

Chemical Demulsification of Oil-in-Water Emulsion from Gas Condensate Field

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Keywords: Emulsion; Produced water; Demulsifier; Demulsification; Oil-in-water content (OiW); Demulsifier OA-KX

Received: Feb 05, 2023 **Revised:** Apr 19, 2023 **Just Accepted Online:** Apr 20, 2023 **Published:** Xxx

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

Please cite this article as:

H. Rajan, N. R. Yusuf, D. F. Mohsim, N. H. B. Halim, (2023) Chemical Demulsification of Oil-in-Water Emulsion from Gas Condensate Field. **Substantia**. *Just Accepted*. DOI: 10.36253/Substantia-2035

1. ABSTRACT

Produced water, also known as oily wastewater, is one of the major wastes in the oil and gas industry. During the hydrocarbon production, formation of emulsion takes place such as oil-in-water emulsion which has a huge financial effect on the sector. Oil and gas industry seeks highly effective and reasonable demulsifying chemicals to separate the oil-in-water emulsions into water and crude oil. Thus, in this publication, resin alkoxyate, cationic polyamine, cationic surfactant and ethylene oxide/propylene oxide (EO/PO) block copolymers are utilized to resolve the oil-in-water emulsion from a gas condensate field. According to the findings of preliminary screening, a unique demulsifier DB was formulated by incorporating resin alkoxyate and cationic surfactant at an optimal weight percentage ratio. Demulsification efficiency (D_e) of 96 % based on measurement of turbidity was attained after treating the oil-in-water (O/W) emulsion with demulsifier DB at a dosage of 7 ppm. To determine the demulsifier's efficiency further, the oil-in-water content (OiW) of the produced water was evaluated after the treatment with demulsifier DB. Oil removal efficiency (OR_e) of 90% was achieved as the formulated demulsifier DB reduced the oil-in-water content (OiW) of O/W emulsion from 1008.3 ppm to 97.1 ppm within 15 minutes at the dosage of 7 ppm. Furthermore, interfacial tension (IFT) and Turbiscan analysis were performed to further study the demulsification process of blank sample and the addition of the demulsifier DB at the optimized dosage of 7 ppm. At demulsifier DB dosage of 7 ppm, the interfacial tension between oil and water reduced significantly compared to blank sample from 24.98 mN/m to 9.38 mN/m. The produced water sample after treatment with 7 ppm of demulsifier DB resulted in a significant increase of Turbiscan Stability Index (TSI) value of 8 which indicates the rate at which the separation of oil and water occurred. The attained results of IFT and Turbiscan analysis further validate that mixed surfactant system is more efficient than single surfactant system. By combining surfactants with different functional groups, mixed surfactant systems can exhibit greater surface activity than single surfactants.

2. INTRODUCTION

The development of alternative energy sources is a significant challenge in today's world, given environmental contamination and the constant need for fresh water. Nevertheless, petroleum is still one of the prominent sources of energy for transportation fuels in most countries. Therefore, there is a steady need to supply the continuous demand for the oil and gas industry. As a result of exploration and development activities, excessive amount of water known as produced water is lifted from the subsurface formations to the earth surface (Veil et al., 2004). Produced water can be present in the form of emulsions which can be harmful to the aquatic organism if it was discharged untreated into the sea. In order to preserve the environment from contamination, these excessive amounts of water should be treated before it can be discharged into the environment. When economically feasible, it is recommended to recycle produced water within the upstream oil and gas sector as it offers several benefits, such as minimizing the need for external water sources, reducing liability concerns associated with managing produced water, and limiting the overall management of produced water. Prior to recycling, specific substances like insoluble oil, microorganisms, iron, and boron are typically removed using fit-for-purpose treatment trains consisting of oil-water separations, solids separation, disinfection, and iron removal methods (Liden et al., 2017). Conventional oil and gas wells are drilled into geological formations where oil and natural gas flow easily to the wellbore. In contrast, unconventional oil and gas wells are drilled into previously unconventional geological sources, such as coalbed methane (CBM), shale gas, tight oil, shale oil, and oil sands. With conventional production, the produced water is often recycled by injecting back into medium-to-high permeability reservoirs to maintain pressure of the reservoir or enhanced oil recovery (EOR) (Scanlon et al., 2019). However, in the case of unconventional production, the excessive produced water cannot be injected back into the low-permeability reservoirs. Therefore, treating produced water is a practical approach for managing the large volumes of water generated during oil and gas exploration and production. The primary objectives of produced water treatment are to remove dispersed oil and grease, desalinate the water, remove suspended solids, eliminate soluble organics, remove dissolved gases, reduce naturally occurring radioactive materials (NORM), disinfect the water, and soften it (Liden et al., 2019). De-oiling is a process of removing any remaining oil and grease that can be harmful to the environment if discharged untreated. Desalination process done using desalters removes any salt from the water to prevent damage to the environment and equipment.

Generally, combination of two non-miscible liquid phases is known as emulsion in which one phase is dispersed in the other phase (Tadros, 2013). An emulsion contains a continuous phase and a dispersed phase which are also known as external and internal phase respectively. The oil droplets are the dispersed phase in the continuous phase which is water or vice versa. Regardless of the phase volume ratio, dispersed phase always has the smaller phase volume compared to the other phase (Schramm, 1992). A water-in-oil (W/O) emulsion is a type of emulsion in which the dispersed and continuous phase is water and oil respectively. Oil-in-water (O/W) emulsion is a form of emulsion in which continuous phase or the dispersion medium is water and the dispersed phase is oil (Auflem, 2002). Multiple emulsions have a more complicated structure, with microscopic droplets suspended in large droplets in a continuous phase. Oil-in-water-in-oil (O/W/O) and water-oil-in-water (W/O/W) emulsions are two types of multiple emulsions (Israelachvili, 1994; Sjoblom, 2001) as shown in the **Fig. 1**.

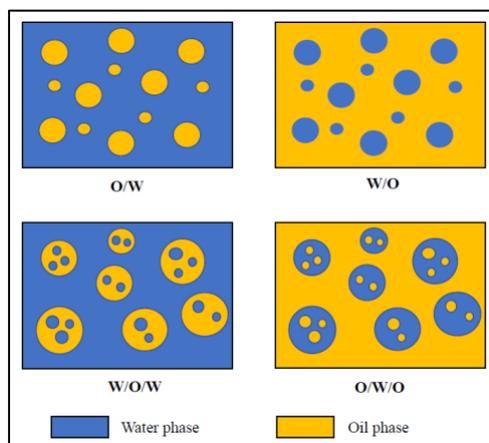


Fig. 1–Types of emulsions

Oil refining, also known as petroleum refining, is the process of transforming crude oil into a range of useful products such as gasoline, diesel, jet fuel, heating oil, lubricants, and various other chemicals. Crude oil is a complex mixture of hydrocarbons, impurities, and contaminants, and refining is necessary to convert this raw material into usable products that meet specific quality and performance standards. The refining process typically involves several stages of processing, each of which is designed to remove different impurities and contaminants from the crude oil. Desalination process done using desalters removes any salt from the water to prevent damage to the environment and equipment. De-oiling is a process of removing any remaining oil and grease that can be harmful to the environment if discharged untreated. These processes of oil refinery are often aided by demulsifier where it helps to separate water and other impurities from the oil more effectively, reducing the amount of contaminants in the final products. Demulsifiers involve desalters and deoilers, which is considered to be about 40% approximately the world oilfield production chemicals market.

Demulsification is the process of segregating an emulsion into two different phases which are water and crude oil. Crude oil can be sent directly to refineries utilising less complex emulsion breakers and chemical technology when crude oil had little to no water during its production in oil and gas industry. Emulsion droplets can range in size from rather big (visible) to sub-micron. Some emulsions are extremely stable and require a demulsification technique to be treated. Destabilization of emulsion is carried out by using either four main methods such as mechanical, chemical, thermal, or electrical (Coca et al., 2011). Chemical method is one of the common approaches applied in the process of demulsification where demulsifiers are added into the emulsion to assist the emulsion breaking process (Razi et al., 2011). Chemical additives' primary role is to counteract the stabilizing impact of emulsifying agents which are asphaltenes and resins (Daniel-David et al., 2008). Demulsifiers are surfactants that helps to separate O/W and W/O emulsions into two phases respectively at low concentrations of dosage. Produced water include a significant amount of oil droplets during the production of hydrocarbon. To minimise complications during the refining process, these oil droplets should be removed from the produced water or viceversa. Asphaltenes and resins are naturally occurring compound of crude oil which can form a stabilizing layer around the water droplets, preventing them from coalescing and separating from the oil (Feitosa et al., 2019). The surface-active chemicals known as demulsifier are absorbed to the oil/water interface and it weaken the rigid film of the droplets. Addition of demulsifier reduces the surface tension of the droplets, which in turn destabilizes the emulsion particles (or droplets). Eventually, it leads to the rupturing of rigid film and enhance coalescence of water droplet (Mhatre et al., 2018). As a result, the particles within the emulsion have a natural tendency to agglomerate and form larger masses which leads to the separation of oil and water. Demulsifiers or surfactants are organic particles comprising of two parts: the polar portion that is attractive to the water phase (hydrophilic) and the non-polar portion that is attractive to the oil phase (hydrophobic) as shown in **Fig. 2**. Effective emulsion breaking using a demulsifier needs a chemical that is

appropriately selected for the specific emulsion, a suitable amount of dosage, appropriate stirring of chemical in the emulsion, and an adequate time for the droplets to settle down (Yi et al., 2017). It may also be necessary to rise the temperature of the system to aid the demulsification process, however, it might increase the cost of treatment.

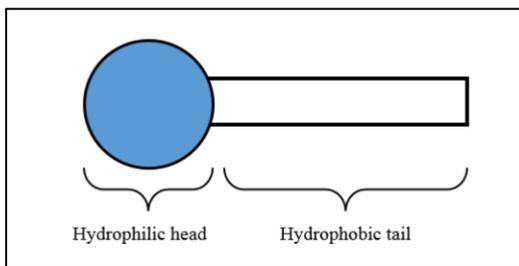


Fig. 2 – Basic structure of demulsifier (Porter, 1991)

There are previous study and research on the types of demulsifiers tested which is important for improving the understanding of emulsions, developing more effective treatments, optimizing their usage, and minimizing their environmental impact. Poly aluminium chloride and quaternary ammonium salt (PAC-QAS), polyamine (PA), and the compound of polyamine and poly aluminium chloride (PA-PAC) were investigated for the treatment of oily produced water in 2020 (Shu et al., 2021). Shu discovered that PA and PA-PAC at 60 mg/L and 90 mg/L respectively showed better performance than PAC-QAS in terms of oil removal efficiency, achieving around 60% and 70%. Due to the cationic polyamine's high positive charge, the stability of emulsified oil droplets was disrupted as the negatively charged oil droplets was counteracted by the chemical and making it surface active (Shu et al., 2021). Wang et al. examined the demulsification of O/W emulsions using block copolymers of ethylene oxide (EO) and propylene oxide (PO), which has amphiphilic characteristics in aqueous solution (Wang et al., 2010). When the concentration of PAE82 and PAE102, which are dendritic copolymers and synthesised by propylene oxide and ethylene oxide reactions, reached 150 mg/L, their demulsification ratios were 91.92% and 91.23% at 15 minutes respectively. This shows that EO/PO block copolymers is capable of a good demulsifier for O/W emulsion. Furthermore, according to the study conducted by Acostal et al., a member of the resin alkoxyolate family, C6 have demonstrated remarkable performance in accordance with industrial norms when tested for the demulsification of W/O emulsion, enabling more than 80% water separation (Acosta et al., 2020). A feasible substitute to the hydrophilic-lipophilic balance (HLB) approach for evaluating the hydrophilic-lipophilic balance of surfactants is the Relative Solubility Number (RSN). RSN has found extensive applications in the surfactant chemical industry for aiding in product selection, quality control, and formulation. It is also beneficial in emulsion research as it facilitates the choice of demulsifiers and stabilizers (Wu et al., 2004). The demulsifier C6 has a relative solubility number (RSN) value of 11. This constant, which is frequently used for screening and benchmarking, categorises demulsifiers as water or oil-soluble. High RSN numbers (>13) are associated as water-soluble demulsifier, whereas low RSN numbers (< 13) numbers are associated with oil-soluble demulsifiers (Marquez-Silva et al., 1997). Intriguingly, C6 lies in the region close to the region of oil-soluble demulsifier which shows that it could be effective in resolving in O/W emulsion. For the O/W emulsions demulsification, water-soluble demulsifiers are typically utilized whereas oil-soluble demulsifiers are commonly utilized to destabilise water-in-oil emulsions (Raya et al., 2020). Hirasaki et al. observed that certain amphoteric and cationic surfactants were efficient at segregating O/W emulsions, which were produced when surfactant/polymer (SP) method was used for enhanced oil recovery (Hirasaki et al., 2011). In his study, adding roughly 200 ppm of cationic surfactant, n-octyltrimethylammonium bromide (C₈TAB) caused a distinct segregation of the oil and water phase. The cationic surfactant decreased electrostatic repulsion between droplets and altered system phase behaviour leading to a balanced state of lipophilic and hydrophilic effects which reduces the emulsion stability. In this article, various types demulsifiers such as resin alkoxyolate, cationic polyamine, cationic surfactant and EO/PO block copolymers were evaluated for the demulsification of O/W

emulsion. The impact of various demulsifiers on the O/W emulsion was investigated based on the turbidity and OiW content of the treated sample. The main objective of this work is to minimize the OiW content of the O/W emulsion from gas condensate field by developing a new formulation using selected effective demulsifiers based on the screening conducted.

3. MATERIALS AND METHODS

3.1 Materials

PETRONAS Research Sdn. Bhd. (PRSB) provided the essential materials for the experiment purpose from gas condensate field such as produced water and condensate. They were selected for the preparation of emulsion as they were raw material obtained from a gas condensate field without undergoing any treatment. The characteristics of the condensate and produced water are shown in **Table 1** and **Table 2**. Several types of chemicals were provided by PETRONAS Research Sdn. Bhd. (PRSB) were used for the treatment of O/W emulsion of gas condensate field are shown in **Table 3**. Demulsifier A, B, C and D are used in this experiment and the chemicals are industrial grade.

Characteristics	Value
Density @15°C	0.8857 g/cm ³
API Gravity @15°C	28.2°
Wax appearance temperature (WAT)	10.7 °C
Kinematic viscosity @60 °C	1.438 mm ² /s
Saturates	52.77 %
Aromatics	46.77 %
Resins	0.41 %
Asphaltenes	0.12 %

Table 1– Characteristics of the condensate

Characteristics	Value
Salinity	100 mg/L
pH	3.7

Table 2– Characteristics of produced water

Demulsifier	Type
A	Cationic polyamine
B	Resin alkoxyate
C	EO/PO block copolymers
D	Cationic surfactant

Table 3– Types of demulsifier

3.2 Emulsion preparation

For the preparation of O/W emulsion, the condensate and produced water from gas condensate field were used as oil and water phases respectively. The O/W emulsion was prepared by using the produced water and condensate at a volume ratio of 85:15. Using a 100 ml beaker, produced water and condensate were added into the beaker at a volume of 34 ml and 6 ml respectively. The total mixture of condensate and produced water was 40 ml in the beaker. In order to form a stable O/W emulsion, the produced water and condensate was then homogenized for 10 mins at 4000 rpm using IKA Ultra-Turrax T-50 Homogenizer.

3.3 Emulsion characterization

The type of emulsions whether O/W or W/O emulsion and the typical size was confirmed visually using a Leica DM LB2 microscope at 40X magnifications. Furthermore, zeta potential (z-potential) gives more information on the O/W emulsion stability, and it is measured by measuring the charged droplets or colloids' velocity in a specified electrical potential field. Zeta-potential of the emulsion were measured to study the electrical charge of any droplet present in the emulsion. Malvern Zetasizer Nano-ZSP was used to test the zeta-potential of emulsion that had no chemical compounds added.

3.4 Bottle test screening

The prepared emulsion according to the experimental procedure mentioned above was then transferred to a bottle. In order to stimulate the real field condition, the bottle containing the emulsion was then immersed in water bath for 30 minutes at 60 °C. After that, the demulsifiers was injected into the bottle using pipette at various dosages and the bottles were shaken 100 times by hand to ensure that the demulsifier was uniformly distributed throughout the emulsion. For the segregation of oil and water to take place, the emulsion was then allowed to settle down for 15 minutes by placing the bottles in water bath. The water sample from the bottom of the bottle was obtained at the end of the retention time. The water sample's turbidity and OiW content were also determined.

3.5 Turbidity measurement

Turbidity is a liquid's relative clarity measurement that has long been used as a fundamental and straightforward indication of water quality. It is an optical property of water in which the amount of light scattered by material in the water is measured when a light is shone on a water sample. The turbidity of the emulsion and treated sample was measured with HACH 2000 turbidimeter at 0.001 NTU, maximum sensitivity. The efficiency of the demulsifier was determined by calculating the demulsification efficiency, D_e (%), using the formula below:

$$\text{Demulsification efficiency, } D_e (\%) = \frac{T_o - T}{T_o} \times 100 \quad (1)$$

where T_o and T are the initial and final turbidities of the produced water.

3.6 Oil-in-water content (OiW) measurement

For the measurement of oil concentration of the sample, TD-500D Handheld Oil in Water Meter from HMA INSTRUMENTATION was utilized. Using infrared detection, the TD-500D Handheld Oil in Water Analyzer determines solvent extractable substances (hydrocarbons, oil, and grease) in water or wastewater. The standard procedure to measure oil concentration is by transferring the

produced water to a tube and add hexane solution at a volume of 10% to the total amount of produced added initially. The tube was then shaken for 2 minutes and the top layer of the tube was taken using a pipette. The solution will be then injected on the surface of the oil analyzer to measure the OiW content. The amount of oil removed from the produced water was evaluated based on the oil removal efficiency, OR_e (%), calculated using the formula below:

$$\text{Oil removal efficiency, } OR_e (\%) = \frac{OiW_o - OiW}{OiW_o} \times 100 \quad (2)$$

where OiW_o and OiW are the initial and final OiW contents of produced water sample.

3.7 Interfacial tension (IFT) measurement

The force between two distinct phases that can be liquid-solid, liquid-liquid, gas-solid or gas-liquid contact is known as interfacial tension (IFT). The interfacial tension of two non-miscible liquids, oil and produced water, was measured at 60°C using the Rame Hart Model 260 by the pendant drop method. Pendant drop is an optical method to measure interfacial and surface tensions of fluid system. They are determined through the drop shape using the following equation:

$$\text{Surface tension, } \gamma = \frac{\Delta\rho g R_0^2}{\beta} \quad (3)$$

Where γ is the surface tension, g is the gravitational constant, $\Delta\rho$ is the difference of densities between liquid, R_0 is the curvature's drop radius at the apex, and β is the shape factor. β is defined as three dimensionless first-order equations through the Young-Laplace equation expressed.

3.8 Turbiscan Lab® Expert demulsification analysis

Turbiscan™ AGS High Throughput Stability Analyzer from Formulaction (France) is intended for examining destabilization mechanisms of emulsions and dispersions. Besides, it characterizes physical properties of substances, or identifies the particle size and concentration in a sample more importantly (Mengual et al., 1999; Paweł et al., 2020). The Turbiscan apparatus utilizes a near-infrared light source with a wavelength (λ) of 880 nm, emitting pulsed signals, in combination with synchronized dual detectors - a transmission (T) detector and a backscattering (BS) detector - to aid in the optical evaluation of dispersion destabilization. At a degree of 0° from the incident beam, the transmission (T) detector detects light that passes through the sample. The light will be then reflected back by the sample at degree of 135° from the incident beam and it will be detected by the back scattering (BS) detector (Celia et al., 2009). This equipment can detect destabilisation by creaming before it is apparent to the human eye. Emulsion destabilisation was investigated utilising profiles of transmission (T) and backscattering (BS) by scanning the sample of emulsion at a wavelength of 880 nm every 5 minutes for 1 hour at 60 °C. It analyses all variances in each sample and generates a unique number that indicates a specific sample's destabilization. TurbiSoft Lab can be utilised to compute the Turbiscan Stability Index (TSI) and analyse any quantity of samples. This will provide an analysis of the sample's stability. This coefficient, TSI is calculated as follows (Zheng et al., 2018; Zhu et al., 2015):

$$\text{Turbiscan stability index, } TSI = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{bs})^2}{n - 1}} \quad (4)$$

where n is the scans number, x_i is the mean backscattering measurement for every minute and x_{bs} is the average value of x_i .

4. RESULT AND DISCUSSION

4.1 Emulsion characterization

The microscopy image of the prepared emulsion is shown in **Fig. 3**. Based on the observation, the continuous phase occupies most of the area which indicates that the phase with the smaller volume is the dispersed phase. Therefore, O/W emulsions were formed based on the emulsion preparation procedure which involved mixing produced water and condensate in a volume ratio of 85:15. The surface charge of particle is linked to the zeta potential. Large readings of z-potential (negative or positive) improve emulsion stability and signify difficulties in droplet coalescence, although z-potential is often pH-dependent, and other important parameters must be addressed for coalescence prediction (Coca et al., 2011). This is a vital parameter for studying the chemistry taken place in evaluating whether an emulsion will remain stable in its intended environment. The prepared emulsion recorded a zeta potential measurement of -29.8 mV that represent a stable emulsion has formed. When the zeta potential in the range of +5 mV to -5 mV, colloidal particles are quite unstable due to agglomeration and it is highly stable when the zeta potential reading is around -30 mV or more negative (Schramm, 1992). A zero-zeta potential implies that the conditions for flocculation of emulsion droplet are at optimum meaning it has a potential for easier emulsion separation. Emulsions are classified as macro-, micro-, and nano-emulsions based on size of droplet and its stability (Komaiko & McClements, 2016). Based on visual observation obtained under microscope, the average size of oil droplets ranges from 20 μm to 5 μm . This shows that the prepared emulsion is a macroemulsion which is also known as conventional emulsion. The typical droplet size of macro-emulsion ranges from 1 – 100 μm and it has a turbid optical property which is the same as the prepared emulsion. Micro- and nano-emulsions has a droplet size of 10 – 100 nm and < 200 nm respectively (Aswathanarayan & Vittal, 2019). Macro-emulsions will lead to a separation of two-phase over time as it is thermodynamically unstable (Yao et al., 2021).

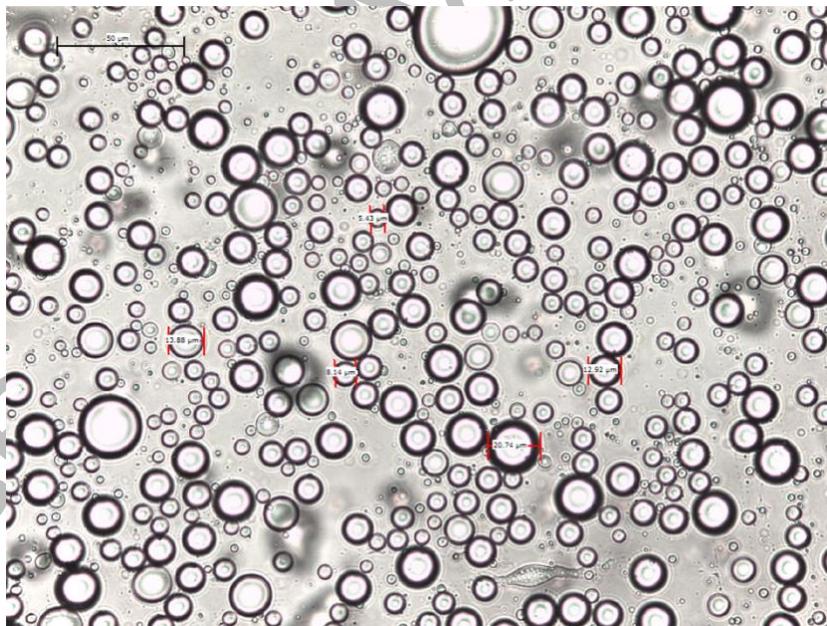


Fig. 3–Photography of prepared emulsion under microscope

4.2 Impact of demulsifier on produced water turbidity

The bottle test screening was conducted according to the experimental procedures on the prepared emulsion. The dosage of demulsifier used are 7 ppm, 10 ppm and 20 ppm. **Fig. 4** illustrate the results obtained from the experiment after the injection of chemicals and immersed in water bath for 15 minutes at 60 $^{\circ}\text{C}$. The impact of demulsifier on the changes in the turbidity reading of the treated produced water sample was studied. The turbidity of the produced water is mainly caused by the presence of oil droplets dispersed in the produced

water. The greater the turbidity reading, the greater the intensity of scattered light. As a result, clear water has a low turbidity value, indicating that there are less oil droplets suspended in the produced water. Based on the results shown in **Table 4**, demulsifier A showed no impact on the turbidity of the produced water as a constant 1000 NTU reading were recorded. As for demulsifier C, a slight change in the turbidity reading of 966 NTU recorded at a dosage of 10 ppm. The impact of demulsifier C is not significant as the reading of turbidity is still high. It can be said that the cationic polyamine and EO/PO block copolymers demulsifier are ineffective in treating O/W emulsion of the gas condensate field. However, as compared to the blank sample, the demulsifiers D and B significantly reduced the turbidity reading of the treated sample. The addition of demulsifier B resulted in a constant decrement of turbidity reading as the dosage increased from 7ppm to 20ppm where the lowest reading of turbidity reading of 210 NTU at 20 ppm. A slight increment in the turbidity reading was recorded as the dosage increased to 30 ppm which is unfavourable. Besides, at a dosage of 7ppm, demulsifier D had the lowest turbidity reading (181 NTU) with the least dosage of demulsifier. The reading of turbidity started to increase when the dosage of demulsifier was increased to 20 ppm where a turbidity measurement of 593 NTU was recorded. The significant reduction in turbidity reading of demulsifiers D is due to the highly active molecules of the demulsifier which can attach to the oil/water interface and lower the stability of dispersed oil droplets. At a dosage of 7 ppm, the adsorption behaviour of demulsifier D molecules on the oil/water interface was remarkable which resulted in a low turbidity reading. Further increase of the dosage of demulsifier D has caused the turbidity reading to increase as the demulsifier D has reached the saturation or optimal point at 7 ppm. The molecules of demulsifier starts to form micelles due to aggregation when the demulsifier dosage exceeded the micelle concentration (CMC) which increased the turbidity of treated produced water sample (Huang et al., 2019). The demulsification efficiency (D_e) of the demulsifiers were calculated based on **Eq. 1**. Based on the results, demulsifier D recorded the highest demulsification efficiency up to 82 % at a minimum dosage of demulsifier which is 7ppm. Demulsifier B was able to achieve a demulsification efficiency of 79 % at a dosage of 20ppm. Therefore, demulsifier D and demulsifier B were further optimized to treat the O/W emulsion of produced water from the gas condensate field.

		Chemical dosage (ppm)				
		0	7	10	20	30
Turbidity (NTU)	Type of demulsifier	1000	1000	1000	1000	1000
	Demulsifier A	1000	421	386	210	325
	Demulsifier B	1000	1000	966	1000	1000
	Demulsifier C	1000	181	194	593	756
	Demulsifier D					

Table 4–Turbidity result of various demulsifiers

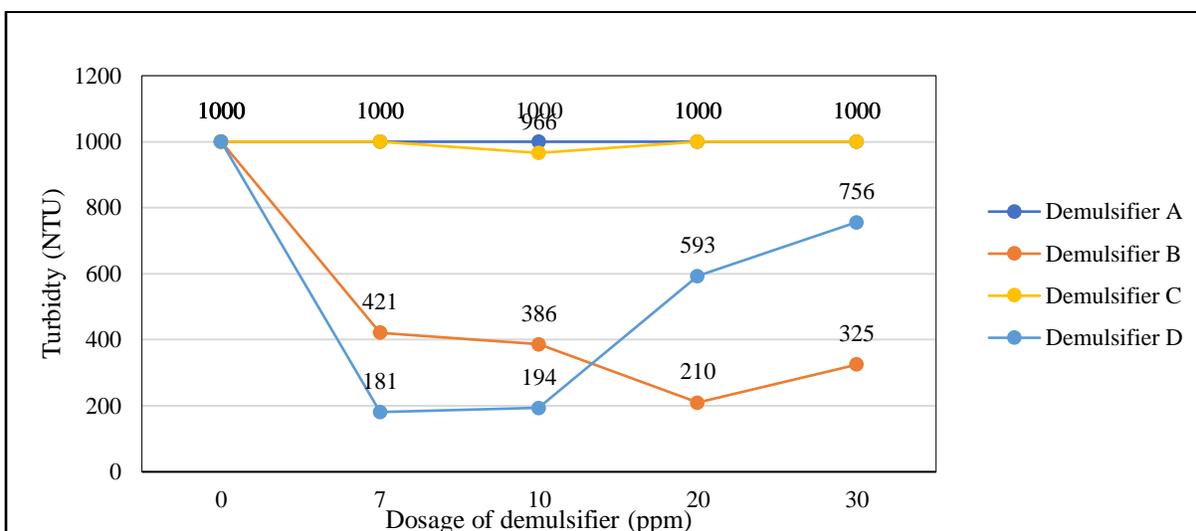


Fig. 4–Impact of demulsifier on the turbidity of treated produced water sample at 60 °C

4.3 Development of demulsifier (DB) formulation

A unique demulsifier was formulated by incorporating demulsifier D with demulsifier B. The unique demulsifier is prepared by adding 10 ml of demulsifier D and 10 ml of demulsifier B into a tube. The mixture is then stirred at 1200 rpm for 10 minutes using Barnstead Thermolyne Maxi Mix II Vortex Mixer as shown in Fig.5. The unique demulsifier DB was then used to conduct bottle test screening at dosage of 7ppm, 10ppm and 20 ppm for treating the O/W emulsion. Fig. 6 illustrate the turbidity results obtained after addition of demulsifier DB. According to the outcome of the testing, the newly formulated demulsifier DB decreased the turbidity reading of treated produced water sample to 45 NTU which is lesser than results attained by the addition of demulsifier D alone (181 NTU). Based on Eq.2, the demulsification efficiency (D_e) of 96 % was attained at 7 ppm of demulsifier DB. The water clarity of the produced water sample is much clearer after the addition of demulsifier DB when compared with blank sample which is very turbid as shown in Fig. 7.



Fig. 5- Preparation of demulsifier DB using Barnstead Thermolyne Maxi Mix II Vortex Mixer

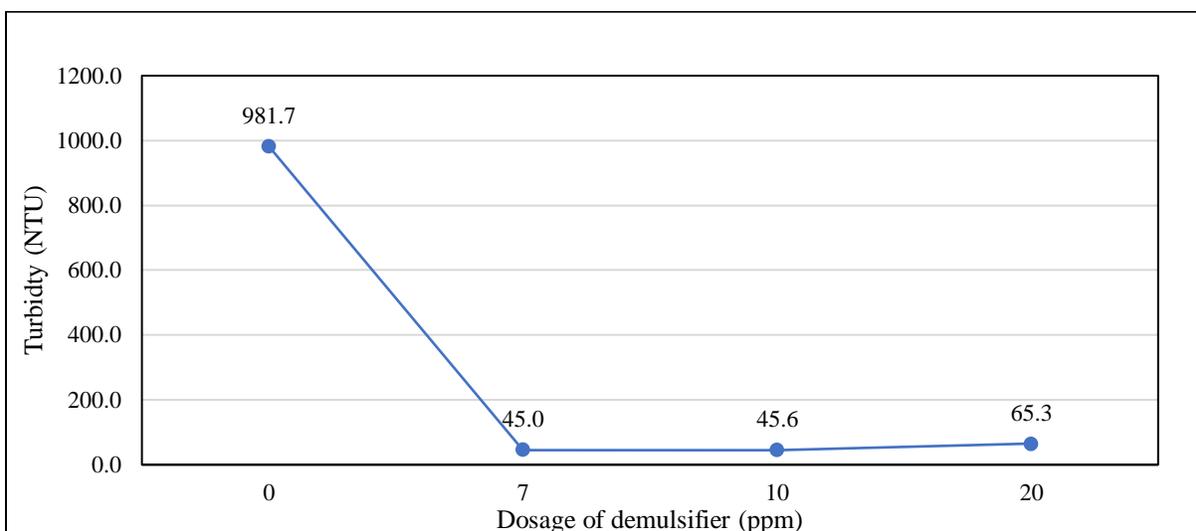


Fig. 6–Impact of demulsifier DB on the turbidity of treated produced water sample at 60 °C

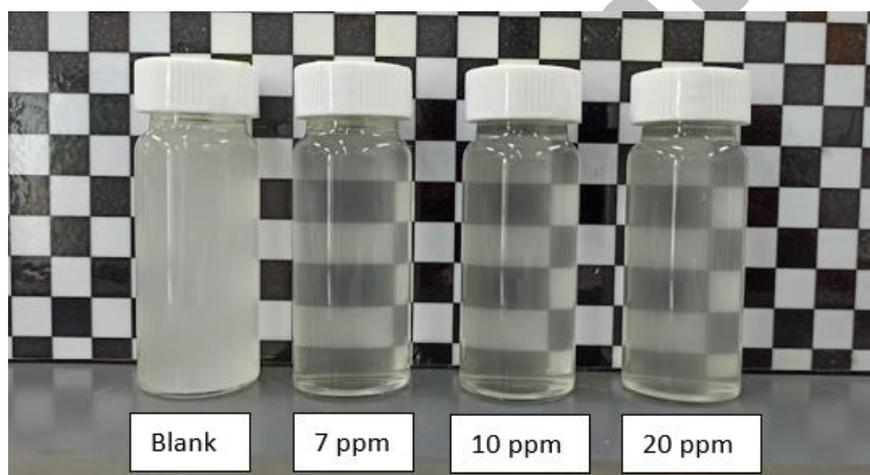


Fig. 7–Produced water after the addition of demulsifier DB

4.4 Impact of demulsifier DB on oil-in-water content (OiW)

The OiW content of the treated produced water sample with demulsifier DB were measured using TD-500 TD-500D Handheld Oil in Water Analyser and the results are shown in Fig. 8. Based on the results obtained, the blank sample without any addition of demulsifier recorded an OiW content of 1008.3ppm. At a dosage of 7ppm, OiW content reading of 97.1 ppm which is the lowest reading was obtained with demulsifier DB. When the unique demulsifier DB was applied, the results demonstrate a substantial drop in OiW content at an oil removal efficiency (OR_e) of 90%. As the dosage of demulsifier was increased after 7 ppm, the OiW content gradually increased. demulsifier DB helps to neutralise the negatively charge oil droplets and reduce zeta potential, lowering repulsion and weakening the oil droplets stability. However, excessive amounts of demulsifier DB may cause the flocs to become positively charged, preventing the production of big flocs from tiny ones. As a result, an excess of the demulsifier DB impedes the oil removal from wastewater which can be seen by the increase of OiW content from 97.1 ppm to 200 ppm as the dosage increase to 20 ppm. Therefore, the optimum dosage of demulsifier DB is 7ppm to achieve the lowest reading of OiW content. The treated produced water sample is further validated with interfacial measurement and Turbiscan analysis to show that the demulsifier DB helps in the demulsification of O/W emulsion.

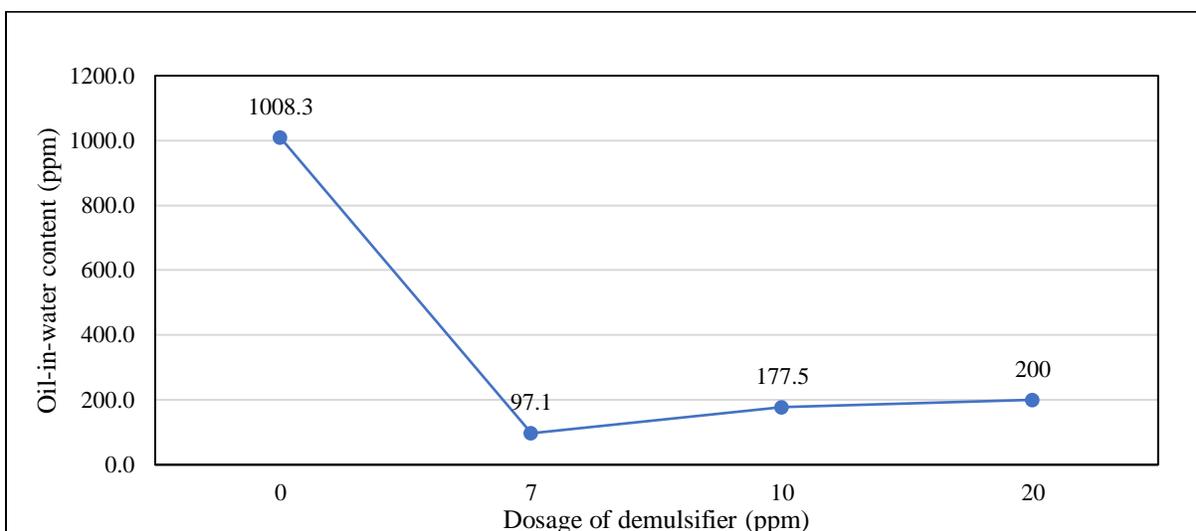


Fig. 8–Impact of demulsifier DB on the OiW content of treated produced water sample at 60 °C

4.5 Impact of demulsifier DB on interfacial tension (IFT)

Produced water was the aqueous phase and condensate was the drop phase in this IFT analysis. The blank sample without addition of chemical has a high IFT value (24.98 mN/m) indicates that a steady emulsion is still present as shown in **Fig. 9**. A high IFT results indicates a highly stable emulsion (Kumar & Mandal, 2018). With the addition of demulsifier DB, it can be seen that the newly formulated demulsifier was able to minimize the interfacial tension at oil/water interface. The interfacial tension between oil and water reduced significantly from 24.98 mN/m to 9.38 mN/m at demulsifier DB dosage of 7ppm. Demulsifiers can significantly lower interfacial tension, which weakens the oil droplets' stability as the rigid film surrounding the oil droplets tends to breakdown readily. The oil droplet with the addition of demulsifier DB has a smaller shape compared to the untreated sample as the demulsifier DB neutralize the natural surfactant present on the oil droplet film. Minimizing the droplets' stability leads to the coalescence of oil droplets which leads to the separation of condensate and produced water (Huang et al., 2019). Demulsifier DB was able to decrease the IFT at the oil/water interface, leading to an increased separation rate of oil and water via enhanced flocculation and coalescence process.

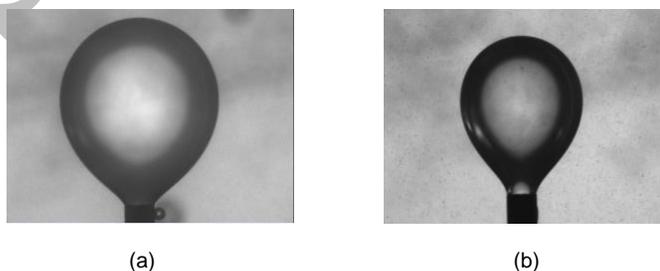


Fig. 9–Image of oil droplet without demulsifier DB (a) and after the addition of demulsifier DB dosage at 7ppm (b)

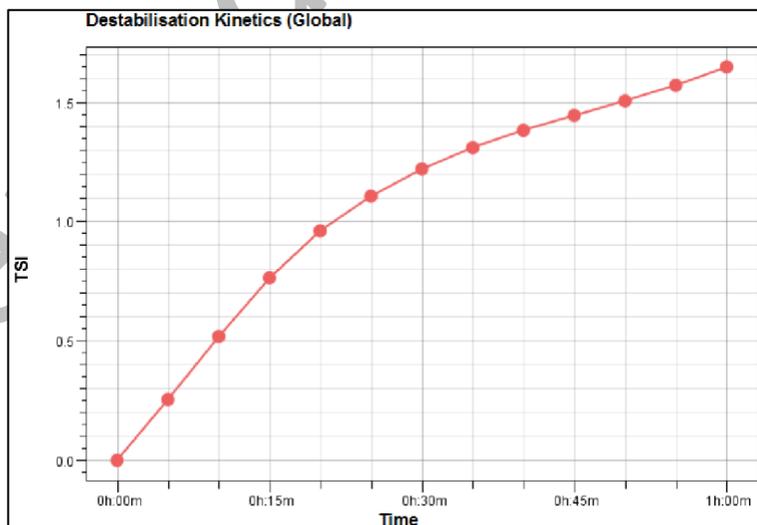
4.6 Demulsification analysis using Turbiscan Lab® Expert

In order to demonstrate how the emulsion ageing process influences the oil droplets, the sample can be optically analysed by the Turbiscan equipment. The Turbiscan Stability Index (TSI), which is used to characterise physical stability, is determined by adding

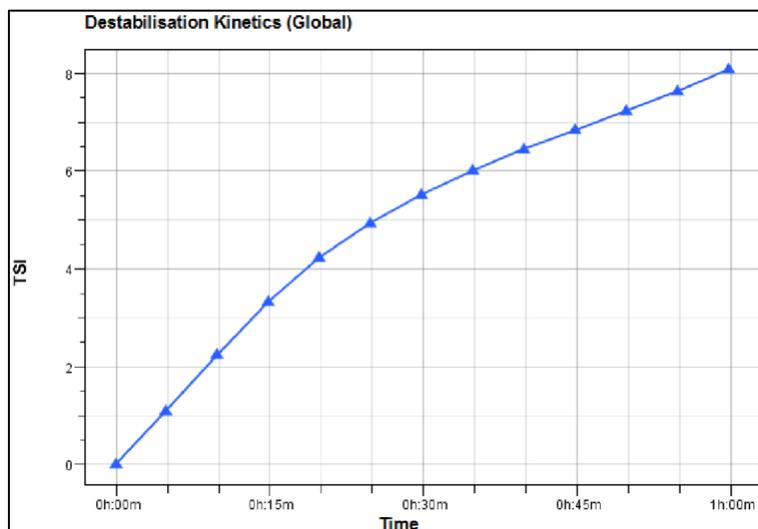
changes in transmission (T) or backscattering (BS) of light over the course of several measurements as a function of sample height (Paweł et al., 2020). The main advantages of TSI measurement are the ability to analyse opaque systems (such as crude oil emulsions) over a short period of time and the samples are undisturbed during TSI measurement from transmission/backscattering data as no dilution is required. TSI measurement has the advantages over several typical stability determination techniques, such as conductivity measurements, and ageing tests (Xu et al., 2013). The TSI value will trend upward for any destabilization occurrence, including coalescence, creaming, sedimentation, flocculation, or Ostwald ripening, because the back-scattered signal and the photon transport mean free route are inversely related ($BS \approx 1/\sqrt{\lambda^*}$) (Acosta et al., 2020). In short, Turbiscan Stability Index (TSI) measurements are utilized to determine how stable an emulsion is. Based on **Fig. 10a** and **10b**, it can be observed that there is a rise in the slope and TSI value after the addition of demulsifier DB compared to blank sample. Over the period of 30 minutes, the slope of the treated sample with demulsifier DB showed a rapid increase which indicates a steady increase of TSI values. The rate of slope change indicates how quickly separation occurs in which higher instability is implied by higher TSI value. (Liu et al., 2011; Mengual, 1999). Compared to TSI value of blank sample without the addition of demulsifier DB which is 1.6, the treated produced water sample with 7 ppm of demulsifier DB resulted in a significant increase of TSI value of 8 as shown in **Table 5**. The emulsion's stability is considered weaker when the TSI value is high (Li et al., 2019). This shows that the demulsifier DB helps in the demulsification of the emulsion efficiently in a short period of time compared to the blank sample without any chemical additives.

Dosage of demulsifier DB (ppm)	TSI value
0	1.6
7	8

Table 5–Turbiscan analysis of DB demulsifier conducted at 60 °C



(a)



(b)

Fig. 10–Comparison of Turbiscan analysis of sample without demulsifier DB (a) and after the addition of demulsifier DB dosage at 7ppm (b) conducted at 60 °C

4.7 Demulsification mechanism of O/W emulsion using mixed surfactant system

Generally, chemical demulsification, as performed in this study, is a process in which an optimum amount of demulsifier is added to emulsions and the emulsion is rapidly agitated to separate the oil and water. Ostwald ripening happens when the dispersed phase which is the oil droplets may readily diffuse in a continuous phase which is the water to come together for flocculation. The demulsifier molecules of a mixed surfactant solution will be absorbed to the oil droplets' surface, thus lowering interfacial tension and rupturing interfacial film strength which holds the oil in droplets form. This will indirectly minimize the oil droplets' stability and allow the oil droplets to accumulate. The accumulation of oil droplets is referred to as the flocculation process in which the oil droplets cluster together in the water continuous phase. This causes the droplets of oil to coalesce and form larger droplets. Finally, depending on the phase density of emulsion's dispersed, the creaming or sedimentation processes take place when the denser phase settles down below the less dense phase (Abdulredha et al., 2020). Since combinations of various surfactant types typically demonstrate synergism in their impact on the characteristics of the system, utilising a mixed surfactant system is more effective than using conventional method of single surfactant (Holland & Rubingh, 1992). Mixed surfactant demulsifiers have been shown to be more effective than single-surfactant demulsifiers in breaking oil-water emulsions. By combining different surfactants with different mechanisms of action, mixed surfactant demulsifiers can more effectively reduce the interfacial tension, provide steric hindrance, and neutralize electrostatic repulsion between the droplets (Kronberg et al., 2014). Besides, mixed surfactant demulsifiers can improve the stability of the demulsification process by providing a broader range of surface activity and surface coverage (Kronberg et al., 2014). This leads to a more complete destabilization of the emulsion, resulting in faster and more efficient separation of the oil and water phases. After analysing the experimental data, considerable impacts at interfaces with the solution can be noticed even at low concentrations of mixed surfactants in the emulsion sample. The most noticeable result is a reduction in interfacial tension caused by adsorption of surfactant molecules at oil droplets interface, as seen in Fig. 11.

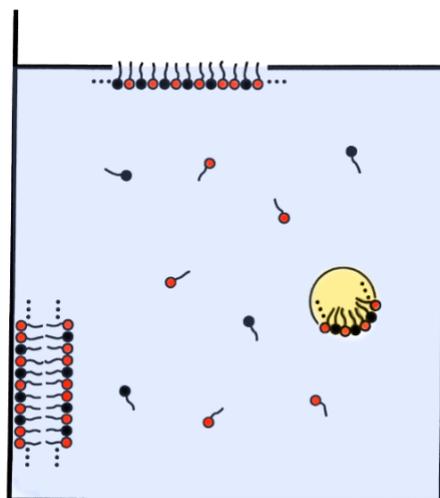


Fig. 11–Occurrence in a mixed surfactant system of two surfactant types

5. CONCLUSION

The O/W emulsion of gas condensate field was treated through demulsification in the present study. Various types of demulsifiers were studied by bottle test and based on the study, the demulsifiers D and B reduced turbidity substantially higher when in comparison with demulsifier A and C. Therefore, an unique demulsifier DB was formulated at an optimal weight percentage ratio of D/B. The unique demulsifier DB exhibited the highest efficiency in removing the dispersed oil droplets of the produced water compared to single demulsifier use. The demulsifier DB was able to neutralize the charge around the dispersed oil droplets leading to coalesces of oil droplets and reduced the OiW content in the produced water. At a temperature of 60 °C, the optimum dosage of demulsifier DB was determined at 7 ppm. An oil removal efficiency (OR_e) of 90% was achieved where the OiW content of the treated produced water sample reduced from 1008.3 ppm to 97.1 ppm under 15 minutes. Moreover, the IFT and Turbiscan analysis exhibited that the utilization of demulsifier DB further validates the results obtained for the OiW content measurements in which the demulsifier helps in minimizing the interfacial tension at oil/water interface and reduce the stability of the produced water sample for the separation of water and condensate to occur. This shows that the resin alkoxyolate (Demulsifier B) and cationic surfactants (Demulsifier D) work together well to treat the O/W emulsion from gas condensate field.

STATEMENTS AND DECLARATIONS

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Nomenclature

D_e	[%]	Demulsification efficiency
T_o	[NTU]	Initial turbidity
T	[NTU]	Final turbidity
OR_e	[%]	Oil removal efficiency
OiW_o	[ppm]	Initial oil-in-water content

OiW [ppm] Final oil-in-water content

Sub- and Superscripts

o Initial
e Efficiency

Abbreviation

OiW Oil-in-water content
IFT Interfacial tension
W/O Water-in-oil
O/W Oil-in-water
W/O/W Water-oil-in-water
TSI Turbiscan stability index
HLB Hydrophilic–lipophilic balance

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