ELUCIDATION OF PHYSIO-CHEMICAL CHARACHTERIZATION OF ULTRASONIC CHEMICALLY DEMULSIFIED CRUDE OIL

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ABSTRACT

Formation of emulsions during oil production and processing is a costly problem, both in terms of chemicals used and production losses. It is necessary to separate the water completely from the crude oils before transporting to refinery. Traditional ways of breaking emulsions using heat and chemicals are disadvantageous from both economic and environmental perspectives. In this thesis, an alternative and multiple frequency energy potential of ultrasonic-assisted chemicals (environmental friendly) in demulsification of water-in-crude oil emulsions were utilized and investigated. Two types of crude oils were used namely; (Tapis and Miri crude oils). The study begun with some characterization studies to provide understanding of fundamental issues such as formation, formulation and breaking of emulsions by both chemicals and ultrasonic approaches. The aim was to obtain optimized operating conditions as well as fundamental understanding of water-in-oil stability, upon which further development of the demulsification process could be developed. The stability studies were carried out by analyzing operating conditions such as surfactant concentration, surfactant type, oil type, temperature and water-oil ratio (30-50%). For stability performance test, four emulsifiers were used namely; Triton X-100, Span 83, Cocamide DEA and SDDS. It was found that there exist a correlation between these factors and emulsion stability. Among these, emulsion stabilized by cocamide DEA was the best and followed by Span 83, SDDS and Triton X-100 respectively. For chemical emulsification performance test, five types of demulsifies with different functional groups were utilized; these are Hexylamine, Dioctylamine, Cocamine, Polyethylene Glycol, PEG 1000 and PEG 600. Among these; Hexylamine was found to be the best in separating water and oil from emulsions (88%) and followed by cocamine (81%), Dioctylamine (79%), PEG 1000 (76%) and PEG 600 (70%). For ultrasonic forces (3, 5, 7 and 9) applied for emulsion breaking, results were significantly enhanced the separation time and amount of water separated. Results showed that, ultrasonic power, 9 and Hexylamine (1.0%) in demulsifying the crude oil A stabilized by Span 83 with maximum water separation of 96% after 150 min. Also, and within the same operating conditions mentioned above, a maximum water separation up to 99% was achieved with crude oil B. The other investigated demulsifiers with ultrasonic force showed also high water separation percentages such as cocamine (1.0%) emulsifier with 91% and 93% for crude oils A and B emulsions respectively. The results obtained in this thesis have exposed the capability of ultrasonic-assisted chemicals technology in demulsification of W/O emulsions. Further works are nevertheless required to provide deeper understanding of the mechanisms involved to facilitate the development of an optimum system applicable to the industry.

ABSTRAK

Pembentukan emulsi semasa pengeluaran dan pemprosesan minyak adalah isu yang kritikal dari segi penggunaan bahan kimia dan masalah kerugian pengeluaran. Langkah pemisahan air yang menyeluruh daripada minyak mentah adalah penting sebelum dibawa ke kilang penapisan. Cara-cara tradisional untuk pengasingan emulsi menggunakan haba dan bahan kimia tidak effisyen dari segi ekonomi dan alam sekitar. Tesis ini mengandungi alternatif dan pelbagai frekuensi tenaga potensi daripada bantuan bahan kimia ultrasonik (mesra alam sekitar) dalam proses pengasingan emulsi air daripada minyak mentah yang telah dikaji dan diaplikasikan. Dua jenis minyak mentah iaitu minyak mentah dari Tapis dan Miri telah digunakan. Kajian ini telah dimulakan dengan penyelidikan ciri-ciri supaya isu-isu asas seperti pembentukan, fomulasi dan pengasingan emulsi dapat difahami menggunakan kaedah bahan kimia dan ultrasonik. Objektif kajian ini adalah untuk memperolehi kondisi optimum serta perfahaman yang mendalam tentang kestabilan air dalam minyak agar kaijan proses pemisahan dapat diperkembangkan lanjut. Penyelidikan stabiliti dijalankan dengan menganalisa keadaan operasi seperti kepekatan surfaktan, jenis surfaktan, jenis minyak, suhu dan nisbah air-minyak (30-50%). Pengemulsi seperti Triton X-100, Span 83, Cocamide DEA dan SDDS telah digunakan bagi mengaji prestasi kestabilan. Kajian telah menunjukkan hubung kait antara faktor-faktor ini dengan kestabilan emulsi. Cocamide DEA adalah yang terbaik di antara emulsi-emulsi yang lain diikuti dengan Span 83, SDDS dan Triton X-100. Terdapat 5 jenis pengasing emulsi yang digunakan untuk kajian pengemulsian bahan kimia. Antaranya adalah Hexylamine, Dioctylamine, Cocamine, Polyethylene Glycol, PEG 1000 dan PEG 600. Kajian ini juga megesahkan bahawa Hexylamine adalah bahan kimia terbaik untuk mengasingkan air daripada minyak (88%), diikuti dengan cocamine (81%), Dioctylamine (79%), PEG 1000 (76%) dan PEG 600 (70%). Keputusan signifikan telah dipertingkatkan dari segi jarak masa dan kuantiti air yang diasingkan dengan menggunakan tenaga ultrasonic (3, 5, 7 dan 9). Selepas 150 min , penceraian maksimum sebanyak 96% telah dicapai dengan aplikasi tenaga ultrasonik 9 dan Hexylamine (1.0%) di dalam proses pengasingan minyak mentah A yang distabilkan oleh Span 83, manakala bagi minyak mentah B adalah sebanyak 99%. Kajian juga menunjukkan peratusan tinggi pengasingan air seperti cocamine (1.0%) dengan 91% dan 93% menggunakkan tenaga ultrasonik untuk emulsi minyak mentah A dan B. Keputusan yang diperoleh daripada kajian ini telah membantu untuk mendedahkan keupayaan teknologi bantuan kimia ultrasonik dalam pengasingan air/minyak emulsi, lantaran memberi kefahaman yang mendalam atas mekanisme yang terlibat untuk membantu dalam perkembangan optimum sistem dalam industri.

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M	Meter
μ_r	Emulsion relative viscosity
μ_e	Emulsion viscosity
μ_o	Continouse phase viscosity
Ø	Disperesed phase volume fraction
K2	Disperesed phase concentration
K	Ratio of dispersed to continouse phases
$\%W_s$	Percentage water separation
V_{ws}	Volume of watewr separated
V_i	Initial water volume in emulsion
TE%	Percentage of time enhancement
T_b	Separation time for lower demulsifier concentration
T_a	Separation time for higher demulsifier concentration
W_{sb}	Maximum water separation at lower concentration
Wsa	Maximum water separation at higher concentration
h	Hours

LIST OF ABBREVIATIONS

W/O	Water in oil emulsion
O/O	Oil in oil emulsion
O/W	Oil in water emulsion
ME	Membrane emulsification
TAN	Total acid number
IFT	Interfacial tension
R/A	Resine to asphaltenes ratio
HLB	Hydrophil-Lipophil balance
CMC	Critical micceler concentration
PPO	Polypropylene –block-Polypropylene oxide

PEO	Polypropylene –block-Polyethylene oxide
SDS	Sodium Dodecylesufate
DSC	Differential Scanner Calorimeter
RSM	Response surface Methodology
LSWR	Low sulfer wax residue
DTAB	Dodecyltrimethylammonium bromide
SPG	Shirasa-porouse-glass
TOC	Total organic carbon concentration
OI	Operational index
TMP	Trous membrane pressure
PVDF	Hydrophilic polyvinyldene difluoride
PES	Polyether sulfate
MWCO	Molecular weight cut off

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The emulsion can be defined as the dispersion (suspension) of one liquid into another immiscible liquid in the form of droplets with the aid of surface active agents. Crude oil is rarely produced alone in commercial oil wells because most of the time it is combined with water in an emulsion form. Emulsions can be formed during almost all stages of crude oil production, starting with the deep oil wells, wellbores, and wellheads; at wet-crude handling facilities, during transportation through pipelines, and petroleum processing. The separation of the water from the crude oil emulsions is an initial step in any crude oil production and processing facility to control the quality of the final product. A good understanding of petroleum emulsions is necessary in order to control and enhance processes at all these stages.

Crude oil emulsions can be classified into three main categories, namely:

1- Week emulsions: where the water is separated within a few minutes of production.
2- Medium emulsions: where the water requires more time than the week emulsions to separate.
3- Tight emulsions: where the water is not separated completely even after a few days.

Generally speaking, emulsions are kinetically stable (stable over a period of time) because there is a natural driving force for the suspended droplets forming the emulsion to colloid and separate in a single phase. The behaviour of emulsions is mainly controlled by the properties of the adsorbed layers which stabilise the oil-water surfaces. The complexity of petroleum emulsions stems from the oil composition in terms of surface-active molecules (surfactants) contained in the crude, such as low molecular weight fatty acids, naphthenic acids and asphaltenes. These surfactants suppress the mechanisms involved in sedimentation, aggregation, coalescence, and phase inversion that would otherwise break down an emulsion.

The emulsion's stability is controlled by a large number of factors such as the solid's content (asphaltenes, waxes, clays, etc.), operation temperature, droplet size and distribution and the ph of the water. The surfactant type (anionic, cationic, amphoteric or non-ionic) also plays a major role in the emulsion formation process and will significantly control the stability of the emulsion and the tendency of the water layer to separate. All of these factors must be taken under consideration in order to achieve an efficient and effective water separation process (Demulsification).

Demulsification (emulsion breaking) is needed in many practical applications such as the petroleum industry, environment technology, and waste-water treatment. Demulsification is the process whereby water is separated from crude oil. Depending on the crude oil emulsion type, a suitable demulsification process is needed so as to ensure a highly efficient as well as low cost emulsion breaking process.

Currently, water-crude oil emulsions are typically destabilised through the use of chemical demulsifiers. The chemical structure of these demulsifiers is usually based on alkylphenol formaldehyde ethoxylated resins. These chemical demulsifiers are effective, but, unfortunately, are now believed to be endocrine disrupters, and thus it is likely that they may be banned by various national environmental protection agencies (Zaki, *et al.*, 1996, 1997, 1998).

Other means of destabilising asphaltene-stabilised W/O emulsions include thermal pressurisation and rapid depressurisation (Ohsol *et al.*, 1999), electrostatic droplet shattering and coalescence. Both of these methods are established around efforts at "cracking" or "disrupting" the rigid, viscoelastic film of asphaltenes which forms around the water droplets. One problem with these methods is the reformation of stabilised water droplets due to readsorption of displaced or "disrupted" asphaltenic film fragments in shear fields under solvent conditions at which the asphaltenes are capable of reassembly (Hart, 1997; Mitchell, 1998).

The present work will present and evaluate a new demulsification technique using ultrasonic force. Four different types of emulsifiers will be used in the formation of crude oil emulsions, namely Triton-X, Span 83, SDDS and Cocoamide. The Cocoamide is applied for the first time as an emulsifier in the crude oil emulsions. The most stable emulsions will be selected and tested for the demulsification processes. Two methods of demulsification process will be adopted, namely the chemically-assisted demulsification process and the Ultrasonic-chemically-assisted demulsification process. The chemically-assisted demulsification process will be adopted with different types of demulsifiers, including Hexylamin, Octylamine, Polyethylene Glycole (600 and 1000), and Cocamine. Cocamine is used for the first time as an alternative environmental friendly demulsification agent. The Ultrasonic-chemically-assisted demulsification process will be applied to the same emulsion and a comparison of the water separation performances will be conducted.

1.2 PROBLEM STATEMENT

Most of the crude oils produced from the oil wells are in the form of emulsions. Generally speaking, crude oil emulsions do exist in the form of oil-in-water (O/W) or water-in-oil (W/O) formation whilst on other occasions it will be in a more complex form such as water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O). Indeed, this depends on the operation factors, including type of emulsifier and the mixing intensity.

Oilfield crude oil usually contains natural emulsifiers which stabilise the emulsion and include surface active agents (surfactants) and fine solids. The value of any crude oil is highly dependent on the type and the tightness of the emulsion formed, which in turn depends on the type of natural emulsifier involved. This is why the price of crude oil varies from country to country. Indeed, the natural emulsifiers usually exist in the heavy fraction of the crude oil. The emulsification intensity of the natural emulsifiers is significantly controlled by the type of crude oil, i.e. different crude oils will have different amounts of heavy components. At a glance, crude oil emulsions with low amounts of natural emulsifier will result in a weak emulsion which can be separated easily whilst other crudes which contain the right type and amount of emulsifier, will result in a very stable emulsion. Artificial emulsifiers are more often used to maintain the emulsion structure and stability during the production of crude oil from the oil wells as well as during the transportation of these crude oils through pipelines. Crude oil emulsions form when oil and water (brine) come into contact with each other, when there is sufficient mixing, and when an emulsifying agent or emulsifier is present. Different types of artificial emulsifying agent exist (mostly anionic and non-ionic surfactants) and are applied commercially in different oil fields depending on the type of crude oil produced. Most of these surfactants are not environmental friendly and their emulsification efficiency can be controlled by operation conditions including pressure, temperature and mixing intensity. Indeed, a more environmental friendly additive is needed. In the present work, natural and environmental friendly emulsifying agents are introduced for the first time in the form of Cocoamide emulsifiers.

One of the key factors controlling crude oil value in the market is the speed and efficiency of water separation in the refining facility. This water separation process is called “Demulsification”. Traditionally, the separation of water from crude oil emulsion is achieved using any, or a combination, of different methods such as the addition of chemical demulsifiers, increasing the temperature of the emulsion, applying electrostatic fields which promote coalescence or lowering the crude oil speed to allow for gravitational separation. Choosing one or more separation processes depends on the type and tightness of the emulsion. Beside the advantages of these methods, several disadvantages also emerge, including the high cost of the chemical demulsifiers involved and the long period of time needed to complete the separation. In addition, most of the demulsifiers used are artificial, chemical, and not environmental friendly. This is why an environmental friendly demulsification agent together with a more efficient and less time consuming demulsification technique are needed. In the present work, ultrasonic force will be utilised to enhance the chemically-assisted demulsification process. A comparison between the water separation performances will be conducted with and without the use of the ultrasonic force to determine its effect in terms of enhancing the water separation and demulsification time.

1.3 OBJECTIVES OF RESEARCH

The objectives of this research are:

1. To evaluate the performance of ultrasonic-assisted chemicals as and alternative and cost effective method for demulsification of crude oil emulsions.
2. To examine and evaluate the performance of a new environmental friendly Cocamide DEA as stabilizer for crude oil emulsions.
3. To introduce Cocamine as a new and environmental friendly chemical for separation of crude oil emulsions.
4. To optimize and analyze the overall potentials of ultrasonic-assisted chemicals demulsification method as an alternative to the conventional chemical demulsification method in demulsifying water-in-oil emulsions.
5. To evaluate the rheological characteristics and stability of W/O emulsions formulated from two different crude oils.

SCOPES OF RESEARCH

1. Characterization of oil and aqueous phases:

Different emulsions are prepared using different operating and emulsification factors such as:

a. Crude oil type; two types of crude oil are investigated (Tapis and Miri crude oils blends) with two blending percentages (30%-70% and 50%-50%).

b. Water cut percentages; to form emulsions the water will be introduce to the crude oil with three different percentages (30, 40 and 50 Vol.%).

c. Emulsifier type; four types of emulsifying agent will be investigated, namely Triton-X100, SDDS, Span83 and Cocamide DEA.