DESTABILISATION OF OIL DROPLETS IN PRODUCED WATER FROM ALKALINE-SURFACTANT-POLYMER FLOODING BY USING ASYMMETRIC PVDF MEMBRANE

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THESIS SUBMITTED IN FULFILLMENT FOR THE MASTER OF ENGINEERING

**FACULTY OF ENGINEERING
UNIVERSITI MALAYSIA SABAH**

2018

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS

JUDUL: DESTABILISATION OF OIL DROPLETS IN PRODUCED WATER FROM ALKALINE-SURFACTANT-POLYMER FLOODING BY USING ASYMMETRIC PVDF MEMBRANE

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DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, excepts, equations, summaries and references, which have been duly acknowledged.

7th February 2018

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ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious and the Most Merciful Alhamdulillah, all praises to Allah SWT for the strength and blessing in completing this study. My gratitude goes to my parents Ramlee Abd. Ghaffar and Noorainnie Abdullah, all my family, and my fiancée Marwan Afnan for giving me full support throughout my student life.

Foremost, I would like to thank my supervisor, Dr. Chiam Chel Ken for the continuous support of my research project, her patience to guide me, motivation enthusiasm and immense knowledge. My sincere appreciation also goes to Prof. Ir. Dr. Rosalam Sarbatly and Miss Zykamilia binti Kamin for their invaluable advices and guidance. Their guidance helped me in all the time of research and writing of this thesis.

I would like to convey my gratitude to Sabah Oil and Gas Terminal who gave us permission to use their crude oil in this research. Additionally, a lot of grateful to Fundamental Research Grant Scheme (FRG0418-TK-1/2015) that provided by Ministry of Higher Education Malaysia for the financial support throughout this research project.

Furthermore, I would also like to acknowledge Mr. Abdullah Tarikim, Mr. Freddy, Mrs. Noridah, Miss Aemi, and staffs for their assistance and guidance during various aspects of my research work in the laboratory.

Last but not least, special thanks to those who have one way or another helped me throughout all this time. Thank you very much.

Azierah binti Ramlee
7 February 2018

ABSTRACT

This thesis presents a study of destabilisation of oil droplets that produced from alkaline-surfactant-polymer (ASP) flooding by using four types of laboratory-fabricated polyvinylidene fluoride (PVDF) membranes. Four formulations of PVDF membranes were fabricated via immersion precipitation method with ethanol (0 – 30 %, v/v) as the coagulant to control the membrane formation. The membrane morphology and structures as well as pore sizes were characterised by using scanning electron microscopy (SEM), while the thickness was measured by a digital micrometre, and the porosity was determined by gravimetric method. The radius of oil droplets in feed and permeate solutions was measured by dynamic light scattering device. The membranes with the effective area of 17.35 cm^2 were tested with synthesized ASP solutions that contained 1500 mg/L of the oil droplets. The oil droplets for feed solution ranged from 10-200 nm to 700-4000 nm with the mean radius 61 nm. Results show that with increasing of ethanol concentration, a pore size at the top and bottom surface become larger. Macrovoid structure formed near to the top surface and the sponge-like structure exhibited at the bottom. As ethanol concentration increased, the membrane porosity increased slightly from 77-83%, while thickness has no significant effects. The distilled water permeation flux increased from 27.37 to 74.69 kg/m^2min at 2 bar transmembrane pressure when the ethanol coagulant increased. Hagen-Poiseuille law and Darcy's law models were suggested to govern the permeation fluxes. The mean values of the membrane thickness, porosity and pore size were used to predict the fluxes. The membrane resistance was approximately 10^{11} m^{-1}. The SEM was defective in the mean pore size measurement. When synthesized ASP produced water used as feed solutions, the flux and fouling resistance increased with the transmembrane pressures from 0 to 4 bars. The oil droplets radius in permeates increased to 20 – 4000 nm with mean radius 200 to 3000 nm. It proved that the destabilisation of the oil droplets took place when the ASP solution permeated through the asymmetric PVDF membranes especially for 2 and 4 bar transmembrane pressure. while no significant influence by the different formulation of asymmetric membrane structures. The membrane fouling increased as the flux decreased over time fitted the Darcy's law.

ABSTRAK

KETIDAKSTABILAN TITSAN MINYAK DALAM AIR YANG DIHASILKAN DARIPADA BANJIR ALKALI-SURFAKTAN-POLIMER DENGAN MENGGUNAKAN PVDF MEMBRAN ASIMETRIK

Tesis ini membentangkan kajian mengenai ketidakstabilan titisan minyak yang dihasilkan daripada banjir alkali-surfaktan-polimer (ASP) dengan menggunakan empat jenis membrane polivinilidena fluorida (PVDF) yang di hasilkan di makmal. Empat formulasi membran PVDF telah dibentuk melalui kaedah pemendapan rendaman dengan etanol (0 – 30 %, v/v) sebagai koaagulan untuk mengawal pembentukan membran. Morfologi, struktur dan saiz liang membran dicirikan dengan menggunakan mikroskop elektron imbasan, manakal ketebalan diukur mengggunakan mikrometer digital dan keliangan di uji menggunakan kaedah gravimetri. Julat jejari titsan minyak di ukur menggunakan alat hamburan cahaya yang dinamik. Membran dengan keluasan kawasan 17. 35 cm^2 diuji dengan sisa air banjir ASP yang mengandungi 1500 mg/L titisan minyak. Titisan minyak di larutan yang di masukkan dalam proses filtrasi mempunyai julat jejari dari 10-200 nm ke 700-4000 nm dengan jejari purata 61 nm. Hasil kajian menunjukkan apabila kepekatan etanol semakin meningkat, saiz liang yang lebih besar di permukaan atas dan bawah terbentuk. Makrovoid struktur terbentuk berhampiran permukaan atas dan struktur seperti span di bahgian bawah. Dengan peningkatan kepekatan etanol, keliangan membran menaik sedikit dari 77 ke 83%, manakalaketebalan membran tidak terpengaruh dengan ketara. Fluks penyerapan air suling meningkat dari 27.37 ke 74.69 kg/m^{2}min pada 2 bar tekanan transmembran apabila kopekatan etanol meningkat. Undang-undang daripada Hagen-Poiseuille dan Darcy digunakan untuk menentukan fluks. Nilai min ketebalan membran, keliangan dan sazi liang digunakan untuk meramal fluks. Rintangan membran adalah 10^{11} m^{-1}. Pengukuran saiz lubang membran menggunakan SEM adalah kurang tepat. Apabila sisa air dari banjir ASP yang disintesis digunakan sebagai larutan yang di masukkan dalam proses filtrasi, rintangan dan fouling rintangan meningkat dengan tekanan transmembran dar 0 ke 4 bar. Julat jejari bagi titisan minyak yang tembus melalui membran meningkat kepada 20-4000 nm dengan jejari purata 200-3000 nm. Ianya telah membuktikan bahawa ketidakstabilal titisan minyak berlaku apabila larutan ASP menyerap melalui PVDF asimetrik membrane terutamanya pada tekanan transmembrane 2 dan 4, manakala tiada kesan ketara oleh struktur membran. Faul membran meningkat apabila fluks bekurangan dari masa ke semasa selari dengan undang-undang Darcy.

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LIST OF ABBREVIATIONS

ASP	-	Alkaline-surfactant-polymer
EOR	-	Enhanced oil recovery
IPA	-	Isopropyl alcohol
MW	-	Molecular weight
PTFE	-	Polytetrafluoroethylene
PVDF	-	Polyvinylidene fluoride
PP	-	Polypropylene
PE	-	Polyethylene
SEM	-	Scanning electron microscopy
TMP	-	Transmembrane pressure (Pa)
DMAc	-	N, N-dimethylacetamide
LiCl	-	Lithium Chloride
PAM	-	Polyacrylamide
°C	-	Degree Celsius
mg/L	-	Milligram per litre
g/L	-	Gram per litre
Wt.%	-	Weight percentage
ε	-	Porosity
ρ	-	Density (g/cm^3)
J	-	Flux (Kg/m^2min)
R_m	-	Resistance of membrane (m^{-1})
D_p	-	Pore diameter (m)
τ	-	Tortuosity
η_e	-	Viscosity (Pa. s)
R_f	-	Fouling resistance (m^{-1})
Δx	-	Membrane thickness (m)

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CHAPTER 1

INTRODUCTION

1.1 Enhanced Oil Recovery

Oil recovery process is divided into three categories; primary, secondary, tertiary as shown in Figure 1.1. Natural flow and artificial lift are considered primary recovery from the well. However, it only collected about 12 to 30 % of the original oil placed in the reservoir. Then secondary recovery technique was introduced, where displacement energy naturally existing in the reservoir which implies the initial production stage (Jelmert et al., 2010). Tertiary recovery techniques were held when the production from secondary technique was declined since the recovery factor can rise up to 50% (Jelmert et al., 2010). This Tertiary technique or also known as 'Enhanced oil recovery' (EOR) used methods including gas injection, thermal recovery, and chemical injection. However, for the oil field industry gaseous and chemical injection (Ko et al., 2014) was more preferable. The common chemical injection method is polymer flooding, alkaline-polymer flooding, and alkaline-surfactant-polymer flooding.

1.2 Alkaline-Surfactant-Polymer (ASP) Flooding

Alkaline-Surfactant-polymer (ASP) EOR is a tertiary technology that injected to the injection well in the reservoir as shown in Figure 1.2. The alkaline chemicals are injected at the first place to allow the alkaline and acidic oil component to create in-situ surfactant, then the water-soluble polymer is injected resulting the improvement in mobility of oil recovered. The oil can be collected by pumping directly from the production well along with the produced water from ASP flooding as a by-product.

This ASP EOR technology application is used in China's oilfield such as Daqing oilfield, Shengli, Gudao and Karamay (Olajire, 2014). While in Canadian, ASP project was conducted at Taber South, Taber Glauconitic, and Suffield (Olajire, 2014). West kiehll, Cambridge Minnelusa, Tanner field, Sho-Vel-Tum field and

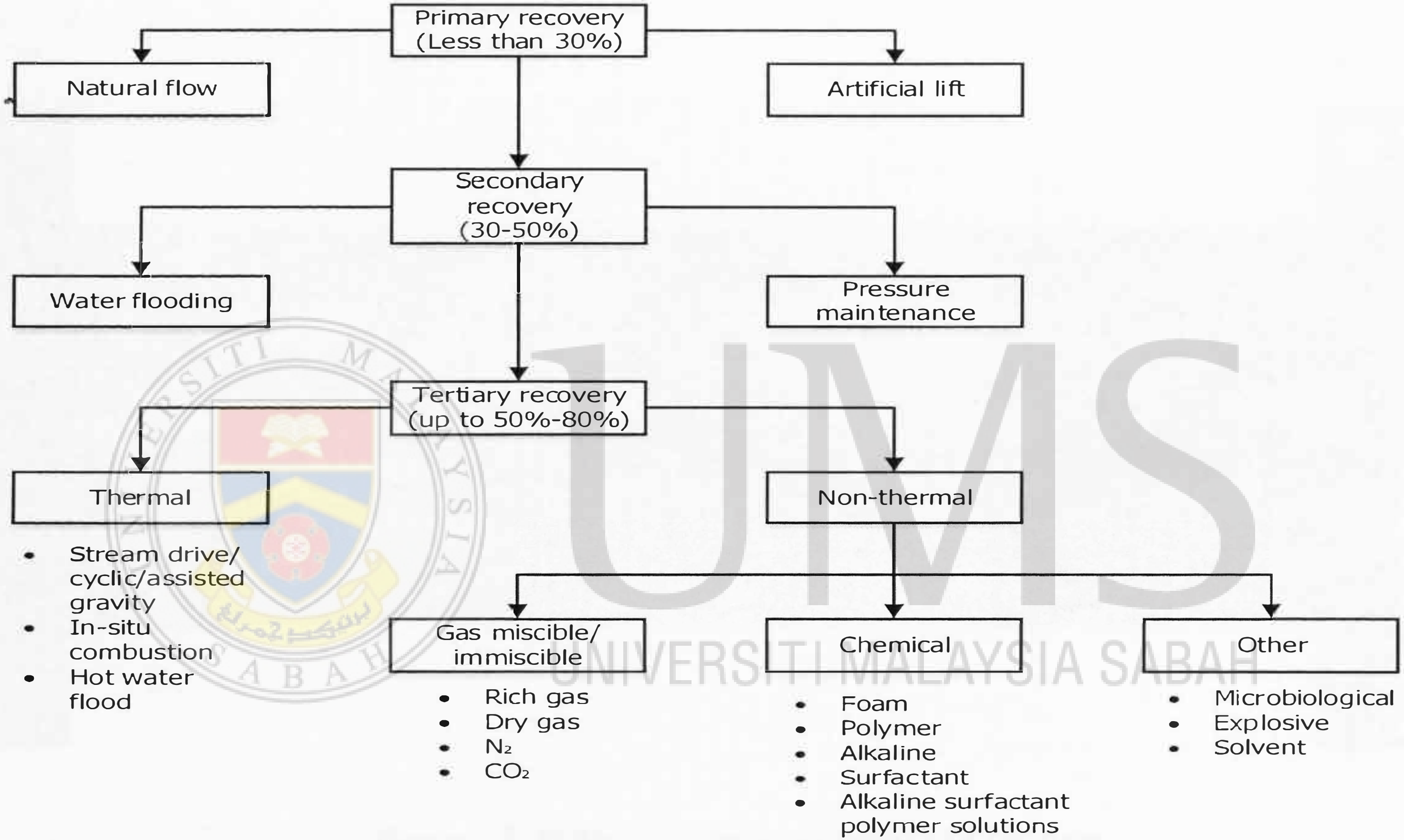

Figure 1.1: Oil recovery process

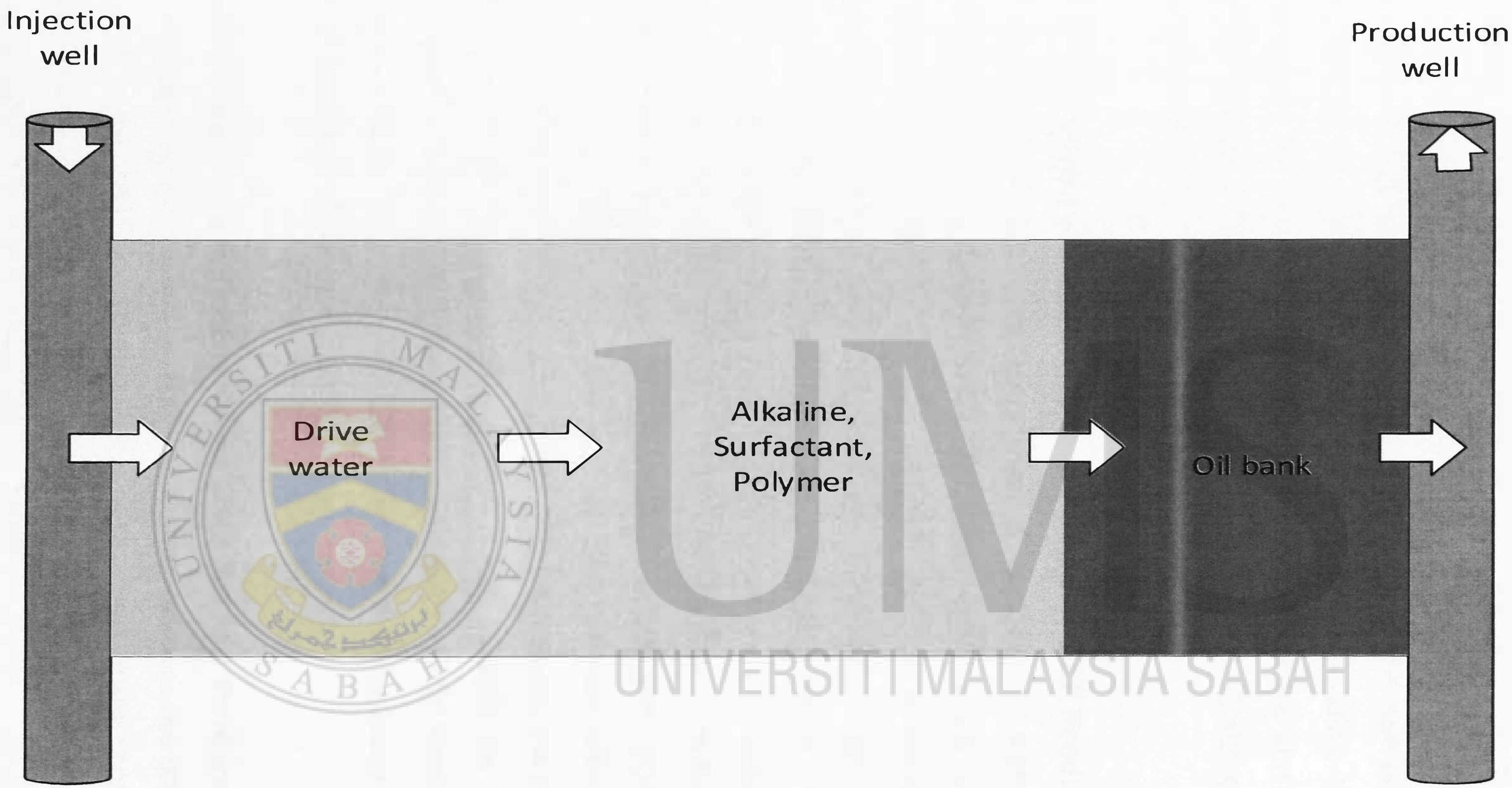

Figure 1.2: Enhance oil recovery using ASP flooding

Lawrence Field Illinois is the oilfield for ASP projects in USA (Olajire, 2014). The common alkaline used was carboxylate, sulphate, sulphonate, hydroxyl, and polyethylene oxides. While polyacrylamide, partially hydrolysed polyacrylamide, and xantham gum for the common polymer used. Unfortunately, there are few challenges associated with ASP EOR technology which is operational difficulties, scaling issues during ASP flooding, surfactant precipitation, and the ASP produced water disposal treatment. The produced water from the ASP flooding that contains alkaline, surfactant and polymer are environmentally destructive and costly since it is more difficult to treat than the water flooding (Deng et al., 2002; Guo et al., 2006; Wang et al., 2011).

1.3 Conventional Treatment Technology for ASP Produced Water

For the purpose of sustainability, reuse of the produced water for re-injection is an attractive option for offshore ASP EOR. Varies action takes to treat produced water, conventionally through physical, chemical, and membrane methods. Even though there are many methods introduced but current technologies cannot remove small-suspended oil particles and dissolved element. Physical treatment like cyclone, flotation tanks, and settling tanks are mostly designed for water and polymer flooding (Deng et al., 2002; Arthur et al., 2005). Then treatment on the produced water from ASP flooding using chemical demulsifiers was widely used especially in China (Gao et al., 2017), chemical demulsifier such as DODY68 was actively studied (Ge et al., 2010; Zhang et al., 2011; Deng et al., 2005). However, the treated produced water that contained the excess demulsifiers is not suitable for reuse and re-injection because it may create a secondary wastewater. Then Membrane treatment being considered. Hence, membrane technology has become active in oil-water separation applications (Padaki et al., 2015).

1.4 Membrane Separation Technology for ASP Produced Water

Membrane-based separation techniques have become the promising technology for the 21st century (Fakhru'l- Razi et al., 2009). Membrane separation technology can be the best option to treat the produced water from offshore ASP EOR due to its advantages (Cleveland, 1999; Baker, 2004):

- No addition of chemical demulsifiers is required, thus no secondary wastewater is produced;
- The requirement of mechanical parts for the membrane system is less, hence the flowsheet of the membrane system is simple and the footprint of the membrane system is small. These make the membrane system become more preferable for offshore application because the space and weight in the offshore production deck are limited;
- A minimal maintenance;
- Easy start-up and shut-down.

Hence, a thin film membrane which is hydrophobic and oleophilic is suggested in this thesis. The hydrophobic characteristic used to allow the membrane to repel a water while oleophilic characteristic used to extract an oil since it is highly permeable to oil droplets. At the same time, a narrow membrane pore size is needed to remove surfactant barrier skin from oil droplet and larger pore sizes are required in order to oil coalescence happened as illustrated in Figure 1.3.

Many researchers studied oily wastewater separation included castrol oil-water emulsion (Rajasekhar et al., 2015), colza oil-water emulsion (Ju et al., 2015), lubricating oil-water emulsion (Ju et al., 2015), soybean oil-water emulsion (Ju et al., 2015), surfactant-stabilized oil-water emulsion (Zuo et al., 2018), machine oil-water emulsion (Zhang and Liu, 2015), and vegetable oil-water emulsion (Pagidi et al., 2014). However, these oil-water separation studies mostly focusing to recover clean water from oily wastewater and it also used a hydrophilic membrane to reject the oil. Up till now, no investigation on ASP produced water treatment using hydrophobic and oleophilic membrane.

1.5 Problem statement

Polypropylene (PP), polytetrafluoroethylene ethylene (PTFE), polyethylene (PE) and polyvinylidene fluoride (PVDF) membranes are suitable for ASP produced water treatment since it is hydrophobic and oleophilic. However, all these types of membrane cannot perform as asymmetric membrane except for PVDF membrane. PVDF membranes with asymmetric structure can be simply fabricated by using phase inversion technique (Liu et al., 2011).

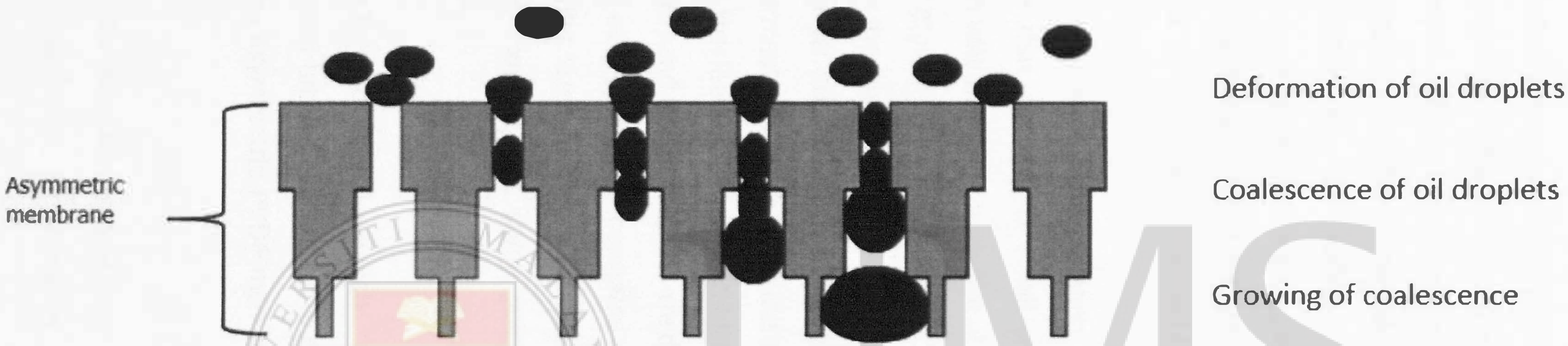

Figure 1.3: Deformation and coalescence of the oil droplets through membrane pores.

The structure consists more than two structural planes that have different morphologies which is non-identical. For top layer structure and morphologies, it is more to dense layer, where finger-like and sponge-like layer in the middle, and macrovoids layer at the bottom. Different layer in this asymmetric membrane gives different pore sizes, these structure formations depend on the coagulation rate during the immersion precipitation process. In general, when fast coagulation rate happened, macrovoids formation induced while sponge-like formation obtained from slow coagulation rate. An addition of a non-solvent in water coagulation bath can reduce the coagulation rate. Hence the concentration of the non-solvent in the water coagulation bath may control the structure and pore size of the membrane (Bottino et al., 1991; Yuliwati and Ismail, 2011).

In concern of destabilisation of the oil droplets, top layer of asymmetric membrane that consists of small pore size are hypothesize for the oil droplet breakdown whereas large pore size at the bottom layer is essential for the coalesced oil droplet growth as shown in Figure 1.3 before, since emulsion breakdown ability is stronger in the smaller pore size membrane while coalesced oil droplet growth ability better in larger pore size (Kwakatsu et al., 1999). Pressure can be used as a driving force to permeate the oil through the membrane. When the transmembrane pressure applied to the feed solution, destabilisation of the oil droplets will take place (Kong and Li, 1999) and the oil droplets are deformed and squeezed through the membrane pores. The oil droplets that permeate through the membrane may have an increasing in oil droplet size since its coalesce and destabilised when passing through the membrane. However, at some point the oil droplets may foul the asymmetric membrane.

1.6 Objectives of the Research

The main goal for this research is to destabilise the oil droplets in the ASP produced water using asymmetric PVDF membrane. The sub-objectives for this study are as follows:

a) To fabricate hydrophobic asymmetric PVDF membranes with different membrane structure by using phase inversion technique; different concentrations of ethanol (0-30% v/v) used in coagulation bath to control the membrane structure.

b) To characterize the membranes such as morphology and structure, thickness, porosity, pore size, membrane resistance and flux; membrane resistance and flux were predicted by using Hagen-Poiseuille and Darcy's law.

c) To destabilise the oil droplets in ASP produced water with fabricated asymmetric membranes by using a crossflow filtration system; the size of the oil droplets before and after destabilisation are observed.

d) To identify the effect of transmembrane pressure on destabilisation of oil droplets by applying three different transmembrane pressure (0,2,4 bar) in filtration process; Membrane fouling resistance are determined by using Darcy's law.

1.7 Outline of Thesis

This thesis consists of five main chapters including introduction in Chapter 1, enhanced oil recovery, alkali surfactant polymer flooding, ASP produced water treatment. While characteristic of ASP produced water, oily wastewater treatment by membrane separation, hydrophobics membrane, membrane structure, and immersion precipitation in Chapter 2. Chapter 3 discussed the methodology, apparatus and equipment for experimental work, and analysis while Chapter 4 discussed the experimental results. Lastly, in Chapter 5 the summarized of the conclusion. This thesis also completed with references and appendices.

CHAPTER 2

LITERATURE REVIEW

2.1 Characteristic of ASP Produced Water

The produced water from the ASP EOR process contains large numbers of residual chemicals, it is because of the use of alkali, surfactant and polymer in the injected aqueous solution in ASP flooding technology. The properties of the produced water from ASP flooding is shown in Table 2.1.

2.2 Oily Wastewater Treatment by Membrane Separation

Membrane separation is a process without heating, it used less energy than conventional thermal separation processes such as distillation, sublimation or crystallization. The separation process is purely physical as shown in Figure 2.1. Permeate is the feed that does pass through the membrane while retentate is a feed that does not pass through. Pressurize membrane processes such as nano/ultra/microfiltration are the pressure exerted on the solution at one side of membrane that used as a driving force to separate the feed into permeate and retentate.

2.2.1 Oil as Retentate/Rejection

Separation of water from oil-water emulsion usually happen when water attached to the membrane and passing through the membrane pores, this separation usually used a hydrophilic membrane where the oil as retentate and water as permeate. Table 2.2 shows a few researchers that used oil as retentate.

2.2.2 Oil as Permeate

Theoretically, the separation of oil involves a series of steps, firstly attachment of oil droplets to the membrane surfaces on the upstream side then, coalescence and penetration of oil into and through the membrane and the last one is the release of