Demulsifier Selection Guideline for Destabilizing Water-in-Oil Emulsion for both non-EOR and EOR Application

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1. ABSTRACT

The most common method for resolving water-in-oil (W/O) emulsions is chemical demulsification. The bottle test is a recommended procedure to analyze a combination of essential parameters such as the demulsifier dosage, residence time, heat, degree of agitation to generate the emulsion and agitation effects after demulsifier injection. It is an extensive and time-consuming selection procedure. Furthermore, the previous demulsifier selection guideline reported in the literature had limitations and was not suitable for the Southeast Asia region. This study describes the development of a new demulsifier selection guideline that relates the demulsifier properties to the crude oil characteristics and is more representative for resolving emulsions in the Southeast Asia environment. In developing the selection guideline, four types of synthetic crude were used, with the crude API ranging from 27˚ to 40˚. Sixteen demulsifiers with a relative solubility number (RSN) ranging from 11 to 21 were evaluated comprising resin alkoxylate and modified polyol base demulsifiers. An emulsion test matrix was developed by creating emulsions with different wax contents, asphaltene content and solid contents in the crude oil; then, the demulsifier was screened for all the matrices. Based on the demulsification bottle test completion for all the test matrices, the demulsifier selection guideline was developed and then validated with the blind test in resolving emulsions from the actual crude. The validation results achieved an 86.7% match rate between the guideline output and the lab experimental result. This proved that good agreement had been established between the demulsifier properties and the crude characteristics.

2. INTRODUCTION

The most common type of emulsions in the petroleum industry are water-in-oil (W/O) emulsion. Once formed, W/O emulsion can adversely impact petroleum dehydration and desalination processes. They cause corrosion, scaling, and mechanical changes in gas–oil separation units, affect the operation of the pumping systems due to the elevated viscosity, influence raw material processing quality

and increase energy consumption (Binks and Rocher, 2009)**.** Crude oil emulsions must be separated almost completely before the oil can be transported and processed further.

W/O emulsion is strongly stabilized by native crude oil emulsifiers (surfactants), which tend to migrate and concentrate at the W/O interface, forming a film that reduces the interfacial tension between the phases, preventing droplet coalescence. Asphaltenes, resins, waxes and fine solid particles are generally considered to be natural emulsifiers and are thought to be responsible for the emulsion stability (Zaki et al., 2000)**.** On the other hand, the use of chemicals such as alkali, surfactants, and polymers in the injected water in EOR technologies not only interacts with rock to change the wettability conditions, but also reacts with oil to form emulsions that improve oil recovery. However, the natural oil–water interfacial properties are also altered, which possibly makes the W/O emulsions much more stable. Thus, while oil field emulsion might possess beneficial effects for oil recovery during oil reservoir Enhanced Oil Recovery (EOR) flooding processes, they create challenging conditions in the subsequent oil processing operations and must be neutralized, reduced, or removed. Therefore, for many decades, understanding their causes, both chemically and physically, and predicting their formation and how to mitigate them, has been a very important technical development objective in the petroleum industries.

Chemical methods are the most common mitigation approach for emulsion resolution in both the oil fields and the refinery (Angle, C.W., 2001)**.** The application of chemicals designed to neutralize the effects of emulsifying agents has the great advantage of being able to break the interfacial film effectively without the addition of new equipment or modification of existing equipment. However, due to the great number of different types of crude oils and EOR process conditions, development, and selection of effective demulsifiers for regional crude oils has become a serious challenge.

Currently, in the oil industry, the selection of a demulsifier is still based mainly on trial and error after some preliminary screening such as bottle testing (Wu et al., 2003)**.** Normal bottle testing duration in screening the demulsifier raw chemicals is very time consuming as there are a lot of raw chemicals to be tested which sometimes can reach 40 to 50 types of raw chemical. There should be a systematic process for selecting a suitable demulsifier based on the increasing knowledge of demulsifier chemistry. Marques-Silva et al. developed a model that relates the crude oil acidity number, water salinity and demulsifier relative solubility number. Correlation between the crude oil nature, the associated water salinity and the demulsifier hydrophilicity (RSN) are described as per Eq. (1) below (Marques-Silva et al., 1997)**:**

$$\ln S = -0.77A - 0.28\ RSN + 8.17 \qquad (1)$$

where S is the associated water salinity and A is the crude oil acidity number.

This model is proposed as a method for demulsifier selection of crude oil/ water systems in which the acidity number and water salinity are easy parameter to be measured in the laboratory.

Cooper et al. studied the hydrophilic–lipophilic balance (HLB) of the demulsifier used to break an emulsion of heavy oil, water, and clay. The degree of demulsification was found to correlate with the HLB of the surfactant. The most effective agents for dewatering had HLB values between either 4 and 6, or 13 and 15. For clay removal, the most useful surfactants had HLB values above 20 (Cooper at al., 1980)**.** Grenoble and Trabelsi agreed on the relationship of HLB with demulsifier performance by mentioning that the initial selection of the most suitable surfactant or surfactant combination based on the intrinsic HLB may be a valid starting point but should not be limiting for fine-tuning the system (Grenoble and Trabelsi, 2018)**.**

Temple-Heald et al. reported that because the RSN of a demulsifier is a measure of its solubility properties, it is a key factor in demulsifier selection because solubility properties dictate whether the chemical will perform effectively as a surface-active agent at the oil/water interface. Demulsifier molecular weight, RSN and functional groups are the keys to provide good separation of the water from

the oil emulsion for heavy oil applications. In terms of the RSN evaluation, all demulsifiers < 8 RSN did not exhibit any separation whilst surfactants with RSN > 11 showed an improvement in the emulsion separation. In terms of the level of alkoxylation levels, the products that had highly mixed alkoxylation levels had better demulsification properties than single alkoxylated products (Temple-Heald et al., 2014). Al-Sabagh and Noor El-Din stated that the optimum demulsification efficiency, with 80% water separation, was obtained by a demulsifier with a high RSN value of 22 (Al-Sabagh and Noor El-Din, 2014).

Many studies have been carried out to evaluate the stability and demulsification of crude oil emulsions. A.A. Pena et al. carried out research on the effect of alkylphenol polyalkoxylated resins and polyurethanes on the stability and properties of brine-in-crude oil emulsions. The phenolic resins promoted coalescence of droplets, supplemented by the cross-linked polyurethanes, which may act as "bridges" between droplets, thus increasing the probability for collisions leading to successful coalescence events. A mixture of 200 ppm of polymer polyurethane and 40 ppm of phenolic resin managed to achieve complete water separation in less than 2 hours at 30 °C (Pena et al., 2005). F. Zhang et al. described that one of the main challenges in demulsifier research and application is the demulsification of Alkali Surfactant Polymer (ASP) flooding produced liquid, because the ASP application induces oil-in-water, water-in-oil and multiple emulsions which are very complex. To tackle this, there is a need to study dual function demulsifiers which can provide demulsification of both O/W and W/O emulsions at the same time (Zhang et al., 2017).

About resin alkoxylate demulsifier application, the literature has reported that ethylene oxide: propylene oxide mixes and resin: alkoxylate ratios are more important for assessing demulsifier performance than the type of resin used. Furthermore, the paper reported that nonylphenol resin alkoxylates were the best performing products for treating emulsions for heavy oil applications (Mohammed et al. 1994). As reported in other literature, the efficiency of a surfactant to act as a demulsifier depends on a few factors related to the surfactant structure, namely, the distribution of the demulsifier molecules throughout the bulk volume of the emulsion, the partition of the demulsifier between the phases, the process temperature, pH, and the salt content of the aqueous phase (Auflem, 2002). In other literature, molecular dynamic simulation software Materials Studio was used to determine the effectiveness of the demulsifier. The simulation results show that the demulsifier with ethylene oxide (EO) and propylene oxide (PO) values of 21 (EO) and 44 (PO) achieved the highest water removal amount of 7.21 ml with an overall error less than 1.83 in which the predicted results are consistent with the experimental screening results (Gent et al., 2022).

This paper will discuss the establishment of a demulsifier selection guideline based on the demulsifier characteristics of Relative Solubility Number (RSN) with the crude oil characteristics including asphaltene content, wax content, and solid content. These three elements are the emulsion stabilizing agents and the impact of them in the emulsion behavior is discussed further in this paper. The previous demulsifier selection guidelines were focusing on the crudes from Northern America (Canada), Europe (UK and France) and Middle East (Egypt) whereas this study are meant for Southeast Asia region which the crudes have higher crude API but some of the fields may contain high wax and solid content as describes in **Table 1.** Nevertheless, the guideline can be used outside Southeast Asia boundary as well since the synthetic crude of API 27 included in this study resembles the heavy crude behavior which is not from this Southeast Asia region.

Table 1- Physical properties of Southeast Asia crude oil.

No	Properties	Value
1	Asphaltene	0.1 – 2 %
2	Wax content	1 – 10 %
3	Crude API	30 - 46°
4	Solid content	0 – 0.2%

Relative solubility number (RSN) is an empirically determined value that characterizes water solubility and the hydrophobic–hydrophilic character of a surfactant. It is commonly used to distinguish demulsifiers from emulsifiers. A demulsifier with an RSN value < 13 is considered insoluble in water or hydrophobic, while 13 <RSN>17 is dispersible at low concentrations, demulsifiers with an RSN > 17 are soluble in water or hydrophilic (Grenoble and Trabelsi, 2018). RSN has similarities with HLB as such that it measures the combined affinity of the hydrophobic part and lipophilic part of the surfactants to oil or aqueous phase. RSN has been widely used by surfactant manufacturers due to the simplicity of the testing in determining the RSN value (Wu et al., 2003).

Two demulsifier groups were studied, namely resin alkoxylate and a modified polyol type of demulsifiers. The resin alkoxylate demulsifier is a versatile demulsifier for covering all emulsion treatment aspects and is usually used as the major portion in demulsifier formulations. It is a fast water dropper, which separates the emulsion quickly, while modified polyol is a good demulsifier for treating emulsions from heavy oil or low API crude oil. In term of resin alkoxylate demulsifier application, Mohammed et al. (1994) has evaluated that the ethylene oxide: propylene oxide mixes and resin: alkoxylate ratio are more important for assessing demulsifier performance than the type of resin used. From this paper as well, nonylphenol resin alkoxylates showed the best performing products in treating emulsion for heavy oil application. Normal demulsifier screening may took 2 or 3 months to obtain the formulation. After the guideline has been developed, team took only around 2 weeks in average to obtain the suitable demulsifier formulation in resolving the emulsion.

3. MATERIALS AND METHODS

3.1 Materials

As the basis for developing the demulsifier selection guideline for non EOR emulsions, four types of synthetic crude oil were used in the demulsifier bottle test with crude oil API ranges from 26˚ to 40˚. Lower API indicates a heavier crude oil. Non EOR emulsion means that the emulsion stabilization is not caused by the EOR chemical surfactant. The synthetic crude oil recipe was developed based on the crude True Boiling Point (TBP) from the crude assay. Light components would involve TBP from C5-150 °C, the intermediate components include TBP of 150-370°C distillate and the heavy components TBP ranging from 370-540°C. Under light components of C5-150°C TBP, the components that need to be included were naphthene and aromatics solvent. For intermediate component, naphthalene needs to be introduced while under heavy components, asphaltene and wax were added into the synthetic crude oil. All these components need to be incorporated to a certain ratio to produce the four (4) types of synthetic crude. The physical properties of the synthetic crude oil are described in **Table 2** below. The synthetic crude oil was used to vary the amount of wax, resin, and solid particles in the crude oil in producing various kind of emulsion behaviors.

Table 2- Physical properties of synthetic crude oil.

Properties	Crude Oil API 27	Crude Oil API 34	Crude Oil API 37	Crude Oil API 40
Wax (wt%)	2.18	6	11.55	2.85
Asphaltene (wt%)	1.6	0.18	0.72	0.36
Saturate (wt%)	29.8	30.1	52.1	37.4
Aromatic (wt%)	4.5	29.1	20.7	28.0
Solid (wt%)	0.1	0.1	0.1	0.1

In the bottle test, 16 different base demulsifiers supplied by CRODA with RSN ranges from 11 to 21 were used, comprising resin alkoxylate and modified polyol groups. The chemical structures are illustrated in **Fig. 1** and **Fig. 2**. For the resin alkoxylate demulsifier, the resins have some aromatic hydroxyl groups that react with ethylene oxide/propylene oxide. For the modified polyol demulsifier, the alkoxylated polyol compound is modified by a quaternary amine capping unit to give the desired characteristics of demulsifier (Scheibel and Menkhaus, 2005).
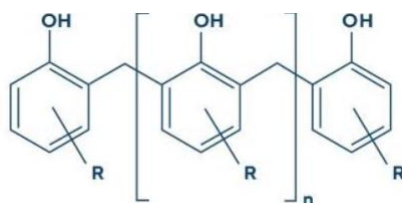
Fig. 1- Chemical structure of resin alkoxylate demulsifier.
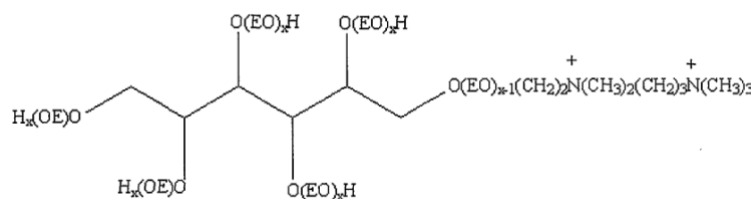
Fig. 2. Chemical structure of modified polyol demulsifier.

For the emulsion-stabilizing agent, asphaltenes were introduced into the synthetic oil by adding vacuum residue in the range of 3 wt% to 26 wt% that had been collected from the distillation process at the PETRONAS Malaysian Refining Company Sdn Bhd (MRCSB). The vacuum residue contained 28% saturate, 37% aromatic, 29% resin and 6% asphaltene. For the effect of solid particles, this study used Aerosil R974, a moderately hydrophobic solid nanoparticle, provided by Evonik Inc. For evaluating the effect of wax on the emulsion stability, 2 wt% to 12 wt% of paraffin wax, namely ACROS organic type, which has a melting point of 42 °C and boiling point of 370 °C, was incorporated into the synthetic oil.

3.2. Emulsion Tendency Test for non-EOR emulsion

Before performing the demulsification test, an emulsion tendency test was conducted for the blank sample without any demulsifier injected to evaluate the stability of the emulsion produced. The formation of the emulsion and observation of the emulsion stability of each synthetic crude oil was performed in the laboratory following the inhouse standardized protocol as below:

1. Place 50 ml of synthetic crude oil and 50 ml of 2% NaCl water and warm to 60 °C in a 100 ml centrifuge tube.
2. Manually shake 100 times to create a homogeneous emulsion.
3. Place the tube in a water bath maintained at 60 °C, except when taking photographic images.
4. Observe, photograph, and record the volume of emulsion left at 5, 10, 15, 20 and 30 minutes.
5. Record the appearance of the emulsion.

3.3. Demulsification Test

For the demulsification bottle test to evaluate non-EOR emulsion, 2% NaCl was used as the synthetic water. This represents the average salinity of the produced water in Malaysian offshore fields. The bottle test is conducted by mixing the crude oil and brine in a 50:50 ratio, because the emulsion behavior is usually at a maximum at this water to crude oil ratio. Each sample was manually shaken 100 times to produce a homogeneous emulsion. A total of 100 ppm of each base demulsifier was dosed into the emulsion mixture. This is the baseline concentration that is normally applied during the demulsifier screening process. After dosing the demulsifier, the samples were shaken by hand for another 20 times before placing the tubes back in the water bath. Monitoring of the emulsion separation was recorded at 30 minutes. The demulsifier bottle tests were performed at two different operating temperatures of 60 °C and 35 °C. These temperature points were selected in accordance with the operating temperature of the demulsifier injection in the Malaysia offshore fields. **Table 3** presents the test matrix of the bottle tests that were conducted to study the relationship between the demulsifier performance and crude oil properties for a non-EOR emulsion.

Table 3- Test matrix of non-EOR demulsification test.

Parameter	Testing Condition
Crude Oil API (°)	27, 34, 37 and 40
Temperature (°C)	35 and 60
Asphaltene content (wt %)	0.09–1.8
Wax content (wt%)	2.85–11.55
Solid effect (wt%)	0.1 and 0.2

For the EOR induced emulsion demulsification guideline development, crude oils from three EOR fields were used, namely from Field A, Field D and Field B. The test matrix of the EOR demulsification test is illustrated in Table 3. For Field A, a chemical EOR (CEOR) application was implemented using a proprietary formulation of surfactant S which is an amphoteric type of surfactant. For Field D and Field B, an enhanced water alternate gas (EWAG) application using surfactant E was implemented, which is a foam surfactant comprising a mixture of anionic and amphoteric surfactants.

During the demulsification bottle testing, an amount of EOR surfactant as shown in **Table 4** was mixed with the synthetic produced water following the water composition from each field. The low concentration (LC) of the surfactant refers to the probable case of the emulsion which will be produced at the surface facilities, allowing for some surfactant adsorption into the rock in the reservoir. The high concentration (HC) of surfactant considers the worst-case scenario of the produced emulsion. The water with surfactant was then mixed with the actual crude oil following the water cut for each field and a test was conducted as per the field process temperature. To produce the emulsion, the mixtures were manually shaken 100 times, and the demulsifiers were dosed at the concentration described in **Table 3.** After 30 minutes of heating in a water bath, the emulsion separation for each sample was monitored.

Table 4- Test matrix of EOR demulsification test.

Parameters	Field A	Field D	Field B
EOR Method	CEOR	EWAG	EWAG
EOR Surfactant	Amphoteric type	Mixture of Anionic and Amphoteric type	Mixture of Anionic and Amphoteric type
EOR Surfactant Concentration (ppm)	250 750	900 2700	900 2700

Process Temperature (°C)	65	55	40
Watercut (%)	60 and 80	80	60 and 80
Demulsifier Concentration (ppm)	20—100	1000—3000	1000—3000

3.4. Blind Test for Demulsifier Validation

Once all the demulsification data sets were completed, the demulsifier selection guideline was established. In validating the guideline, a blind test was conducted in testing the demulsifier performance with the actual crude oil from during the development phase. For the blind test, 15 crude oil samples from 5 fields were tested with base demulsifiers in which their RSN were matched with their crude oil property data. The demulsifiers were tested using the bottle test method to evaluate whether they could resolve the emulsion from these actual crude oil samples.

4. RESULT AND DISCUSSION

4.1. Emulsion Tendency Test (Non-EOR Emulsion)

When crude oil and water are mixed, there is an intrinsic risk that they will stabilize and create an emulsion. The purpose of this emulsion tendency test is to create a stable and robust emulsion in the middle phase of the prepared synthetic crude oil for each individual API. **Fig. 3** shows the emulsion produced from each of the synthetic crude oils when mixed with 2% NaCl at 50:50 crude oil: water volume ratio after 30 minutes at 60 °C; and **Fig. 4** illustrates the emulsion separation times within the 30-minute time, with respect to different crude oil APIs. As can be observed from the graph, for the low crude oil API of API 27 and API 34, the emulsion was stable, which means no separation at all after 30 minutes. The most stable emulsion was from the crude oil of API 27, and the least emulsion produced from the crude oil of API 40. This is due to the increasing amount of vacuum residue in the heavy crude oil of API 27. It contained the highest asphaltene and saturate content, which are the stabilizing agents for the emulsion. The content of the vacuum residue in each of the crude oil were 26.2% for crude oil of API 27, 5.5% for crude oil of API 34, 4.4% for crude oil of API 37 and 3% for crude oil of API 40.

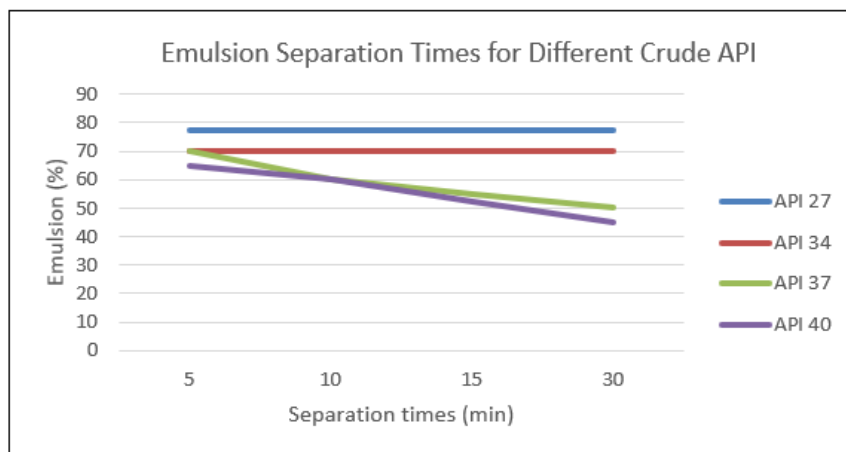**Fig. 3- Test matrix of non-EOR demulsification test.**

Fig. 4- Emulsion separation time of crude oil API 27, API 34, API 37, and API.

4.2. Demulsification Test (Non-EOR Emulsion)

After completing the emulsion tendency test, the next step was to conduct the demulsification test by dosing a certain concentration of demulsifier into the emulsion. In this case, 100 ppm demulsifier concentration was used to resolve the produced emulsion. The effect of different crude API, wax content, asphaltene content and solid content to the emulsion and demulsification behavior are discussed further in each subsection.

4.2.1 Effect of Crude API and Wax Content

From the demulsification test result, the most effective demulsifier in terms of their RSN for variation of crude oil API and wax content at 60 °C, are tabulated in **Fig. 5**. The demulsifiers are defined as working when they can completely resolve the emulsion or there is 1% or less remaining in the solution. The demulsification result from the two demulsifier chemistry groups shows that on average, the demulsifier with the high RSN, which is from 19 to 21, works best in resolving the emulsion compared to the low RSN demulsifiers. Increase in HLB/ RSN value increases the solubility of the demulsifier in the aqueous phase which is water. When the demulsifier is initially introduced to the water in oil emulsion, it will be thermodynamically stable at the interface of water droplets. Accordingly, the surfactants possessing high RSN migrate faster to the interface than those having low RSN. As a result of such enhanced migration toward the interface, the surfactant forms a continuous hydrophilic pathway between the dispersed water droplets. This leads to a rapture of the interfacial film surrounding the water droplets (Atta et al., 2009).

The high RSN demulsifier is a water soluble demulsifier which worked well in resolving the water-in-oil emulsion of this emulsified synthetic crude oil. Compared to this high RSN demulsifier, the demulsifier with RSN 19 was the most effective demulsifier in resolving the emulsion for all the crude oil APIs except for crude oil API 37. The crude oil of API 37 had the highest wax content, 11.55%, and that required a higher RSN, of RSN 21, for it to work effectively.
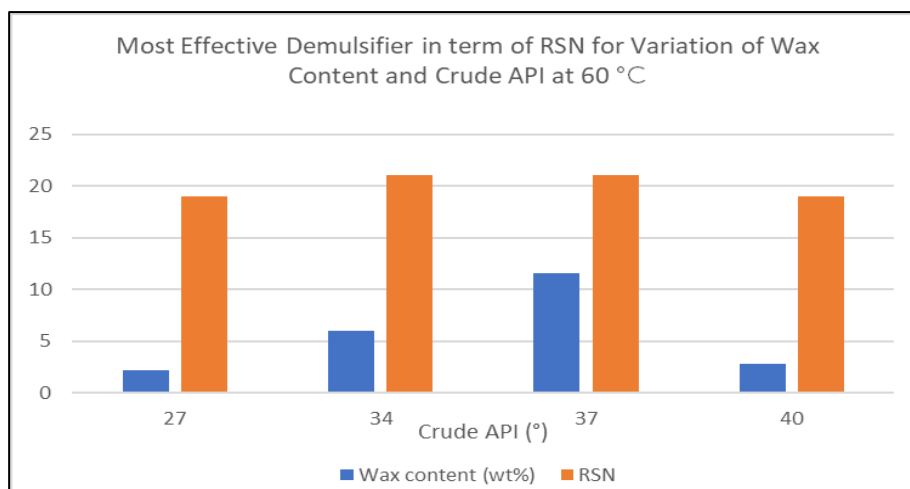
Fig. 5- Most effective demulsifier based on the RSN for variation in crude oil API and wax content at 60 °C.
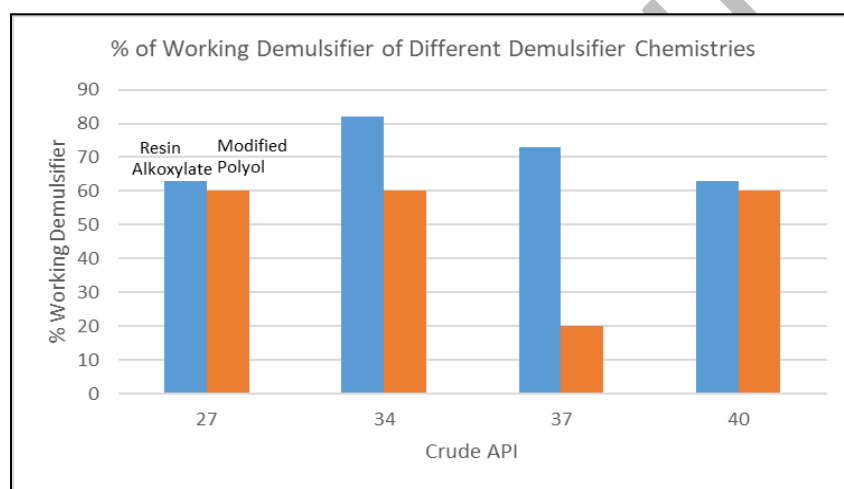

Fig. 6- Percentage (%) of working demulsifier at 60 °C based on different demulsifier chemistries.

The demulsification data, based on each demulsifier chemistry group at 60 °C for all the crude oil APIs are illustrated in **Fig. 6**. As determined by the demulsifier chemistry trend, the resin alkoxylate type was better in dehydrating the crude oil compared to the modified polyol type especially for crude oil API 37 where the crude oil was a bit waxy and the wax content was high, up to 11.55%. The percentage of the working demulsifier was higher for the resin alkoxylate which was about a 53% difference compared to the modified polyol type.

4.2.2 Effect of Temperature

Temperature plays an important role in the destabilization of emulsions. Demulsification evaluation also was conducted at lower temperature of 35 °C to determine the demulsifier performance at lower process temperature, as per **Fig. 7.** The test could not be conducted for crude oil at API 27 since this crude oil contains a high vacuum residue of 26.2% and comprises high asphaltene and saturates until it solidifies at this low temperature. Referring to the results in **Fig. 7.,** the demulsifier performance was decreased at 35 °C, especially for crude oil at API 37, which had a high wax content.
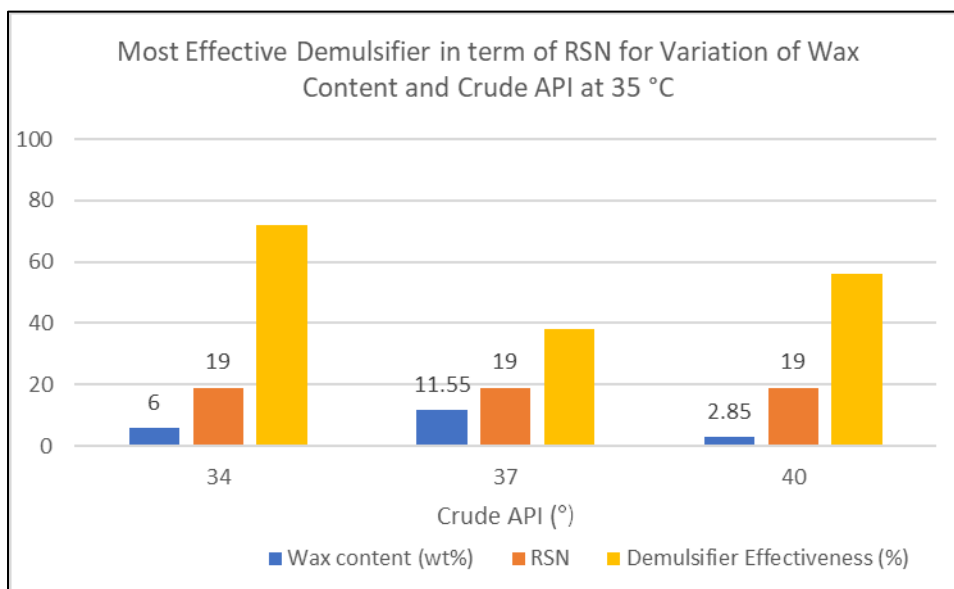
Fig. 7- Most effective demulsifier based on the RSN for variation in crude oil API and wax content at 35 °C.

At low temperatures, especially below the wax appearance temperature (WAT), waxes precipitate and interact with water droplets, forming a physical network between the droplets (Freitas et al., 2018). The formation of a network structure occurs by crystal aggregations through inter- and intramolecular non-covalent interactions in which wax concentration and crystal size affect the stabilization mechanism (Ghosh and Rousseau, 2011). This network can increase the emulsion stability (Visintin et al., 2008). Low temperature conditions hinder the collision of droplets thus increasing the oil viscosity. This increases the strength of the stabilizing agents at the droplets, thus providing low chances of settling. Despite this, demulsifiers at RSN 19 continue to work with high efficiency even at low temperatures, which implies the robustness of these demulsifiers.

4.2.3 Effect of Asphaltene

As mentioned in the introduction, asphaltene content and solid content stabilized the emulsion (Zaki et al., 2000). These two parameters have been studied in detail regarding their demulsification, by varying both components in the synthetic crude oil. SARA analysis of the Vacuum Residue shows the asphaltene content was 6%. This equated to the asphaltene content in the original synthetic crude oil being 1.6% (26.2/100*6%) in heavy crude oil of API 27, and 0.18% (3/100*6%) in the light crude oil, API 40.

Fig. 8 describes the demulsifier performance of each individual RSN upon varying the asphaltene content in the synthetic crude oil of the lowest and highest crude oil API. From the figure, the demulsifier performance reduced when the asphaltene content increased for both low and high crude oil API. (Zaki et al., 2000) illustrated that the higher the concentration of asphaltene, the higher the emulsion stability, which caused the demulsifier performance to reduce. Due to the large molecular weight of asphaltene, it forms a steric barrier to coalescence between two approaching water droplets which is considered the important factor in emulsion stabilization.

For a heavy crude oil of API 27, demulsifiers with RSN 16 work best for all asphaltene content between 1.2% and 1.8%, while for a light crude oil of API 40, demulsifiers with RSN 19 work best for all asphaltene content between 0.36% and 0.72%. Surfactant species that are available in the crude oil, such as asphaltenes and resins results in a HLD > 0. HLD is a dimensionless hydrophilic–lipophilic deviation from a reference state. The usual technique to dehydrate the crude oil is to break the W/O emulsion by adding a hydrophilic demulsifier surfactant that migrates at the drop interface and combines with the natural surfactants to attain an exact HLD = 0 mixture

formulation (Salager and Forgiarinni, 2012). Grenoble and Trabelsi, (2018) also supported this theory and mentioned that asphaltenes, which have a more lipophilic character, require a more hydrophilic demulsifier (oil soluble or less water soluble demulsifier) to shift the hydrophilic lipophilic deviation (HLD) towards zero. The optimum condition for demulsification is when the HLD is 0. Both references support the result that a lower RSN (less water soluble) demulsifier works better than a demulsifier with high RSN in resolving the emulsion for a crude oil with high asphaltene content. To promote good destabilization at the interfacial phase, the demulsifier must competitively adsorb at the interface, remove, and break up the asphaltenic aggregates and reduce the interfacial tension between the hydrocarbon aqueous phases and hence facilitate the droplet coalescence kinetics (Salager and Forgiarinni, 2012).
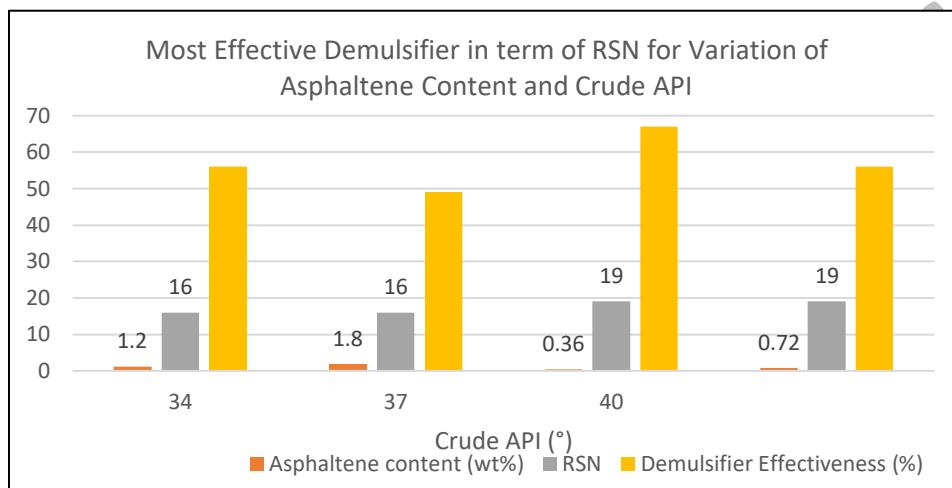

Fig. 8- Most effective demulsifier based on the RSN for variation in crude oil API and asphaltene content.

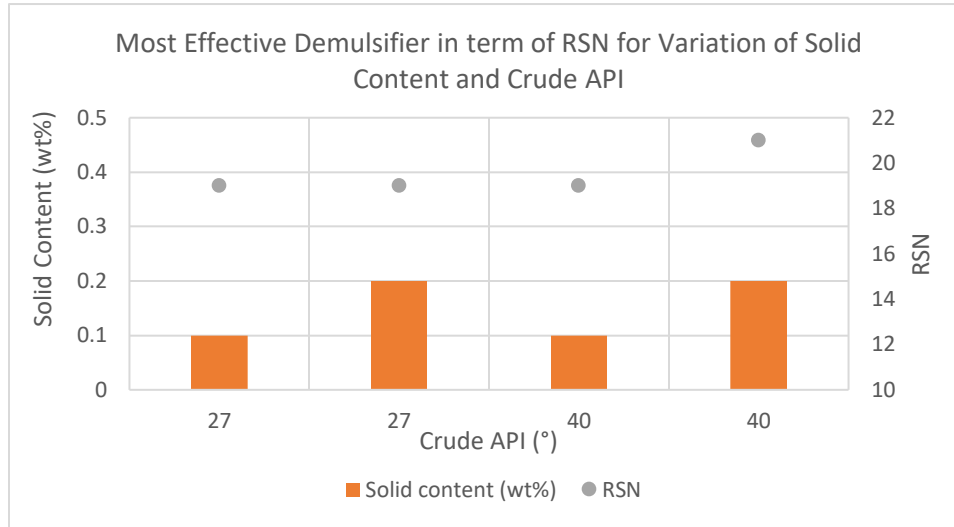### 4.2.4 Effect of Solid Content

Evaluation was continued to observe the demulsification effect when solid content was varied in the mixture of synthetic crude oil and water. To study the solid content effect to the emulsion stabilization, 0.1 and 0.2 wt% of Aerosil R974, a silica particle was mixed into the mixture of crude and water using a mechanical shaker. Aerosil R974, is a moderate hydrophobic type which tend to stabilize water-in-oil emulsions (Perino et al., 2013). This type of silica particle, with a contact angle of 143.7° helps water droplets disperse in oil phases, resulting in stabilization of water-in-oil emulsions (Wu et al., 2020).

Table 5 illustrates the percentage of working demulsifier at different solid amounts for both crude oil APIs. For crude oil API 27, because it had the highest amount of asphaltene at 1.6%, the combination of this asphaltene and solid caused the emulsion to become very stable, thus the percentage of working demulsifier was very low at about 16% compared to the high API crude oil that is easier to treat, and in which 63% of demulsifiers were still working to resolve the emulsion. Small particles strongly enhance water–crude oil emulsion stability when interactions with asphaltenes promote particle adsorption at the oil–water interface (Sullivan and Kilpatrick, 2002). The higher emulsion stability observed in the presence of hydrophobic particles results from the addition of severel effects: the tendency to form a structure in the oil dispersed phase and the influence of the attached particles at the interface (Perino et al., 2013). Due to this tighter emulsion, the demulsifier to resolve the emulsion is limited, especially for low API crude oil of API 27.

Fig. 9 presents the results of the best demulsifier RSN when solid effect is the main factor in stabilizing the emulsion for the lowest and highest API crude oils. The results indicate that the demulsifier with RSN 19 worked best for all solid content except for the light crude oil of API 40%, which need a higher water soluble demulsifier, which is a demulsifier of RSN 21, to resolve the emulsion at the higher solid content of 0.2 wt%.
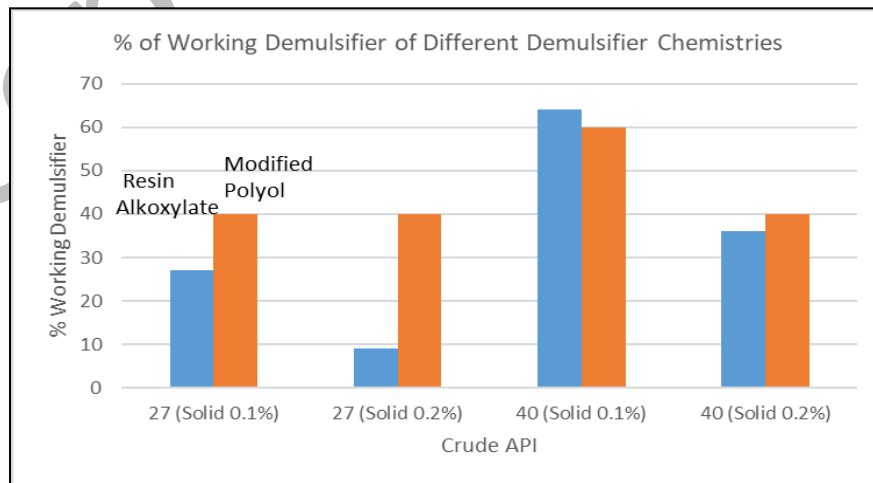
Table 5- Percentage of working demulsifier for both solid contents and different crude oil APIs.

Crude Oil API (°)	Solid content (wt%)	Working Demulsifier (%)
27	0.1	31
27	0.2	16
40	0.1	63
40	0.2	38

Fig. 9- Most effective demulsifier based on the RSN for variation in crude oil API and solid content.

With respect to the different demulsifier chemistries, the chart in **Fig. 10** illustrates the comparison between the modified polyol and resin alkoxylate demulsifiers with the presence of solids in the synthetic crude oil emulsion. For heavy crude oil, modified polyol demulsifiers are good for resolving the emulsion with the presence of solids but for light crude oil, the performance of both demulsifier chemistries is comparable. In addition, polyol demulsifiers are claimed to work effectively in resolving bituminous emulsions in Canada. This bituminous hydrocarbon is known to be very viscous or even non flowable under reservoir conditions, thus it produces highly stable emulsions which are made even more stable by the usual presence of clays (LaBerge and McCoy, 1982).

Fig. 10- Percentage of working demulsifier of different demulsifier chemistries with the variation in solid content.
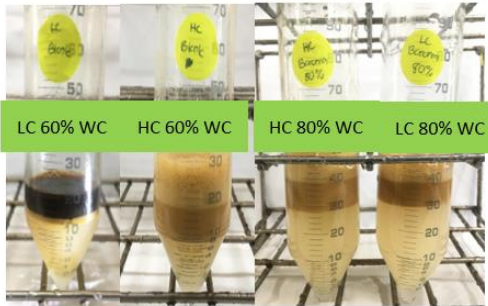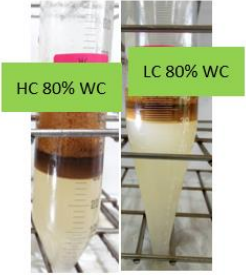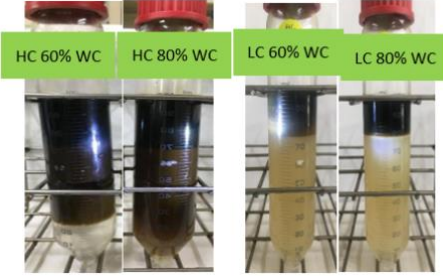
4.3. Emulsion Tendency Test (EOR Emulsion)

The effect of amphoteric EOR surfactant concentration on the emulsion separation was studied with the concentrations of 250 ppm and 750 ppm for Field A CEOR application. For Field B EWAG and Field D EWAG application, the EWAG surfactant concentrations were 1000 ppm and 2700 ppm. For EWAG surfactant, it comprises of a mixture of amphoteric and anionic type of surfactant. **Table 6** presents the EOR induced emulsion due to EWAG surfactant foam and CEOR surfactant chemical. HC is defined as High Surfactant Concentration and LC is Low Surfactant Concentration.

The results showed a general increase in emulsion volume at the high surfactant concentration. For the Field B EWAG case, for the high surfactant concentration, the emulsion was worst at 60% water cut in which the emulsion is about 40% compared to the 80% water cut in which the emulsion is about 25%; however, the foam produced was higher for the 80% water cut. Chen et al. showed that foam stability decreased when oil saturation increased (Chen et al., 2020). However, for emulsions, the emulsion stability increases as the oil saturation rises. In another study, it was observed that as the water cut increased, the tendency of emulsion formation was reduced for foam assisted CO_2 WAG applications (Borhan et al., 2014). These results support the findings of Field B EWAG emulsion tendency test for the high EWAG surfactant concentration case. For the Field D EWAG case, the test was only conducted at the 80% water cut as that was the current water cut of that field. The emulsion was quite comparable between the low and high surfactant concentration except that it produced a higher foam height compared to the low surfactant concentration.

For the emulsion induced by the CEOR application of injecting amphoteric surfactant in Field A, it seems that the emulsion was worse for the 60% water cut compared to 80% water cut. At this water cut, the emulsion behavior can be either the oil-in-water or water-in-oil type (Borhan et al., 2014). However, due to the nature of this CEOR amphoteric surfactant, which is a less water-soluble type of surfactant, it tends to produce a water-in-oil emulsion which is why a higher volume of crude oil is needed to produce a more stable emulsion. Furthermore, from the observation the higher CEOR surfactant concentration produced a more severe emulsion than the lower CEOR surfactant concentration. Nguyen et al., (2012) showed that the EOR surfactant decreased the size of oil droplets, increased the surface charge of oil droplets and increased the film elasticity, thus making the oil–water separation more difficult, which was depicted in a CEOR emulsion tendency test.

Table 6- Emulsion behavior of EOR induced emulsion.

No	Field	Emulsion Behavior
1	Field B EWAG	Field B EWAG emulsion at 60% and 80% water cut for low and high surfactant concentrations

| 2 | Field D EWAG |
Field D EWAG emulsion at 80% water cut for low and high surfactant concentrations. |
|---|---|---|
| 3 | Field A CEOR |
Field A CEOR emulsion at 60% and 80% water cut for low and high surfactant concentrations. |

4.4 Demulsification Test (EOR Emulsion)

A demulsification system was then formulated to address the emulsion formed by this EOR application. A demulsifier in the range 20 ppm to 100 ppm was used for treating the Field A CEOR application, and a 1000 ppm to 3000 ppm demulsifier concentration was used to treat the EWAG emulsion. This demulsifier can be further optimized as this screening is only referring to a single base demulsifier without combining with other demulsifiers or solvents, thus becoming a formulation. **Table 7** describes the recommended demulsifier RSN for each EOR demulsification case with respect to the different fields, water cuts and surfactant type and concentration breakthrough.

Table 7- EOR demulsification result.

Field	Process Temperature (°C)	Water Cut (%)	Surfactant Type	Surfactant Breakthrough (wt%)	Workable RSN
Field A	65	60	CEOR Surfactant	0.075	19 and 20
				0.025	17 to 21
		80		0.075	19 to 21
				0.025	17 and 20
Field B	40	60	EWAG Foam Surfactant	0.27	11 to 16
				0.09	11 to 17
		80		0.27	16 to 17
				0.09	16 to 17
Field D	55	80		0.27	11 to 16
				0.09	11 to 16

The EOR demulsification is mostly impacted by the EOR surfactant properties and its concentration thus the EOR demulsification guideline was developed based on the EOR surfactant being the causative factor in EOR emulsion stability. For the Field D EWAG application, the effective demulsifiers had an RSN of 11 to 16, which was a lower RSN than the high RSN demulsifiers used for resolving non-EOR emulsions. The EWAG Surfactant E was highly water soluble which means it is highly hydrophilic thus it tends to produce an oil-in-water emulsion. This emulsion needs an oil soluble or less water-soluble demulsifier with a low RSN to resolve the emulsion. For the Field B EWAG application, the workable demulsifier RSN range was larger, being from 11 to 17 (low to medium RSN range) even though they were using a similar EWAG surfactant. Field B crude oil which is lighter than the Field D waxy crude oil may make the workable demulsifier RSN range bigger compared to Field D. At 80% water cut, the emulsion was more severe and the workable RSNs were between 16 and 17 only.

For Field A CEOR application, generally the effective demulsifiers had the RSN from 17 to 21. Properties of the CEOR Surfactant S which is less water-soluble (less hydrophilic) than foam surfactant, tends to produce the water-in-oil emulsion. This emulsion needs a highly water-soluble demulsifier that has a high RSN to resolve the emulsion. In one study, decreasing the extent of the interfacial tension acted on by the water solubility demulsifiers was bigger than the oil solubility demulsifiers for the surfactant polymer flooding application. With the increase in the demulsifier concentration for these demulsifiers, the interfacial tension decreased, and the dewatering rate increased (Yimei, 2014). (Zhang et al., 2006) revealed that a non-ionic water-soluble mixed demulsifier was used successfully to treat the produced liquid from ASP flooding. The demulsifier increased the zeta potential and Interfacial Tension (IFT) and reduced the water content from 30.5 to 7.6%, at a 50 mg/kg dose. This demulsifier also managed to reduce the oil concentration in the water phase from 1623 mg/l to 530 mg/l which was about a 67% reduction.

Fig. 11 illustrates the comparison of the demulsifier performances between the resin alkoxylate and the modified polyol for EOR demulsification. The performance was comparable between the two demulsifier groups for all three EOR applications except for the Field B EWAG demulsification where the resin alkoxylate demulsifier worked better than the modified polyol. The results also showed that not many demulsifiers effectively resolved the EWAG emulsion compared to the CEOR emulsion, as the effect of foam really increased the emulsion severity.
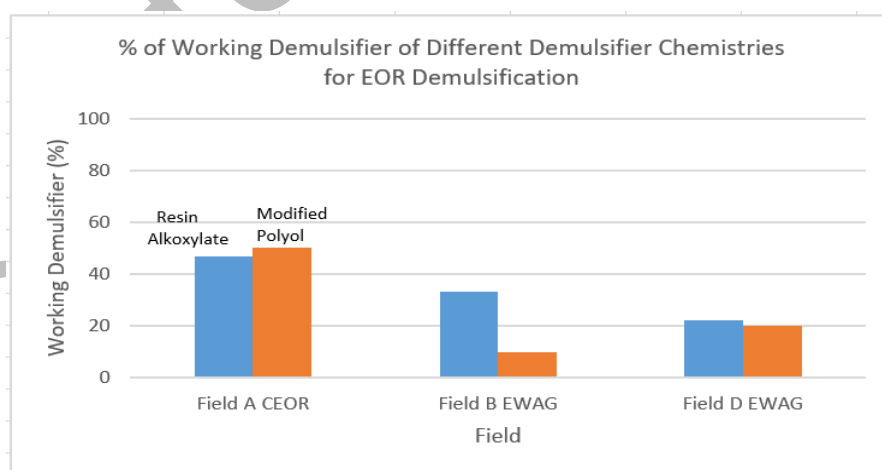
Fig.11- Percentage (%) of working demulsifier based on different demulsifier chemistries for EOR demulsification.

4.5. Demulsifier Selection from Demulsification Guideline

Based on the demulsification database that was developed earlier, the demulsifier selection guideline is summarized as below:

1. For a non-EOR emulsion, generally the best demulsifier ranges that work for all API crude oil are high, which is between 19 to 21.

2. The demulsifier with RSN 19 works for wax content 6% and below.

3. For a higher wax content, the demulsifier RSN needs to be higher, which is 21, for the demulsifier to work.

4. The demulsifier with RSN 19 works best at low process temperature of 35 °C.

5. For heavy crude oil, demulsifiers with RSN 16 work best for all asphaltene content between 1.2% to 1.8%; while for light crude oil, demulsifiers with RSN 19 work best for all asphaltene content between 0.36% to 0.72%.

6. On the solid effect, for heavy crude oil, demulsifiers of RSN 19 performed the best in resolving the emulsion at all solid content. For light crude oil, demulsifiers worked at RSN 19 for solid content of lesser than 0.2%. For higher solid content of more than 0.2%, they need a higher water soluble demulsifier which is demulsifiers of 21 to resolve the emulsion.

7. For Field B EWAG application, demulsifier with RSN 16 and 17 work best and for Field D EWAG application, demulsifier with RSN 11 and 16 work best in resolving the EWAG emulsion.

8. For Field A CEOR application, the effective demulsifiers have an RSN from 17 to 21.

4.6. Demulsifier Blind Test

After the demulsifier selection guideline was developed, a blind test was conducted to test the demulsifier performance with the actual crude oil. The most important parameters when applying the selection guideline are asphaltene content, wax content, solid content and API gravity, and the crude oil properties are presented in **Table 8.** For the blind test, 15 crude oil samples from 5 fields were tested with base demulsifiers, and their RSN was matched with their crude oil property data. The results of the blind test are depicted in **Table 7** and some of the bottle test images are illustrated in **Fig. 12.**

Table 8- Demulsifier blind test result.

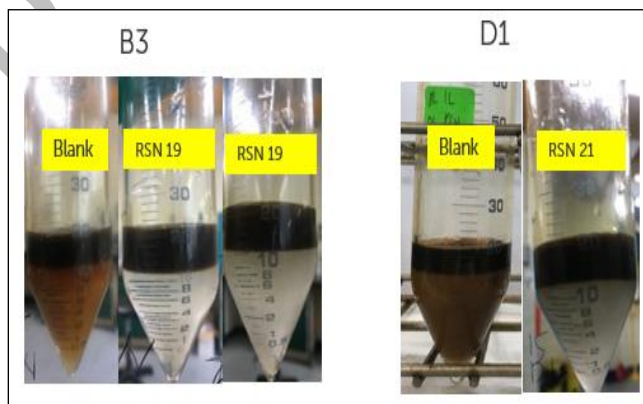| No	Crude Oil	Crude Oil Properties				Demulsifier Properties	No. of Working Demulsifier of Similar RSN	Matching Rate (%)
		API	Wax (%)	Solid (%)	Asph (%)	RSN		
1	D1	34	13	0.29	1.19	21	2 out of 3	66
2	G2	46	6	0.2	1.2	21	1 out of 2	50
3	B3	39	2.7	0.14	0.1	19	2 out of 2	100
4	B4	35	4.3	0.12	0.1	19	2 out of 2	100
5	B5	37	3	0.1	0.04	19	2 out of 2	100
6	D6	31	4.7	0.1	0.53	19	2 out of 2	100
7	B7	44	2	0.01	1.78	19	2 out of 2	100
8	S8	36	4.8	0.09	0.09	19	2 out of 2	100
9	T9	24	6.9	0.08	2.19	19	2 out of 2	100
10	T10	23	1.3	0.06	1.25	19	2 out of 2	100
11	T11	25	3.3	0.09	2	19	2 out of 2	100
12	T12	26	1.3	0.04	3.6	19	2 out of 2	100
13	D13	33	25	0.4	0.1	19	2 out of 2	100
14	B14	41	4	0.2	0.1	19	2 out of 2	100
15	S15	19	2.1	0.17	1.25	16	1 out of 1	100

Fig. 12- Blind test image of B3 and D1 crudes before and after addition of base demulsifier.

For B3 crude oil, based on the crude oil properties data in **Table 7**, it was a high-API type of crude oil, which is close to 40°. The wax content was quite low, about 2.7%. Based on this data, because the wax content is lesser than 6%, the demulsifiers chosen should

be under RSN 19. In terms of the solid's relationship, B3 crude oil had a solid content of 0.14% which was less than 0.2%, and based on this, RSN 19 also worked best. For the D1 crude oil, it was a bit waxy, and the solid content was also higher than B3 crude oil. Because the wax content was 13% and the solid content was 0.29%, base demulsifiers from the RSN 21 group were chosen for testing. In addition to this, the blind test results in **Table 8** show that almost recommended demulsifiers worked efficiently in resolving the emulsion except for D1 and G2 crude oils. This led to a high matching rate of 86.7% based on the number of working demulsifiers between the guideline output and the experimental lab results.

5. CONCLUSION

This paper establishes a demulsifier selection guideline in resolving W/O emulsions based on the relationship of demulsifier properties with the crude oil characteristics. Based on the bottle test completion for all the test matrices, the demulsifier selection guideline was developed and then validated with the blind test in resolving the emulsion from the actual crude oil. The high matching rate of 86.7% between the selection guideline outputs versus laboratory test proved that good agreement was established between the demulsifier properties and the crude oil characteristics.

STATEMENTS AND DECLARATIONS

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

Abbreviation

RSN	Relative Solubility Number
EOR	Enhanced Oil Recovery
CEOR	Chemical Enhanced Oil Recovery
EWAG	Enhanced Water Alternate Gas
W/O	Water-in-Oil
O/W	Oil-in-Water
HLB	Hydrophilic–Lipophilic Balance
HLD	Hydrophilic–Lipophilic Deviation
SARA	Saturate Aromatic Resin Asphaltene
ASP	Alkaline Surfactant Polymer
API	American Petroleum Institute
HC	High Surfactant Concentration
LC	Low Surfactant Concentration
IFT	Interfacial Tension
TBP	True Boiling Point

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