

ENC-2022-0536

## EXPERIMENTAL STUDY ON DROPLETS BREAKAGE OF OIL-WATER EMULSIONS (O/W) ACROSS A VARIABLE PRESSURE DROP DEVICE

**Alex Roger Almeida Colmanetti**

**Gabriel Furlan**

**Gherhardt Ribatski**

Heat Transfer Research Group, São Carlos School of Engineering, University of São Paulo, HTRG – EESC – USP  
Av. Trabalhador São-carlense, 400 – Centro 13566-590. São Carlos – SP – Brasil  
alex.colmanetti@usp.br, gabriel.furlan.sf@gmail.com, ribatski@sc.usp.br

**Luiz Fernando Barca**

**Érika A. Carvalho**

**Thais Lamoglia**

The Nucleus of Compact Separators, Federal University of Itajubá, NUSEC – UNIFEI  
Av. Benedito Pereira Santos, 1303, Itajubá – MG – Brasil, 37500-903  
barca@unifei.edu.br, erikacarvalho22@gmail.com, thaislamoglia93@gmail.com

**Aloisio Euclides Orlando Junior**

Centro de Pesquisas, Desenvolvimento e Inovação Leopoldo Américo Miguez de Mello – CENPES/PETROBRAS  
Av. Horácio Macedo, 950 – Cidade Universitária da Universidade Federal do Rio de Janeiro, Rio de Janeiro – RJ, 21941-915  
aloisio.orlando@petrobras.com.br

**Abstract.** *Emulsions occur in several industrial applications covering different engineering fields, such as pharmaceutical, food, cosmetics, and petrochemical industries. Especially in the oil-gas industry, emulsions are observed in most of the processes, including crude oil extraction, transport, and refining. The injection of water in mature wells, which is a technique recurrently employed to increase crude oil productivity, favors the formation of emulsions during the oil extraction stage. In offshore environments, the effluents from the extraction process are usually treated; however, this operation is challenging in such conditions due to limited space and the inherent difficulty in separating stable oil-water emulsions (O/W). Currently, there are several investigations focusing on emulsion separation, however, this type of study necessarily requires the production and characterization of emulsions with a certain droplet size distribution (DSD). The present study presents an experimental evaluation of the emulsion production process in a mixing device (“mixing tee”) and oil droplets breaking in a variable pressure drop device (globe valve). Both devices are part of an experimental facility developed for this study. The emulsion was produced by injecting water in crude oil with API Gravity of 21.31, dynamic viscosity of 229.83 mPa.s, density of 0.9216 g/cm<sup>3</sup>, surface tension of 30.9 mN/m, and interfacial tension of 22.0 mN/m (properties at 20°C). Emulsion characterization was performed through measurements of oil and grease content (TOG) and also of droplet size and its distribution (DSD). The stability of emulsions was also evaluated through measurements of the Oil and Grease Content (TOG) over time, which were obtained for the following time intervals: i) 0 min (online), ii) 15 min (after the experiments in the glass separating funnel) and iii) 60 min (after the experiments in the glass separating funnel). The results show that the DSD decreases by increasing the pressure drop ( $\Delta P$ ) at the flow restriction device.*

**Keywords:** *Oil-water emulsions (O/W), droplet breakage, oil and grease content (TOG), droplet size distribution (DSD), globe valve.*

### 1. INTRODUCTION

In oil platforms, the disposal of produced water (combination of water, oils and heavy metals resulting from the oil exploration and production process) has faced regulations that become progressively more restricted in terms of temperature and concentration of contaminants, reflecting the increase in evidence of damage caused by improper disposal of water with oil (Bakke et al., 2013; Moosai and Dawe, 2003). For the properly discharged of produced water into the oceans or its reinsertion in the network of reservoirs, in addition to being cooled, the produced water must go through

physical treatment steps (such as the use of activated carbon, copolymers, sand filters, water evaporation, and condensation), chemicals (as agents for stimulating flocculation, oxidants and electrolysis) and/or biological (use of microorganisms) (Cabral and Santos, 2019; Al-Ghouti et al., 2019). The selection of the produced water purification method is based on both the fluid conditions (i.e. the concentration and characterization of pollutants), as well as the installation conditions, whether space, weight, or available capital.

Schramm (1992) relates the stability of the emulsions with the reduced size of the droplets and the presence of an interfacial film in the emulsion dispersed droplets. In this way, the drops do not easily coalesce or float, which makes difficult the treatment process. Emulsions with smaller droplet sizes are usually the most stable ones, and the variation in average size with time can be used to measure their stability. However, the characterization of droplet size is not a simple process, as emulsions are usually polydispersed (Tadros, 2013), that is, they have different droplet diameters, thus requiring a droplet size distribution function to characterize them. This function directly influences the emulsion viscosity, which value tends to increase as the droplet size becomes homogeneous (Becher, 1965). A high viscous emulsion makes it difficult for the droplets to coalesce, generating additional operating costs to pump the emulsion. Further, the properties of the formed interfacial film is another important factor for analyzing the generation and destabilization of emulsions. This importance occurs because the droplet size distribution is characterized by reduced dimensions of droplets, which results in large surface area between the droplets of the dispersed phase and the fluid of the continuous medium.

In this context, the present work aims to develop and characterize an oil-in-water emulsion, which includes oil and grease content measurement (TOG), oil droplet size measurements (DSD), and stability of oil-in-water emulsions (O/W). The effects of variable pressure drop device ( $\Delta P$ ), and mixing tee diameter on (O/W) emulsion characteristics are also evaluated.

## 2. DEVELOPMENT AND CHARACTERIZATION OF OIL-IN-WATER EMULSIONS (O/W)

The experiments of generation and characterization of oil-water (O/W) emulsions were performed in the Nucleus of Compact Separator (NUSEC) of the Federal University of Itajubá (UNIFEI). A setup was specially designed and built to study the generation of (O/W) oil-in-water emulsions which characteristics close to those observed in oil platforms. This section describes the experimental apparatus and physical properties of the handling fluids used in this study. Furthermore, the experimental matrix is also presented.

### 2.1 Setup

Figure 1 presents the experimental facility used in the present study. The setup was composed of three water reservoirs with a volumetric capacity of 20 m<sup>3</sup> (each one) and one positive displacement pump (B1, Figure 1), which drives the water from the reservoirs to the test section. The water volumetric flow rate was measured through a Coriolis-type flow meter (M1, Figure 1).

The (O/W) oil-water emulsions were produced by injecting crude oil into the water through a mixing tee (device highlighted in red, Figure 1). A piston-metering pump (B2, Figure 1) was used to drive the crude oil from its reservoir (R2, Figure 1) through the mixing tee. Relief valves were installed in both pumps for safety purposes. A globe valve (VG1, Figure 1) was installed downstream of the mixing tee to be used as a variable pressure drop device. This device is required to induce the droplet breakage of oil-water emulsions. Two pressure gauges (P1 and P2) are used to measure the pressure upstream and downstream of the mixing tee, respectively. Furthermore, a third pressure gauge (P3) was used to measure the pressure downstream of the globe valve (VG1, Figure 1). The pressure drop in the globe valve (VG1) was obtained from the difference between the measurements from the pressure transducers P2 and P3 ( $\Delta P = P2 - P3$ ).

The size of the oil drops dispersed in the (O/W) emulsions was measured through the Malvern Panalytical® Particle Size Analyzer (Insitac Wet model). This Particle Size Analyzer (PSA) was installed downstream of the mixing tee and measures the in-situ droplet size. The Particle Size Analyzer (PSA) required a specific condition of volume flow rate to properly measure the oil drop size. Therefore, the flow inside the Particle Size Analyzer (PSA) was controlled through a by-pass line that handled a fraction of the emulsion flow directly to the R5 reservoir and the other part of the (O/W) emulsion flow directly to the PSA to carry out the online measurements of the size of the oil drops (DSD). A globe valve (VG 2, Figure 1) was also used to control the mass flow rate and it was installed downstream of the PSA. A flow meter (M2) and a pressure gauge (P4) were also employed to monitor the flow rate through the Particle Size Analyzer (PSA).

The oil-in-water emulsions (O/W) generated in the tests were stored in the intermediary reservoir (R5, Figure 1). Later, at the end of each experiment, the (O/W) emulsions were pumped from the reservoir (R5) to a larger reservoir (R3, Figure 1). It is used to store the wastewater produced in the test. The wastewater treatment from reservoir R3 was performed through a centrifuge (C1, Figure 1), which separated the oil phase from the water phase. The oil phase was stored in reservoir R4. The specifications of the equipment used in the test setup are presented in Tab. 1.

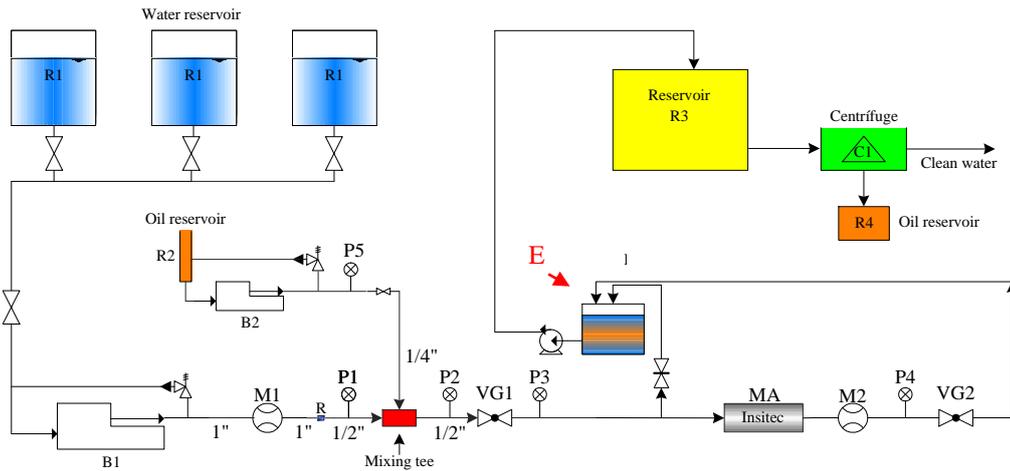
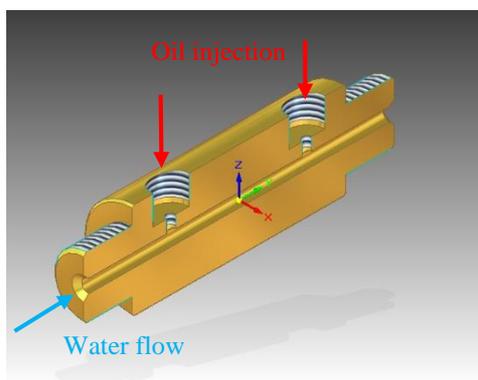


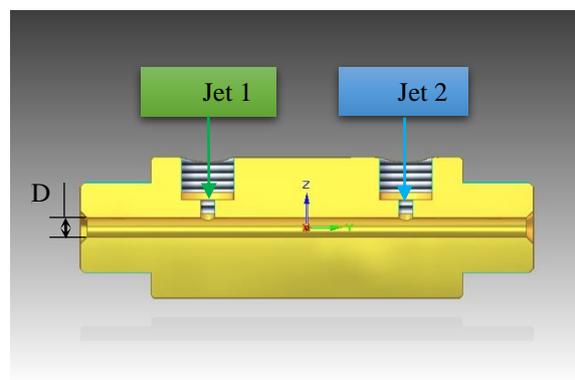
Figure 1. Diagram of the experimental facility used in the study.

Table 1. Equipment of the experimental apparatus.

Symbol	Description	Operating range
B1	Positive displacement pump – water	–
B2	Omel® piston metering pump – oil, model NSP – M5	0 – 780 (cc/h)
C1	GEA Westfalia® Centrifuge, model WSE120-01-937	–
MA	Malvern Panalytical® Particle Size Analyzer, <i>Insittec Wet</i> model	0.1 – 2500 $\mu\text{m}$
M1	Coriolis flow meter	
M2	Magnetic flow meter	
P1	Valmec® pressure gauge	0 – 25 bar
P2	Valmec® pressure gauge	0 – 25 bar
P3	Valmec® pressure gauge	0 – 25 bar
P4	Valmec® pressure gauge	0 – 25 bar
P5	Valmec® pressure gauge	0 – 25 bar
R1	Water reservoirs (Quantity: 3)	0 – 10.000 L
R2	Oil reservoir (before experiments)	0 – 500 mL
R3	Emulsion reservoir	0 – 10.000 L
R4	Oil reservoir (after separation)	–
R5	Oil-in-water emulsion (O/W) reservoir	0 – 1000 L
VG1	Globe valve (Worldval®, NPS 1/2", class 800)	–
VG2	Globe valve (Worldval®, NPS 1/2", class 800)	–



a)



b)

Figure 2. a) Diagram of the “mixing tee”, b) Diameter (D) of the “mixing tee”.

The generation of the (O/W) emulsions were performed through orthogonal injection of oil in the water flow, as schematically shown in Figure 2. The injection of the crude oil was performed through the mixing tee (see Figure 2 for details). In this component, the water phase flows in the main circular channel with diameter D (see Table 2). At the entrance of the mixing tee, there was a reduction in the diameter of the pipe of nominal diameter of 1/2" (internal diameter

of 13.15 mm) to the diameter D of the mixing tee (Figure 2.b). This configuration induced a significant increase in the water velocity (around 340 %). In the present study, the effect of the diameter size (D) of the mixing tee was evaluated through experiments of generation of (O/W) emulsion for two different diameters of mixing tee, as shown in Table 2. The oil phase injection was performed by injecting oil perpendicular to the water flow through jet 1 (Figure 2.b), which has an injector with a 0.5 mm diameter orifice. The jet 2 is used in the generation of (O/W) emulsions with concentrations higher than that investigated in this study, and therefore, it was not employed in the present study.

Table 2. Diameter (D) of mixing tee used in the generation of (O/W) emulsion.

Diameter of mixing tee	D (mm)
Diameter 1	5.0
Diameter 2	7.0

## 2.2 Characterization of the crude oil used

The transport properties of the oil affect the characteristics of (O/W) oil-water and (W/O) water-oil emulsions. Table 3 presents the density ( $\rho$ ), the dynamic viscosity ( $\eta$ ), and kinematic viscosity ( $\nu$ ) of the crude oil used in the experiments for generation of (O/W) oil-water emulsions. These properties were measured in an Anton-Paar® viscometer (model SVM 3000) for temperature ranging from 15°C to 60°C (Table 3). Figure 3 shows in the left y-axis the dynamic viscosity (highlighted in red) as function of temperature and it can be observed that the dynamic viscosity noticeably decreases with increasing oil temperature. The dynamic viscosity ranged from 318.16 mPa.s (at 15°C) to 28.988 mPa.s (at 60°C), corresponding to a decrease of around 90% in dynamic viscosity with an increase of only 45°C in temperature. In the right y-axis (highlighted in blue) in Figure 3, it can be observed a decrease around 3% in the density ( $\rho$ ) of the crude oil for temperatures ranging from 15°C (0.924 g/cm<sup>3</sup>) to 60°C (0.8962 g/cm<sup>3</sup>). The BSW (Basic Sediment and Water) of the crude oil is 0.46 % and the analysis was performed using the volumetric titration method with the Karl Fisher reagent. The superficial tension and interfacial tension (oil/water) of the crude oil were measured in the tensiometer Kruss® (model k9-MK1), and the results are presented in Table 4. The analysis of the crude oil shows that it presented an API grade of 21. The characterization of the oil was developed at the Nucleus of Compact Separators from the Federal University of Itajubá (NUSEC – UNIFEI).

Table 3. Physical properties of crude oil used in the experiments of generation of (O/W) emulsions.

T <sub>nominal</sub> (°C)	T <sub>real</sub> * (°C)	Viscosity**		Density***	Basic Sediment and Water (BSW)
		Dynamics $\eta$ (mPa.s)	Kinematic $\nu$ (mm <sup>2</sup> /s)	$\rho$ (g/cm <sup>3</sup> )	KF%
15	15.00	318.2	344.0	0.9248	0.46
20	20.00	229.8	249.4	0.9216	
25	25.00	167.3	182.1	0.9183	
30	30.00	123.7	135.2	0.9149	
35	35.00	93.7	102.8	0.9113	
40	40.00	72.1	79.5	0.9075	
45	45.00	55.6	61.4	0.9061	
50	50.00	44.3	49.1	0.9026	
55	55.00	35.5	39.5	0.8995	
60	60.00	28.9	32.4	0.8962	

\*T  $\pm$  0.005°C, \*\*  $\eta \pm$  0.1%, \*\*\*  $\rho \pm$  0.0002 (g/cm<sup>3</sup>)

Table 4. Superficial tension and interfacial tension of crude oil obtained at 20°C.

Superficial tension (mN/m)	Interfacial tension (mN/m)	SG	API grade
30.9	22.0	0.9260	21

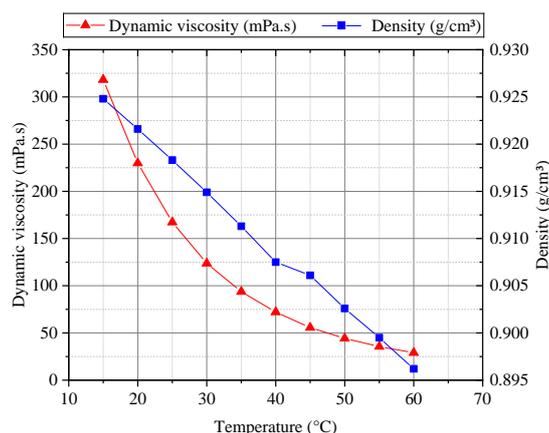


Figure 3. Dynamic viscosity (mPa.s) and density (g/cm<sup>3</sup>) of crude oil as a function of temperature (°C).

### 2.3 Experimental matrix

The experiments of generation of (O/W) oil-water emulsions were performed for the conditions given in the experimental matrix shown in Table 5. A total of 13 experiments were carried out. The experiments were developed for volumetric water flow rates ranging from 1.0 m<sup>3</sup>/h to 2.0 m<sup>3</sup>/h and mass oil flow rates ranging from 1.46 g/min to 8.76 g/min. Furthermore, two diameter of mixing tee (D, Figure 2) were also evaluated and the water velocity inside the mixing tee ranged from 7.22 m/s ( $Re = 5.5 \times 10^4$ ) to 28.29 m/s ( $Re = 1.5 \times 10^5$ ) (see Table 5).

Table 5. Experimental conditions used for the emulsion generation assay.

ID	Water volumetric flow rate (m <sup>3</sup> /h)	Oil mass flow rate (g/min)	D (mm)*	Reynolds number (Re) x 10 <sup>5</sup>	v (m/s)
A1	2.0	2.92	5.0	1.5492	28.3
A2	1.1	2.92	5.0	0.8521	15.6
A3	2.0	2.92	7.0	1.1066	14.4
A4	2.0	2.92	7.0	1.1066	14.4
A5	2.0	2.92	7.0	1.1066	14.4
A6	1.0	2.92	7.0	0.5533	7.2
A7	1.0	2.92	7.0	0.5533	7.2
A8	1.0	2.92	7.0	0.5533	7.2
A9	2.1	2.92	7.0	1.1619	15.2
A10	2.0	8.76	7.0	1.1066	14.4
A11	2.0	8.76	7.0	1.1066	14.4
A12	1.0	1.46	7.0	0.5533	7.2
A13	1.0	1.46	7.0	0.5533	7.2

\*diameter of mixing tee

### 2.4 Methodology

In this work, the following characteristics of the emulsions were evaluated: (i) oil and grease content (TOG), ii) oil droplet size (DSD), and iii) stability of oil-in-water emulsions (o/w). The methodology used in these analyses are described in the next subsection.

#### 2.4.1 Oil and grease content measurement (TOG)

The oil and grease content (TOG) is a parameter that is widely used to evaluate the oil concentration in produced water in the oil and gas industry (Cirne et al, 2016). In this study, the oil and grease content (TOG) of the oil-in-water emulsions (O/W) were measured through the spectrometry technique (Queirós et al, 2015; Cirne et al, 2016). The oily water collected from the experiments (around 50 mL of oil-water emulsion (O/W) stored in 100 mL volumetric flask) was initially acidified with 0.5 mL of pure hydrochloric acid (HCL with a purity of 37.7%), and next the mixture was shaken for 3 min. Then, the sample was transferred from the volumetric flask to a separating funnel to begin the process of chemical extraction of oil.

The oil phase was extracted from aqueous phase by addition of 30 mL of organic solvent (n-hexane) in the separating funnel. Then, the mixture was strongly shaken for 3 min and later the mixture rests for a period of 5 min, which induced

the separation of the following phases: (i) oil and solvent and (ii) water. These steps described above were used in the procedures of chemical extraction and phase separation, respectively. The organic phase (oil and n-hexane) was filtered in a second volumetric flask. The water obtained from the extraction was submitted through a second step of chemical extraction (addition of n-hexane), in order to separate the residual oil that was still in the water. After the second chemical extraction, the volume of water was measured through a graduated test tube.

The second volumetric flask (where the organic phase was stored) was filled with n-hexane until reaching a volume of 100 ml ( $V = 100$  mL). After this step, the DR 2800 spectrophotometer (©Hach Company) was used to measure the absorbance value (ABS) of the organic phase. Then, the oil and grease content (TOG) was determined according to the following equation:

$$\text{TOG} = (\text{ABS} \times F \times V \times f) / A \quad (1)$$

where ABS is the absorbance of the organic phase (oil and n-hexane), F is an oil calibration factor (specific for the oil used in this experiment), V is the volume of volumetric flask used to store the organic phase, f is the factor of dilution ( $f = 1$ ), and A is the initial volume of sample collected for analysis (O/W emulsion).

#### 2.4.2 Oil droplet size measurement

The droplet size measurements were performed using the Malvern Insitac in-line equipment, which analyses the diffraction of a laser beam to characterize the DSD. The deconvolution of the diffraction pattern relies upon the Mie theory, which it is based on the solution of Maxwell equation for light propagation through spherical homogeneous particle with plane wave excitation. The size of the particles is greater than the wavelength of the light. As explained by Eremin (2005), the scattered light field is represented as an infinite series of fields of spherical multipoles, orthogonal at the sphere surface. It considers that the particles are optically homogeneous and spherical.

#### 2.4.3 Stability of oil-in-water emulsions (O/W)

The stability assessment of oil-in-water emulsions (O/W) were developed through the measurements of oil and grease content (TOG) of three samples of (O/W) emulsions, which were extracted from each experimental condition (Table 5) at position E in the setup (Figure 1). The emulsion samples were extracted (using the entrance 1 in Figure 4) and stored in upward reservoirs with volume capacity of 1.0 L (Figure 4). The TOG measurement was performed over three periods of time (t): (i) 0 min, (ii) 15 min, (iii) 60 min. After the settled time (t) for each sample, a fraction of emulsion (around 50 mL) was collected at position 2 from the reservoir (Figure 4) and stored in a 100 mL volumetric flask. After collection of all three samples, the measurement of TOG was carried out according to the procedure previously described.

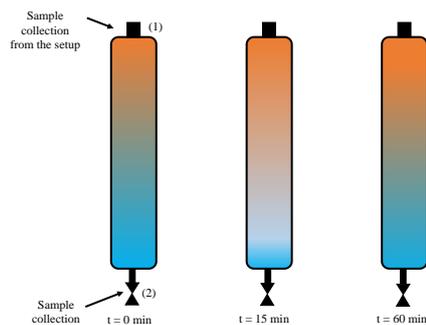


Figure 4. Evaluation of stability of oil-in-water emulsions (O/W) as a function of time (t).

### 3. RESULTS AND DISCUSSION

This section presents the results and the analyses of the data obtained in this study, which includes: (i) the effect of changing of pressure drop ( $\Delta P$ ) across the globe valve (VG1) on the characteristics of oil-in-water emulsions (O/W) and, (ii) on the stability of oil-in-water emulsions (O/W).

#### 3.1 Effect of variable pressure drop device in (O/W) emulsion

Table 6 shows water ( $Q_a$ ) and oil ( $m_o$ ) flow rates, the pressure drops across the globe valve ( $\Delta P$ ), the oil droplet sizes (DSD), and the oil and grease contents (TOG) obtained for A1 to A13 experimental conditions. The experiments A3 – A5 were developed under similar conditions of water ( $Q_a$ ) and oil ( $m_o$ ) volumetric flow rates. The water volumetric flow

rate ( $Q_a = 2.00 \text{ m}^3/\text{h}$ ) and oil mass flow rate ( $m_o = 2.9 \text{ g}/\text{min}$ ) adopted for these experiments were  $2.00 \text{ m}^3/\text{h}$  and  $2.9 \text{ g}/\text{min}$ , respectively. Hence, the emulsions produced in these tests (A3 – A5) are nearly similar, since the oil and grease contents (TOG) obtained for those experiments were  $55.5 \text{ mg}/\text{l}$ ,  $56.0 \text{ mg}/\text{l}$ , and  $54.7 \text{ mg}/\text{l}$ , respectively, leading to an average TOG of  $55.40 \text{ mg}/\text{L}$  (standard deviation of  $0.7 \text{ mg}/\text{l}$ ). The pressure drop ( $\Delta P$ ) across the globe valve (VG1, Figure 1) has been changed for each experimental condition to investigate its effect on the oil drop size of the (O/W) emulsions. The pressure drop ( $\Delta P$ ) at the globe valve (VG1) was 4.0, 2.0, and 1.0 for the experiments A3 – A5, respectively. The experimental results revealed that the sizes of the oil droplets (DSD) dispersed in each emulsion were significantly different (Table 6), e.g., the oil droplet sizes (DSD) measured via Particle Size Analyzer (PSA) were  $24.14 \mu\text{m}$  for the experiment A3 and  $44.31 \mu\text{m}$  for experiment A5, which indicated an increase of nearly 85 % in the DSD. From the analysis of these data (Table 6), it can be concluded that an increase in the pressure drop ( $\Delta P$ ) across the globe valve (VG1) leads to a decrease in the oil droplet size (DSD). This trend is clearly observed in Figure 5, which shows the size of oil droplets (DSD) dispersed in the emulsion as a function of pressure drop ( $\Delta P$ ) across the globe valve (VG1). The oil droplet size (DSD) for the experiments A3 – A5 (highlighted in red) systematically dropped as the pressure drop ( $\Delta P$ ) at the globe valve increased.

The same trend of decreasing DSD with the increase of  $\Delta P$  was observed for the experiments A6 – A8 (highlighted in blue in Figure 5), which were developed for the same oil mass flow rate ( $m_o = 2.9 \text{ g}/\text{min}$ ) and a water volumetric flow rate of  $1.00 \text{ m}^3/\text{h}$  (half of flow rate adopted for the experiments A3 – A5). The oil and grease contents (TOG) obtained for the A6 – A8 experiments were approximately 220% higher than the TOG obtained for the A3 – A5 experiments (Table 6). Such a result was already expected since the oil mass flow rate ( $m_o$ ) was kept constant, and the water volumetric flow rate ( $Q_a$ ) was decreased by half compared to the conditions of the tests A3 – A5. Regarding the oil droplet size (DSD) for experiments A6 – A8, Figure 5 shows that the oil droplet size (DSD) decreases from approximately  $33 \mu\text{m}$  (experiment A7) to  $15 \mu\text{m}$  (experiment A8) for a change in pressure drop ( $\Delta P$ ) across the globe valve from 2.0 bar to 8.0 bar. From Figure 5, it can be concluded that the higher the pressure drop at the globe valve, the lower the oil droplet size (DSD). This behavior agrees with the results observed by Silva (2019), which associated the decrease in the oil droplet size with the increase in shear stress resulting from the increase in pressure drop at the globe valve (VG1, Figure 1).

Table 6. Experimental data obtained in the present study.

ID	$Q_a$ ( $\text{m}^3/\text{h}$ )	$m_o$ ( $\text{g}/\text{min}$ )	$M_2$ ( $\text{kg}/\text{min}$ )	P1 (bar)	P2 (bar)	P3 (bar)	P4 (bar)	$\Delta P$ * (bar)	DTG** ( $\mu\text{m}$ )	SD*** ( $\mu\text{m}$ )	TOG ( $\text{mg}/\text{L}$ ) $t = 0 \text{ min}$
A1	1.99	2.92	3.0	15.5	9.0	5.0	-	4.0	12.78	0.08	54.7
A2	1.06	2.92	3.0	6.5	5.0	1.0	-	4.0	19.61	0.04	110.9
A3	2.01	2.92	2.9	7.5	6.0	2.0	2.0	4.0	24.14	0.15	55.5
A4	2.01	2.92	2.9	5.5	4.0	2.0	2.0	2.0	36.06	0.18	56.0
A5	2.00	2.92	2.9	5.0	3.0	2.0	2.0	1.0	44.31	0.23	54.7
A6	0.99	2.92	3.0	5.0	4.5	0.5	0.0	4.0	22.1	0.05	124.2
A7	0.99	2.92	2.8	3.5	2.5	0.5	0.0	2.0	33.35	0.09	122.0
A8	1.00	2.92	2.9	8.5	8.5	0.5	0.0	8.0	13.58	0.06	125.0
A9	2.05	2.92	3.0	12.0	10.5	2.5	1.0	8.0	14.50	0.03	37.8
A10	2.00	8.76	2.9	5.0	30	2.5	1.0	0.5	49.50	0.18	180.2
A11	2.00	8.76	2.9	7.5	6.0	2.0	1.0	4.0	26.34	0.09	199.5
A12	0.99	1.46	2.9	5.5	5.0	1.0	0.0	4.0	22.59	0.05	52.8
A13	1.02	1.46	3.0	3.0	2.5	0.5	0.0	2.0	38.62	0.15	55.9

\* $\Delta P = P2 - P3$ , \*\*  $D_{v(50)}$ , \*\*\*standard deviation

Figure 6 also presents the oil droplet size (DSD) as a function of the pressure drop at the globe valve ( $\Delta P$ ) obtained for a wide range of oil grease content (TOG): from  $55.35 \text{ mg}/\text{l}$  to  $189.84 \text{ mg}/\text{l}$ . The graph shows that the oil concentration (TOG) had no significant effect on the oil droplet size (DSD) obtained in oil-water emulsions (O/W). The oil droplet size (DSD) was approximately  $35 \mu\text{m}$  for the conditions corresponding to the green, red, and blue symbols (Figure 6), obtained for a pressure drop at the globe valve of 2.0 bar. The oil and grease content (TOG) for blue symbols is approximately 120 % larger than the TOG obtained for the red symbols. However, the oil droplet size (DSD) for red symbols was around 8.2% larger than for the blue symbols (Figure 6). The results show that the pressure drop (shear stress) makes a major role on the development of the oil droplet size (DSD). As well, the DSD for the black, green, red, and blue symbols seems not to be affected by the TOG of the oil-in-water emulsions (O/W), which were developed for a pressure drop of 4.0 bar (Figure 6). Furthermore, the increase of the pressure drop at the globe valve ( $\Delta P$ ) leads to a decrease in the oil droplet size (DSD) for the condition highlighted in black and green, which properly agreed with the trend already observed for the conditions highlighted in blue and red. It can be speculated that the oil droplet size tends to a value around  $10 \mu\text{m}$  (Figure 6) with increasing the pressure drop across the globe valve.

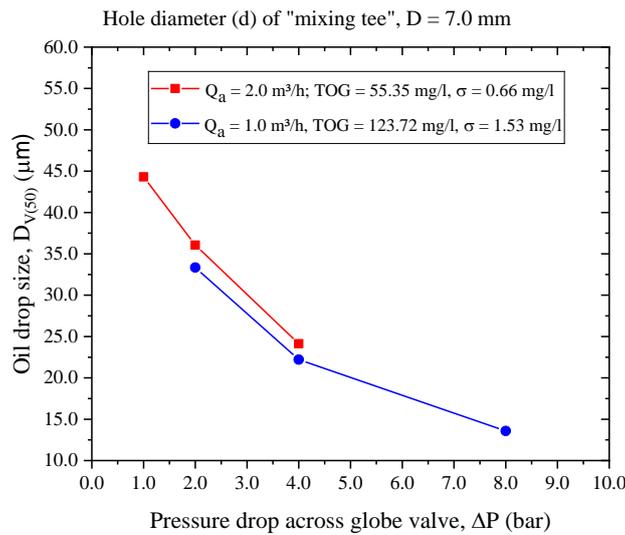


Figure 5. Oil droplet diameter (DTG) in oil-in-water emulsion (O/W) as a function of the pressure drop ( $\Delta P$ ) at the globe valve.

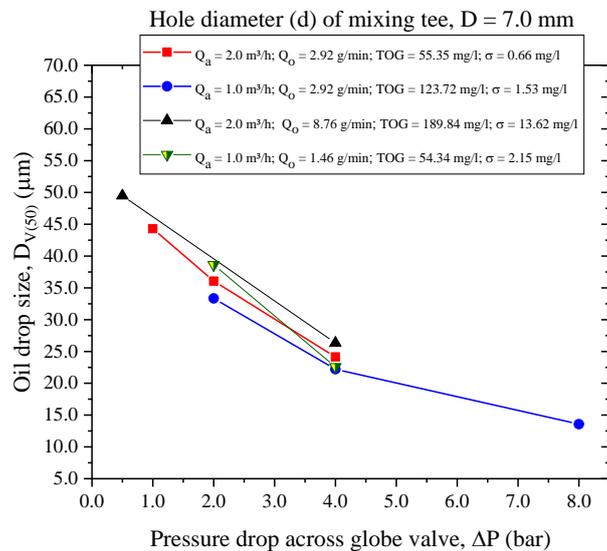


Figure 6. Oil droplet size (DTG) in oil-in-water emulsion (O/W) as a function of pressure drop ( $\Delta P$ ) at the globe valve.

### 3.2 Stability of oil – water emulsion (O/W)

The stability of the oil-in-water emulsion (o/w) was evaluated through the measurements of oil and grease contents (TOG) over time, which were performed according to the methodology described in section 2.4. Table 7 show the results of the TOG measurements for the experiments A1 – A13 and Figure 7 show the TOG data for the experiments A1 – A7. The evolution of oil and grease content (TOG) for experiments A6 and A7 (Figure 7) over 60 min is presented in Figure 7. It is noted that the TOG for experiment A7 was about 17% lower than the TOG for the experiment A6. Both experiments started with similar initial conditions levels of TOG (122 mg/l). Furthermore, the oil droplet size for A6 (DSD = 22.1  $\mu\text{m}$ ) was 50 % smaller than for A7 (DSD = 33.35  $\mu\text{m}$ ). From these results, it is clear that the lower the DSD, the higher the stability of the emulsion, because the TOG value is higher for the A6 experiment over 60 minutes. This in agreement with Schramm (1992). In his study, he associates the stability of the emulsions with the reduced size of the droplet.

Figure 8 shows the results of oil and grease content (TOG) measured through spectrophotometry technique (y-axis) and the measurements of oil concentration provided by the Malvern Panalytical® particle size analyzer (Insittec Wet), which provides the in-situ measurements of oil and grease content (Volumetric TOG as Cv in ppm). The results provided by both techniques agree within a band of  $\pm 20\%$ . For dispersed oil, the spectrophotometry technique is more accurate as previously verified through the gravimetric technique (previously developed by the technical staff of NUSEC). The advantage of the Particle Size Analyzer (PSA) technique is that it presents a good correlation to the spectrophotometry technique, which is more accurate. Furthermore, the Particle Size Analyzer (PSA) allows in-situ real-time measurements of TOG as opposed to the spectrophotometry technique by solvent extraction.

Table 7. Oil and grease content (TOG) for tests A1 – A13 as a function of time.

ID	TOG (mg/l) *	TOG (mg/L) t = 0 min	TOG (mg/L) t = 15 min	TOG (mg/L) t = 60 min
A1	84.9	54.7	51.3	59.4
A2	113.5	110.9	106.5	99.2
A3	51.7	55.5	45.2	32.0
A4	47.7	56.0	30.0	20.3
A5	48.6	54.7	41.4	26.7
A6	110.2	124.2	105.9	77.8
A7	107.3	122.0	95.8	64.2
A8	113.2	125.0		
A9	34.6	37.8		
A10	153.5	180.2	28.8	10.6
A11	169.4	199.5	71.2	26.2
A12	61.7	52.8	29.9	13.6
A13	59.7	55.9	13.5	6.7

\*Online measurement through Malvern Panalytical® particle size analyzer (*Insittec wet model*).

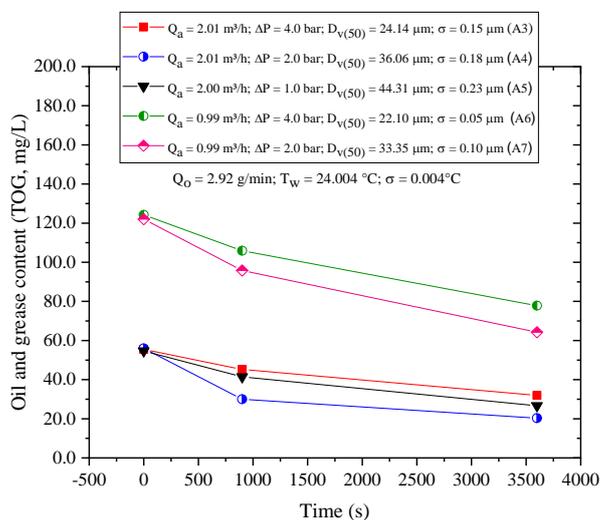


Figure 7. Oil and grease content (TOG) as a function of time (s) for tests A3 – A7 (emulsion stability test).

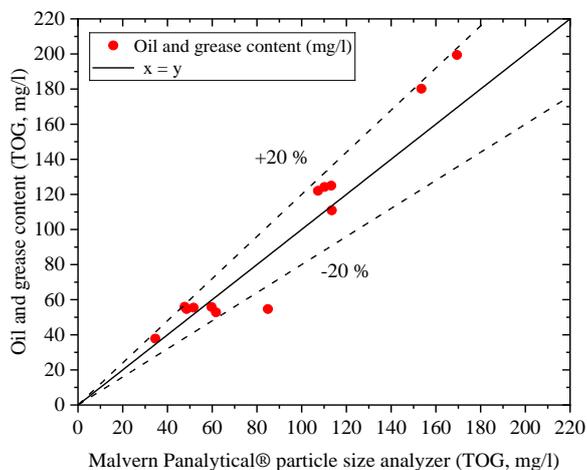


Figure 8. Comparison of the oil and grease content (TOG) measured through spectrophotometry technique (axis-y) and the Malvern Panalytical® particle size analyzer (axis-x).

#### 4. CONCLUSIONS

The present study investigates the droplets breakage of oil-water emulsions (o/w) flowing across a variable pressure drop device (globe valve) downstream a pre-mixing device (mixing tee). The experimental work was focused on oil-in-water (o/w) emulsions produced by injecting (in water) crude oil with API Gravity of 21.31, dynamic viscosity of 229.83 mPa.s, density of 0.9216 g/cm<sup>3</sup>, surface tension of 30.9 mN/m, and interfacial tension of 22.0 mN/m (properties at 20°C). The emulsion characterization was performed through measurements of oil and grease content (TOG) and the oil droplet size and its distribution (DSD). The stability of emulsions was also evaluated through measurements of the Oil and Grease Content (TOG) over time, which were obtained for the following time intervals: i) 0 min (online), ii) 15min (after the experiments in the glass separating funnel) and iii) 60 min (after the experiments in the glass separating funnel). The main conclusions of this study are: i) The oil droplet size (DSD) decreases by increasing the pressure drop at the flow restriction device ( $\Delta P$ ), ii) the TOG result was directly affected by the increase in the water volumetric flow rate ( $Q_a$ ). For the same condition of oil injected into the oil-in-water emulsion (O/W), an increase in the water volumetric flow rate ( $Q_a$ ) caused a decrease in the TOG value. Furthermore, as the injected oil mass flow rate was substantially lower than the water volumetric flow rate ( $Q_a$ ), the variation in the oil mass flow rate ( $m_o$ ) did not affect the DTG measurement, which was mainly affected by the pressure drop at the globe valve, iii) the in-situ oil and grease content (TOG) measurements by the spectrometry technique and through the Particle Size Analyzer (PSA) agrees within a range of  $\pm 20\%$ , (iv) and the oil-in-water emulsions (O/W) with a reduced oil droplet size (DSD) are more stable.

#### 5. ACKNOWLEDGEMENTS

This study was financed in part by the Coordination for the Improvement of Higher Education Personnel – Brazil (CAPES) – Finance Code 001. The authors also thanks Petrobras and the ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis) for their financial support, CNPq (National Council for Scientific and Technological Development) through the grant number 312337/2021-3, and the technical staff of NUSEC (The Nucleus of Compact Separators from Federal University of Itajubá, NUSEC – UNIFEI), headed by Prof. Marcos Aurélio de Souza.

#### 6. REFERENCES

- Al-Ghouti, M. A.; Al-Kaabi, M.A., Ashfaq, M.Y.; AdelDa'na, D. 2019. "Produced water characteristics, treatment and reuse: A review". *Journal of Water Process Engineering*, Vol. 28, pp. 222–239.
- Bakke, T.; Klungsoyr, J.; Sannic, S., 2013. "Environmental impacts of produced water and drilling waste discharges from the Norwegian offshore petroleum industry". *Marine Environmental Research*, Vol. 92, pp. 154–169.
- Becher, P., 1965. *Emulsions: theory and practice*. Reinhold Publishing Corp, New York, 2<sup>nd</sup> edition.
- Cabral, R.C.; Santos, D.F., 2019. "Estudo das principais técnicas para o tratamento de água produzida de petróleo. Uma análise das principais metodologias utilizadas em campo". *Ciências Exatas e Tecnológicas*, Vol. 5, pp. 175–184.
- Cirne, I.; Boaventura, J., Guedes, Y., Lucas, E. 2016. "Methods for determination of oil and grease contents in wastewater from the petroleum industry". *Chemistry & Chemical Technology*, Vol. 10, No. 4, pp. 437 – 444.
- Da Silva, F.S., 2019. *Detecção Estudo de quebra de gotas de dispersões de água em óleo frente a queda de pressão localizadas*. Ph.D. thesis, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brasil.
- Eremin, Y.A., 2005. "Scattering: Scattering theory". *Encyclopedia of Modern Optics*, pp. 326 – 330.
- Moosai, R. and Dawe, R.A., 2003. "Gas attachment of oil droplets for gas flotation for oily wastewater cleanup". *Separation and Purification Technology*, Vol. 33, pp. 303–314.
- Queirós, Y. G. C., Clarisse, M. D., Oliveira, R. S., Reis, B. D., Travalloni, A. M. L. and Lucas, E. F., 2005. "Determinação e correlação do teor de total de óleos e graxas por meio de diferentes técnicas espectroscópicas e gravimétrica". In *Proceedings of the 3rd Congresso Brasileiro de P&D em Petróleo e Gás - IBP 2005*. Fortaleza, Brazil.
- Schramm, L. L., 1992. "Fundamentals and applications in the petroleum industry". *Adv. Chem*, Vol. 231, pp. 3 – 24.
- Tadros, T. F., 2013. *Emulsion formation and stability*. John Wiley & Sons., 1<sup>st</sup> edition.

#### 7. RESPONSIBILITY NOTICE

The author(s) is (are) the only responsible for the printed material included in this paper.