformation of the droplets when subjected to high transmembrane pressure during filtration, by increasing the interfacial tension between the oil droplet and water. For the measurement of interfacial tension the Du Nouy ring method with a White Electric Instrument tensiometer (model DB2KS) was used. Filtration tests were performed using a dead-end candle microfiltration system with a slotted membrane of 4 μ m slot width and 400 μ m slot length (Micropore Technologies Ltd, UK) see Figure 5.2 for an image of an example slotted membrane and Figure 5.3 for schematic diagram of the equipment used. To prevent coalescence of droplets vegetable/water oil emulsion was gently stirred with a magnetic stirrer (Stuart Scientific, SM1, 13519, UK). The membrane was cleaned with Ultrasil 11 and an ultrasonic bath (Fisher Scientific, FB 15046, Germany) was used to agitate the beaker containing Utrasil 11 water solution to clean the membrane.



Figure 5.2 Image of the surface of a slotted pore membrane.

5.3.2 Interfacial tension measurement

The Du Nouy ring method was used to measure the interfacial tension. A ring is placed inside the dense liquid (water) and pulled out towards the light liquid (oil) until it detached from the dense phase. The force (F') required to pull the ring from one phase to another is equal to the interfacial tension between the two liquids multiplied by the length of the perimeter of the ring.

$$F' = 4\pi\sigma\beta' \tag{5.14}$$

Where *R* is the radius of the ring, β' is the correlation factor and σ is the interfacial tension [McClements, 1999].

5.3.3 Filtration

A 4 μ m slot width membrane was used for filtration experiments using the dead-end candle microfiltration system as illustrated in Figure 5.3.



Figure 5.3 Schematic view of dead-end candle microfiltration system.

The presence of large droplets in the permeate would indicate deformation of the droplets through the slots of the membrane. Grade efficiency can be calculated using the following equation [Cumming et al., 1999]:

$$grade \ efficiency = \ (1 - \frac{permeate mass concentration in size \ grade}{feed \ mass \ concentration \ in size \ grade})100$$
(5.15)

Permeate with various flux rates was passed through the membrane, and the influence of the flux rate on grade efficiency and 100% cut-off was studied. Before and after each run the membrane was cleaned with 2% Ultrasil 11 and hot (50 ^oC) filtered water. At different transmembrane pressures various permeate flux rates were obtained and compared with clean water flux rates at the respective trans-membrane pressures. When these flux rates were similar to the flux rates of the clean water, the membrane was considered cleaned and ready for reuse.

5.4 Results and discussion

According to the mathematical model presented in this chapter, according to equation 5.1, a system needs more energy for the deformation and squeezing of the droplets through the slots

of the membrane when there is a higher interfacial tension. Similarly, a higher pressure is required for drops with a higher interfacial tension to pass through circular pore membranes [Cumming et al., 2000]. Mainly, the drag force and the static force are taken into account in the model. Drag force is the one that drags the droplets through the slots [Kosvintsev et al., 2007]. It is the function of droplet size and fluid velocity around the droplet [Kosvintsev et al., 2007]. It increases linearly with the droplet size. Static force always acts in the opposite direction to the drag force, and tries to reject the droplets through the slots. It mainly depends on interfacial tension between the two fluids. Static force increases linearly with interfacial tension and exponentially with the size of the droplets.

To compare the influence of the drag force and the static force on the droplets was the main focus of the study. Higher drag force than static force leads to higher deformation, and passage of the droplets through the slots [Kosvintsev et al., 2007]. In the case of higher static force than drag force oil drop rejection is higher [Kosvintsev et al., 2007]. Equilibrium condition is when drag force equals of static force without shear rate applied to the surface of the membrane. When the equilibrium condition is reached, the droplets are assumed to stay on the surface of the membrane.

The membrane slot width (4 μ m) was specified by Micropore Technologies UK. To confirm the slot width, non-deformable silica particles were filtered at various flux rates. The width of the slots would be 4 μ m if it rejected silica particles at 4 μ m, and above, with different flux rates. Figure 5.4 shows that at various flux rates the 100% silica particles cut-off was close 4 μ m. So, the slot width was assumed to be 4 μ m for the mathematical model and for the filtration of vegetable oil and crude oil droplets at different flux rates. A linear fit in Figure 5.4 is obtained by drawing a straight line connecting the 100% cut-off theoretical value with the origin of the graph. It provides a reasonable correlation of rejection below the 100% cutoff value.



Figure 5.4 Grade efficiency against particle size to slot width ratio (d/2h) of silica particles at various flux rates (2000, 4000, 6000 l m⁻² hr⁻¹) using a 4 μ m slotted pore membrane.

Figure 5.5 illustrates the comparison of 100% cut-off (rejections) points against drop to slot ratio (d/2h) of all the droplets obtained from experimental measured points and theoretical predications. d is the drop size and 2h is the slot width, in our case slot width is 4 μ m. The static force was obtained using equation (5.12), and drag force from equation (5.13). For a given system theoretical 100% cut-off is when static force balances drag force and at different flux rates various predicted 100% cut-off values are obtained. Different 100% cut-off predicted points are connected with a line that is referred as 'Predicted' in Figure 5.5. A satisfactory agreement of theoretical points and the experimental measured points shows that this model can be used to predict the 100% cut-off values the different types of oil tested here.



Figure 5.5 Experimental measurements and theoretical points of 100% cut-off (when eqn. 5.12 balances eqn. 5.13) during filtering vegetable oil droplets with various surfactants, (Silica + gum Arabic, Gum Arabic, PVA, Tween 20) and Crude oil (27 °API) and crude oil (22 °API) with different flux rates (2000, 4000 and 6000 l m⁻² hr⁻¹) using a 4 µm slotted pore membrane.

Various interfacial tensions were observed with the different surfactants used. Interfacial tension of vegetable oil/water emulsion was increased by dispersing hydrophobic silica (SiO₂) particles in the oil phase as shown in Table 5.1. At a flux rate of 2000 1 m⁻² hr⁻¹, 4000 ppm of oil in the inlet feed is reduced to 30 ppm in the outlet permeate using 0.5 wt% silica along with 1 wt% of gum Arabic as illustrated in Table 5.1. 100% droplets were cut-off at 4.5 μ m with 2000 1 m⁻² hr⁻¹. Increasing flux rate to 4000 1 m⁻² hr⁻¹ also increased drag force over droplets and 50 ppm oil was observed in the permeate. This time 100% cut-off of oil droplets was observed at 5 μ m. Concentration of oil in the permeate further increased (60 ppm) with increasing flux rate (6000 1 m⁻² hr⁻¹) and 100% rejection of oil droplets moved to 5.5 μ m as illustrated in Figure 5.6 (a).

Table 5.1 Interfacial tension, mass of oil in the feed and permeate and 100% rejection of oil droplets with various surfactants at 2000 l m⁻² hr⁻¹.

Substance	Interfacial Tension (mN m ⁻¹)	Mass in Feed (ppm)	Mass in Permeate (ppm)	100% Cut-off (d/2h)
Crude oil (22 °API)	47.0	400	14	1.0125
Crude oil (27 °API)	40.0	400	18	1.025
0.1 wt% Silica + 1 wt% Gum Arabic	17.0	400	30	1.05
1 wt% Gum Arabic	13.0	400	50	1.1
1 wt% PVA	10.0	400	70	1.15
1 wt% Tween 20	5.0	400	100	1.3



Figure 5.6 (a) Grade efficiency of vegetable oil droplets against drop size to slot ratio (d/2h) using gum Arabic and silica combined for droplets stability at various flux rates (2000, 4000, 6000 l m⁻² hr⁻¹) using a 4 μ m slotted pore membrane.

Slightly lower interfacial tension (13 mN m⁻¹) was observed with gum Arabic without silica. Taking into account the idea that a decrease in interfacial tension would decrease the amount of energy required for the squeezing of the droplets through the slots. So, a decrease in interfacial tension would lead towards more passage of the droplets through the membrane and the 100% rejection point will be increased. Therefore, higher concentration of oil was observed (50 ppm) with lower interfacial tension emulsion (13 mN m⁻¹) as compared to higher interfacial tension emulsion (17 mN m⁻¹) at the same flux rate (2000 1 m⁻² hr⁻¹). Similarly, an increase in flux rate increased drag force over the droplets and higher concentrations of oil and higher 100% rejection points occurred with increasing in flux rate as can be seen in Figure 5.6 (b).



Figure 5.6 (b) Grade efficiency of vegetable oil droplets using gum Arabic for droplets stability at various flux rates (2000, 4000, 6000 l m⁻² hr⁻¹) using a 4 μ m slotted pore membrane.

Furthermore, the system with PVA showed lower interfacial tension than gum Arabic and gum Arabic and silica combined. At different flux rates (2000, 4000 and 6000 1 m⁻² hr⁻¹) higher concentrations of oil (70, 80 and 90 ppm) in the permeate were obtained respectively. Again, using the above mentioned conditions higher 100% cut-off was observed in the case of PVA than gum Arabic as shown in Figure 5.6 (c). Interfacial tension was lowest with Tween

20 as compared to all the surfactants used (5 mN m⁻¹). Lower energy will be required for droplets to squeeze through the membrane in the case of using Tween 20 as compared to other surfactants (gum Arabic and silica combine, gum Arabic and PVA). In this case, 100, 120 and 140 ppm oil was observed with flux rates of 2000, 4000 and 6000 l m⁻² hr⁻¹ respectively. Similarly, with the above mentioned flux rates, 100% cut-off of vegetable oil droplets occurred at 6, 7, and 8 µm respectively as illustrated in Figure 5.6 (d).



Figure 5.6 (c) Grade efficiency of vegetable oil droplets using PVA for droplets stability at various flux rates (2000, 4000, 6000 l m⁻² hr⁻¹) using a 4 μ m slotted pore membrane.



Figure 5.6 (d) Grade efficiency of vegetable oil droplets using Tween 20 for droplets stability at various flux rates (2000, 4000, 6000 l m⁻² hr⁻¹) using a 4 μ m slotted pore membrane.

Two types of crude oil (27 °API, 22 °API) were used to assess the response of filtration of crude oil to the mathematical model used. Without using any surfactant crude oil shows higher interfacial tension (40 mN m⁻¹ with 27 °API, 47 mN m⁻¹ with 22 °API) as compared to vegetable oil. Hence, 100% rejection at 4 and 4.1 μ m with crude oil 22 °API and 27 °API respectively, a better separation efficiency than vegetable oil droplets using the same flux rate (2000 1 m⁻² hr⁻¹). Increase in flux rates decreased rejection through the membrane, due to higher passage and deformation of crude oil droplets, as illustrated in Figure 5.6 (e) and Figure 5.6 (f).



Figure 5.6 (e) Grade efficiency of crude oil (27 $^{\circ}API$) droplets at various flux rates (2000, 4000, 6000 l m⁻² hr⁻¹) using a 4 μ m slotted pore membrane.



Figure 5.6 (f) Grade efficiency of crude oil droplets (22 °API) at various flux rates (2000, 4000, 6000 l m⁻² hr^{-1}) using a 4 μ m slotted pore membrane.

In all cases, once below the 100% cut-off, it is possible to provide an approximate 'linear fit' of rejection against droplet size. This is true for the oil drops as well as the solid silica particles. The two limits of the 'linear fit' are: the theoretical 100% cut-off value, and the origin. Hence, this 'linear fit' also quantifiably is predicted from the model presented in this chapter. Thus, for a given feed drop size distribution of oil drops in water, it is possible to predict the 100% cut-off value and the rejection efficiency at drop sizes below the 100% cut-off. Thus, the total oil drop distribution and mass concentration of oil in water in the permeate can be predicted, if the feed concentration and feed size distribution is known.

5.5 Conclusions

Interfacial tension between oil and water is an important factor that can strongly influence deformation of droplets through the slots of the membrane. It was found that an increase in interfacial tension decreased deformation of oil droplets. Interfacial tension of oil/water can be increased by dispersed particles at the interface. Higher interfacial tension was observed for crude oil than vegetable oils. This led to better rejection of crude oil droplets than vegetable oil droplets, but tests used both types in order to validate the numerical model predicting 100% cut-off. Good agreement of experimental measured points with the theoretical points shows that the concept of drag and static force over a droplet can be efficiently applied for filtering deformable droplets using slotted pore membranes. This work can be applied for filtration of emulsions created by produced water in the oil and gas industry that contain deformable droplets, for the prediction of 100% cut-off values and below, by using a 'linear fit' to the origin on a grade efficiency (rejection) against drop size figure, as well as the final dispersed phase oil drop concentration from a known feed emulsion.

Chapter 6

Membrane oscillations and rejection of drops

This Chapter is based on

A. Ullah, R.G. Holdich, M. Naeem, V.M. Starov, Shear enhanced microfiltration and rejection of crude oil drops through a slotted pore membrane including migration velocities, Journal of Membrane Science 421-422 (2012) 69-74.

6.1 Introduction

Shear enhanced microfiltration of crude oil/water emulsion is investigated and the influence of an applied shear rate on the rejection of drops by the membrane is reported. Applying vibration provides shear at the membrane surface leading to an inertial lift of drops/particles. This phenomenon tends to move the drops away from the membrane surface. The inertial lift migration increases with increasing shear rates. A mathematical model is presented to account for the presence of inertial lift phenomenon. The developed model is used for theoretical prediction of 100% cut-off of crude oil drops by the membrane with, and with-out, vibration applied. An agreement of the model predictions with experimental data shows that the model can be used as a starting point for a theoretical prediction of 100% cut-off of drops by slotted pore membranes. However, a slightly better experimental rejection was noticed than the theoretical one with the applied shear rate that might be due to the turbulence present in the system with the membrane oscillations. When applying a shear rates of 8000 s⁻¹ and 400 1 m⁻² hr⁻¹ flux rate, 2-3 µm radius drops were almost completely rejected using a 4 µm slotted pore membrane; reducing 400 ppm of crude oil (30 °API, interfacial tension in produced water is: 24 mN m⁻¹) in the feed to 7 ppm in the permeate.

6.2 Theory

Static force (F_{c_x}) is the force responsible for the rejection of drops through the membrane without shear applied to the surface of the membrane and can be expressed as follows: (equation (5.12)),

Where σ is interfacial tension between oil/water, R_{sp} is the radius of the drop, and *h* is the half width of slot of the membrane.

The drag force exerted on a sphere moving between two plates is given in [Soubiran and Sherwood, 2000; Keh and Po, 2001] as:

$$F_d = k_w \ 12 \ \pi\eta \ R_{sp} U \tag{6.2}$$

Where k_w is a wall correction factor and for a similar system its value is equal to 4.3 [Kosvintsev et al., 2007]. η is viscosity of the fluid, R_{sp} is the radius of the spherical droplet and U is the velocity of the fluid through the slot. The drop is under steady state conditions inside the pore, when F_{cx} becomes equal to F_d and the drops will be captured in this position. The drop will deform and will pass through the membrane when $F_d > F_{cx}$ and it will be rejected by the membrane in the case of $F_d < F_{cx}$.

Cross-flow of fluid created a shear on the surface of the membrane in microfiltration processes [Belfort et al., 1994]. Shear rate on the membrane surface can also be created by vibrating the membrane with various frequencies [Akoum et al., 2002]. Applied shear rate on the membrane surface caused migration of the particles away from the membrane surface [Belfort et al., 1994; Hudson, 2003]. Migration of the drops/particles away from the membrane surface may be due to shear-induced diffusion, Brownian diffusion, inertial lift and wall migration [Belfort et al., 1994; Hudson, 2003; Gomaa and Rao, 2011]. In shear-induced diffusion, drops/particles migrate away from the membrane surface due to particle-particle interactions and this phenomenon is prominent when particle-particle interactions are higher [Belfort et al., 1994; Kromkamp et al., 2002]. A dilute emulsion is used and therefore, particle-particle interactions are negligible here in this study. While, the Brownian diffusion occurs pronouncedly with submicron drops/particles [Belfort et al., 1994].

Migration of particles/drops away from the membrane surface due to the applied shear rate is referred as wall migration and velocity of the particles/drops away from membrane surface is named as migration velocity [Hudson, 2003]. Wall migration theory is valid when dispersed and continuous phases viscosities ratio was less than 1 [Hudson, 2003]. For a higher dispersed and continuous phases viscosities ratio, wall migration theory had a poor agreement with the experimental data [Hudson, 2003]. Also, wall migration theory hold upto a few radii distance

from the membrane [Hudson, 2003]. Therefore, wall migration theory is not considered in our case due to its limitation for the study presented here.

Inertial lift migration created due to applied shear rate that opposed permeate velocity [Belfort et al., 1994]. Migration velocity under fast laminar flow (the model is used as a starting point) conditions of a drop due to inertial lift, v_{if} , was deduced in [Belfort et al., 1994]:

$$v_{if} = \frac{0.036\rho_f \dot{\gamma}^2 R_{sp}^3}{\eta}.$$
 (6.3)

Where ρ_f is density of the fluid, η is viscosity of the fluid, $\dot{\gamma}$ is the applied shear rate and R_{sp} radius of the drop.

Dilute oil/water emulsion is used, so, particle to particle interaction is assumed to be negligible in our case. Inertial lift velocity can be calculated using equation (6.3). Migration velocity due to inertial lift is directed oppositely to the convection, v'_0 , caused by the flowing liquid. This consideration shows that drops reach the surface of the membrane with a velocity, v', which is lower than the velocity of the flowing liquid:

$$v' = v_0' - v_{if} = v_0' - \frac{0.036\rho_f \dot{\gamma}^2 R_{sp}^3}{\eta}.$$
(6.4)

This expression is used for comparison with the experimental data.

For a given shear rate and convection velocity (v'_0) , critical drop size would be the one at which v' become negative. Critical radius can be obtained using equation (6.4). For a given convection velocity, critical radius of drops would different at different shear rates. If velocity of the drops on the membrane surface becomes negative then the drops cannot pass the membrane into the permeate and will be transferred away from the membrane.

For a given drop size and convection velocity, critical shear rate $(\dot{\gamma}_{cr})$ is the one at which migration velocities of drops due to inertial lift become greater than convection velocity of the
drops. For a given drop size and convection velocity, critical shear rate can be obtain using equation 6.4. For a given convection velocity, drops with different sizes having different critical shear rates. Similarly, for a given drop size, at different convection velocities critical shear rate would be different.

6.3 Results and discussion

Drops approach the membrane surface at the same velocity as the surrounding fluid velocity without imposed shear. Due to the drag force created by the flow of the surrounding fluid, drops smaller than the slot width pass through the membrane . Static force (F_{cx}) acts in the opposite direction to the drag force (F_d) when the drops are bigger than the slot width (Figure 5.1). Drops may deform and pass through the membrane when drag force is higher than static force ($F_d > F_{cx}$). The drops are rejected by the membrane in the case of higher static force than the drag force ($F_d < F_{cx}$).

The membrane is oscillated at various frequencies that created turbulence in the surrounding fluid. The intensity of turbulence is the surrounding fluid can be evaluated by oscillatory Reynolds number (R_{eo}) and is calculated as follows:

$$R_{eo} = \frac{2\pi F a \rho D}{\eta} \tag{6.5}$$

Where *F* is membrane oscillation frequency, *a* is membrane amplitude, ρ is fluid density, *D* is diameter of the membrane and η viscosity of the fluid. Oscillating the membrane at 20 and 25 Hz frequencies provided 4500 and 5700 oscillatory Reynolds number (R_{eo}) respectively. At 20 and 25 Hz membrane oscillation frequencies R_{eo} is higher than 3460, it means that turbulence occurred for all the cycles [Salon et al., 2007].

Inertial lift due to the applied shear rate for a fast laminar flow provided by [Belfort et al., 1994] is assumed as a starting point here and in the future, solution of Navier-Stokes equation for oscillating flow in our system may be possible that would provide an exact model for the lift present in an oscillating flow. Higher turbulence due to the oscillation of the membrane is

present and a higher experimental rejection is expected than the predicted model at different flux rates.

When shear is applied to the membrane, inertial lift migrations velocity is created, which is directed away from the membrane surface [Belfort et al., 1994]. Migration velocity is a function of drop size and applied shear rate [Belfort et al., 1994]. Critical drop size would be the one above which drops would not pass the surface of the membrane into the permeate, i.e. migration velocities due to applied shear rate are higher than the initial filtration velocity (Figure 6.1). It is possible to compare the drop rejection at different shear rates to determine the influence of the "back-transport" of inertial lift migration for drop sizes below the 100% rejection value, and this is illustrated in Figure 6.2. Drops would reach the surface of the membrane if velocity (v'_0) of drops due to filtration of the surrounding fluid is higher than inertial lift velocity (v_{if}). A relation between the static force and the applied drag force is responsible for the rejection or transport of the drop through the membrane, once, the droplet reaches the inside membrane surface. Migration velocity (v_{if}) of drops due to the applied shear rate is worked out using equation 6.3. Subtracting migration velocity (v_{if}) from convection velocity (v'_0) gives the net convection velocity (v') of drops to the membrane surface with the applied shear rate. Net convection velocity of drops is lower due to the lateral migration of drops than the convection velocity of the surrounding fluid with the applied shear rate. With lower convection velocity drops due to the applied shear rate rejection would be higher.



Figure 6.1 Predicted drop size that would not pass the surface of the membrane into the permeate due to migration velocities created by the fixed applied shear rate according to eq. 6.4 using a 4 µm slotted pore membrane.



Figure 6.2 Rejection of drops (R (%)) against surrounding fluid velocity (m s⁻¹) of a 2 μ m drop with, and with without applied shear rate. With the applied shear rate, convection velocity of a drop decreased and reduction in convection velocity of a drop can be calculated using equation 6.4 that would increase rejection.

Figure 6.3 illustrates theoretical and experimental 100% cut-off of crude oil drops through a slotted pore membrane at various flux rates with, and without, applied shear rate. Drag force is strongly dependent on the fluid velocity around the drops. Without shear rate theoretical 100% cut-off would be when $F_d \leq F_{cx}$.

Applying shear rate to the membrane produced inertial lift which is directed away from the membrane surface [Belfort et al. 1994]. Migration velocities away from the membrane surface increases with increase in drops size, a stage is reached when drops would migrate away from the membrane surface, would not pass through the surface of the membrane into the permeate, and that stage is referred to as 100% theoretical cut-off. 100% theoretical cut-off can be obtained using equation 6.4. As smaller number of drops pass the membrane surface into the permeate when shear rate is applied as compared to without shear rate. The reduction in the number of drops passing the membrane surface is a function of the applied shear rate. Table 6.1 shows that higher the shear rate the lower would be number of drops experimentally obtained in the permeate. It is expected that rejection of drops through the membrane would be higher with the applied shear rate. The migration velocities (inertial lift) are a function of drop size: higher the drop size higher would be the migration away from the surface of the membrane [Belfort et al., 1994]. So it can be seen (Figure 6.3) that experimentally and theoretically 100% cut-off points decreased with the applied shear rate. A reasonable agreement of the experimental data with the theory shows that the presented mathematical model can be used as a starting point for the prediction of the 100% cut-off, with and without, shear rate applied to the membrane.



Figure 6.3 Experimental measurements and theoretical points of 100% cut-off against drop to slot ratio during filtration of crude oil drops (30°API) at various shear rates (0, 8000 s⁻¹, 10000 s⁻¹) and different flux rates (400, 600 and 1000 l m⁻² hr⁻¹). Predicted 100% cut-off points at various flux rates without oscillating the membrane are obtained when equation 6.1 and 6.2 balances each other. For a given flux rate with membrane oscillations, when value of v' (using equation 6.4) becomes negative is assumed as 100% cut-off point. Lines obtained by connecting various predicted 100% cut-off at different flux rates with, and without, membrane oscillating are referred as 'Predicted' in Figure 6.3.

Table 6.1 Number of crude oil drops (30 $^{\circ}$ API) and concentration of oil in the feed and permeate obtained at various shear rates and 400 l m⁻² hr⁻¹ flux rate.

Shear rate (s ⁻¹)	No of drops per 0.4 ml sample	Concentration of crude oil	Concentration of crude oil
		in the feed (ppm)	in the permeate (ppm)
10,000	1020	400	5
8000	1606	400	7
0	5092	400	21

Figure 6.4 (a), (b) and (c) show 100%, and below 100%, rejections of crude oil drops at various shear rates applied at different flux rates following the linear fit to rejection used previously. It was found that 400 ppm of oil in the feed solution was reduced to 5 ppm in the permeate with the highest shear rate (10,000 s⁻¹) and at flux rate of 400 l m⁻² hr⁻¹. The derived

model and the linear fit assumption can be used to asses overall oil drop rejection under different operating conditions.



Figure 6.4 (a) Rejection against drop to slot ratio of crude oil drops (30 °API) at flux rate (400 l m⁻² hr⁻¹) and various shear rates (0 s⁻¹, 8000 s⁻¹, 10,000 s⁻¹) using a 4 μ m slotted pore membrane.



Figure 6.4 (b) Rejection against drop to slot ratio of crude oil drops (30 °API) at flux rate (600 l m⁻² hr⁻¹) and various shear rates (0 s⁻¹, 8000 s⁻¹, 10,000 s⁻¹) using a 4 μ m slotted pore membrane.



Figure 6.4 (c) Rejection against drop to slot ratio of crude oil drops (30 °API) at flux rate (1000 l m⁻² hr⁻¹) and various shear rates (0 s⁻¹, 8000 s⁻¹, 10000 s⁻¹) using a 4 µm slotted pore membrane.

6.4 Conclusions

Applied shear rates create inertial lift migrations, which are directed away from the surface of the membrane. Due to inertial lift migrations drops are convected towards the membrane at lower velocity as compared to the drops without shear rate applied. Inertial lift migrations are linear functions of the applied shear rate and the size of the drops. Applied shear rates increased rejection of oil drops through the membrane. Rejection is found to be a linear function of the applied shear rate. At a shear rate of 8000 s⁻¹ and at flux rate of 400 l m⁻² hr⁻¹, 100% rejection of drops occurred at 3 μ m, reducing 400 ppm of oil in the feed to 7 ppm in the permeate. The study presented here can be applied on an industrial scale for separation of crude oil drops from Produced water with the oscillation of the membrane for a better separation, provided the feed concentration and drop size distribution are known.

Chapter 7

Prediction of size distribution of crude oil drops in the permeate

This chapter is based on

A.Ullah, R.G. Holdich, M. Naeem, V.M. Starov, Prediction of permeate size distribution of crude oil drops in the permeate, using a slotted pore membrane, Chemical Engineering Research and Design, 2014, in press.

7.1 Introduction

As explained in the previous chapters, drops pass through the membrane due to the drag force created by the flow of fluid around the drops. Static force acts in the opposite direction to the drag force and is responsible for the rejection of drops through the membrane. Without shear rate applied, 100% cut-off point of drops through the membrane would be when drag and static forces become equal. At 100% cut-off and above, all the drops would be rejected by the membrane. The 100% cut-off point is a linear function of permeate flux rate. While, 100% cut-off is an inverse function of the interfacial tension between dispersed and continuous phases. Extrapolating 100% point to the origin of the rejection graph gives a straight line, referred to as linear fit. The linear fit can be used for predicting drop rejection below 100% cut-off. The portion of oil that would not be rejected by the membrane and would pass through the membrane into the permeate can be calculated using this approach. For a given size of drops in a feed suspension, permeate size distribution can be predicted by multiplying the fraction of oil passing through the membrane and the feed size distribution data.

Crude oil (22, 27, 30 °API) drops were passed through the membrane at various flux rates and based on 100% cut-off points, permeate size distribution is investigated. Applying shear rates of various intensities created migration velocities of drops away from the membrane surface that increased rejection of drops from the membrane. Prediction of size distribution of crude oil (30 °API) drops in the permeate at different applied shear rates was also studied. In this chapter, the published data of Kuwait oil companies is used in order to demonstrate the linear fit approach for predicting permeate size distributions of various crude oil drops obtained at different locations around the world: investigating the possibilities for slotted pore microfiltration in pollution control.

7.2 Theory

Feed size distribution based on mass of crude oil drops can be obtained using equation (3.1). Without shear rate applied, 100% cut-off of drops can be calculated when equations (5.12) and (5.13) become equal. When shear rate is applied, drops above a critical radius cannot reach the surface of the membrane due to migration velocities created. With the applied shear rate, 100% cut-off would be when drops cannot reach the surface of the membrane or are rejected completely by it; and this can be obtained using equation (6.4).

Due to the drag force offered by the flow of fluid, drops may pass through the membrane. Below the slot/pore size of the membrane, a portion of drops pass through the membrane, and passage of drops decreases with increase in drop size until the 100% cut-off is obtained. While, static force acts in the opposite direction to the drag force, and that is responsible for rejection of drops through the membrane. The membrane also rejects drops below the slot/pore size of the membrane. The line obtained by extrapolating the theoretical 100% cut-off is referred to as linear fit. Linear fit can be used for predicting rejection of drops below 100% cut-off. The idea of linear fit can be used for theoretical size distributions of drops in the permeate. For a given size of drops, theoretical size distributions in the permeate can be obtained by multiplying the portion of drops passing through the membrane to the feed size distribution. 100% cut-off of drops changes with the flux rate, so, different permeate oil drop size distributions are expected at different flux rates, and consequently different overall oil drop rejection values.

7.3 Materials and Method

All the materials used during experiments were described in previous chapters. Without applying shear rate, the experimental set-up is explained in Chapter 5, while, oscillations of membrane provide a shear to the surface of the membrane and experimental procedure and set-up is provided in Chapter 4.

7.4 Results and discussion

Drops of crude oil (22, 27 and 30 °API) from crude oil provided by North Sea oil operating companies were made in produced water, with a food blender, operated for 12 mins at its highest speed, and feed size distributions can be seen in Figure 7.1. Once the drops are produced, then the feed size can be nearly maintained constant by gently stirring the emulsion. The difference in feed size distribution of different crude oil drops may be due to different viscosities, interfacial tensions and densities. It has been noticed that the higher the API value of a crude oil, the lower interfacial tension between dispersed and continuous phases (Kosvintsev et al., 2007). It means that the higher the interfacial tension between dispersed and continuous phases; the higher would be rejection of crude oil drops through the membrane; and a lower portion of drops would be passing through the membrane

into the permeate. Similarly, 100% cut-off point is an inverse function of interfacial tension between dispersed and continuous phases. Applied shear rate to the membrane surface also influences the 100% cut-off of drops through the membrane. Shear rates produce migration velocities of drops away from the surface of the membrane and due to it some drops do not reach the surface of the membrane. Migration velocities away from membrane surface are a linear function of the applied shear rate [Belfort et al., 1994]. So, applied shear rate decreases the 100% cut-off value of drops through the membrane.

Drops pass through the membrane into the permeate due to drag force offered by the flow of fluid around the drops [Kosvintsev et al., 2007]. Drag force is a linear function of permeate flux rate: higher the flux rate, higher would be the drag force around the drops [Kosvintsev et al., 2007]. This shows that at higher flux rate a larger number of drops would pass through the membrane as compared to low flux rates. Similarly, like drag force, 100% cut-off point is a linear function of flux rate. Extrapolating 100% cut-off point to the origin of the graph produced a straight line and was referred as linear fit. Linear fit can be used for predicting rejection of drops below the 100% cut-off. The idea of linear fit can be further extended for predicting size distributions of drops in the permeate. For a given size of drop, predicted permeate size distribution can be obtained by multiplying the fraction of drops passed through the membrane to the feed size distribution. Permeate size distribution mainly depends on feed size distribution, interfacial tension between dispersed and continuous phases, flux rate and size of slot/pore of the used membrane.



Figure 7.1 Drop size distribution of crude oil from North Sea operating companies (22, 27, 30 °API)) in terms of mass of oil per 2 ml of feed challenge as measured by the Coulter Multisizer.

Figures 7.2 (a)-(c) show predicted and experimental permeate size distributions of crude oils 22, 27, 30 °API respectively. Predicted lines in Figures 7.2 (a)-(c) means data obtain from the 'linear fit' approach. The crude oils were provided by North Sea oil operating companies. From the linear fit, at different points, the fraction of oil drops through the membrane is obtained. The fraction of oil drops passed through the membrane decreased moving from down to up on the linear fit line and reached zero at the 100% cut-off point. At the same flux rate, the fraction of oil drops passed through the membrane is higher for crude oil having high API values as compared to lower API crude oil due to the fact that higher API crude oil offers lower interfacial tension. Lower interfacial tension means a lower static force, which is responsible for the rejection of drops through the membrane [Kosvintsev et al., 2007]. It is also clear from Figures 7.2 (a), (b) and (c) that an increase in the flux rate increases the passage of drops through the membrane for all crude oil drops tested during experiments. It has been noticed that a large portion of oil by mass passed through the membrane below the size of slot/pore was a minimum. Due to a higher resistance offered by the static force to the drops above slot size,

a lower portion of drops above slot size passed through the membrane. Coulter analysed 2 ml sample, and the mass recovered both in the feed and in the permeate by the Coulter was actually mass of oil in 2 ml sample. Based on 2 ml sample calculations, mass of oil in the feed and in the permeate in ppm can easily be obtained.



Figure 7.2 (a) Predicted and experimental size distributions by mass of crude oil (22 °API) drops in terms of mass of oil per 2 ml of feed challenge as measured by the Coulter Multisizer, provided by North Sea operating companies without shear rate, reducing 400 ppm in the feed into 16, 19 and 21 ppm at 2000, 4000 and 6000 l m⁻² hr⁻¹ respectively. Predicted point mean data came from the 'linear fit' approach.



Figure 7.2 (b) Predicted and experimental size distributions by mass of crude oil (27 °API) drops in terms of mass of oil per 2 ml of feed challenge as measured by the Coulter Multisizer, provided by North Sea operating companies without shear rate, reducing 400 ppm in the feed into 18, 22 and 24 ppm in the permeate at 2000, 4000 and 6000 l m⁻² hr⁻¹ respectively.



Figure 7.2 (c) Predicted and experimental size distributions by mass of crude oil (30 °API) drops in terms of mass of oil per 2 ml of feed challenge as measured by the Coulter Multisizer, provided by North Sea operating companies without shear rate, reducing 400 ppm in the feed into 21, 24 and 26 ppm in the permeate at 400, 600 and 1000 l m⁻² hr⁻¹ respectively.

Oscillating the membrane with various frequencies created shear rates of different intensities over the surface of the membrane [Gomaa and Rao, 2011]. Migration velocities (Inertial lift migration velocities) away from the surface of the membrane are created due to the applied shear rate to the membrane [Belfort et al., 1994]. Migration velocities are a linear function to the applied shear rate [Belfort et al., 1994]. Its means lower mass of crude would pass through the membrane with the higher shear rate. Figure 7.3 (a) and (b) show experimental and predicted size distributions by mass of crude oil (31 °API) at different shear rates and flux rates. The theory is in satisfactory agreement with the experiments that shows that the linear fit idea can be successfully applied to predict permeate size distribution of deforming drops with, and without, shear.



Figure 7.3 (a) Predicted and experimental size distributions of crude oil (30 °API) drops in terms of mass of oil per 2 ml of feed challenge as measured by the Coulter Multisizer, provided by North Sea operating companies with 10,000 s⁻¹ shear rate, reducing 400 ppm in the feed into 4, 6 and 8 ppm in the permeate at 400, 600 and 1000 l m⁻² hr⁻¹ respectively.



Figure 7.3 (b) Predicted and experimental size distributions of crude oil (30 °API) drops in terms of mass of oil per 2 ml of feed challenge as measured by the Coulter Multisizer, provided by North Sea operating companies with 8000 s⁻¹ shear rate, and reducing 400 ppm in the feed into 7, 9, 10 ppm in the permeate at 400, 600 and 1000 l m⁻² hr⁻¹ in the permeate respectively.

Table 7.1 shows a measured size distribution of published data for crude oil (32 °API, 29 °API) samples in various continuous phases of a Kuwait oil company [Alanezi, 2009]. This data is used in order to demonstrate the linear fit approach for predicting size distribution in the permeate for various crude oil drops obtained at different locations. It can be seen in Table 7.1 that a large number of drops are above 4 μ m. Based on their API values, interfacial tensions between dispersed and continuous phases can be assumed. 100% cut-off points through a 4 μ m slotted pore membrane can be assumed on the basis of API values. On the basis of 100% cut-off and linear fit approach, permeate size distributions at different flux rates for crude oil obtained from this Kuwait oil company can be predicted. Feed size distribution of crude oil drops in different continuous phases is provided in Figure 7.4 (a) and (b). Predicted permeate size distributions based on a linear fit for crude oil (29, 32 °API) at different rates are illustrated in Figures 7.5 (a), (b) (c) and (d).

Table 7.1 Reported size distribution of crude oil (29 and 32 °API) drops per 0.1 ml sample in various continuous phases provided by a Kuwait oil company.

Drop size	No of (29 °API) per	No of drops (29 °API)	No of drops (32 °API)	No of drops (32 °API)
(µm)	0.1 ml of sample in	per 0.1 ml of sample in oil	per 0.1 ml of sample	per 0.1 ml of sample in
	Bair Aquifer water	field effluent water	in Bair Aquifer water	Produced water
1.5	7566	3519	-	-
2	3298	1400	22511	46352
3	745	576	21622	23841
5	117	175	1899	2219
8	22	50	170	320
10	5	4	79	150
12	1	16	49	71
15	0	7	18	22
20	0	0	4	4



Figure 7.4 (a) Feed size distributions of crude oil from Kuwait crude oil operating company (29 °API).



Figure 7.4 (b) Feed size distributions of crude oil from Kuwait crude oil operating company (32 °API).



Figure 7.5 (a) Prediction of permeate size distributions of crude oil drops (29 °API) in Oil Field Effluent Water, provided by Kuwait oil company at different flux rates without shear rate applied.



Figure 7.5 (b) Prediction of permeate size distributions of crude oil drops (29 °API) in Bair Aquifer Water, provided by Kuwait oil company at different flux rates without shear rate applied.



Figure 7.5 (c) Prediction of permeate size distributions of crude oil drops (32 °API) in Bair Effluent Water, provided by Kuwait oil company at different flux rates without shear rate applied.



Figure 7.5 (d) Prediction of permeate size distributions of crude oil drops (32 °API) in Produced Water, provided by Kuwait oil company at different flux rates without shear rate applied.

Size distributions of crude oil drops in the permeate can be predicted knowing size distribution of the feed; size of membrane slot/pore; interfacial tension between continuous and dispersed phase and permeate flux rate. This idea can be used for permeate size distributions of crude oil obtained from various locations and dispersed in different continuous phases. The concept of predicting permeates size distributions can also be applied to the filtration of other deforming materials like yeast and stem cells.

Table 7.2 Predicted mass of permeate (ppm) of various crude drops in different continuous phases at different flux rates and the feed size distribution data is reported by a Kuwait company.

Flux rate (l m ⁻² hr ⁻¹)	Mass in permeate of crude oil (29 °API) in Oil Field Effluent Water (ppm)	Mass in permeate of crude oil (29 °API) in Bair Aquifer Water (ppm)	Mass in permeate of crude oil (32 °API) in Bair Aquifer Water (ppm)	Mass in permeate of crude oil (32 °API) in Produced Water (ppm)
200	0.017	0.015	0.09	0.3
400	0.022	0.02	0.13	0.36
600	0.03	0.027	0.15	0.46

Table 7.2 shows the predicted mass of 29 °API and 32 °API crude oil drops in the permeate at different flux rates. Mass of 29 °API crude oil drops in Oil Field Effluent Water and in Bair Aquifer water is reported as 1.5 and 1 ppm respectively [Alanezi, 2009]. Similarly, mass of crude oil (32 °API) in Bair Aquifer Water and Produced Water is 17 and 26 ppm respectively [Alanezi, 2009]. Using the linear fit approach the mass of crude oil drops in the permeate reduced significantly at different flux rates as can be seen in Table 7.2. Theoretically, the mass of various crude oil (29 and 32 °API) in the permeate is reduced by more than 20 times that to the mass of crude oil in the feed at different flux rates. From the above study it can be concluded that if a stream coming from an oil rig containing 500 ppm of crude oil, can be reduced to 25 ppm of crude oil in the permeate using a 4 µm slotted pore membrane.

7.5 Conclusions

Mainly, drag force created by the flow of fluid around drops is responsible for the passage of oil drops through the membrane. While, static force acts in the opposite direction to the drag force and it tries to reject the drops from the membrane. A balance in static and drag force is

assumed at the 100% rejection point. Extrapolating 100% rejection or cut-off point to the origin of a graph gives a straight line which is referred to as linear fit. The linear fit approach can be used for predicting permeate size distribution of deforming drops such as oil drops. For a given size, permeate size distribution can be obtained by multiplying the fraction of material passed through the membrane to a size distribution of the feed. The approach of predicting permeate size distribution has been demonstrated with a genuine feed size distribution using published data of a Kuwait oil company. Higher mass of oil was obtained at lower interfacial tension due to the fact that higher deformation and passage of drops occurred. Similarly, increase in flux rate results in increased mass of drops in the permeate. By knowing the feed size distribution, interfacial tension, slot/pore size of the membrane and flux rates, size distribution for permeate can be predicted for crude oil obtained at various oilfields and locations and, therefore, the total concentration of dispersed oil in water.

Chapter 8

Conclusions and future work

8.1 Conclusions

In this thesis an efficient technique for separating crude oil drops from produced water has been described. A number of steps were involved and various challenges were faced for achieving the set targets: production of specific size of drops and their stability, influence of interfacial tension on deformation and passage of drops through the membrane, influence of shear rate on slot blocking and rejection of drops through the membrane.

Material is retained on the surface of the membrane in the form of drops or particles and creation of specific size of drops is important during microfiltration of oil/water separation. For this reason oil drops (1-15 μ m) were produced with a food blender operated at its highest speed for the duration of 12 mins. To avoid coalescence and breaking, drops were stabilised with 1% polyvinyl alcohol (PVA), Tween 20 and gum Arabic. Stability of drops was established on the basis of consistency in size distribution and number of drops in the samples analysed at 30 mins intervals. Drops stabilised with all surfactants (polyvinyl alcohol (PVA), Tween 20 and gum Arabic) used during the filtration experiments, as they provided different interfacial tensions to enable model testing.

Oil drops deform when passing through the slots/pore of the membrane. The influence of oil/water interfacial tension on deformation and passage of drops through the slots was studied. The higher the interfacial tension the lower is the deformation and passage through the slots of the membrane. Two forces act on the drops reaching the surface of the membrane: drag force (F_d) created by the flow of the fluid tries to push the drops through the membrane, while, static capillary force (F_x) acts in the opposite direction to the drag force. A mathematical model was developed based on drag and static forces applied to the drops pass through the slots in the case when the drag force overcomes the static force ($F_d > F_x$). The drops are rejected by the membrane when static force, it is assumed to be at the 100% cut-off of the drops through the membrane. A satisfactory agreement between the model predictions and the experimental data showed that the model can be efficiently applied for 100% cut-off prediction of deforming drops by the slotted pore membranes. By extrapolating to the origin of the graph the predicted theoretical 100% cut-off dependency of drops, a relation was

obtained which is referred to as a linear fit. This curve can be used for predicting rejection below 100%.

Membranes were vibrated with various frequencies that created shear of different intensities on the surface of the membrane used. The influence of the applied shear rate on the membrane blocking was investigated. A blocking theory was modified in this case and used to predict the trans-membrane pressure during filtration. The applied shear rate reduced the blockage of the membrane and that was the reason that lower trans-membrane pressure was obtained both experimentally and theoretically as compared to the same value obtained without applied shear rate. Reducing blockage of the membrane was found as a function of the applied shear rate: the higher applied shear rate the lower was the blockage. Trans-membrane pressure reduced 4 times at 8000 s⁻¹ as compared to the value without applied shear rate, keeping all other conditions constant.

The influence of the applied shear rate on the rejection of drops through the membrane was studied. The applied shear rate forces the drops to move away from the membrane surface. This was caused by inertial lift migration velocity. A theory is developed, which takes into account inertial lift migration velocities. The theory predicts 100% cut-off of the drops when shear rate is applied and the critical size of the drop that does not reach the membrane surface due to the applied shear rate was predicted. Inertial lift migration velocities are functions of the applied shear rate and size of the drops: the higher the shear rate applied and the bigger the size of the drops the higher will be the inertial lift velocities.

The developed theory is in reasonable agreement with experimental data at 10,000 and 8000 s⁻¹ shear rate. At 8000 s⁻¹ shear rate 400 ppm feed suspension crude oil was reduced to 7 ppm in the permeate at 400 l m⁻² hr⁻¹ that is a major reduction compared to the feed suspension.

The idea of a linear fit can be extended for the prediction of permeate size distribution of different crude oil drops at various flux rates, with, and without, shear rates applied. The theoretical fraction of drops rejected and passed through the membrane is obtained from the linear fit. For a given size of drops, theoretical size distributions of drops in the permeate is obtained by multiplying the fraction of drops passed through the membrane to the size

distribution of drops in the feed. Both the 100% cut-off and the linear fit changed with the flux rates, so, different permeate size distributions were obtained at different flux rates.

8.2 Future work

The study can be extended for separation of deforming crude oil drops from produced water with various sizes of slotted pore membranes (2, 5, 10 μ m), to investigate the response of different sizes of slots to the separation of oil drops with and without oscillation of the membrane. Filtering oil drops with various sizes of slotted pore membranes will help to understand the influence of slot size on the slot/pore blocking during the process both experimentally and theoretically with and without oscillating the membrane. Filtration of silica suspensions can provide an idea how oscillation of the membrane can influence separation of non-deforming particles.

Separation of living organisms (stem cells) is an issue that has attracted researchers recently. This process requires more attention and care during the separation due to the sensitivity of stem cells and deformation when passing through the membrane. Filtration of stem cells and yeast would provide a new insight in the applicability of slotted pore membranes for living organism separation. Oscillating of the membrane could provide information on the influence of applied shear induced separation of living organisms. The theoretical model developed above could be used for predicting 100% cut-off of living organisms by slotted pore membrane. Also, the study can be extended further to the membrane surface interactions (electro-static) with both the deforming and non-deforming materials with, and without, membrane oscillations.

The threshold flux rate region is very important on industrial scale that separates high fouling region from low one or constant fouling region. The study of threshold flux rates region of crude oil/water emulsions at different shear rates applied experimentally and theoretically would be a useful application of the developed methods, to test further the applicability of the modelling approach suggested here. Finally, the modelling approach could be used to investigate the influence of 'surface porosity' of the slotted microfilters: the current surface porosity is very low (1.4%) and higher porosity would reduce the approach velocity of drops

in the convective flow. Hence, an analysis of the benefits of membrane open area (surface porosity) can be provided in a quantitative way.

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Appendix A

 Table A.1 Mass balance of vegetable oil drops produced with various devices operated at different speeds

 and duration when different volumes of samples are analysed in the Coulter.

Oil Material	Device Type	Speed Setting	Time	Sample Value	Oil Recovered from
(-)	(-)	(-)	(mins)	(ml)	Balance (%)
Vegetable oil	Stirrer	Highest	20	1	130
Vegetable oil	Blender	Lowest	15	1	101
Vegetable oil	Blender	Lowest	20	1	107
Vegetable oil	Blender	Lowest	30	1	94
Vegetable oil	Blender	Highest	3	1	77
Vegetable oil	Blender	Highest	4	1	73
Vegetable oil	Blender	Highest	12	1	190
Vegetable oil	Blender	Highest	12	0.6	131
Vegetable oil	Blender	Highest	12	0.4	92

The oil recovered from balance is a mass balance comparison between the oil that was added to form the emulsion (1 ml) and that calculated by taking the Coulter analysis, and number of counts in each size grade, and determining the mass of oil present using the dilution used for the analysis. Obtaining calculated mass higher than 100% was due to coalescence of drops.

Table A.1 Mass balance calculations when vegetable oil/water emulsion is prepared with magnetic stirrer operated at highest speed for 20 mins

INPUT VALUES:		
density of vegetable oil	0.92	g/ml
density of saline	1	g/ml
Mass of vegetable oil used	0.67	G
Mass of Water and gum Arabic used	500	G
volume of vegetable oil	0.7283	Ml
Total mass of emulsion	500.73	G
mass of emulsion added to coulter	1	G
Mass of saline in Coulter beaker	185	G
Volume sampled by Coulter	2	Ml
CALCULATED VALUES:		
Mass of oil determine in Coulter sample	4E-06	G
Concentration of oil in Coulter sample	2E-06	g/ml
Dilution factor	974.68	
Concentration oil in mixture	0.0017	g/ml
Volume of oil added to coulter	0.0015	Ml
Mass of oil added to coulter	0.0013	G
Mass oil in mixture, by Coulter	0.0017	G
Amount of measured mass determined	130	%
Error in mass determined	-30	%
Number of particles measured	11755	



Figure A.1: Cumm mass undersized against drops size, when vegetable oil/water emulsion is prepared with megnatic stirrer operated at highest speed for 20 mins

Table A.2 Mass balance calculations when vegetable oil/water emulsion is prepared with a food blender operated at lowest speed for 15 mins

INPUT VALUES:		
density of vegetable oil	0.92	g/ml
density of saline	1	g/ml
Mass of vegetable oil used	1	G
Mass of Water and gum Arabic used	1110	G
volume of vegetable oil	1.0870	Ml
Total mass of emulsion	1111.1	G
mass of emulsion added to coulter	0.9	G
Mass of saline in Coulter beaker	186	G
Volume sampled by Coulter	2	Ml
CALCULATED VALUES:		
Mass of oil determine in Coulter sample	3E-06	G
Concentration of oil in Coulter sample	2E-06	g/ml
Dilution factor	548.06	
Concentration oil in mixture	0.0009	g/ml
Volume of oil added to coulter	0.001	Ml
Mass of oil added to coulter	0.0009	G
Mass oil in mixture, by Coulter	0.0009	G
Amount of measured mass determined	101	%
Error in mass determined	-1	%
Number of particles measured	8593	



Figure A.2 Cumm mass undersized against drops size, when vegetable oil/water emulsion is prepared with a food blender operated at lowest speed for 15 mins

Table A.3 Mass balance calculations when vegetable oil/water emulsion is prepared with a food blender operated at lowest speed for 20 mins

INPUT VALUES:		
density of vegetable oil	0.92	g/ml
density of saline	1	g/ml
Mass of vegetable oil used	1	G
Mass of Water and gum Arabic used	1110	G
volume of vegetable oil	1.0870	Ml
Total mass of emulsion	1111.1	G
mass of emulsion added to coulter	0.92	G
Mass of saline in Coulter beaker	167	G
Volume sampled by Coulter	2	Ml
CALCULATED VALUES:		
Mass of oil determine in Coulter sample	4E-06	G
Concentration of oil in Coulter sample	2E-06	g/ml
Dilution factor	429.21	
Concentration oil in mixture	0.001	g/ml
Volume of oil added to coulter	0.001	Ml
Mass of oil added to coulter	0.0009	G
Mass oil in mixture, by Coulter	0.001	G
Amount of measured mass determined	107	%
Error in mass determined	-7	%
Number of particles measured	11738	



Figure A.3 Cumm mass undersized against drops size, when vegetable oil/water emulsion is prepared with a food blender operated at lowest speed for 20 mins

Table A.4 Mass balance calculations when vegetable oil/water emulsion is prepared with a food blender operated at lowest speed for 30 mins

INPUT VALUES:		
density of vegetable oil	0.92	g/ml
density of saline	1	g/ml
Mass of vegetable oil used	1	G
Mass of Water and gum Arabic used	1110	G
volume of vegetable oil	1.0870	Ml
Total mass of emulsion	1111.1	G
mass of emulsion added to coulter	0.4	G
Mass of saline in Coulter beaker	190	G
Volume sampled by Coulter	2	Ml
CALCULATED VALUES:		
Mass of oil determine in Coulter sample	e 4E-06	G
Concentration of oil in Coulter sample	2E-06	g/ml
Dilution factor	476	
Concentration oil in mixture	0.0008	g/ml
Volume of oil added to coulter	0.001	Ml
Mass of oil added to coulter	0.0009	G
Mass oil in mixture, by Coulter	0.0008	G
Amount of measured mass determined	94	%
Error in mass determined	6	%
Number of particles measured	11253	



Figure A.4 Cumm mass undersized against drops size, when vegetable oil/water emulsion is prepared with a food blender operated at lowest speed for 30 mins

Table A.5 Mass balance calculations when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 3 mins

INPUT VALUES:		
density of vegetable oil	0.92	g/ml
density of saline	1	g/ml
Mass of vegetable oil used	0.85	G
Mass of Water and gum Arabic used	1100	G
volume of vegetable oil	0.9239	Ml
Total mass of emulsion	1100.9	G
mass of emulsion added to coulter	0.78	G
Mass of saline in Coulter beaker	167	G
Volume sampled by Coulter	2	Ml
CALCULATED VALUES:		
Mass of oil determine in Coulter sample	2E-06	G
Concentration of oil in Coulter sample	1E-06	g/ml
Dilution factor	507.06	
Concentration oil in mixture	0.0006	g/ml
Volume of oil added to coulter	0.0008	Ml
Mass of oil added to coulter	0.0008	G
Mass oil in mixture, by Coulter	0.0006	G
Amount of measured mass determined	77	%
Error in mass determined	23	%
Number of particles measured	7221	



Figure A.5 Cumm mass undersized against drops size, when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 3 mins

Table A.6 Mass balance calculations when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 4 mins

INPUT VALUES:		
density of vegetable oil	0.92	g/ml
density of saline	1	g/ml
Mass of vegetable oil used	0.98	G
Mass of Water and gum Arabic used	1100	G
volume of vegetable oil	1.0652	Ml
Total mass of emulsion	1101.1	G
mass of emulsion added to coulter	0.89	G
Mass of saline in Coulter beaker	187	G
Volume sampled by Coulter	2	Ml
CALCULATED VALUES:		
Mass of oil determine in Coulter sample	2E-06	G
Concentration of oil in Coulter sample	1E-06	g/ml
Dilution factor	551	
Concentration oil in mixture	0.0006	g/ml
Volume of oil added to coulter	0.001	Ml
Mass of oil added to coulter	0.0009	G
Mass oil in mixture, by Coulter	0.0006	G
Amount of measured mass determined	73	%
Error in mass determined	27	%
Number of particles measured	8678	



Figure A.6 Cumm mass undersized against drops size, when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 4 mins

Table A.7 Mass balance calculations when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 12 mins and 1 ml sample is analysed.

INPUT VALUES:		
density of vegetable oil	0.92	g/ml
density of saline	1	g/ml
Mass of vegetable oil used	0.8	G
Mass of Water and gum Arabic used	502	G
volume of vegetable oil	0.8696	Ml
Total mass of emulsion	502.87	G
mass of emulsion added to coulter	0.91	G
Mass of saline in Coulter beaker	192	G
Volume sampled by Coulter	2	Ml
CALCULATED VALUES:		
Mass of oil determine in Coulter sample	2E-05	G
Concentration of oil in Coulter sample	1E-05	g/ml
Dilution factor	315.75	
Concentration oil in mixture	0.003	g/ml
Volume of oil added to coulter	0.0017	Ml
Mass of oil added to coulter	0.0016	G
Mass oil in mixture, by Coulter	0.003	G
Amount of measured mass determined	190	%
Error in mass determined	-90	%
Number of particles measured	54636	



Figure A.7 Cumm mass undersized against drops size, when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 12 mins and 1 ml sample is analysed.

Table A.8 Mass balance calculations when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 12 mins and 0.6 ml sample is analysed.

INPUT VALUES:		
density of vegetable oil	0.92	g/ml
density of saline	1	g/ml
Mass of vegetable oil used	0.7	G
Mass of Water and gum Arabic used	507	G
volume of vegetable oil	0.7609	Ml
Total mass of emulsion	507.761	G
mass of emulsion added to coulter	0.53	G
Mass of saline in Coulter beaker	184	G
Volume sampled by Coulter	2	Ml
CALCULATED VALUES:		
Mass of oil determine in Coulter sample	5.5E-06	G
Concentration of oil in Coulter sample	2.7E-06	g/ml
Dilution factor	658.143	
Concentration oil in mixture	0.00181	g/ml
Volume of oil added to coulter	0.0015	Ml
Mass of oil added to coulter	0.00138	G
Mass oil in mixture, by Coulter	0.00181	G
Amount of measured mass determined	131	%
Error in mass determined	-31	%
Number of particles measured	22602	



Figure A.8 Cumm mass undersized against drops size, when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 12 mins and 0.6 ml sample is analysed.

Table A.9 Mass balance calculations when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 12 mins and 0.4 ml sample is analysed.

INPUT VALUES:		
density of vegetable oil	0.92	g/ml
density of saline	1	g/ml
Mass of vegetable oil used	0.6	G
Mass of Water and gum Arabic used	502	G
volume of vegetable oil	0.6522	Ml
Total mass of emulsion	502.652	G
mass of emulsion added to coulter	0.34	G
Mass of saline in Coulter beaker	177	G
Volume sampled by Coulter	2	Ml
CALCULATED VALUES:		
Mass of oil determine in Coulter sample	2.6E-06	G
Concentration of oil in Coulter sample	1.3E-06	g/ml
Dilution factor	843.857	
Concentration oil in mixture	0.00109	g/ml
Volume of oil added to coulter	0.0013	Ml
Mass of oil added to coulter	0.00119	G
Mass oil in mixture, by Coulter	0.00109	G
Amount of measured mass determined	82	%
Error in mass determined	18	%
Number of particles measured	13944	



Figure A.9 Cumm mass undersized against drops size, when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 12 mins and 0.4 ml sample is analysed.

Table A.10 Mass balance calculations when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 12 mins and 0.4 ml sample is analysed.

INPUT VALUES:		
density of vegetable oil	0.92	g/ml
density of saline	1	g/ml
Mass of vegetable oil used	0.7	G
Mass of Water and gum Arabic used	501	G
volume of vegetable oil	0.7609	Ml
Total mass of emulsion	501.761	G
mass of emulsion added to coulter	0.3	G
Mass of saline in Coulter beaker	184	G
Volume sampled by Coulter	2	Ml
CALCULATED VALUES:		
Mass of oil determine in Coulter sample	3.9E-06	G
Concentration of oil in Coulter sample	2E-06	g/ml
Dilution factor	682.481	
Concentration oil in mixture	0.00133	g/ml
Volume of oil added to coulter	0.00152	Ml
Mass of oil added to coulter	0.0014	G
Mass oil in mixture, by Coulter	0.00133	G
Amount of measured mass determined	85	%
Error in mass determined	15	%
Number of particles measured	14056	



Figure A.10 Cumm mass undersized against drops size, when vegetable oil/water emulsion is prepared with a food blender operated at highest speed for 12 mins and 0.4 ml sample is analysed.

Appendix B

List of journal papers published in refereed academic journals

1. A. Ullah, V.M. Starov, M. Naeem, R.G. Holdich, Microfiltration of deforming oil droplets on a slotted pore membrane and sustainable flux rates, *Journal of Membrane Science* 382 (2011) 271-277.

2. A. Ullah, R.G. Holdich, M. Naeem, V.M. Starov, Stability and deformation of oil droplets during microfiltration on a slotted pore membrane, *Journal of Membrane Science* **401-402** (2012) 118-124.

3. A. Ullah, R.G. Holdich, M. Naeem, V.M. Starov, Shear enhanced microfiltration and rejection of crude oil drops through a slotted pore membrane including migration velocities, *Journal of Membrane Science* **421-422** (2012) 69-74.

4. A. Ullah, M. Naeem, R.G. Holdich, V.M. Starov, S. Semenov, Microfiltration of deforming droplets, *Progress in Colloid and Polymer Science* **139** (2012) 107-110.

5. A. Ullah, V.M. Starov, M. Naeem, R.G. Holdich, S. Semenov, Filtration of suspensions using slit pore membranes, *Separation and Purification Technology* **103** (2013) 180-186.

6. A. Ullah, S.W. Khan, A. Shakoor, V.M. Starov, Passage and deformation of oil drops through non-converging and converging micro-sized slotted pore membranes, *Separation and Purification Technology* **119** (2013) 7-13.

7. A. Ullah, R.G. Holdich, M. Naeem, S.W. Khan, V.M. Starov, Prediction of size distribution of crude oil drops in the permeate using a slotted pore membrane, Chemical Engineering Research and Design (2014) in press

8. A. Ullah, V.M. Starov, Membrane oscillation and particle rejection, submitted to Water Research (2014)

Appendix C

List of conference presentations

1. A. Ullah, Deformation based on interfacial tension during microfiltration of oil drops on a slotted pore membrane, American Chemical Engineering Society (AlChE) annual meeting, 2013 San Francesco, CA, USA.

2. A. Ullah, R.G. Holdich, V.M. Starov, "Permeate flux rate and trans-membrane pressure during microfiltration of oil/water emulsion", Oral presentation, PSA, 2011, Edinburgh UK.

3. A. Ullah, "Shear enhanced vibratory microfiltration on a slotted pore membrane, Poster presentation", UK Particle Technology Forum, 2012, Loughborough University UK.

4. A. Ullah, R.G. Holdich, V.M. Starov, "Shear enhanced vibrating microfilration and membrane pore blocking, Poster Presentation" 12 International conference on Inorganic Membranes, 2012, Enschede, The Netherlands.