



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Chemical Demulsification of Water-in-Crude Oil Emulsions

Abdurahman, H. Nour, Rosli Mohd Yunus and Zulkifly Jemaat
Faculty of Chemical and Natural Resources Engineering,
Universiti Teknologi Malaysia, 81310 Skudai, Johor-Malaysia

Abstract: Demulsification (emulsion breaking) is necessary in many practical applications such as the petroleum industry, painting and waste-water treatment in environmental technology. Chemical demulsification is the most widely applied method of treating water-in-crude oil emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The effect of chemical demulsification operations on the stability and properties of water-in-crude oil emulsions was assessed experimentally. In this regard, Amine Demulsifier, Polyhydric Alcohol, Acid and Polymeric demulsifiers were used. Using samples of w/o, the data presented for several commercial-type demulsifiers show a strong connection (correlation) between good performance (fast coalescence) and the demulsifiers. The relative rates of water separation were characterized via beaker tests. The amine group demulsifiers promoted best coalescence of droplets. In contrast, polymeric demulsifier group is the least in water separation.

Key words: Demulsification, efficiency, w/o emulsion, coalescence, chemicals

INTRODUCTION

The breaking of emulsions (demulsification) is necessary in many applications such as environmental technology, painting, petroleum industry and waste-water treatments. Methods currently available for demulsification can be broadly classified as chemical, electrical and mechanical. Chemical demulsification is the most widely applied method of treating water-in-oil and oil-in-water emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The formulation of an emulsion demulsifier for a specific petroleum emulsion is a complicated undertaking. In petroleum system, asphaltenes and resinous substances comprise a major portion of the interfacially active components of the oil (Sjoblom *et al.*, 1992; Johansen *et al.*, 1989; Urdahl *et al.*, 1992; Corbett and Petrossi, 1978; Shiffert *et al.*, 1984).

Asphaltenes and resinous are large polyaromatic and polycyclic condensed ring compounds containing heteroatoms Urdahl *et al.* (1992) and Moschopedis *et al.* (1976). Chemically, asphaltenes and resins are represent the pentane or hexane insoluble portion of the oil Anderson and Bird, (1990, 1991), Moschopedis *et al.* (1976) and Ferworn *et al.* (1993). Understanding and controlling demulsification is of primary importance for breaking waste emulsions and for using emulsions in industrial processes that require emulsion destabilization

as a main step. Anklam (1997) reported that in the oil industry water comes into contact with crude oil on many occasions, creating emulsions stabilized by various components in the oil, including the asphaltenes and resins. At drilling site, the recovered oil will contain some water and hydrophilic impurities which need to be removed before shipping and processing. The water concentration may vary, but a target specification for water and sediments removal may be 1% or less (Rowan, 1992).

There are many procedures for the neutralization and reduction of the emulsifying agent has been used, for example, Hennessey *et al.* (1995) are used the gravity separation, while electrostatic coalescence has used by Bailes *et al.* (1997). Also centrifugal and filtration methods mentioned by Lissant (1983) as techniques used for breaking the emulsion.

This research conducted to study the influence of chemical demulsifiers on the destabilization of emulsions. Experimental results showed a strong connection (correlation) between good performance (fast coalescence) and the demulsifiers.

MATERIALS AND METHODS

In this study, four chemical demulsifiers; Amine groups, Polyhydric Alcohol, Acid and Polymeric demulsifiers were used for water-in-crude oil emulsions

demulsification. A 900 mL graduated cylindrical glass was used as sample container.

Sample preparations and procedures: The crude oil samples were obtained from Petronas Refinery. A detailed procedure for the w/o emulsion preparation and their procedures, including the formulation of w/o emulsion, their characteristics and the method of preparation is thoroughly described in a previous research by Abdurahman *et al.* (2006). Here the study merely describes the main steps of the experimental procedure. Water-in-crude oil emulsions were prepared at room temperature with a standard three blade propeller at speed of 1800 rpm. For w/o preparations, distilled water was used as the water phase (dispersed phase) and crude oil as oil phase (continuous phase). The surfactants used in this study for emulsion formulation and stabilization were; Low Sulfur Wax Residue (LSWR) and Triton X-100. The emulsifying agents were used as received without further dilution. For chemical demulsification performance study, water-in-crude oil emulsions were prepared and tested. Four

groups of demulsifiers with different functional groups were utilized in this paper namely, polymeric, polyhydric alcohols, amines and sulphonate groups, respectively. Demulsifiers used were listed in Table 1. The water separation in percent was calculated as separation efficiency (e) from volume of water observed in the beaker as follows:

$$(\% \text{ water separated (e)}) = \frac{\text{Volume of separated water, mL}}{\text{Original volume of water in the emulsion, mL}} \times 100 \quad (1)$$

The prepared emulsion was used to check for w/o or o/w emulsions. All emulsions investigated were found w/o emulsion (oil continuous). Table 2 and 3 show the effect of amine group demulsifiers on crude oil emulsion stability (% of water and oil separation v/v), respectively.

Table 1: The demulsifiers and their concentrations which were used in emulsions demulsification tests

| Group | Demulsifier | Concentration (mole/l) | HLB Number |
|------------------------|--|------------------------|------------|
| A/ Polymeric | Polyethylene block PEG | 800 | 8.30 |
| | Poly PO terminated | 800 | 7.32 |
| | Polyethylene Oxide (PEO) 600,000 | 0.2485 | 8.80 |
| | Polyethylene Oxide (PEO) 1000,000 | 0.2485 | 8.88 |
| B/ Polyhydric alcohols | Polyethylene glycol (PEG) 600 | 0.2485 | 13.20 |
| | Ethylene glycol (EG) | 0.2485 | 9.85 |
| | Propylene glycol (PG) | 0.2485 | 9.40 |
| | Polyethylene glycol (PEG) 1000 | 0.2485 | 16.00 |
| C/ Amines | Hexylamine | 0.2485 | 6.98 |
| | Trioctylamine | 0.2485 | 5.00 |
| | Dioctylamine | 0.2485 | 6.75 |
| | Octylamine | 0.2485 | 6.88 |
| | Pentylamine | 0.2485 | 6.87 |
| | Propylamine | 0.2485 | 6.86 |
| D/ Sulphonate | Decylamine | 0.2485 | 6.93 |
| | Sodium di-2-ethylhexyl sulphosuccinate (AOT) | 0.0013 | 13.65 |
| | Dodecyl benzene sulphonic acid (DBSA) | 0.0013 | 7.35 |
| | Sodium dodecyl benzene sulphonic (NaDBS) | 0.0013 | |

Table 2: Effect of amine group demulsifiers on crude oil emulsion stability (%water separation v/v)

| Time (min) | Decyl-amine (%) | Octyl-amine (%) | Hexyl-amine (%) | Pentyl-amine (%) | Dioctyl-amine (%) | Trioctyl-amine (%) | Propyl-amine (%) |
|------------|-----------------|-----------------|-----------------|------------------|-------------------|--------------------|------------------|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 85 | 12 | 8 | 6 | 4 | 3 | 0 | 0 |
| 193 | 12 | 10 | 8 | 6 | 4 | 2 | 0 |
| 347 | 16 | 16 | 12 | 9 | 6 | 4 | 1 |
| 490 | 23 | 22 | 18 | 12 | 9 | 6 | 3 |
| 656 | 34 | 30 | 27 | 18 | 13 | 9 | 5 |
| 800 | 36 | 41 | 38 | 27 | 19 | 11 | 8 |
| 880 | 51 | 55 | 49 | 38 | 28 | 15 | 11 |
| 937 | 68 | 62 | 59 | 46 | 34 | 22 | 15 |
| 1050 | 78 | 67 | 64 | 57 | 46 | 30 | 25 |
| 1333 | 80 | 67 | 64 | 57 | 44 | 30 | 28 |
| 1600 | 80 | 68 | 64 | 58 | 43 | 31 | 25 |
| 1800 | 80 | 67 | 64 | 57 | 43 | 30 | 25 |

Table 3: Effect of amine group demulsifiers on crude oil emulsion stability (%oil separation v/v)

| Time (min) | Decyl-amine (%) | Octyl-amine (%) | Hexyl-amine (%) | Pentyl-amine (%) | Dioctyl-amine (%) | Trioctyl-amine (%) | Propyl-amine (%) |
|------------|-----------------|-----------------|-----------------|------------------|-------------------|--------------------|------------------|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 85 | 15 | 11 | 8 | 5 | 6 | 3 | 1 |
| 193 | 23 | 19 | 16 | 11 | 7 | 6 | 2 |
| 347 | 31 | 28 | 25 | 17 | 12 | 9 | 6 |
| 490 | 44 | 36 | 31 | 27 | 21 | 13 | 10 |
| 620 | 57 | 47 | 43 | 36 | 30 | 23 | 18 |
| 687 | 65 | 58 | 52 | 43 | 36 | 29 | 23 |
| 733 | 73 | 66 | 60 | 50 | 42 | 37 | 29 |
| 937 | 84 | 73 | 69 | 61 | 54 | 43 | 38 |
| 1050 | 86 | 75 | 74 | 68 | 58 | 47 | 39 |
| 1333 | 87 | 77 | 74 | 68 | 58 | 47 | 39 |
| 1600 | 87 | 77 | 74 | 68 | 58 | 47 | 39 |
| 1800 | 87 | 77 | 74 | 68 | 58 | 47 | 39 |

RESULTS AND DISCUSSION

Figure 1-3 shown some typical results of demulsification experiments conducted to test the influence and performance of the amine group demulsifiers on the crude oil emulsion stability. The stability of the emulsions was determined visually by measuring the water and oil separation from emulsions at 30°C as a function of time. After about 2% of amine, the separation of water and oil are stagnates. Figure 1 and 2 shows separation of water and oil from water-in-oil emulsions as a function of time, respectively. As shown in Fig. 1 and 2, all amine groups showed the water and oil separations. This could be attributed to a very specific interaction between the amine added and the naturally occurring constituents in the interfacial film.

As shown in Fig. 1, after 85 min, the amount of water separated from the emulsion for decylamine, octylamine, hexylamine, pentylamine and dioctylamine were found as 12, 8, 6, 4 and 3%, respectively. After a prolonged duration (1085 min), decylamine separated highest percentage of water separation (80%), followed by octylamine (67%), hexylamine (64%), pentylamine (57%), dioctylamine (43%), trioctylamine (30%) and propylamine (25%), respectively. After 1050 min, there was no further water separation observed in the entire sample tested. Figure 2, shows the oil separation from water-in-oil emulsions through the addition of amine group. It was found that the percentage of oil separated achieved the maximum values, in the descending order of decylamine (87%), octylamine (77%), hexylamine (74%), pentylamine (68%), dioctylamine (58%), trioctylamine (47%) and propylamine (39%), respectively.

From the results, the amine group demulsifiers on crude oil emulsion stability can be arrange as: decylamine has highest separation capacity (87%), followed by octylamine (77%), hexylamine (74%), pentylamine (68%), dioctylamine (58%), trioctylamine (47%) and propylamine (39%). The observed descending sequence of amine demulsifier efficiency was due to high molecular weight

factor of amine which acts as flocculants in adsorption and interaction activities. These molecules act more slowly due to their lower diffusivities and more effective in removing remaining small water drops and tight, fine emulsions once most of the dispersed phase has been removed by the water droppers. Figure 3 depicts the influence of decylamine demulsifier on crude oil emulsion stability for crude oils, A, B, C and D. In this regard, crude

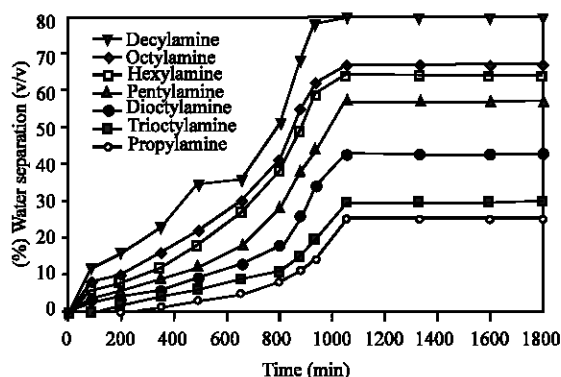


Fig. 1: The influence of amine group demulsifiers on crude oil emulsion stability (percentage of water separation)

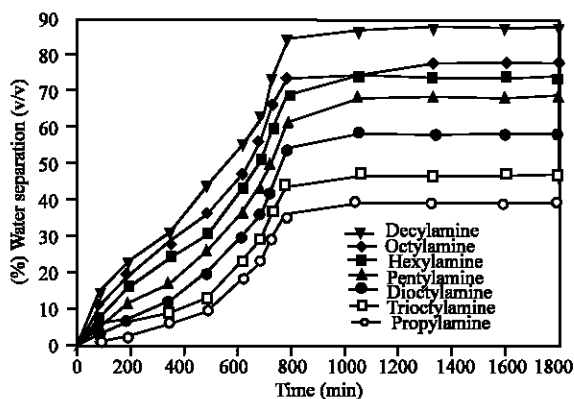


Fig. 2: The influence of amine group demulsifiers on crude oil emulsion stability (percentage of oil separation)

oil D (Miri) produced the highest percentage of water separation (80%). Followed by crude oil A (74%), crude oil B (67%) and Crude oil C (63%). Based on solubility properties, pentylamine, propylamine, dioctylamine and trioctylamine are insoluble in water but they are soluble in less polar solvents such as benzene, alcohol and ether. However, decylamine, octylamine and hexylamine are slightly soluble in water due to their hydrophobic chain, which is shorter than of the pentylamine and dioctylamine.

The influence of polyhydric alcohol demulsifiers on crude oil emulsion stability also studied. Table 4 shows the effects of polyhydric alcohol demulsifiers on crude oil emulsion stability. Figure 4 and 5 shows the separation of water and oil from water-in-oil emulsions as a function of time, respectively. All polyhydric alcohols (polyethylene glycol PEG 1000), polyethylene glycol PEG 600, ethylene glycol EG and propylene glycol PG are aliphatic alcohol compounds which contain two hydroxyl groups as their functional groups. As illustrated in Fig. 4, the PEG 1000 and PEG 600 are able to separate water from the emulsion. In this regards, their water separation found as PEG 1000 (46%) and PEG 600 (40%), respectively. While for EG and PG, there was no separation of water. The percentage of

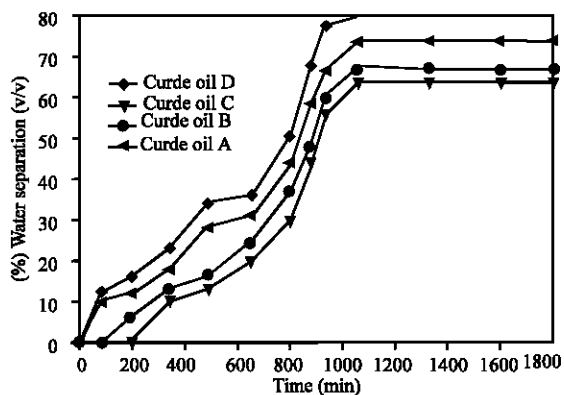


Fig. 3: The influence of Decylamine demulsifier on crude oil emulsion stability (percentage of water separation)

oil separation is shown in Fig. 5. As shows in the Fig. 5, all polyhydric alcohol demulsiers are able separating oil from the emulsion. After 30 h (1800 min), the percentage of oil separated for each demulsifier can be arranged as follows: polyethylene glycol PEG 600 has the highest separation (58%), followed by polyethylene glycol PEG 1000 (55%), ethylene glycol EG (25%) and propylene glycol PG (15%).

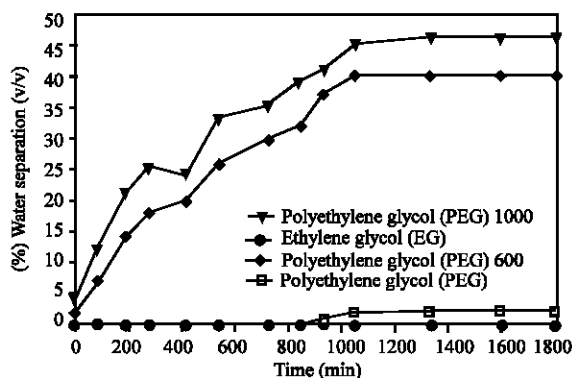


Fig. 4: The influence of polyhydric alcohols group on crude oil emulsion stability (Percentage of water separation%)

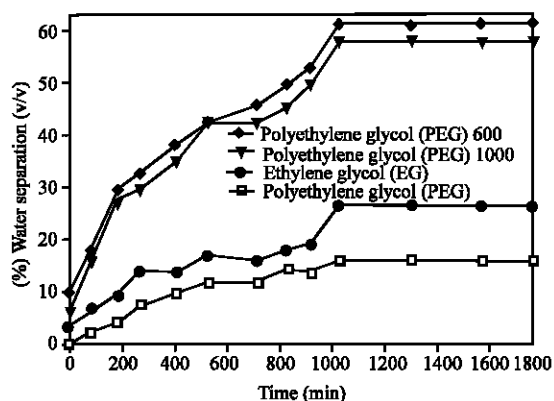


Fig. 5: The influence of polyhydric alcohols group on crude oil emulsion stability (Percentage of oil separation%)

Table 4: Effects of polyhydric alcohol demulsifier on emulsion stability: water separated, % (v/v)

| Time (min) | Polyethylene glyco IPEG 1000 | Propylene glycol (PG) | PEG 600 | Propylene glycol PG |
|------------|------------------------------|-----------------------|---------|---------------------|
| 0 | 4 | 0 | 2 | 0 |
| 85 | 12 | 0 | 7 | 0 |
| 193 | 21 | 0 | 14 | 0 |
| 374 | 25 | 0 | 18 | 0 |
| 490 | 33 | 0 | 20 | 0 |
| 656 | 35 | 0 | 26 | 0 |
| 800 | 41 | 0 | 30 | 0 |
| 880 | 45 | 0 | 37 | 0 |
| 937 | 46 | 5 | 40 | 0 |
| 1058 | 46 | 7 | 40 | 0 |
| 1333 | 46 | 7 | 40 | 2 |
| 1600 | 46 | 7 | 40 | 2 |
| 1800 | 46 | 7 | 40 | 2 |

Based on the solubility properties, the water solubility of alcohols can be explained as; low molecular weight alcohols are water soluble such as methanol and ethanol. However, four carbon alcohols and higher, have much lower water solubility. This can be explained by considering the way that water molecules can disperse solute molecules into a solution. The polar water molecules are attracted to the hydroxyl group by hydrogen bonding that occurs between the hydrogen of water molecules and the oxygen in the alcohol molecules. As the hydrocarbon portions of the alcohol become more extensive, they would be in a higher molecular weight.

The influence and effectiveness of emulsion breaking between the amine group demulsifiers and polyhydric group demulsifiers can be compared in terms of their ability in separating the water and oil from emulsions. From experimental results obtained in this paper, it was found that the amine demulsifiers were more effective in emulsion breaking than polyhydric demulsifier group. There were no water separations for EG and PG in polyhydric demulsifiers and maximum water separation from this group found to be 46 and 40% for PEG 1000 and PEG 600, respectively. In contrast, the water separations in amine demulsifiers were in the range 25 to 80%. The maximum amount of water separation was 80% in the case of decylamine followed by octylamine 67%, hexylamine 64% and propylamine 25%. From literature view point, both functional groups of amine and polyhydric alcohols have the hydrogen bonding ability. However, from these results, it may be concluded that, the amine demulsifiers for hydrogen bonding in much stronger than polyhydric alcohols demulsifier groups. The affect and performance of acid demulsifier group in separation of water and oil from emulsion also studied. Six acid demulsifiers were tested separately and their performances were compared. This group involves formic acid, pentanoic, butanoic, hexanoic, heptanoic and octanoic acid. The percentage of both water and oil separation as a function of time is shown in Fig. 6 and 9, respectively. Figure 6 shows the best performance in terms of total amount of separated water achieved with butanoic acid (42%), followed by formic acid (38%). In the case of octanoic acid demulsifier, it showed quite a long time of induction where no separation was observed (approximately 800 min), but the maximum amount of water separated after 1800 min is (40%) was very close to that observed with butanoic acid (42%). In the case of hexanoic, pentanoic and heptanoic, there were no separation of water before 800 min, but after 800 min, the separation of water obtained were 2, 2 and 1%, respectively.

Considering the amount of separated water after 800 min of test, the classification of the demulsifiers in terms

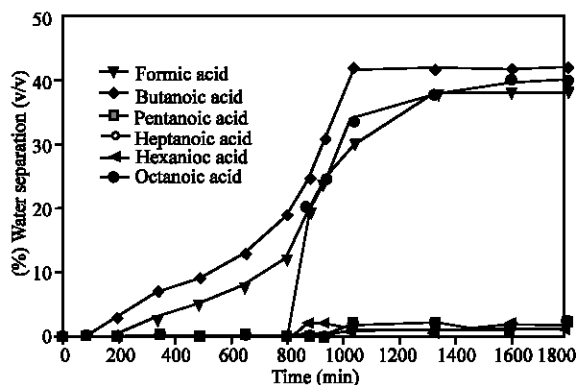


Fig. 6: Influence of acid demulsifiers group on emulsion stability (% water separation)

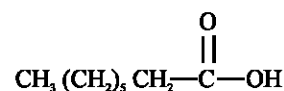


Fig. 7: Structure of Octanoic acid demulsifier

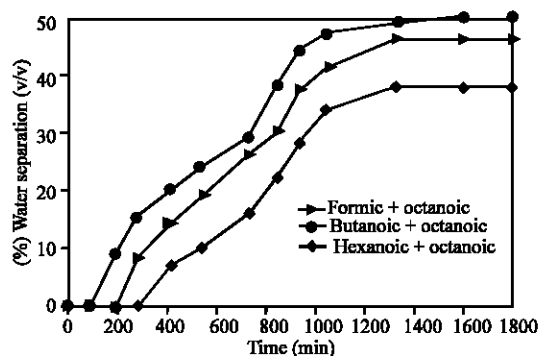


Fig. 8: Water separations from acid demulsifier with octanoic blends

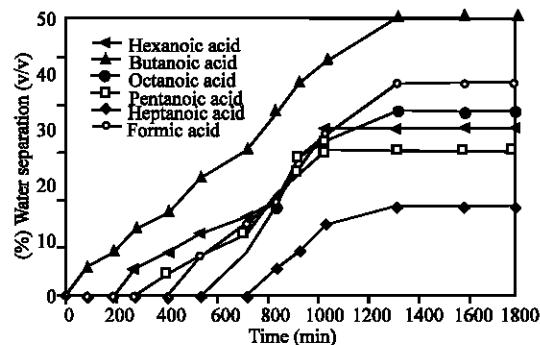


Fig. 9: Influence of acid demulsifiers group on emulsion stability (% oil separation)

of decreasing efficiency is therefore the following: butanoic>formic>octanoic>hexanoic>pentanoic>heptanoic. The specific behavior of octanoic acid demulsifier encouraged, further to be undertaken to perform some tests on acid blends. Fig. 7 shows the structure of the octanoic acid, which has the molecular formula as examination $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ and molecular weight of 144.21. Figure 8 shows the efficiency of separation of blended butanoic/octanoic, formic/octanoic and hexanoic/octanoic (50/50 w/w). As shown in Fig. 8, the performance of blended demulsifiers was better than the single demulsifier. The water separation for the blended demulsifiers was found to be: butanoic/octanoic (50%), formic/octanoic (48%) and hexanoic/octanoic (38%), respectively. This may be attributed to the presence of the low molecular weight octanoic acid which effectively increases the efficiency of water separation compared to the performance of each demulsifier used alone.

The percentages of oil separation from acid demulsifiers as a function of time are shown in Fig. 9. As show, all acid demulsifiers permit oil separation. The maximum percentage was given by butanoic acid (50%) after 1340 min, followed by formic acid (38%). The minimum percentage of water separation was given by heptanoic acid (27%) after 1340 min in comparison to polyhydric demulsifiers group, acid demulsifiers were less in terms of both water and oil separations.

CONCLUSIONS

Water-in-crude oil emulsion has great importance in the oil industry. Chemical demulsifiers thoroughly investigated for breaking water-in-oil emulsions (w/o). From experimental results obtained in this research, it can conclude that, Amine demulsifiers group were more effective in emulsion breaking than polyhydric and acid demulsifiers. Decylamine demulsifier is the best in terms of separation both water and oil from emulsion. It obtained 80% water and 87% oil, respectively.

REFERENCES

Abdurahman, H.N., M.Y. Rosli and J. Zulkifly, 2006. Study on demulsification of water-in-oil emulsions via microwave heating technology. *J. Applied sci.*, pp: 6: 2060-2066.

Anklam, M.R., 1997. *The Flow and Stability of Water-in-oil Emulsions and the Behavior of Thin Oil Films*. A Bell and Howell Company.

Anderson, S.I. and K.S. Birdi, 1990. Influence of Temperature and Solvent on the Precipitation of Asphaltenes, *Fuel Science and Technology Intl.*, pp: 8: 93-615.

Anderson, S.I. and K.S. Birdi, 1991. Aggregation of Asphaltene as Determined by Calorimetry, *J. Colloid And Interface Sci.*, pp: 142, 497-502.

Bailes, P.J., D. Freestone and G.W. Sam, 1997. Pulsed Dc field for electrostatic coalescence of water-in-oil emulsions. *Chem. Eng.*, 23: 34-39.

Corbett, L.W. and U. Petrossi., 1978. Differences in distillation and solvent separated asphalt residua, *Ind. Eng. Chem. Prod. Res. Dev.*, 17: 342-346.

Ferworn, K.A., W.Y. Svrcek. and A.K. Mehrotra, 1993. Measurement of asphaltene particle size distributions in crude oils diluted with n-heptane. *Ind. Eng. Chem. Res.*, 32: 955-959.

Hennessey, P.M., M. Neuman, B.A. Kalis and G. Hellinx, 1995. Use coalescing methods to solve emulsion problems. *Hydrocarbon processing*, 74: 107-124.

Johansen, E.J., I.M. Skjarvo, T. Lund and J. Sjoblom, 1989. Water-in-crude oil emulsions from the norwegian continental shelf, part I. Formation, characterization and stability correlations, *colloids and surfaces*, 34: 353-370.

Lissant, K.L., 1983. *Demulsification, Industrial Applications*. Vol. 13. New York. Marcel Dekker. Inc.

Moschopedis, S.E. and J.G. Speight, 1976. Oxygen functions in asphaltenes, fuel, pp: 55, 334-336.

Moschopedis, S.E., J.F. Fryer and J.G. Speight, 1976. Investigation of Asphaltene Molecular Weight, *Fuel*, 55: 227-232.

Rowan, B., 1992. *The Use of Chemicals in Oilfield Demulsification*. In: *Industrial Applications of Surfactants*. III. Royal Society of Chemistry, Cambridge.

Shiffert, B., C. Bourgeois and E. Papirer, 1984. Structure and water-oil emulsifying properties of asphaltenes. *Fuel*, 63: 835-837.

Sjoblom, J., L. Mingyuan, A.A. Christy and T. Gu. 1992. Water-in-crude oil emulsions from the norwegian continental shelf, 7. Interfacial pressure and emulsion stability. *Colloids and surfaces*, 66: 55-62.

Urdahl, O., T. Brekke and J. Sjoblom, 1992. 13 C n.m.r and multivariate statistical analysis of adsorbed surface-active crude oil fractions and the corresponding crude oils. *Fuel*, 71: 739-746.