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Dimensionless evaluation and kinetics of rapid and ultradeep desulfurization of diesel fuel in an oscillatory baffled reactor†

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The oxidative desulfurization (ODS) of dibenzothiophene in diesel fuel cut using a homogeneous liquid catalytic system in a novel reactor is presented. Hydrogen peroxide was the oxidizing agent and acetic acid was the liquid catalyst. The oxidation process was conducted in a meso-oscillatory baffled reactor ("mesoOBR") under mild operating conditions: atmospheric pressure, and 60 to 80 °C. The reactor was operated over a range of residence times (1–3 min), and frequencies and amplitudes of oscillation, leading to oscillatory Reynolds numbers in the range 64–383, and net flow Reynolds numbers in the range 5 to 16. The results showed that dibenzothiophene (DBT) removal in the OBR was significantly higher than in conventional processes under the same conditions (pressure of 1 atm and temperature near room temperature). The maximum DBT conversion was 94%, which was achieved in 3 min at 4 Hz and 6 mm amplitude. A significant improvement in the removal efficiency of DBT was achieved in OBR within only 3 minutes compared to previous studies, which required at least a half-hour reaction time to achieve the same or less removal efficiency. A reaction kinetic model was developed using the optimum experimental results achieved in the OBR. The apparent reaction order was 1, with significantly low apparent activation energies (24.7–29.0 kJ mol⁻¹).

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1. Introduction

Among the wide variety of contaminants in fossil fuels (*e.g.*, crude oil, jet fuel, gasoline, diesel, *etc.*), naturally occurring organic sulfur compounds (OSCs) are the most abundant.^{1–3} The most common OSCs in fossil fuels are sulfides, disulfides, mercaptans, and thiophene (Th), and their derivatives. These types of OSCs release toxic SO_x, upon combustion, leading to health and environmental problems.^{3–6} The most common technique for removing these compounds is hydrodesulfurization, however, the hydrodesulfurization (HDS) process requires severe operating conditions (high pressure and temperature), expensive hydrogen gas, and it is less useful in the removal of thiophene and its derivatives like DBT. Among the alternative desulfurization technologies to hydrodesulfurization, oxidative desulfurization (ODS) has received a great deal of attention in academia and industry.^{7,8} ODS involves organic sulfur compounds being oxidized to their corresponding sulfoxides and/or sulfones.^{9–11} Nawaf *et al.*¹² investigated the ODS of DBT in light gas oil (LGO) using air as an oxidant under moderate operating conditions (atmospheric

pressure, temperature range (130–200) °C) with MnO₂/γ-Al₂O₃ as a catalyst in a trickle bed reactor under various operating conditions as follows: atmospheric pressure, temperature (403 K, 443 K, 473 K), initial sulfur content (600 ppm, 800 ppm, 500 ppm), and LHSV (1 h⁻¹, 2 h⁻¹, 3 h⁻¹). They showed that the highest DBT conversion (81.2%) was achieved at 600 ppm, temperature = 473 K, and residence time = 1 h. Joskić *et al.*¹³ investigated the ODS of model gas oil using H₂O₂ as an oxidant and acetic acid as a catalyst in a batch reactor. The degree of sulfur removal increased to 90% at 90 °C, over 80 min. Numerous researchers studied the oxidative desulfurization process and suggested various kinetic models that describe the oxidation process, including first-order,^{14–17} second-order model,^{17,18} and nth-order models.^{19–22}

Various types of reactor designs have been used to oxidize sulfur compounds in diesel fuel in batch and flow processes. Li *et al.*²³ studied oxidative desulfurization of model oil (BT or DBT in *n*-octane) with sulfur content 1000 ppm, using hydrogen peroxide as oxidant and tetra alkyl ortho-titanates (TAOTs) as catalysts in a batch reactor. The typical operating conditions required to reduce the sulfur content from 1000 to 10 ppm were: 10 min, molar ratio of O/S = 6, room temperature, and ambient pressure. Sobati *et al.*²⁴ proposed a four-impinging-jets reactor (FIJR) for the ODS of kerosene. They examined the ODS at different operating and design parameters such as feed flow rate, inter nozzle distance, jet diameter, and jet Reynolds number. They found that the rate of ODS of kerosene increased

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because of the impinging process and shear forces exerted on the phases and the rate of ODS in the FIJR increased significantly compared to that obtained by a conventional reactor system such as continuous stirred-tank reactor because of decreasing the mass-transfer resistance due to high intensity mixing. Moreover, about 92% sulfur removal of kerosene has been obtained in FIJR. Various reactor designs have been used to oxidize sulfur compounds in fuel as shown in Table 1.

A new generation of near-plug flow reactors that can achieve plug flow under laminar flow conditions or flowing of large reactant molecules is OBR; it consists of a tubular device with baffles superimposed with fluid oscillation. OBR is considered in the present study for the first time in the desulfurization research field as an alternative for conventional plug flow reactors. In OBRs, uniform mixing and enhanced transport rates are achieved by the interaction of baffles with the oscillatory motion of the fluid, while maintaining flow conditions approximating plug flow^{27,28}

The net Reynold's number (Re_n) is defined as:

$$Re_n = \frac{\rho u D}{\mu} \quad (1)$$

where u is the superficial net flow velocity through the tube ($m s^{-1}$), D is the tube diameter (m), ρ ($kg m^{-3}$), and μ ($kg m^{-1} s^{-1}$) are the feed density and viscosity respectively. The residence time is expressed as:

$$\tau = \frac{V}{v_0} \quad (2)$$

where V is the OBR volume and v_0 is the volumetric flow rate of the feed.

And the velocity of feed flow is;

$$u = \frac{v_0}{A_c} \quad (3)$$

where A_c is the cross-section area of the OBR (m^2).

Three dimensionless numbers can describe the dynamic nature of OBRs. Firstly, the oscillatory Re_o :

$$Re_o = \frac{2\pi f x_o \rho D}{\mu} \quad (4)$$

where x_o is the center-to-peak amplitude (m), and f is the oscillation frequency (Hz). The oscillatory Re_n is dependent on $2\rho f x_o$, the maximum oscillation velocity ($m s^{-1}$).²⁹ Re_o indicates mixing intensity. An increase in Re_o can be achieved by increasing the amplitude (x_o) or frequency (f) of oscillation, which produces a wide range of mixing intensities from 'soft' ($50 \leq Re_o \leq 500$), where vortex formation occurs, to the most

intense ($Re_o > 5000$) corresponding to mixed flow conditions with the OBR acting as an STR.³⁰ Another dimensionless group is the Strouhal number (St):

$$St = \frac{D}{4\pi x_o} \quad (5)$$

The Strouhal number relates the amplitude of oscillation (inversely proportional) to the baffle spacing (a multiple of D) and measures vortex propagation (degree of eddy propagation).^{29,31,32} Large St values are achieved at small amplitudes, giving poor vortex formation and *vice versa*. The previous studies in the literature showed that the tested range for St is 0.01–9;^{33,34} however, the range used most commonly is 0.15–4.^{35–37}

The velocity ratio is described as the ratio of Re_o to Re_n , as shown in eqn (6).³⁸

$$\psi = \frac{Re_o}{Re_n} \quad (6)$$

The most common scale-up methodology for commercial reactors that has been reported in the literature is based on matching the dimensionless groups. Thus, this study aimed to investigate the effect of conducting the ODS of diesel fuel at various oscillatory flow dimensionless groups at milder conditions, with significant 1-pass conversion and continuous reactors, thereby reducing time and efforts of scaling up process.

2. Experimental

ODS was performed in the liquid phase using a homogeneous catalyst (acetic acid) and hydrogen peroxide oxidant. The experimental work can be summarized *via* the following steps:

1. Designing, installation, and operation of an oscillatory baffled reactor using a helical baffle with a central rod.
2. Evaluating the performance of the OBR utilizing oxidation of sulfur compound in OBR at different mixing and operating conditions, which are temperature, residence time, the amplitude of oscillation, and the frequency of oscillation using acetic acid as a catalyst and H_2O_2 as an oxidant for DBT oxidation reaction.

2.1 Materials

The feedstock used was diesel fuel (total sulfur content 9 ppm), obtained from Pendik Company, Turkey. The physical properties of oil feedstock are given in Table S1,† below. Dibenzothiophene (DBT) was used as the model sulfur compound in the oil feedstock in this study. The DBT was obtained from Alfa

Table 1 Previous fuel desulfurization studies by H_2O_2 in different types of reactors

Feedstock	System, catalyst/oxidant	Residence time	Type of reactor used	Ref.
Model diesel fuel	tetra alkyl ortho-titanates (TAOTs)/ H_2O_2	10 min	Batch reactor	23
Kerosene	Formic acid/ H_2O_2	20 min	Four-impinging-jets reactor (FIJR)	24
Model diesel fuel	Isopropanol/ H_2O_2	24 h	A film-shear reactor	25
Diesel fuel	Acetic acid/ H_2O_2	3 min	OBR	Present study ²⁶



Aesar Company, U.K. The specifications of the DBT used are summarized in Table S2.† Hydrogen peroxide (H_2O_2) was obtained from Merck Millipore Company, Germany. Its specifications are also summarized in Table S2.† Acetic acid (CH_3COOH , 99% purity, J.T. Baker Company, USA) was used as a liquid catalyst in this work.

2.2 Experimental setup

The continuous oxidation of DBT was carried out in an OBR unit. Fig. 1 is a diagram of the unit.

The OBR unit consisted of an 8 mm inner diameter and 380 mm length fitted with 1.5 mm helical baffles with a 1.2 mm

central insert, and a 12 mm pitch (Fig. 1), providing a volume of 19 mL. The OBR is connected to two Confluent PVM C-Series syringe pumps *via* PTFE tubing and a custom-built Swagelok union. Syringe pump 1 was used for feeding the diesel fuel and the catalyst from the feed tank to the reactor and syringe pump 2 was used for providing the fluid oscillation inside the reactor and for varying the frequency of oscillation from 0 to 4.34 Hz and the amplitude of oscillation from 0 to 12 mm. The pumps were made of 316 stainless steels, and were supplied by Eurodyne, Ltd, U.K. Both the oscillation amplitude and frequency were controlled by commands written in “Sapphire Commander” software. A liquid dosing pump made of 316 stainless steel type by CoMetro Technology, Ltd, U.K., was used for feeding the hydrogen peroxide solution to the tubular reactor Fig. 2.

2.3 Experimental runs

The first part of this study was conducted to evaluate the performance of OBR in the removal of the sulfur compounds (DBT) removal from diesel fuel *via* the ODS process using H_2O_2 as oxidant and acetic acid as catalyst under the operating conditions shown in Table 2. The volumetric ratio of diesel fuel to the oxidant (H_2O_2) and the ratio of the diesel fuel to the liquid catalyst (CH_3COOH) were 25 and 10, respectively.³⁹ To conduct the experimental runs, the temperature of the reactor was set to the desired temperature using the temperature controller. The liquid catalyst (acetic acid) was added to the feed tank and well mixed with the oil, then fed to the reactor as an emulsion. The desired flow rate was obtained by regulating the syringe pump using the software. Hydrogen peroxide was fed to the reactor at the desired flow rate by regulating the dosing pump. The fluid oscillation was achieved by oscillating the second syringe pump 2, which was set at the desired frequency and amplitude of oscillation by the Sapphire Commander software. When the system was at a steady state, the liquid samples were withdrawn

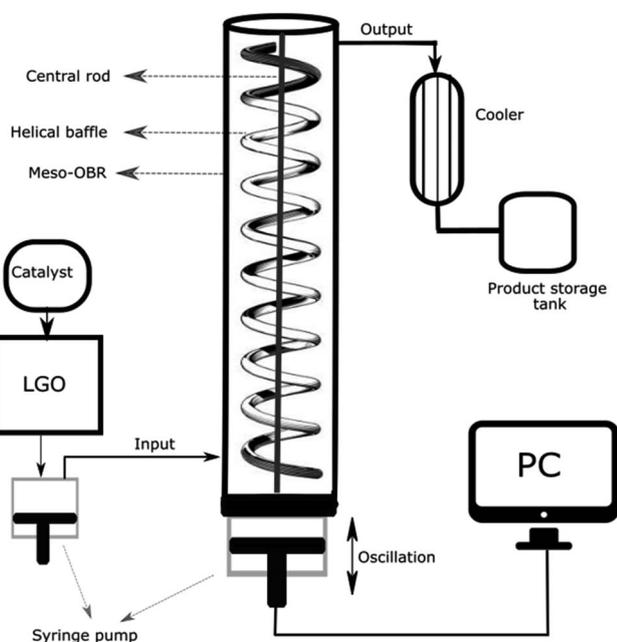


Fig. 1 Experimental setup of the OBR Unit.

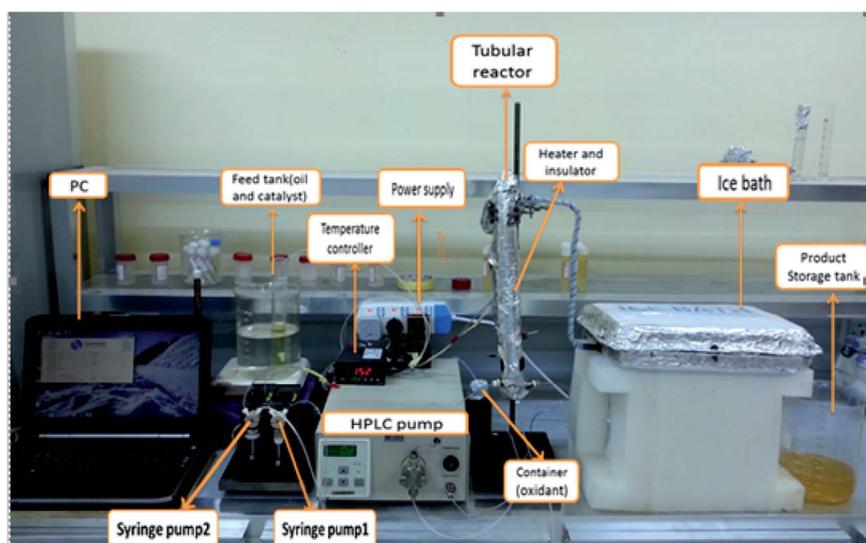


Fig. 2 Experimental setup of the OBR unit.



Table 2 Experimental variables for ODS of DBT in the OBR

Variable	Value
Temperature, °C	60, 70, 80
Residence time, min	1, 2, 3
Oscillation amplitude, mm	2, 4, 6
Oscillation frequency, Hz	2, 3, 4
Strouhal number, St	0.3, 0.2, 0.1
Oscillatory Reynolds number, Re_o	64–383
Net flow Reynolds number, Re_n	5, 8, 16
Velocity ratio, $\psi = Re_o/Re_n$	4–72

from the liquid outlet of the cooling system and extraction process to remove the remnant of hydrogen peroxide (the oxidant), catalyst and the ODS products from the sweet fuel. Samples of the treated fuel were left to settle to allow for separation by extraction. The residue oil obtained from oxidation step subsequently then to be continued with the liquid–liquid extraction step by mixing the oxidized residue oil with solvent (ethanol) into the conical flask with the residue oil/solvent ratio (v/v) of 1/1. The mixture was heated to temperature of 30 °C accompanied by constant stirring for 60 min. Then the raffinate and extract phase was separated using separation funnel. Then, the samples were labeled for testing and analysis for the remaining sulfur content against the fresh sample. The reactor was left to cool to room temperature; then, it was removed and cleaned. Nitrogen was used to get rid of the by-product gases; then, ethanol was flown to wash the streams of the OBR unit.

2.4 Kinetic studies

The second part of this project dealt with investigating the kinetics of the oxidation reaction in the OBR. The kinetic parameters determined were the order of reaction (n), constant of reaction (k), pre-exponential factor (k_0), and activation energy (E). The parameters were estimated at the optimal oscillation conditions obtained in the first part of this work. The kinetic runs were conducted at various times of reaction (0.5 min to 3 min) and at three different temperatures (60, 70, and 80 °C). DBT content in the feedstock and the desulfurized diesel fuel was tested in the HPLC system (EX-1600 FLD, Selon, China, C18 reverse-phase column (Philips, 5 μm \times 0.4 cm), wavelength = 287). The mobile phase was *n*-hexane (HPLC grade, J.T. Baker, USA) flows at 1.0 mL min^{-1} . The DBT percent conversion was calculated by eqn (6):

$$X_{\text{DBT}} = \frac{C_{\text{DBTin}} - C_{\text{DBTout}}}{C_{\text{DBTin}}} \times 100 \quad (7)$$

3. Results and discussion

3.1 Effect of the net flow on DBT conversion

The conversion of the DBT as a function of Re_n (5, 8, and 16) and Re_o (pressure, reaction temperature, the amplitude of oscillation, and frequency of oscillation) are shown in Fig. 3. It shows that the DBT conversion in OBR increased with increasing agitation. The conversion of DBT was increased when Re_n was

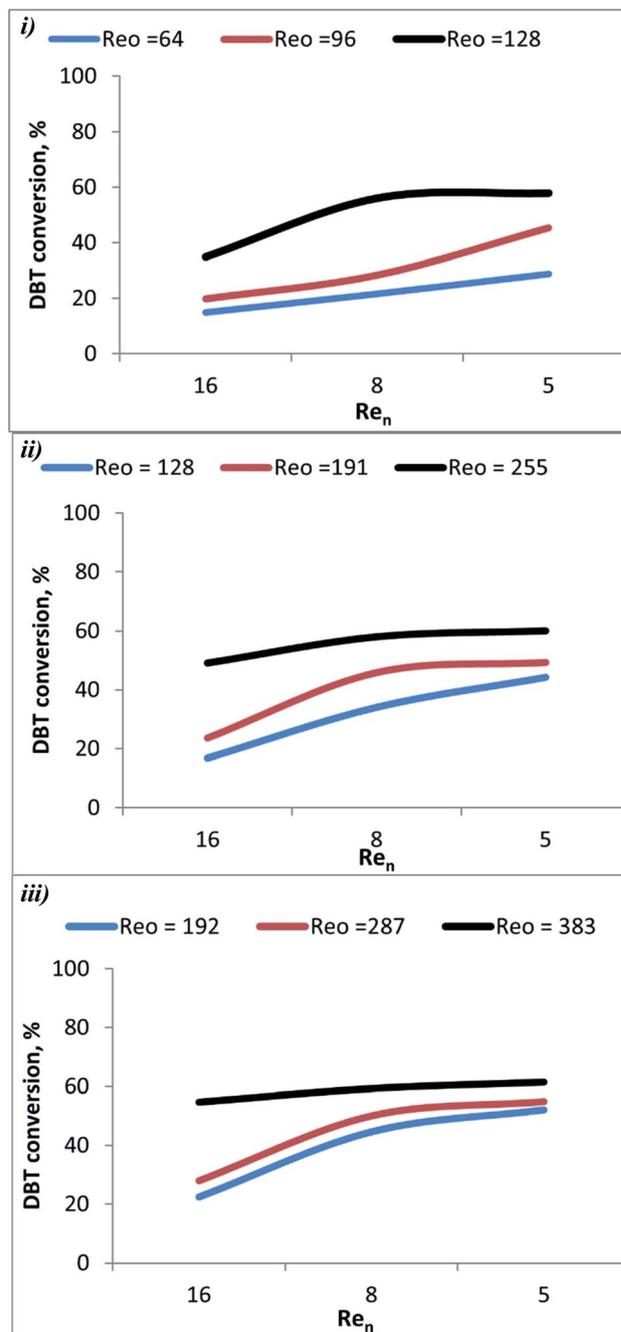


Fig. 3 Effect of Re_n on DBT conversion at different oscillation conditions and 60 °C (i) $St = 0.3$ (ii) 0.2 (iii) 0.1.

reduced as depicted in Fig. 4. This may be due to Re_n being directly proportional to the diesel flow rate and inversely proportional to the residence time of reactants inside the OBR. So, the residence-time of reactants decreases with the increase of Re_n . Hence DBT removal efficiency decreased. Also, laminar flow conditions were enhanced with a decrease in Re_n . Thus, DBT removal efficiency was enhanced in OBR due to applying $Re_n \leq 16$ in the present study. The effect is more pronounced at higher Re_n as the activity of the acetic acid catalyst decayed due to the high load of the reactant (feedstock) flown to the OBR.



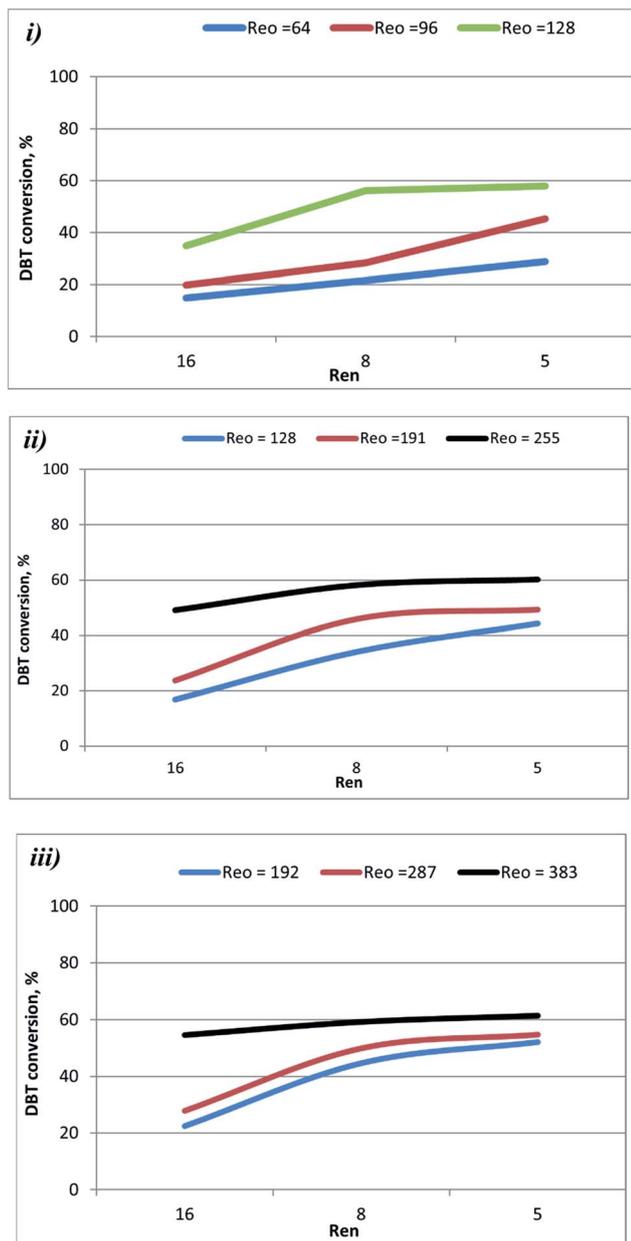


Fig. 4 Effect of Re_n on DBT conversion at different oscillation conditions and 70 °C. (i) $St = 0.3$ (ii) 0.2 (iii) 0.1.

Fig. 5 shows that DBT conversion in the OBR was enhanced by decreasing flow rate (increasing residence time) and hereby decreasing Re_n . At $T = 60$ °C and $x_o = 2$ mm, and $f = 2$ Hz, the conversion of the DBT increased from 15.0% to 22% as Re_n decreased from 16 to 8. As the Re_n was decreased to 5, the DBT conversion increased to 29.0%. At $x_o = 4$ mm and $f = 3$ Hz, the increase to 70 °C with reducing the Re_n from 16 to 5 resulted in raising the DBT conversion from 54.0% to 65.0%. At $x_o = 6$ mm, $f = 4$ Hz, a significant increase in DBT conversion from 68.0% to 94.0% was observed as the temperature was raised to 80 °C, and the Re_n was decreased from 8 to 5. In the present study, Re_n was ≤ 16 , suggesting that the flow was oscillating laminar. DBT conversion decreases as Re_n increases as the residence time

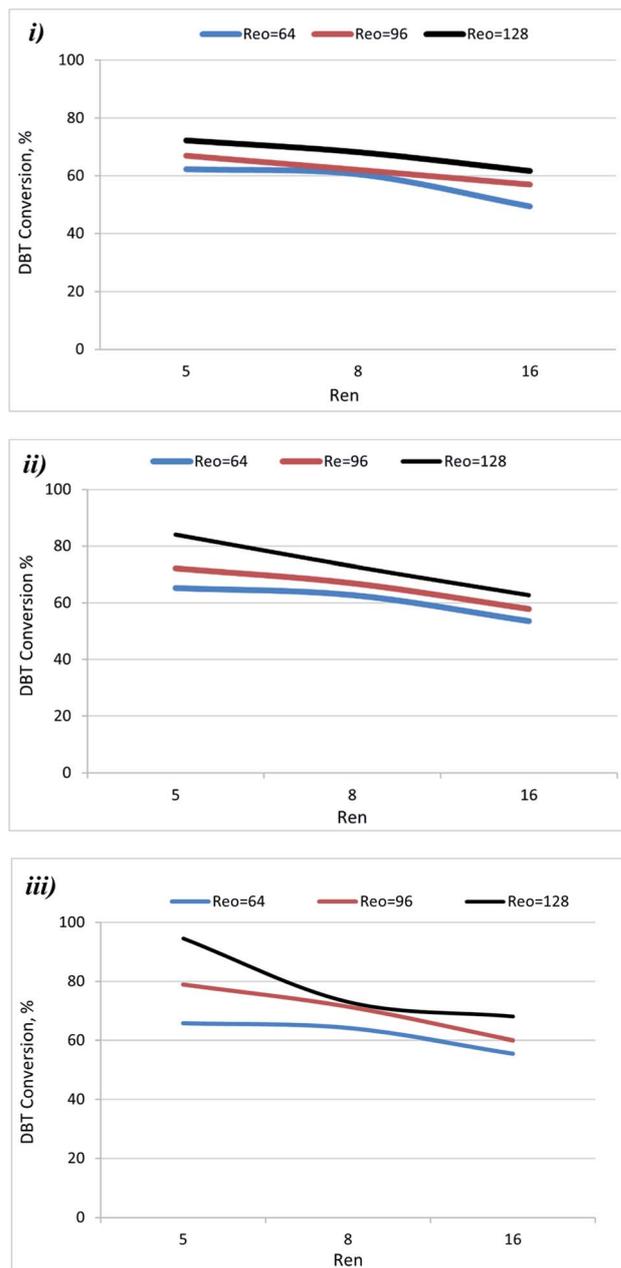


Fig. 5 Effect of Re_n on DBT conversion at different oscillation conditions and 80 °C. (i) $St = 0.3$ (ii) 0.2 (iii) 0.1.

decreases. In a previous study,⁴⁰ it was shown that good plug flow was obtained in a 350 mm length helically baffled meso-OBR at $Re_n = 2.55$ –7.2, $Re_o = 50$ –800 using a $St = 0.1$, and $Re_o = 50$ –300 using a $St = 0.2$. Their finding supports that the design of the reactor and the operating conditions in the present study are compatible with the requirements of achieving the plug flow conditions that resulted in the high conversion of DBT in the diesel fuel.

3.2 Effect of amplitude on DBT conversion

The Strouhal number (St) is the ratio of column diameter to stroke length, measuring the effective eddy propagation.²⁸ The



influence of St on DBT removal in the OBR was investigated at different St values (0.1, 0.2, and 0.3) and operation conditions. In general, the results showed that decreasing St led to enhancing the DBT removal.

Fig. 6 shows that decreasing St led to enhancing DBT removal. The St is inversely proportional to the amplitude of oscillation and measures vortex propagation.^{29,31,32} The results showed that the oxidative desulfurization was enhanced by decreasing St due to increasing oscillation amplitude at constant tube diameter, which provides efficient mixing of reactants. As an emulsion reaction system oil (diesel fuel)-hydrogen peroxide, it appeared that the dispersion properties of the peroxide within the oil phase were not affected by the net flow rate, enabling dispersion-independent control of the

residence time. Oscillation amplitudes and frequencies are the main parameters responsible for droplet breakage and initiation of the oxidation reaction. It has been reported that the mass transfer coefficient, $k_{L,a}$, decreases with increasing St (lowering the oscillation amplitude).⁴¹ The low value of the coefficient was due to the absence of the phase separation within the emulsion (oil containing DBT) and the hydrogen peroxide, which produced an extractive reaction effect.

All these conditions caused a reduction in DBT conversion as St increases. The range of the St analyzed in the literature was in the range of 0.01–9. High St ($St > 0.2$) indicates that there is insufficient eddy generation to mix the baffle cavity effectively. In contrast, low St ($St < 0.1$) indicates intense eddy generation causing vortex propagation into adjacent baffle cavities.⁴⁰

3.3 Effect of mixing (Re_o) on DBT conversion

Different Oscillatory Reynolds Numbers (Re_o) were examined in the present study to obtain the agitation rate that gives the highest DBT conversion in the OBR. The DBT removal efficiency was studied at the Re_o range of 64–383, 80 °C, different residence times, and oscillation conditions. Generally, DBT removal increased with increasing Re_o .

Fig. 7 shows the profiles of desulfurization efficiency *versus* mixing intensity (Re_o). As noted, an increase in Re_o from 64 to 128 leads to increased desulfurization, from 66% to 94% at $T = 80$ °C and residence time of 3 min. Also, increasing the Re_o from 64 to 128 leads to increasing desulfurization efficiency from 72% to 94% at $T = 80$ °C and a residence time = 3 min.

The removal of DBT was increased by utilizing the oscillatory flow mixing (as measured by the Re_o), due to enhanced mixing, as the Re_o increased. As the ODS by hydrogen peroxide depends on the contact between the liquid–liquid reacting phases, therefore, mass transfer in the system becomes a crucial factor, and the contact between reacting phases increases the mixing quality of the liquid–liquid system in an OBR.⁴² Therefore, oscillatory mixing, which is governed by Re_o , can be an effective method of removing mass transfer limitations in liquid systems. A dispersed flow regime is predicted at high Re_o (high frequency and amplitude of oscillation) with droplet diameter small enough to limit interactions with the reactor walls. In this case, oscillation frequency was found to have a more significant impact than amplitude on the mass transfer coefficient.

The enhancement of Re_o led to improved radial mixing as a result of the periodic vortices generated thereby enhanced plug flow conditions, and this enhancement led to raising the DBT conversion.⁴³ The experiments showed that to achieve an efficient DBT removal conversion in the OBR and reach a very low sulfur content in the fuel, in compliance with the new environmental protection regulations, a combination of oscillation frequency 4 Hz and amplitude 6 mm was required. This is within the range required for high levels of plug flow.⁵¹

3.4 Effect of the velocity ratio (ψ) on DBT conversion

In this work, the oxidation reaction was conducted at various ψ (4–72). The experimental data showed that ψ significantly influences the DBT removal from diesel fuel. DBT conversion

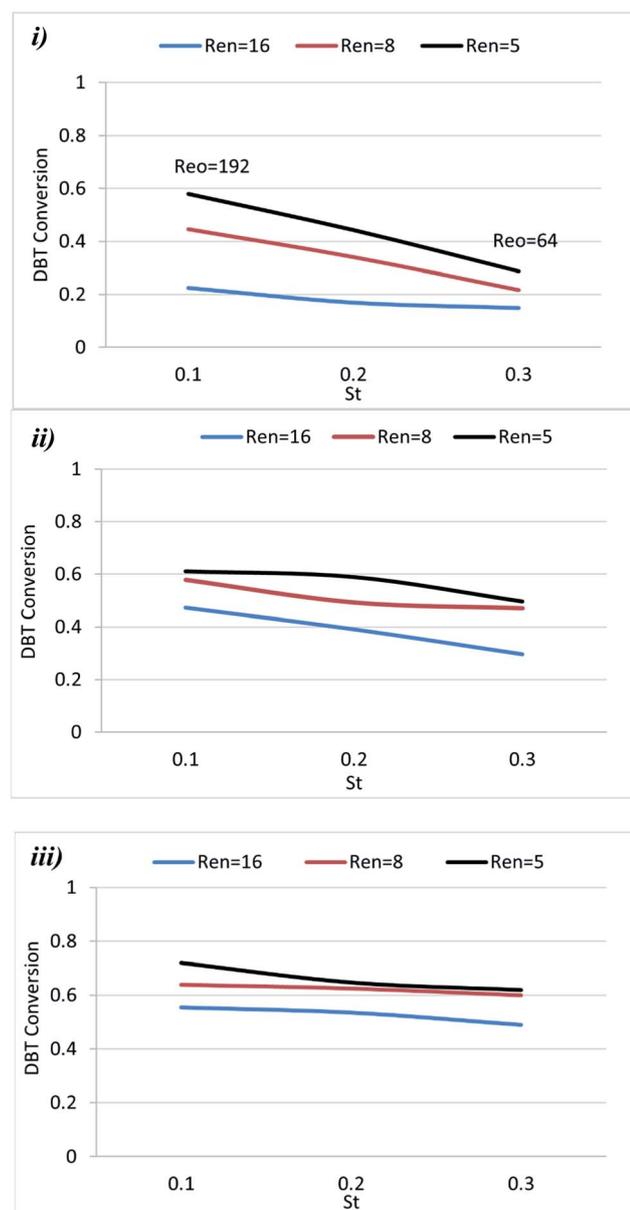


Fig. 6 Effect of St on DBT conversion at (i) 60 °C, (ii) 70 °C, (iii) 80 °C, and different operation conditions.



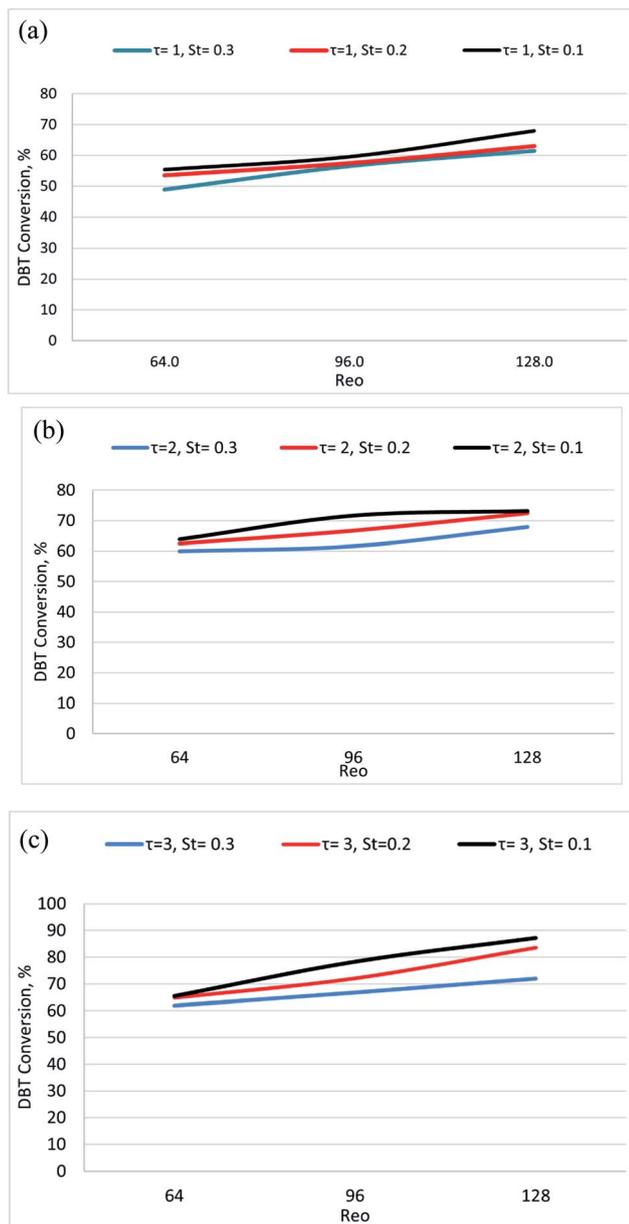


Fig. 7 Effect of Re_o on DBT conversion at $80\text{ }^\circ\text{C}$ at a different residence time (a) 1 min (b) 2 min (c) 3 min.

increases from 72% to 94% as ψ increases from 24 to 72 due to increasing Re_o (oscillation amplitude) at $T = 80\text{ }^\circ\text{C}$ and $Re_n = 5$ as shown in Fig. 8.

Fig. 9 shows that DBT oxidation was enhanced from 66% to 94% with rising ψ from 36 to 72 due to increasing Re_o (oscillation frequency) at $T = 80\text{ }^\circ\text{C}$ and $Re_n = 5$.

As can be observed in Fig. 10, DBT removal efficiency increases from 68% to 94% with an increasing velocity ratio from 24 to 72 due to decreasing Re_n at $T = 80\text{ }^\circ\text{C}$ and $Re_o = 383$. Also, the DBT conversion due to the ODS process in the OBR is significantly enhanced by raising the ψ and increasing temperature, as shown in Fig. 11.

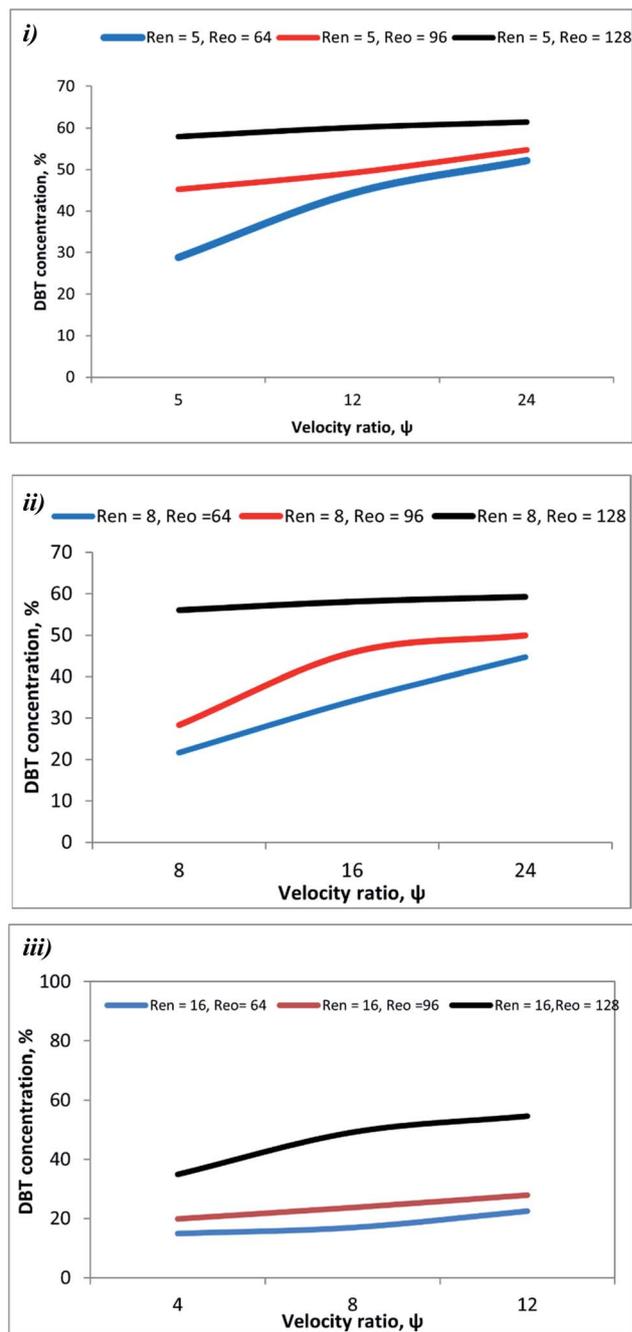


Fig. 8 Effect of velocity ratio (ψ) on DBT conversion at $T = 80\text{ }^\circ\text{C}$ and different Re_n .

Phan *et al.*⁴⁴ showed also that the plug flow behavior could be achieved in OBRs with a ratio of 2–10 or higher for mesoscale oscillatory helically baffled reactors.⁴⁴ The present experimental work showed that the highest DBT removal efficiency was achieved at $Re_n = 5$, $Re_o = 383$, and $\psi = 72$.

3.5 The kinetic study of the ODS process in an OBR

The conditions for maximum DBT conversion were $f = 4\text{ Hz}$ and $x_o = 6\text{ mm}$ at all temperatures (60 , 70 , and $80\text{ }^\circ\text{C}$). Hence, these conditions were used in the ODS kinetic experiments to obtain



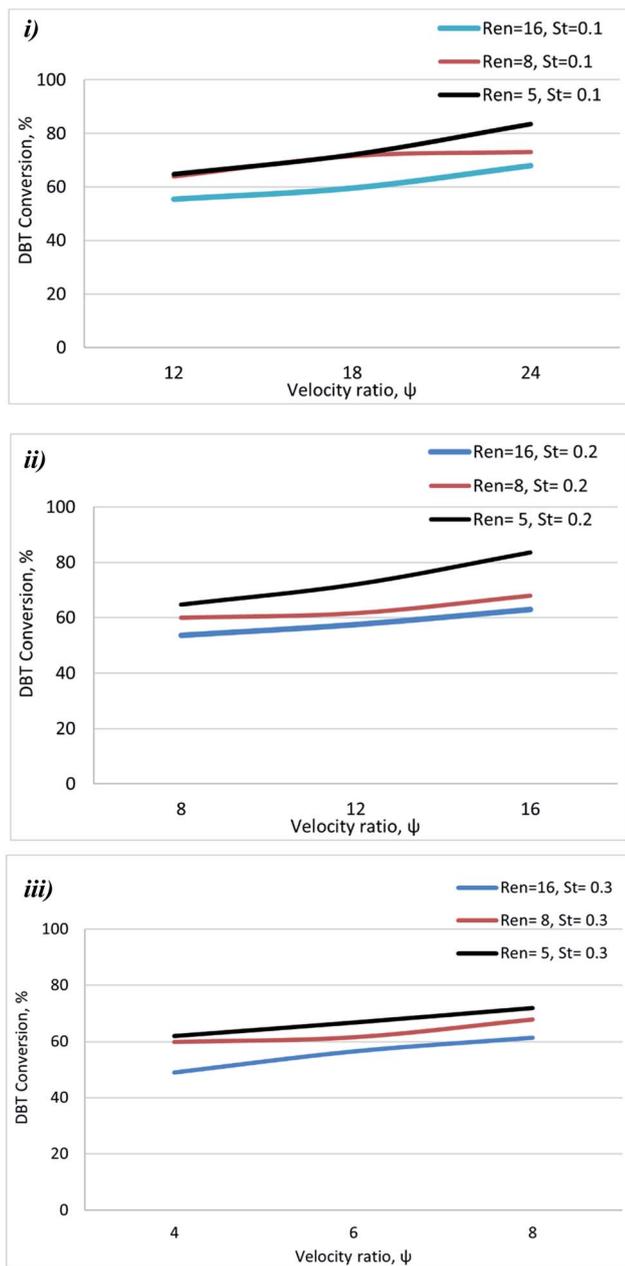


Fig. 9 Effect of velocity ratio (ψ) on DBT conversion at $T = 80\text{ }^{\circ}\text{C}$ and different St.

the kinetic parameters model towards these reaction variables (temperature and residence time). Fig. 12 shows the DBT conversion as a function of reaction time at different temperatures. The experiments showed that increasing the reaction time from 0.5 min to 3 min led to increasing DBT removal efficiency at the three oxidation temperatures.

The DBT conversion increased from 19% to 64% at $60\text{ }^{\circ}\text{C}$, 25% to 82% at $70\text{ }^{\circ}\text{C}$, and 36% to 86% at $80\text{ }^{\circ}\text{C}$ as reaction time increases from 0.5 min to 3 min as shown in Fig. 12. It can be seen from Fig. 12 that the DBT removal efficiency increased with reaction time, and the time needed to achieve a high (94%) conversion was very short, at 3 min.

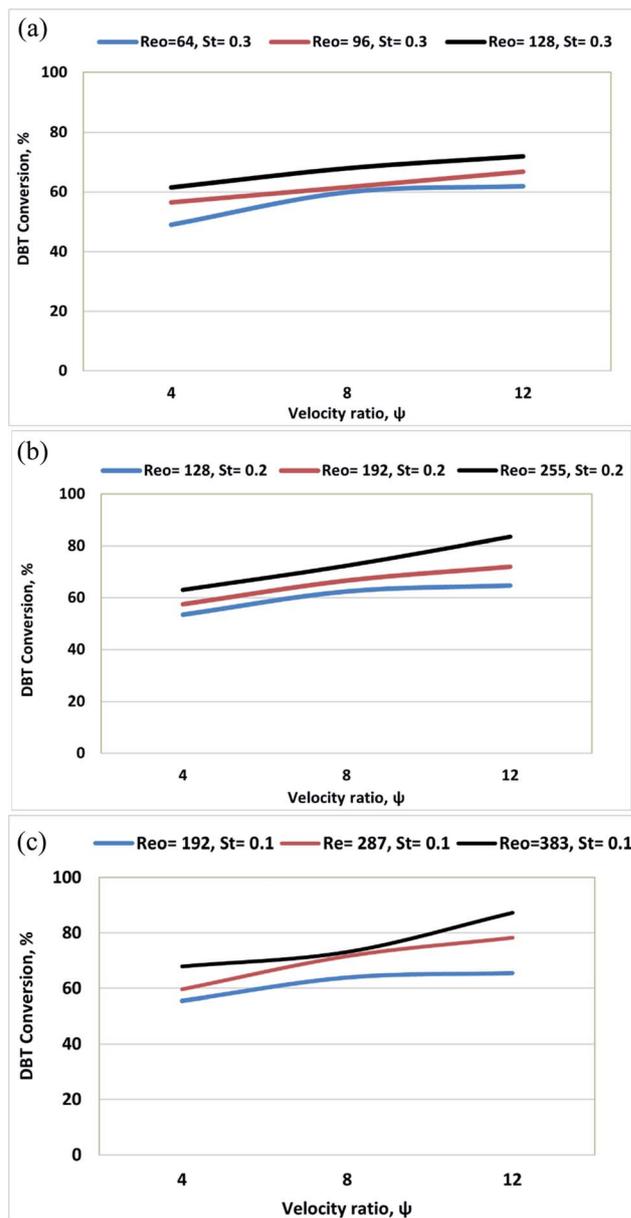


Fig. 10 Effect of velocity ratio (ψ) on DBT conversion at $80\text{ }^{\circ}\text{C}$ and different Re_o and St.

In this analysis, the integral method of kinetic data was used to determine the ODS of DBT kinetic parameters.

The rate law for DBT conversion is written as;

$$-r_{\text{DBT}} = -\frac{dC_{\text{DBT}}}{dt} = kC_{\text{DBT}}^n \quad (8)$$

Assuming that the ODS of DBT in the diesel fuel obeys a first-order rate equation ($n = 1$);

$$-r_{\text{DBT}} = -\frac{dC_{\text{DBT}}}{dt} = kC_{\text{DBT}} \quad (9)$$

By separating and integrating eqn (9), we obtain:



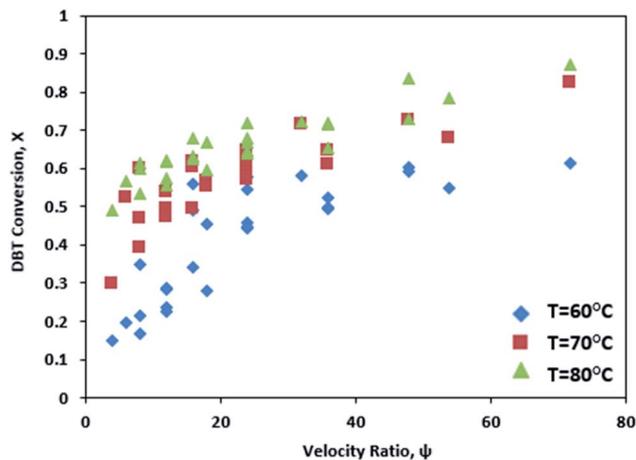


Fig. 11 Effect of velocity ratio (ψ) on DBT conversion at different temperatures.

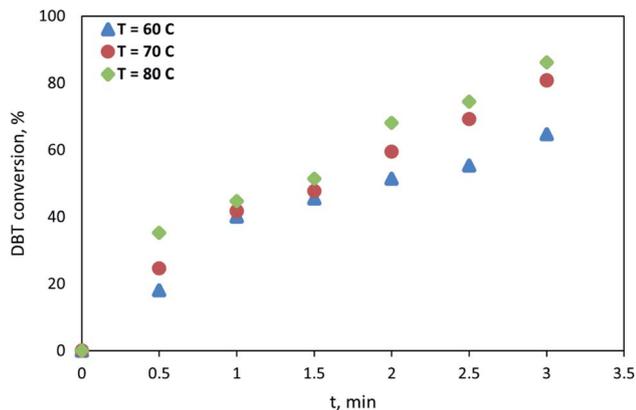


Fig. 12 The kinetics profiles of the ODS of DBT in the OBR at = 4 Hz, $x_o = 6$ mm, and different temperatures, conversion versus reaction time.

$$-\int_{C_{DBT0}}^{C_{DBT}} \frac{dC_{DBT}}{C_{DBT}} = k \int_0^t dt \quad (10)$$

$$\ln \frac{C_{DBT0}}{C_{DBT}} = kt \quad (11)$$

where r_{DBT} is the rate of DBT oxidation reaction, ($\text{mol L}^{-1} \text{min}^{-1}$), k is the reaction rate constant, (min^{-1}), C_{DBT0} is the initial concentration of DBT (inlet concentration of DBT into the reactor), (mol L^{-1}), C_{DBT} is the outlet concentration of DBT from the reactor, (mol L^{-1}), t is the reaction time, (min), and n is the reaction order (—).

Fig. 13 shows the fitting of the kinetic data of the ODS of DBT in the OBR, according to eqn (11).

The reaction followed a first-order rate law at all temperatures (60, 70, and 80) with an R^2 of 0.987, 0.973, and 0.96, respectively. The reaction rate constants were 0.3561 min^{-1} at 60°C , 0.5 min^{-1} at 70°C , and 0.5951 min^{-1} at 80°C . It has been previously reported that the rate of oxidation reaction was well-represented by a first-order model [95, 207, 241].

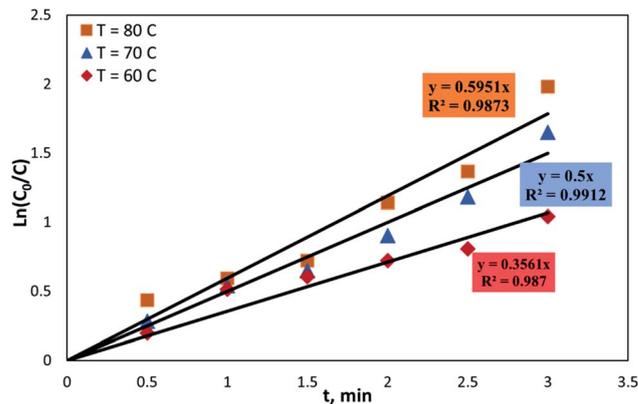


Fig. 13 First-order kinetic data at different temperatures 60°C , 70°C , and 80°C .

The apparent activation energy for the oxidation of DBT can be obtained from the slope of the Arrhenius plot according to the linearized form of 1.1 as follow:

$$-\ln k = -\ln k_0 + \frac{E}{RT} \quad (12)$$

where T is the reaction temperature (K), R is the gas constant ($\text{kJ mol}^{-1} \text{K}$), E is the activation energy (kJ mol^{-1}), and k_0 is the Pre-exponential factor.

A plot of $(-\ln k)$ vs. $(1/T)$ is shown in Fig. 14 and fitted to a straight line. It is found that the activation energy (E) and the pre-exponential factor (k_0) of DBT oxidation reaction in the OBR were $24.87 \text{ kJ mol}^{-1}$ and 0.805 s^{-1} , respectively.

The activation energy reveals that this catalytic OBR system could quickly oxidize DBT homologs compounds in OBR. The low pre-exponential factor of the oxidation reaction indicates the non-spontaneity of this reaction.⁴⁵ Table 3 summarizes the activation energies of the ODS reaction with the first-order kinetics of the present study and previous studies.

The activation energy values reported by the previous studies were higher than the ones obtained in the present study in the OBR system. The oxidation reactivity of the sulfur-containing fuel increases with the increase in the electron density of the sulfur compound and leads to reducing the activation energy of

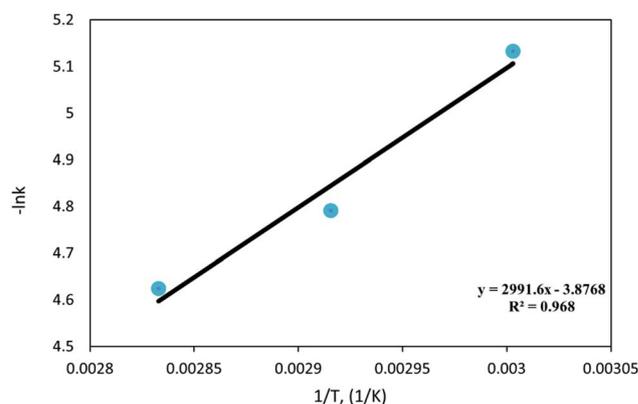


Fig. 14 Arrhenius Plot of DBT oxidation reaction of DBT in the OBR.



Table 3 The activation energy of oxidation reaction with first-order kinetics for some studies

Feedstock	Sulfur compound	Oxidant/Catalyst system	Activation energy (kJ mol ⁻¹)	Ref.
Diesel fuel	DBT	H ₂ O ₂ /acetic acid	57	46
Diesel fuel	DBT	H ₂ O ₂ /formic acid	53.8	14
Diesel fuel	DBT	H ₂ O ₂ /acetic acid	28.9	47
Diesel fuel	DBT	H ₂ O ₂ /acetic acid	24.87	Present study

the oxidation reaction.^{48,49} Therefore, this low activation energy can be attributed to the electrophilic addition of oxygen or the high electron density on S of the DBT.⁵⁰

4. Conclusions

The oxidative desulfurization of dibenzothiophene (DBT) in diesel fuel was conducted at a laboratory scale in a mesoscale oscillatory baffled reactor (*meso*-OBR). The parameters studied included: temperature (60–80 °C), residence time (1–3 min), Reynolds number (5–16), oscillatory Reynolds number (64–383), and Starhul number (0.1–0.3). The catalyst used was acetic acid (CH₃COOH), and hydrogen peroxide (H₂O₂) as the oxidant. The reaction was performed at atmospheric pressure. Within this parameter residence, the DBT conversion increased with temperature, residence time, oscillation frequency, and oscillation amplitude. The maximum single-pass conversion of DBT achieved was 94%. This was achieved at 80 °C, oscillatory Reynolds number of 382, and a net flow Reynolds number of 5. While other studies showed the use of other types of reactors, such as the batch, fixed, CSTR, and FIJR reactors, which achieved DBT removal efficiency similar to or less than those achieved in the present study but at a reaction time of not less than 30 min. The DBT conversion could not be increased further by increasing the temperature (more than 80 °C), as this would lead to H₂O₂ decomposition. However, the *meso* OBR design allowed a closer approach to the decomposition temperature, which is an advantage of using a tubular flow reactor for this application. The removal of the DBT from the diesel fuel *via* the homogeneous ODS reaction in the OBR was first order with respect to DBT concentration with lower apparent activation energy in comparison with the previous studies and higher frequency factor, of 24.9 kJ mol⁻¹ and 0.805 s⁻¹, respectively. The combination of the oscillatory motion and the helical baffle design provided sufficient mixing to accelerate the reaction. The operation of the mesoscale OBR at Ren between 5–8 along with Reo of 96–128 offered plug flow behavior. This enables the ODS to be upgraded in the OBR at a substantially short residence time. It was possible to achieve a high-performance continuous ODS process under milder operation conditions.

Conflicts of interest

There are no conflicts to declare.

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