

DEMULSIFIER SELECTION FOR WATER SEPARATION FROM HEAVY CRUDE OIL EMULSIONS OF IRANIAN OIL FIELD

Fatemeh Yazdanmehr¹, Iulian Nistor²

¹National Iranian Oil Company, PEDEC, Iran, Petroleum – Gas University of Ploiesti (PhD Student), **Romania**

²Universitatea Petrol-Gaze din Ploiești, **Romania**

e-mail: fyazdanmehr@pedec.net

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ABSTRACT

In this study, various demulsifiers have been chosen for emulsion separation from heavy Iranian oil. The 16 types of water and oil based demulsifiers were tested using the selection procedure. Further, the current study assessed the effect of parameters like concentration, water cut and residence time on demulsification. Water emulsion separation has been found to be improved with selected oil-based demulsifiers. The results show that the oil based demulsifiers with a pH between 7-8 and dosage more than 100 ppm have more dehydration efficiency.

The efficiency of water-based demulsifiers is lower than that of oil-based demulsifiers. Using the Qualitec-4 software, the possibility of increasing the efficiency of the former was investigated. The results show that the selection of water-based demulsifiers, with pH = 7.76, dose = 100, time = 600, had the best performance.

Keywords: emulsion, demulsification, water oil separation, demulsifiers, oil base, water base, Qualitec-4

INTRODUCTION

Oil-water emulsions were formed in the process of crude oil production, which is almost associated with water. During operation, a certain percentage of water was often distributed through the crude oil produced in the form of small drops. Oil operators must avoid the formation or breakage of these emulsions in order to reduce the impact on the operating process and in the alternative on environmental issues.

Demulsification is vital in the processing of crude oil, used in the process of removing the content of water and salts from them. The water is distributed in the form of fine drops of oil, and most salts are contained in the water. Because water contains salts, dehydration and desalination technology were applied simultaneously. Let's suppose contaminants, such as salt and water that are present in crude oil, have not been removed. In this case, there is a potential for severe corrosion and clogging problems in

downstream installations etc. [1]. Crude oil produced in most fields of the world contains a significant amount of water and salts, and crude oil produced in the fields of Iran is no exception.

Regarding those mentioned above, the separation of the water emulsion is mandatory, but strong oil desalination of crude oil is required in order to balance the export oil cost and standard oil specification. Also, increasing water and brine by about 1 ppm (part per million), reduces the oil price by around 0.85 - 1.3 \$ for each barrel. To date, several techniques have been used such as the use of emulsifiers, gravitational separation or centrifugal decantation, pH modification, filtration, oil heating, separating membranes and electrostatic desalination. The percentage of associated water after processing must be less than 0, 1 - 0, 5 per cent in most crude oil-water mixture treatment processes according to crude oil marketing specifications.

Because of the immiscibility between two liquids, demulsification oil is challenging. The mixing effect between the surfactants produced and existing on crude oil also causes the formation of emulsions. [2]. Naturally, emulsifying formations were located in the polar molecules of crude oil with a higher molar weight [3]. This includes resins, asphaltenes and organic acids (soluble in crude oil, such as naphthenic, carboxylic oil, etc.) and bases which are the main parts of the interfacial layer that determine the stabilized emulsion.

Also, some other factors that impact interfacial film stability are the pH of the water and the additive content [4]; however, for various oil sources, these results indicate different effect [5]. For example, Daaou et al. (2011) investigated the pH effect on Algerian oil emulsions and proposed a neutral medium with greater efficiency than the acidic or basic environment to stabilize the emulsions [6]. Fourtuny et al. (2007) studied the salinity impacts, water content, temperature and pH on the oil emulsions stability based on microwave processing. They observed which the demulsification efficiency is high in emulsions with high water content, except when high pH and salt content are involved simultaneously. It is shown that in emulsions with high water content, the demulsification rate is high, unless the pH and salt content were simultaneously high. [7]. In addition, by evaluation the droplet-size distribution described by an optical microscopy method, Moradi et al. (2011) studied the salinity impact on crude oil-water emulsions and noted that emulsions are more stable at lower aqueous phase ionic strength [8].

In the current research, the focus is on the investigation of demulsifiers pH effect on one of Iranian heavy crude oil emulsions stability. In order to improve the efficiency of water separation, a wide range of influence of chemical emulsifiers (water-based / oil-based) on the emulsion is available.

Qualitec-4, experimental design software, has been applied to obtain an optimized demulsifier for water separation. The effects of demulsifier type, residence time and injection dosage in the range of various water cuts have studied.

1- PROCESS, SUBSTANCES AND MATERIAL DESCRIPTION

1-1- Crude oil characterization

The crude oil desalting specification is shown in Table 1. In order to find the best desalination efficiency, it is important to optimize the design parameters such as

temperature, electric field, demulsifiers, etc.

In this research, efforts have been taken to minimize the demulsifier volume and residence time in one of the existing Iranian heavy oil production units' desalination. The operation conditions are given in Table 2.

Table 1. Crude oil characterization

Parameter	Value
Original water cut, %	2.37 - 2.45
Pour point, °C	-24
Relative density (25 °C)	0.9430
Viscosity (20 °C), mPa·s	604.67
Sulphur content, %	4.35
Acid number, mg KOH/g	0.37
Wax content, %	1.84
Asphaltenes content, %	12.79
Resin content, %	36.55
Ash content, %	0.416
Initial boiling point, °C	100
Wax precipitation point, °C	19.1

Table 2. Range of Operating Parameter

Parameter	Value	Unit
Water cut	2%-40%	Volume
Chemical content	20-200	ppm
Residence time	15 – 1200	minute
Temperature	95	°C

Table 3. Demulsifier specifications

Demulsifier specification	Value	Unit
pH	3 -10	-
Viscosity	13-270	mPa.s
Flash point	22-80	g/cm ³

The American standards (ASTM) have used for measuring the oil density (ASTM D 1298, 2001), the water density (ASTM D 362, 2001), the based and sediments and water (BS&W) (ASTM D4007-2016) and the salt content (ASTM D 326, 1997).

The original water cut of a crude oil sample is given in Table 1. The crude oil characteristics and its properties have been tested in RIPI (Research Institute of Petroleum Industry) laboratory in IRAN. Also the study has been done based on different water cuts.

The emulsion's stability is depended on the properties of the oil and water and the interfacial film behavior. The stability of the emulsion is also influenced by external factors such as temperature and electrical field. In this study, the emulsion stability was investigated studied by gathering experimental data showing the water separated amount from the emulsion and the water and oil interfacial tension by adjusting the demulsifier concentration, type and residence time. Some of the characteristics of the demulsifiers used in the research are listed in table 3.

1-2- Materials

Table 4 have demonstrated the chemicals used in this study. Most of the chemicals have supplied from SEMNAN, CEDEC, KING, and FALIZAN companies.

According to ASTM D 4006-81 “Standard Test Method for Water in Crude Oil by Distillation”, the water cut of emulsions was tested by distillation.

Table 4 Type of chemical demulsifiers

No.	Name	Base	Supplier
1	Dw-1	Water	SEMNAN
2	Dw-2	Water	SEMNAN
3	Dw-3	Water	KING
4	Dw-4	Water	KING
5	Dw-5	Water	CEDEC
6	Dw-6	Water	FALIZAN
7	Dw-7	Water	FALIZAN
8	Dw-8	Water	FALIZAN
9	Do-1	Oil	SEMNAN
10	Do-2	Oil	FALIZAN
11	Do-3	Oil	KING
12	Do-4	Oil	KING
13	Do-5	Oil	KING
14	Do-6	Oil	CEDEC
15	Do-7	Oil	FALIZAN
16	Do-8	Oil	FALIZAN

1-3- Emulsion Preparation

The reference method (SPE 65041) "*Development of New green Demulsifiers*" was used in oil production a centrifuge tube functioned as a dehydration vessel according to the test conditions. Based on reference method, the Water/Oil emulsion was made up of sampled crude oil from well. Formation water was used and then the mixture of water and crude oil was preheated. Withdrew simulated formation water and crude oil at different proportion according to water cut in emulsion and also 1000 RPM was applied as a Stirring rate.

1-4- Screening of the Demulsifiers

The screening method has carried out at constant pH and temperature. Different demulsifiers (oil/water base) concentration and residence time were applied for other water cut crude oil. The experimental data has analyzed, and the most effective demulsifier was determined based on water separation efficiency in the existing emulsion system in RIPI laboratory. The kinds of demulsifiers, including water base and oil base, have tested for a heavy crude sample from an Iranian oil field. The specification and type of tested oil/water base demulsifiers have shown in Tables 5 and 6.

Table 5 Water based demulsifiers specification

Name	pH	Viscosity (mPa.s)	Density (g/cm ³)	Flash point (°C)	Solidification point (°C)
Dw-1	7.76	65.90	0.985	28.1	< -15
Dw-2	3.22	2.40	1.011	58.0	-1
Dw-3	6.28	270.30	1.018	80.1	< -5
Dw-4	6.36	184.60	1.018	36.1	< -5
Dw-5	8.10	61.20	0.984	22.2	< -5
Dw-6	10.38	147.60	0.999	55.1	< -5
Dw-7	10.91	14.80	0.995	57.6	< -5
Dw-8	5.44	34.10	1.042	>85	< -5

Table 6 Oil based demulsifiers specification

Name	pH	Viscosity (mPa.s)	Density (g/cm ³)	Flash point (°C)	Solidifying point (°C)
Do-1	4.05	66.61	0.914	53.1	< -5
Do-2	7.59	42.95	0.948	65.2	< -5
Do-3	7.17	102.21	1.002	22.2	< -8
Do-4	7.35	112.43	0.988	>85	< -5
Do-5	8.90	247.83	1.012	57.1	-4.5
Do-6	6.70	25.46	0.938	32.1	< -5
Do-7	7.88	13.20	0.997	>80	< -5
Do-8	7.10	225.69	0.985	71.2	< -8

2- RESULTS AND DISCUSSION

2-1- Oil / Water demulsifiers, base demulsifiers effect

In this part of the study, the optimal conditions for removing water from heavy crude oil were found following laboratory tests. The sample was heated with an adequate heating bath to meet the temperature. At a specific temperature, the demulsifiers have injected into the emulsion.

- **Oil base demulsifiers**

The eight types of oil base demulsifiers (mentioned in table 4) have been tested. Each type of demulsifier is evaluated with the dosage of 50ppm, 100ppm, 150ppm, and 200ppm. The experimental data of dehydration efficiency in different water cuts (2%, 7.8%, 20%, and 40%) with above-mentioned dosage for oil base demulsifiers are collected. The dehydration efficiency changes versus different demulsifiers dosage in constant water cut (7.8%) at different residence time are reflected in the figures 1-4. The result shows that when the dose was over 100 ppm, the use of Do-1 demulsifier was most effective.

When dosage was below 120ppm, the use of demulsifiers Do-5 and Do-8 was the highest demulsifier efficiency. Demulsifier efficiency were over 96% when dosage at 200ppm of Do-1 and dosage at 100ppm of Do-5 & Do-8. So the demulsifiers Do-5, Do-8 and Do-1 have been chosen as three of best oil base demulsifiers. Optimal dosages are 100ppm, 100ppm, 200ppm respectively. This study shows the oil base demulsifiers with pH between 7-8 and dosage more than 100 ppm, have similar behavior. In addition, oil base demulsifiers with high viscosity and high pH have more dehydration efficiency.

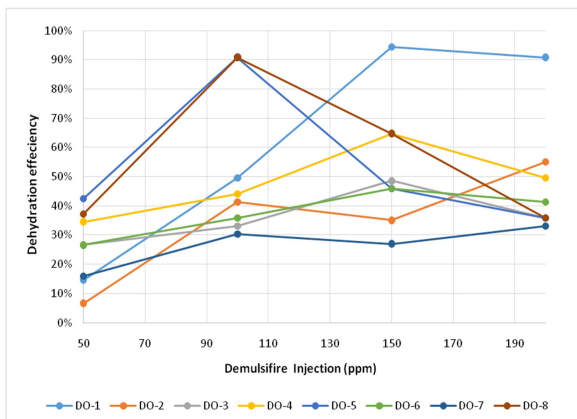


Figure 1. Dehydration efficiency of oil base demulsifiers for a residence time of 120 minutes

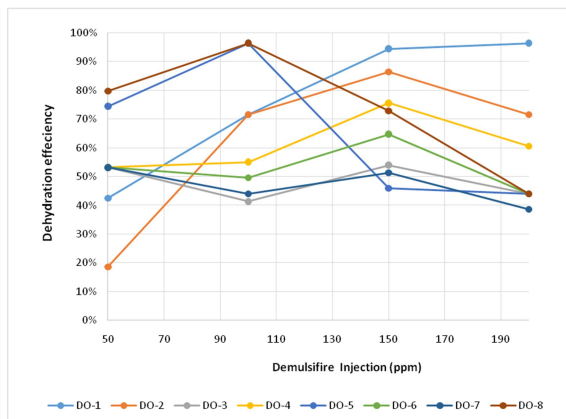


Figure 2. Dehydration efficiency of oil base demulsifiers for a residence time of 240 minutes

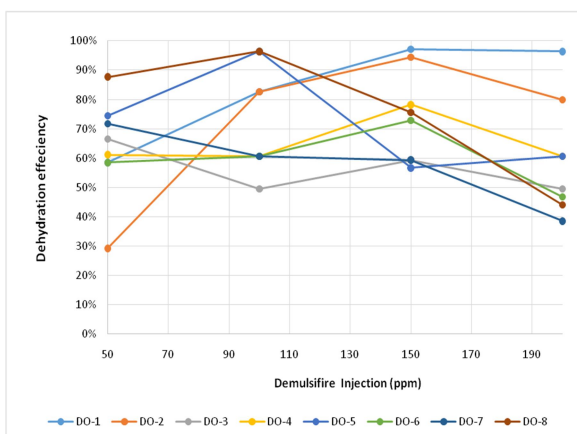


Figure 3. Dehydration efficiency of oil base demulsifiers for a residence time of 360 minutes

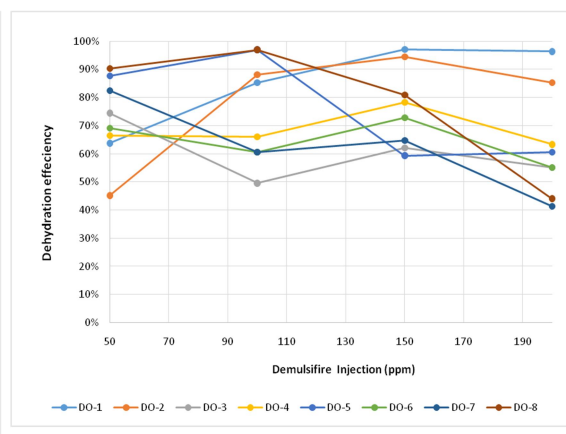


Figure 4. Dehydration efficiency of oil base demulsifiers for a residence time of 480 minutes

• **Water base demulsifiers**

Following the research, 8 types of water-based demulsifiers were tested. Each kind of demulsifier is evaluated with the dosage of 50 ppm, 100 ppm, 150 ppm, and 200 ppm. The experimental data of dehydration efficiency in different water cuts (2%, 7.8%, 20%, and 40%) with above-mentioned dosage for water base demulsifiers are collected. The results of water base demulsifiers efficiency versus different dosage in constant water cut (7.8%) at different residence time are reflected in the figures 5-8.

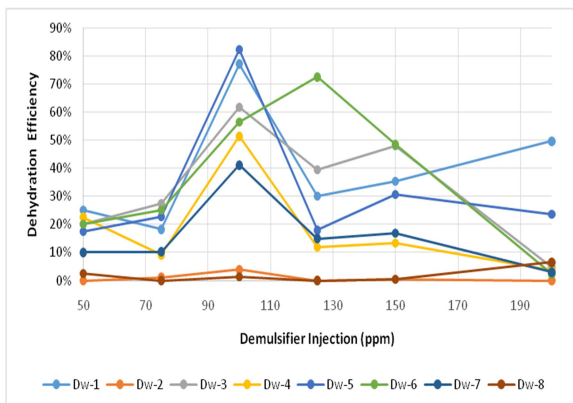


Figure 5. Dehydration efficiency of water base demulsifiers for a residence time of 120 minutes

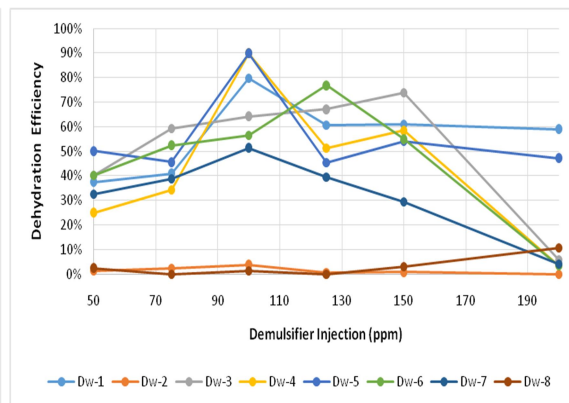


Figure 6. Dehydration efficiency of water base demulsifiers for a residence time of 240 minutes

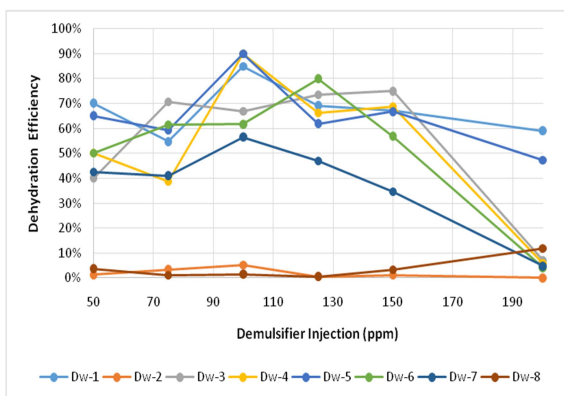


Figure 7. Dehydration efficiency of water base demulsifiers for a residence time of 360 minutes

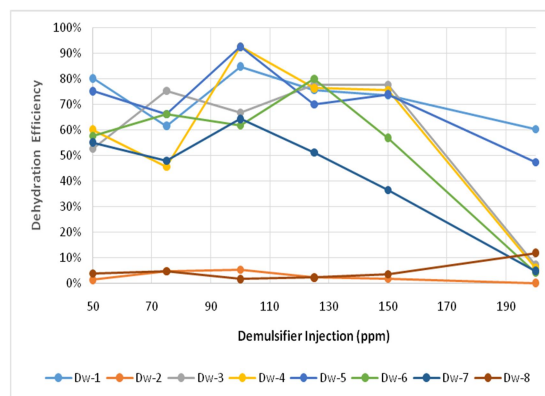


Figure 8. Dehydration efficiency of water base demulsifiers for a residence time of 480 minutes

For long period demulsification, it can be seen that water base demulsifiers performances were approximately same excepting Dw-2, Dw-7, and Dw-8. For short period demulsification, it can be seen that water base demulsifiers performances are different. Dw-2, Dw-4, Dw-7 and Dw-8 were abandoned but Dw-6 at dosage 75 mg/L~150 mg/L have excellent performance in demulsifiers efficiency curve of water base demulsifiers in 120 & 240 minute, especially in 120 minute. Dw-3 also had advantage to Dw-1 & Dw-5 in demulsifiers efficiency curve of water base demulsifiers in 120 & 240. Therefore, Dw-3 and Dw-6 have been chosen as two best water base demulsifiers. Optimal dosage is 125 mg/L.

2-2- Demulsifiers type effect with water cut consideration

The results of oil/water base demulsifiers study have been shown on figures 9-12, based on different water cuts with 100 ppm dosage in 240 and 480 minute as residence time.

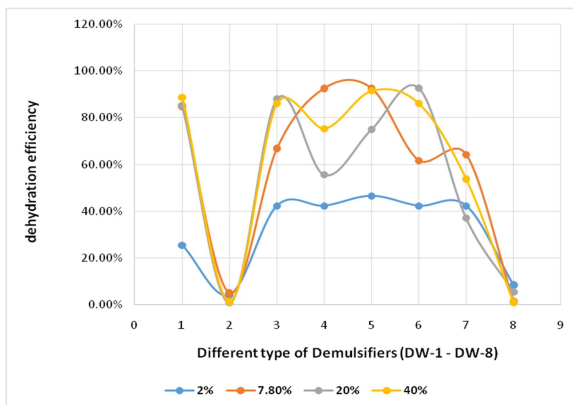


Figure 9. Dehydration efficiency for different water base demulsifiers type in different water cut (100 ppm, 480 minute)

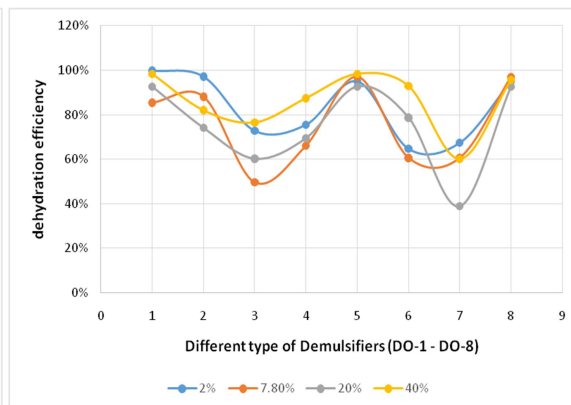


Figure 10. Dehydration efficiency for different oil base de emulsifiers type in different water cut (100 ppm, 480 minute)

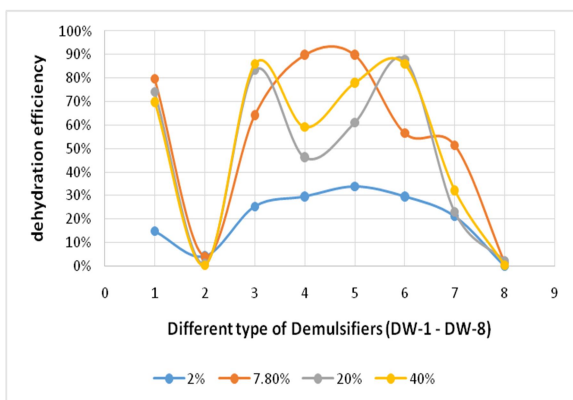


Figure 11. Dehydration efficiency for different water base demulsifiers type in different water cut (100 ppm, 240 minute)

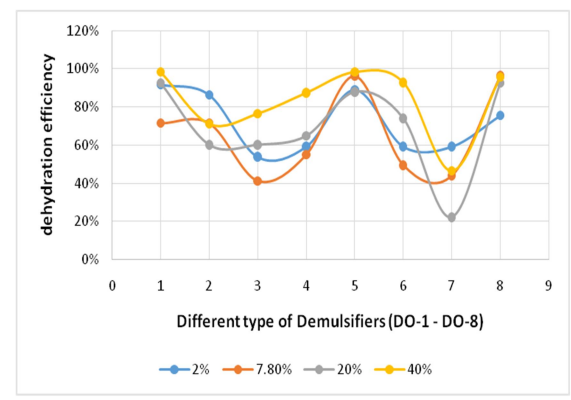


Figure 12. Dehydration efficiency for different oil base de emulsifiers type in different water cut (100 ppm, 240 minute)

The results show that the water base demulsifiers have less efficiency in less crude oil water cuts and it is demonstrated that the water separation by using oil base demulsifiers has a better efficiency. In addition, increasing the residence time has no effect on dehydration efficiency.

3- PARAMETERS INVESTIGATION ON DEHYDRATION EFFICIENCY BY THE SOFTWARE

The effect of demulsifiers pH as an independent parameter was studied on demulsifiers performance. For this goal, the Software Qualitec-4 was used.

The Qualitec-4 Software is windows operating software for the Taguchi experimental design technique. It can automatically design experiments based on user specified parameters and levels. It offers variants for experiments, analyzes the results and much more. Table 7 shows the three independent variables' range and levels for the water base demulsifiers investigated in this study.

Table 7. Experimental range and levels of independent parameters for chosen water base demulsifiers

Parameters	Dw-1 (level 1)	Dw-2 (level 2)	Dw-3 (level 3)	Dw-6 (level 4)
pH	7.76	3.22	6.28	10.38
Dosage (ppm)	50	75	100	200
Time (minutes)	360	480	600	600

The experimental results of each level based on variables for water base demulsifiers (dehydration efficiency) have been mentioned in table 8.

Table 8 Experimental level dehydration efficiency for chosen water base demulsifiers

Water base demulsifiers	
Levels	Efficiency
Dw-1	70.10%
Dw-2	4.56%
Dw-3	84.78%
Dw-6	4.13%

In this regard, sixteen different runs were performed for water base demulsifiers in order to investigate each parameter effect, as shown in Table 9.

Table 9 Recommended runs by Qualitec-4 software for selected water base demulsifiers

Run	Variables			Dehydration efficiency (%)
	pH	Dosage	Time	
1	7.76	50	360	70.1
2	7.76	75	480	61.53
3	7.76	100	600	97.62
4	7.76	200	600	60.21
5	3.22	50	480	1.25
6	3.22	75	360	3.42
7	3.22	100	600	17.98
8	3.22	200	600	0
9	6.28	50	600	65.09
10	6.28	75	600	77.48
11	6.28	100	360	66.08
12	6.28	200	480	7.08
13	10.38	50	600	60.09
14	10.38	75	360	70.64
15	10.38	100	480	61.66
16	10.38	200	360	4.13

Based on the results in Table 9, the effective separation for water-based demulsifiers occurred in experiment 3 with about 97% dehydration efficiency, while in experiment 8, the water separation was 0%, being at the end of the list. In these runs, the mean separation rate was about 45.3%.

Table 10 shows that pH is the most influential parameter in separating water (56.079%), while time had the lowest effect on separation, around 9.8%. The total error for the results of the above experiments is 10.1%.

Table 10. Investigation of variances for chosen water base demulsifiers

Factors	DOF	Sum of sqrs.	Variance	F ratio	Pure sum	Percent (%)
pH	3	9571.326	3190.442	28.767	9238.613	56.079
Dosage	3	4290.921	1430.307	12.896	3958.209	24.026
Time	3	1946.519	648.839	5.85	1613.807	9.795
Total	15	665.423				10

The information about the selected parameter is shown in Table 11. In this table, the optimal value related to each factor, corresponding to its level, was revealed.

Table 11. The optimum levels for all selected water base demulsifiers

No.	Factors	Level description	Level	Contribution
1	pH	7.76	1	27.092
2	Dosage	100	3	15.562
3	Time	600	3	13.065

CONCLUSIONS

A screening process was used to choose the most efficient demulsifiers, taking into account their price. The oil base demulsifiers have better dehydration efficiency, about 96% based on water/oil base results. Using this type of demulsifiers, cover crude oil with wide water cut range (2%-40%). So the demulsifiers Do-5, Do-8 and Do-1, have chosen as three of the best oil-based demulsifiers. The optimal dosages are 100 ppm, 100 ppm and 200 ppm, respectively.

In the second part of the research, because water-based demulsifiers have a lower water separation efficiency, Qualitec-4 software investigates the effect of the pH parameter and the best efficiency for water-based demulsifiers. This is obvious: the water separation percentage using water base/oil base demulsifiers varies, and the difference in separation depends on dosage, residence time, and demulsifiers properties such as pH.

The result shows that the pH of demulsifiers can affect about 27% on dehydration efficiency, and other conditions such as dosage and residence time have less impact. In this regard, selecting the water base demulsifier with pH =7.76, dosage=100, time=600, has the best performance (approximately 100% dehydration efficiency considering 10% error).

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