EMULSIFICATION AND DEMULSIFICATION OF WATER-IN-CRUDE OIL EMULSION VIA MICROWAVE-ASSISTED CHEMICAL TREATMENT

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ABSTRACT

Formation of emulsions during oil production and processing is a costly problem, both in term of chemicals used and production losses. The traditional ways of breaking emulsion using heat and chemicals are disadvantageous from both economic and environmental prospective. In this thesis, a new natural demulsifier knowing as “Cocamine MEA” in addition to an alternative energy potentials of microwave-assisted chemical approach were utilized and investigated in the demulsification of water-in-crude oil emulsion. Two types of crude oils were used, namely; crude oils A, and B. The study begun with some characterization studies to provide understanding of fundamental issues such as formation and characterization of the emulsion upon which further development on demulsification process could be achieved. The aim was to evaluate the performance of the new natural demulsifier compare with the existing demulsfiers as well as to obtain an optimized operating conditions of the demulsification process. For the stability performance test, three non-ionic emulsifiers were used, namely; Triton X-100, Span 80, and Cocamide DEA. Among these emulsifiers, Span 80 and Cocamide DEA permit the highest stability for the prepared emulsion. For the chemical demulsification performance test, six emulsifiers having different properties were utilized, namely: Octylamine, Hexylamine, Dioctylamine, Cocamine MEA, Polyethylene Glycol (PEG 600), and Polyethylene Glycol (PEG 1000). Among these demulsifiers, Octylamine was found to be the best in separating water and oil phases (90-100%) followed by Hexylamine (80-90%) for emulsion based on Span 80 at different phase ratios, respectively. Meanwhile, Cocamine MEA at the dose of 1 vol.% was found to be the best in separating water and oil phases (90-100%) followed by Octylamine and Hexylamine (90-100 %) at the dose of 1.5 vol.% for emulsion based on Cocamide DEA at different phase ratios. However, Dioctylamine, PEG 1000, and PEG 600 promote the monophase separation in separating the emulsion. Optimization of the microwave-assisted chemical demulsification using Face Centered Central Composite Design (FCCCD) under Response Surface Methodology found that Octylamine (1.5 vol.%) promotes a superior effect on demulsification rate of different types of emulsion, the exposure time (0.5-8) minutes and the MW power (270-360) watt were the most significant factors at different types of emulsion that consist with lower demulsifier utility, crude oil A emulsions needed higher MW power to separate the two phases. Based on the optimum conditions, the demulsification rate was accelerated by achieving a complete water separation for most types of emulsions. Characterizing the microwave generation and absorption at the optimum conditions showed that the w/o emulsion heated uniformly and deeply by long microwaves with less energy consumption. Results obtained in this thesis have exposed the potential application of Cocamine MEA as a natural composite for demulsification the water-in-crude oil emulsion. Moreover, results proved the capability of microwave-assisted chemical technology in developing the demulsification of w/o emulsions. Further works are nevertheless required to provide a deeper understanding of the mechanisms involved to facilitate the development of an optimum system applicable to the industry.

ABSTRAK

Pembentukan emulsi di dalam pemprosesan dan pengeluaran minyak mentah adalah mahal dari segi penggunaan bahan kimia yang digunakan dan kos operasi pengeluarannya. Pemecahan emulsi melalui teknik tradisional iaitu menggunakan haba dan bahan kimia bukanlah satu kelebihan dari segi ekonomi dan alam sekitar. Di dalam thesis ini, demulsifikasi baru semulajadi yang dikenali sebagai "Cocamine MEA" adalah sebagai tambahan kepada tenaga alternatif yang berpotensi di dalam gelombang mikro berbantukan bahan kimia telah dikaji dan digunakan di dalam teknik demulsifikasi emulsi air di dalam minyak mentah. Dua jenis minyak mentah telah digunakan, iaitu; minyak mentah A dan B. Kajian ini telah dimulakan dengan beberapa kajian pencirian untuk memberikan kefahaman tentang isu-isu asas seperti pembentukan dan pencirian emulsi di mana pembangunan lanjut mengenai proses demulsifikasi boleh dicapai. Tujuannya adalah untuk menilai prestasi demulsifikasi baru semulajadi dibandingkan dengan demulsifikasi sedia ada dan juga untuk mendapatkan keadaan operasi optimum bagi proses demulsifikasi. Untuk ujian prestasi kestabilan, tiga pengemulsi bukan ionik telah digunakan, iaitu; Triton X-100, Span 80, dan Cocamide DEA. Diantara pengemulsi ini, Span 80 dan Cocamide DEA mempunyai kestabilan tertinggi berdasarkan emulsi yang disediakan. Untuk ujian kimia bagi prestasi demulsifikasi, enam jenis demulsifier dengan kumpulan berfungsi yang berbeza telah digunakan, iaitu: Octylamine, Hexylamine, Dioctylamine, Cocamine MEA, Polyethylene Glycol (PEG 600), dan Polyethylene Glycol (PEG 1000). Diantara demulsifier ini, Octylamine didapati adalah yang terbaik dalam fasa pemisahan air dan minyak untuk emulsi (90-100%), diikuti oleh Hexylamine (80-90%). Cocamine MEA pada dos 1 peratusan isipadu didapati adalah yang terbaik di dalam pemisahan fasa minyak dan air (90-100%) diikuti oleh Octylamine dan Hexylamine (90-100 %) pada dos 1.5 peratusan isipadu. Sementara itu, Sementara itu, Dioctylamine, PEG 1000, dan PEG 600 memisahkan hanya minyak. Pengoptimuman demulsifikasi kimia gelombang berbantukan bahan kimia adalah menggunakan Rekabentuk Permukaan Berpusat Komposit (FCCCD) dan didapati Octylamine telah menggalakkan kesan yang unggul pada kadar demulsifikasi bagi pelbagai jenis emulsi, iaitu masa pendedahan (0.5-8) minit dan kuasa (270-360) watt adalah faktor yang paling penting di dalam pelbagai jenis emulsi, serta minyak A emulsi mentah memerlukan kuasa MW yang lebih tinggi untuk memisahkan kedua-dua fasa pada keadaan optimum. Berdasarkan kondisi optimal, kadar pemisahan emulsi dipercepatkan dengan mencapai pemisahan air lengkap untuk sebahagian besar jenis emulsi. Mencirikan penjanaan gelomtang mikro dan penyerapan pada kondisi optimum menunjukkan bahawa emulsi w / o dipanaskan secara seragam dan mendalam oleh gelombang mikro panjang dengan penggunaan tenaga yang lebih sedikit. Keputusan yang diperolehi di dalam tesis ini telah mendedahkan keupayaan gelombang mikro berbantukan teknologi kimia dalam demulsifikasi air kepada minyak emulsi. Kajian seterusnya diperlukan untuk memberikan pemahaman yang lebih mendalam mengenai mekanisme yang terlibat bagi memudahkan pembangunan sistem optimum yang sesuai dengan industri.

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LIST OF SYMBOLS

ε̈	dielectric constant
ὲ	dielectric loss
λ	wavelength
$\mathcal{D}_p$	penetration depth
Tan δ	loss tangent
q_{MW}	volume rate of heat generation
μ	viscosity
Dz	droplet size
Y	response (water separation rate)
β_0	interaction coefficient,
β_1	linear terms
β_{11}	quadratic terms,
A	processing time
B	microwave power
C	demulsifier concentration
R^2	coefficient of determination
ΔT	temperature increases
dt	time increases
f	frequency
C	light velocity
Cp	heating capacity
P	volumetric absorption of microwave
ρ	density
(dT/dt)	rate of temperature increases

LIST OF ABBREVIATIONS

w/o	Water-in- crude oil emulsion
o/w	Oil-in- water emulsion
w/o/w	Multiple emulsion
MWHT	Microwave heating technology
MW	Microwave
Crude A	Heavy crude oil
Crude B	Blended crude oil
SARA	Asphaltenes, Aromatic, Resins, and Saturated compounds
R/A	Resins to Asphaltenes ratio
ASTM	American Society for Testing and Materials
OCLC	Open-Column Liquid Chromatography
SG	Specific gravity
˚API	API gravity
DEA	Diethanolamide of coconut fatty acid
MEA	Monoethanolamine of coconut fatty acid
Span 80	Sorbitan Oleate
PEG 1000	Polyethelen Glycol 1000
PEG 600	Polyethelen Glycol 600
HLB	Hydrophilic-Lipophilic Balance
rpm	Rotational speeds (rotation per minute)
CMC	Critical Micelle Concentration
SFT	Surface Tension
IFT	Interfacial Tension

DOE	Design-Expert software
RSM	Response Surface Methodology
CCD	Central Composite Design
FCCCD	Faced Centered Central Composite Design
ANOVA	Analysis of variance
MHz	Mega Hertiz

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Petroleum or the “black gold” as known famously, in one form or another, has been used since ancient times, and is now important across society, including economy, politics, and technology. The rise in importance was mostly due to the invention of the internal combustion engine and the rise in commercial aviation (Hnasnidal et al., 2007). Crude oil is a complex mixture of hydrocarbons (the most commonly found molecules are alkanes, cycloalkanes, aromatic hydrocarbons, or more complicated chemicals like asphaltenes), with small amounts of sulphur, oxygen and nitrogen, as well as various metallic constituents, particularly vanadium, nickel, iron and copper (Speight, 1999). One of particular interest in the petroleum industry is the Asphaltenes component because of their depositions effect on production equipment such as tubulars in oil wells. In addition, asphaltenes impart high viscosity to crude oils, and negatively impacting production. The variances of the asphaltenes concentration in the crude oils within individual reservoirs create a myriad of production problems.

The world consumption of oil, according to the calculations made by the Organization of Petroleum Exporting Countries (OPEC, 2010), was about 79.6 million barrels per day in 2003 alone. The forecast was for an increase in consumption to almost 91 million barrels per day in 2010 and to 103 million barrels a day by 2020. Based on the same source, the world proven crude oil reserves stood at 1,074,850 million barrels (approximately 153 billion tones) at the end of 2001. Because of the great demand for oil and the existence of these large reserves, the production of crude oils has become an economist, not to mention political, a necessity for many nations.

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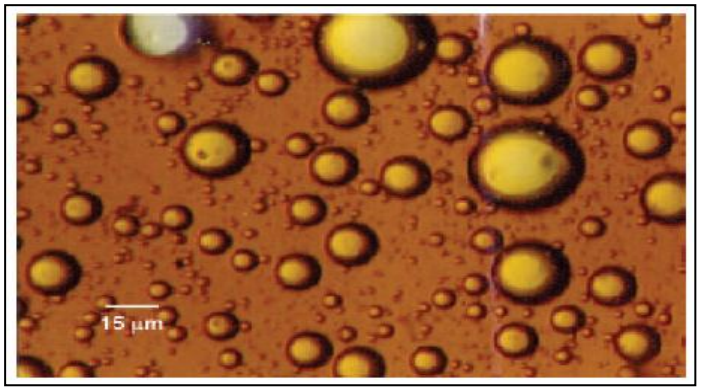

Figure 1.1: Photomicrograph of a water-in-oil emulsion

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Particularly, all w/o emulsion (perhaps with the exception of micro-emulsions) are physically stable but thermodynamically unstable. Nevertheless, the destabilization may take considerable time, and a stable emulsion is unable to resolve itself in a defined time period without some form of mechanical or chemical treatment. Destabilization or demulsification has been observed to reduce the interfacial viscosity (Kim et al., 1995). It is one of the most critical processes in chemical, metallurgical and food industries, where a large amount of liquid waste, including water-in-oil (w/o) and oil-in-water (o/w) emulsions, are frequently generated (Masato and Masahiro, 2008). Methods to induce phase separation in water-in-crude oil emulsions can be classified into three main categories: mechanical, electrical, and chemical (Borges et al., 2009).

Over the years, microwave energy is receiving an extensive attention from researchers for a wide spectrum of applications (Dumbaugh et al., 2001; Belanger et al., 2008). It's clean, inexpensive, and convenient method of heating, which often result in higher yields and shorter reaction times. The directly delivering energy to microwave-absorbing materials, complications such as long heat up periods, thermal gradients, and energy lost to the system environment can often be avoided, in addition to the advantage of the penetrating capacity of microwave as an alternative to conventional thermal-processing methods (Sateesh et al., 2010).

In this sense, demulsification of the petroleum emulsion using an efficient method is required for faster processing to improve the oil quality based on industry demand. Accordingly, the study suggests using the microwave heating method that could be a good solution due to the advantages of rapid, controlled, selective, and uniform heating effects.

1.2 PROBLEM STATEMENT

During the oil production operation, water is generally present in crude oil either because water is naturally exists in the reservoir, or intentionally introduced in order to enhance the production, or to maintain constant extraction pressure. Therefore, the crude oil extracted with high water content is in term of emulsion. All over the world, about

80% of exploited crude oils exist in an emulsion state that associated with the price reduction.

The more common emulsions in the petroleum industry are of the water-in-oil type (w/o) (Ese et al., 1997). The stability of such emulsions is very high due to the emulsion aging that tends to increase its stability as well as the presence of indigenous surface-active substance, mainly resins and asphaltenes in crude oil even in small amounts, it can cause huge problems for separation of water-in-oil emulsions as they gradually concentrate in the interfacial layer in separators as shown in Figure 1.2 (Mclean and Kilpatrik, 1997; Jones et al., 1987; Bridie et al., 1980). Therefore, for economic and operational reasons, the emulsified water must removed completely from the produced crude oil and breaking must be carried out as soon as possible in the production facility to reduce the water content at values generally below 1% to fulfill the quality criteria (Lisiane et al., 2009).

Figure 1.2: Asphaltenes deposited in the pipeline

The traditional method for emulsion breaking include high heat and chemical consumption. However, these methods are expensive and harmful to the environment when the chemical carried into the waste stream or follow the hydrocarbon into the refining. Since the discharge of emulsion to the dump site prohibited by regulation of the Malaysian Department of Environment (DOE) (1979). Hence, an efficient separation technique of emulsion is required for faster processing based on industrial demand to fit the requirement of discharge to public water safely and to enhance the demulsification efficiency.

1.3 SIGNIFICANCE OF THE STUDY

The study focused on the water-in-crude oil emulsion that found in the petroleum industry. It has attracted a specific attention of researchers over years, as they encountered in reservoirs, in the well bore, at the platform, in transportation systems and refineries. Typically, emulsion is undesirable and can result in high pumping costs, reduced throughput and special handling equipment. The removal of the extremely stable emulsified water from crude oil has been a major challenge to the petroleum industry worldwide.

In the last decades, Enhance Oil Recovery (EOR) methods have received considerable attention as the petroleum industry faces the challenge every day of resolving several types of emulsions to improve crude oil production from aging oil fields. The disadvantages of emulsion are catalyst fouling, high volume and viscosity than the crude oil that leads to severe downstream separation problems such as posing a severe problem for the equipment involved in recycling water, which consider a tough task for the companies to comply with legislation on permitted discharge limits as well as the difficulty in routine maintenance. This demand needs expense efficient emulsion separation equipment that leads to significant increase in the capital and operating cost as well as increase the cost of petroleum transportation and refining.

Various methods of demulsification and separation have been proposed to break down the emulsion, however, the physical and chemical methods including; heating, electrical, and ultrasonic have attracted the attention over the mechanical methods. However, heating with the addition of the chemicals “Thermal Chemical Method” and the electrical techniques are the most popular methods, but they have many disadvantages such as power-wasting, a large addition of the demulsifier, and the bad water quality associated with environmental pollution since the separated water may contain an excess chemical to be discharged to public water.

In recent years, Microwave Heating Technology (MWHT) has drawn much more attention as an advanced high frequency heating method that assures clean and efficient energy. The advantages of this new technology are: speed up the heating process

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

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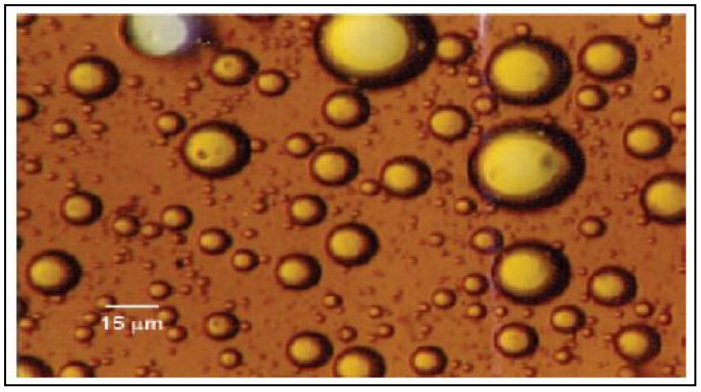

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CHAPTER THREE

MATERIALS AND METHODS

3.1 INTRODUCTION

This chapter describes and details the methods and approaches used in this study to achieve each specific objective. The study focus on four main parts: characterization of the oil samples, formation and characterization of the emulsion, destabilization (breaking) of the emulsion, in addition to optimizing the demulsification rate and the microwave parameters.

In Section 3.2, materials and chemicals that used during the experimental lab-work is presented. In Section 3.3 the general procedure adopted under the study scope is clarified. Section 3.4 detailed the main approaches that applied to identify and characterized the crude oil samples. In Section 3.5, the methods of emulsifier selection, emulsion preparation and examining, as well as the method of emulsion stability are highlighted. Section 3.6 represents the rheological study that used to characterize the water-in-crude oil emulsion. Section 3.7 detailed the methods of demulsification in term of chemical and thermal-assisted chemical approaches to break the water-in-oil emulsion. Finally, the experimental design and the statistical modeling using Design-Expert software is presented in Section 3.8 to identify and predict the optimal condition.

3.2 MATERIALS AND CHEMICALS

3.2.1 Crude Oil Samples

The research was conducted using two types of crude oil samples donated by PETRONAS Sdn. Bhd. (Kertih Kemaman and Melaka refinaries, Malaysia) for investigation. The crude oil samples were marked as crude oil A for the original crude as purchased from refinery without further treatment or dilution, whereas crude oil B that prepared by blending and homogenizing (60 vol.%) of sample A with (40 vol.%) of the second crude oil sample followed by filtration to remove the contaminants. The main task of blending the crude oil samples is to observe and evaluate the stability behavior of emulsion for different types of crude oil under similar processing conditions.

3.2.2 Chemicals

Three surfactants were used as an emulsifying agent to stabilize the w/o emulsion. These agents are; Sorbitan Oleate (Span 80), and Triton X-100, were purchased from MERK, Germany, whereas diethanolamide of coconut fatty acid (Cocamide DEA), was purchased from Shanghai Sunny Scientific Collaboration Co., Limited, China. Some other surfactants were used as a demulsifying agent to break the w/o emulsion. These agents are; Cocamine MEA, Octylamine, Polyhydric alcohol (PEG 1000, and 600) were supplied by MERK, Germany, while Hexylamine was supplied by Sigma-Aldrich, USA. Other chemicals used in this research, such as solvents used in the SARA method of analysis, are summarized in Table 3.1

Table 3.1: Chemical used in research

Chemical	Properties	Supplier
n-Hexen	Assay 99%	R&M Chemicals, Essex,UK
Toluene	Assay 99.5%	MERK, Germany
Fumed silica	Particle size 0.014µ, surface area 200m^2 /g	Sigma-Aldrich, USA
Methanol	99.8%	MERK, Germany

3.3 GENERAL PROCEDURE

The experimental methods are carried out according to the flow diagram presented in Figure 3.1.

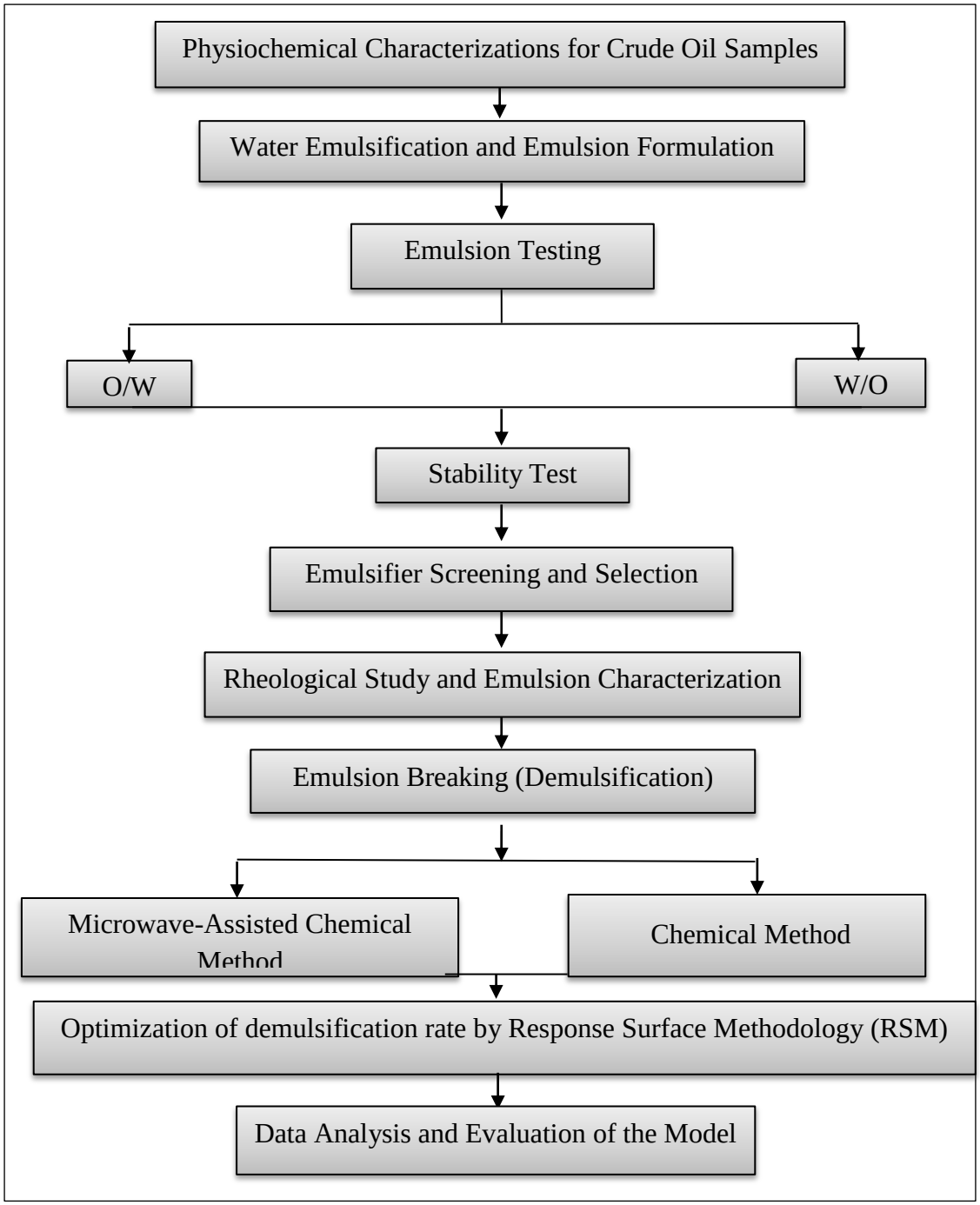

Figure 3.1: A complete flow diagram of the research methodology for experimental studies