



THE ROLE AND EFFECT OF AERATION ON COMBINED DEMULSIFICATION PROCESS FOR STUBBORN WATER-IN-OIL EMULSION FROM SLOP OIL TANK

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ABSTRACT

Various demulsification methods have been proposed and reported in literatures to solve water-in-oil (W/O) emulsion. Nevertheless, there is a case where demulsification process cannot break the emulsion 100%. The process left behind some amount of rag layer (stubborn emulsion) with greater stability than the original emulsion. Common combined demulsification method (heating, demulsifier injection, and gravity settling) is found ineffective to give expected residence time. Therefore, the work aims to propose aeration into the combined demulsification method for better separation efficiency and as a cheap alternative to solve the stubborn emulsion. The effects of the combination methods are investigated through a designed experiment. The best operating conditions are identified through an optimization using Design Expert software. The optimization goals are to maximize oil recovery and water separation, to minimize the rag layer and to reduce the demulsification cost. Based on the results, the best operating condition is at $\approx 42^\circ\text{C}$ with injection of 200 ppm chemical demulsifier and ≈ 73 cc/min. of aeration rate. The solution was able to provide 58.23% of oil separation fraction with only 12.42% rag layer within 30 min. The demulsification cost is as low as US\$0.13/barrel.

Keywords: combined demulsification method, stubborn emulsion, optimization.

INTRODUCTION

Emulsion can be technically defined as dispersion of droplets of a liquid in another liquid which is incompletely immiscible [1]. Two immiscible liquids, mixing energy, and surfactant must be present for macro emulsion (kinetically stable) formation. Mixing energy disperses the two phases into small droplets and followed by surfactant adsorption on oil-water interface to stabilize the emulsion. Oil soluble surfactants will stabilize water-in-oil (W/O) emulsion while water soluble surfactants will stabilize oil-in-water (O/W) emulsion. W/O emulsion is normal and commonly occur in petroleum industry; especially in the upstream operations [2]. The emulsion formed during flow through pumps, chokes and valves can be very stable if the crude oil contains natural surfactants e.g. asphaltenes [3, 4]. According to the degree of kinetic stability, emulsion can be classified into loose emulsions which will separate in matter of few minutes, medium emulsions which will separate in matter of tens of minutes and tight emulsions which will fully or partially separated in hours, days or weeks [5].

Nano- or micro-solid particles contained in crude oil can also act as surfactant and stabilize an emulsion [6]. This emulsion is called "Pickering emulsion". The particles are typically less than few microns in size while the droplet size is generally 10 μm or less. The role of the particles depends on the contact angle (θ) made by the particles on oil-water interface. Hydrophilic particles (e.g. metal oxides) normally have θ below 90° and leads to O/W emulsions. Hydrophobic particles (e.g. suitably treated silica) have θ greater than 90° and leads to W/O emulsion. Various efforts have been conducted to treat W/O emulsion. The treatment methods widely used in oil and gas industries can be grouped into four: mechanical, thermal, chemical and electrical method [3]. Under

mechanical treatment, gravity settling at high and low pressure is commonly used as the last stage in a separator. It breaks the emulsion due to gravitational force based on density difference between water and oil [7]. Gravity settling alone cannot solve emulsion problem in most of the cases due to long settling time required. The application of heat assists demulsification process by decreasing the viscosity of the continuous phase. Nevertheless, heating method is expensive and only effective if coupled with other remediation method such as addition of demulsifier [8]. Another method for demulsification is via the applications of electricity current. It promotes electro-coalescence due to various mechanisms such as chain formation of droplets, dipole coalescence, etc [9]. Sophisticated electrocoalescer have been proposed in the literature but exhibit short circuit problem at high water content [10, 11].

Chemical demulsifier usually comprises of solvents, surface-active ingredients and flocculants. It is usually injected in the range of 1 - 1000 ppm to neutralize the stabilizing effect of emulsifying agents at oil-water interface [7, 12]. It is a widely applied method to treat emulsion and involves the use of chemical additives to increase the rate of emulsion separation process [3]. Demulsifier added into emulsion will weaken the rigid film at oil-water interface and enhance water droplet coalescence. The demulsifier needs to have a close contact with interfacial film between water and oil, be thoroughly mix with the emulsion, and have sufficient retention time for the demulsification process to take place effectively [7, 13].

Aeration is another cheap mechanical treatment that is usually used to break oil-in-water (O/W) emulsion. Nevertheless, the application of aeration method to solve stubborn W/O emulsion is still rare in literature. Aeration



can be potentially used to solve W/O emulsion as the bubble movement could enhance flocculation or coalescence. The bubble movement could also facilitate faster demulsifier attachment on oil-water interface.

Currently, even optimum combined demulsification method (with heating, demulsifier injection, and gravity settling) cannot 100% solve the emulsion, leaving behind some amount of rag layer (stubborn emulsion). The rag layer has stability higher than the original emulsion. It cannot be separated within the expected residence time even after undergo several demulsification cycles. In addition, expectation of a cheaper demulsification cost is another challenge (economically) that should be taken into account.

Therefore, this paper aims to investigate the performance of aeration combined with heating, demulsifier and gravity settling in breaking the stubborn emulsion. Based on the results, the best operating conditions are identified by using Design Expert software.

STUBBORN EMULSION SAMPLE

Emulsion sample regarded as “stubborn emulsion” and a chemical demulsifier were collected from operator from a slop oil tank. The sample is an unresolved emulsion after undergo several cycles of demulsification process (with heating, demulsifier injection and gravity settling). The emulsion consists of approximately 65% oil, 30% water, 5% unknown solids and demulsifier residue. The water salinity is 1.018% wt. (measured by using KF Titrator T70 from Mettler Toledo) and the specific gravity of is 1.0082 g/cm³. Basic properties of the crude oil (taken from separated oil layer) are presented in Table-1.

Table-1. Basic properties of the crude oil sample.

Parameter	Value
Water cut	0.30
Viscosity @35°C (mPa.s)	8.6
Density @35°C (g/cm ³)	0.8966
API degree	23.8
Unknown solid (vol. %)	Approx. 5%
Asphaltene (%wt.)	N/A
WAT of the oil (°C)	16.57

The density and API gravity are determined by KEM Densito Meter DA 650 which comply with ASTM D1250, D4052, and D5002 and also ISO 12185 and 15212 standards. High API degree of the oil is believed due to the demulsifier residue as the emulsion has undergone several demulsification cycles. The viscosity is measured under rheometer AR-G2. The WAT is determined by using Micro-DSC 7 Evo from Setaram Instrument with cooling rate of 1°C/min.

METHODOLOGY AND EXPERIMENTAL DESIGN

Upon received, the initial conditions of the sample were recorded (the oil and water fraction as well as the emulsion stability). The sample was re-used for the study and was re-emulsified by using IKA T25 Ultra Turrax high speed stirrer for 15 minutes at 12,000 rpm under elevated temperature (according to the heating temperature for emulsion treatment). Following that, 300 mL of emulsion sample was treated by means of heating, chemical demulsifier, and aeration under an in-house demulsification test rig (batch process). Jacket heater is utilized to heat the glass reactor chamber where the emulsion sample is placed. Two temperature sensors were placed at two different height and position for better temperature sensing and control. Gas aeration was induced to the emulsion chamber from the bottom of the chamber via a nozzle with diameter 4 mm and air pressure at 27 Psi. The demulsification treatments were designed by using Design Expert 6 (DX06) software with surface respond method with three level factorial design models to completely map the effect of the combinations of the three demulsification methods. 32 sets of experiments were required to cover all parameters ranges as presented in Table-2. The treatment time was set to 30 minutes in compliance with [14, 15] as the International Petroleum Standards. After the treatment, the standard bottle test was conducted and the separation quality was monitored over periodic time intervals of 5 minute, 15 minute, 30 minute, 1 hour, 2 hour and 4 hour. The emulsification step and bottle test activity were conducted in accordance to [16].

Table-2. Range of parameters considered during demulsification process.

W/O Emulsion treatment		Parameter values
Method	Heating at 3 temperature	35 °C, 57.5 °C, 80 °C 200, 400, 600 ppm 30, 65, 100 cc/min.
	Demulsifier injection at 3 different concentration	
	Aeration	

After mapping the effects of combined demulsification processes under 32 different conditions, optimization was done using Design Expert 6 Software (response surface (RSM) method) to achieve 4 goals as below:

- Volume (%) of oil separated at 30th minutes of settling time was set at maximum.
- Volume (%) of rag layer formed at 30th minutes of settling time was set at minimum.
- Volume (%) of water layer formed at 30th minutes of settling time was set at maximum.
- Total associated operating cost (US\$) was set at minimum.

Total associated operating cost can be distinguished into three sub-costs: Demulsifier cost, heating cost and aeration cost. Nevertheless, only the demulsifier and heating costs are feasible to be calculated



due to difficulties on collecting the information. It is assumed that aeration cost will be relatively small. The cost of the demulsifier is approximately US\$ 1622.84/tonne of oils.

The heating cost analysis would be performed by simulating separator-sized sample volume using ASPEN HYSYS. In the simulation, the separator volume is assumed to have a capacity of 7670 barrels/day of crude oil. As a fluid barrel is equal to ≈ 159 liter, thus 7670 barrel/day is equivalent to 1.22×10^6 L/day. Then, the cost of the demulsifier used for 200, 400 and 600 ppm are US\$ 395.97/day, US\$ 791.95 /day and US\$ 1,187.91/day, respectively.

Separator process simulation by using ASPEN HYSYS was performed at 35 °C, 57.5 °C and 80 °C heating temperature to determine the power required to operate the separator at respective temperatures. The composition of fluid used was set at 70:30 oil-water ratios which indicate the original composition of the stubborn emulsion. The solid content was included in the oil portion since it is soluble in the oil phase. The inlet temperature of the emulsion was set at 27 °C as this is the average of minimum daily operating temperature (approximately). The power required to operate the separator at 35 °C, 57.5 °C and 80 °C based on the simulation are 233, 900 and 1,585 kW. On daily basis, the heating power ratings are 5,592, 21,600 and 38,040 kWh/day, respectively.

In offshore facilities operations, fuel gas is commonly used as the main source of energy to operate the electric generator thus the cost of the fuel was mainly considered for the separator heating cost calculation. On average, the price of fuel gas was taken at approximately US\$ 5.07 per Million British Thermal Unit (MMBTU). Note that 1 MMBTU is equivalent to 293 kWh. Then, the heating cost to operate the separator at 35 °C, 57.5 °C and 80 °C are US\$ 96.76/day, US\$ 373.76/day and US\$ 658.24/day, respectively.

RESULTS AND DISCUSSIONS

Emulsion stability of initial emulsion sample was determined through a bottle test as a base case. The evolution of percentage volume of each layer was recorded and presented in Figure-1. The percentage volume was calculated from the volume of each layer divided by the total volume. Rapid oil separation occurred only after 30 minutes of gravity settling and is negligibly small after 1h. The best separation process can be achieved after 3h with 55.9% volume of oil layer, 17.44% volume of rag layer, and 26.67% volume of water layer.

Demulsification processes under 32 different experimental conditions have been conducted and three layers were observed during bottle test.

Effect of heating and aeration

In order to analyze the role and effect of heating and aeration, percentage volume of oil separated during bottle test under different aeration rate and demulsifier dosage were presented in Figure 2-4 at temperature 35, 57.5, and 80 °C, respectively.

The pattern clearly showed that higher temperature would slow down the separation process. It can be observed from the percentage volume of oil separated at the end of observation time. The percentage volume varied from approximately 60% at 35 °C to 50% at 57.5 °C and only 35% (in average) at 80 °C. This fact contradicts the theory that heating would speed up the separation process by reducing the continuous phase viscosity. The reason for this was believed due to the role of aeration.

At lower temperature the aeration would give lower hydrodynamic force due to higher continuous phase viscosity that favor good mixing of the demulsifier added as also mention by [7]. At proper aeration rate, bubbles movements also provide kinetic energy that facilitates inter droplets collision. It enhances flocculation and coalescence processes. As the temperature increase, the viscosity decreased and the hydrodynamic force may become big enough to induce re-emulsification and prevent coalescence between droplets. This was supported by the result at 80 °C where the percentage volume of separated oil had tendency to decrease at higher aeration rate. Higher rag layer formation (the results are not presented here) at higher temperature was another supportive fact that aeration would re-emulsify the emulsion above certain temperature. As a consequence, the percentage volume of rag layer at the end of observation time was increased from 12% at 35 °C to 17% at 57.5 °C and to 37% (in average) at 80 °C. Based on the results obtained, aeration could be used to enhance the demulsification process and reduce the heating requirement.

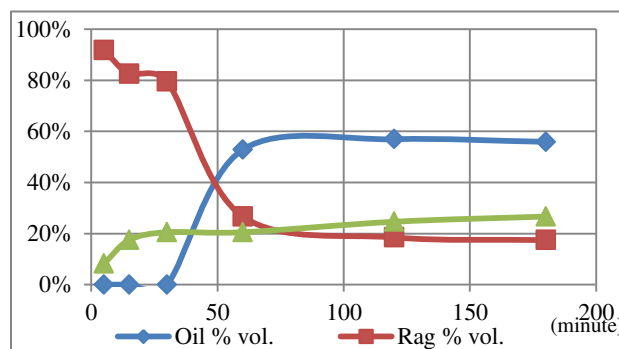
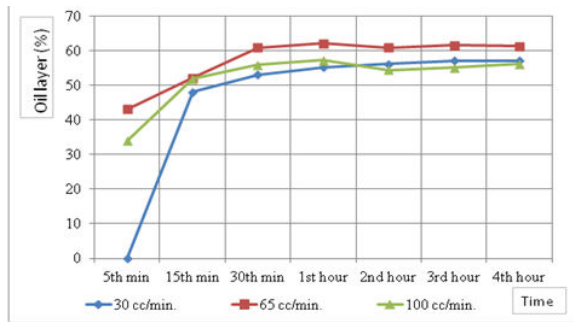
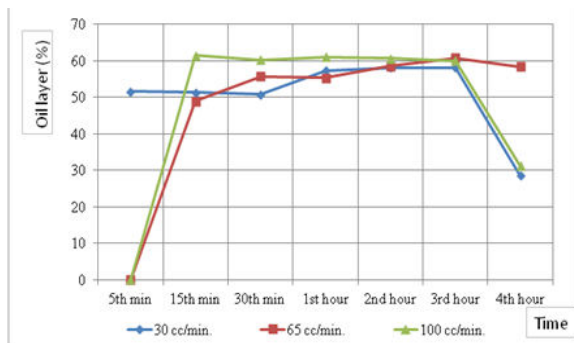


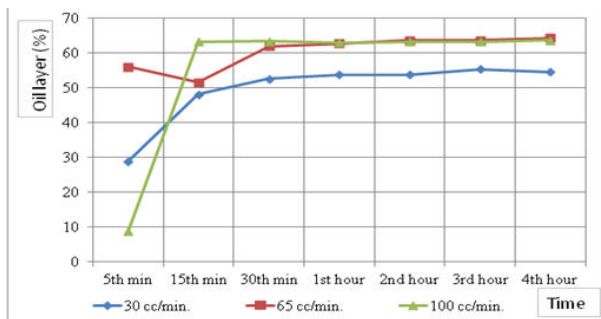
Figure-1. Initial emulsion stability of the emulsion sample collected from operator.



(a)



(b)

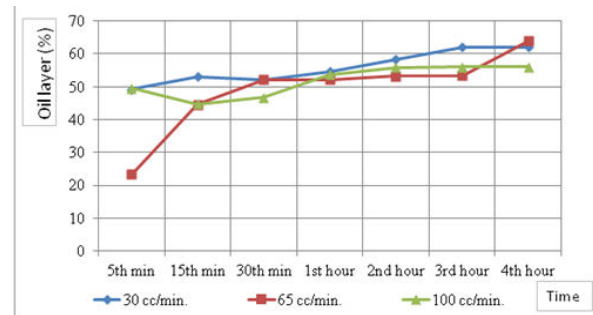


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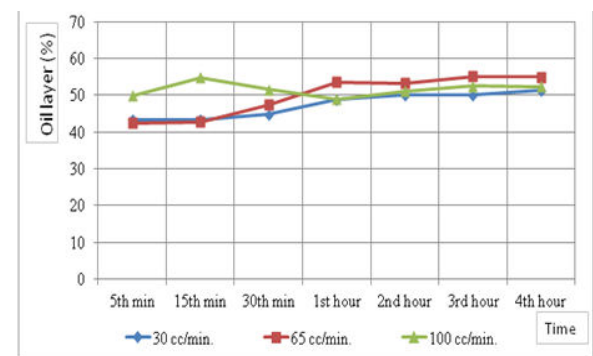
Figure-2. Volume of oil separated (%) at temperature 35 °C with, a). 200 ppm demulsifier, b). 400 ppm demulsifier, and c). 600 ppm demulsifier

During emulsification, it was also observed that there were two different emulsion colors. Emulsification at 35 °C and 57.5 °C produced black colored emulsion while emulsification at 80 °C produced light brown emulsion color. The color of rag layer formed during bottle test also followed the same trend. The phenomena indicated a phase inversion temperature. A rheological test was conducted by using rheometer DHR-1 to measure viscosity of both of the rag layers at 35 °C. Viscosities of black and light brown rag layers are 157.6 and 52 mPa.s, respectively, which is higher than the oil viscosity. High viscosity value of black rag layer is a typical case for water-in-oil emulsion. Lower viscosity for light brown rag layer could be due to phase inversion from water-in-oil emulsion to oil-in-water emulsion. Microscopy observations were conducted (as shown in Figure-5) to observe and confirm the emulsion type. The results show

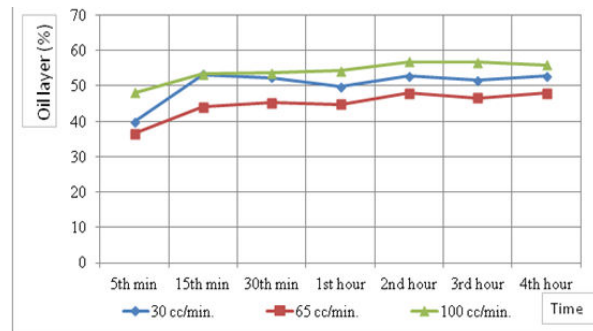
that black rag layer is a W/O emulsion while the brown rag layer is an O/W emulsion.



(a)



(b)



(c)

Figure-3. Volume of oil separated (%) at temperature 57.5 °C with, a). 200 ppm demulsifier, b). 400 ppm demulsifier, and c). 600 ppm demulsifier.

Effect of demulsifier concentration

At temperature 35 °C and 57.5 °C, the effect of increasing demulsifier dosage (in average) was insignificant and had tendency to give similar results (as presented in Figure 2-4). It means that 200 ppm of demulsifier dosage was enough to give maximum performance of the demulsifier in counteracting the role of natural surfactant. Under high temperature (80 °C), the performance of separation process reduced considerably (in average) with increasing demulsifier dosage.

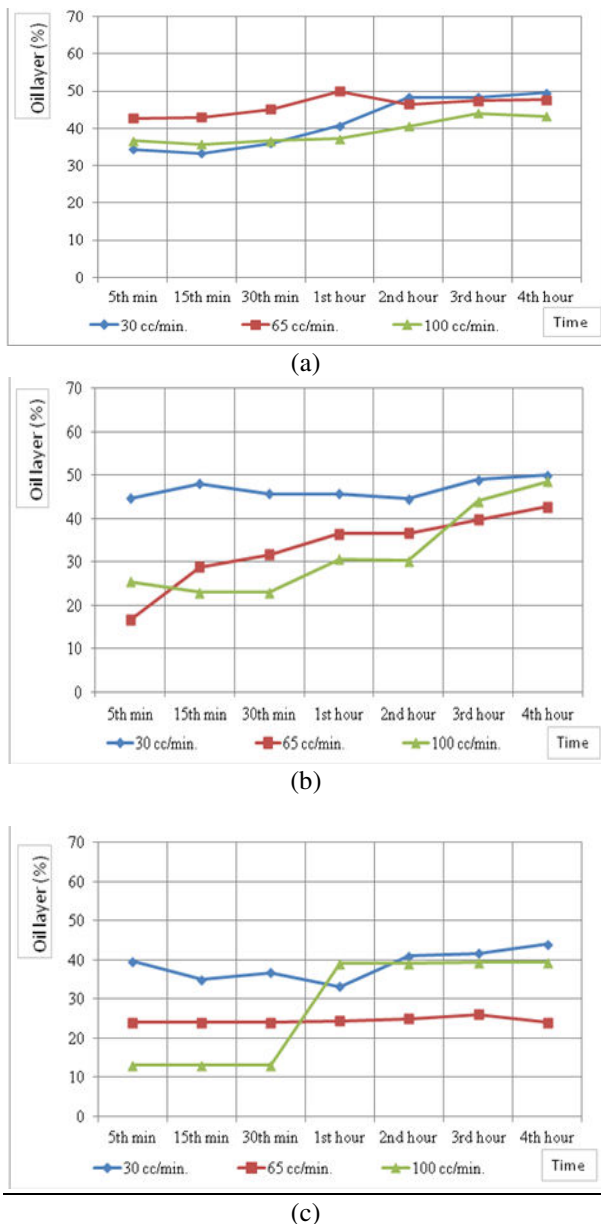


Figure-4. Volume of oil separated (%) at temperature 80 °C with, a). 200 ppm demulsifier, b). 400 ppm demulsifier, and c). 600 ppm demulsifier.

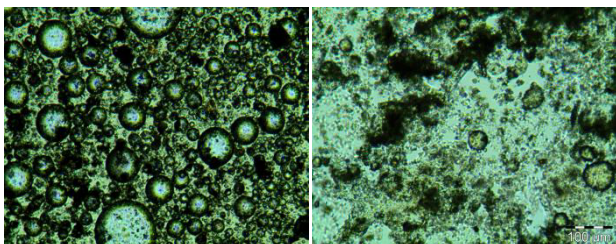


Figure-5. Rag layer image of, a). Black rag layer and b). Light brown rag layer.

The reason for this was believed due to the effect of temperature. Solubility of the demulsifier may be changed from oil soluble (since it is prepared to solve water-in-oil emulsion) into water soluble at high

temperature. Consequently, the demulsifier would become a surfactant that stabilizes O/W emulsion. This phenomenon refers to phase inversion temperature. The emulsion and rag layer colors show agreement with this argument. Oil-in-water emulsion is always lighter in color than water-in-oil emulsion for the same fluid system. In addition, it was observed that more rag layer volume was observed as the demulsifier increased at 80 °C. This fact supports the argument.

Overtreatment effect was also observed from the bottle test result at temperature 57.5 °C as the amount of the rag layer tends to increase at higher demulsifier addition. The excess amount of surfactant may re-stabilize the emulsion. The argument was also supported by [7] and the work done by [17].

OPTIMIZATION

With all the experimental data, the optimum operating conditions for the combined demulsification process was analyzed by using Design Expert software. Based on the criteria explained previously, the optimum operating conditions is by operating the separator or emulsion treater at temperature of 41.94°C, demulsifier injection at 200 PPM concentration and gas aeration injection at rate of 73.05 cc/min. It can approximately recover 58.23% oil within 30 minutes of retention time.

Water content of the oil fraction was also tested by using KF titrator and found to have only 0.14% wt. of water content. The emulsion residue can be reduced down to 12.42% within the period. This approach could be achieved with a cost of US\$ 974/day or US\$ 0.13/barrel. In term of separation performance, this result is obviously better and faster than the base case.

CONCLUSIONS

Investigation on the effect of aeration in a combined demulsification process of stubborn emulsion from slop oil tank has been investigated through a designed experiment. In general, some conclusion can be made as below:

- At low temperature (≤ 57.5 °C), aeration support demulsification process by enhancing inter droplets collisions and demulsifier attachment on oil-water interface. However, the aeration rate (hydrokinetic energy from gas bubble movement) should be maintained such that it will not induce re-emulsification.
- A phase inversion temperature was observed at temperature between 57.5 °C to 80 °C.
- Aeration and heating method has mutual correlation on the combined demulsification process. Aeration could reduce the need of heating and give better separation performance.
- The optimum operating conditions are by operating the separator at ≈ 42 °C with injection of 200 PPM demulsifier dosage and ≈ 73 cc/min gas aeration rates. The treatment cost is as low as US\$ 0.13/barrel.



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