

COMPARISON OF SEPARATION EFFICIENCY OF OIL IN THE PRESENCE OF ALKALI SURFACTANT POLYMER (ASP) PRODUCED FLUID USING PACKED BED AND FLOATATION MODELS

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS TRONOH, PERAK Sept 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

Separation of oil that is recovered from the reservoir is very important for the downstream processes. The alkali surfactant polymer (ASP) flooding used in enhanced oil recovery produces a fluid that contains large residual chemicals which inhibits an efficient separation of oil and water. This causes corrosion of pipes and other problems in downstream process which needs attention. Thus optimum parameters have to be identified to predict the separation efficiency in order to determine both operational safety and economic performance. In this project, several important factors that influence the separation such as operating temperature, retention time, and surfactant and polymer concentration are investigated using packed bed and floatation models found in literature to identify the best model that can predict the effect on separation when a standard set of parameters used. Based on the results obtained, the floatation model is selected as best model (76% of efficiency) and analyzed further to optimize the parameters using function value based method to enhance the separation. The key parameter values were varied and optimum values obtained was used to predict the separation efficiency. It was found that after optimizing, the performance of model is increased by 32% where 99.90% of separation efficiency is obtained. A trade-off between the parameters is discussed for each parameters in this project that enhances the separation efficiency.

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Nomenclature

С	Concentration of oil
K	Oil droplet removal rate constant
N	Kinetic order
C _e	Final Concentration of oil (mg/l)
<i>C</i> ₀	Initial Concentration of oil (mg/l)
t	Time (min)
Т	Temperature (°C)
C_P	Polymer concentration (mg/l)
C_S	Surfactant concentration (mg/l)
Q	Volumetric flow rate of gas (m ³ /h)
k _{rec}	Rectifying factor
v_t	Terminal velocity (m/s)
и	Velocity water flow (m/s)
h	Height of corrugated plate (m)
L	Length of packing (m)
$ ho_e$	Density of emulsion (kg/m ³)
$ ho_o$	Density of oil (kg/m ³)
g	Gravitational acceleration (kg/m ² .s)
D	Oil droplet size diameter (m)
μ_e	Viscosity of emulsion (Pa.s)
А	Constant = 13.37
b	Constant = 1.87
Re	Reynold number = $\frac{du\rho}{\mu}$
v'	Terminal velocity of emulsion (m/s)
α	Volume fraction of oil
μ_o	Viscosity of oil (Pa.s)
φ	Water cut (fixed at 0.6)
а	Factor for type of emulsion (5.5 for tight emulsion)
d	Diameter of vessel (m)

CHAPTER 1

INTRODUCTION

1.1 Background

This project is related to the primary separation of alkali surfactant polymer (ASP) produced fluid from the crude oil recovered from the enhanced oil recovery. Advanced crude oil extraction methods have been developed over the past years in order to meet the increasing oil demand from different industries. Alkali surfactant polymer (ASP) flooding technology is found to be one of the efficient ways that enhances the oil recovery by increasing the sweeping efficiency and displacing efficiency. However, the separation of oil from produced fluids (water, sedimentation and salts) has always been a challenging task in the industry. Several conventional oilwater separation methods are being used currently has proven not to be very effective. Many researches have recently studied some of these methods and the factors that influence the oil-water separation to develop methods that are more effective. The ultimate aim of this research is to explore certain key factors that influence the separation of oil from ASP produced fluid after the recovery process and model a separator to find the optimum conditions that enhances the primary separation efficiency. The main aspects that will be studied in this research are operating temperature, retention time, and surfactant and polymer concentration.



Figure 1: Typical Industrial Multiphase Separator (Source: (Craddock, 2014))

1.2 Problem Statement

In the recent years, the demand for crude oil has increased tremendously. In order to increase the yield by at least 40% of the assumed recoverable oil reserves in a reservoir, enhanced oil recovery process is being used for decades now. Several strategies have been introduced along the years and it is found that the use of alkali surfactant polymer (ASP) flooding promises better yield compared to other chemical methods.

However, the produced fluid from the process contains a huge amount of residual chemicals, which forms a complex and stable emulsion, thus making the separation harder. As a result, this water-in-oil type of emulsion causes problems such as deposition behavior that decreases the transport capacity of the pipelines, corrosion of pipes, pumps, and processing equipment (Behin & Aghajari, 2008), foam production in produced fluid, scaling and damage of heating furnace, along with the deactivation of catalysts in downstream processing (Zhihua, et al., 2013). Therefore, higher separation efficiency is essential in avoiding the problems caused by stable emulsion in the downstream process.

Based on the findings from literature review, two models have been identified to meet the requirement of this type of emulsion formed. These models have to be studied to determine the best option for better separation efficiency.

1.3 Objectives

The objectives of this project are:

- 1. To identify the main factors that influence the separation efficiency of the oil in the presence of ASP produced fluid.
- 2. To compare packed bed and floatation model from previous research with standard parameters to predict the effect on separation when a standard set of parameters used.
- 3. To propose of a set of parameters that would optimize and enhance the separation efficiency of chosen model.

1.4 Scope of Study

This project will utilize the previous research paper findings to identify the most important factors that are influencing the separation of the oil in the presence of ASP produced fluid and their governing equations that are readily available. The equations that are obtained will be utilized to compare the models selected analyze the effect of the factors identified with standard parameters. Due to the time frame of the project, only few key factors such as operating temperature, retention time, and surfactant and polymer concentration are studied in this project for both models. This is to ensure the prevention of overgeneralization of the project. The modeling will be repeated with different combination set of parameters for the chosen model in order for an enhanced separation to be achieved.

CHAPTER 2

LITERATURE REVIEW

2.1 Enhanced Oil Recovery

Oil recovery process is divided into three major categories: primary, secondary and tertiary (enhanced) oil recovery. Donaldson, Chilingarian and Yen (1989) claims that the primary oil recovery process is mainly influenced by the presence of natural pressure in the petroleum reservoir. This primary process is further enhanced with the combination of artificial pumps and jacks (Enhanced Oil Recovery, n.d.). However, Craddock (2014) emphasizes that this method of recovery will only yield up to 20% of the reservoirs total volume maximum because as the oil is produced, the gas held in the reservoir is also released which causes the reservoir pressure to reduce and energy is lost.

In order to extend the production of oil to 20-40%, the secondary recovery process is used by injecting water or gas to displace the oil and transport it a production wellbore (Enhanced Oil Recovery, n.d.). This process is referred as water flooding and gas drive method. The main purpose of injecting water and gas is to increase the pressure required artificially to force the oil out of the reservoir (Donaldson, Chilingarian, & Yen, 1989).

Whereas, the tertiary (enhanced) oil recovery process that is now being used for many decades, promises much higher yield (30-60%) from the reservoir. The three common used techniques in EOR that have been found to be commercially successful are thermal recovery, gas injection and chemical injection. Thermal recovery introduces heat to either lower the viscosity or improve the flow ability through the reservoir. Over 40 percent of U.S. EOR production, primarily in California uses this technique. Gas injection on the other hand, involves the injection gases that expand in a reservoir to push the oil to wellbore (Enhanced Oil Recovery, n.d.). According to Craddock (2014), chemical injection usually uses three main treatments known as polymer flooding, surfactant polymer flooding and alkali surfactant polymer (ASP) flooding.

2.2 Alkali Surfactant Polymer (ASP) Flooding

As mentioned by Craddock, Alkali Surfactant Polymer (ASP) flooding technology is one of the most effective chemical injection methods in EOR process. This technology combines the key mechanisms of alkali, surfactant and polymer to force the oil out from the reservoir. This method is conventionally applied to sandstone reservoir (Craddock, 2014) and found to be used in large scale in China, especially Daqing Oilfield (Zhihua et al., 2013)

Moderate pH alkali such as sodium carbonate (Na₂CO₃) and sodium bicarbonate (NaHCO₃) are used in these ASP formulations to alter the rock wettability, alter the rock chemistry by reducing the adsorption, regulate the phase behavior, and increase ionic strength (Craddock, 2014). This statement is supported by Zhihua et al. (2013) where it is mentioned that strong base usage such as sodium hydroxide (NaOH) causes stratum corrosion and scale formation in surface system which is why the moderate pH alkali are preferred.

As for the surfactant, the most common type of surfactants that are used are petroleum sulphonates and synthetic alkyl sulphonates. These surfactants require alcohols as their co-surfactant or co-solvent (Craddock, 2014). According to Lu-hong, Hong, Hai-tai, Li-juan and Dan (2007), surfactants such as alkylbenzene sulphonate promotes the mobilization of trapped oil droplet by reducing the oil-water interfacial tension. However, Zhihua et al. (2013) claim that the use of alkylbenzene sulphonate causes high cost of EOR process, thus promoting a cheaper locally produced surfactant from the reaction of alkali with oil.

Craddock (2014) states that the addition of polymer to the injected formulation has huge impact in the EOR process where the introduction of polymer, usually, polyacrylamides, increases the viscosity of the oil solution and decreases the effective permeability when adsorbed into the formation. Thus, the sweep efficiency increases as the water mobility is reduced. This statement is similar with the claim of Lu-hong et al. (2007), where it is mentioned that the greater volumetric swept efficiency is achieved by adding a polymer into the injected formulation. In conclusion, alkali plus surfactant plus polymer flooding greatly enhances the oil recovery by increasing the displacing efficiency and sweeping efficiency.

2.3 Separation of Oil in the Presence of ASP Produced Fluid

ASP produced fluid is referred to the emulsion that is produced from the combination of alkali, surfactant and polymer that is used in the EOR to force 30% to 60% yield of the total volume of the reservoir. This fluid is carried along with the oil and gas that is recovered to the surface.

2.3.1 Importance of the Separation

Oil recovered from a reservoir consists of the mixture of oil, water, sediments and salts which is generally referred as produced fluid. The separation of oil in the presence of ASP produced fluid is very essential to prevent the downstream problems such as corrosion of pipes, pumps, and processing equipment, along with the deactivation of catalysts in downstream processing (Behin & Aghajari, 2008).

Other than that, the produced fluid has a serious deposition behavior in long term scale where the transport capacity is greatly reduced and the pressure of the well head is raised which in time affects the oil production. Besides that, due to the complex properties of the ASP produced fluid, the heating furnaces are scaled and damaged over a period. This scaling is mainly composed of silica scale (50-60 wt %) and other compositions (Zhihua et al., 2013).

Apart from that, Zhihua et al., (2013) also claims that pump efficiency of transfer station is lowered which in result increases the energy consumption of the surface processes due to foams that are formed gradually from the presence of surfactant in the fluid. As the foam is formed, the oil-water interfacial properties are changed. Therefore, in order to avoid the mentioned problems, the phases are usually separated before being transported for oil refinery.

2.3.2 Factors Affecting the Separation

Upon study over the years, the key factors that influence the separation of oil in the presence of ASP produced fluids have been identified. They are as below:

- a) Operating temperature
- b) Retention time
- c) Surfactant concentration
- d) Polymer concentration

Operating temperature as mentioned by Wei-Kang, Zhong-Chen, Yu-Yu and Yu-You (2013), is very important in the floatation techniques where kinetic models are used to calculate the removal rate of oil are temperature dependent. Other than that, temperature is also used to break the emulsion in oil phase (Hirasaki, et al., 2010).

Simmons, Komonibo, Azzopardi and Dick (2004) claims that the study of retention time of both aqueous and organic phases in the oil-water separation are vital for diagnostics of flow behavior. Flow behavior is one of the important criteria that determines the separation of oil.

Lastly, the polymer and surfactant concentration also greatly influences the emulsion stability of the produced fluid, which leads to separation difficulties (Biao, et al., The Effects of Oil Displacement Agents on The Stability of Water Produced from ASP (Alkaline/Surfactant/Polymer) Flooding, 2011). Biao et al., (2011) mention that polymer used in the ASP flooding enhances the emulsion stability by increasing the viscosity of water. It is stated that above 300mg/L of concentration, the polyacrylamide polymer increase the viscosity thus reducing the rising velocity of an oil droplet.

As for the surfactant, Ruiquan et al., (2006) claims that the interfacial tension and size of oil droplets are highly affected by the use of surfactant. Increase in the use of surfactant decreases the interfacial tension between water and oil by decreasing the size of the oil droplet. Thus separation becomes harder.

2.3.3 Separation and Treatment Technologies

Conventionally, separation of crude oil involves mainly the gravity separator and centrifugal separator (Yong-tu, Sheng-qiu, Xia-xue, Xian-qi, & Wang, 2013). According to Wikipedia, gravity separation uses gravity as the dominant force to separate mixtures with different specific weight. Flocculation, coagulation and suction are the other methods applied together with gravity separators to make the separation faster and efficient (Gravity Separation, n.d).

On the other hand, centrifugal separation involves the use of centrifugal force to separate the heterogeneous mixtures. The rate of centrifugation is specified by the angular velocity measured in revolutions per minute (RPM), or acceleration expressed as g (Centrifugation, n.d). Apart from these two traditional separators, there are other technologies that are being used currently such as corrugated plate separator, hydro cyclone, gas floatation, extraction, ozone, adsorption, lime softening, ion exchange, rapid spray evaporation, freeze-thaw evaporation, microfiltration, ultrafiltration, reverse osmosis, and activated sludge (Ahmadun, et al., 2009). The comparison between these technologies can be found in the Appendix section.

However, in the presence of the alkali, surfactant and polymer, the separation becomes harder as the produced fluid is more stable. Thus, regular methods have less separation efficiency. Therefore, numerous studies have been carried addressing the problems present in the separation of oil in the presence of alkali surfactant polymer and enhancing the process. Wei Kang et.al, (2013) studied on the removal of emulsion oil from oilfield ASP wastewater by internal circulation flotation and kinetic models. In their study, volumetric flow rate of gas, temperature and concentration of alkali, surfactant and polymer have been studied experimentally to determine the removal rate of oil from ASP wastewater.

Behin and Aghajari, (2008) has investigated on the influence of water level on oil-water separation by residence time distribution (RTD) curves investigation. They used the radioactive tracer injection to identify the RTD as the water level is manipulated. Separator performance increased when the RTD increased due to the water level increase. In another study, Simmons et al., (2004) used RTD to determine the flow behavior. The flow behavior then used to enhance the separation efficiency.

Lu-hong et al., (2007) have also studied on the optimal design of novel oilwater separator by investigating on the structure and material of coalescent packing as well as the operating conditions. They discovered a separation efficiency of 98 % by studying on the packing length, packing type, inlet part and steady flow plate. On the other hand, Hirasaki et al., (2010) explored on the separation of produced emulsion from surfactant enhanced oil recovery process. They found temperature and different type of surfactant greatly influences the separation efficiency.

Apart from the mentioned studies, there are still more studies that are being done even today to enhance the separation. This project will utilize all the findings from the literatures to further enhance the separation efficiency. Therefore, important factors that are identified will be analyzed to suggest an optimized condition for separation.

2.4 Corrugated Plate Separation

Corrugated Plate Separator (CPS) is the most effective separation and treatment technologies used so far in separating the oil from the ASP produced fluid. It provides an economical and effective oil and solid removal using gravitational force. Thus, with no moving parts, this type of separators provides an efficient automatic flow and consistent operating results (Siemens Water Technologies Corp., 2009).

According to Siemens Water Technologies Corp (2009), this type of separators are typically one-fifth the size of in-ground API separators that are used conventionally. However these have greater features and benefits such as better effluent quality, superior solids handling, low maintenance design and has quality construction compared to API separators.

2.4.1 Corrugated Plate Interceptor

Situated at the heart of the CPS, these Corrugated Plate Interceptors (CPIs) minimizes the distance of rising of the oil droplet before it comes into contact with other oil droplets (Siemens Water Technologies Corp., 2009). Basically, this is an advanced version of Parallel Plate Interceptor (PPI) where the plates are placed in basin at certain angle (normally 45") of inclination which allows the oil to rise along the lower parts of the plates and coagulate to become larger droplets via peak of the corrugation (Fischer, 2012).

2.4.2 Operating Process

As the oil/water emulsion enters the CPS to the influent receiving compartment, the velocity is slowed and the flow is directed in to the zone above CPI packs. The larger oil droplets rise to the top while the smaller oil droplets with chemical residuals enters the CPI in laminar flow. The CPIs then allow the oil droplets to coalesce and separate from the carrier fluid. The separated droplets then rise to the peaks of corrugations and a gutter protects them from the flow that is entering CPI.

At top of the CPS, an adjustable weir or trough skims the separated oil layer. The clean effluent that is coming out of CPI flows upwards and exits the separator through effluent outlet. As for the separated solids, they flow down the valleys of corrugation to the bottom of the CPS. Another gutter protects them from the flow leaving the plate pack. The down-flow pack usage would ensure the entire water phase passes through the plate pack as the pack would be positioned at 45" inclination, which minimizes the risk of plugging the media (Siemens Water Technologies Corp., 2009).



Figure 2: Corrugated Plate Separator (Source: (Siemens Water Technologies Corp., 2009))

2.5 Separator Models

There are various models proposed by many papers that can be used for separation of oil-water solution that utilizes the corrugated plate separation methods. After a comprehensive review, two models were found to have significant results in predicting the separation efficiency of oil in the presence of ASP fluid which uses the corrugation separation technique that found to be very effective in removing oil from the emulsion. The first model, which is the internal circulation floatation and kinetic model, was proposed by Wei-Kang et. al. (2013) in their research paper. The second model is the model of the corrugated plates packing oil-water separator (Lian & Yuan, 1994).

2.5.1 Internal Circulation Flotation and Kinetic Model Separator

Wei-Kang et. al. (2013) has utilized the floatation technology in predicting the separation efficiency. They experimentally tested a pilot plant with two-stage flotation reactor including the flotation and separator stages as shown in Figure 3. The air is introduced to the system at the bottom of the floatation stage and the stabilized oil-water emulsion is pumped into the bottom of the separator stage. The oil overflows from the top of the separator stage and the water is discharged from the floatation discharge pipe.



Figure 3: Schematic diagram of internal circulation floatation and kinetic model separator (Source: (Wei-Kang, Zhong-Chen, Yu-Yu, & Yu-You, 2013))

Since the microscopic modeling for the plant setup was too complex and not practical, a simple generalized rate expression has been derived to denote the floatation process,

$$-\frac{dC}{dt} = kC^n \tag{1}$$

In order to simplify the equation, first order of kinetic integration model where $C = C_0$ at $t = t_0$ was assumed. Therefore the Equation 1 is integrated to give Equation 2:

$$C_e = C_0 e^{-kt} \tag{2}$$

The k value from Equation 2 is calculated by using Equation 3 as follows:

$$k = -0.747 + 1.31e^{0.000221C_0 - 20.4/T} - 0.00186C_P - 0.0117C_S + 0.164Q - 0.00373Q^2$$
(3)

2.5.2 Corrugated Plates Packing Oil-Water Separator

Lian and Yuan (1994) proposed a high efficiency corrugated plates packing oil water separator. They modified the API separator design into a very packed bed model where except for the intake and outlet of oil and water chambers, the main body of the separator is packed with corrugated plates used as separation medium. This is shown in Figure 4 below.



Figure 4: Corrugated Plates Packing Oil-Water Separator (Source: (Lian & Yuan, 1994))

As can be seen from Figure 4, the following are the specification of the separator:

1 - intake pipe; 2 - intake chamber; 3 - oil collecting chamber; 4 - vertical plates section;
5 - horizontal plates section; 6 - corrugated plates; 7 - case body; 8 - grid; 9 oil outlet pipe;
10 - water outlet chamber; 11 - water outlet pipe .

The authors represented the liquid flow in the packing in a simple manner equivalently so that the shape of the flow is rectangle, the height is equal to corrugation height, h and the length equals to total length, L of corrugated plates. The velocity distribution of liquid is considered as even. This is shown in Figure 4.



Figure 5: The equivalent liquid flow (Source: (Lian & Yuan, 1994))

Following the Figure 4, Lian and Yuan (1994), described the changes in the concentration of oil droplets in water as

$$-dC = k_{rec} C \frac{v_t}{uh} dz \tag{4}$$

By conducting an integration with the respect to the length, L, Equation 5 is obtained.

$$\frac{c_e}{c_0} = exp\left[-k_{rec}\frac{v_t}{uh}L\right] \tag{5}$$

Using Stokes equation:

$$v_t = \frac{(\rho_w - \rho_0)gD^2}{18\mu}$$
(6)

The terminal velocity can be expanded and thus the oil separation efficiency can be expressed as follows:

$$\eta = 1 - \exp\left[-\frac{k_{rec}(\rho - \rho_0)gD^2L}{18\mu_e uh}\right]$$
(7)

The rectifying factor, k is expressed as in Equation 8,

$$k_{rec} = ARe^b \tag{8}$$

This model that was proposed by Lian and Yuan (1994), only took into account for separation of dispersed oil in emulsion where the emulsion is not very stable and easily can be coagulated to separate the oil from water. For the oil separation from a stable emulsion, Lakehal et. al. (2010) has proposed Equation 9 to compute for the terminal velocity.

$$v' = \frac{v_t (1-\alpha)}{\left(1 + \alpha^{1/3}\right) \exp\left[\frac{5\alpha}{3(1-\alpha)}\right]}$$
(9)

The viscosity of an emulsion can be estimated by using Equation 10 (SPE International, 2014).

$$\mu_e = \mu_o e^{5\varphi} (1 - 3\varphi + a\varphi^2) \tag{10}$$

Both models that has been found is assumed to be ideal for the separation of oil in the presence of ASP produced fluid. Thus, both of this models will be compared with a typical set of data obtained from literature to determine the best among the two and the best model will be further optimized for better result. The data is assumed to be the same in the St. Joseph oilfield in Malaysia. The typical data obtained from Daqing oilfield is tabulated as below:

Oil Concentration (mg/l)	<2000
HPAM Concentration (mg/l)	48-630
Surfactant Concentration (mg/l)	48-630
NaOH Concentration (mg/l)	<1500
Temperature (°C)	<45
Viscosity of Oil (cP)	3.0 - 5.0
Density of Oil (kg/m ³)	700 - 900
Viscosity of Water (cP)	1.0
Density of Water (kg/m ³)	1000
Diameter of Droplet (µm)	1 - 50
Retention Time (min)	2 - 10
Emulsion Velocity (m/s)	<0.01
Water cut	0.6
Volume fraction of oil	0.4

Table 1: Typical Data obtained from ASP flooding in the Daqing oilfield.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

As mentioned in Chapter 2, the internal circulation floatation and kinetics model (floatation model) will be compared with the modified corrugated plates packing oil-water separator model (packed bed model) to determine the best among the two and the best model will be further enhanced and optimized. Explained below are the research methodology and project activities of this project.

- Based on the literature, few key parameters such as operating temperature, retention time, surfactant and polymer concentration are identified
- Two different model equations as well as some typical data used in plant is identified from the previous literature too.
- Using the model equations and data obtained, both models are compared to determine the best model with higher separation efficiency.
- The best model is further studied by manipulating the key parameters identified from the literature to enhance the separation efficiency. Trade-off points are identified in the process of optimizing the parameters.
- The results obtained will be studied and analyzed using graphs obtained from excel and reported in final thesis. Key parameter settings that will provide higher separation efficiency will then be suggested to be used in real plant environment.

After identifying the best model, key parameters that are present in the model equation will be manipulated one by one to enhance the performance of the separator to the highest value possible. However, several factors such as demulsifier agents, the chemicals for alkali, surfactants and polymers are kept constant in the model in order to narrow down the scope of study. The demulsifier agent to be used for this study is water soluble and mainly composed of ethylene oxide, ethylene oxide copolymer, polypropylene acid ramification, ethanol and water with a dosage of 50mg/kg. Petroleum sulphonate (WPS) and polyacrylamide (HPAM) are used as surfactant and polymer respectively. Initial concentration of oil is also kept constant throughout the study. Steady state of flow is assumed for both model.



Figure 6: Workflow of Project

3.2 Key Milestone



3.3 Gantt Chart

Week Time Task name 1 5 1 9 2 2 0 1 $\begin{array}{ccc} 2 & 2 \\ 2 & 3 \end{array}$ 2 4 2 5 2 6 2 7 2 8 1 7 1 3 1 1 1 2 5 1 3 4 9 6 7 8 6 8 4 0 2 Research proposal Topic research Literature review Proposal preparation & submission Proposal Defense Model Equations Obtain and finalize model equations Obtain and finalize oilfield data Compare and determine the best model Submission of Interim Draft Report Submission of Interim Report Separation Efficiency Analysis Optimization of parameters of selected model Evaluate efficiency using optimized parameters **Results Discussion** Research documentation Submission of Progress report Submission of Draft Final Report Dissertation writing Submission of Technical Paper Submission of dissertation Viva Voce Pre- SEDEX presentation **Final Presentation**

Table 2: Gantt Chart of Project

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Model Comparison

Since there are two models that is being compared, the equation for each model are as below:

4.1.1 Internal Circulation Flotation and Kinetic Model Equation

$$C_e = C_0 e^{-\left[\begin{pmatrix} -0.747 + 1.31e^{0.000221C_0 - 20.4/T} \\ 0.00186C_P - 0.0117C_S + 0.164Q - 0.00373Q^2 \end{pmatrix} \times (t)\right]}$$
(11)

The separation efficiency for this model equation is calculated by Equation 12:

$$\frac{c_0 - c_e}{c_0} \times 100\%$$
 (12)

Using Equation 11 and the average values of oilfield data, the concentration of oil after the separation is calculated. The calculations are as follows:

 C_e

 $= 2000e^{-[(-0.747+1.31e^{0.000221(2000)-20.4/(35)}-0.00186(300)-0.0117(100)+0.164(15)-0.00373(15)^2)\times(5)]}$ = 484. 31mg/l

The separation efficiency for this model is:

$$\frac{2000 - 484.31}{2000} \times 100\% = \mathbf{75.78\%}$$

The calculations shows that the final oil concentration is 484.31 mg/l, which gives about 76% of efficiency. All the parameters such as polymer concentration, surfactant concentration, temperature, and flow rate and retention time obtained from the oilfield data are inserted into the equation in order to obtain the final concentration oil. The reaction rate, k, used in the equation is an empirical formula derived from experimental results by Wei-Kang et.al. (2013) where all the parameters have been standardized to be expressed in single unit (1/t) that facilitates the analysis.

4.1.2 Modified Corrugated Plates Packing Oil-Water Separator Model Equation

Combining all the Equations 5 - 10, the following model equation is developed to predict the separation efficiency of the oil in the presence of ASP fluid.

$$\frac{c_e}{c_0} = exp\left[\frac{-A\left(\frac{d \times u \times \rho_e}{\mu_0 e^{5\varphi}(1-3\varphi+a\varphi^2)}\right)^b \times \left(\frac{(\rho_e - \rho_0)gD^2}{18\left(\mu_0 e^{5\varphi}(1-3\varphi+a\varphi^2)\right)} \times \frac{(1-\alpha)}{\left(1+\alpha^{1/3}\right)\exp\left[\frac{5\alpha}{3(1-\alpha)}\right]}\right)}{uh}L\right]$$
(13)

The separation efficiency is calculated using Equation 11 as well for this model.

Using Equation 13 and the average values of oilfield data, the concentration of oil after the separation is calculated. The vessel size is estimated to be 10 m in height, 50 m in length and 3 m in diameter. The calculations are as follows:

$$\frac{c_e}{2000} = exp \left[-13.37 \left(\frac{3 \times 0.01 \times 1010}{0.003 e^{5(0.6)} (1 - 3(0.6) + 5.5(0.6)^2)} \right)^{1.87} \times \frac{\left(\frac{(1010 - 900)9.81 (0.00001)^2}{18 \left(0.003 e^{5(0.6)} (1 - 3(0.6) + 5.5(0.6)^2) \right)} \times \frac{(1 - 0.4)}{(1 + 0.4^{1/3}) \exp\left[\frac{50.4}{3(1 - 0.4)} \right]} \right)}{0.01 (10)} \times 50 \right] = 949.34 mg/l$$

The separation efficiency for this model is:

$$\frac{2000 - 949.34}{2000} \times 100\% = 52.53\%$$

The calculations for this model resulted in final oil concentration of 949.34 mg/l, which has the separation efficiency of 53%. This model is a modified version where the base is equation is obtained from Lian and Yuan (1994) who proposed a high efficiency corrugated plates packing oil water separator. However, since that mathematical model is to just represent the separation of dispersed oil in water, several other publications were used to modify the equation as shown in Equation 13, which can represent for the separation of oil from the ASP produced fluid.

Model	Final Oil Concentration (mg/l)	Separation Efficiency (%)
Internal Circulation Flotation and Kinetic Model	484.31	75.78
Modified Corrugated Plates Packing Oil-Water Separator	949.34	52.53

4.1.3 Selection of the best model Table 3: Comparison of Model

Based on results in table 4, the internal circulation floatation and kinetic model (floatation model) is concluded to be the best among the two models compared. Even though the separation efficiency of the modified corrugated plates packing oil-water separator (packed bed model) can be considered as quite high in a real plant situation, however, it did not outperform the floatation model. Hence, floatation model is chosen to be the best model.

Besides the separation efficiency, floatation model also has other advantages over packed bed model. One of them is the space conservation. Since floatation model is a vertical vessel the space needed to set up the vessel is less compared to packed bed model which is a horizontal vessel that requires much larger space to set up. Other than that, based on the model equation developed for the floatation model, all the key factors that influence the separation efficiency has been specified. This ease the identification and manipulation of variable to analyze and manipulate them to achieve better performance of the separator. However, the model equation that is developed for the packed bed model, contains parameters that cannot easily identify the key factors that influences the separation. For instance, in floatation model, effect of temperature change can be easily studied with the presence of term for temperature in the equation. But, this is rather difficult in the packed bed model because there is no specific term for temperature. In packed bed model, the change in the temperature can only be correlated to the equation by using temperature vs density data and temperature vs viscosity data that are obtained after few analysis. This would make the adjustment or optimization calculation to be more complex compared to floatation model.

Therefore, in conclusion, the floatation model is found to be the best and easiest model to optimize compared to packed bed model.

4.2 Optimization of Selected Model Parameters

As per the findings from literature review there are five main key parameters that can be optimized in the internal circulation floatation and kinetic model (floatation model) separator. They are temperature, flow rate of gas, retention time, and surfactant and polymer concentration. This section of the report will report the effect of changing the values of parameter to the separation efficiency.

4.2.1 Temperature

Temperature	Reaction rate, k	Final Oil	Separation
(°C)	(1/min)	Concentration (mg/l)	Efficiency, η (%)
35	0.283634	484.3146	75.78427
40	0.369631	315.0547	84.24726
45	0.440987	220.5152	88.97424
50	0.501056	163.3056	91.83472
55	0.552269	126.4132	93.67934



Figure 7: Temperature vs Separation Efficiency Graph

Table 4 illustrates the effect of temperature on the reaction rate, final oil concentration and separation efficiency of oil in the presence of the ASP produced fluid. This is depicted in graphical manner as shown in Figure 7. From the graph obtained, it can be seen that the separation efficiency increases as the temperature increases. The increase in separation efficiency is relatively higher from 35°C to 40°C compared to the increase in the subsequent intervals. Based on the curve and the equation obtained, it is predicted that the efficiency would achieve about 99% and would not vary much after the temperature reaches around 70°C.

However, the operating temperature of the vessel at 70°C is not recommended due the high maintenance cost that would be required to handle the vessel. The literature also recommends that temperature of produced fluid should not be more than 45°C as that would affect the oil recovery itself.

Increase in temperature generally favors the separation as the added heat to the emulsion reduces the viscosity of the oil phase which was increased exponentially due to the injection of ASP into the reservoir. According to Stokes equation, when the viscosity of the oil is reduced, more rapid rising of oil droplets is allowed and thus faster the separation occurs. Other than that, higher temperature can dissolve small crystals of paraffin and asphaltenes and therefore, neutralizes their effect as potential emulsifiers. Besides, higher temperature causes the zeta potential (ζ) of the oil droplets to decrease apart from causing higher interfacial tension (IFT) between emulsion and oil droplets which destabilize the emulsion for easier separation.

Zeta potential is the scientific term for the electro kinetic potential which is the key indicator of the stability of colloidal dispersions. On the other hand, interfacial tension is the force that holds the surface of two phase (oil-water) together. However, adding excessive heat can cause significant loss of light ends (lower boiling point hydrocarbons) which may lead to a phenomena called "shrinkage" of oil where volume is loss and the API gravity is lower.

In this case, the process can be explained as follows: the oil particles near each other deforms, the interfacial tension between the particles is squeezed under the capillary pressure and destabilizes before rupturing and merging together into one large particle. The change in temperature then further alter the adhesion properties of oil particles and accelerate the coalescence rate. Therefore, the removal rate is improved with increase of temperature.

In conclusion, appropriate temperature must be set to balance the volume loss and effective separation. In this case, it can be safely assumed that the temperature of vessel should be maintained around 40 - 45°C which will still produce a separation efficiency about 85% in average.

Flow Rate of Gas (m ³ /h)	Reaction rate, k (1/min)	Final Oil Concentration (mg/l)	Separation Efficiency, Ŋ (%)
15	0.283634	484.3146	75.78427
20	0.450884	209.8693	89.50654
25	0.431634	231.0732	88.44634
30	0.225884	646.4428	67.67786
35	-0.16637	4595.049	-129.752

4.2.2 Flow Rate of Gas

Table 5: Effect of Flow Rate of Gas Manipulation



Figure 8: Flow Rate of Gas vs Separation Efficiency Graph

Figure 8 shows separation efficiency of oil in the presence of ASP produced fluid based on the flow rate of gas. The values are plotted using the data tabulated in Table 5. From the Figure, it can be seen that the separation efficiency increases from $15 - 20 \text{ m}^3/\text{h}$ of gas flow rate and decreases rapidly in the interval afterwards. The value reaches negative after the flow rate of 33 m³/h which indicates that the model equation is only valid until that point of flow rate.

Therefore, the boundary for the model equation where the flow rate of gas that can be modified is from 15 - 33 m³/h only. Beyond these values the equation cannot be used to predict the separation efficiency of the oil.

Gas flow rate in this model affects the residence time of the oil droplets where the different gas hold up causes the bulk density (emulsion and gas bubbles) to differ between regions. When the down-flow velocity of the fluid is greater than of small rising bubbles pumped into the system (refer Figure 3), the bubbles flow down and reenter the central region. This cause higher collision frequency between particles and bubbles which enable effective separation as the residence time is increased. However, if the gas volume increases beyond specific threshold, the bubbles would merge together and become volatile. Besides, higher gas supply causes the turbulence of the reactor to increase which results the back mixing of destabilized emulsion. This would block the floatation of oil particles to the surface where the oil droplets merge together to form oil layer and separates form the emulsion.

In conclusion, from the graph it can be observed that, as the flow rate increases above 20 m³/h, the separation efficiency is found to be decreasing which makes that value as the optimum value for the flow rate of gas that need to be supplied for this model.

4.2.3 Retention time Table 6: Effect of Retention Time Manipulation

Retention	Reaction rate,	Final Oil	Separation
Time (min)	k (1/min)	Concentration (mg/l)	Efficiency, Π (%)
5	0.283634	484.3146	75.78427
6	0.283634	364.7095	81.76452
7	0.283634	274.6418	86.26791
8	0.283634	206.817	89.65915
9	0.283634	155.742	92.2129



Figure 9: Retention Time vs Separation Efficiency Graph

Retention time, when manipulated illustrated a high separation efficiency with the increase of the time. From table 6, it can be observed that the reaction rate is constant for all manipulated values while the increase in separation efficiency is getting slower with the increase of retention time. From Figure 9 and equation obtained, 100% of efficiency is expected to be achieved when the retention time is at 60 minutes (1 hour). However, this is not ideal in real plant situation where continuous flow of oil from the reservoir into the vessel is required to meet the daily target of oil production.

Besides that, the literature also suggest that the retention time should not be more than 10 minutes. Therefore, taking into the account of oil production and processing, the optimum retention time is suggested to be around 7 minutes which can produce a separation efficiency of 86%.

Generally, the more the retention time the higher the separation of oil in the presence of dispersed oil phase in an emulsion. However, in a tight emulsion formed by the ASP flooding, retention time alone would not have much effect on the separation. Nevertheless, in the presence of demulsifer and electrostatic coalescer in the ASP containing emulsion, retention time can enable better separation. In this case, 7 minutes is considered to be optimum.

Surfactant Concentration (mg/l)	Reaction rate, k (1/min)	Final Oil Concentration (mg/l)	Separation Efficiency, I] (%)
60	0.751634	46.65288	97.66736
70	0.634634	83.74151	95.81292
80	0.517634	150.3152	92.48424
90	0.400634	269.8145	86.50927
100	0.283634	484.3146	75.78427

4.2.4 Surfactant Concentration Table 7: Effect of Surfactant Concentration Manipulation



Figure 10: Surfactant Concentration vs Separation Efficiency Graph

The data from Table 7 is presented in Figure 10 where the relationship between the surfactant (WPS) concentration and separation efficiency is shown to be inversely proportional. From the graph, it can be seen that the separation efficiency decreases at a constant rate when the concentration of WPS is increased. This indicates that the higher the amount of WPS present in the produced fluid, the harder the separation.

Generally, during the ASP flooding, increase in the WPS concentration is preferred normally due to the effect of surfactant to increase the stability of the oil droplets. This stability is due to the properties of surfactants where they adsorb to the surface of oil droplets with its polar head group extending in water while the non-polar head attach to the oil droplets. Therefore, the surface of oil droplets are changed to hydrophile and hard to attract each other for coalescence to occur. This stability thus results in higher percentage of oil recovery. Thus, the WPS concentration must be lowered during the separation process in order to ensure the zeta potential and IFT is sufficiently low for coalescence to occur. As two oil droplets attracts each other, the thin aqueous film of continuous phase that formed must be broken in order for them to merge to become one big oil droplet. The strength of this water film is affected by this WPS concentration where it plays an important role in the coalescence rate.

Therefore, based on the Figure 10, it is predicted that 100 mg/l of WPS concentration would be an optimum value which would produce a 75% separation efficiency. Even though much lower concentration could produce much better efficiency, this would cause much complex demulsification process where the cost of process could be possibly compromised.

4.2.5 Polymer Concentration Table 8: Effect of Polymer Concentration Manipulation

Polymer Concentration (mg/l)	Reaction rate, k (1/min)	Final Oil Concentration (mg/l)	Separation Efficiency, Ŋ (%)
100	0.655634	75.39453	96.23027
150	0.562634	120.0292	93.99854
200	0.469634	191.0881	90.44559
250	0.376634	304.215	84.78925
300	0.283634	484.3146	75.78427



Figure 11: Polymer Concentration vs Separation Efficiency Graph

Polymer's (HPAM) effect on separation is almost similar to the effect of the surfactant. This can be seen in Table 8 and also Figure 11. The trend of the curve is inversely proportional to the separation efficiency. Since, HPAM concentration in the oil affects the separation efficiency similarly to the WPS, it can be assumed that the optimum concentration can be almost similar to surfactant concentration.

During ASP flooding, HPAM improves the sweep efficiency of the oil by reducing the mobility ratio of the aqueous phase with the increase in viscosity and interfacial elasticity of water which stabilizes the oil droplets. High amount of HPAM results in the oil droplets to rise very slowly thus, reducing the oil removal rate.

However, even though the HPAM causes the stability of the emulsion during flooding, experimentally, it is proven that at specific amount, it also promotes the flocculation of oil droplets. Therefore, demulsification process should not account for high conversion or removal of HPAM from the ASP produced fluid.

In conclusion, from Table 8, it can be seen that, with the presence of 100 mg/l of polymer concentration the separation efficiency is the highest, which is about 96%. This is accepted as the optimum HPAM concentration.

4.3 Separation Efficiency Prediction with Optimum Parameters

Temperature (°C)	45
Flow Rate of Gas (m^3/h)	20
Retention Time (min)	7
Surfactant Concentration (mg/l)	100
Polymer Concentration (mg/l)	100

Table 9: Optimum Parameter Predicted

Using Equation 10 and the data from Table 9, the concentration of oil after the separation is calculated. The calculations are as follows:

 C_e

 $= 2000e^{-[(-0.747+1.31e^{0.000221(2000)-20.4/(45)}-0.00186(100)-0.0117(100)+0.164(20)-0.00373(20)^2)\times(7)]}$ = 2.09 mg/l

The separation efficiency is:

$$\frac{2000 - 2.09}{2000} \times 100\% = 99.90\%$$

Increase in performance (%) is:

$$\left|\frac{75.78 - 99.90}{75.78}\right| \times 100\% = \mathbf{31.83\%}$$

The calculations shows that the final oil concentration is 2.09 mg/l, which gives about 99.90% of efficiency. This has increase the performance of the vessel by approximately 32% which is a very good result. Thus, the Internal Circulation Floatation and Kinetic Model Separator is recommended to be used in the St Joseph oilfield to separate the oil recovered from the ASP produced fluid.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The main purpose of this project is to identify the key factors that influences the separations efficiency and compare two possible model that can predict the separation efficiency of oil from ASP produced fluid. Further to the project, after identifying the best model, the selected model will be further analysed to obtain optimum parameter values that can enhance the separation efficiency.

After comparing Internal Circulation Floatation and Kinetic Model (floatation model) and modified corrugated plate packing separator model (packed bed model), it is found that floatation model has higher separation efficiency, which is 75.78% compared to packed bed model, which only had 52.53 % of separation efficiency.

Floatation model is then further studied and the parameter is the model equation for floatation model is varied in order to obtain the optimum set of values. It was found that the optimum temperature for better separation efficiency is around 40- 45° C. As for the gas flow rate, 20 m³/h produced the highest separation efficiency. Thus, the obtained flow rate is predicted to be the optimum value. Next is the retention time. The optimum time that a separation process should occur is estimated around 7 minutes. Increase in surfactant and polymer concentration further increase the stability of the oil/water emulsion. Therefore, minimum amount of surfactant (100 mg/l) and polymer concentration (100 mg/l) is estimated to yield a higher separation efficiency.

By using all the estimated optimum parameters, the efficiency is found to have increased from 76% to 99.9%. This depicts the performance of the vessel is increased about 32%.

Apart from the key factors that are being discussed in this project, there are other factors such as oil droplet size diameter, water cut percentage, type of surfactant and polymer, type and amount of demulsifier used which also greatly influence the separation efficiency of the oil in the presence of ASP produced fluid. These factors can be investigated in future to enhance the findings of this research.

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APPENDICES



Appendix 1: CPI Oil Separator



PLATE PACKS

Appendix 2: Plates and Plate Packs



Appendix 3: CPS system for Emulsified Oils



Appendix 4: CPI plate pack working mechanism



Appendix 5: Micrographs of Oil Droplet in wastewater at different ASP Concentration



Appendix 6: Impact of (a) HPAM, (b) temperature, (c) volumetric flow rate of floatation gas, and (d) oil droplet distribution on the oil removal rate R and the rate constant k.

Appendix 7: Current Separation and Treatment Technologies

Treatment	Description	Advantages	Disadvantages	Waste stream	Oil and gas produced water applications	
Corrugated plate separator	Separation of free oil from water under gravity effects enhanced by flocculation on the surface of corrugated plates	No energy required, cheaper, effective for bulk oil removal and suspended solid removal, with no moving parts, this technology is robust and resistant to breakdowns in the field	Inefficient for fine oil particles, requirement of high retention time, maintenance	Suspended particles slurry at the bottom of the separator	Oil recovery from emulsions or water with high oil content prior to discharge. Produced water from water-driven reservoirs and water flood production are most likely feed stocks. Water may contain oil and grease in excess of 1000 mg/L.	
Centrifuge	Separation of free oil from water under centrifugal force generated by spinning the centrifuge cylinder	Efficient removal of smaller oil particles and suspended solids, lesser retention time high-throughput	Energy requirement for spinning, high maintenance cost	Suspended particles slurry as pretreatment waste		
Hydroclone	Free oil separation under centrifugal force generated by pressurized tangential input of influent stream	Compact modules, higher efficiency and throughput for smaller oil narticles	Energy requirement to pressurize inlet, no solid separation, fouling, higher maintenance cost			
Gas floatation	Oil particles attach to induced gas bubbles and float to the surface	No moving parts, higher efficiency due to coalescence, easy operation, robust and durable	Generation of large amount of air, retention time for separation, skim	Skim off volume, lumps of oil		
Extraction	Removal of free or dissolved oil soluble in lighter hydrocarbon solvent	No energy required, easy operation, removes dissolved oil	Use of solvent, extract handling, regeneration of solvent	Solvent regeneration waste	Oil removal from water with low oil and grease content (<1000 mg/L) or removal of trace quantities of oil and grease prior to membrane processing. Oil reservoirs and thermogenic natural gas reservoirs usually contain trace amounts of liquid hydrocarbons.	
Ozone	Strong oxidizers oxidize soluble contaminant and easy operation, efficient for primary treatment of soluble constituents remove them as	Easy operation, efficient for primary treatment of soluble constituents	On-site supply of oxidizer, separation of precipitate, byproduct CO ₂ , etc.	Solids precipitated in slurry form		
Adsorption	Porous media adsorbs contaminants	Compact packed bed modules,	High retention time, less efficient at	Used adsorbent media,		
Lime softening	Addition of lime to remove carbonate, bicarbonate, etc. hardness	Cheaper, accessible, can be modified	Chemical addition, post-treatment necessary	Used chemical and precipitated waste	These technologies typically require less power and less pretreatment than membrane technologies. Suitable produced waters will have TDS values between 10,000 and 1000 mg/L. Some of the treatments remove oil and grease	
Ion-exchange	Dissolved salts or minerals are ionized and removed by exchanging ions with ion-exchangers	Low energy required, possible continuous regeneration of resin, efficient, mobile treatment possible	Pre- and post-treatment require for high efficiency, produce effluent concentrate	Regeneration chemicals		
Rapid spray evaporation	Injecting water at high velocity in heated air evaporates the water which can be condensed to obtained treated water	High quality treated water, higher conversion efficiency	High energy required for heating air, required handling of solids	Waste in sludge form at the end of evaporation	contaminants and some of them require oil and grease contaminants to be treated before these operations.	
Freeze-thaw	Utilize natural temperature cycles to	No energy required, natural process,	Lower conversion efficiency, long	-		
evaporation	freeze water into crystals from contaminated water and thaw crystals to produce pure water	cheaper	operation cycle			
Microfiltration	Membrane removes micro-particles from the water under the applied pressure	Higher recovery of fresh water, compact modules	High energy required, less efficiency for divalent, monovalent salts, viruses, etc.	Concentrated waste from membrane backwash during membrane deaning, concentrate	Removal of trace oil and grease, microbial, soluble organics, divalent salts, acids, and trace solids. Contaminants can be targeted by the selection of	
Ultrafiltration	Membrane removes ultraparticles from the water under the applied pressure	Higher recovery of fresh water, compact modules, viruses and organics etc. removal	High energy, membrane fouling, low MW organics, salts, etc	stream from the filtration operation	the membrane.	
Reverse osmosis	Pure water is squeezed from contaminated water under pressure differential	Removalent salts, dissolved contaminants, etc., compact modules	High pressure requirements, even trace amounts of oil and grease can cause membrane fouling		Removal of sodium chloride, other monovalent salts, and other organics. Some organic species may require pretreatment. While energy costs increase with higher TDS, RO is able to efficiently remove salts in excess of 10.000m/l	
Activated sludge	Using oil degrading microorganisms to degrade contaminants within water	Cheaper, simple and clean technology	Oxygen requirement, large dimensions of the filter	Sludge waste at the end of the treatment	Removal of suspended and trace solids, ammonia, boron, metals, etc. Post-treatment is normally required to separate biomass, precipitated solids	
Constructed wetland treatment	Natural oxidation and decomposition of contaminants by flora and fauna	Cheaper, efficient removal of dissolved and suspended contaminants	Retention time requirement, maintenance, temperature and pH effects		dissolved gases, etc.	