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Evaluating the efficiency of demulsifiers for water-in-oil emulsions and the influence on the chemical composition of the dehydrated petroleum

João Vitor Q. Pardo[1], Danilo C. da Silva[1], Laercio L. Martins[1], Alexsandro A. da Silva[2], Georgiana F. da Cruz[1]

[1]Petroleum Engineering and Exploration Laboratory/State University of the North Fluminense Darcy Ribeiro, Brazil, * joaovitorpardo@gmail.com
[2]Chemistry Institute/State University of Rio de Janeiro, Brazil

Abstract
Due to the complexity of water-in-oil emulsions (W/O) stability, choosing the proper demulsifier during oil production is challenging. Therefore, it is necessary to understand how these emulsions are formed to determine the best demulsifier (most common chemical method) that can be used to treat undesirable emulsions. Therefore, it is necessary to study the type and composition of the oil and the aqueous phase that forms the emulsion. In this context, the stabilities of two W/O emulsions from 1616 and blend crude oils were investigated regarding the separation efficiency of five demulsifiers at different concentrations. The demulsification efficiency was examined using bottle tests at 40 °C in graduated tubes for water separability tests by adding a constant quantity of each tested demulsifier. In addition, the separated oil was characterized, and the influence of concentration and type of demulsifier on its chemical composition was evaluated. The results showed that the best performance was obtained for the 1D and 2D demulsifiers for the 1616 sample and the 2D and DM1580/359 demulsifiers for the blend sample. Importantly, none of the evaluated demulsifiers interfered with the chemical composition of the dehydrated oils in any of the concentrations used, providing reassurance in their application.

Keywords
Petroleum composition; W/O Emulsion; Demulsifier

Introduction
Chemical demulsifiers, such as polymeric flocculants, ethoxylated phenolic resins, and alkylphenol formaldehyde resins, have proven to be highly effective in expediting the separation of oil and water in water-in-oil emulsion and oil-in-water [1]. These demulsifiers migrate to the water-oil interface and counteract the stabilizing function of emulsifying agents, thereby breaking the emulsion [2]. This is possible since natural petroleum surfactants, such as resins, asphaltenes, and acid compounds, exhibit weak adsorption at the water-oil interface and can be easily displaced by various demulsifiers [2]. Given the complexity of the demulsification process and the multitude of chemical products used as demulsifiers, a clear-cut relationship between the emulsion type and the most suitable demulsifier for its destabilization is yet to be established [3]. Currently, the industry approach is more empirical. Therefore, the crucial first step in resolving this issue is to thoroughly understand the emulsion's composition. This involves understanding the chemical composition of the oil and water that form the emulsion and, from there, striving to establish more concrete relationships to accurately select demulsifiers.

Within this context, this work aimed to evaluate the performance of five demulsifiers (D1, D2, DM1580/359, DM1580/Z, and DM1580/T) on emulsion separation capability and characterizing the oil and water recovered. Only the results of the oil characterization by GC-FID were presented in this work.

Methodology
Samples
Two crude oil samples (1616 and blend oils) were obtained from different fields in Brazil and provided by oil and gas companies to be used in this work. The samples were dehydrated for chemical characterization by gas chromatography coupled to a flame ionization detector (GC-FID) [4], and the water-in-oil emulsions from these samples were used in the bottle tests. The bottle test method was used to evaluate the percentage of water separated. The properties of the two used crude oils are tabulated in Table 1.

Bottle Testing Procedure
The performance of five demulsifiers (D1, D2, DM1580/359, DM1580/Z, and DM1580/T) was evaluated by bottle test experiments. The bottle experiments were performed according to the

approach outlined by Loufakis et al. [5]. First, 100 mL of emulsion sample (1616 and blend) were added into graduated glass bottles and were set in a water bath at 40 ºC for 20 minutes. Second, once the temperatures of the content of the bottles were reached, each sample was dosed with a demulsifier at 500, 750, and 1000 ppm. After that, the bottles were shaken for five minutes and were submerged in the water bath. The amount of separated water in each sample was observed and recorded at 0, 5, 10, 20, 30, 40, and 60 minutes. The bottle tests were performed using the operating parameters, as shown in Table 1.

Table 1. Experimental parameters used in the bottle tests

Parameters	Value
Temperature (ºC)	40 ± 0.1
Mixing time of the demulsifier with the crude oil sample (min.)	5
Demulsifier concentration (ppm)	500, 750, 1000
Time to read analyzes (min.)	0, 5, 10, 20, 30, 40, 60
API of the crude oil sample	23 (1616); 23-24 (blend)
pH of the crude sample	7.6 (1616); 7.5-7.8 (blend)
Crude oil salt content (Cl^-, mg/L)	22665
Crude oil salt content (NaCl, mg/L)	37364

Demulsification efficiency

The results were expressed regarding the water percentage separated (WS) (%) as a function of time (min), using Eq. (1).

$$WT(\%) = \frac{V(t)}{V(T)} \times 100 \quad Eq.(1)$$

V(*t*) is the volume of water separated at t = 0, 5, 10, 20, 30, 40, and 60, and V(*T*) is the total volume of water in the bottle test (measured by BSW). All the experiments were triplicated.

Results and Discussion

Oil characterization by GC-FID

For breaking a water-in-oil emulsion, the right demulsifier is selected by an old but well-accepted method in the oil industry, the bottle test [6]. However, in this work, we conducted a study that evaluated the influence of the chemical composition of the oil on the performance of the evaluated demulsifiers. This involved the characterization of dehydrated oils by GC-FID to evaluate the hydrocarbon profile, followed by the evaluation of demulsifier efficiency considering the chemical composition of each oil previously analyzed. In the assessment of the chemical composition of the two crude oil samples by GC-FID (Fig. 1), the blend oil showed a bimodal profile with a maximum in nC_{15}, a greater abundance of *n*-alkanes range nC_8 to nC_{36}, and lower UCM (unresolved complex mixture), which reflects on characteristics of a lighter and low biodegraded oil [6]. The crude oil 1616, on the other hand, presents an unimodal profile with maximums in nC_{14} and nC_{15} and a lower abundance of high molecular weight *n*-alkanes compared to the blend oil.

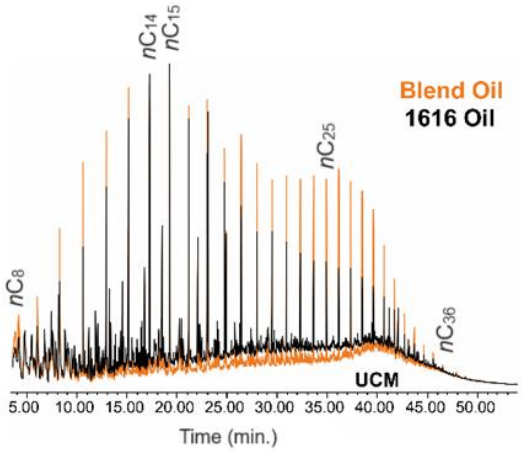


Figure 1. Overlay of the GC-FID chromatograms of the two dehydrated oil samples, blend and 1616 oil. nC_8, nC_{14}, nC_{15}, nC_{25} and nC_{36} = *n*-alkanes; UCM: Unresolved Complex Mixture.

Bottle tests

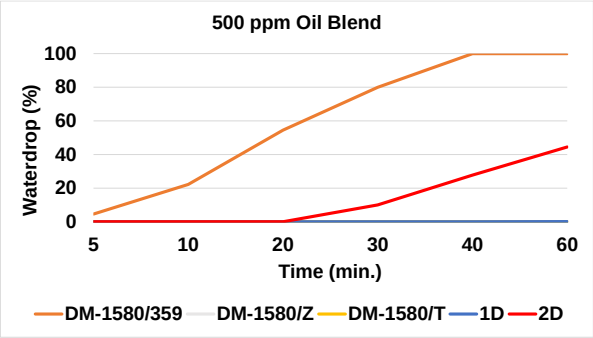
During the bottle test experiment, every demulsifier was evaluated based on its ability to separate the water phase as a function of time (Fig. 2 and 3).

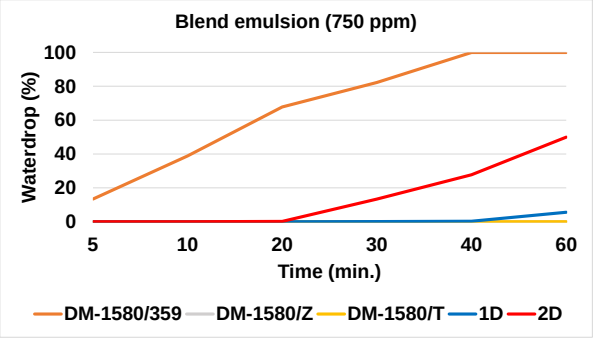
For all concentrations evaluated (500, 750, and 1000 ppm), the demulsifiers DM1580/359 and 2D were the ones that presented the highest separation efficiency of the aqueous phase for the blend emulsion sample (Fig. 2). This shows that these demulsifiers are efficient even at low concentration (500 ppm) for lighter oils (with high *n*-alkane content). On the other hand, the other demulsifiers (DM1580/Z, DM1580/T, and 1D) did not present any demulsification activity at the concentration of 500 ppm, and the demulsifier 1D showed an initial separation of the aqueous phase only after 40 minutes at the concentrations of 750 ppm (3,85% waterdrop) and 1000 ppm (24,42% waterdrop).

When the bottle test was carried out with the 1616 emulsion sample, all demulsifiers showed some water separation in the different concentrations evaluated (Fig. 3), highlighting the demulsifiers 1D, 2D e DM1580/539, which showed greater efficiency in separating the aqueous phase, over 80% water resolution after 20 minutes at a concentration of 500 ppm. The 1616 crude oil is more biodegraded and has a lower *n*-alkane content when compared to the blend crude oil sample (Fig. 1).

Therefore, all the demulsifiers tested showed good performance when used with a more biodegraded oil (with probably a higher content of polar compounds). These results suggest that the

evaluated demulsifiers are recommended for heavy oils.





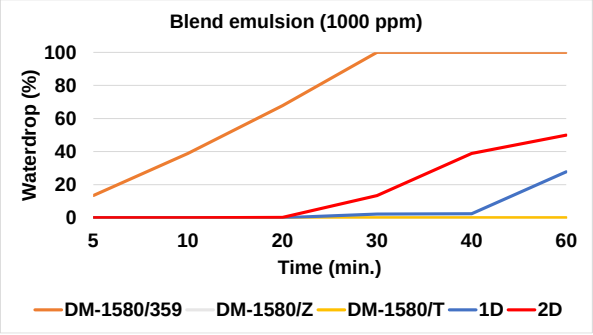
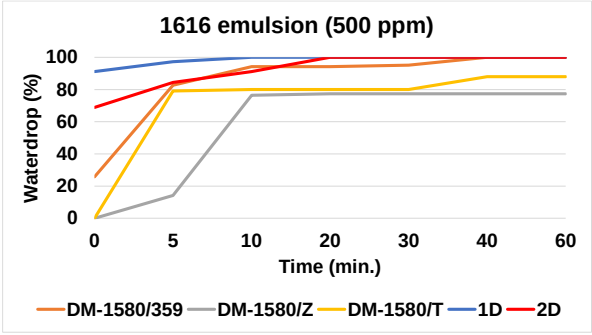
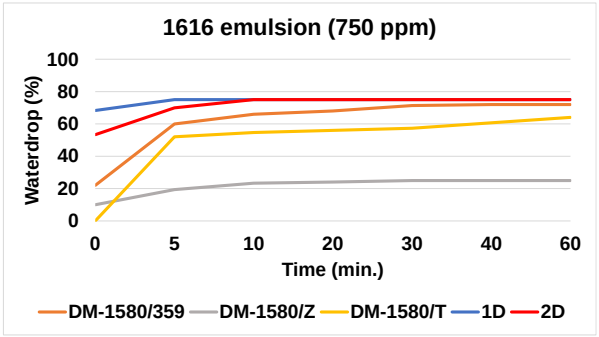


Figure 2. Waterdrop from the blend emulsion sample over time for each of the demulsifiers at the concentrations: 500 ppm; 750 ppm; and 1000 ppm.





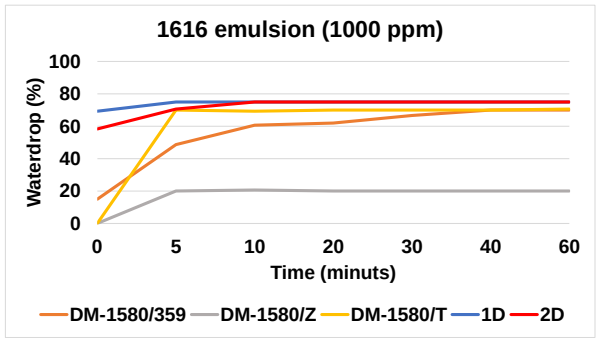


Figure 3. Waterdrop from the 1616 emulsion sample over time for each of the demulsifiers at the concentrations: 500 ppm; 750 ppm; and 1000 ppm.

It is important to note that the nature of the demulsifier, including molecular weight, chain size, and solubility in water, among others, impacts the interfacial activity of the emulsion. However, the characteristics of the crude oil must also be considered for the correct selection of demulsifier, as it was assessed in this work.

Effect of demulsifier on the chemical composition of oils

Another critical point is to evaluate whether the demulsifier used to break the emulsion interferes with the chemical composition of the oil. This is important because changing the chemical composition of the oil may imply additional steps in its treatment. Therefore, this study characterized the oils containing the tested demulsifiers by GC-FID (Fig. 4 and 5).

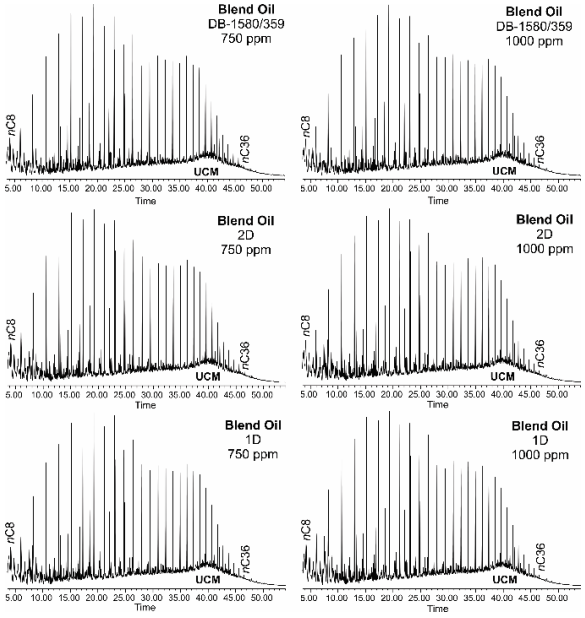


Figure 4. GC-FID chromatograms of the blend crude oil, after the bottle tests and for each demulsifier and concentration. UCM: Unresolved Complex Mixture.

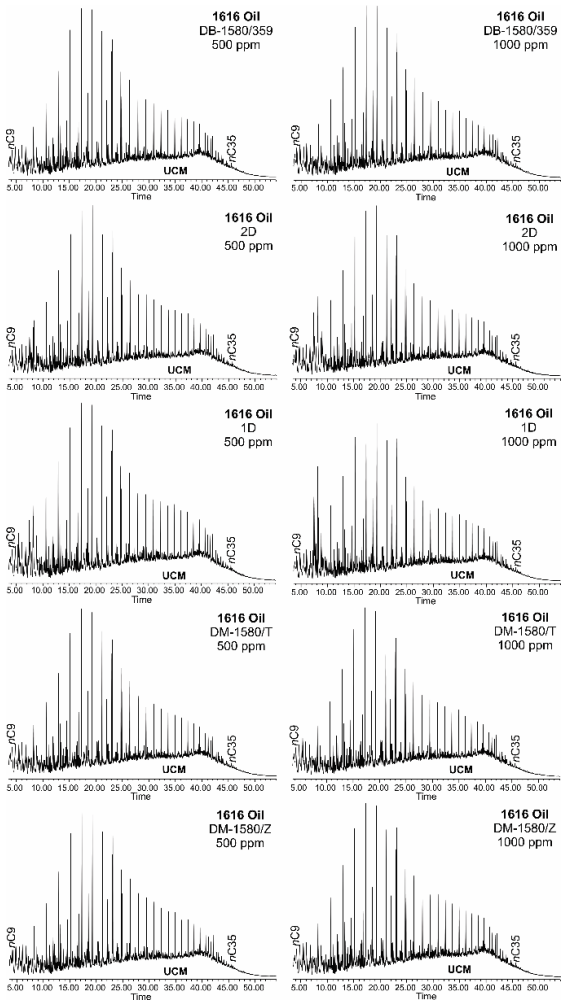


Figure 5. GC-FID chromatograms of the dehydrated 1616 oil, after the bottle tests and for each demulsifier. UCM: Unresolved Complex Mixture.

Considering only the hydrocarbon profile, it is noted that the demulsifiers did not alter the composition of the oils or are not present in the oily phase. Therefore, a comprehensive analysis of both the aqueous and oily phases is necessary to obtain a more appropriate result on the effect of the demulsifier on the chemical characteristics of the oil.

Conclusions

Five distinct demulsifiers tested for oil/water emulsion separation of two Brazilian crude oil samples showed potential. However, the best performance was obtained for the 1D and 2D demulsifiers for the 1616 oil sample (more biodegraded) and the 2D and DM1580/359 demulsifiers for the blend sample (light oil). Additionally, none of the studied demulsifiers influenced the chemical composition of the oils.

It is worth mentioning that this work presents novelties in evaluating the efficiency of demulsifiers by considering the chemical composition of the oil, which allows for an accurate choice of the demulsifier.

Acknowledgments

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Responsibility Notice

The authors are the only responsible for the paper content.

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