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AN EXPERIMENTAL COMPARISON BETWEEN TWO METHODS FOR BIOFUELS EMULSIFICATION

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Abstract. The scope of this investigation is to formulate and characterize emulsified fuels using a micro-channel emulsifier and compare this against emulsions produced using a magnetic stirrer. The emulsified fuels are formulated using a blend of rapeseed oil in diesel fuel as continuous phase and water as dispersed phase, as well as Sorbitan Sesquioleate as surfactant. Several stable dispersed systems classified as emulsions based on their optical appearance and dispersed droplet size are obtained. A better stability time and smaller mean droplet size for the emulsions formulated with micro-channel emulsifier is observed, compared to the same systems obtained through magnetic stirrer. The dynamic viscosity measured as a function of shear rate indicated non-Newtonian behavior with a shear-thinning response for all emulsions. An increase of water percentage led to emulsified fuels with higher viscosity levels, highlighting a strong dependency of the dispersed phase content on dispersed system viscosity.

Keywords: Micro-channel emulsifier, magnetic stirrer, emulsified fuel, rapeseed oil, diesel fuel.

1. INTRODUCTION

In many countries, fossil fuels represent one of the most used energy source. The limited fossil fuel reserves, greenhouse gas emissions, global warming, recent changes in fossil fuel prices and their influence on the energy scenario are currently worldwide problems. This situation has motivated governments, automotive industries, energy-producing industries and the scientific community around the world to search for suitable alternatives and strategies to reduce fossil fuel usage.

In this context, the emulsification method applied to animal fats, diesel fuel, vegetable oils and their derivatives is a promising techniques reported in order to reach an environmentally friendly fuel with proper physicochemical properties, allowing improvements in the atomization process, combustion and exhaust emissions (Senthil Kumar *et al.*, 2006, Melo *et al.*,2016, Ithnin *et al.*, 2015). Emulsified fuels might be applied as alternative fuels for diesel engines, fired boilers and power plants. For this reason, several researches have been conducted fueling emulsified fuels in different applications (Strandell and Schab, (1986); Melo *et al.* (2015)).

On the other hand, emulsified fuels are formulated generally applying magnetic stirrer, mechanical stirrer, (ultra)sonic device, membrane emulsifier and micro-channel emulsifier. Among the above-mentioned methods, micro-channel emulsifier applied to alternative fuels production has not been often reported. Nevertheless, interesting contributions in this field have been recently reported by Belkadi *et al.* (2015, 2016a, 2016b). These studies are focused on a biofuel emulsifier using different velocity impinging flows and singularities in micro-channels, as well as the use of one or two micro-channels. Depending on applied flow-rates and water fraction, a strong influence represented the use of two micro-systems in series on dispersed water droplets sizes. Regarding to dispersion process into micro-channel, a swirl and convective flow during the emulsification process was noted.

For the above mentioned reason, the scope of this investigation is to formulate and characterize emulsified fuels using a micro-channel emulsifier, as well as develop a comparison with the same fuels obtained through magnetic stirrer (as a reference).

2. MATERIALS AND METHODS

The emulsified systems are formulated based on stabilization zones reported in our previous experiments (Melo *et al.*, 2016) using a blend of rapeseed oil in diesel fuel as continuous phase (i.e. 20% Rapeseed oil and 80% diesel fuel). In the present work, additional components such as tap water as dispersed phase and Sorbitan Sesquioleate as surfactant are used. The emulsified fuels are prepared using 2% and 4% of surfactant (by volume). The physicochemical properties of diesel fuel and rapeseed oil are shown in Table 1.

Table 1. Physicochemical properties of neat fuels

Properties	Unit	Diesel fuel	Rapeseed oil
Dynamic viscosity @40ºC	mPa·s	3.5	28
Density @40ºC	g/cm3	0.810	0.901
Water content	%	<0.05	<0.05

The emulsification process is conducted using two methods (i.e. magnetic stirrer and micro-channel emulsifier). As stirrer, a VWR hotplate magnetic stirrer VMS-C4 lab device is used. The volume prepared during the magnetic stirrer formulation is 50 mL with continuous agitation during 2 hours (see Table 2). The needed amount of surfactant is added into the continuous phase (blends of rapeseed oil in diesel fuel); then the water is slowly added. After each addition, the dispersed systems are vigorously stirred at 1000 rpm.

The emulsification process using micro-channel emulsifier is based on the matrices shown in Table 3. Emulsified fuels are obtained using the same methodology previously mentioned. Nevertheless, it might be pointed out that the continuous phase and surfactant are previously blended as a first step before the use of micro-channel emulsifier.

Table 2. Composition used for the emulsification process using magnetic stirrer

	Components (% by volume)		
Emulsified fuel	RO-Diesel	Surfactant	Water
ERO1	88	2	10
ERO2	78	2	20
ERO3	68	2	30
ERO4	86	4	10
ERO5	76	4	20
ERO6	66	4	30

ERO: Emulsified rapeseed oil

Table 3. Compositions and flow process conditions used with micro-channel technology

	Components (% by volume)			Flow rate (mL/min)	
Emulsified fuel	RO-Diesel	Surfactant	Water	Continuous phase	Dispersed phase
ERO7	88	2	10	225	25
ERO8	78	2	20	200	50
ERO9	68	2	30	175	75
ERO10	86	4	10	225	25
ERO11	76	4	20	200	50
ERO12	66	4	30	175	75

ERO: Emulsified rapeseed oil

The schematic diagram of the experimental set-up used for the micro-channel emulsification process is shown in Fig. 1. The geometry of the micro-channel is an optimized one, which has been recently presented by Belkadi *et al.* (2016b). It is based on the impinging flow (Fig. 2). The pressure drop required to perform the emulsions is around 10 bars in the Diesel loop for the configuration of the Table 3.

A high-speed camera model 675K-M1 (HighSpeedStar series) provided by LaVision is used for visualization of flow into micro-channel emulsifier. This camera works with a frequency range between 50 Hz and 650 kHz. The used photographic objective is from LaVision (Ref. 1108548) and is equipped with lenses that allow 12 focus ranges (12x zoom). The range of exposure time sensor is between 1 µs and 0.02 s. The maximum resolution of images reaches 1 Megapixels.

The stability assessment of emulsified fuels is analyzed through a direct method like visual observation. The main criterion for stable emulsified fuels is the preservation of only one phase (Ghannam and Selim, 2009). The separation layer during the stability test is analyzed using graduate scale test tubes under static condition and following the procedure reported by Lin and Wang (2004).

The dispersed water droplet sizes are measured through a microscope Olympus BX61. The dispersed systems are analyzed on a PolyMethyl MethAcrylate (PMMA) homemade hemocytometer cell type. All measurements are repeated thrice and the averages of the replicates were used in the analysis.

The rheological behavior of dynamic viscosity-shear rate relationship is assessed using a Thermo Scientific Haake Mars III rheometer. The viscosities are determined at 40°C using a closed temperature chamber and a shear rate range from 20 to 260s^{-1}.

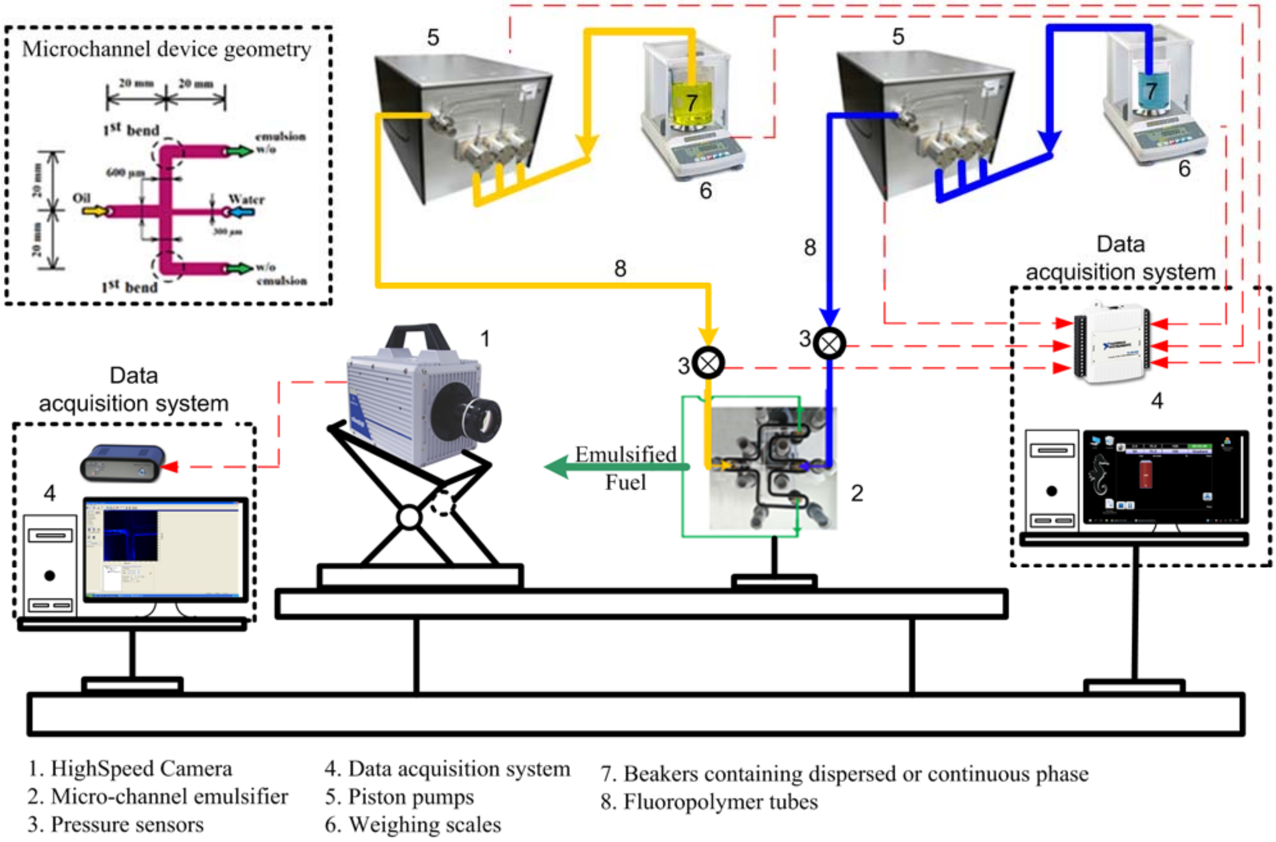


Figure 1. Schematic diagram of the micro-system setup

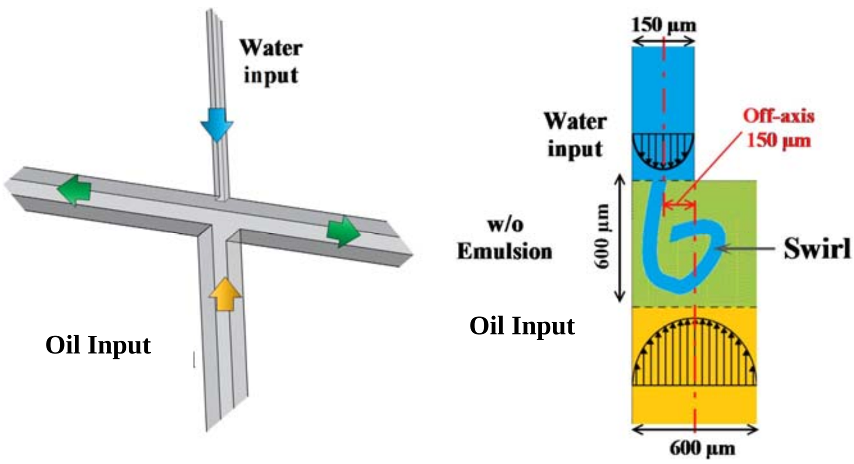


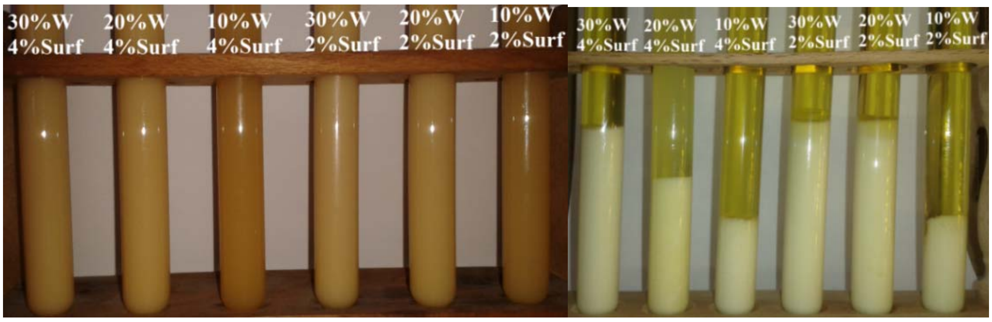
Figure 2. Schematic diagram of impinging flow principle with swirl effect into micro-channel emulsifier

3. RESULTS

3.1 Assessment of emulsified fuels stabilities

Based on spontaneous tendency for phase separation and their optical appearance (turbid appearance), all emulsified fuels formulated are classified as emulsions. The stability assessments are shown in Fig 3 and Fig 4. As can be noted the maximum stabilization time period reached was 120 minutes for ERO10. In addition, the surfactant percentages used during the formulation represented an acceptable amount to assure stability using both methods of emulsification (overall with micro-channel emulsifier). However, better results were achieved with 4% (by volume).

On the other hand, better stability performance for the emulsified fuels obtained through micro-channel emulsifier was reported. These improvements are not only consequence of the previous agitation step of the continuous phase just before the micro-channel emulsification process. This process represents an advantage and promotes a better dispersion avoiding a sudden agglomeration and coalescence process. Nevertheless, increasing the mass flow rate in the micro-channel emulsifier improve significantly the stability results.



a) b)

Figure 3. Emulsified fuel´s optical appearance: a) after preparation process, b) after breakdown process

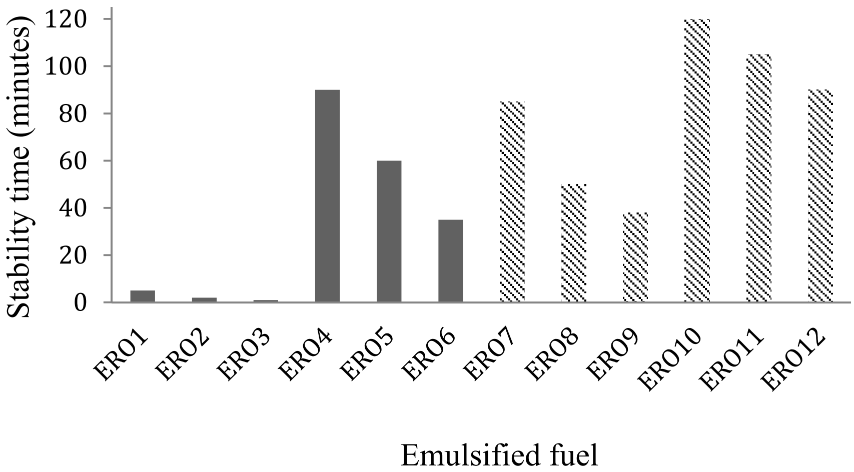
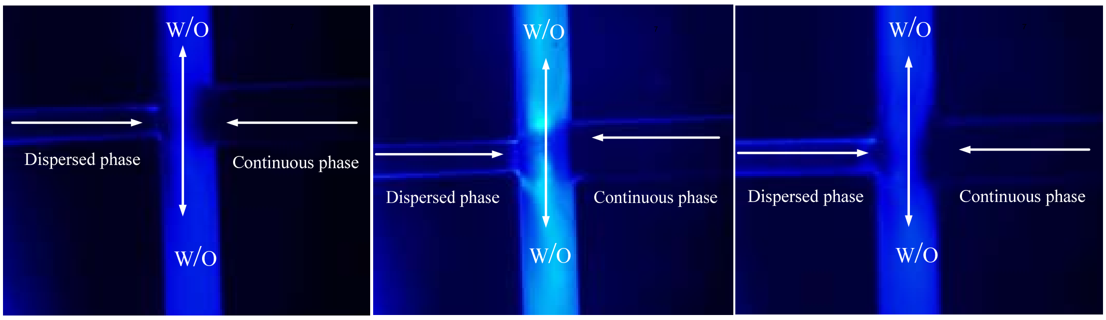


Figure 4. Emulsified fuel stability. Black bars: emulsions formulated with magnetic stirrer, Shaded bars: emulsions formulated with micro-channel emulsifier

3.2 Flow visualization into micro-channel emulsifier

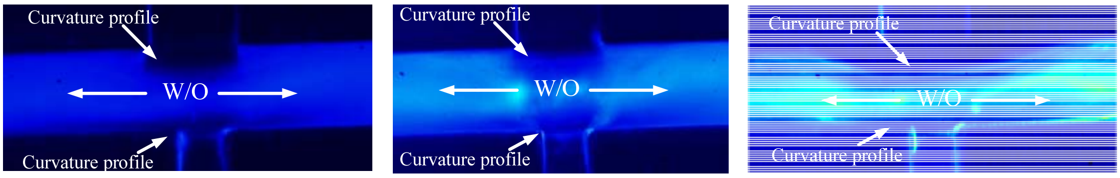
The evolution profile and flow curves achieved inside the micro-channel are shown in Fig. 5 and Fig 6. For each case, continuous and dispersed phases were pumped from opposite channels. The dispersed systems are immediately formed after impinging flows process between continuous and dispersed phase.

Variation on curvature profiles prior to impinging zone is reported (see Fig 6). This trend is observed for all emulsified fuels produced. This observation is also reported by Belkadi *et al.* (2015) regarding to emulsified diesel fuel. The topology velocity profile and structure at each case is linked to micro-channel emulsifier characteristic and flow rate conditions. Variations in the flow rate conditions also promoted change on curvature profile (see the outlet of each channel in Fig. 5 and Fig 6) which might be accompanying to swirl effect in the impinging zone.



(a) (b) (c)

Figure 5. Flow topology into micro-channel emulsifier: a) emulsified fuel with 10% of water, b) emulsified fuel with 20% of water, c) emulsified fuel with 30% of water

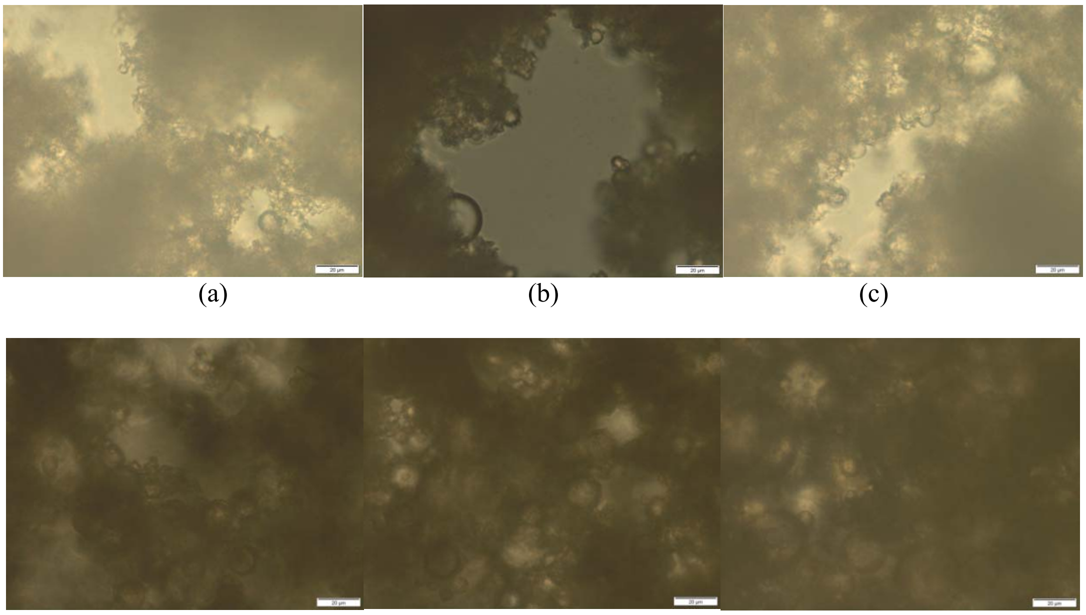


(a) (b) (c)

Figure 6. Curvature profile into micro-channel emulsifier: a) emulsified fuel with 10% of water, b) emulsified fuel with 20% of water, c) emulsified fuel with 30% of water

3.3. Microscope observation and droplet size characterization

According to the microscope observation, there is not a well dispersion of the surfactant and water into emulsified fuel matrix when magnetic stirrer was used (see Fig. 7: a, b and c). In fact, bigger water droplets are observed. This result might be correlated with the preparation conditions and dispersed system viscosity. Magnetic stirrer is generally recommended for homogenization process of fluids with lower viscosity. As was previously mentioned, all these drawbacks promote a quick coalescence and sedimentation process which leads to shorter stability times.



(a) (b) (c)

(d) (e) (f)

Figure 7. Microscope observation of emulsified fuels (scale bar: 20 μm): a) ERO4, b) ERO5 c) ERO6, d) ERO10, e) ERO11, f) ERO12

Moreover, dispersed systems formulated using micro-channel emulsifier brings better- homogenization in the emulsified fuel matrix (see Fig. 7: d, e and f). This improvement reached is linked to micro-channel emulsifier geometry used because of it ensures a homogeneous droplet size in the impinging zone. Furthermore, it is valid to point out that the agitation step used just before the micro-channel emulsification process also played an important role. Nevertheless, increases of flow rate conditions during the emulsification with micro-channel enhance the dispersion quality as consequence of vigorous swirl process in the impinging zone (see Fig. 2).

The mean values of dispersed water droplets size are shown in Fig 8. The emulsions analyzed are the only ones that report better stability time per each sets of emulsified fuels (see section 3.1). The systems prepared with micro-channel emulsifier reported smaller mean dispersed droplet size compared to emulsified fuels formulated with a magnetic stirrer device.

In both sets of emulsified fuels, an increase of water content led to bigger water droplets size. Significant differences between both emulsification methods were mainly reported at 30% of water. All this are associated with the limited capacity of the magnetic stirrer to disperse higher water content under the defined experimental condition. It is in coherence with the stability study developed (decrease of dispersed water diameter leads longer stability time).

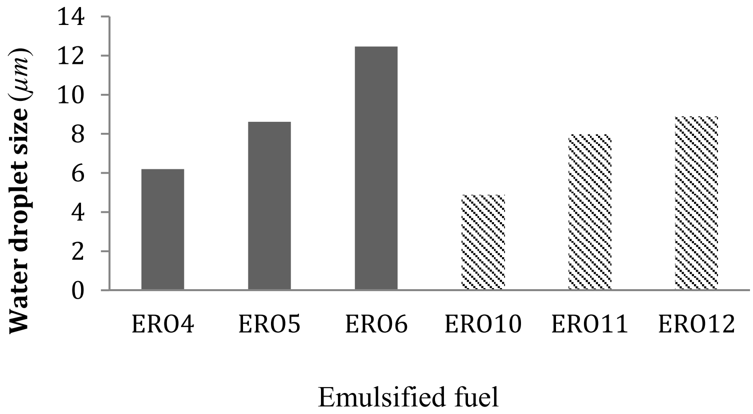


Figure 8. Mean value of water droplet size. Black bars: emulsions formulated with magnetic stirrer, Shaded bars: emulsions formulated with micro-channel emulsifier

On the other hand, a frequency distribution analysis of water droplet size in the emulsified fuels is developed (see Fig. 9). The analysis is performed fitting a normal distribution to the data on water droplets measured per each dispersed system. This analysis shows the results of number of occurrences vs. droplet size.

Water droplet sizes smaller than $1\mu m$ were not included due to limitation of the measurement set-up used. Nevertheless, the maximum occurrence bars are close to the average of the water droplet size obtained for all emulsified fuels. The best regular dispersion frequency was achieved with ERO10.

3.4 Rheological behavior of dynamic viscosity-shear rate relationship

The assessment of emulsified fuels viscosity-shear rate relationship is shown in Fig. 10. A slight difference between both sets of dispersed systems is observed. For this reason, only three systems are plotted. A strong correlation of viscosity upon the shear forces applied to the emulsified fuels is observed. Based on this fact, all emulsified fuels are classified as non-Newtonian fluids with a shear-thinning behavior (pseudo-plastic response). Viscosity decreases when the shear rate increases. Same trend was also reported by Ghannam and Selim (2016).

On the other hand, an increase of water percentage leads to emulsified fuels with higher viscosity levels (see Fig. 11), highlighting a strong dependency of the dispersed phase content on dispersed system viscosity. This is one of the most important facts to take into account in this field because there might be a standard or accepted range of emulsified fuels viscosity for a given application. Nevertheless, emulsified fuels involve several complex factors which might promote further improvements on atomization, combustion process and exhaust emissions.

4. CONCLUSIONS

Several emulsified fuels with different water and surfactant percentage were obtained using two different methods. All these emulsions may be applied as alternative fuels in oil-fired boilers and diesel engines. Based on the experimental results the following conclusions are established:

- Emulsified fuels addressed with micro-channel emulsifier reported better stability time and smaller dispersed droplet size compared to emulsions formulated with magnetic stirrer.
- The best dispersion performance was achieved with the emulsion formulated with 10% water and micro-channel emulsifier.
- Dynamic viscosity measured as a function of shear rate indicated non-Newtonian behavior with a shear-thinning response for all emulsified fuels studied.

- An increase of water percentage led to emulsified fuels with higher viscosity levels, highlighting a strong dependency of the dispersed phase content on dispersed system viscosity.

Finally, many of these emulsions may be applied as alternative fuels in oil-fired boilers and diesel engines. However, it is important to analyze the effect of the water dispersed on atomization and combustion. For this reason, the atomization and combustion of these emulsified fuels are currently investigated.

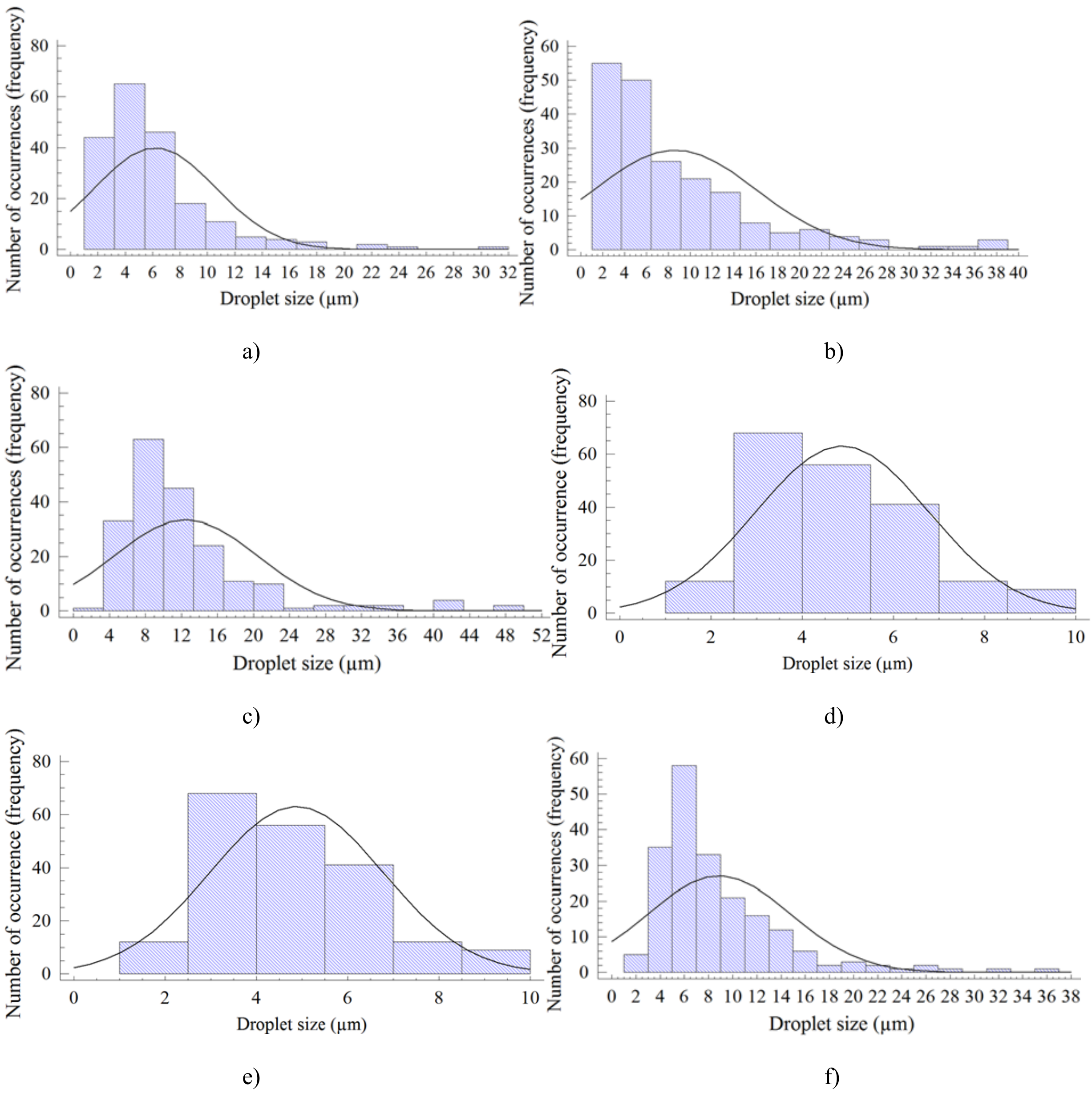


Figure 9. Distribution of water droplet size for 200 repeated tests:
a) ERO4, b) ERO5, c) ERO6, d) ERO10, e) ERO11, f) ERO12

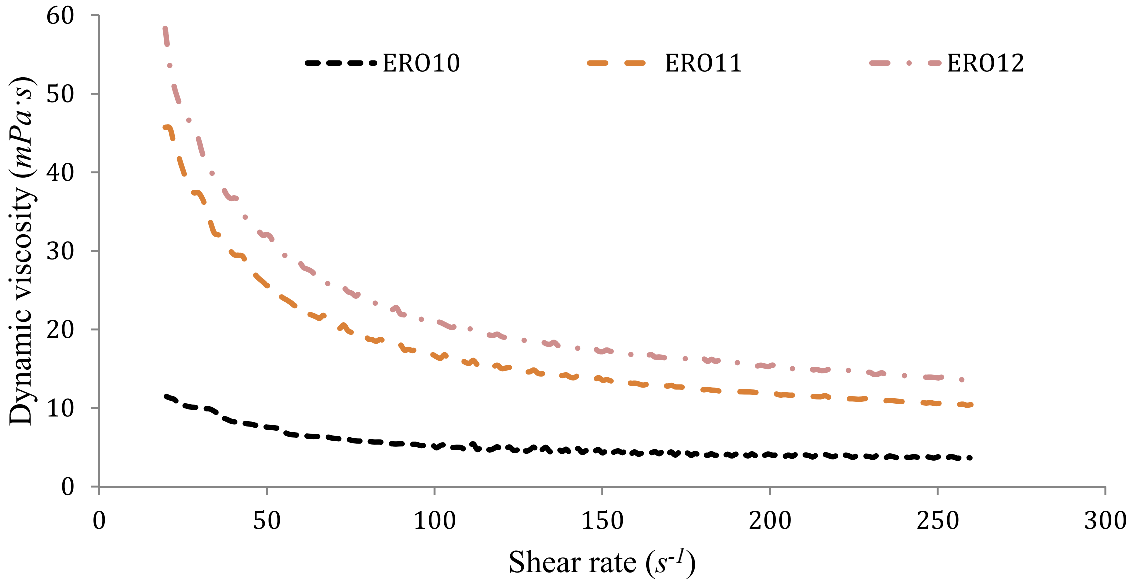


Figure 10. Rheological behavior of dynamic viscosity over shear rate

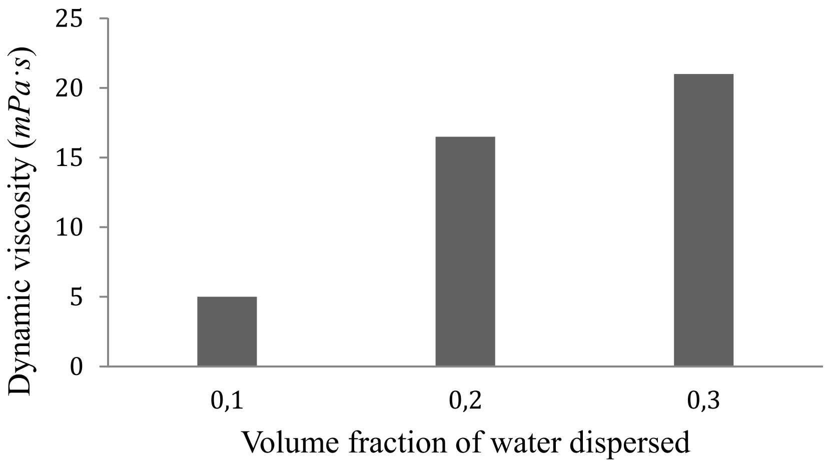


Figure 11. Effect of water dispersed volume fraction on emulsified fuel viscosity at a shear rate of 100 s^{-1}

5. ACKNOWLEDGEMENTS

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