

# SEPARATION OF SULFUR-CONTAINING COMPOUNDS FROM DIESEL BY OXIDATION FOLLOWED BY SOLVENT EXTRACTION IN A SINGLE DROP COLUMN

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(Submitted: November 3, 2018 ; Revised: March 16, 2019 ; Accepted: March 24, 2019)

**Abstract** - Oxidative desulfurization (ODS) is an attractive complementary or alternative process for the hydrodesulfurization (HDS) process due to advantages such as mild operating conditions. In the ODS process, the sulfur-containing compounds are oxidized first to polar sulfoxide and sulfone products and then these polar compounds are separated using solvent extraction or an adsorption process. In the present study, the separation of oxidized sulfur-containing compounds of diesel as a real fuel has been investigated using extraction in a single drop column. The oxidation system was hydrogen peroxide/formic acid. The selected solvent for the extraction of oxidized sulfur-containing compounds was dimethylformamide (DMF). In single drop tests, the effect of various parameters including the drop size (1.70-4.60 mm) and column height (228-550 mm) on the different parameters such as drop velocity and sulfur concentration in the dispersed and continuous phases has been investigated. The outcome of this study provides valuable insights for designing the extraction column for separation of oxidized sulfur-containing compounds from middle distillate fuels in an ODS process.

**Keywords:** Oxidative desulfurization (ODS); Diesel; Dimethylformamide (DMF); Single drop system; Drop diameter; Column height.

## INTRODUCTION

Increasing the consumption of crude oil and its derivatives in the world leads to an increase in environmental pollution. The presence of sulfur-containing compounds in fossil fuels leads to corrosion problems and inactivation of the pollution control catalysts in internal combustion engines. Furthermore, sulfur oxides ( $\text{SO}_x$ ), produced during the combustion of untreated fossil fuels, are the main source of acid rain and air pollution. Due to these environmental concerns, very stringent standards on the sulfur content of transportation fuels have been legislated in different countries. Therefore, different methods for removal of the sulfur-containing compounds from fuels have been

studied by many researchers (Babich and Moulijn, 2003; Dehkordi et al., 2009b; Fan et al., 2009; Mjalli et al., 2014). Nowadays, the hydrodesulfurization (HDS) process is the conventional technology applied for the removal of sulfur-containing compounds from oil derivatives. In this process, deep desulfurization needs high temperatures (up to 400 °C), high pressures (up to 100 bar), and expensive catalysts, which lead to an increase in the capital and operating costs. Furthermore, this process has limited capability for removal of several refractory sulfur-containing compounds, including heterocyclic sulfur-containing compounds such as dibenzothiophene and its derivatives. Thus, various new desulfurization technologies, such as electrochemical oxidation

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(Wang et al., 2007), extraction using ionic liquids and polar solvents (Seeberger and Jess, 2010), oxidative desulfurization (ODS) (Ismagilov et al., 2011), selective adsorption (Wang et al., 2012; Hernández-Maldonado and Yang, 2003), and bio-desulfurization (Soleimani et al., 2007) have been proposed as HDS alternative or complementary methods. The oxidation/extraction desulfurization process is an attractive method due to its mild operating conditions, no need of hydrogen, and high potential to remove HDS refractory sulfur-containing compounds (Hassan et al., 2013; Ito and Van Veen, 2006; Mjalli et al., 2014). The ODS process has two stages. The first stage is the oxidation of sulfur-containing compounds to their corresponding sulfoxides and sulfones (Ismagilov et al., 2011). The polarity of these oxidized sulfur-containing compounds is higher in comparison with the original sulfur-containing compounds (Zannikos et al., 1995). Different oxidants can be used for the oxidation of sulfur-containing compounds but hydrogen peroxide is widely used as oxidant due to its high active oxygen content, commercial availability, and its relatively low cost (Ismagilov et al., 2011; Campos-Martin et al., 2010; Dehkordi et al., 2009b). In addition, the common catalysts for the oxidation of sulfur-containing compounds are organic and mineral acids and the salts of transition metals (Dehkordi et al., 2009a; Dehkordi et al., 2009b; Ismagilov et al., 2011). The second stage is the removal of the oxidized sulfur-containing compounds by a liquid-liquid extraction process using a polar solvent or selective adsorption. Applying direct extraction without oxidation of sulfur-containing compounds does not have a good performance due to the low polarity of these compounds (Sobati et al., 2010). Sulfoxide and sulfone waste management is an important issue that should be resolved before commercialization of the ODS process. Processes such as hydrodesulfurization (HDS), coking, gasification and hydrocarbon recovery are among the ideas proposed for the management of sulfone waste. For example, the sulfone waste can be sent to a HDS unit. It is claimed that the reactivity of sulfones in HDS is higher in comparison with sulfides (Ito and van Veen, 2006). A delayed coking process is proposed to minimize the residual materials such

as sulfone waste with the help of extreme thermal cracking. The gasification process is another plan for the management of sulfone waste. More details regarding different strategies for sulfone waste management can be found in Ito and van Veen (2006). According to a literature review, no commercial plant has been reported for desulfurization based on an oxidation process followed by liquid-liquid extraction. However, a few experimental investigations were performed to remove sulfur-containing compounds using an oxidative/extractive method on the pilot plant scale. Some of the oxidative/extractive desulfurization processes which were developed for pilot and demonstration plants are summarized in Table 1.

In the liquid-liquid extraction step, extraction columns with high removal capability for sulfur-containing compounds should be applied. Various extraction columns, including a rotating disk contactor (Torab-Mostaedi et al., 2017; Asadollahzadeh et al., 2016), Kuhni column (Hemmati et al., 2015; Arab et al., 2017; Oliveira et al., 2008), packed column (Rahbar-Kelishami and Bahmanyar, 2012; Torab-Mostaedi and Safdari, 2009), pulsed column (Amani et al., 2017; Khooshechin et al., 2013; Usman et al., 2009), tray column (Sincuba et al., 2017), and spray column (Salimi-Khorshidi et al., 2013), are available. Single drop tests can provide valuable insights regarding the hydrodynamics of the complex systems in the liquid-liquid extraction. These specifications include the drop form (Al-Hassan et al., 1991; Henschke and Pfennig, 1999; Clift et al., 2005), drop oscillation (Al-Hassan et al., 1991; Brunson and Wellek, 1970) and circulation (Al-Hassan et al., 1991; Wegener et al., 2010; Slater et al., 1988), the boundary layer around the moving drops (Kumar and Hartland, 1999), the initial concentration of solute (Wegener et al., 2007; Wegener et al., 2009; Mao and Chen, 2004; Engberg et al., 2014; Paschedag and Wegener, 2006; Burghoff and Kenig, 2006), and drop velocity (Adinata and Pfennig, 2011; Torkaman et al., 2014). In liquid-liquid extraction, the selection of appropriate solvents is important. Indeed, the selected solvent should have high dipole moment and thermal stability, as well as low viscosity, corrosivity, toxicity, and combustibility. In addition, a suitable solvent must be inexpensive and its boiling point should differ

**Table 1.** Some available processes for oxidative/extractive desulfurization of middle distillate fuels in the pilot plant scale.

Company name	Oxidation system	General specification	References
Petrostar conversion/extraction desulfurization (CED) process	Hydrogen peroxide/ acetic acid	<ul style="list-style-type: none"> <li>• Sulfone separation by liquid-liquid extraction</li> <li>• API gravity and Cetane number improvement</li> <li>• Further development is needed before licensing and commercialization</li> </ul>	Stanislaus et al., (2010); Jalali and Sobati, (2017)
Lyondell process	Tert-Butyl hydroperoxide/ solid catalyst	<ul style="list-style-type: none"> <li>• Fixed bed single liquid oxidation system</li> <li>• Sulfone removal by liquid-liquid extraction</li> <li>• Production of t-butyl alcohol as new by-product</li> </ul>	Ito and Van Veen (2006); Jalali and Sobati, (2017)

More details can be found elsewhere (Jalali and Sobati, 2017).

from the oxidized sulfur-containing compounds. On the other hand, solvents with high boiling points are not suitable (Babich and Moulijn, 2003; Otsuki et al., 2000; Mjalli et al., 2014; Sobati et al., 2010; Heidari et al., 2013). Dimethylformamide, dimethyl sulfoxide, methanol, ethanol, acetonitrile, sulfolane, N-methyl-2-pyrrolidone, and lactones are some of the most important polar solvents (Sobati et al., 2010). Previous studies regarding the removal of oxidized sulfur-containing compounds from fuels using the extraction process are summarized in Table 2.

In addition, important studies have been done with single drop systems. Azizi and Rezaeimanesh (2016) measured the effect of drop diameter on the mass transfer coefficient of rising drops in a spray and packed column with random and structured packing in a liquid-liquid extraction operation and chemical system of toluene/acetic acid/water with high interfacial tension. Wegener et al. (2010) presented a correlation to describe the rising velocity of toluene drops in water with different drop diameters and different nozzle materials based on Grace (1976) semi-empirical theory. Hashem and El-Bassuoni (2007) also investigated the influence of various parameters such as the formation time, needle size, and flow rates of the continuous and dispersed phase on the mass transfer rate for an acetic acid/toluene/water system. Wegener

et al. (2007) conducted an experimental study to investigate the rising velocity of drops and mass transfer in a single drop system containing toluene/acetone/water. They also studied the effect of adding the solute (acetone) and its initial concentration on the different drop diameters.

Based on our knowledge, there is no report available regarding the separation of oxidized sulfur-containing compounds from diesel in a single drop system. Therefore, the main aim of the present study is the investigation of the hydrodynamic aspects of the separation of oxidized sulfur-containing compounds from diesel as a real fuel in a single drop system. In this regard, after solvent selection, the effects of different parameters, including the drop diameter, column height, terminal, and maximum velocity, are investigated.

## MATERIALS AND METHODS

### Materials

Non-hydrotreated diesel with a total sulfur content of 1550 ppm was used as feedstock. Table 3 shows the specifications of the diesel feedstock. Chemical compounds used in the present study, including formic acid (98-100%), hydrogen peroxide (30 wt%), dimethylformamide (DMF) ( $\geq 99.8\%$ ) and dimethyl

**Table 2.** Previous studies regarding the separation of oxidized sulfur-containing compounds by solvent extraction.

Source	Extraction system	Studied parameters
Sobati et al. (2010)	Acetonitrile, methanol, ethanol 96 vol. %	<ul style="list-style-type: none"> <li>The effect of solvent to fuel ratio</li> <li>The effect of number of extraction stages</li> <li>Evaluation of solvent effectiveness factor</li> </ul>
Ramirez-Verduzco et al. (2004)	Acetonitrile, C <sub>4</sub> H <sub>6</sub> O <sub>2</sub> , DMF, C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	<ul style="list-style-type: none"> <li>The comparison of sulfur, aromatics, and nitrogen removal after the extraction and oxidation/extraction using different solvents</li> </ul>
Ali et al. (2006)	Acetonitrile	<ul style="list-style-type: none"> <li>The comparison of extraction and extraction/oxidation on the removal of sulfur containing compound</li> <li>The effect of solvent on fuel quality</li> </ul>
Zannikos et al. (1995)	Methanol, DMF, NMP	<ul style="list-style-type: none"> <li>The effect of different solvents on the desulfurization in the extraction/oxidation and extraction processes</li> <li>solvent effectiveness factor by using different solvents</li> </ul>
Hassan et al. (2013)	DMSO	<ul style="list-style-type: none"> <li>Present a three-phase equilibrium diagram for oxidized diesel fuel</li> <li>study of sulfur and aromatic containing compound removal after the extraction and oxidation/extraction</li> </ul>
Otsuki et al. (2000)	DMF, DMSO, acetonitrile, methanol, Sulfolane	<ul style="list-style-type: none"> <li>Study of the desulfurization and fuel recovery after the extraction and oxidation/extraction using different solvents</li> <li>The effect of number of extraction stages on the different fuels</li> </ul>
Heidari et al. (2013)	Methanol, propanol, acetone, acetonitrile	<ul style="list-style-type: none"> <li>The effect of solvent concentration, solvent to fuel ratio, temperature, mixing time and number of extraction stages on the desulfurization and fuel recovery in the oxidation/extraction process using different solvents</li> </ul>
Palaić et al. (2015)	DMF, acetonitrile	<ul style="list-style-type: none"> <li>The effect of solvent to fuel ratio on the extraction efficiency</li> <li>Comparison of the effect of ultrasound and mechanical stirrer on the oxidation</li> </ul>
Dehkordi et al. (2009b)	Methanol, ethanol, propanol	<ul style="list-style-type: none"> <li>The effect of different solvents on the extraction process</li> </ul>
Maity et al. (2014)	Acetonitrile, DMSO, 1-ethyl 3-methyl imidazolium ethyl sulfate	<ul style="list-style-type: none"> <li>The effect of stirring time, extraction temperature, amount of solvent on the desulfurization, comparison of extraction, oxidation and simultaneous oxidation extraction methods</li> </ul>
Otaibi et al. (2015)	DMF, DMSO, ethanol, ethylene glycol, furfural	<ul style="list-style-type: none"> <li>Optimization of the oxidation and extraction conditions using different fuels</li> </ul>

**Table 3.** The specifications of the diesel feedstock.

Characteristic	Content	Test method
Density at 15 °C (kg/m <sup>3</sup> )	832	ASTM D4052
Sulfur content(ppm)	1550	ASTM D4294
Kinematic viscosity at 40 °C(cSt)	3.10	ASTM D445
Flash point(°C)	62	ASTM D93
Water content(ppm)	38	ASTM D6304
Cetane index	55.77	ASTM D4737
Distillation range(°C)		ASTM D86
Initial boiling point(I.B.P)	168.0	
10%	198.5	
20%	221.0	
30%	245.0	
40%	264.5	
50%	281.5	
60%	296.5	
70%	313.0	
80%	327.0	
90%	347.0	
95%	360.0	
Final boiling point(F.B.P)	375.0	

sulfoxide (DMSO) ( $\geq 99.9\%$ ), were obtained from Merck Co. (Germany). All of the mentioned chemicals were used as received without further purification.

### Analysis method

A Rigaku NEXQC+ (Rigaku, Japan) was used to determine the total sulfur content of samples in accordance with ASTM D4294. Rigaku NEXQC+ has the total sulfur detection range of 0-5 wt% and a lower detection limit of 25 ppm. The other fuel specifications such as flash point, water content, cetane index and distillation range were measured according to ASTM D93, ASTM D6304, ASTM D4737, and ASTM D86, respectively.

### The procedure of oxidation of diesel

Appropriate conditions for the oxidation of diesel were selected from Sobati et al. (Sobati et al., 2010). Oxidation was performed in a 1L three-necked glass reactor equipped with a condenser and thermometer. The reactor was placed in a circulating water bath in order to set the temperature. 415 mL of diesel with a total sulfur content of 1550 ppm was introduced into the reactor and then 44.25 mL of formic acid was added to the reaction container. The mixture was heated to 55 °C and was stirred continuously for 30 min. Then, 8.52 mL of hydrogen peroxide (30 wt. %) was added to the reactor as an oxidizing agent and the mixture was stirred vigorously for 150 minutes. After passing the reaction time, the mixture was introduced to a separatory funnel to separate aqueous and hydrocarbon phases. Then, the lower phase (i.e., the aqueous phase) was removed and the upper phase (i.e., the oxidized hydrocarbon phase) was washed three times with distilled water to remove any entrained aqueous phase. Finally, the oxidized diesel was used for solvent extraction experiments in a single-drop system.

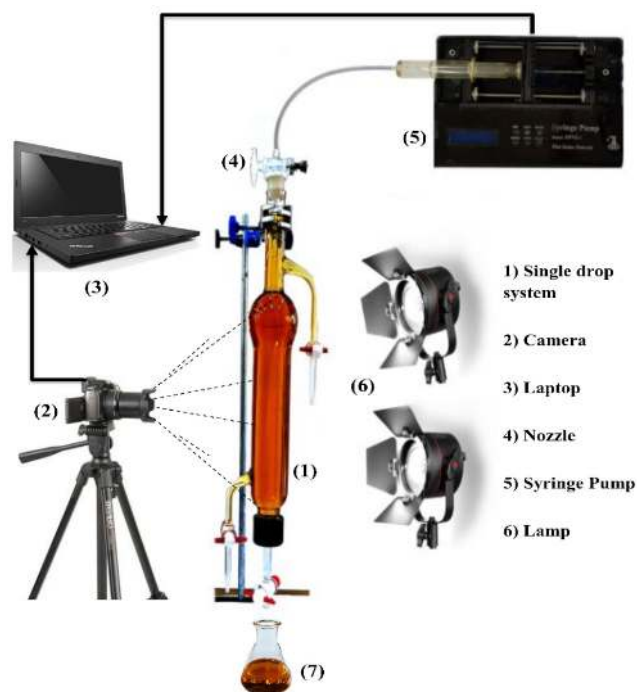
### The procedure of diesel extraction for solvent selection

The effects of different parameters such as volume ratio of solvent to fuel and the number of extraction stages on the desulfurization were investigated to choose the appropriate solvent for separation of oxidized sulfur-containing compounds from diesel.

Extraction of oxidized sulfur-containing compounds was carried out in a 250 mL flask at ambient temperature with the stirring rate of 875 rpm for 30 min. In each experimental extraction run, 40 mL of the oxidized diesel was introduced into the flask and the pre-determined volume of solvent was added to the extraction flask. After extraction experiments, the mixture was introduced into a separatory funnel to separate aqueous and hydrocarbon phases. Then, the hydrocarbon phase was washed three times with distilled water to remove any entrained solvent. It should be noted that the procedure was repeated for some experiments in which the effect of number of extraction stages was investigated. Finally, the treated diesel samples were used to determine total sulfur content.

### The procedure of single-drop experiments

The applied experimental set up for single drop tests is shown in Figure 1. In single drop experiments, the oxidized diesel and the selected solvent (i.e., DMF) were used as feed and extraction solvent, respectively. DMF and oxidized diesel were selected as the dispersed and continuous phases, respectively. DMF was injected into the continuous phase (i.e., oxidized diesel) in the form of drops from the top of the

**Figure 1.** The experimental set-up for single drop test



column because the DMF density was higher than the oxidized diesel density. In addition, six glass nozzles with different diameters were selected to cover a wide range of drop size from the rigid sphere region to the oscillation region. It should be noted that ambient temperature and pressure conditions were selected for the single drop test. A syringe pump (made by Zist rahe danesh Co., Iran) was used to inject the solvent in the form of regular drops with a specific flow rate. It should be added that, in all experiments, 10.79 mL of solvent was used. Table 4 shows the diameter of the equivalent sphere with the volume of drop produced using different nozzles.

In addition to the drop diameter, the column height (H) was considered as a variable. In this regard, three columns with the heights of 228, 400, and 550 mm and volumes of 465, 700 and 980 mL were built. Internal and external diameters of the columns were 4.60 and 5 cm, respectively. Considering 6 different drop diameters and 3 different column heights, 18 different experimental runs should be carried out. Also, to get the instantaneous and terminal velocities of drops, it was necessary to video record the tests. For this purpose, a Nikon D3200 camera was used. In all experiments, a frame rate of 30 Hz was used. The camera position was vertical and standing against the columns, and all directions of drop motion were video recorded throughout the columns. The applied lighting system also included two simple bulbs that had low thermal radiation for the camera and created a stable illumination for the entire system. Afterwards, a computer code was used for image processing in order to obtain the ratio of drop displacement with time interval (i.e., drop falling velocity). In this regard, the videos were converted into the corresponding images. Then, the drop distances from a same point in two consecutive images were obtained. The drop displacement between two consecutive images was equal to the difference between these distances. In addition, the time interval between two consecutive images was the inverse value of the frame rate for each video. Finally, the drop falling velocity between two images was obtained by dividing the drop displacement by the time interval.

**Table 4.** Drop diameter produced by different nozzles.

Nozzle	Drop diameter (D, mm)	Nozzle	Drop diameter (D, mm)
1	1.70	4	3.70
2	2.50	5	4.10
3	3.10	6	4.60

## RESULTS AND DISCUSSION

### Characteristics of oxidized diesel

The characteristics of the oxidized diesel are shown in Table 5.

**Table 5.** General specifications of the oxidized diesel before the extraction step.

Characteristic	Content	Test method
Density at 15 °C (kg/m <sup>3</sup> )	828	ASTM D4052
Sulfur content (ppm)	1230	ASTM D4294
Kinematic viscosity at 40 °C (cSt)	2.94	ASTM D445
Water content (ppm)	39	ASTM D6304

The untreated diesel had a total sulfur content of 1550 ppm. Desulfurization percent for the treated fuels was calculated by equation (1):

$$\text{Desulfurization (\%)} = 100 \times \frac{(S_i - S_f)}{S_i} \quad (1)$$

where  $S_i$  and  $S_f$  are the total sulfur content of untreated and treated fuels, respectively.

It was observed that the total sulfur content of diesel decreased to 1230 ppm after oxidation. In other word, the desulfurization after the oxidation step is about 20.65 %. It should be noted that the mentioned sulfur removal is achieved by *in situ* extraction of oxidized sulfur-containing compounds into the aqueous phase of the oxidation system (i.e., a mixture of formic acid and hydrogen peroxide). It should be added that the presence of formic acid in the aqueous phase increases the polarity of the aqueous phase, which in turn leads to *in situ* extraction of part of the polar oxidized sulfur-containing compounds.

### The choice of an appropriate solvent

Dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were selected as polar solvents to investigate the sulfur removal experimentally. Tables 6 and 7

**Table 6.** Effect of solvent to fuel ratio on the desulfurization of the oxidized diesel using DMSO and DMF: extraction time=30 min, stirrer rate=875 rpm, extraction temperature= 28 °C, No. of extraction stage =1.

Volume ratio of solvent to fuel (mL/mL)	0.50	1	2	3
Desulfurization (%) using DMSO	79.50	84.50	90.40	91.70
Desulfurization (%) using DMF	85.50	92.30	94	95.50

**Table 7.** Effect of number of extraction stages on the desulfurization of the oxidized diesel using DMSO and DMF: extraction time=30 min, stirrer rate=875 rpm, extraction temperature=28 °C, Volume ratio of solvent to fuel =1.

Number of extraction stages	1	2	3
Desulfurization (%) using DMSO	84.50	92.60	94.20
Desulfurization (%) using DMF	92.30	97.40	97.80

show the desulfurization of the oxidized diesel using different solvent to fuel volume ratios and number of extraction stages, respectively.

As can be seen, the desulfurization increases upon increasing the volumetric ratio of solvent to fuel and the number of extraction stages. Also, DMF showed the best performance in term of desulfurization. Therefore, DMF solvent was selected for the single drop tests.

### The effect of drop diameter and column height on the terminal and maximum velocity of drops

The maximum falling velocity of a drop, obtained from image processing, is the average of all maximum velocities for a given drop diameter, considering at least three consecutive drops. This velocity usually occurs after the first acceleration of the drop released from the nozzle. The terminal velocity is also the average of all obtained velocities after the maximum velocity. Various studies show that the terminal velocity is increased by an increase in the drop diameter. However, a maximum velocity is achieved for large diameter drops and then a decreasing trend is observed for the terminal velocity. The difference between the values of maximum and terminal velocities is increased when the Weber number is close to the critical value (Wegener et al., 2010). The critical diameter can be obtained using the Edge and Grant equation (Edge and Grant, 1971).

$$d_{cr} = \frac{1.62}{\left(\frac{\Delta\rho}{\rho_d}\right)^{0.5}} \quad (2)$$

where  $d_{cr}$ ,  $\rho_d$ , and  $\Delta\rho$  are the critical diameter (cm), dispersed phase density ( $\text{g/cm}^3$ ), and the difference between the values of density for the dispersed and hydrocarbon phases ( $\text{g/cm}^3$ ), respectively. The critical diameter in our system was calculated as 4.55 mm. According to eq.2, the critical diameter is not dependent on the column height.

The data obtained for the terminal velocity were also compared with the results predicted using the Grace correlation. It should be mentioned that, since the majority of the single drop systems are contaminated, the terminal velocity can be obtained from equations (3-5) provided by Grace (1976):

$$\text{Re} = \frac{\rho_c d_e U_\infty}{\mu_c} = (J - 0.857) M^{-0.149} \quad (3)$$

where:

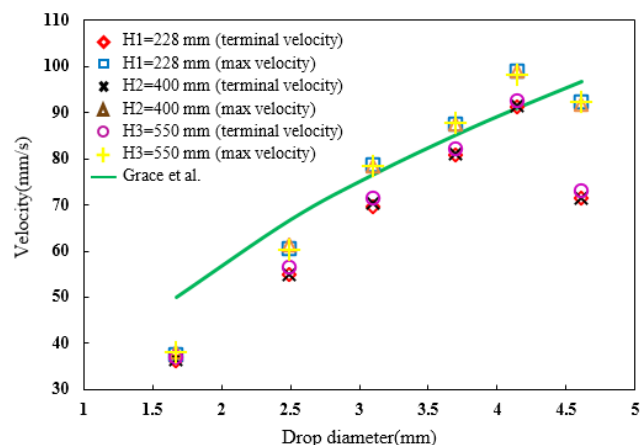
$$J = \begin{cases} 0.94N^{0.757} & 2 < N \leq 59.30 \\ 3.42N^{0.441} & N > 59.30 \end{cases} \quad (4)$$

and  $N$  is expressed by the following equation:

$$N = \frac{4}{3} \text{Eo} \cdot M^{-0.149} \left(\frac{\mu_c}{0.0009}\right)^{-0.14} \quad (5)$$

In these equations,  $d_e$ , and  $\mu_c$  are the drop diameter and the viscosity of the oxidized diesel in SI units, respectively. Also,  $\text{Re}$ ,  $M$ , and  $\text{Eo}$  are the Reynolds number, Morton number, and Eötvös number, respectively. Figure 2 shows the values of terminal and maximum velocities versus drop diameter.

As can be observed in Figure 2, increasing the drop diameter leads at first to an increase in the terminal and maximum velocities. Then, these velocities are slightly decreased after reaching a critical diameter. It was also observed that increasing the column height does not affect the maximum velocity and terminal velocity of the drops. In addition, the difference between the values of maximum and terminal velocities increases upon increasing the drop diameter. Besides, this increase is greater in the oscillating region in comparison with the circulating and rigid sphere regions. Also, the values of terminal velocity obtained from the correlation of Grace (i.e., eq. 3-5) are plotted in Fig. 2. It is observed that there is a fair agreement between the experimental data and the data predicted using the Grace (1976) correlation. This agreement in the circulation region is more pronounced in comparison with the rigid sphere and the oscillation regions (Table 8). This is because the Grace correlation is usually applied for elliptical drops in the circulation region (Grace, 1976).



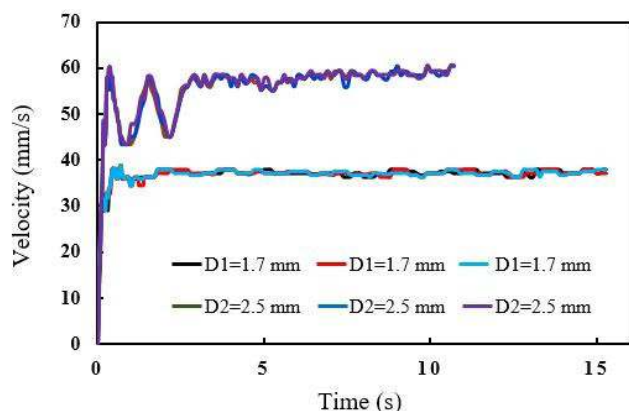
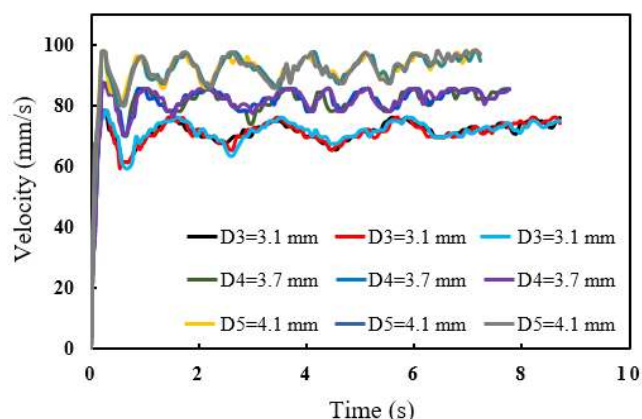
**Figure 2.** Comparison of the terminal and maximum velocity for different drop diameters and column heights.

### Investigation of the instantaneous and terminal falling velocities of drops

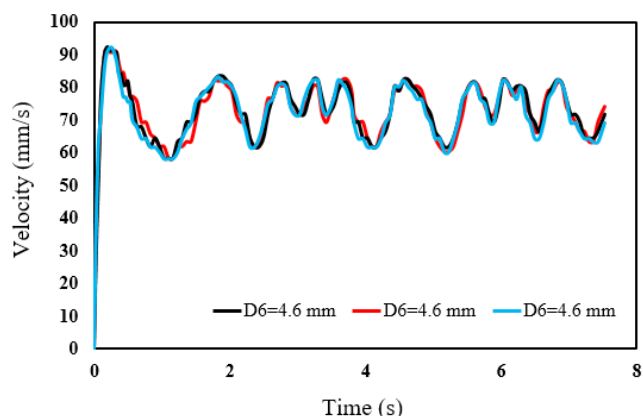
Figures 3, 4 and 5 show the variations of the instantaneous velocity of drop versus time for different drop diameters. It should be noted that the plots are provided for three consecutive drops. As can

**Table 8.** Prediction error of the Grace correlation for terminal velocities in different conditions.

Run	Column height (mm)	Drop diameter (mm)	% Error
1	228	1.70	38.20
2		2.50	21.43
3		3.10	9.76
4		3.70	5.33
5		4.10	0.21
6		4.60	35.13
7	400	1.70	36.60
8		2.50	20.86
9		3.10	8.76
10		3.70	4.59
11		4.10	0.70
12		4.60	35.25
13	550	1.70	34.81
14		2.50	18.03
15		3.10	6.96
16		3.70	3.28
17		4.10	1.82
18		4.60	32.50

**Figure 3.** Variations of the drop instantaneous velocity versus time for drops in the rigid sphere and semi-rigid sphere regions.**Figure 4.** Variations of the drop instantaneous velocity versus time for drops in the circulating region.

be observed, the instantaneous velocity profiles are in good agreement for these three drops.

**Figure 5.** Variations of the drop instantaneous velocity versus time for drops in the oscillation region.

As shown in Figs. 3, 4 and 5, four different behaviors are observed for drops with different diameters. For small drops (i.e., diameter 1 with the size of 1.70 mm), the value of the drag coefficient is closer to the value of the drag coefficient of a rigid sphere and the inertial forces are negligible in comparison with interfacial tension and viscous forces. For this drop diameter, no significant deformation occurs and the drops usually exhibit the rigid sphere behavior. In this region, the drop accelerates immediately after its release and then the drop velocity does not change and fluctuates slightly around the same velocity. In fact, for this drop diameter, the difference between the values of maximum and terminal velocities is very low. Upon increasing the diameter from 1.70 to 2.50 mm (D2), the drop oscillation begins a short period after releasing the drop, but the intermediate surface forces are stronger than the inertial forces. In this case, the drop is stretched at the nozzle tip. In this region, the deformation is quickly adjusted and the velocity is fixed after 3s and reaches a value on the order of magnitude close to the value of the maximum velocity, and no more fluctuations occur. Also, for this diameter and larger diameters, the tangential shear stress is applied on the drop interface by the continuous phase and droplet circulation occurs. These intermediate surface movements reduce the drag and increase the velocity in comparison with the velocity related to the rigid sphere region (Fig. 3).

For diameters of 3.10, 3.70 and 4.10 mm (i.e., D3, D4, D5), the velocity is maximized after the drop is released. Then, the velocity decreases and fluctuates around a lower value. Unlike drops with a diameter of 2.50 mm, the velocity remains constant at this low value. As a result, the terminal velocity is lower than the maximum velocity, but the difference between the values of these two velocities is small for these drops and the drops are not oscillating. Also, for these drops, increasing drop diameter leads to a decrease in the drag coefficient to the minimum drag point. The



higher velocity of drops with a larger diameter ( $D3 < D4 < D5$ ) can be attributed to the lower values of drag coefficient, which in turn increases the circulations for these drops and as a result increases the drop velocity (Fig. 4).

By increasing the drop diameter from 4.10 to 4.60 mm (i.e., D6), the drop velocity decreases and its oscillation becomes more intense in comparison with other drop sizes. In other words, the drop with this diameter is in the oscillating region. In addition, the oscillations are due to a high deformation rate of the drop. The deformation leads to an increase in the drag coefficient and a subsequent decrease in the drop velocity. For this diameter, the drop velocity decreases after reaching a maximum value and fluctuates around a lower value, but with more variations. As a result, there is a large difference between the maximum and terminal velocities of the drop in this region (Fig. 5).

The effect of drop diameter on terminal and transient drop rise velocity of single toluene droplets in water was investigated by Wegener et al. (2010). They observed that the drop velocity increases after releasing it from the nozzle tip, so that the velocity reached a maximum value. For rigid drops, the terminal velocity is equal to the maximum velocity. Upon increasing the drop diameter, circulations begin inside the drop and the instantaneous velocity fluctuates around a mean value. Finally, increasing the drop diameter beyond the critical diameter leads to drop oscillation and a subsequent decrease in the terminal velocity. The same behavior was observed by different researchers (Edge and Grant, 1971; Wegener et al., 2007; Wegener et al., 2014).

As was already mentioned, drop deformation is the main factor affecting the drop velocity. The deformation can change the drag coefficient and the forces applied to the drop, and thus affect the drop velocity. According to Figs. 3, 4, and 5, the observed high variations in the velocity profile at the beginning of the diagrams are due to changing the drop shape from prolate to oblate spheroid after release from the nozzle. This deformation alters the drag coefficient, which in turn leads to the drop velocity change (Fig. 6) (Popovich et al., 1971; Wegener et al., 2010).

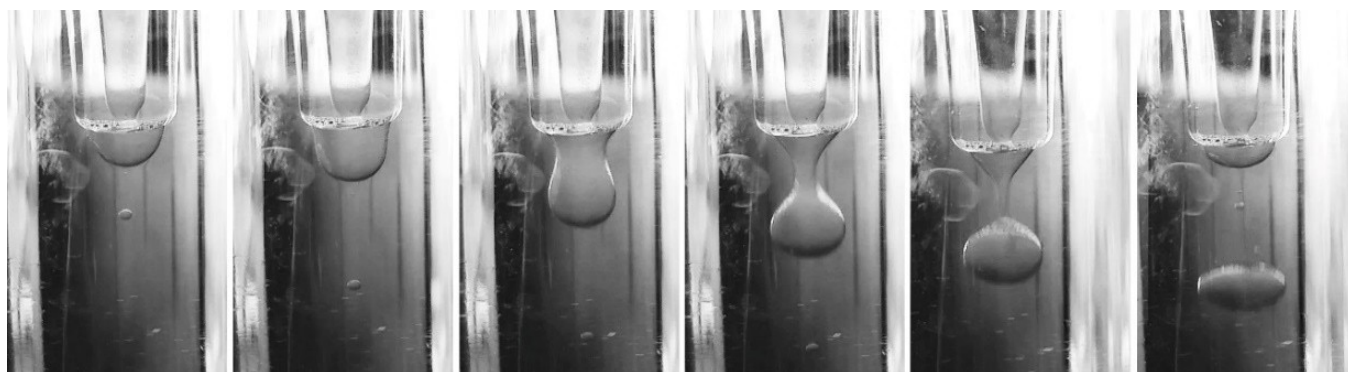


Figure 6. Drop deformation after releasing from the nozzle tip.

The drop falling time decreases with increasing drop diameter to the critical diameter, but in the oscillating region (i.e., the diameter beyond the critical diameter), the drop falling time increases. The profiles shown in Figs. 3, 4, and 5 are related to the column with the largest height, but for the other columns, the aforementioned subjects can also be applied. The only difference for these columns is the falling time of drops, which is higher for the columns with larger heights (Fig. 7).

Figure 8 shows the variations of drop velocity versus the falling time for different drop diameters and column heights.

It should be noted that the drop velocity was measured twice for different drop diameters and column heights. The reported values for the instantaneous and terminal velocities in Figures 3, 4, 5, and 8 are the mean drop velocity for two different experiments with the relative standard deviations lower than 4%.

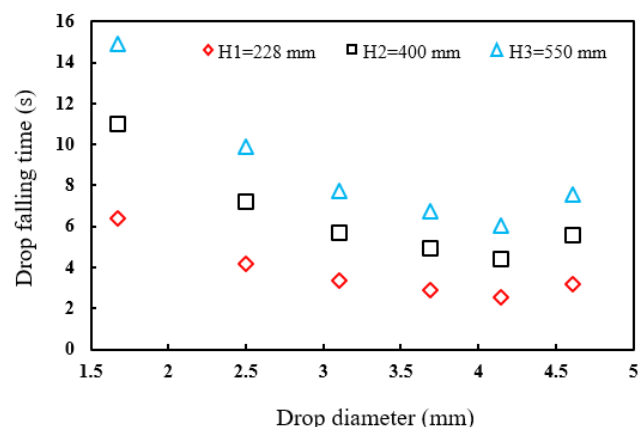
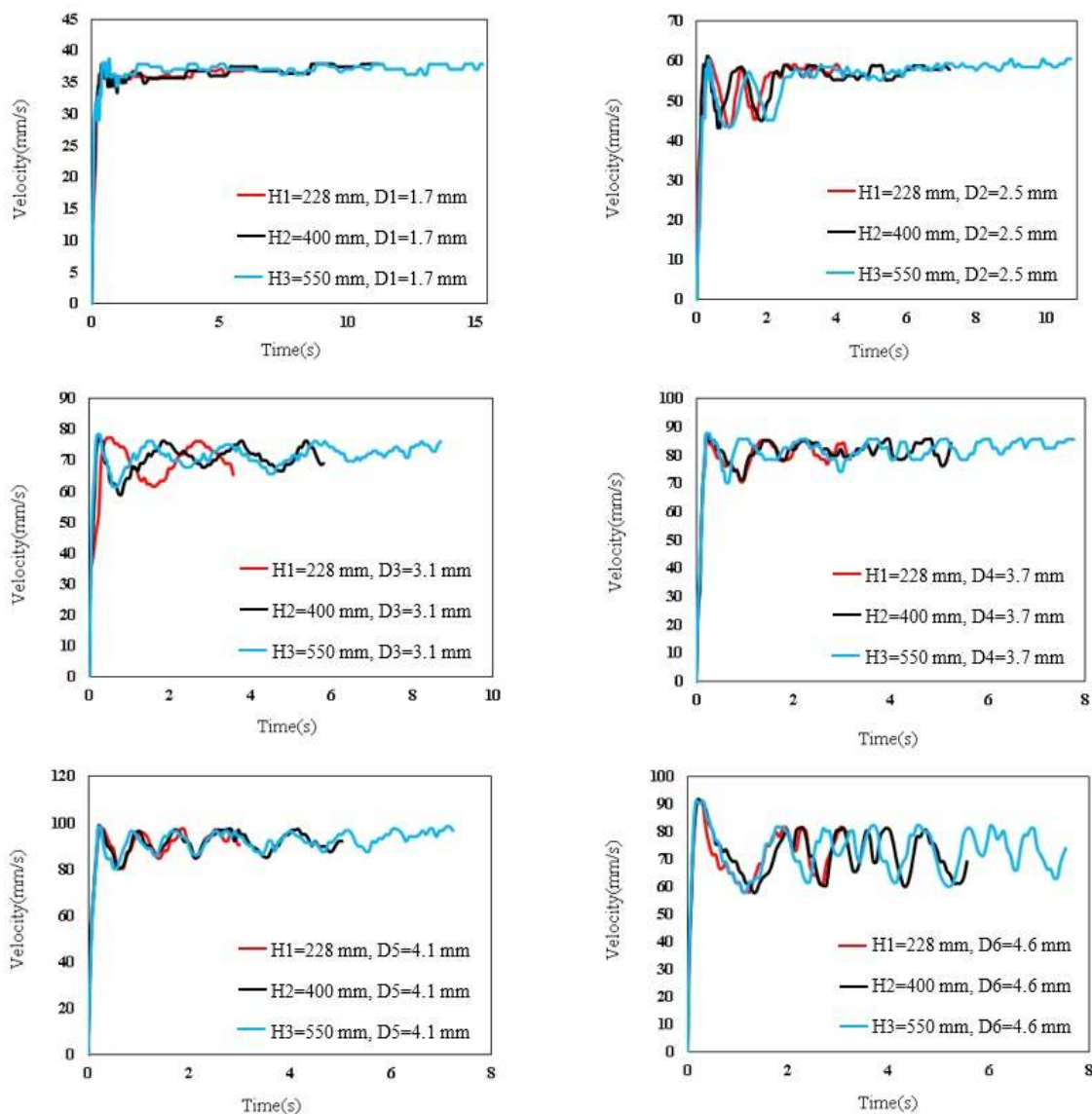


Figure 7. Drop falling time versus drop diameter for different column heights.

### The concentration of sulfur in the continuous and dispersed phases

After conducting the single-drop experimental runs, the sulfur concentration in the dispersed phase was determined using the total sulfur analyzer. Afterwards, the concentration of sulfur in the hydrocarbon phase was predicted using eq. 6:





**Figure 8.** Variations of drop velocity versus the falling time for different drop diameters and column heights.

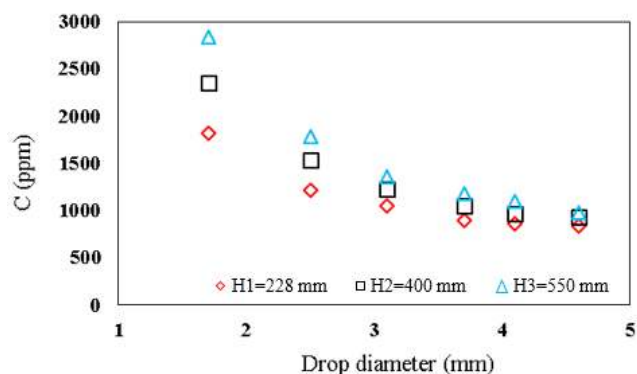
$$C_{\text{fuel}} = 1230 - \frac{C_{\text{solvent}} \times \rho_{\text{solvent}}}{\rho_{\text{fuel}}} \times \frac{V_{\text{solvent}}}{V_{\text{fuel}}} \quad (6)$$

where  $C_{\text{solvent}}$ ,  $C_{\text{fuel}}$  are the concentration of sulfur in the solvent and oxidized diesel after extraction (ppm), respectively.  $\rho_{\text{solvent}}$  and  $\rho_{\text{fuel}}$  are the values of the density of the solvent and the oxidized diesel, respectively.  $V_{\text{solvent}}/V_{\text{fuel}}$  is the volumetric ratio of solvent to oxidized diesel. 1230 ppm is the total sulfur content of oxidized diesel feedstock. It should be noted again that the total sulfur content of diesel decreased from 1550 to 1230 ppm after oxidation due to *in situ* extraction of some of the oxidized sulfur-containing compounds into the aqueous phase of the oxidation medium (i.e., hydrogen peroxide-formic acid mixture).

Figure 9 shows the variations of sulfur concentration in the dispersed phase versus drop diameter at different column heights.

It should be noted that the measurements were carried out twice in order to verify the accuracy of the experimental data. The relative standard deviation (%) for the sulfur content of the dispersed phase was less than 2%, which confirms the accuracy of the experiments.

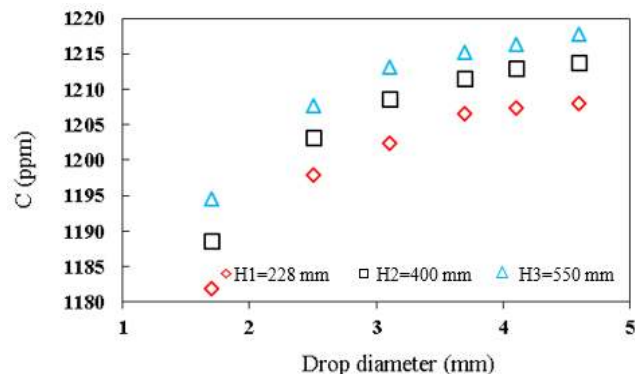
As can be observed in Fig. 9, an increase in the drop diameter leads to a decrease in the sulfur concentration in the dispersed phase. This behavior can be explained as follows: using the constant volume of the dispersed and hydrocarbon phases (i.e., constant height), the number of small drops produced is larger in comparison with that of the large drops and, as a result, the overall contact surface will be larger for the small drops in comparison with large drops. Also, the residence time is longer for the small drops in comparison with large drops, which leads to an increase in the mass transfer time of the dispersed and hydrocarbon phases. As a



**Figure 9.** Variations of sulfur concentration in the dispersed phase versus drop diameter at different column heights.

result, the extent of total sulfur mass transfer (i.e., total desulfurization) for the dispersed phase with small drops is larger in comparison with the large drops. In addition, the variation in the concentration with drop size is large at first and decreases gradually. This behavior is due to the fact that the differences between the residence time and the number of produced drops for the first two drop sizes are larger in comparison with those of the next two larger drops, which makes the difference between the mass transfer extent more pronounced for the small drop sizes at the beginning of the graph. It should also be noted that increasing the column height for the same drop diameter leads to an increase in the sulfur concentration in the dispersed phase. This finding can be explained as follows. Using the same volume of the dispersed phase, the drop residence time at higher column height is large, and thus the extent of mass transfer from the continuous phase to the dispersed phase will be greater. In addition, upon increasing the column height, the difference in the values of sulfur concentration between two heights 1 and 2 is larger in comparison with the difference between heights 2 and 3. This behavior can be attributed to two points. The first point is that the difference in height (i.e., the difference in the residence time) between columns 1 and 2 is greater than that for columns 2 and 3. The second reason may be that, by increasing height, the concentration gradient and changes in the mass transfer extent are reduced, which in turn results in the changes in the mass transfer between the two heights of 1 and 2 being greater in comparison with those of 2 and 3. Also, the effect of increasing column height on the sulfur concentration decreases upon increasing the drop diameter. Figure 10 shows the variations of sulfur concentration in the hydrocarbon phase versus drop diameter of the dispersed phase using different column heights.

As can be observed in Fig. 10, increasing the drop diameter and column height leads to an increase in the remaining sulfur content in the hydrocarbon phase. An increase in the column height leads to a decrease in



**Figure 10.** Variations of the sulfur concentration in the hydrocarbon phase versus drop diameter of the dispersed phase at different column heights.

the value of volumetric ratio of solvent to fuel, which in turns leads to a subsequent decrease in the sulfur removal from the continuous phase (i.e., oxidized diesel). It should be noted that the low sulfur removal from the continuous phase can be attributed to the selected low values of the solvent to fuel volumetric ratios, which are 1/43.1, 1/64.9, and 1/90.9 for column heights of 228, 400, and 550 mm, respectively.

## CONCLUSION

In the present study, an experimental investigation was conducted on the desulfurization of diesel by oxidation followed by extraction in a single drop column. The effects of solvent to fuel ratio and number of extraction stages on the desulfurization were studied in batch extraction mode using DMF and DMSO as solvents. After the solvent screening stage, a single drop system was used to remove the oxidized sulfur-containing compounds from diesel using DMF. According to the results, the drop velocity in the rigid sphere region is minimum, but the drop velocity increases upon increasing the drop diameter, starting drop circulation. The oscillations reduce the drop velocity for drop sizes greater than the critical diameter. Therefore, the drop falling time decreases at first upon increasing the drop diameter and then increases beyond a certain drop size. It was found that the column height did not affect the terminal and maximum velocities of drops. It was also observed that the velocity oscillations at the column entrance zone were greater in comparison with other zones due to the large deformation rate of the drop. It was found that the difference between the values of terminal and maximum velocity increases upon increasing the drop diameter. In addition, a fair agreement was observed between the experimental terminal velocities and predicted terminal velocity using the Grace correlation (Grace, 1976). It was also found that the concentration of sulfur in the dispersed phase decreases upon

increasing the drop diameter. However, it was also found that the concentration of sulfur in the dispersed phase increases upon increasing the column height. Also, the total desulfurization of the hydrocarbon phase as the continuous phase was decreased upon increasing the drop diameter and column height.

### ACKNOWLEDGMENTS

The authors would like to acknowledge the support provided by the National Iranian Oil Engineering and Construction Company (NIOEC).

### NOMENCLATURE

$C_{\text{fuel}}$	Concentration of sulfur in the oxidized diesel after extraction, ppm
$C_{\text{solvent}}$	Concentration of sulfur in the solvent after extraction, ppm
$d_{\text{cr}}$	Critical diameter, m
$d_e$	Drop diameter, m
EO	Eötvös number
M	Morton number
Re	Reynolds number
$S_f$	Total sulfur content of treated fuel, ppm
$S_i$	Total sulfur content of untreated fuel, ppm
$U_{\infty}$	Terminal velocity, m/s
$V_{\text{solvent}}/V_{\text{fuel}}$	Volumetric ratio of solvent to oxidized diesel
$\rho_c$	Continuous phase density, kg/m <sup>3</sup>
$\rho_d$	Dispersed phase density, kg/m <sup>3</sup>
$\rho_{\text{fuel}}$	Density of oxidized diesel, kg/m <sup>3</sup>
$\rho_{\text{solvent}}$	Density of solvent, kg/m <sup>3</sup>
$\Delta\rho$	Difference between the values of density for the dispersed and hydrocarbon phases, kg/m <sup>3</sup>
$\mu_c$	Viscosity of the oxidized diesel, Pa.s

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