

Surfactants Efficiency in Oil Reserves Exploitation

IULIANA GHETIU¹, IOANA GABRIELA STAN¹, CASEN PANAITESCU^{1*}, COSMIN JINESCU², ALINA MONICA MARES³

¹ Petroleum Gas University of Ploiesti, Drilling, Extraction and Transport of Hydrocarbons Department, 39 Bucharest Blvd., 100680, Ploiesti, Romania

² University Politehnica of Bucharest, Mechanical Engineering Faculty, Process Equipment Department, 313 Splaiul Independenței, 77206, Bucharest, Romania

³ University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Chemical and Biochemical Engineering Department, 1-7 Polizu Str., 011061, Bucharest, Romania

The use of surfactants in the process of water separation from crude oil emulsions formed at extraction is an effective solution in the treatment of crude oil. But perfecting this technology to a higher degree of efficiency, in order to destabilize the emulsion formed, requires the determination of the parameters involved in the design and the correlation of the obtained results. This research also aims at finding optimal solutions that increase the degree of water separation from emulsions using surface-effective solutions to destabilize the emulsion layer. This research was based on data from two wells that extract oil from Barcău reservoir. To achieve this objective, the composition of crude oil was analyzed, the emulsion characteristics were established and the elected demulsifiers were tested. The study highlights the efficiency of destabilization up to 97.9 mass %.

Keywords: surfactants, demulsification process, efficiency of destabilization

Exploitation of oil is subjected to physical phenomena occurring at system's liquid-solid interface or in the separation process of two fluids of different nature [1].

In choosing the optimal water separation technology from emulsions one must consider both the process' efficiency in terms of technical-economic features, as well as environmental compliance [2-5].

The appearance of water in the immediate vicinity of the wall layer of the well, has the effect of reducing the effective permeability to oil and, alongside the crude oil from the formation, creates an emulsion layer of high viscosity, which flows at slow speed through the porous environment.

Currently, demulsification includes chemical and/or physical methods. In most cases the two methods are combined. The physical methods can generate secondary pollution phenomena [6-8], thus, adding surface-active substances or polymers represents a modern and actual approach. The correct dosage of these substances will speed up the demulsification process and promote the flow of oil to the wellbore. In emulsion breaking operations the stimuli used are mostly chemicals, flocculants such as cationic polyacrylamide, polyaluminium chloride, etc [9, 10].

Surfactants commonly used in such treatments are cationic, anionic and nonionic. The cationic surfactants are: amine, salts and quaternary nitrogen bases. The category of anionic surfactants includes: soaps, phenols, petroleum sulfonates, aryl alkyl sulfonate, alkyl benzene sulfonate. Ethoxylated products, fatty alcohols, polyethoxylated alkyl - phenol polyethoxylates, polyethoxylated fatty acids or their derivatives are part of the nonionic surfactants category [11]. The demulsification process with the help of surfactants has been improved based on Shinoda's [12, 13] and Salager's [14] studies regarding the influence of temperature on emulsion destabilization.

The demulsification process is influenced by: temperature, oil composition, electrolyte concentration, surfactant type and concentration.

Selection of active agents must be done in order to ensure:

- reducing interface tension in the water - oil system;
- minimal losses in the deposit;
- close mobility to the one of the fluids to which it comes in contact with;
- chemical stability in the reservoir water;
- solubility in water or oil [15].

In literature [16], the type of emulsion depends on the degree of dispersion of water droplets achieved. The classification of emulsions by the size of water droplets is shown in table 1.

Table 1
EMULSION TYPE ACCORDING TO WATER DROPLET SIZE

Water droplet size, μm	Emulsion type
< 20	Finely dispersed
20 - 50	Medium dispersed
> 50	Highly dispersed

The stability of emulsions [11] falls under four intervals of stability (table 2).

In this study we proposed based on existing technologies removing produced water using two types of surface active substances for two wells located in Barcău area. A previous study showed great stability of emulsions having characteristics similar to those used in this study, thus the need to add demulsifiers.

The study was necessary because of the difficulties in the operation of oil wells. Thus it was of great importance

* email: c.panaitescu@gmail.com; Tel: (+40) 751172458

Table 2
ASPHALTENE STABILITY OR INSTABILITY
DEPENDING ON THE VALUES OF THE CIS INDEX

CIS	Asphaltene stability
< 0.7	Stable asphaltens
0.7 – 0,9	Moderate instability
> 0.9	Unstable asphaltens

to find solutions to destabilize the emulsion and increase water separation.

Experimental part

In the present study six samples of emulsion from two wells (three samples from each well) located in Barcau area (tokens M and N), were collected.

The following properties were determined for the collected samples:

- the content of saturated hydrocarbons (S), aromatics hydrocarbons (A), resins (R) and asphaltenes (A) are determined by chromatographic SARA analysis;
- colloidal stability index, CSI- determined based on the data of SARA analysis;
- density of the reservoir fluids determined by SARA analysis in range of 15 – 75 °C (crude oil, emulsion and water formation);
- dynamic viscosity of reservoir fluids necessary to determine the rheological profile; measurements were done at temperatures of 25, 50 and 75°C with a Brookfield rheometer.

A dye, methylene blue, has been added to the samples, to determine their complexity. The water content of the two types of emulsions from the M and N wells was determined by centrifugation. For the separation of water from emulsion samples taken from the M and N wells, surface-active substances were used (table 3).

Table 3
CHARACTERISTICS OF THE SURFACTANTS TESTED FOR THE
ELIMINATION OF WATER FROM EMULSIONS

Surfactant	Ionic charge	Structural composition
Ecostim	Nonionic	glycols, polioxipropilen - polioxietilen copolymers, ethoxylated alcohol and sulfosuccinic esters
Adirol P4	Anionic+nonionic	surfactants with anionic and neionic groups, superior alcohols, polymers and amines

To intensify the activity of the demulsifier was used an addition of Na_2CO_3 .

The experimental study on the removal of water from the emulsion was carried out in a thermostatic reactor at temperatures of 25, 50 and 75 °C, operating at atmospheric pressure.

Results and discussions

The processing of samples from the two wells was carried out according to a monitoring program established before. The results presented here in represent average values of six samples taken from wells M and N.

The composition of the oil samples taken from M and N wells, i.e. content of resins, aromatics, saturates and asphaltenes was analyzed. Thin layer chromatography was

Table 4
THE SATURATE, AROMATIC, RESIN AND ASPHALTENE CONTENT
OF OIL CRUDE SAMPLES

Well	Resin, mass %	Saturate, mass %	Aromatic, mass %	Asphaltene, mass %
M	24.68	38.84	33.41	3.07
N	13.21	48.72	34.56	3.51

used. The average values of experimentally determined concentrations of the components are shown in table 4.

The two types of crude oil can be distinguished as follows: in the oil sample from the M well, the content of the resin is higher than in the oil sample coming from the N well (24.68 % - M well, to 13.21 % - N well). The ratio resin/asphaltene is of 8.03 for M well, to 3.76 for N well.

The cumulative concentration of resins and asphaltenes is higher for M well than for the N well (27.75 to 16.72).

The colloidal stability index, CSI, calculated using equation (1), was lower for the crude oil sample from the M well, 0.72, to 1.09 for the crude oil sample from the N well.

$$CSI = \frac{S+A_1}{A_2+R} \quad (1)$$

where: S, saturated hydrocarbon total content, mass %; A_1 , asphaltene content, mass %; A_2 , aromatic content, mass %; R, resin content, mass %.

To adequately choose the better reactive for eliminating the water from the emulsion requires knowing the values of density and viscosity of the analyzed oil.

Fluid reservoir densities were measured using an Oscillating Tube Densimeter in the temperature range 15 – 75 °C. The variation of density in reservoir fluids, based on temperature, is shown in figures 1, 2 and 3.

For the temperature of 50°C the density of water reservoir amounts to 985 kg/m³ for both wells (M and N). At 75°C the density decreases to the value of 962 kg/m³ for N well, and to 970 kg/m³ for M well.

Oil density variation is as follows:

-at 50 °C is 881 kg/m³ for N well and 911 kg/m³ for M well;

-at 75 °C is 855 kg/m³ for N well and 887 kg/m³ for M well

The emulsion's density was determined for the two temperatures; the measured values are as follows: 955 kg/m³, for both N and M wells, at 50 °C and 939 kg/m³ for N well and 928 kg/m³ for M well, at 75°C.

For a complete characterization of the samples and for choosing the optimal technological solution for emulsion breaking, we need to determine the variation of viscosity with temperature for both crude oil and the emulsion. The formation water viscosity is not relevant for the present study.

The results obtained for viscosity at temperatures of 25°C, 50°C and 75°C are shown in figures 4 and 5.

Analyzing the values in figures 4 and 5 result that both crude oil and emulsion viscosity recorded significant decreases as the temperature increased.

It was also noticed that samples from M well have higher viscosity than samples taken from the N well.

Coloring tests applied to samples of crude oil from M and N wells have led to results shown in figure 6.

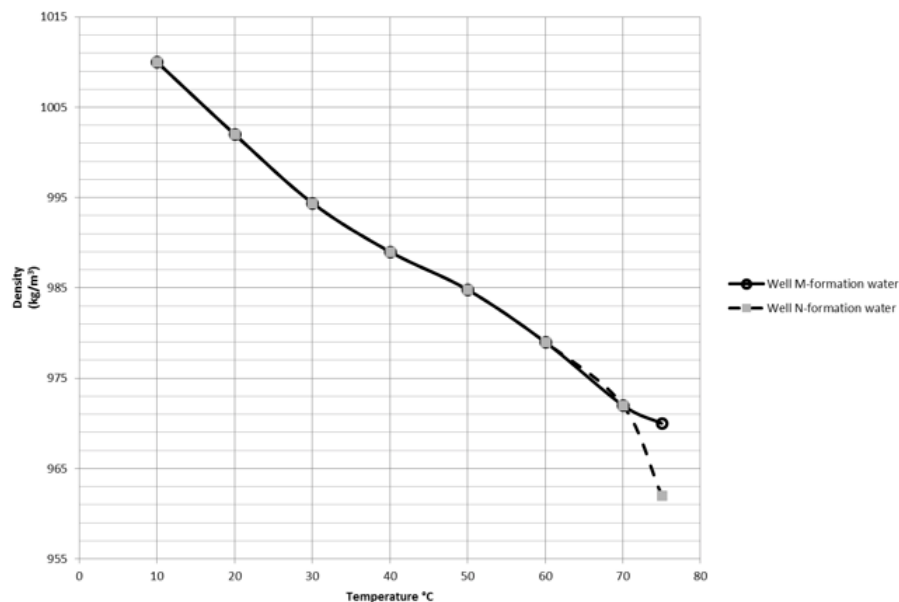


Fig. 1. The variation of formation water density with temperature

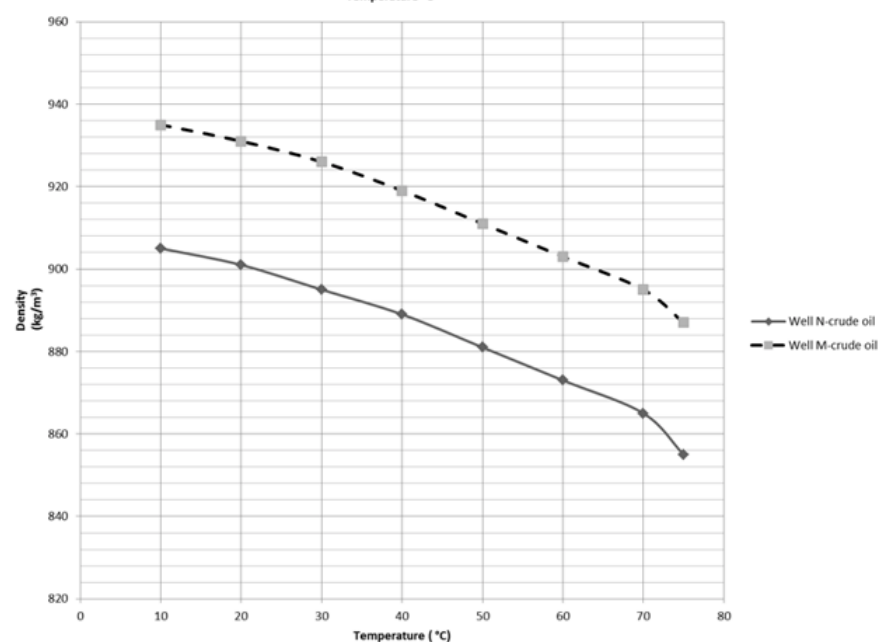


Fig. 2. The variation of crude oil density with temperature

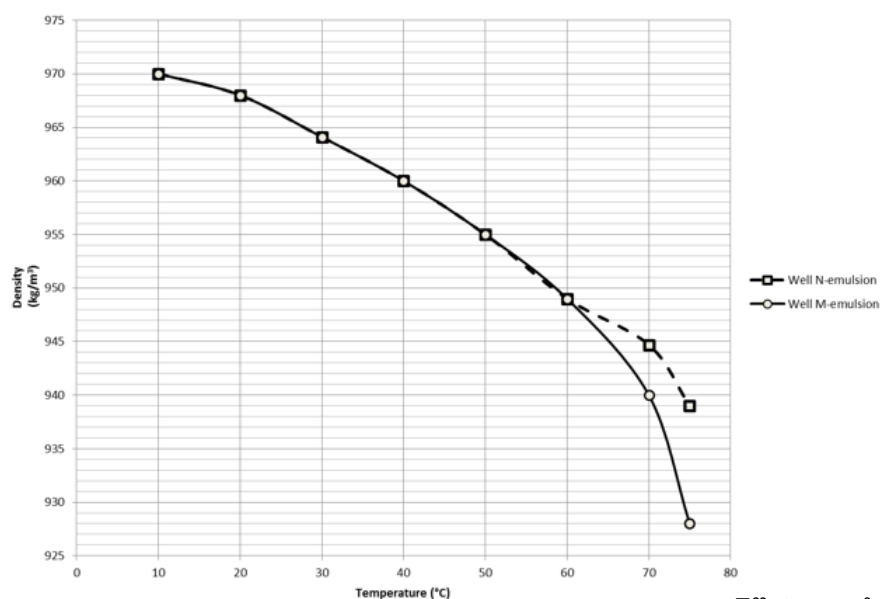


Fig. 3. The variation of emulsion density with temperature

It is observed that emulsion from N well stained with methylene blue shows more complexity than the one from M probe.

Demulsibility tests lead to the results shown in table 6.

Efficiency of the emulsion destabilization was calculated and the obtained results are shown in table 7.

Surfactant's efficiency of destabilization was calculated for a 100 mL emulsion sample to which was added 50 mL surfactant. The calculations were done considering the

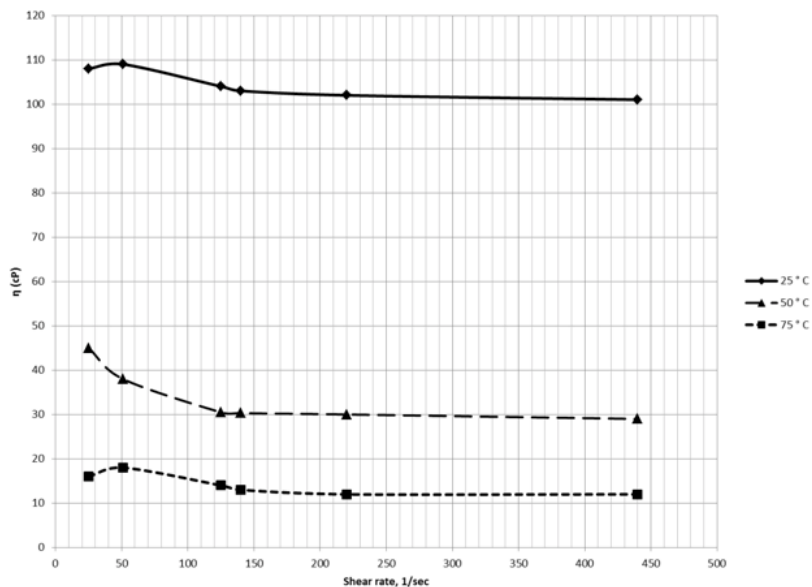


Fig.4. (a). The rheological behaviour of *crude oil* for M well, at different temperatures

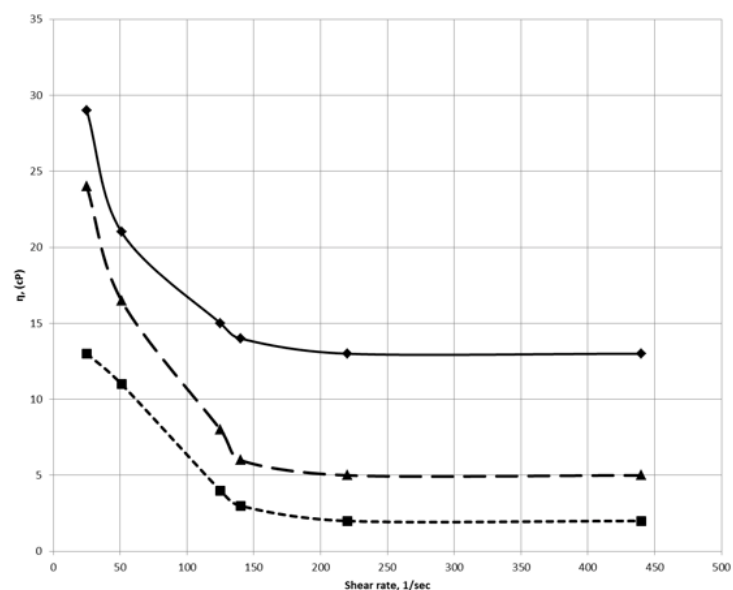


Fig.4 (b). The rheological behaviour of *crude oil* for N well, at different temperatures

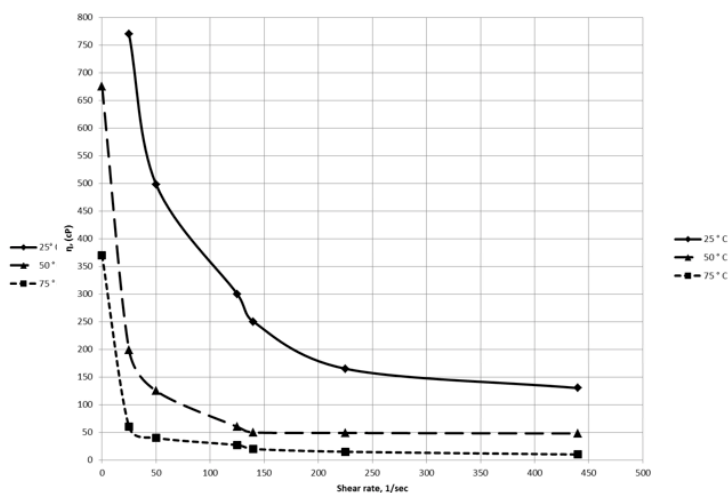
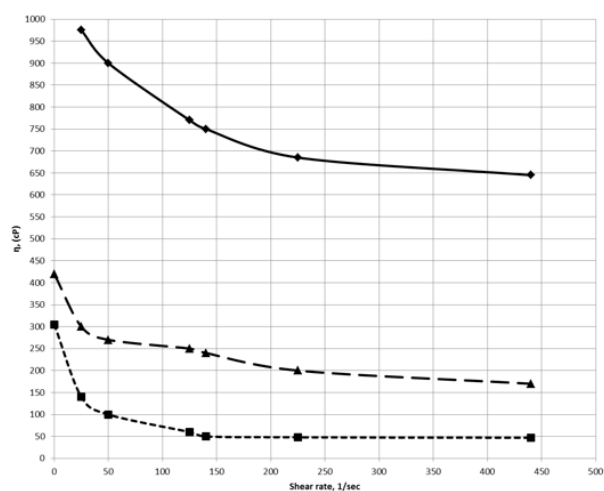


Fig. 5. The rheological behaviour of *emulsion* at different temperatures: a) for M well; b) for N well

water formation content of the Barcau reservoir from geological analyses (60 % mass, water formation).

In the first phase, the percentage of separated water from the samples taken is calculated. After adding of surfactant a new amount of water will be separated. Final

surfactant destabilization efficiency is calculated using the above data.

For testing conducted with **Adirol**, the efficiency for samples from M well spiked between 81.4 and 86.9 mass %, at a temperature of 75°C and between 79.2 and 86.9 mass % for N well.

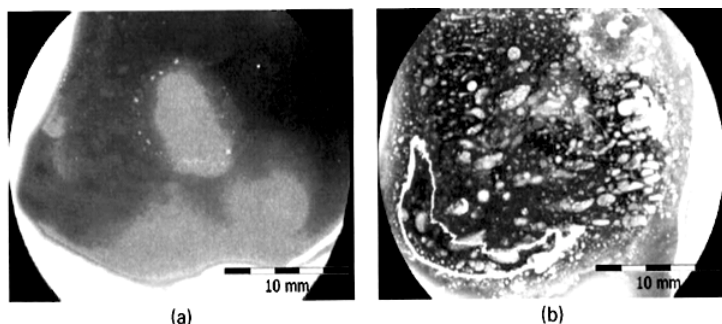


Fig. 6. Close-ups for emulsions: (a) - well M; (b) - well N

Table 6
THE SEPARATED WATER QUANTITY, IN mL

Surfactant	Temperature, °C	Well M			Well N		
		Sample 1 (ml)	Sample 2 (ml)	Sample 3 (ml)	Sample 4 (ml)	Sample 5 (ml)	Sample 6 (ml)
Adirol	25	48	48	34	34	52	32
	50	53	57	52	49	65	46
	75	74	79	74	72	79	72
Adirol +1% Na ₂ CO ₃	25	52	57	47	46	66	39
	50	61	68	64	73	78	47
	75	71	82	81	84	84	87
Ecostim	25	39	34	39	37	34	46
	50	42	52	57	56	52	64
	75	88	79	79	89	86	82
Ecostim +1%Na ₂ CO ₃	25	48	49	49	32	58	51
	50	72	64	61	46	72	68
	75	89	81	81	72	87	89

Table 7
SURFACTANT'S EFFICIENCY OF DESTABILIZATION FOR M AND N WELLS, IN THE PERCENTAGE OF SEPARATED WATER

Surfactant	Temperature, °C	Well M			Well N		
		Sample 1 mass %	Sample 2 mass %	Sample 3 mass %	Sample 4 mass %	Sample 5 mass %	Sample 6 mass %
Adirol	25	52.8	52.8	42.9	37.4	57.2	35.2
	50	58.3	62.7	46.2	53.9	71.5	50.6
	75	81.4	86.9	81.4	79.2	86.9	79.2
Adirol +1% Na ₂ CO ₃	25	57.2	62.7	51.7	50.6	72.6	42.9
	50	67.1	74.8	79.2	80.3	85.8	51.7
	75	78.1	90.2	89.1	92.4	92.4	95.7
Ecostim	25	42.9	37.4	42.9	40.7	37.4	50.6
	50	46.2	57.2	62.7	61.6	57.2	70.4
	75	96.8	86.9	86.9	64.9	94.6	90.2
Ecostim +1% Na ₂ CO ₃	25	52.8	53.9	53.9	35.2	63.8	56.7
	50	79.2	70.4	67.1	50.6	79.2	74.8
	75	97.9	89.1	89.1	79.2	95.7	97.9

For testing conducted with **Adirol+Na₂CO₃** the efficiency for samples from M well spiked between 78.1 and 90.2 mass %, at a temperature of 75 °C and between 92.4 and 95.7 mass % for N well.

For testing conducted with **Ecostim** the efficiency for samples from M well spiked between 86.9 and 96.8 mass %, at a temperature of 75 °C and between 64.9 and 94.6 mass % for N well.

For testing conducted with **Ecostim+Na₂CO₃** the efficiency for samples from M well spiked between 89.1 and 97.9 mass %, at a temperature of 75 °C and between 79.2 and 97.9 mass % for N well.

Conclusions

Testing of new demulsifiers to separate water from oil wells aligns to actual trends.

Improving stimulation treatment requires determination of the parameters. Running compatibility tests of reservoir fluids with treatment solutions is done in order to avoid or mitigate undesired effects (insoluble salt precipitation,

slugging, direct or inverse emulsion formation, swelling and disintegration of clay minerals, a.s.o.)

By observing the analysis of the density of reservoir fluids we can notice that oil from the M well has a greater density than that of the N well, although emulsions and formation water have a similar behaviour. This is due to different oil quality, since different oils can incorporate different amounts of water. The higher density of oil from M well in comparison to the one from the N well confirms that the emulsion of the M well is more stable than that of the N well. These must be combined also with the viscosity of the crude oil for a correct interpretation of density analyses concerning the stability of emulsions. Demulsifiers **Adirol+Na₂CO₃** and **Ecostim+Na₂CO₃** have the maximum efficiency of destabilization (90.2 mass% at a temperature of 75 °C for samples of the M well with **Adirol+Na₂CO₃**).

Following the conducted study resulted that the process of stimulating oil flow using emulsion destabilization can be applied on an industrial scale only after going through

laboratory testing of surfactant solutions on emulsions samples taken from the wells.

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