FORMATION OF WATER IN CRUDE OIL EMULSIONS AND MICROWAVE-ASSISTED CHEMICAL DEMULSIFICATION

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Thesis submitted in fulfillment of the requirements for the award of the degree of Master of Engineering (Chemical)

Faculty of Chemical and Natural Resources Engineering

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JUNE 2016

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LIST OF SYMBOLS

Cp	Heating capacity
η	Viscosity
Ƭ	Shear stress
γ	Shear rate
V	Sedimentation velocity
R	Particle radius
ρ	Density
g	Force
Qmw	Volume rate of heat generation
dT/dt	Rate of temperature increase
Ø	Phase content
ε	Relative permitivity
έ	Dielectric constant
ε̋	Dielectric loss
tan δ	Loss factor
T	Temperature
λ	Wavelength
λo	Wavelength in free space
Dp	Penetration depth
Ƒ	Frequency
Y	Response
β_0	Constant term
β_i	Coefficient of linear factor
β_{ii}	Coefficient of quadratic parameter
β_{ij}	Coefficient of interaction parameters
K	Number of variables
T_0	Room temperature

LIST OF ABBREVIATIONS

DEA	Diethanolamide of coconut fatty acid
LSWR	Low sulphur wax residue
Span 80	Sorbitan Oleate
PEG 600	polyethylene glycol
Span 83	Sorbitan sesquiester
W/O	Water-in-oil emulsion
O/W	Oil-in-water emulsion
W/O/W	Water-in-oil-in-water emulsion
MWHT	Microwave heating technology
Mw	Microwave
SARA	Saturate, Aromatic, Resin, Asphaltene
RSM	Response Surface Methodology
HLB	Hydrophilic-lipophilic balance
PAH	Polycyclic aromatic hydrocarbons
PAC	Polycyclic aromatic compounds
HPV	High production volume
TBP	True boiling point
HPLC	High performance liquid chromatography
GC	Gas chromatography
TLC-FID	Thin layer chromatography with flame ionization detection
API	American petroleum institute
ASTM	American society for testing materials
SI	International system
IFT	Interfacial tension
CMC	Critical micelle concentration
FCC	Federal communications commission
ELM	Emulsion liquid membrane
KF	Karl fisher
OCLC	Open-column liquid chromatography
DCM	Dichloromethane
CCD	Central composite design

FCCD	Face centered composite design
Vol	Volume
ANOVA	Analysis of variance
R/A	Resin asphaltene ratio

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ABSTRACT

With the increasing energy prices and the drive to reduce CO_2 emissions, universities and industries are challenged to find new technologies in order to reduce energy consumption, to meet legal requirements on emissions, and for cost reduction and increased quality. Formation of emulsions during oil production and processing is a costly problem, both in terms of chemicals used and production losses. In this thesis, an alternative and cost effective microwave heating technology in demulsification of water-in-crude oil (W/O) emulsions was utilized and investigated. Two different types of Malaysian crude oils namely; heavy and light were mixed together at a volume ratio of (50-50%). The experimental studies began with some important physical and chemical characterizations of crude oil such as density, viscosity, shear rate, shear stress, water content, pour point, interfacial properties, and chemical fractionation of saturates, aromatics, resins, and asphaltenes (SARA), respectively, to provide understanding of fundamental issues such as formation, formulation and breaking of emulsions by chemicals, microwave approaches, and conventional heating. The aim was to obtain the best conditions as well as fundamental understanding of water-in-oil stability, upon which further development on demulsification process could be developed. The stability studies were carried out by analyzing operating conditions such as emulsifier concentration (1.5-2.5 vol.%), emulsifier type, and water-oil ratio of (20-80%), (30-70%), and (40-60%). For stability performance test, five emulsifiers were used namely; Span 80, Span 83, Triton X-100, DEA and low Sulphur wax residue (LSWR). Among these, emulsion stabilized by Span 80 was the best for emulsion stability because it produced the emulsions with smallest size of droplets. For emulsion demulsification performance test, three methods were used which are; chemicals, microwave assisted chemicals and conventional method (hot plate). For chemical demulsification test, four demulsifiers with different concentrations (1.5-2.5 vol%) and functional groups were utilized; which are: Octylamine, Hexylamine, Dioctylamine, and Polyethylene Glycol (PEG 600). Among these, Octylamine was found to be the best in separating water and oil from emulsions due to its lower molecular size. For microwave factorial analysis, three factors namely; processing time (1-5 minutes), microwave power (180-540 watt), and demulsifier concentration (1.5-2.5vol.%) using face centered composite design (FCCD) under RSM were employed. The evaluation of microwave demulsification indicated that for microwave heating demulsification the best condition for water separation efficiency was achieved at 3 (minutes), 360 (watt), and 2.50 vol. %. Whereas, the separation efficiency reached at 100 % within 24 hours in emulsion with 40 % water content. The best condition for conventional heating demulsification using FCCD and processing parameters of time (1-5 minutes), temperature (30-160˚C), and demulsifier concentration (1.5-2.5 vol.%) was obtained at 5 minutes, 160˚C, and 1.5 vol.%, where it reached to 96 % within 36 hours in emulsion with 40 % water. The results obtained in this thesis have exposed the capability of microwave-assisted chemical technology in 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

Dengan harga tenaga yang semakin meningkat dan pemacu untuk mengurangkan pelepasan CO_2, universiti dan industri telah dicabar untuk mencari teknologi baru untuk mengurangkan penggunaan tenaga, untuk memenuhi keperluan undang-undang pelepasan dan pengurangan kos dan peningkatan kualiti. Pembentukkan emulsi semasa pengeluaran minyak dan pemprosesan adalah satu masalah yang mahal, baik dari segi penggunaan bahan kimia dan kerugian dalam pengeluaran. Dalam kajian ini, satu alternatif dan kos teknologi gelombang mikro pemanas dalam demulsifikasi yang berkesan dari air-dalam-minyak mentah (W/O) emulsi telah digunakan dan dikaji. Dua jenis minyak mentah yang berbeza dari Malaysia iaitu; berat dan ringan telah dicampur bersama-sama pada nisbah isipadu (50-50%). Kajian eksperimen telah dimulakan dengan beberapa ciri fizikal penting dan sifat kimia minyak mentah seperti ketumpatan, kelikatan, kadar ricih, tekanan ricih, kandungan air, titik tuang, sifat-sifat antara muka dan pemecahan kimia dari tepu, aromatik, resin dan *asphaltenes*, masing-masing untuk memberi kefahaman mengenai isu-isu asas seperti pembentukan, perumusan dan pemecahan emulsi oleh bahan kimia, pendekatan ketuhar gelombang mikro dan pemanas konvensional. Tujuannya adalah untuk mendapatkan parameter terbaik serta kefahaman asas akan kestabilan air-dalam-minyak, yang mana lagi perkembangan pemprosesan demulsifikasi boleh dibangunkan. Kajian kestabilan ini telah dijalankan dengan menganalisis keadaan operasi seperti kepekatan pengemulsi (1.5-2.5 isipadu%), jenis pengemulsi dan nisbah air-minyak ialah (20-80%), (30-70%), dan (40-60%). Bagi ujian prestasi kestabilan, lima pengemulsi telah digunakan iaitu; Span 80, Span 83, Triton X-100, DEA dan low Sulphur wax residue (LSWR). Antaranya, kestabilan emulsi oleh Span 80 adalah yang terbaik untuk kestabilan emulsi kerana ia menghasilkan emulsi titisan yang paling kecil. Bagi ujian prestasi demulsifikasi emulsi, tiga kaedah yang telah digunakan iaitu; bahan kimia, gelombang mikro bantuan bahan kimia dan kaedah konvensional (plat panas). Untuk ujian kimia demulsifikasi, empat demulsifer dengan kepekatan yang berbeza (1.5-2.5 isipadu %) dan kumpulan fungsian digunakan; antaranya ialah: Oktilamina, Heksilamina, Dioktilamina, dan Polietilena glikol (PEG 600). Dikalangan ini, Oktilamina telah ditemui sebagai yang terbaik dalam pengasingan air dan minyak dari emulsi. Bagi Analisis Faktor ketuhar gelombang mikro, tiga faktor iaitu; pemprosesan masa (1-5 minit), kuasa gelombang mikro (180-540 watt) dan kepekatan demulsifer (1.5-2.5 isipadu%) dengan menggunakan Face Centered Composite Design (FCCD) di bawah RSM telah digunakan. Penilaian gelombang mikro demulsifikasi menyatakan bahawa parameter terbaik bagi ketuhar gelombang mikro pemanas demulsifikasi untuk kecekapan air pemisah telah dicapai pada 3 (minit), 360 (watt) dan 2.50% isipadu. Manakala, kecekapan pemisahan dalam emulsi telah mencapai 100% dalam masa 24 jam dengan 40% kandungan air. Parameter terbaik bagi demulsifikasi pemanas konvensional dengan menggunakan FCCD dan pemprosesan parameter masa (1-5 minit), suhu (30-160˚C), dan kepekatan demulsifer (1.5-2.5 isipadu%) telah diperolehi pada 5 minit, 160˚C dan 1.5 isipadu%, di mana ia sampai ke 96% dalam tempoh 36 jam dalam emulsi dengan 40% air. Keputusan yang diperolehi dalam kajian ini telah menunjukkan keupayaan teknologi kimia yang dibantu ketuhar gelombang mikro dalam demulsifikasi W/O emulsi, kerja-kerja selanjutnya, namun perlu untuk menyediakan pemahaman yang lebih mendalam daripada mekanisme yang terlibat bagi memudahkan perkembangan sistem optimum yang berkaitan dengan industri.