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Water-in-Crude Oil Emulsions: Its Stabilization and Demulsification

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Abstract: Traditional ways of breaking emulsions using heat and chemicals are disadvantageous from both economic and environmental perspectives. In this research, the potentials of microwave technology in demulsification of water-in-crude oil emulsions are investigated. The study began with some characterization studies to provide understandings of fundamental issues such as formation, formulation and breaking of emulsions by both chemical and microwave approaches. The aim was to obtain optimized operating conditions as well as fundamental understanding of water-in-oil emulsion stability upon which further developments on demulsification processes could be developed. It was found that emulsion stability was related to some parameters such as, the surfactant concentration, water content, temperature and agitation speed. Experimental results found that microwave radiation method can enhance the demulsification of water-in-oil emulsions in a very short time compared to the conventional heating methods. The results obtained in this study have exposed the capability of microwave technology in demulsification of water-in-oil emulsion. 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.

Key words: Stability, microwave, demulsification, w/o emulsion, concentration, surfactant

INTRODUCTION

Crude oil is a complex fluid comprising colloidal particles such as asphaltenes and resins dispersed in a mixture of aliphatic and aromatic solvents. Water-in-oil (w/o) emulsions are extremely stable because of the presence of these particles. For economic and operational reasons, it is necessary to separate the water completely from the crude oils before transporting or refining them. To reduce the water content of the produced crude oil, the water/crude oil emulsions have to be broken (demulsified). Therefore, it is necessary to understand the mechanisms responsible for stabilization of these emulsions (Berger et al., 1987; Mohammed et al., 1993a, b; Sjoblom et al., 1990, 1992, 1995). The effect of asphaltene solvency on the stability of water-in-crude oil emulsions has been studied by Kilpatrick and McLean (1997). The role of asphaltenes in the stability of water-in bitumen emulsions has reported by Yan et al. (1999).

Based on the crude oil aliphatic/aromatic ratio which governs the solubility of asphaltene-resins and their interfacial activity, one can expect three major stabilization mechanisms for a crude oil film between water droplets (Krawczyk et al., 1991; Wasan and Nikolov, 1993) steric stabilization due to an adsorbed layer of asphaltene at a low concentration of asphaltene-resin submicron particles; depletion destabilization due to an excluded-volume effect, leading to attraction between water droplets and structural stabilization due to long-range colloidal structure formation inside the film in the presence of a sufficient effective volume fraction of colloidal particles, generally, an emulsion system is expected to have a combination of these three mechanisms. The concept of microwave demulsification of emulsions was first introduced by Klaila (1983) and Wolf (1986). Fang and Lai (1995) presented demulsification of water-in-oil emulsions used microwave heating and separation method.

The objective of the present research is conducted to examine the factors effect emulsion stability as well as the influence of microwave heating in demulsification of water-in-crude oil emulsions.

MATERIALS AND METHODS

Microwave radiation: To accomplish the objective of this research, Elba domestic microwave oven model: EMO 808SS was used in heating emulsion samples. The microwave oven rated power output is 900 watts at 2450 MHz, its power consumption is 1400 watts (microwave) and 1000 watts (heater) as shown in Fig. 1.
A number of studies were carried out on Microwave Heating (MW) of oil and water systems. Microwave heating because of its volumetric heating effects, offers a faster processing rate, also microwave has another unique feature other than how it interacts with matter, that it’s penetrating power. Microwave distributes energy within the bulk of most materials, rather than just on it surface. Any heat produced at the surface must then be conducted or convected into the material. Microwave because the wave length is relatively long and the method of interaction so mild, can penetrate deeply into a substance. Penetration energy deposition by microwave overcomes many surface-limiting characteristics of normal heating. The purpose of heating water-in-crude oil emulsions with microwave radiation, is to separate water from oil. Therefore, when water-in-oil emulsions are heated with microwave radiation, two phenomenons will occur, the first one is the increase of temperature, which causes reduction of viscosity and coalescence. The result is separation of water without addition of chemicals (Fang et al., 1989; Fang and Lai, 1995). According to Stoke’s law, it oil is the continuous phase, the settling velocity of water droplets is given by:

\[ v_w = \frac{gD^2(\rho_w - \rho_o)}{18 \mu_o} \]

Where:
- \( D \) = The diameter of the droplets

The viscosity of oil is very sensitive to temperature, as temperature increases, viscosity decreases much faster than the density difference \((\rho_w - \rho_o)\), the result when viscosity decreases, the droplets size increases. Therefore, microwave heating increases the velocity of water \((v_w)\) and accelerates the separation of emulsion. The second phenomenon is coagulation; the higher temperature and lower viscosity make the coagulation process easier. The results are larger particle diameter \(D\) and rapid separation.

**Preparation of w/o emulsions:** In this research, three crude oils were used, crude A from Iran oil field, while crude oil B and C from Malaysia oilfields. These crude oils were obtained from Petronas refinery at Melaka. Their respective compositions and fractions were shown in Table 1 and 2, respectively.

Different samples of water-in-crude oil emulsions were prepared. A detailed procedures for the w/o emulsion preparation and their procedures, including the formulation of w/o, their characteristics and methods of preparation were thoroughly described in a previous research by Abdurahman et al. (2006). Here the research merely describes the main steps of the experimental procedures. For preparation of water-in-crude oil emulsions, the agent in oil method was followed, that is, the emulsifying agent dissolved in the continuous phase (oil) and water added gradually to the mixture (oil + emulsifying agent). Emulsions were agitated vigorously using a standard three blade propeller at room temperature (28-30°C). The volume of the water settled to the bottom was read from the scale on the beaker with different times. The amount of water separation in percent was calculated as separation efficiency from the water observed in the beaker. The prepared emulsions were used to check for w/o or o/w emulsions. All emulsions investigated were type of water-in-oil emulsions (oil continuous). The surfactants used in this research are sodium dodecyl sulphate (SDDS), Low Sulphur Wax Residue (LSWR), Sorbitan monoleate (Span 83) and triton X-100. The emulsifying agents were used as received without further dilution. For chemical emulsification (breaking emulsion) performance, microwave heating method was utilized.

**Measuring the stability of the prepared emulsions:** The different prepared samples of w/o emulsions were tested for their stability. An emulsion sample of 100 mL was taken and tested for stability under gravity at room
temperature. The amount of water resolved is a measure of the emulsion stability. The measurements were done in glass beakers and after two days, the amount of water was recorded.

**Determination of interfacial tension:** For the measurements of interfacial tension, a standard test method for surface and interfacial tension of solutions of surface active agents (ASTM) was used. The equipment used is Du Nouy Interfacial Tensiometer, equipped with 6 cm circumference platinum ring. Since oil is lighter than water, the aqueous solution (water) was first placed in the sample vessel and the ring was immersed therein. The oil on top of the water solution then oil was poured to form the two-layer system (emulsion). Contact between the oil and the ring was avoided during the operation. After following sufficient time (5 min) for the interfacial tension to come to its equilibrium value, measurements were taken.

**Determination of the emulsions apparent dynamic viscosity:** The apparent dynamic viscosity for the prepared emulsions was determined by Brookfield Rotational Digital Viscometer Model LV/DV-III with UL adapter and spindles No. 16 and 31. Brookfield Viscometer apparatus was equipped with a water bath thermostat.

**RESULTS AND DISCUSSION**

This present investigation, the various factors affecting the stability and viscosity of three water-in-crude oil emulsions stabilized by a non-ionic water soluble surfactant Triton-X-100 and an ionic surfactant sodium dedocyl sulphate SDS, low sulphur wax residue and Sorbitan monooleate were thoroughly studied. These factors are the oil content of the emulsion, the surfactant concentration, temperature, agitation speed and salinity of water.

**Effect of water content of the emulsion:** The first part of this study deals with the formation, production and stabilization of w/o emulsions, while in the second part discusses the emulsion breaking (demulsification) of w/o. The effect of water content of the emulsion on its stability, processing time, dynamic shear viscosity, density and pour point was investigated. In this respect, the water content of the emulsion was varied from 30 to 70 vol % (for stability purpose) with respect to the total volume of the emulsion. LSWR and Triton X-100 water-in-oil (w/o) emulsions were made with 50, 55, 60 and 70% (v/v) internal phase (water) (Table 3). For the 50 and 55 emulsion, a higher solids concentration was found (6 mg mL⁻¹ oil versus 2 mg mL⁻¹) allowed easier emulsification and slowed the settling process. The 60 and 70% emulsions were appeared fairly stable with little settling. The LSWR and Triton X-100 stabilized emulsions exhibited only slight coalescence over three days. Some globule formation was observed and settling occurred. In contrast, the Span 83 emulsions were different from LSWR and Triton X-100 emulsions, even at similar dispersed phase volume fractions. Emulsions were made at 50 and 55% (v/v) internal phase with surfactant concentrations in the oil phase of 1.5 and 4.5% (w/w), at 60% (v/v) (3% w/w) and at 70% (v/v) (6.8% w/w). The different between surfactant concentrations for the 50 and 55% emulsions made by Span 83 appeared very significant on emulsions stability. High Span 83 concentrations increased emulsion stability; therefore, for high concentration of Span 83, the viscosity of w/o emulsion increased considerably and the emulsion droplets lost their shape. The effect of the dispersive phase on the stability of emulsion systems also examined with sodium dodecyl sulphate (SDDS) as the emulsifying agent. In this regards, the SDDS emulsions were made with 65, 70, 75 and 80% (v/v) (1 to 3.5 w/w in oil) internal phase. An increase in the concentration of SDDS in oil did not cause an increase but decrease of demulsification rate. The decrease would be induced by the increase of the surface potential of water droplets arising from the increase of the density of SDDS anion on the surface, which overcame the decrease of the surface potential by the increase ionic concentration in oil.

The emulsion stability for crude oils A, B and C were examined as function of processing time and emulsifier applied (surfactant). Stability evaluated via the ratio of the total water separated. The evaluation was carried out with agitation speed at 1800 rpm at 30°C. As demonstrated in Fig. 2 and 3, in most cases stability of emulsion increases with processing time.

It is worth noticing that all surfactants permit a very long time for separation of the water phase (emulsion.
Fig. 2: Change of emulsion stability for Crude oil A emulsions (50-50% w/o), as function of processing time and emulsifier applied

Fig. 3: Change of emulsion stability for crude oil B emulsions (50-50% w/o), as function of processing time and emulsifier applied

more stable). However, the maximum amount of water separated from crude oil A was (50%) and crude B was (60%), crude C was (67%). From these observations, the classification in terms of decreasing stability efficiency is therefore the following: SDDS > Triton X-100 > LSWR > Span 83, respectively.

Effect of the speed of mixing on the stability and viscosity of the emulsion: The apparent dynamic viscosity of the crude oil emulsion (w/o) was investigated for the three crude oils for different mixing speeds at 30°C for 30 min. As shown in Fig. 4, which is a plot of apparent dynamic viscosity as a function of different mixing speed, it is clear from this Fig. 4, there is a correlation between dynamic viscosity and mixing speed, which is; as increasing the mixing speed, result in increasing the viscosity of the emulsion.

Fig. 4: Dynamic viscosity of the emulsion as a function of mixing speed

Again to confirm the effect of stirring time and phase ratio on emulsion stability, water-in-crude oil with various volume ratios as shown in Fig. 5 was investigated. At low internal phase ratio water/oil (10-90%), only low stability was obtained, the increment of internal phase (water) continued till (75-25%). It’s interesting to observe that, increasing the phase ratio, surfactant availability increases accordingly leading to highly stable emulsion. The variation in stability of the emulsions with phase ratio (75-25%) it is very difficult to explain its behavior especially during the first 8 min of the processing. When the volume of dispersed phase reached to (90-10%), the emulsion behavior completely has changed as shows in Fig. 5. The emulsion changed from w/o to o/w, from these measurements and observations, it can be deduced that the phase inversion point should be in the range of 68-72% water. As the volume of the dispersed phase increases, the continuous phase must spread out farther to cover all of the droplets, this causes the likelihood of impacts to increase, thus decreasing the stability of the emulsion. This means that, the emulsion might not break as increase the volume of the dispersed phase. In fact this increment caused an emulsion to invert from one phase (w/o) to another (o/w).

Effect of resin/asphaltene ratios on emulsion stability:
The presence of asphaltene and resin in crude oil can stabilize the emulsion. Asphaltene and resin act as an emulsifying agent, which reduce the interfacial tension and to induce repulsive forces between the droplets. Therefore, the resin/asphaltene ratio (R/A) is an important parameter to predict the emulsion stability. Resins increase the solubility of asphaltene in the crude and minimize the asphaltene interaction with water droplets. The resin/asphaltene ratio (R/A) may be expected to
provide valuable information on tight emulsion formation. In this regards, the R/A ratio for crude oils A, B and C were found as 5, 8 and 13, respectively. The experimental results of this study show that, crude oil C fractions which have higher R/A ratio (13) were separated easily than that of lower R/A ratio (Crude A and B). It may concluded that, when R/A ratio decreased, the emulsions are become tighter and harder to break. High resin concentration keeps more of the asphaltene dissolved in the oil phase. In this study, crude oil A was found more stable than crude B and C, respectively.

Emulsion breaking via microwave heating: In terms of emulsion breaking, as shown in Fig. 6: the separation is much faster with microwave heating than room temperature and conventional heating separation. In this regard, Fig. 6 shows that at the end of 35 min of gravity settling, there is no separation of water layer was observed. For conventional heating (hotplate), at 90 sec, the separation was 38%, while at 90, 120, 150 and 180 sec of microwave irradiation showed 57, 73, 82 and 88% of separation water, respectively. These results showed that microwave radiation can raise the temperature of emulsion, reduce viscosity and the result a separation of water from oil as mentioned by Fig. 1.

CONCLUSIONS

The effect of the R/A ratio, surfactant concentration, water content, agitation speed and temperature on crude oil emulsion stability has been shown. High R/A ratios decrease the water-in-oil emulsion stability. The effect of water-in-oil emulsion stabilization increases with increasing surfactant concentration and decreases with increasing temperature. Results have shown that microwave radiation can be an effective tool to separate emulsified water from oil mixtures. The microwave separation does not require chemical addition.

REFERENCES


