INTERNATIONAL JOURNAL OF INTEGRATED ENGINEERING
ISSN: 2229-838X e-ISSN: 2600-7916

Vol. 16 No. 1 (2024) 189-200
https://publisher.uthm.edu.my/ojs/index.php/ijie

IJIE

Demulsifier Performance Study: Relationship between Demulsifier Properties with Crude Characteristics

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DOI: https://doi.org/10.30880/ijie.2024.16.01.015

Article Info

Received: 13 December 2023
Accepted: 6 November 2023
Available online: 21 April 2024

Keywords

Demulsifier, RSN, chemistry group, wax, API

Abstract

Due to the vast range of different types of crude oil characteristics which differ from region to region, wells and even day to day, developing and selecting effective demulsifiers for regional crude oils has been a time-consuming and tedious process. This experimental study defined a relationship between the crude characteristics of wax, asphaltene and crude API with relative solubility number (RSN) properties and chemistry groups of demulsifiers with their performances accordingly. Twenty-five different types of demulsifiers with RSN ranging from ten to twenty-three were tested using demulsifier bottle test. The demulsifiers comprise resin alkoxylate, modified polyol and polyimine derivative. Synthetic crude is used throughout the study with API of 27, 34 and 40. The wax and asphaltene contents of each crude API are varied. Based on the three chemistry groups, resin alkoxylate showed the best performance, while polyimine derivative-based demulsifiers had the poorest performance. The demulsifier with high RSN from 19 to 23 works best in resolving the emulsion compared to the low RSN demulsifiers. These findings provide valuable insights for the petroleum industry, offering guidance on demulsifier selection based on crude characteristics to optimize production, reduce operational costs, and effectively address emulsion-related challenges.

1. Introduction

Demulsifiers are surface-active substances that destabilize emulsions by dividing the water from the oil phase. The demulsifiers replace the natural emulsifiers, resulting in the development of an emulsion. The natural emulsifiers are typically organic-based and function by adsorbing at the interphase of water droplets. The film around the water droplets weakens, leading to coalescence and phase separation [1]. The demulsification of water-in-crude oil happens through the quick clumping of the particles to form a continuous phase and through the interfacial film-breaking process. The entrapped water droplets move towards each other, forming a thin film of continuous oil phase between the water streams. Interfacial tension difference happens by the outward flow of the film, which then hinders the drainage. The concentration and the forces that either enhance or weaken the contact between the dispersed water droplets in the emulsion affect how quickly the particles cluster together. In the context of demulsification in crude oil, the concentration of demulsifiers and various intermolecular forces, such as Van der Waals forces, influence the interaction and contact between these water droplets. The droplets tend to come together through the Van der Waals forces, which occurs readily when the lamellae are thin enough.

The demulsification mechanism using demulsifier surfactants is initiated with the adsorption of the surfactant molecules. The surfactant molecules at the oil-water interface reduce the interfacial tension, which causes the change in interfacial film structure to decrease its hydrophobicity [2]. The interfacial film is more hydrophilic, and its wettability increases. The viscosity of the interfacial film reduces. The surfactant is amphiphilic and commonly used. The hydrophilic segments of the demulsifier move to the water surface while the hydrophobic segment moves toward the oil. The viscosity of interfacial film reduces as the asphaltene moves from the emulsion to the oil phase.

The classification of demulsifiers is mainly done according to the hydrophilic group. The combination of lipophilic and hydrophilic surfactants gives good performance based on the synergistic effect of the mixture. Oxyethylene, hydroxyl, carboxyl, and amine groups are the hydrophilic part, while the hydrophilic part includes clusters of alkyl, alkylphenols, or oxypropylenes. Different products can be found by varying the ratio and types of the two groups [3]. There are four types of demulsifiers used to break emulsions in crude oil. These are namely anionic, cationic, nonionic, and amphiphilic. The earlier demulsifiers were based on hydrophilic ionic demulsifiers and emulsion-reversal types. Oil-compatible nonionic surfactants have recently been used based on ethylene oxide and propylene oxides. The most efficient demulsifier formulations combine nonionic, cationic, and anionic demulsifiers. Generally, oil-soluble demulsifiers are used to destabilize water-in-oil emulsions [4].

Emulsions have many applications in a wide range of chemical industries. However, an emulsion in the upstream petroleum industry is highly undesired [5], [6], [7]. Emulsion causes corrosion, which leads to equipment failure. Most importantly, the Basic Sediments and Water (BS&W), which refers to water and salt content, affects crude oil's commercial value besides failing to meet the company and pipeline specifications. The emulsion also causes constrained flow line pressure, pump failure, poisoning of catalysts in downstream refineries, other problems to production equipment, and overhead distillations [6], [8], [9]. Separating the water, brine, and crude oil into two phases before transporting or refining is crucial in producing crude from the reservoir [10]. Searching for ways to break or destabilize emulsions helps mitigate economic losses and operational challenges. Usually, water emulsification in oil is laborious as both phases are immiscible. However, the shear force from crude mixing and natural surfactants' presence causes emulsification. The emulsifying surfactants are asphaltene, resins, waxes, inorganic solids, and oil-soluble organic acids, which act as natural emulsifiers [5], [11], [12]. The surface-active materials attach to the oil-water interface, forming a stable interfacial layer. Asphaltene, the heaviest component, increases the interfacial film strength and prevents the water droplets from coming together and forming a separate continuous phase.

Most crude oil emulsions are treated using the chemical demulsification method. It is done by injecting chemical additives known as demulsifiers into the emulsion [7], [13], [14], [15]. The operational cost is low using the chemical demulsifiers as opposed to the other methods besides the less space required. Chemical demulsifiers affect the impact of emulsifying agents and separate the interfacial film. The demulsifier surfactant molecules adsorb at the oil-water interface to reduce the interfacial tension and viscosity, which causes rapid film thinning and separation of the emulsion into respective water and oil phases. It is done without adding new equipment or modification of the existing equipment.

Different types of crude oils and process conditions lead to a big challenge in developing and selecting effective demulsifiers. The bottle test method is the most used in analyzing parameters such as demulsifier dosage, residence time, heat, and degree of agitation [16], [17]. [18], [19], [20]. This method synthesizes the emulsion and agitation effects after injecting the demulsifier into the emulsion. Understanding how demulsifiers interact with crude oil is essential for selecting more effective demulsifiers and improving demulsifier formulation, even though this method is efficient but time-consuming.

The previous study of the demulsifier relationship with crude oil has declared that the relationship exists. It indicates the relationship between the performances of the demulsifiers and the RSN, but the study is mainly for heavy oil-produced emulsion. The study demonstrated the relationship between the performances of demulsifiers with the demulsifier's RSN and molecular weight properties [21]. In this study, the demulsifier performances considering the medium crude API 27, API 34, and API 40 produced emulsions. The relationship between overall demulsifier performance with crude oil API and wax content was investigated. Next, the demulsifier performance of RSN 10 to RSN 23 was analyzed accordingly with different crude API and wax content. The performance of several demulsifier chemical groups, such as resin, polyol, and polyimine derivatives, was then examined in crude oil with variable wax contents.

2. Methodology

2.1 Materials

Synthetic crude is a blended fluid comprised of base oil components, diluent and heavy hydrocarbon components of wax and asphaltene, which mimics the behaviour of crude oil. Generally, base oils with the same viscosity, density, and interfacial tension as crude oil have been tried as synthetic oils. The base oil used in the synthetic oil combines Primol 352, hexane, heptane, octane and cyclohexane. The diluent is an aliphatic or aromatic solvent such as toluene, xylene, benzene and Solvessol 150. This synthetic oil also used Exxsol D grade hydrocarbons as the diluent. It also contains anthracene and naphthalene, two more solid polycyclic aromatic hydrocarbons. These are dearomatized hydrocarbons and offer ideal diluent properties.

Three types of synthetic oil comprised of the API gravity of 27, 34, and 40 have been developed. The resins and asphaltenes, which are interfacial active, are present in crude and may be mimicked using a particulate component. This study introduced asphaltenes, resin, and saturate into the synthetic oil by adding some vacuum residue collected from the distillation process in PETRONAS Penapisan Melaka (PPM). The vacuum residue contains 28% saturated, 37% aromatic, 29% resin, and 6% asphaltene. This synthetic oil also used Paraffin Wax granular, ACROS Organics type, with a melting point of 42 ^{o}C and a boiling point of 370 ^{o}C to mimic wax and crude oil.

2.2 Process Conditions

This study establishes the relationship between crude API, asphaltene, wax characteristics with RSN properties, and the chemical group of demulsifiers with their corresponding performances. The demulsifier bottle test evaluated 25 different demulsifiers with RSNs ranging from 10 to 23. The demulsifiers comprise resin alkoxylate, polyol alkoxylates, and polyimine derivatives. Synthetic crude was used throughout the study with API of 27, 34 and 40, as this range of API falls into a normal range for Malaysian crude oil. The wax and asphaltene contents of each crude API were varied. The study used 2% NaCl water, representing the average salinity of the produced water in Malaysian offshore fields.

The demulsification test used a 50:50 ratio of crude and brine volume. 100 ppm demulsifier dosed into an emulsion mixture, and the separation is then monitored and recorded after 30 minutes of observation. The demulsifier bottle test is conducted at 60 °C, which is comparable to the operational temperature for the demulsifier injection in the Malaysian offshore field. The API of all the synthetic crude prepared was then calculated to ensure the synthetic crude prepared was according to the required API. The calculation of API was done using Equation (1). The specific gravity, SG is measured by using the density meter. The demulsifier chemicals kit used in this study was purchased from Croda International.

$$API = \left(\frac{141.5}{SG}\right) - 131.5 \quad (1)$$

2.3 Testing on Emulsions

The most common emulsion tendency and bottle tests were carried out using synthetic crude formulated with varying crude API consisting of API 27, API 34 and API 40. The wax content ranged from 1 g, 3 g, 4 g, and 5 g. It is to test the performance of demulsifier in different varying crude API and wax content. The various wax contents were set in this study to investigate the effect of different levels of wax deposition on the emulsion stability and demulsifier performance. Wax can increase the viscosity and density of crude oil, reduce the flow rate and efficiency of pipelines, and cause blockages and corrosion. Therefore, it is important to study how different amounts of wax influence the emulsion tendency and the effectiveness of demulsifiers. Fig. 1 shows the overall test procedure in this study. The water settling rate from oil in various demulsifiers in the emulsion sample is compared. After a specific time, the extent of phase separation and the appearance of interphase separating the phase is noted. The test tube was shaken to mix the demulsifier and homogenize the emulsion. The emulsion's interface clarity and the water phase's turbidity are used to gauge the degree of phase separation when the demulsifier is added. The test was conducted on loose emulsion; as the emulsion separated within 5 minutes, the demulsifier was injected. If only 1 ml or less of the emulsion remained after the demulsification bottle test, the demulsifier was considered successful in treating the emulsion. The total number of non-working demulsifiers was determined by counting the number of tests where the demulsifier failed to treat the emulsion within the specified time limit. If more than 1 ml of the emulsion remained, the demulsifier was considered not working for that particular test. The performance analysis is then done by considering the number of successful demulsification tests obtained over the total number of tests done. Their RSN and chemical groups characterized the demulsifiers. The total working demulsifier percentage was calculated using Equation (2).

$$\frac{\textit{Total test on emulsions} - \textit{Total not working demulsifier}}{\textit{Total test on emulsions}} \times 100\% \qquad (2)$$

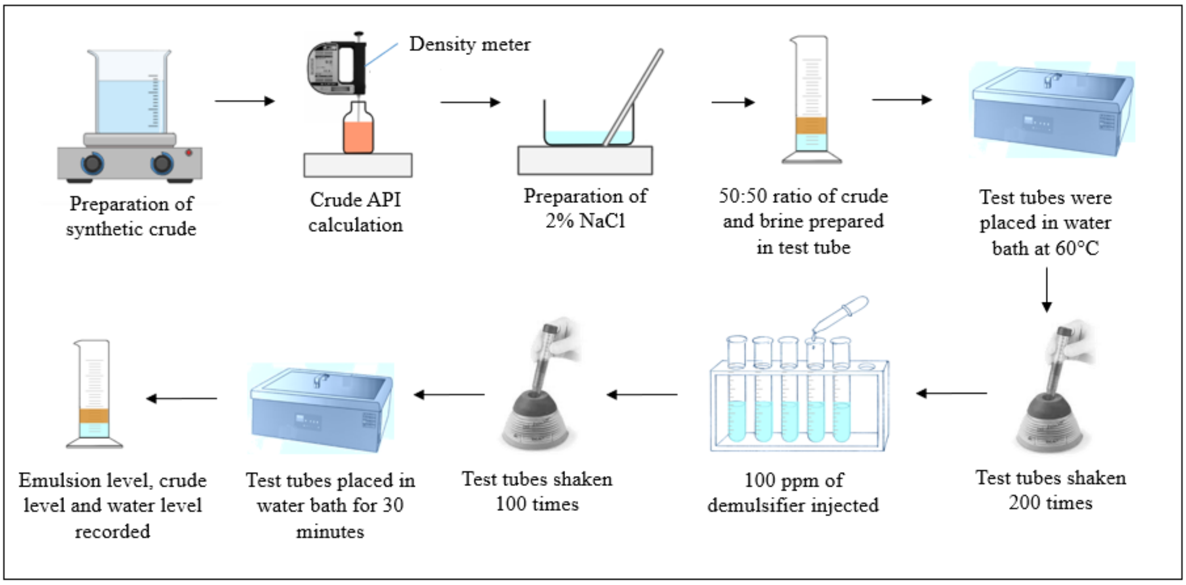

Fig. 1 *Overall procedure of testing on emulsions*

3. Results and Discussion

3.1 Analysis of Working Demulsifier According to Crude API

Table 1 shows the details of the working demulsifier according to crude API 27, API 34 and API 40, with 50 tests for each crude API sample. The percentage of working demulsifiers has decreased from 74% using the crude of API 27, 68% for API 34, and 62% for API 40. According to Fig. 2, demulsifier performance declines when crude API gravity rises. Due to an increase in asphaltene concentration, demulsifier performance improves as crude API increases. The contribution of interfacial film around the suspended particles hinders the coalescence of bigger droplets coming together. Instead, the results in this study align with previous research by Oloro [23], which concluded that light crude oil with high API gravity values forms a more stable emulsion than heavier crude oil with low API gravity values.

One of the hypotheses drawn is that the emulsion in crude API 40 may be more stabilised than the emulsions formed in other heavier crudes tested. It may be due to the strong shear force from shaking the crude with saline water. The mixing may be vigorous as the crude is lightweight. The demulsifier surfactants adsorbed on the emulsion surface will form a stress gradient when shear stress is applied to the emulsion [22]. The shear stress will then cause the elastic component of the emulsion to increase, which means an increase in elastic behaviour leads to a decrease in the coalesce mechanism among emulsions. It causes the production of very stable emulsions.

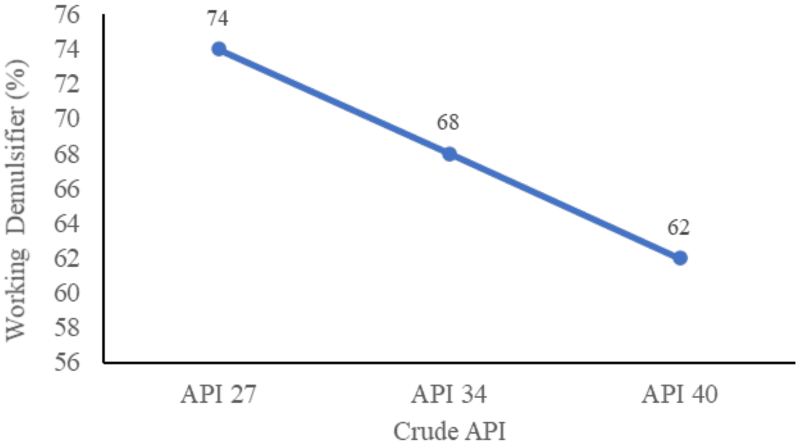

Fig. 2 *Demulsifier performance according to crude API*

Table 1 *Details of working demulsifier according to crude API*

		API 27 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 34 (Wax 8)		API 40 (Wax 1)		API 40 (Wax 5)	
No	RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
1	6	✓		✓		✓		✓		✓		✓	
2	7	✓		✓		✓		✓		✓			✓
3	9		✓	✓			✓	✓			✓		✓
4	10		✓		✓		✓	✓		✓			✓
5	10	✓			✓		✓		✓		✓	✓	
6	11	✓		✓		✓		✓		✓		✓	
7	11	✓			✓		✓		✓	✓		✓	
8	11	✓			✓		✓	✓			✓		✓
9	15		✓	✓			✓	✓			✓		✓
10	16		✓	✓		✓			✓		✓		✓
11	16	✓		✓		✓		✓		✓		✓	
12	16	✓			✓	✓		✓		✓			✓
13	17	✓		✓		✓			✓		✓		✓
14	17	✓			✓		✓	✓			✓		✓
15	17	✓		✓			✓		✓	✓		✓	
16	17	✓		✓			✓		✓	✓			✓
17	19	✓		✓		✓		✓		✓		✓	
18	19	✓		✓		✓		✓		✓		✓	
19	20	✓			✓	✓		✓		✓		✓	
20	20	✓		✓		✓		✓		✓		✓	
21	20	✓		✓			✓	✓		✓			✓
22	21	✓			✓	✓		✓		✓		✓	
23	21	✓		✓		✓		✓		✓		✓	
24	21	✓			✓	✓		✓		✓		✓	
25	23	✓		✓		✓		✓		✓			✓
	Total	21	4	16	9	15	10	19	6	18	7	13	12

3.2 Analysis of Working Demulsifier According to Wax Content

Table 2 shows the details of demulsifier performance according to the wax content. The study was for a total of 25 tests for each API and wax content, API 27 (Wax 1 g), API 40 (Wax 1 g), API 27 (Wax 3 g), API 34 (wax 4 g) and API 40 (Wax 5 g). Based on Fig. 3, 78% of success for API 27 and API 40 with 1 g of wax content. The value drops to 64%, 60%, and 52%, with wax content of 3 g, 4 g and 5 g. The rate of success decreases as the wax content in the crude increases, and it is because tighter emulsions are formed with the increase in the wax content of the crude. Moreover, high-melting paraffin forms many wax crystals in crude oil, creating a barrier at the interface between water and oil. The barrier increases the strength of the interfacial film, which avoids the aggregation and flocculation of the droplets and stabilizes the emulsion. The efficiency of the demulsifier also decreases with the decrease in the interfacial tension gradient. The increase of interfacial viscosity is caused by the presence of wax in the crude oil, leading to a longer time for film thinning.

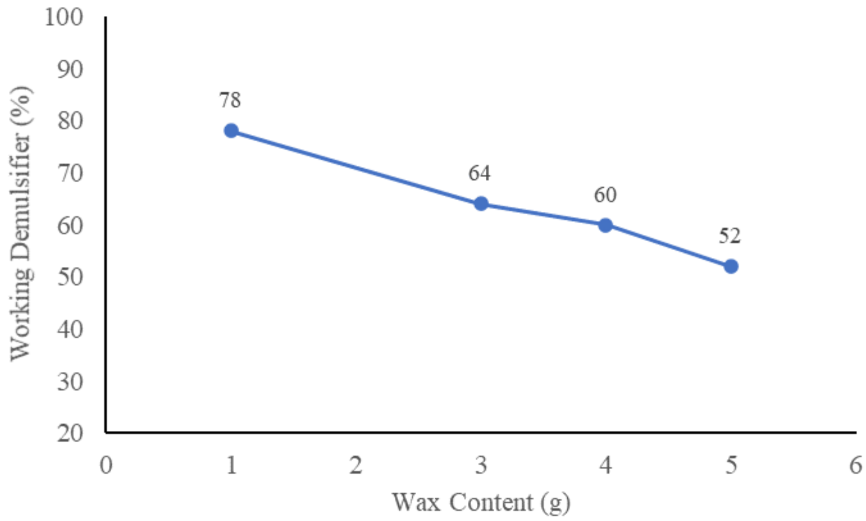

Fig. 3 *Demulsifier performance according to the wax content*

Table 2 *Details of working demulsifier according to the wax content*

		API 27 (Wax 1)		API 40 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 40 (Wax 5)	
No	RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
1	6	✓		✓		✓		✓		✓	
2	7	✓		✓		✓		✓			✓
3	9		✓		✓	✓			✓		✓
4	10		✓	✓			✓		✓		✓
5	10	✓					✓		✓	✓	
6	11	✓		✓		✓		✓		✓	
7	11	✓		✓			✓		✓	✓	
8	11	✓			✓		✓		✓		✓
9	15		✓		✓	✓			✓		✓
10	16		✓		✓	✓		✓			✓
11	16	✓		✓		✓		✓		✓	
12	16	✓		✓			✓	✓			✓
13	17	✓			✓	✓		✓			✓
14	17	✓			✓		✓		✓		✓
15	17	✓		✓		✓			✓	✓	
16	17	✓		✓		✓			✓		✓
17	19	✓		✓		✓		✓		✓	
18	19	✓		✓		✓		✓		✓	
19	20	✓		✓			✓	✓		✓	
20	20	✓		✓		✓		✓		✓	
21	20	✓		✓		✓			✓		✓
22	21	✓		✓			✓	✓		✓	
23	21	✓		✓		✓		✓		✓	
24	21	✓		✓			✓	✓		✓	
25	23	✓		✓		✓		✓			✓
	Total	21	4	18	6	16	9	15	10	13	12

3.3 Performance of Demulsifier RSN According to the Crude API

Tables 3, 4, and 5 show the details of demulsifier performance according to the crude API for low-demulsifier RSN, medium-demulsifier RSN and high-demulsifier RSN, respectively. The study was performed for 30 tests of low-demulsifier RSN, 48 for medium-demulsifier RSN, and 54 for high-demulsifier RSN. The performance of demulsifiers increases as the demulsifier RSN value rises, as shown in Fig. 4. The RSN value measures the relative solubility of the demulsifier in the organic solvent or water. The hydrophilic nature of the demulsifier increases as the RSN increases. The low-demulsifier RSN value category showed 50% success in demulsification, followed by the medium range of RSN, performing at a 54% success rate. The highest RSN range showed 89% of successful emulsion treatment. In the higher RSN category, which includes RSN 19, 20, 21 and 23, the RSN 19 demulsifier showed a performance of 100%. The demulsifiers of RSN 20, RSN 21, and RSN 23 showed performances of 80%, 87%, and 80%, respectively.

Table 3 *Details of working low-demulsifier RSN according to crude API*

	API 27 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 34 (Wax 8)		API 40 (Wax 1)		API 40 (Wax 5)	
RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
10		✓		✓		✓	✓		✓			✓
10	✓			✓		✓		✓		✓	✓	
11	✓		✓		✓		✓		✓		✓	
11	✓			✓		✓		✓	✓		✓	
11	✓			✓		✓	✓			✓		✓
Total	4	1	1	4	1	4	3	2	3	2	3	2

Table 4 *Details of working medium-demulsifier RSN according to crude API*

	API 27 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 34 (Wax 8)		API 40 (Wax 1)		API 40 (Wax 5)	
RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
15		✓	✓			✓	✓			✓		✓
16		✓	✓		✓			✓		✓		✓
16	✓		✓		✓		✓		✓		✓	
16	✓			✓	✓		✓		✓			✓
17	✓		✓		✓			✓		✓		✓
17	✓			✓		✓	✓			✓		✓
17	✓		✓			✓		✓	✓		✓	
17	✓		✓			✓		✓	✓			✓
Total	6	2	6	2	4	4	4	4	4	4	2	6

Table 5 *Details of working high-demulsifier RSN according to crude API*

	API 27 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 34 (Wax 8)		API 40 (Wax 1)		API 40 (Wax 5)	
RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
19	✓		✓		✓		✓		✓		✓	
19	✓		✓		✓		✓		✓		✓	
20	✓			✓	✓		✓		✓		✓	
20	✓		✓		✓		✓		✓		✓	
20	✓		✓			✓	✓		✓			✓
21	✓			✓	✓		✓		✓		✓	
21	✓		✓		✓		✓		✓		✓	
21	✓			✓	✓		✓		✓		✓	
23	✓		✓		✓		✓		✓			✓
Total	9	0	6	3	8	1	9	0	9	0	7	2

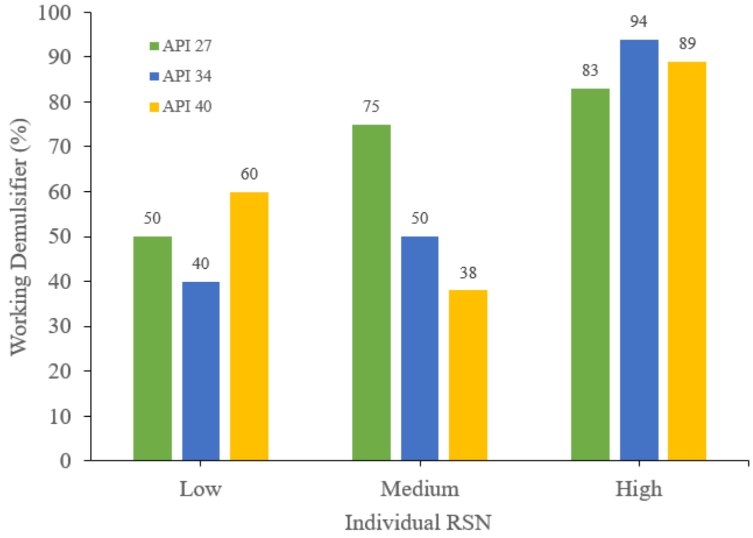

Fig. 4 *Demulsifier RSN performance analysis according to the crude API*

From RSN 17 onwards, the demulsification performance gets even better than the lower RSN. It may be due to the demulsifier of RSN lesser than 13 being insoluble in water while demulsifiers above RSN 17 value being water-soluble in nature. As for the demulsifier with RSN value between 13 to 17, the product disintegrates in water at a lower concentration. The demulsifiers should be interfacially active to meet the field applications. The hydrophilic segment of the demulsifier is known as the polar group, while the hydrophobic segment is known as the non-polar group. The effect produced by a polar hydrophilic group is more significant than the non-polar hydrophobic group; therefore, the surfactant is more soluble in water.

A higher RSN demulsifier that is hydrophilic in nature exhibits a higher interfacial elastic modulus as it is more water-soluble and shows high interfacial adsorption. Increased adsorption time reduces the interfacial tension and increases the interfacial elastic modulus. The interfacial elastic modulus refers to the strength of the interaction of molecules between the oil and water interface. Therefore, the performance of demulsifiers gets better with increasing the RSN value of the demulsifiers.

3.4 Performance of Demulsifier RSN According to Wax Content

Tables 6, 7, and 8 show the details of demulsifier performance according to the wax content for low-demulsifier RSN, medium-demulsifier RSN, and high-demulsifier RSN, respectively. The study was performed for 25 low-demulsifier RSN tests, 40 for medium-demulsifier RSN, and 45 for high-demulsifier RSN. Fig. 5 shows the demulsifier RSN performance analysis according to wax content. The performance of the demulsifier increases with the increasing demulsifier RSN. The lower RSN category has a demulsification percentage of 48%. The medium RSN range showed 55% successful demulsification, while the highest RSN values have an 87% success rate in treating the emulsion. In the higher RSN category, which includes RSN 19, 20, 21 and 23, the RSN 19 demulsifier showed a performance of 100%. The demulsifier of RSN 20, RSN 21 and RSN 23 showed successful performance of 83%, 89% and 17%, respectively.

The higher demulsifier RSN showed better performance as the demulsifiers have longer hydrophilic chains. It helps treat the stable emulsions caused by the wax, and the wax surface is hydrophobic. Therefore, increasing the demulsifier hydrophilicity with the increase in RSN value helps to further separate the interfacial film from hydrophobic and hydrophilic balancing action.

Generally, emulsions are not thermodynamically stable. It is due to the large interface area of the oil-water interface, which provides free positive energy. The demulsifier surfactant adsorption reduces the interface film energy. The wax increases interfacial viscosity and acts as a barrier for the collisions of the water droplets to occur [23]. However, the stability caused by wax does not happen through action at the interface. The wax acts in the oil phase to prohibit the interfacial film from shrinking, thereby preventing the droplets from coalescing. Moreover, the wax also acts as a demulsifier scavenger, whereby the efficiency of the demulsifier further reduces with the increase in the wax content [24].

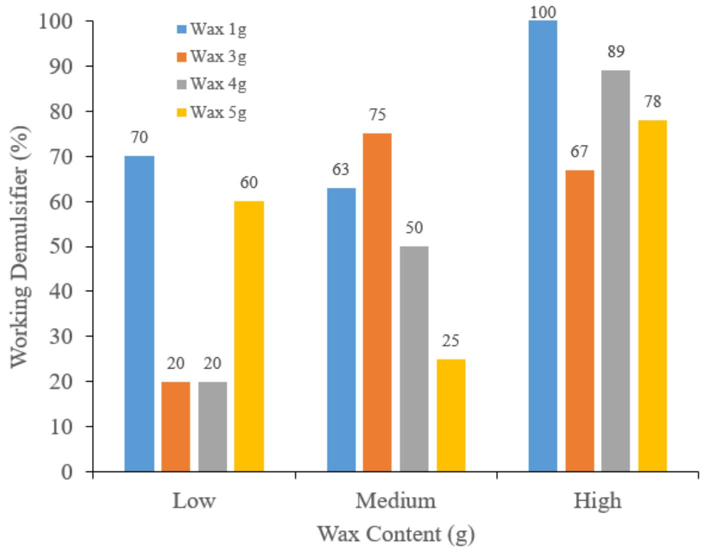

Fig. 5 *Demulsifier RSN performance analysis according to the wax content*

Table 6 *Details of working low-demulsifier RSN according to wax content*

	API 27 (Wax 1)		API 40 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 40 (Wax 5)	
RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
10		✓	✓			✓		✓		✓
10	✓			✓		✓		✓	✓	
11	✓		✓		✓		✓		✓	
11	✓		✓			✓		✓	✓	
11	✓			✓		✓		✓		✓
Total	4	1	3	2	1	4	1	4	3	2

Table 7 *Details of working medium-demulsifier RSN according to wax content*

	API 27 (Wax 1)		API 40 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 40 (Wax 5)	
RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
15		✓		✓	✓			✓		✓
16		✓		✓	✓		✓			✓
16	✓		✓		✓		✓		✓	
16	✓		✓			✓	✓			✓
17	✓			✓	✓		✓			✓
17	✓			✓		✓		✓		✓
17	✓		✓		✓			✓	✓	
17	✓		✓		✓			✓		✓
Total	6	2	4	4	6	2	4	4	2	6

Table 8 *Details of working high-demulsifier RSN according to wax content*

	API 27 (Wax 1)		API 40 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 40 (Wax 5)	
RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
19	✓		✓		✓		✓		✓	
19	✓		✓		✓		✓		✓	
20	✓		✓			✓	✓		✓	
20	✓		✓		✓		✓		✓	
20	✓		✓		✓			✓		✓
21	✓		✓			✓	✓		✓	
21	✓		✓		✓		✓		✓	
21	✓		✓			✓	✓		✓	
23	✓		✓		✓		✓			✓
Total	9	0	9	0	6	3	8	1	7	2

3.5 Relationship between Demulsifier Chemistry Groups with Crude Oil Wax Content

The demulsifier chemistry groups involved in the testing are resin alkoxylate, polyol alkoxylate, and polyimine derivative. Tables 9, 10, and 11 show the details of demulsifier chemistry groups' performance at different wax content for resin alkoxylate, polyol alkoxylate, and polyimine derivative, respectively. The study was performed for 65 resin alkoxylate tests, 20 for polyol alkoxylate and 35 for polyimine derivative. Fig. 6 shows the demulsifier chemistry performance according to wax content. The resin alkoxylate demulsifier performs best in resolving emulsion in crude oil with wax. The percentage of success for resin alkoxylate is 74%, while polyol alkoxylate showed 70% success rate. The lowest success rate follows it by using polyimine derivative, which is 49%.

The resin alkoxylate performance depends on its ethoxylated groups and the hydrophilic-hydrophobic interactions [25]. Natural emulsifiers such as asphaltenes and resins are known to be lipophilic compounds. The lipophilic property of the surfactants was reverted by hydrophilic demulsifiers, which are added to the system. The hydrophilic-lipophilic interactions contribute to the rupturing of the interfacial film. Being a hydrophilic fraction, the demulsifier molecules change the asphaltene from previously lipophilic to hydrophilic. The more superior interaction will affect the emulsion stability. Demulsifiers have higher surface activity than natural emulsifiers. Therefore, the natural surfactant in resin alkoxylate can displace the emulsifiers and weaken the interfacial film to promote coalescence. The interaction between asphaltene and the demulsifier is superior to the interaction between asphaltene compounds. In this case, the interaction pertains to hydrophilic-lipophilic interaction and interfacial film thinning, which contributes to the destabilization of the emulsion. The interaction between the asphaltene-asphaltene molecules will result in a stronger interfacial film, while the interaction between the asphaltene and demulsifier results in the thinning of the interfacial film.

Resin alkoxylate performs better than the other two groups due to its high RSN values and molecular weight. These two factors contribute mainly to the performance in treating high wax content emulsions. The resin alkoxylates typically have higher molecular weights (500 – 5000 g/mol) than polyol alkoxylate (500 – 2000 g/mol) and polyimine derivatives (500 – 1000 g/mol). The higher molecular weight of resin alkoxylates is one of the reasons why they perform better than polyol alkoxylates and polyimine derivatives in demulsification. The higher the RSN, the more hydrophilic, indicating higher ethylene oxide chains than propylene oxide chains. The higher the hydrophilic characteristic of the demulsifier, the better it reverts to the lipophilic characteristic of the emulsifiers. In the industry, resin alkoxylate is the most widely used as it is the cheapest and most versatile chemistry developed for a long time.

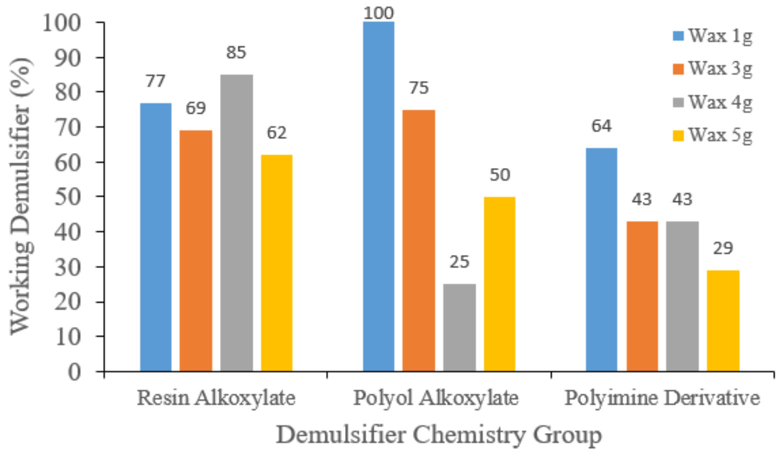

Fig. 6 *Different demulsifier chemistry group performances according to the wax content*

Table 9 *Details of working resin alkoxylate in different wax content*

		API 27 (Wax 1)		API 40 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 40 (Wax 5)	
No	RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
1	16		✓		✓	✓		✓			✓
2	19	✓		✓		✓		✓		✓	
3	11	✓		✓		✓		✓		✓	
4	21	✓		✓			✓	✓		✓	
5	19	✓		✓		✓		✓		✓	
6	23	✓		✓		✓		✓			✓
7	20	✓		✓			✓	✓		✓	
8	21	✓		✓		✓		✓		✓	
9	17	✓			✓	✓		✓			✓
10	21	✓		✓			✓	✓		✓	
11	16	✓		✓		✓		✓		✓	
12	17	✓			✓		✓		✓		✓
13	15		✓		✓	✓			✓		✓
	Total	11	2	9	4	9	4	11	2	8	5

Table 10 *Details of working polyol alkoxylate in different wax content*

		API 27 (Wax 1)		API 40 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 40 (Wax 5)	
No	RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
1	11	✓		✓			✓		✓	✓	
2	20	✓		✓		✓		✓		✓	
3	20	✓		✓		✓			✓		✓
4	17	✓		✓		✓			✓		✓
	Total	4	0	4	0	3	1	1	3	2	2

Table 11 *Details of working polyimine derivative in different wax content*

		API 27 (Wax 1)		API 40 (Wax 1)		API 27 (Wax 3)		API 34 (Wax 4)		API 40 (Wax 5)	
No	RSN	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working	Working	Not Working
1	9		✓		✓	✓			✓		✓
2	16	✓		✓			✓	✓			✓
3	7	✓		✓		✓		✓			✓
4	10		✓	✓			✓		✓		✓
5	10	✓			✓		✓		✓	✓	
6	11	✓			✓		✓		✓		✓
7	6	✓		✓		✓		✓		✓	
	Total	5	2	4	3	3	4	3	4	2	5

4. Conclusion

A decreasing trend is observed with the increasing crude API for the general demulsifier performance. The lighter crude with lower asphaltene content forms stable emulsions as the shear force impact is high. The high shear force increases the elastic component's elastic behaviour in crude oil. The greater the wax content results in a lower percentage of success as the wax creates a barrier between the water and oil phase, increasing the strength of the interfacial film and preventing coalescence between droplets. As the demulsifier RSN increases, it becomes more effective with crude API and wax content variation. Overall, the demulsifier of RSN 19, with a 100% success rate, is the best in de-emulsifying emulsion in different crude API and wax content. The higher the demulsifier RSN, the more hydrophilic it is, and the better the hydrophilic-hydrophobic interaction. In comparison to polyol alkoxylate and polyimine derivatives, resin alkoxylate is the most effective demulsifier for resolving emulsions in crude oil with lower wax concentrations.

Acknowledgement

The authors gratefully acknowledge the support from the Centre of Excellence for Research, Value Innovative and Entrepreneurship (CERVIE), UCSI University, School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, and PETRONAS Research Sdn Bhd.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Amritpal Kaur Manjit Singh, Nor Hadhirah Halim;* ***data collection:*** *Amritpal Kaur Manjit Singh;* ***analysis and interpretation of results:*** *Amritpal Kaur Manjit Singh, Mohd Fadhil Majnis;* ***draft manuscript preparation:*** *Amritpal Kaur Manjit Singh, Mohd Fadhil Majnis, Elhassan Mostafa Abdallah Mohammed. All authors reviewed the results and approved the final version of the manuscript.*

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