A PLANT-BASED NATURAL SURFACTANT FOR ENHANCED OIL RECOVERY APPLICATION

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DEDICATION

This thesis is dedicated to my beloved family and friends for their love, support and encouragement.

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ABSTRACT

It is generally known that only one-third of the petroleum present in known reservoirs can be recovered economically using established technology. To improve the recovery of oil from these reservoirs various Enhanced Oil Recovery (EOR) methods have been tested and implemented worldwide. One of the most widely used methods is surfactant flooding. The use of synthetic surfactant usually has serious environmental and financial implications, which have made it important to find new surfactants to solve these problems.

In this study, saponin was extracted from the leaves of *Vernonia Amygdalina* by ultra-sonication and used to formulate surfactant solutions capable of achieving low interfacial tension (IFT). Saponins are a group of naturally occurring plant glycosides, characterized by their strong foam-forming properties in aqueous solution. In addition, the effect of the surfactant solution on the IFT and emulsion stability of the surfactant solution as well was evaluated. Finally, oil displacement efficiency of the formulated surfactant solution was examined and compared.

The surfactant solution can effectively emulsify oil and could reduce the IFT with crude oil from 18 mN/m to 3.9 mN/m. The displacement experiments through 100 – 170 mD sandstone cores indicated that the EOR could reach 11.2% OOIP by the surfactant flooding after water flooding. The newly formulated surfactant based on saponin extract from *Vernonia Amygdalina* can efficiently enhance oil recovery after water flooding. This work adds *Vernonia Amygdalina* to the list of plant-based surfactant to be used in the petroleum industry.

ABSTRAK

Umumnya diketahui bahawa hanya satu pertiga daripada petroleum yang terdapat dalam reservoir yang diketahui dapat diperoleh dengan menggunakan teknologi yang mapan. Untuk meningkatkan perolehan minyak dari reservoir ini, pelbagai kaedah perolehan minyak tertingkat (EOR) telah diuji dan dilaksanakan di seluruh dunia. Salah satu kaedah yang paling banyak digunakan ialah banjiran surfaktan. Penggunaan surfaktan sintetik biasanya mempunyai implikasi kepada alam sekitar dan kewangan yang serius. Oleh itu adalah penting untuk mencari surfaktan baru untuk menyelesaikan masalah ini.

Dalam kajian ini, saponin diekstrak daripada daun *Vernonia Amygdalina* dengan ultrasonikasi dan digunakan untuk merumuskan penyelesaian surfaktan yang mampu mencapai ketegangan antara muka (IFT) yang rendah. Saponin adalah kumpulan glikosida tumbuh-tumbuhan yang terbentuk secara semulajadi, yang dicirikan oleh sifat pembentukan busa yang kuat dalam larutan akueus. Di samping itu, kesan larutan surfaktan pada IFT dan kestabilan emulsi larutan surfaktan juga dinilai. Akhirnya, kecekapan anjakan minyak bagi larutan surfaktan yang dirumus diperiksa dan dibandingkan.

Larutan surfaktan didapati dapat mengemulsikan minyak secara berkesan dan dapat mengurangkan nilai IFT antara larutan surfaktan dengan minyak mentah daripada 18 mN/m kepada 3.9 mN/m. Eksperimen anjakan melalui teras batu pasir 100 - 170 mD menunjukkan bahawa perolehan minyak melalui EOR dapat mencapai 11.2% OOIP oleh banjiran surfaktan setelah banjiran air. Surfaktan yang baru dirumuskan berdasarkan ekstrak saponin daripada *Vernonia Amygdalina* didapati dengan cekap dapat meningkatkan perolehan minyak selepas banjiran air. Kerja ini menambah *Vernonia Amygdalina* kepada senarai surfaktan berasaskan tumbuhan untuk digunakan dalam industri petroleum.

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LIST OF ABBREVIATIONS

EOR	-	Enhanced Oil Recovery
FTIR	-	Fourier Transform Infrared
HPLC	-	High Performance Liquid Chromatography
CO2	-	Carbon dioxide
CMC	-	Critical Micelle Concentration
OOIP	-	Original Oil In Place
SAGD	-	Steam Assisted Gravity Drainage
MMP	-	Minimum Miscible Pressure
IFT	-	Interfacial Tension
VA	-	Vernonia Amygdalina
WOR	-	Water oil ratio
NaCl	-	Sodium Chloride

LIST OF SYMBOLS

Nc	-	Capillary Number
Krw	-	Relative permeability to water
Kro	-	Relative permeability to oil
μ_o	-	Oil viscosity
μ_w	-	Water viscosity
λ_o	-	Oil mobility
λ_w	-	Water mobility
μ	-	Fluid viscosity
V	-	Fluid Velocity
M	-	Mobility ratio

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

It is generally known that only one-third of the petroleum present in known reservoirs can be recovered economically using established technology which includes the primary reservoir drive mechanisms such as water drive, solution gas drive and gas cap drive and secondary recovery by water flooding. To recover as much oil as possible various types of Enhanced Oil Recovery (EOR) method has been introduced over the years. Based on the types of injectants, Lake (1989) classified enhanced oil recovery method into three group: thermal (including steam flooding, hot-water injection, surface mining and extraction, etc.), gas (including CO_2 flooding, nitrogen injection, hydrocarbon flooding) and chemical methods (including alkaline flooding, surfactant flooding, alkaline/surfactant/polymer flooding, microemulsion)"

Most of the oilfields in Malaysia and other parts of the world are mature field in which the reservoir is unable to sustain production due to its primary energy. The alternative ways to increase production is either by finding new fields or by applying new technology to enhanced production from these mature fields. The estimated average cost of developing a new well in the Deepwater environment is USD 50 million (The Edge Daily, 2007). Due to this expensive cost and low crude oil prices, alternative ways to increase oil production economically must be sought after. To improve the recovery of oil from these mature field various EOR method have been tested and implemented worldwide. One of the most widely used EOR method is surfactant flooding, which entails the reduction of the interfacial tension between reservoir oil and water to ultra-low values. However, the cost of surfactants has been one of the main reason for its limited use in the EOR processes.

Surfactant flooding attempts to mobilize the oil that is trapped in pore spaces during a more conventional fluid injection project, such as water flooding. Decreasing interfacial tension and altering reservoir wettability are the main mechanisms of surfactant flooding in the reservoirs. Surfactants are compounds that tends to focus on boundary surfaces between two fluids, which reduces the surface tension between these two fluids and thereby release the oil to be easily moved out of the reservoir by water displacement. Various types of surfactants have been used for EOR process but recent advances have seen the formulation of natural surfactant from plant and agricultural products.

The use of synthetic surfactant usually has serious environmental implications. These leads to a growing interest in developing surfactants from natural sources that are environmentally friendly and less expensive compared to synthetic surfactants. In recent years, there have been many researches on the use of natural surfactant in Chemical EOR processes. One of the most popular plant based surfactants are the Saponins. These naturally occurring chemical compounds generate foam or lather similar to soap in water (Chhetri et al., 2009). A natural surfactant named Quillaja Saponaria Molina, which was extracted from a soar bark tree in Chile was, formulated (Rigano and Lionetti, 2009). Their interfacial tension and oil recovery capabilities have been tested in the laboratory. Various leaf-derived surfactants have also been formulated and there interfacial tension (IFT) with oil measured.

Vernonia Amygdalina is a shrub tree distributed mainly in tropical regions of Africa and Asia, which is popularly known as Bitter Leaf because of its bitter taste (Odugbemi et. al, 2007). It has been extensively used as a medicinal supplement over the years and in diseases treatment (Brendler et. al, 2010). Some of its components have been used in the pharmaceutical and cosmetic industries. *Vernonia amygdalina* contains various bioactive compounds such as alkaloids, saponins, terpenes, lignans, flavonoids, phenolic acids, steroids, anthraquinone, coumarins, sesquiterpenes, xanthanoes and edotides (Cimanga et al., 2004).

Saponins are a group of naturally occurring plant glycosides, characterized in aqueous solution by their strong foam-forming properties (Sahu et al., 2011). The common names of plant species rich in saponin were often derived from this feature, e.g. soaproot (Chlorogalum pomeidianum), soapbark (Quillaya saponaria), soapwort (Saponaria officinalis), soapberry (Sapindus saponaria), soapnut (Sapindus mukurossi) and soapjacob (Wieslaw and Arafa, 2010). Saponins have mainly found an industrial interest as surface-active or foaming agents. Most natural surfactants also contain saponins.

Most surfactant solutions are formulated to achieve miscibility with reservoir fluids or to achieve displacement of residual oil by reduction of the IFT. To achieve the above conditions, it is important that three criteria be satisfied; the surfactant as injected must be capable of mobilizing residual oil, the capability of the surfactant to displace reservoir oil must be maintained as the injected fluid moves towards production wells and certain mobility relationships must be satisfied. The formulated surfactant was tested to achieve the above stated criteria and its shows very favourable results.

In the early 1900s the concept of the application of surfactants in EOR was introduced. Variations in water salinity, oil composition and formation temperature are some of the factors that can affect the surfactant performance by altering the interfacial tension and wettability. Over the years, surfactant flooding have encountered various problems such as loss of surfactant to the rock matrix through adsorption, precipitation and phase behaviour changes (Clara, 2009). Several methods have been suggested as ways of reducing or eliminating the above stated problem. The use of plant-based surfactants has been experimentally tested to be useful in EOR process (Chhetri et al., 2009). Due to the above stated problem associated with surfactant flooding, a highly effective natural surfactant solution is needed in the industry.

1.2 Problem Statement

Oil recovery processes can be improved by the injections of surfactant solutions into the reservoir that release the residual oil. The work of Shidong and Ole (2015) gives the results of interfacial tension alteration experiments indication that hydrophilic synthetic surfactants have the ability of reducing IFT and thereby making oil wet sandstone reservoir to be more water wet. However, the high cost and significant adsorption of synthetic surfactant on to rocks surface have been limiting surfactant EOR development and the profitability of the process. Plant based natural surfactant are attracting interest in diverse fields because of their availability, low cost and their environmental friendly nature. A new natural surfactant was formulated and evaluated as a surfactant, which is capable of percolating through the reservoirs pores and mobilizing additional oil after water flooding. This will be achieved by lowering the interfacial tension between the fluids and increasing oil recovery.

This work focuses on the formulation of a new natural surfactant from *Vernonia Amygdalina* (bitter leaf) and the evaluation of its influence on interfacial tension between water and oil and increase in oil recovery. This work should address the following:

- Is the solid crude extract from *Vernonia amygdalina* actually saponin?
- What are the concentrations of surfactants to be formulated from *Vernonia amygdalina*?
- Is the surfactant solution compatible with the formation water?
- When will a phase behaviour change occur in the new natural surfactant solution?
- What is the influence of the surfactant concentration on interfacial tension and oil recovery?

1.3 Objectives

The objectives of this research are:

(a) To extract and characterize a new natural surfactant from *Vernonia Amygdalina*.

(b) To formulate natural surfactant solutions from the extracts.

(c) To examine and analyse surfactant concentration influence on interfacial tension, critical micelle concentration (CMC) and oil recovery.

1.4 Scope of the Study

The scopes of this research are based on the objectives stated above. They are as follows:

- Extracting saponins from the leaves of *Vernonia Amygdalina* by ultra-sonication.
- Investigating different concentrations of surfactant during the formulation. Seven surfactant concentrations (0.1wt%, 0.25wt%, 0.5wt%, 1wt%, 1.5wt%, 2wt% and 3wt %) was considered.
- Conducting various test such as; saponin characterization, emulsion ability test and core flood test.
- Analysing surfactant concentration influences on parameters such as: interfacial tension, critical micelle concentration (CMC) and oil recovery.

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