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Investigation of non-toxic demulsifiers and comparison to standard equivalents in the Paris Basin (France) oil mines

Introduction

The crude oil obtained from a well is comprised of a mixture of hydrocarbons and water. Oil-in-water and water-in-oil emulsions can exist, although the latter is the most common (Fink 2012). When crude oil is destined for the transportation line, a demulsifier is added to accelerate the separation between water and oil. Dai and Zhao (2018) showed that natural emulsifiers in water-in-oil emulsified crude oil mainly included active acidic oils (e.g., naphthenic acid, colloid acid) and oil-wet solid particles (e.g., asphaltenes, wax). Oilinwater emulsions are typically stabilized by alkali metal salts of active acidic oils, water-soluble surfactants, or water-wet solid particles (e.g., clay). According to Pu et al. (2022), asphaltenes

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and waxes are the main crude oil components responsible for emulsifying properties. Other important natural emulsifiers are resins. Asphaltenes and resins have a polar structure that provides a stable emulsion (Pickering emulsion) between a polar water molecule and a non-polar hydrocarbon phase (Yonguep et al. 2022). Naphthenates can be added to the final demulsifier formula to prevent naphthenate deposition (mostly calcium naphthenate) and provide excellent surface separation between the oil and water phases (Korzec and Sapińska-Śliwa 2023).

Gravity-induced separation in the presence of a demulsifier at elevated temperature is the most common approach to separate water from the oil phase at an oil and gas mine (Kelland 2014). Kelland claimed that a bottle test was the most effective method for determining the optimal demulsifier. The relative solubility number (RSN) is an important value for selecting the demulsifier group suitable for the oilfield based on the crude oil type. The lower the RSN value, the more oil-soluble the product (Kelland 2014). The main advantage of employing an oil-soluble demulsifier is that it will not transfer to the aqueous phase (i.e., the water does not require treatment to remove the demulsifier).

Many demulsifiers used in the oilfield industry contain toxic compounds, such as aromatic hydrocarbons, as solvents or active components. Khani and Razaeye (2018) claimed that aromatic hydrocarbons and toxic alcohols (e.g., methanol) are commonly used as solvents for many demulsifiers. Moreover, many active components can be toxic or not easily biodegradable (Dai and Zhao 2018). In the presented study, more toxic demulsifiers were compared during bottle tests with more environmentally friendly, non-toxic equivalents.

The dangers posed by the selected demulsifier components are presented in Table 1. This study aims to determine an effective, non-toxic, and highly biodegradable demulsifier that can be used in the oilfields of the Paris Basin. Many common demulsifier components negatively influence the natural environment and/or human health (Allison and Mandler 2018). These materials further complicate issues related to logistics, worker safety, and possible leaks. A review of relevant green technologies published by Dhandhi et al. (2021) provided

Table 1. Example of health hazards cited in the material safety data sheets of industrial demulsifier components

Tabela 1. Przykłady zagrożeń dla zdrowia podanych w kartach charakterystyki składników demulgatorów przemysłowych

H304	May be fatal if swallowed and enters the airways
H314	Causes severe skin burns and eye damage
H336	May cause drowsiness or dizziness
H351	Suspected of causing cancer
H411	Toxic to aquatic life with long-lasting effects

Source: MSDS of industrial demulsifier of Brenntag – EN_MSDS_713245.

crucial information regarding the possibility of using non-toxic reagents as demulsifiers, and data clarifying the toxicity of commonly used reagents.

Dalmazzone and Noïk (2001) pioneering work applied green chemistry in a demulsification process. They demonstrated that silicone-based chemicals could effectively separate water from crude oil. The technical aspects were comprehensively presented, but the influence of silicone on the refinery process was not considered. Later, Zhou et al. (2012) tested a series of commercial demulsifier formulas and evaluated their efficiencies before and after replacing the solvents and active components. The results indicated that more environmentally friendly solvents and surfactants could be employed to optimize the system efficiency. Zhou et al. (2012) described a similar study to that present in our work because both strategies relied on grind-out (centrifuge) tests (see the Materials and Methods section).

Another important approach towards crude oil separation using non-toxic products employs magnetic fluorinated polyether composite demulsifiers (Jia et al. 2023). The product provided excellent demulsification properties, nevertheless, the dosages suggested by the authors started from 600 ppm, which is considerably higher than in many industrial cases.

Several reports have discussed other sophisticated (non-standard) chemical methods. Abdurrahim (2018) used a non-ionic surfactant based on chitosan to effectively separate water from crude oil. It was found that the separation process could be accelerated with this type of surfactant, but it was uncommon, hence, the economic factors prevented its implementation in the oilfield. A similar disadvantage occurred when using a synthetic demulsifier based on the ester of oleic acid and polyethylene glycol to dehydrate crude oil emulsions. Despite the excellent bottle test results, the dosage suggested was at least 731 ppm (Dhandhi et al. 2024). Dhandhi et al. (2023) also tested a novel demulsifier synthesized via the esterification of fatty acid, having low cost and biodegradability, and generated excellent results in treated crude oil samples.

Plant extracts have also been investigated to determine their separation properties (Yaakob and Sulaiman 2017), and indeed, several substances obtained from various plants can be used as demulsifiers. Despite promising results, the dosages (20,000 to 60,000 ppm per crude oil emulsion) far exceeded those used in commercial products. For example, in this work, the dosage examined was 75 ppm per oil (hydrocarbons) volume when water was not considered in the calculation.

1. Materials and methods

Standard bottle tests were conducted on the demulsifiers to estimate the efficiency of the investigated products. This is one of the most common methods for selecting demulsifiers (Zolfaghari 2016; Loufakis 2017).

The tests involved pouring crude oil samples into glass bottles, which were heated for approx. 1 h at a temperature similar to that in the installation line (approx. 35°C). Next, they were removed and hand-shaken for 2 min. The demulsifiers were added to each bottle,

where the dosage was calculated according to the amount of oil in the corresponding emulsion (measured before the test using a centrifuge or a Karl-Fischer titrator). The samples were hand-shaken for 2 min and then placed in a water bath at the temperature of the installation line or separator (35°C).

The separation process on an installation line took less than 2 h, and the tests were performed for approx. 1 h. The results were recorded at regular intervals (depending on the test).

After each test, 5 mL of oil from the middle of the oil layer was mixed with 5 mL of xylene in a plastic tube. The tubes were centrifuged for 10 min at 2,300 rpm, and the amount of water separated from the oil was recorded. Finally, a large amount of another demulsifier (solution prepared to separate the whole water content in high dosage) was added to each tube, and the samples were centrifuged again. It was assumed that the total volume of water in the oil was obtained after the second centrifugation. After each cycle, the obtained results were similar (i.e., after the two centrifugation processes), indicating that the quantity of water separated after a dose of demulsifier was comparable to the total potential water separation.

The separation time, demulsifier dosage, water isolated after centrifugation (grind-out), separation surface, and clarity of the separated water were the considered factors to evaluate the overall efficiency of each product (Bęben et al. 2007; Grenoble and Trabelsi 2018).

Bottle tests of the demulsifiers were performed using crude oil from four locations (mines) and one mixture of oils from the mines. The samples were obtained from a small area in the Champagne region of France (Figure 1). Testing demulsifiers at the oil mining

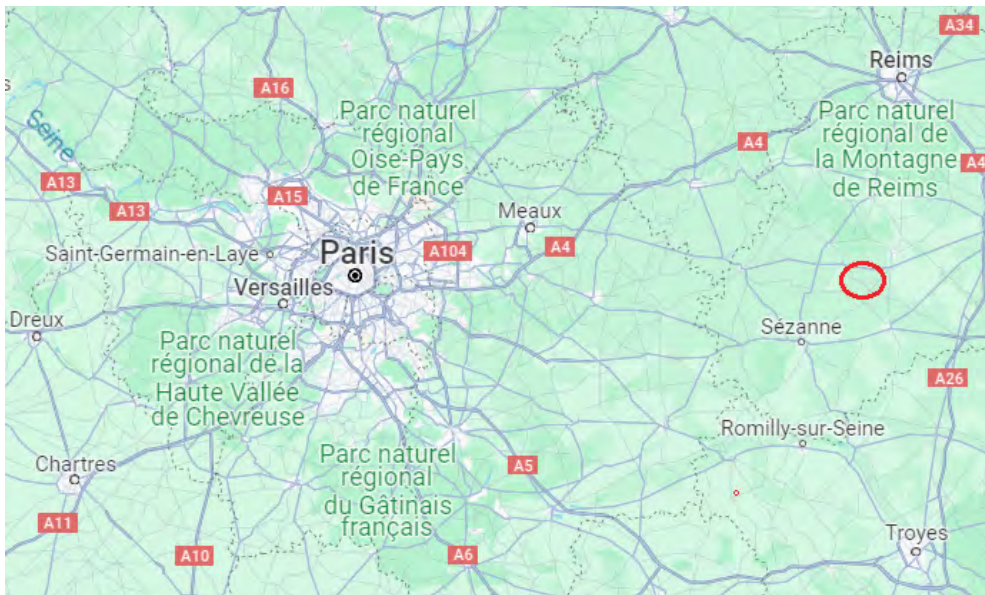


Fig. 1. The region where samples were obtained (area in a circle)
Source: M. Korzec, Google Maps Table 2 (Water contents in all tested oil samples)

Rys. 1. Region, z którego pobrano próbki (pole w okręgu)

facilities was advised because the oil aged over time. Specifically, the volatile components of the crude oil evaporated over time, changing the oil's properties and influencing the demulsifier efficiency (Ferreira et al. 2012). Before each test, the water content in the oil was measured using a standard dynamic centrifugation technique (Yaakob and Sulaiman 2017). Specifically, small samples from the wells (5 mL) were mixed with xylene (5 mL), and then a knock-out demulsifier was added. A knock-out demulsifier is a product that is added in large quantities to separate all the water during this test. The resulting mixture was centrifuged for 10 min at 2300 rpm. The water contents in the tested oil samples are presented in Table 2.

Table 2. Samples parameters

Tabela 2. Parametry próbek

Sample	Water content in the oil (%)	Water parameters (average)		
		sulfides (mg/L)	dissolved iron (mg/L)	total iron (mg/L)
No. 1	81	1.50	2.65	6.01
No. 2	70	13.00	0.10	1.00
No. 3	35	2.03	7.44	8.63
No. 4	25	not measured	not measured	not measured
No. 5 – MIX Oil 1 – 16% Oil 2 – 24% Oil 3 – 3% Oil 4 – 57%	35	not measured	not measured	not measured

Density of oil No 5 is $0.841 \text{ g}\cdot\text{cm}^{-1}$ at 25°C and $0.853 \text{ g}\cdot\text{cm}^{-1}$ at 15°C .

When the water content in the oil was determined, the bottle test was initiated. First, the oil samples were hand-shaken for 10 min to obtain a homogenous solution. Then, 80 mL of oil was poured into each bottle (bottles were shaken for 2 min after every two samples), and the samples were heated to 35°C (i.e., the oil temperature in the transportation line) for 1 h. In total, 75 ppm of the demulsifier (similar to the amount present in the installation line, adjusting for the oil quantity in the sample) was added to each oil sample (14 test samples), while one blank sample was used as a control. Each bottle was shaken for 2 min and placed in a water bath at 35°C for 60 min. The obtained results (i.e., water separation, surface quality, water quality) were recorded after 10, 20, 30, and 60 min.

After 60 min, the water content in the oil samples was measured using a centrifuge. Specifically, 5 mL of oil (from the top of the bottle) was mixed with 5 mL of xylene in a tube. The tubes were shaken and then centrifuged for 10 min at 2,300 rpm. The amount of water

separated from 5 mL of oil was determined, and the test was repeated with a knock-out demulsifier. The lower the water content in the oil, the better. The difference between the water contents in the oil before and after the use of the knock-out product was another important factor. A lower difference between these values indicated a more efficient and effective demulsifier (according to the internal procedure for selecting demulsifiers provided by the Brenntag company).

2. Results

The number of samples varied depending on the test, and a screening test was conducted to select the products that could be demulsifiers for the oils in a particular oilfield. Therefore, one aim of this study was to determine at least one product that was compatible with every type of crude oil.

2.1. Test results for crude oil No. 1

This stage also involved a screening test, in which 13 demulsifiers were investigated. Based on this test, 6 of the most efficient products were used for further stages, together with the product already used at the installation (a blank sample was used in every stage). Currently used demulsifiers were not tested due to the requirement of internal permission to use the product. Hence, the screening test commenced without such demulsifiers, which were added in further tests. Table 3 presents the active components and types of solvents for every sample. Depending on the formula, the content of active components corresponded to 20% to 50%. The dosage of the product (demulsifier) in every stage (excluding the blank sample) was 75 ppm, which was calculated based on the oil content (the water content was not considered during calculations). This dosage was used at the installation due to the pump's specifications (they cannot dose lower quantities).

The test outcomes for oil No. 1 are presented in Figures 2–7.

Separation occurred after 10 min, due to the step in the internal procedure, it was visible that the oil separated after dosing of the demulsifiers. The properties of the emulsion were compared to the blank sample, in which separation of 50 mL of water indicated that the emulsion was unstable to some extent (still needs to be treated with demulsifier).

Samples 3, 6, 7, 11, and 12 had the most transparent water (bottom layer in Figures 4–7). Another critical factor was the quality of the interfacial surface, where Samples 3, 4, 6, 7, 8, 9, 13, and 14 had a smooth appearance, and the other samples containing demulsifiers had a rough interfacial surface, except for Sample 1 (blank) and Sample 10. The grind-out results (from the centrifuge test) are presented in Figure 3. The first grind-out value described the amount of unseparated water in the oil during the test, and the grind-out after using a knock-out demulsifier indicated the total water content in the separated oil. The ideal outcome was

Table 3. Characteristics of products tested with oil No. 1

Tabela 3. Charakterystyka produktów badanych z olejem nr 1

Sample number	Active component	Molecular weight (Da)	Solvent
1	None (blank sample)	Not applicable	none (blank sample)
2	EO/PO (ethylene oxide/propylene oxide) polymer (RSN* = 10)	4,400	dimethyl esters
3	Polyimine derivative + EO/PO polymer (RSN = 10) (ratio 1:2)	10,000 + 4,400	dimethyl esters
4	Fatty acids derivative (RSN = 9,1)	Unknown	dimethyl esters
5	A mix of anionic surfactants, ethoxylated (RSN = 8,6)	Unknown	dimethyl esters
6	Oxyalkylated phenolic resin	Unknown	aromatic
7	Oxyalkylated phenolic resin	Unknown	aromatic
8	Oxyalkylated phenolic resin	Unknown	aromatic
9	Calixarene	Unknown	aromatic
10	EO/PO polymer (RSN = 21)	2900	aromatic
11	Mix of oxyalkylated phenolic resins	ca. 10,000 + ca. 5,000	aromatic
12	A mix of oxyalkylated phenolic resin	ca. 5,000	aromatic
13	Oxyalkylated phenolic resin	ca. 5,000	aromatic
14	Oxyalkylated phenolic resin + EO/PO polymer (RSN = 17) + silicone oil	ca. 5,000 + ca. 2,900 + ca. 5,000	aromatic
15	Product currently used in the installation line, dosed at the wellhead	Unknown	aromatic

* RSN – Relative Solubility Number.

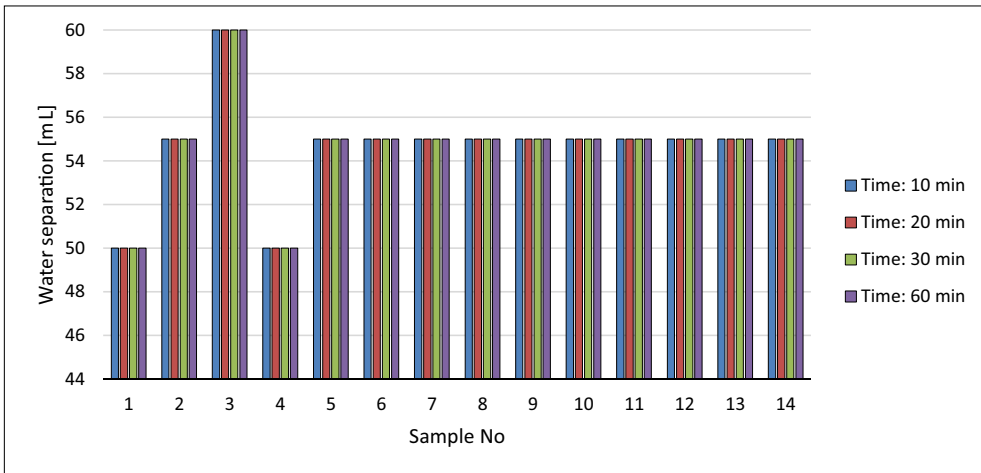


Fig. 2. Water separation from each oil No. 1 sample after 10, 20, 30, and 60 min

Rys. 2. Wydzielenie wody z każdej próbki oleju nr 1 po 10, 20, 30 i 60 min

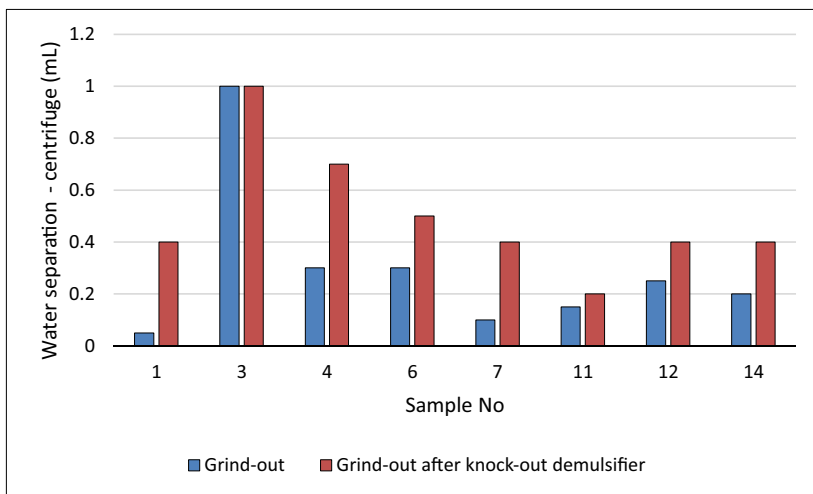


Fig. 3. Grind-out before and after the use of a knock-out demulsifier on oil No. 1 samples

Rys. 3. Rozdrobienie przed i po zastosowaniu demulgatora wybijającego na próbkach oleju nr 1

a low value and the lower the difference between the obtained values. When there was no difference (e.g., Sample 3), the demulsifier had the potential to completely separate from the water.

The demulsifier products used in Samples 3, 4, 6, 7, 11, and 12 were subjected to further tests. These products were selected based on the interfacial surface quality, the visual



Fig. 4. Test results after 60 min, from the left: Blank and Samples 2, 3, and 4

Rys. 4. Wyniki testu po 60 min, od lewej: próba ślepa oraz próbki 2, 3 i 4



Fig. 5. Test results after 60 min, from the left: Samples 5, 6, 7, and 8

Rys. 5. Wyniki testu po 60 min, od lewej: próbki 5, 6, 7 i 8



Fig. 6. Test results after 60 min, from the left: Samples 9, 10, 11, and 12

Rys. 6. Wyniki testu po 60 min, od lewej: próbki 9, 10, 11 i 12



Fig. 7. Test results after 60 min, from the left: Samples 13 and 14

Rys. 7. Wyniki badania po 60 min, od lewej: próbki 13 i 14

quality of the separated water, and the centrifugation test results obtained with oil No. 1. Due to complete water separation after 10 min, the water separation rate was not considered as a crucial factor in this investigation.

2.2. Test results for crude oil No. 2

Products 3, 4, 6, 7, 11, and 12 were used for the subsequent testing stage, along with the demulsifier currently used on the oilfield (number 15) and a blank (Sample 1). The results are presented in Figures 8–11. A mix of Samples 6 and 7 was used due to the high water clarity and excellent interfacial surface quality (especially in Sample 7). Other samples rejected for further investigation did not provide either clean water (visually) or a smooth interfacial surface. The dosages were maintained at 75 ppm for Samples 3, 7, 11, 12 and 15. For Sample 4,

the dosage was doubled to 150 ppm, and for Sample 6+7 mix, the dosage was divided among the two products (20 ppm of Product 6, and 55 ppm of Product 7).

In total, 55 mL was separated for every sample immediately (noted after 10 min), even for the blank sample. That is why, for this sample, only grind-out results were presented.

All of the water was separated from the oil within 10 min. Each bottle contained a similar number of water droplets on the glass, except for Sample 15 (Figures 9 and 10). The grind-out results (Figure 8) were similar for all tested samples, however, Samples 3, 4, 7, and 11 separated negligible water content from the oil after centrifugation tests. The water in each sample was clear, where Samples 3, 11, and 12 interfacial separation surfaces were smooth, while the others were rough.

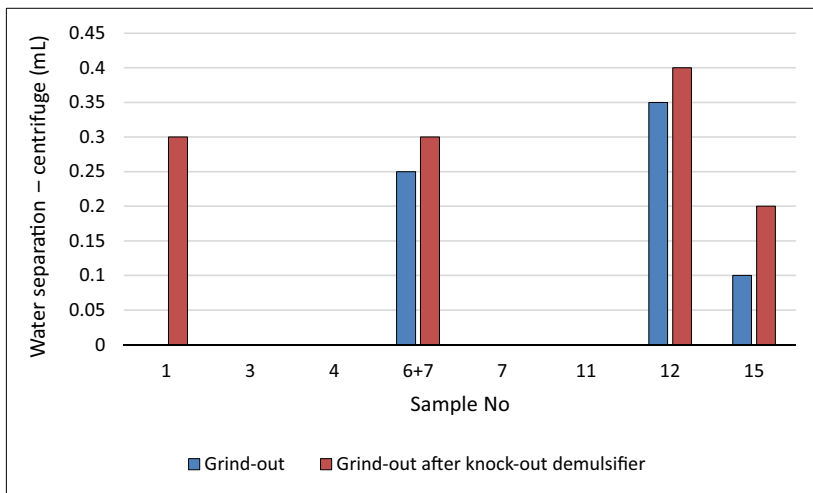


Fig. 8. Grind-out before and after the use of a knock-out demulsifier in oil No. 2

Rys. 8. Rozdrobienie przed i po zastosowaniu demulgatora wybijającego w oleju nr 2



Fig. 9. Test results after 60 min, from the left: Blank and Samples 3, 4, and 6+7

Rys. 9. Wyniki testu po 60 min, od lewej: próba ślepa oraz próbki 3, 4 i 6+7



Fig. 10. Test results after 60 min, from the left: Samples 7, 11, 12, and 15

Rys. 10. Wyniki testu po 60 min, od lewej: próbki 7, 11, 12 i 15

2.3. Test results for crude oil No. 3

The test results obtained for oil No. 3 are presented in Figures 11–14. The results were recorded after 30 and 50 min, and the dosages were the same as those used for oil No. 2.

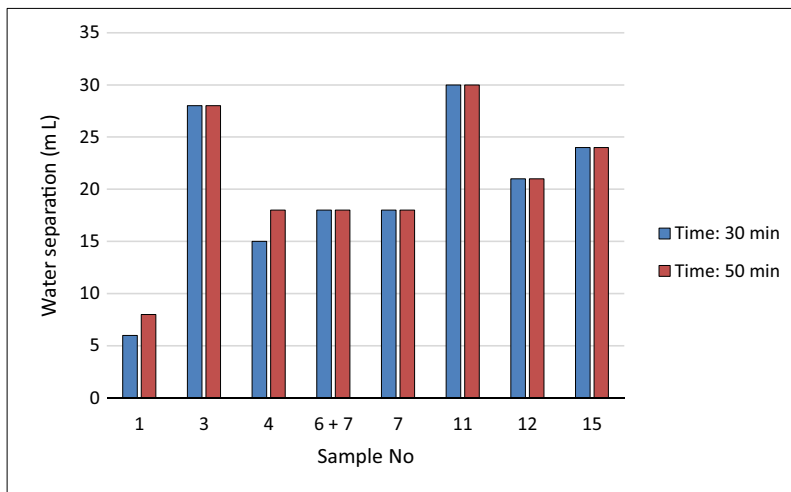


Fig. 11. Water separation from oil No. 3 with each sample after 30 and 50 min

Rys. 11. Wydzielanie wody z oleju nr 3 dla każdej próbki po 30 i 50 min

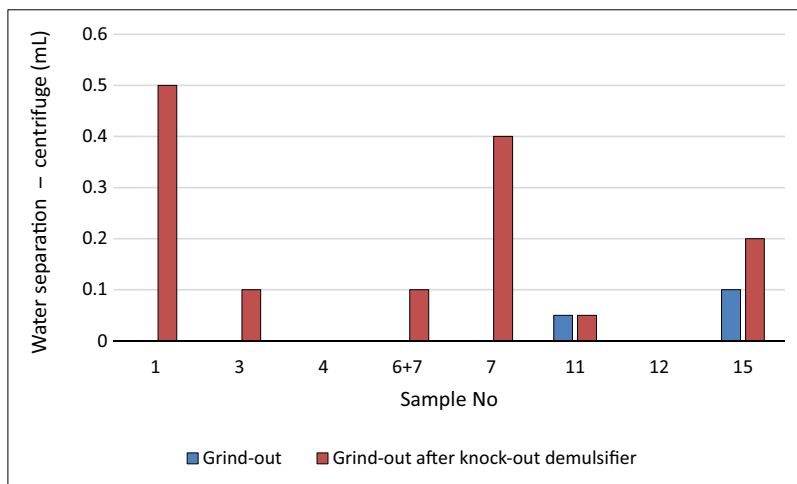


Fig. 12. Grind-out before and after the use of a knock-out demulsifier on oil No. 3

Rys. 12. Rozdrobnienie przed i po zastosowaniu demulgatora wybijającego na oleju nr 3

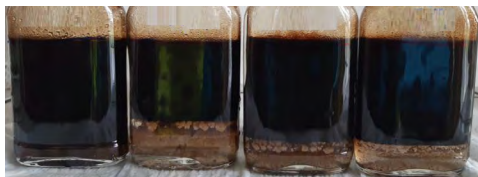


Fig. 13. Test results after 50 min, from the left: Blank and Samples 3, 4, and 6+7

Rys. 13. Wyniki testu po 50 min, od lewej: próba ślepa oraz próbki 3, 4 i 6+7



Fig. 14. Test results after 50 min, from the left: Samples 7, 11, 12, and 15

Rys. 14. Wyniki testu po 50 min, od lewej: próbki 7, 11, 12 i 15

Samples 3 and 11 exhibited the most apparent separation, specifically, 28 mL of water separated after the addition of Product 3, and 30 mL separated after the addition of Product 11. The separated water was the clearest in Samples 11 and 12. Samples 6+7, 11, and 12 showed smooth interfacial surfaces (Figures 13 and 14). The blank sample had a baggy interfacial surface, while the remaining samples had rough surfaces. In terms of grind-out (Figure 12), all samples, except for the blank and Sample 7, induced a small degree of water separation following centrifugation.

2.4. Test results for crude oil No. 4

Figures 15–17 present the test results for oil No. 4. The results were recorded after 10, 30, and 60 min, and the dosages were comparable to those used for tests on oils No. 2 and 3.

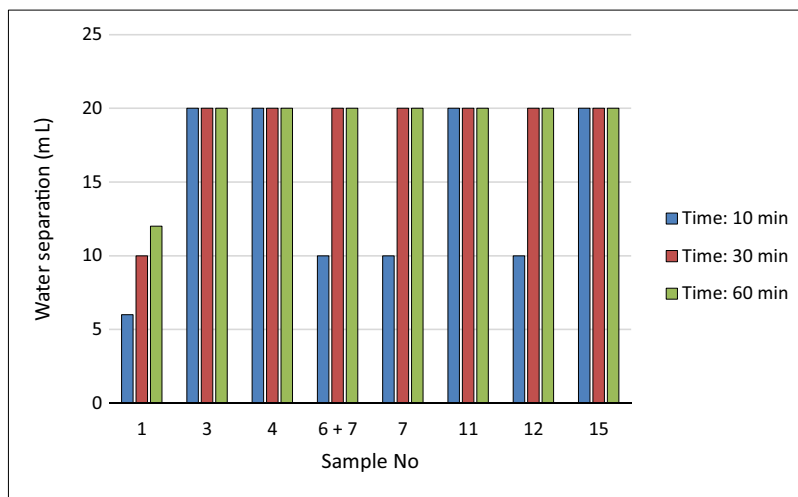


Fig. 15. Water separation from oil No. 4 using each sample after 10, 30, and 60 min

Rys. 15. Wydzielanie wody z oleju nr 4 przy użyciu każdej próbki po 10, 30 i 60 min

A grind-out chart was not included for this oil because water separation did not occur in every sample. Hence, all the water in the bottles was perceived as separated (resulting in the absence of water in the oil during the centrifuge test). Every additive demulsifier product gave a smooth separation surface, and only the blank sample had a baggy surface (Figures 16 and 17). Moreover, the separated water was clear in every sample. The fastest separation was obtained with Samples 3, 4, and 15.



Fig. 16. Test results after 60 min, from the left: Blank and Samples 3, 4, and 6+7

Rys. 16. Wyniki testu po 60 min, od lewej: próba ślepa oraz próbki 3, 4 i 6+7



Fig. 17. Test results after 60 min, from the left: Samples 7, 11, 12, and 15

Rys. 17. Wyniki testu po 60 min, od lewej: próbki 7, 11, 12 i 15

2.5. Test results for crude oil No. 5

Five of the best demulsifier products were used to test oil No. 5, a mixture of previously investigated oils. The product dosages were 75 ppm.

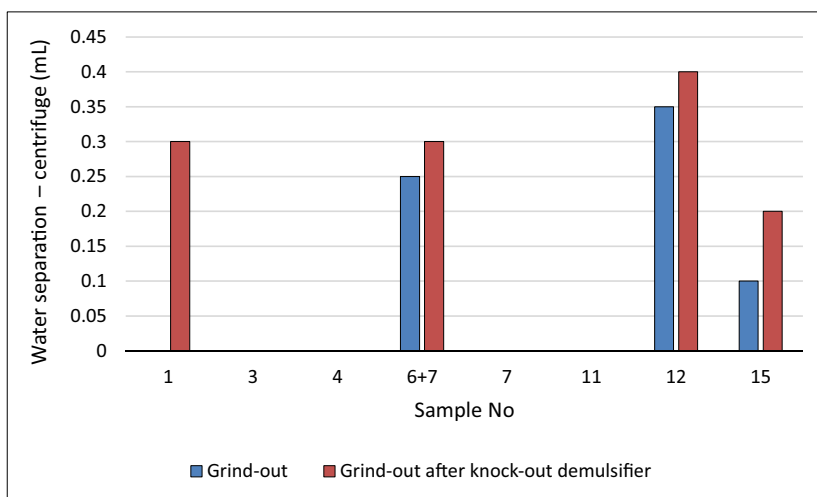


Fig. 18. Water separation from oil No. 5 using each sample after 10, 30, and 60 min

Rys. 18. Wydzielanie wody z oleju nr 5 przy użyciu każdej próbki po 10, 30 i 60 min

The results of the bottle tests are presented in Figures 18–21. These results were recorded after 10, 30, and 60 min.

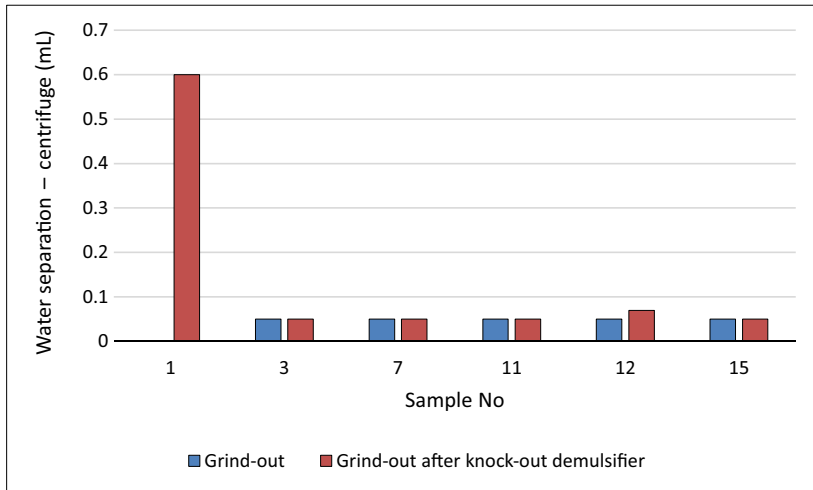


Fig. 19. Grind-out before and after the use of a knock-out demulsifier on oil No. 5

Rys. 19. Rozdrobnienie przed i po zastosowaniu demulgatora wybijającego na oleju nr 5



Fig. 20. Test results after 60 min, from the left: Blank and Samples 3 and 7

Rys. 20. Wyniki testu po 60 min, od lewej: próba ślepa oraz próbki 3 i 7



Fig. 21. Test results after 60 min, from the left: Samples 11, 12, and 15

Rys. 21. Wyniki testu po 60 min, od lewej: próbki 11, 12 i 15

The fastest separation was observed using Samples 11 and 15, followed by Samples 7 and 3. The separated water was clear in every sample, although Sample 3 provided the best water clarity. Regarding the interfacial surfaces, all samples (except that containing Product 7) provided smooth surfaces. The blank sample exhibited a baggy surface, indicating that the addition of a demulsifier was necessary.

Discussion and conclusions

The test results showed that all examined oils displayed good separation without any added demulsifier (Sample 1, blank). Oils No. 1 and 2 gave almost complete water separation after 60 min, whereas oils No. 3 and 4 and oil mixture No. 5 required treatment with a demulsifier.

The product was comprised of polyimine derivatives and EO/PO block polymers (ratio 1:2) in highly biodegradable solvents (Sample 3), generating the optimal (i.e., non-toxic and biodegradable) environment.

According to the material safety data sheets of the active components and dimethyl esters, this product sample contained no hazardous substances. Biodegradation of dimethyl esters can reach 97% after 28 days in freshwater environments. This parameter for the EO/PO block polymer was 30%, and it was not measured by the provider for polyimine. Ultimately, the amount of biodegradable solvent in the final formula accounted for >60%. The main advantage of this formula, relative to green demulsifiers tested by other researchers, was that the required dosage of the product was much lower, thus, making it more economical (75 ppm in the final formula vs. ~500–2,000 ppm of active component in other reports (Pal 2021)). Yaakob and Sulaiman (2017) also used high dosages of plant extract-derived demulsifier to separate water from oil. The formulas used in our work have commercialization potential because they introduce much lower contents of the demulsifier into the oil stream. Venkatesham et al. (2018) also investigated the use of high dosages of plant extracts (e.g., 0.25–1.5 mL of demulsifier in 10 mL of oil emulsion). They obtained similar results, where a sample of cotton seed oil gave a high rate of separation (90%), but the dosage was much higher than that commercially acceptable (i.e., 20–250 ppm, depending on the location. In refineries, the dosage range is even lower).

The results suggest that the product can work effectively and replace standard, toxic demulsifiers, however, this potential can only be confirmed with field tests on location. Moreover, the biodegradation of polyimine derivatives was not evaluated by the producer, hence, the demulsifier was classified as “non-toxic” rather than green. None of the compounds (active components or solvents) were classified as dangerous according to the current CLP (Classification, Labelling, and Packaging) regulations.

Biodegradation of the final formula was investigated using the OECD 301 F method and showed >60% after 28 days. Therefore, this product was more biodegradable than many other solutions available on the market.

The solution developed in this work offers a potential alternative to the standard types of demulsifiers that are used in the Paris Oil Basin. It mitigates logistical challenges (e.g., a lack of hazardous materials reduces the need for specialized transport) and reduces the hazards associated with possible fluid leakages. Moreover, products with a high flash point, low pour point, and no irritating components enable safer and more comfortable work environments.

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REFERENCES

- Abdulraheim, A.M. 2018. Green polymeric surface active agents for crude oil demulsification. *Journal of Molecular Liquids* 271, pp. 329–341, DOI: 10.1016/j.molliq.2018.08.153.
- Allison, E. and Mandler, B. 2020. *Petroleum and the environment*. American Geosciences Institute, Alexandria (VA).
- Bęben et al. 2007 – Bęben, D., Jewulski, J. and Janocha, A. 2007. Demulsifiers and their influence on oil exploitation processes (*Demulgatory i ich wpływ na procesy eksploatacji ropy naftowej*). *Wiertnictwo, Nafta, Gaz* 24(1), pp. 99–108 (*in polish*).
- Dai, C. and Zhao, F. 2018. *Demulsification of the emulsified crude oil and defoaming of the foaming crude oil*. [In:] *Oilfield Chemistry*, pp. 313–331, DOI: 10.1007/978-981-13-2950-0_12.
- Dalmazzone, C. and Noik, C. 2001. Development of new “green” demulsifiers for oil production. *SPE International Symposium on Oilfield Chemistry*, Houston, Texas. DOI: 10.2523/65041-MS.
- Dhandhi et al. 2021 – Dhandhi, Y., Chaudhari, R.K. and Naiya, T.K. 2021. Development in separation of oilfield emulsion toward green technology – A comprehensive review. *Separation Science and Technology* 57(10), pp. 1642–1668, DOI: 10.1080/01496395.2021.1995427.
- Dhandhi et al. 2023 – Dhandhi, Y., Saw, R.K., Singh, R. and Naiya, T.K. 2023. Application of a novel surface-active green demulsifier for demulsification of field crude oil emulsion. *Separation Science and Technology* 58(9), DOI: 10.1080/01496395.2023.2198108.
- Dhandhi et al. 2024 – Dhandhi, Y., Naiya, T.K. and Guria, C. 2024. Development of high-performance biodegradable and non-toxic demulsifier for dehydration of field crude oil emulsion: Statistical design and process optimization. *Geoenergy Science and Engineering* 234(7), DOI: 10.1016/j.geoen.2024.212677.
- EN_MSDS_713245 – *Safety Data Sheet of commercial demulsifier of Brenntag company*.
- Ferreira et al. 2023 – Ferreira B.M.S., Ramalho, J.B.V.S. and Lucas, E.F. 2023. Demulsification of water-in-crude oil emulsions by microwave radiation: effect of aging, demulsifier addition, and selective heating. *Energy & Fuels* 27(2), pp. 615–621.
- Fink, J. 2012. *Petroleum engineer’s guide to oil field chemicals and fluids*. DOI: 10.1016/C2009-0-61871-7.
- Grenoble, Z. and Trabelsi, S. 2018. Mechanisms, performance optimization and new developments in demulsification processes for oil and gas applications. *Advances in Colloid and Interface Science* 260, DOI: 10.1016/j.cis.2018.08.003.
- Internal procedure of selection of demulsifiers delivered by Brenntag
- Jia et al. 2023 – Jia X., Wei, L., Fu, M., Liu, C., Gu, Y., Qin, W., Zhang, L., Geng, X. and Guo, H. 2023. One-pot preparation of environmentally friendly, high demulsification rate and novel functional magnetic demulsifier: Used for oil and water separation in crude oil emulsion. *Arabian Journal of Chemistry* 16(10), DOI: 10.1016/j.arabjc.2023.105134.
- Kelland, M. 2014. *Production chemicals for the oil and gas industry*. Second edition, CRC Press, Taylor & Francis Group. DOI: 10.1201/b16648.
- Khani, M.J. and Razaeye, M. 2018. A review in solvent uses in petroleum industry. *Revista Publicando* 5, 15(2), pp. 1197–1216.
- Korzec, M. and Sapińska-Śliwa, A. 2023. Prevention and Removal of Naphthenate Deposits in Oil and Gas Production – Historical Background and Novel Attitude towards Inhibition and Solution. *Energies* 16(20), DOI: 10.3390/en16207104.
- Loufakis et al. 2017 – Loufakis, D.N., Schmitt, A.K., Nelson, C., Hoyles, S., Goodwin, J., White, B. and Ayers, C. 2017. A microfluid technique for the evaluation of demulsifiers. *SPE International Conference on Oilfield Chemistry*, Texas, USA, 3–5.04.2017, DOI: 10.2118/184538-MS.
- Pal et al. 2021 – Biswadeep Pal, B., Kumar, R. and Naiya, T.K. 2021. Demulsification of crude oil-water emulsion using naturally formulated demulsifier. *Petroleum Science and Technology* 39(2), DOI: 10.1080/10916466.2021.1983599.
- Sun et al. 2022 – Sun, Z., Pu, W., Zhao, R. and Pang, S. 2022. Study on the influence of heavy oil group components on the formation and stability of W/O emulsion. *Journal of Petroleum Science and Engineering* 209, DOI: 10.1016/j.petrol.2021.109899.

- Venkatesham et al. 2018 – Venkatesham V, Marshoom, N., Joy, R.M., Ginto, G. and Murshid. 2018. Studies on demulsification of crude oil emulsion using plant extracts as green demulsifiers. *Asian Journal of Applied Science and Technology* 2(2), pp. 999–1004.
- Yaakob, A.B. and Sulaimon, A.A. 2017. Performance Assessment of Plant Extracts as Green Demulsifiers. *Journal of the Japan Petroleum Institute* 60(4), DOI: 10.1627/jpi.60.186.
- Yonguep et al. 2022 – Yonguep, E., Kapiamba, F., Jonathan Kabamba Katende, J.K. and Chowdhury, M.R. 2022. Formation, Stabilization and Chemical Demulsification of Crude Oil-In-Water Emulsions: A Review. *Petroleum Research* 7(4), pp. 459–472, DOI: 10.1016/j.ptlrs.2022.01.007.
- Zhou et al. 2012 – Zhou, H., Dismuke, K.I., Lett, N.L. and Penny, G.S. 2012. Development of more environmentally friendly demulsifiers. *SPE International Symposium and Exhibition on Formation Damage Control*, Lafayette, Louisiana, USA. DOI: 10.2118/151852-MS.
- Zolfaghariet al. 2016 – Zolfaghari, R., Fakhru'l-Razi, A., Chuah, A.L., Elnashaie, S. and Pendashteh, A. 2016. Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry. *Separation and Purification Technology* 170(1), DOI: 10.1016/j.seppur.2016.06.026.

INVESTIGATION OF NON-TOXIC DEMULSIFIERS AND COMPARISON TO STANDARD EQUIVALENTS IN THE PARIS BASIN (FRANCE) OIL MINES

Keywords

demulsifier, crude oil, Paris Basin, non-toxic, green solutions

Abstract

Demulsifiers are widely used to increase the separation between oil and water. The more common ones contain hazardous ingredients (aromatic solvents, non-biodegradable active components), which can negatively affect human health (especially the respiratory system) and the environment. The presented study evaluates the feasibility of implementing a non-toxic, highly biodegradable, and environmentally friendly demulsifier in oil mines in the Paris Oil Basin (France). The standard commercial demulsifiers were tested together with four other, non-toxic and biodegradable ones. This investigation employed the bottle test of demulsifiers, which contained grind-out tests using the centrifuge. The test determined the residual water content in separated water. Four types of oil were used for this test, plus a fifth sample, which contained a mix of oil from the four wells, based on the ratio that existed in the installation. The investigations took place at four oil mines in Paris Basin, France.

The tests proved that, for all oil types, a novel, highly biodegradable, oil-soluble demulsifier containing polyimine derivative and EO/PO block copolymer (RSN = 10) in a non-toxic solvent, could be used to treat oil during the exploitation process in the reservoir. This provided the best separation properties of all tested samples and the lowest water content in the oil.

This solution can potentially mitigate numerous logistical, storage, and environmental issues while enhancing job-related safety aspects. Our proposed approach provides a greener method that could be implemented in the industry field.

**MOŻLIWOŚCI POTENCJALNEGO ZASTOSOWANIA NIETOKSYCZNYCH
DEMULGATORÓW W KOPALNIACH ROPY NAFTOWEJ W BASENIE PARYSKIM
(FRANCJA) I PORÓWNANIE Z PRZEMYSŁOWYMI ODPowiednikami**

Słowa kluczowe

demulgator, ropa naftowa, Basen Paryski, nietoksyczne, ekologiczne rozwiązania

Streszczenie

Demulgatory przyspieszają separację wody od ropy naftowej podczas jej wydobycia. Te bardziej powszechne często zawierają substancje niebezpieczne (rozpuszczalniki aromatyczne, czy słabo biodegradowalne składniki aktywne), które mogą działać negatywnie na zdrowie ludzi (szczególnie układ oddechowy) oraz na środowisko. Artykuł ocenia możliwość zastosowania środków nietoksycznych, o wysokim stopniu biodegradacji, przyjaznych środowisku, podczas badań przeprowadzanych dla ropy naftowej pochodzącej z kopalni znajdujących się w Basenie Paryskim. Powszechne, komercyjne demulgatory były testowane wraz z czterema nietoksycznymi i biodegradowalnymi. Badanie polegało na przeprowadzeniu testu butelkowego demulgatora oraz testu badającego zawartość wody w wirówce. Analizowane były cztery próbki ropy naftowej wraz z piątą próbką, będącą mieszaniną tychże czterech, mieszaną w stosunku znanym z procesu produkcyjnego dla danej instalacji. Miejscem pracy były cztery kopalnie ropy naftowej w Basenie Paryskim, we Francji.

Na podstawie badania udowodniono, iż dla wszystkich czterech próbek nowy, wysoce biodegradowalny, rozpuszczalny w ropie demulgator, zawierający pochodne poliiiminowe wraz z polimerami EO/PO (o RSN = 10) w rozpuszczalniku nietoksycznym, skutecznie może być użyty w celu poprawienia separacji podczas eksploatacji ropy. Nie tylko zapewnił najlepsze właściwości separacji dla wszystkich analizowanych próbek, ale również najniższą zawartość wody w ropie po separacji spośród wszystkich analizowanych produktów.

Rozwiązanie to ma potencjał w wyeliminowaniu wielu problemów związanych z logistyką produktu, składowaniem oraz aspektami środowiskowymi. Jest również bardziej bezpieczne pod kątem pracy z produktem. Wnioski te w zupełności spełniają aktualny trend dotyczący użycia jak najbardziej ekologicznych rozwiązań w każdej możliwej pracy przemysłowej.

