UNIVERSITI PUTRA MALAYSIA

DEMULSIFICATION EFFICIENCY OF WATER-IN-OIL EMULSION USING NON-IONIC SURFACTANTS

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By

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Faculty : Engineering

One of the main problems faced by the petroleum industry is growth in the presence of salty water that is accompanies crude oil productions. However, the spread of small water droplets in the oil phase produces a very stable emulsion. The contents of crude oil contribute to enhancing the stability of the water droplets dispersed in crude oil, making petroleum demulsification of emulsion more difficult and the development of a new demulsification method and desalting crude oil is necessary. Water-in-oil emulsion is very common in the petroleum industry.

In this study, the chemical method used for demulsification emulsion by using surface active agents. The main objective of this study is to determine the capability of three surface-active agents as non-ionic demulsifiers, namely Propargyl Alcohol (PA), Triethylene Glycol (TG) and Glycerol (G), in breaking water-in-oil emulsion by using bottle test tube method. The findings sought are the optimal value of temperature, toluene concentration, surfactant dose, pressure and setting time on demulsification efficiency.

Design Expert software was used as an approach to study the effects of five parameters on output response. Factorial designs were utilised to describe the effect of factors on the response by using the Pareto chart. The result shows that Glycerol has the highest effect on demulsification efficiency. Central Composite Design (CCD) based on Response Surface Methodology (RSM) was employed to design the experiments and establish a mathematical model for finding the optimal value for the demulsification process. The results show that the three surfactants achieved high performance in separating the water. Glycerol shows high capability compared to Triethylene Glycol and Propargyl Alcohol because the hydrophilic-lipophilic balance for Glycerol was higher than that of the other two surfactants. It was concluded from the analysis of variance (ANOVA) that the main parameters were surfactant dosage,

temperature and time with highest F-values. While toluene concentration and pressure had a limited effect on breaking emulsion. Temperature played an essential role in the process of demulsification of water by reducing the viscosity of the oil and increase the kinetics energy of water droplets. Additionally, the sitting time was very important parameters in destabilizing emulsion stability through diffusing surfactant in the emulsion and adsorbing surfactant molecules on the interfacial film between two phase's water and oil. Moreover, it was found that the maximum separation of water occurred approximately at high temperature for three models approximately above 85℃ for three surfactants. The difference between predicted R^2 and adjusted R^2 was reasonable for three models as well as diagnostic plots all showed that the developed models for three surfactants could adequately predict the experimental outcome. The optimal value for temperature and sitting time were approximately above 85℃ and 100min, respectively, for three models.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYAHEMULSIAN KEBERKESANAN EMULSI AIR DALAM MINYAK MENGGUNAKAN SURFAKTAN BUKAN IONIK

Oleh

MURTADA MOHAMMED ABDULREDHA

April 2019

Pengerusi : Profesor Madya Datin Ir. Siti Aslina Binti Hussain, PhD
Fakulti : Kejuruteraan

Salah satu masalah utama yang dihadapi industri petroleum ialah peningkatan kewujudan air masin yang hadir bersama penghasilan minyak mentah. Walau bagaimanapun, penyebaran titisan air kecil dalam fasa minyak telah menghasilkan emulsi yang sangat stabil. Kandungan minyak mentah membantu dalam penggalakan kestabilan titisan air yang terserak dalam minyak mentah, menyebabkan penyahemulsian emulsi petroleum menjadi lebih sukar dan pembangunan suatu kaedah baharu dihidrasi dan penyahmasinan minyak mentah adalah perlu. Emulsi air dalam minyak merupakan perkara biasa dalam industri petroleum.

Dalam kajian ini, kaedah kimia menggunakan emulsi penyahemulsian adalah dengan menggunakan agen permukaan aktif. Objektif utama kajian ini adalah untuk menentukan kapabiliti tiga agen permukaan aktif sebagai penyahemulsi bukan ionik yang dikenali sebagai Propil Alkohol (PA), Trietilena Glikol (TG) dan Gliserol (G), dalam pemecahan emulsi air dalam minyak dengan menggunakan kaedah tiub ujian botol. Dapatan yang disasarkan ialah nilai optimal suhu, konsentrasi toluene, dos surfaktan, tekanan dan masa seting ke atas keberkesanan penyahemulsian.

Perisian pakar reka bentuk telah digunakan sebagai suatu pendekatan bagi mengkaji kesan lima parameter ke atas respon hasil. Reka bentuk faktorial digunakan untuk menjelaskan kesan faktor tersebut ke atas respon dengan menggunakan carta Pareto. Dapatan menunjukkan bahawa Gliserol mempunyai kesan tertinggi ke atas keberkesanan penyahemulsian. Bentuk Komposit Pusat (CCD) berdasarkan Metodologi Permukaan Respon (RSM) telah digunakan untuk reka bentuk eksperimen, mewujudkan suatu model matematikal dan mencari nilai optimal bagi proses penyahemulsian. Dapatan menunjukkan bahawa ketiga-tiga surfaktan memperoleh prestasi tinggi dalam pengasingan air. Gliserol menunjukkan kapabiliti yang tinggi berbanding dengan Trietilena Glikol dan Propil Alkohol kerana

keseimbangan hidrofilik - lipofilik bagi Gliserol adalah lebih tinggi daripada dua surfaktan yang lain. Kajian ini menyimpulkan dari analisis varians (ANOVA) bahawa parameter utama ialah dos surfaktan, suhu dan masa dengan nilai F tertinggi. Manakala konsentrasi toluene dan tekanan mempunyai kesan yang terhad ke atas pemecahan emulsi. Suhu memainkan peranan yang penting dalam proses penyahemulsian air melalui pengurangan kelikatan minyak dan meningkatkan tenaga kinestik titisan air. Tambahan pula, masa seting merupakan parameter yang penting dalam penyahstabilan kestabilan emulsi melalui resapan surfaktan dalam emulsi dan serapan molekul surfaktan ke atas film antaramuka antara dua fasa air dan minyak. Di samping itu, pengasingan air maksimum berlaku lebih kurang pada suhu yang tinggi bagi ketiga-tiga model lebih kurang atas 85℃ bagi ketiga-tiga surfaktan. Perbezaan antara R^2 teranggap dan R^2 terlaras adalah wajar bagi ketiga-tiga model, juga bagi plot diagnostik, semua menunjukkan bahawa model yang dibangunkan bagi ketiga-tiga surfaktan sewajarnya dapat meramalkan hasil eksperimen. Nilai optimal bagi suhu dan masa seting adalah masing-masing lebih kurang atas 85℃ dan 100min, bagi ketiga-tiga model.

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Declaration by graduate student

I hereby confirm that:

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Signature:	______________________
Name of Member of Supervisory Committee:	Professor Dr. Luqman Chuah Abdullah

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LIST OF SYMBOLS

Symbol	Expression	Unit
A	Demulsifier dosage	ppm
B	Toluene concentration	mL
C	Constant of the asphaltenic thickness film	nm
C	Pressure	mmHg
Co	Experimental number at centre point	
D	Temperature	℃
E	Time	minute
Ɛ oil	Oil dielectric constant	
Ɛ0	Electric vacuum permittivity constant	C V-1 m-1
fc	Correction factor respectively	
H	Hamaker constant	J
K	Number of factor	
K	Volumes ratio	
kB	Boltzmann constant	J/K
m	Dipole momentum	D
N	Number of the experiment	
r	The distance between two droplets	nm
R2	Coefficient of determination	
T	Temperature	K
uµ	Dipole interaction	
uD	Dispersion energy	J
us	Steric repulsive	

VA	Volume of droplet A	µm
VB	Volume of droplet B	µm
Vo	Volume of separated water	mL
Vt	Total volume of the water in emulsion	mL
xi	Parameters	
Y	Output response	
βi	Slope influence of input variables	
βii	Quadratic influence	
βij	Cross output term	
βo	Constant coefficient	
γA	The coefficient of the interfacial tension between the droplet A and host	mN/m
γAB	Interfacial tension between droplet A and B	mN/m
γB	The coefficient of the interfacial tension between the droplet B and host	mN/m
ε	Statistical error	
θ	Contact angel	
ϵi	Residual error	
γi	Parameters	
yi	Total mean value	
σ	Residual mean square	

LIST OF ABBREVIATIONS

CBM	Coal Bed Methane
ANOVA	Analysis of Variance
HF	Hydraulic Fracturing
O/W	Oil-in-Water
W/O	Water in Oil
W/O/W	Water-in-Oil-in-Water
SMD	Sauter Mean Diameter
SEM	Scanning Electron Microscopy
HLB	Hydrophilic Lipophilic Balance
RSM	Response Surface Methodology
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
DE	demulsification Efficiency
fFD	Fractional Factorial Design
FFD	Full Factorial Design
BBD	Box Behnken design
CCD	Central Composite Design
DF	Degrees of Freedom
PA	Propyl Alcohol
TG	Triethylene Glycol
G	Glycerol
RSS	Sum of Squares of Residual Errors
SS	Sum of Squares
Adj R2	Adjusted of Coefficient of Determination
p	Number of factors
n	Number of experiments
V2	Variance of experimental error

ED	Effect of factor
Mi	Response of individual values
Mo	Average of values response
SE	Standardized effect
EV	Effect values
Se	Standard deviation

CHAPTER 1

INTRODUCTION

1.1 Background

The issue of separating water or breaking water-in-oil emulsion returns to the beginnings of crude oil production. The emulsion in the petroleum industry is very undesirable and at the same time, the formation of the emulsion is ineluctable. The emulsion should be broken into two phases before the transportation and refinery process and meet the specific water standard and salt residual. Meanwhile the water content should be less than 1% (Fink, 2015; Zhang et al., 2016a).

The light hydrocarbons compounds travel to gap locations in the reservoirs and convert the location of the water from the formation to hydrocarbon reservoirs. Consequently, these reservoir rocks will usually contain petroleum hydrocarbons (liquid and gas) together with water. The flow of underground water may rise from above or below the hydrocarbon region, flowing from inside the hydrocarbon area, or stream from injected fluids and additives during production activities. This type of water is frequently considered as “connate water” or “formation water” and becomes produced water when the reservoir is produced as these fluids are carried to the surface. Produced water can be defined as the water that is raised to the surface with the hydrocarbon resource and is brought to the surface along with crude oil or natural gas (Veil et al., 2004). Figure 1.1 presents the geological layers of reservoir and gives a general imaginary of reservoir layers, where generally water sits below the hydrocarbon seams as well as the formation water is generally slightly acidic.

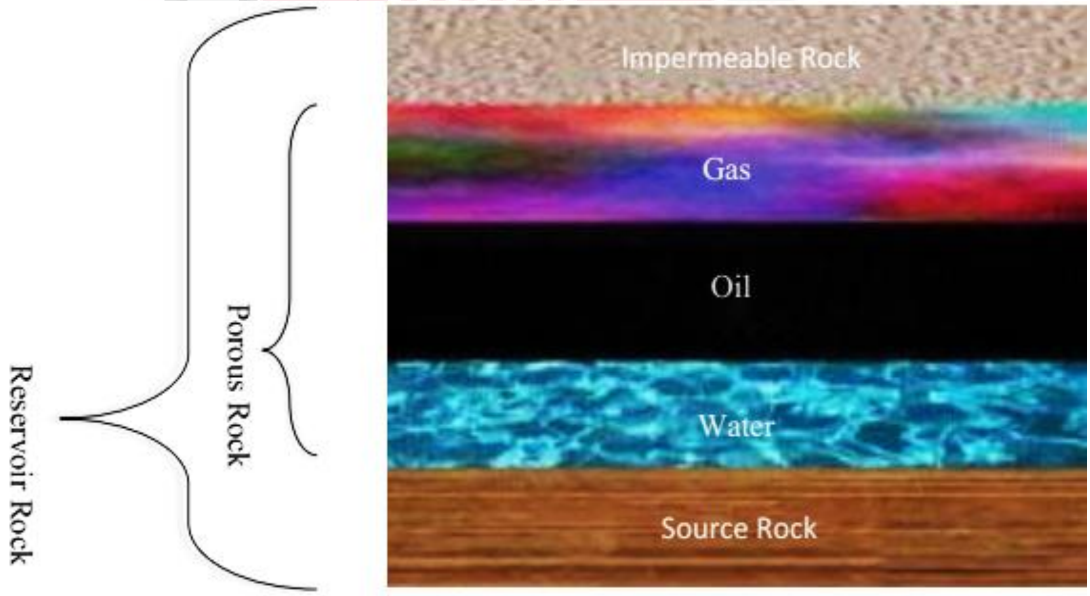

Figure 1.1 : Reservoir Layers (Igunnu and Chen, 2012)**.**

However, the hydrocarbon compounds are presented as a fluid mixture on the surface. The combination of mixture usually depends on the nature of hydrocarbons being extracted. The combination normally contains liquid and gaseous hydrocarbons, dissolved or solid contaminants, water, solid particles like salts, silt, sand, iron and additives, such as chemical compounds and injected fluids during the production and exploration activities. Furthermore, the process of extraction includes disarmament of water and this may lead to natural gas migration to other wells.

Moreover, most crude oil fields often have a higher content of water and fines, while the combination of fines and high water content produces very stable crude oil emulsions. The increase in emulsion viscosity occurs due to the large number of small water droplets often leading to an increase in the operational condition cost. The emulsion can be produced due to contact between two immiscible liquids, the presence of emulsifying compounds in crude oil as well as turbulence during production activates. Water-in-oil emulsion is very common in petroleum industry as compared to other types of emulsion (De Oliveira et al., 2018; Sellman et al., 2013).

The process of breaking emulsion into two phases is referred to by the demulsification term. Furthermore, the demulsification process is a very intricate process, which generally has three basic methods, namely physical, chemical and biological demulsification. The efficiency of the methods depends on the capability to minimize the emulsion stability until the separation occurs. In the petroleum industries, the emulsion must be broken into two phases before proceeding with further refining process. The use of chemical additives, which is known as demulsifers, is the prevalent method in breaking emulsion (Issaka et al., 2015; Zolfaghari et al., 2016).

The most important aspect in the demulsification process is removing impurities, salt and water from mixture. The demulsification technique depends on the concentration of salt in content and the compatibility of technique under high concentration of contaminants in produced water. There are several techniques of demulsification emulsion. The most common are electric separation, chemical treatment and membrane filtration. Demulsification can be defined as the process of separation crude oil emulsion into two-phase crude oil and water. Generally, demulsification method can be assessed in three-point as below (Arthur et al., 2005).

- Time or speed of broken emulsion process.
- Efficiency of process in separating crude oil emulsion.
- Goodness of removal separated water.

High efficiency of separation with minimum time and best way for disposal water are centrally preferred by crude oil producers. There are specifications about crude oil before it is sent to refinery or transported in pipelines. These specifications include that crude oil should contain less 0.2% water and sediment and less 10PTB of salt. The specifications also vary according to crude oil producer (Arthur et al., 2005).

1.2 Problem Statement

In recent years, the most challenging confrontation in the petroleum industry is the increase in water production during crude oil and gas extraction. Most of this water produces an emulsion in surface facilities, pipelines and wellbore. Subsequently, water contain organic and inorganic compounds, chemical materials that are used during the extraction process and heavy materials. Accordingly, these compounds cause a series of problems in petroleum refinery, like fouling, corrosion and erosion in equipment and pipelines and toxicity of catalysts in the upstream facility (Ammar and Akbar, 2018; Aryafard et al., 2016; Zheng et al., 2016). Also, the spread of small water in crude oil increases the viscosity of crude oil leading to increase the operation cost.

However, containment of crude oil on surface-active compounds increases the stability of emulsion and difficulty in breaking emulsion. There are many variables influence on emulsion stability including the heavy material i.e. solids particles, pH, temperature, brine to oil ratio, droplet size, the difference between two density and interfacial tension. At the same time, the main challenges in petroleum refining process are found to be the selection of the most effective variables to destabilise water-in-crude oil emulsion. Also, one of the essential methods to break emulsion into two phases is by using surface-active agents or demulsifiers. Meanwhile there is a limitation in efficiency by using non-ionic surfactants to destabilise water-in-oil emulsion (Lu et al., 2014).

Moreover, by conducting an in-depth literature review, it is found that there is still a significant gap in information for using the other variables with demulsifier that can be used to enhance the oil recovery, depending on resolving the basic reason for water droplets stability in oil (asphaltenes) and providing the best condition for the demulsifier to achieve maximum separation in a short time. Additionally, asphaltenes in crude oil are the most problematic components through absorbing the molecules on the interface between oil and water which makes a high rigid film. The highest level of stability emulsion can reach is when the asphaltenes are at precipitation point or close to it (Langevin and Argillier, 2016). As a result, reduction in asphaltene precipitation is a promising technique to enhanced oil recovery. Consequently, this study investigates this hypothesis by using variables that reduce asphaltenes precipitation on the interfacial film between two phases with a demulsifier to achieve high demulsification efficiency in a short time. To the best of our knowledge, we could not detect a study on dissolving asphaltenes film with using a demulsifier, which can be a promising technique in maximising the demulsification efficiency of water from crude oil and enhance the demulsification process of the emulsion by using non-ionic surfactants.

1.3 Study Objectives

The main study objectives are:

1) To investigate the demulsification efficiency of water-in-oil emulsion using non-ionic surfactants namely Propargyl Alcohol, Triethylene Glycol and Glycerol.
2) To optimize the parameters influencing demulsification efficiency using Response Surface Methodology (RSM).

1.4 Scope of Work

The present work studies the efficiency of various non-ionic surface-active agents compounds in demulsification of water-in-oil emulsion. The surfactants that were used as demulsifiers for breaking the emulsion were Propargyl Alcohol, Triethylene Glycol and Glycerol. Generally, the three surfactants possess high capability in reducing the interfacial tension between the two phase. Therefore, the efficiencies of the surfactant were evaluated by using bottle test method.

Moreover, the variables including surfactants concentration, temperature, setting time, pressure and toluene concentration in breaking water-in-oil emulsion were studied in a specific range. The range of parameters that are used in the experiment was fixed depending on literature of previous studies to ensure that the parameter have high influence on breaking emulsion into two phases.

The two-level factorial design was applied to characterize the significant variables by using the Pareto chart. Then, a Central Composite Design based on the Response Surface Methodology (RSM) was utilized for experimental design runs, modelling and statistical analysis based on the analysis of variance (ANOVA). Numerical optimization was used to find the optimal condition for surfactant dose, toluene concentration, pressure, sitting time and temperature for three models to achieve maximum water separation was found by Central Composite Design.

1.5 Study Limitation

Crude oil is a very complex mixture of hydrocarbon components, making it difficult to analyze the pure components in crude oil by refineries. In the last few decades the correlations between pressure-temperature-volume properties of crude oil have been approached. The specific gravity, pressure and temperature and other relative components were used to describe crude oil properties. However, many of organic chemical compounds form crude oil. Crude oil types differ largely in their chemical and physical properties from different oil platforms. The variance in chemical and physical characteristics is dependent on the percentage of hydrocarbon compounds, including alkenes, alkanes, cyclo compounds, alkynes and aromatics in crude oil as well as heteroatoms materials like oxygen, sulphur and nitrogen besides the organic compounds, alcohol (−OH) and carboxylic (−COOH) (Eneh, 2011; Onyema and Manilla, 2010). As a result, the synthetic oil (diesel fuel) was used in the experiment instead of crude oil due the limitation in crude oil source as well as the high similarity between crude oil and diesel fuel (Demirbas et al., 2015).

1.6 Outline of Thesis

The thesis is classified into five chapters to describe the research in a consecutive order. Chapter 1 introduces the background study on demulsification of water-in-oil emulsion and formulation problem. Chapter 2 surveys the major lines of general study aspects, and the variable optimizations by using the response surface method. The chapter also surveys literature on treatment methods of water-in-oil emulsion to address the method development. Chapter 3 presents in detail the materials and methods utilized in the experimental study. Chapter 4 shows the results and discusses the research findings. Lastly, Chapter 5 includes the result conclusions and recommendations for future work.

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