

Fast, Non-Extractive, and Ultradeep Desulfurization of Diesel in an Oscillatory Baffled Reactor

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Abstract

Sulfur compounds are major contaminants in diesel fuels and cause significant negative impacts on the environment, human health, and petroleum product quality. Oxidative desulfurization (ODS) has gained attention due to relatively mild operating conditions. However, ODS requires significant improvements in terms of productivity, reaction time, and conversion. This study reports the development of a highly efficient, rapid ODS process, in an oscillatory baffled reactor (OBR), to allow continuous, safe dibenzothiophene (DBT) removal. DBT conversion was studied as a function of temperature, residence time, oscillation frequency, and oscillation amplitude. By optimizing the operating conditions, up to 94% DBT could be removed without further extraction in 3 min, at 80°C, 4 Hz, and 6 mm. This is a substantial increase over comparable processes at this temperature and furthermore has been conducted in a reactor that scales up predictably, hence it is probable that this performance can be realized at an industrial scale.

Keywords: Oxidative desulfurization, oscillatory baffled reactor (OBR), acetic acid, hydrogen peroxide.

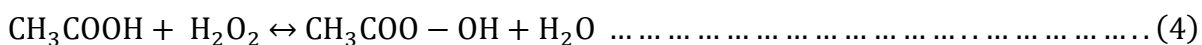
1. Introduction

Although considerable efforts have been put into producing alternative fuel, petroleum or crude oil remains the largest (33.1%) and most economical source of energy to meet global energy demands, particularly in the transportation sector (Dudley, 2020). However, crude oil reservoirs are currently depleting and the oil quality is declining, particularly with regard to sulfur content (from 4500 to more than 6000 ppm over 2014-2025) and increasing density (Huirache-Acuña et al., 2009). As a result, they constitute a significant source of sulfur emissions (Al-Malki, 2004).

Disulfides, mercaptans, and thiophene (T.H.) and its derivatives, e.g., benzothiophene (B.T.), dibenzothiophenes (DBTs), and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) are typical organic sulfur compounds (OSCs) in fuels. These forms of organic sulfur compounds emit toxic SO_x when combusted and cause serious health/environmental issues, including air and water contamination, global warming (indirectly), ecosystem disruption, and acid rain, as well as adverse impacts on living organisms (Colvile et al., 2002; Pawelec et al., 2011). To protect the environment as well as fuel processing technology, the European Union (E.U.) and the U.S. have introduced new legislation. The maximum permissible sulfur content set by the Environmental Protection Agency (EPA) and E.U. were 10 and 15 ppm respectively (Colvile et al., 2002; Jeong et al., 2013; Kulkarni and Afonso, 2010; Song and Ma, 2003; Stanislaus et al., 2010). Conventional reaction processes, such as hydrodesulfurization (HDS) in catalytic packed bed reactors require high temperatures and pressures (50-100 bar and 200-450 °C)(Berhault, 2016), expensive noble metal catalysts (Yoshimura et al., 2004), and long processing times (0.0833 h-3 h)(G. Wu et al., 2020). Operation at these conditions results in significant hydrogen usage (H₂/Oil, SCF/bbl=300-2000)(Gary et al., 2007) and decreased catalyst lifetime, due to the extreme operating conditions (Bokare and Choi, 2016). Deep desulfurization refers to processes to remove sulfur to below 15 ppm for diesel fuels

These products (sulfone and sulfoxide) are more polar than DBT. The sulfoxides/sulfones produced were expected to migrate from the oil phase, which is mostly the non-polar phase to the polar aqueous phase.

Peracetic acid (CH_3COOOH), which is a selective oxidizing agent, is an equilibrium product generated from the reaction of hydrogen peroxide and acetic acid (reaction 4)



Mamaghani et al. (Haghighat et al., 2013) studied ODS of model fuels containing benzothiophene, dibenzothiophene, and DBT-derivatives. Formic acid (HCOOH) was used as the catalyst and H_2O_2 as the oxidizing agent in a batch reactor. Conversion of sulfur compounds has reached 60% under the optimal reaction conditions of formic acid to a sulfur molar ratio of 222:1, H_2O_2 to sulfur 2:1, 65 °C, and a reaction time of 56 min. Joskic et al. (Joskic et al., 2014) investigated an ODS process for model gasoil using H_2O_2 as oxidant and acetic acid as a catalyst in a batch reactor. The percentage of sulfur removal (conversion) reached 90% at reaction conditions of 90 °C and 80 min 200:1 acetic acid to sulfur molar ratio and 2:1 H_2O_2 to sulfur. Farsi et al. (Farshi and Rabiei, 2005) studied the removal of sulfur compounds from heavy oil by an ODS-extraction system. They used acetic acid and hydrogen peroxide in a batch reactor. They found that ODS reaction is limited by the speed of rotation i.e the mass transfer within the reaction volume and low conversion of 58% was achieved by applying a stirring rate of 750 rpm, the long reaction time of 90 min, and 60°C. Jie et al. (Zhu et al., 2020) constructed 3D catalysts with the integral structure for oxidative desulfurization of DBT, 4-MDBT, and 4, 6-DMDBT in dodecane using H_2O_2 /acetic acid in a batch catalytic process. They achieved almost 100% conversion with an initial sulfur content of 200 ppm. Wu et al. (Wu et al., 2020) conducted oxidative desulfurization (ODS) in a batch catalytic process using graphene analogous hexagonal boron nitride (h-BN) as a metal-free catalyst with

hydrogen peroxide (H_2O_2) as the oxidant. They obtained a 99.4% of sulfur removal in octane fuel of 500 ppm sulfur content. Suryawanshi et al. (Suryawanshi et al. , 2017) studied ODS of thiophene as a model sulfur compound, using an orifice and vortex diode as a mechanical cavitating device and generated hydrogen peroxide from water *in situ* at three different pressures (2, 5, and 10 bar). The results showed that the highest sulfur removal was achieved above 90% at a pressure of 5 bar. ODS has been investigated in various flow reactors including trickle bed reactors, continuously stirred tank reactors, and fluidized bed reactors. However, all these studies showed that severe conditions such as high pressure, highly active catalysts, and long residence time are needed to achieve a satisfactory removal of sulfur compounds. As homogeneous ODS processing of sulfur compounds is a mass transfer controlled reaction process(Rivoira et al., 2018), it is expected that the sulfur compounds conversion going to be much improved as mass transfer being enhanced. The oscillatory baffled reactor (OBR) is a continuous tubular flow reactor containing an insert supporting equally spaced orifice baffles, operated with an oscillatory fluid motion superimposed upon the continuous net flow (Ahmed et al., 2018; Phan and Harvey, 2010). In OBRs, uniform mixing and enhanced transport rates are achieved by the interaction of the baffles with the oscillatory motion of the fluid, while maintaining flow conditions approximating plug flow (McDonough et al., 2019; Phan and Harvey, 2010; Rasdi et al., 2013). A reduced residence time would be expected when using an OBR for the reaction if it is mixing-limited(Abbott et al. 2014). Here, the OBR was evaluated for a non-extractive ODS process, to demonstrate proof-of-concept for a more economically viable process for obtaining sulfur-free diesel fuel.

2. Experimental work

2.1 Chemicals

The feedstock used was diesel fuel (total sulfur content 9 ppm), obtained from Pendik Company, Turkey. The physical properties are given in Table 1:

Table 1. Physical properties the diesel fuel.

Physical property	Value	Physical property	value
Specific gravity@15.5°C	0.8333	Colour	0.9
API at 60F	38.31	Initial boiling point (°C)	165
Total sulfur, (ppm)	9	Distillation, (°C)	
Kinematic viscosity@40°C (mm ² /sec)	3.15	10%	202
Cetane Index	53.9	50%	276
Flash point, (°C)	61	90%	338
Pour point, (°C)	< - 20	Final boiling point (°C)	357

Dibenzothiophene (DBT) was used as the model sulfur compound in the diesel fuel feedstock in this study. DBT was obtained from Alfa Aesar Company, UK. The specifications of the DBT used are summarized in Table 2. Hydrogen peroxide (H₂O₂) was used as an oxidizing agent. This oxidant was obtained from Merck Millipore Company, Germany. The specifications of the oxidant used are summarized in Table 2. Acetic acid (CH₃COOH, 99% purity) was used as a liquid catalyst in this work. J.T. Baker Company, USA supplied the acetic acid.

Table 2. Specifications of DBT.

Properties	DBT	Hydrogen peroxide
Chemical formula	C ₁₂ H ₈ S	H ₂ O ₂
Molecular weight (g/mol)	184	34
Physical form	Solid	Liquid
Purity	98 %	29.0 – 31.0 %
Density (g/cm ³) at 20 °C	1.44	1.11

2.2 Experimental setup

The continuous oxidation of DBT was carried out in a mesoscale OBR unit, as shown in Figure 1, below. This unit is a fully automated reactor. The diesel fuel was stored in a feed tank, which was connected to a syringe pump 1 (C3000 syringe pump with 120deg 3-port valve PEEK/PTFE, Eurodyne Limited, UK). The fuel net flow rates and oscillation were generated using syringe pump 1 which was connected to the base of the meso-OBRs via a custom Swagelok union and 1/16 in and 1/8 in PTFE tubing. Syringe pump 1 provided the oscillatory flow using a 12.5 mL syringe from the feed tank. The oscillation amplitude was controlled using the volume of dispensed liquid, whilst the frequency was controlled by adjusting the speed and acceleration settings of the lead screw. The liquid oxidant (H₂O₂) was stored in an appropriate container, which was connected to a dosing pump. The oscillation inside the reactor is provided by syringe pump 2 (oscillator). A tubular reactor was connected to syringe pump 2 (C3000 syringe pump with 120deg 3-port valve PEEK/PTFE, Eurodyne Limited, UK) via PTFE tubing and a custom-built Swagelok union. The C-Series comprises syringe pump modules for automated instrumentation is used in this study. The oscillation motion inside the reactor is generated by syringe pump 2, which is used for

providing the fluid oscillation inside the reactor. It is also used to vary the frequency of oscillation from 0 to 4.0 Hz and the amplitude of oscillation from 0 to 6 mm. The amplitude (center-to-peak) was controlled by varying the volume of the displaced liquid, while the frequency was controlled by varying the speed and acceleration settings of the plunger. Both oscillation amplitude and frequency were controlled via text input commands of the Sapphire software. The pump is made out of 316 stainless steel types by Eurodyne, Ltd., UK. This pump provides extremely low flow rates at minimum pulsation and sets new standards for syringe pumps. The advantages of the syringe pump are:

1. A seamless replacement for industry-standard pumps
2. High Resolution options available up to 192,000 steps/full stroke
3. Proprietary high-efficiency and maintenance-free drive system
4. Direct-drive design (no belts to stretch or break)
5. Long-life rotary shear valves (up to 24 times the life of competing valves)

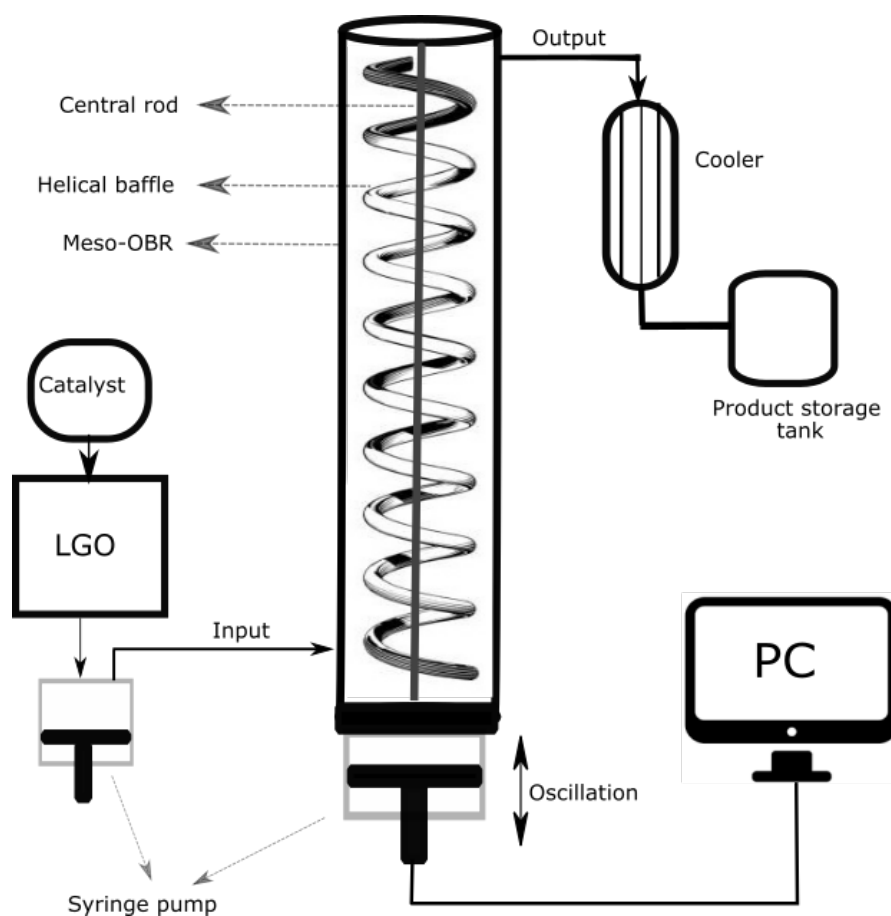


Figure 1. Schematic diagram of the experimental OBR setup

2.2.1 OBR setup

The tubular reactor was made of stainless steel (Grade 316 L) with 8 mm inner diameter (ID) and 380 mm length. Helical baffle which was inserted into the reactor exhibit plug flow over a wide range of operating conditions (McDonough et al., 2015). A 0.5 mm diameter central rod was coupled with the helical baffle (6 mm outer diameter (OD), 4 mm ID, and a pitch = 12 mm) to avoid any channeling flow, as suggested in previous work (Phan and Harvey, 2012). The reactor contains three inlet slots, two for feeding the reactants, and one for generating the oscillation motion inside the reactor, and one slot for the product outlet. Other accessories included a heater jacket (dispense the temperature from 0 to 100 °C), and a glass wool insulator. Two syringe pumps via

polytetrafluoroethylene (PTFE) tubing and a custom-built Swagelok union by Eurodyne, Ltd., U.K.(Figure 1), were used to pump the diesel fuel and catalyst from the feed tank into the reactor (pump 1) and generating oscillation motion inside the reactor (pump 2) as shown in Figures 1 and 2. The oscillation frequency (f) was controlled by adjusting the speed of the piston movement, while the oscillation amplitude (center-to-peak, x_0) was adjusted by setting the amount of volume dispensed. These parameters were monitored via a computer to be 0-4.45 Hz oscillation frequency and 0-12 mm oscillation amplitude. Both amplitude and frequency were controlled by commands written in Sapphire Commander software. Also, a liquid dosing pump made of 316 stainless steel type by CoMetro Technology, Ltd, UK, was used to feed the oxidant (H_2O_2) to the reactor. To control the system temperature, a temperature controller, REX-C series intelligent industrial (PID, 0-400 $^{\circ}$ C, $\pm 0.5\%$ F.S $\pm 1^{\circ}$ C), was used in this work.

The parts of the OBR unit were combined as shown in Figure 2. The heart of this unit is a reactor. The reactor is a cylindrical tube surrounded by an efficient heater, which is controlled by a temperature controller, and thermally insulated by an insulator.

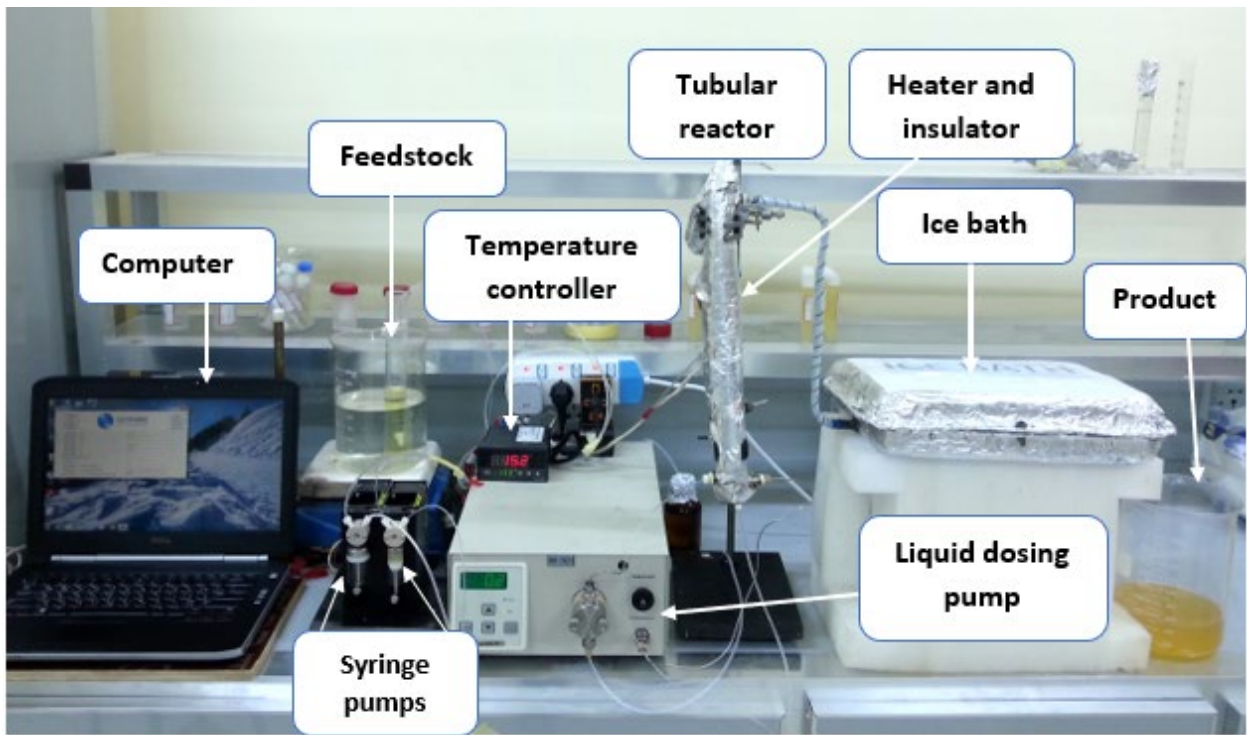


Figure 2. Experimental setup of the OBR unit.

The oscillation conditions can be characterized by two dimensionless groups: the oscillatory Reynold's number (Re_o) and the Strouhal number (St) as presented in Table 3. The ranges shown in this table were selected based on relevant previous studies (Wu, 2020; Ahmed, 2018, Phan, 2010). The oscillatory Reynold's number represents the intensity of mixing inside the reactor, while the Strouhal number measures the propagation of eddies. Other dimensionless oscillation parameters were chosen at specified ranges as shown in Table 3:

$$\text{Reynold's number of oscillations, } Re_o = 2\pi f x_0 \rho D / \mu$$

$$\text{Net flow Reynold's number, } Re_n = \rho u D / \mu$$

$$\text{Baffle space ratio} = l/D$$

$$\text{Velocity ratio, } \psi = Re_o / Re_n$$

$$\text{Cross sectional area parameter, } \alpha = (D_o / D)^2$$

Where:

L: Length of the OBR tube.

D: Internal diameter of the OBR tube

D_o : Baffle diameter

ρ =Density of flowing fluid

μ =Viscosity of flowing fluid

Table 3. The dimensionless groups of the OBR in this study.

Parameter	Range / Value
Baffle space ratio	1.5
Strouhal number, St	0.32, 0.16, 0.11
Cross-sectional area, α	25 %
Reynold's number of oscillations, Re_o	64 - 383
Net flow Reynold's number, Re_n	5.0, 8.0, 16.0
Velocity ratio, ψ	4.0 – 72.0

2.2 Experimental conditions

Table 4 shows the experimental variables (temperature, residence time, the oscillation amplitude, and the oscillation frequency) of the present work based on a Full Factorial Design of experiments:

Table 4. Experimental variables for ODS of DBT in the OBR.

Variable	Level	Value
Temperature, °C	3	60, 70, 80
Residence time, τ , min	3	1, 2, 3
Net flow Reynold's number, Re_n	3	5.0, 8.0, 16.0
Oscillation amplitude, x_o , mm	3	2, 4, 6
Oscillation frequency, f , Hz	3	2, 3, 4

The initial DBT concentration was 569 ppm in all experimental runs. The total number of runs was 81 with three replications. All experiments were conducted at atmospheric pressure. The fuel dosing pump, the two syringe pumps, and the temperature controller were calibrated and connected to the electrical connection of the two syringe pumps to a convector, power supply, and computer. They were connected to the mesoscale OBR, which was insulated and equipped with a heater and a cooling system. The system was checked for leaks by feeding water to the reactor using all pumps under the most severe operating conditions ($T= 80$ °C (where the hydrogen peroxide begins to decompose), $f= 4$ Hz, $x_o = 6$ mm) for one hour. The unit was flushed with an ethanol solution before each experiment. The feedstock (diesel fuel) was fed to the reactor along with the oxidant and the catalyst, each via the pump connected to it at the desired operating conditions.

The ODS process was carried out in the OBR using H_2O_2 as oxidant and acetic acid as catalyst under the different operating conditions shown in Table 4.(Ali, 2006). To conduct the experimental runs, the temperature of the reactor was set to the desired temperature (60, 70, or 80°C) using the temperature controller (± 0.1 °C). The liquid catalyst (acetic acid) and the diesel fuel were mixed before fed to the OBR. The flow rate of the feed was adjusted via syringe pump 1 to achieve the desired residence time for each run. The mixture was oscillated using syringe pump 2 set at the desired

oscillation frequency and oscillation amplitude by the “Sapphire Commander” software. The liquid samples were withdrawn from the liquid outlet of the cooling system and labeled. To get rid of the sulfur compounds, the sample of the product (treated fuel) was left to settle to allow for separation of the polar aqueous phase. The aqueous phase contains the sulfones and sulfoxides and the acetic acid recovered from the process, which can be separated and recycled by distillation due to the different boiling points of the components of the aqueous phase mixture (H₂O, H₂O₂, CH₃COOH, sulfones, and sulfoxides). Then, the sample was analyzed for the remaining sulfur content against the fresh sample. After completing the experiments, diesel fuel syringe pump 1, syringe pump 2, the dosing pump, temperature controller were turned off, all open valves were closed, and all heating systems were brought to off mode. The reactor was left to cool to room temperature; then, it was removed and cleaned. To investigate the effect of mixing on the ODS reaction of DBT in the diesel fuel, preliminarily ODS tests were conducted at different reaction temperatures (60, 70, and 80 °C) and residence times (1, 2, and 3 min) in a batch reactor (round bottom flask). For each set of experiments, a replication experiment was conducted to estimate the random error. The error of the experimental data for all experiments was up to 5%.

2.5 Analysis of samples

The DBT contents of the feedstock of diesel fuel and the treated samples were determined using X-ray fluorescence (EDXRF) (RX-360SH, Tanaka Scientific, Ltd, Japan) apparatus according to ISO 9454 and ASTM D4294-03. The specifications of this automatic petroleum tester are shown in Table 5. The DBT percent conversion was calculated by equation 1.

$$X_{DBT} = \frac{C_{DBTin} - C_{DBTout}}{C_{DBTin}} \times 100 \dots \dots \dots (5)$$

Table 5. The main specifications of the X-ray sulfur meter.

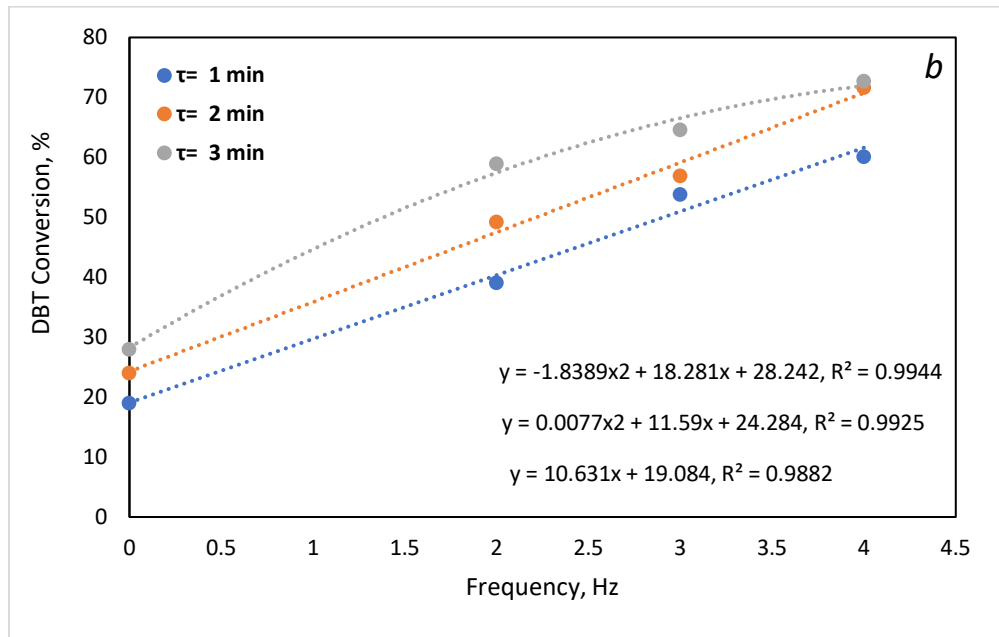
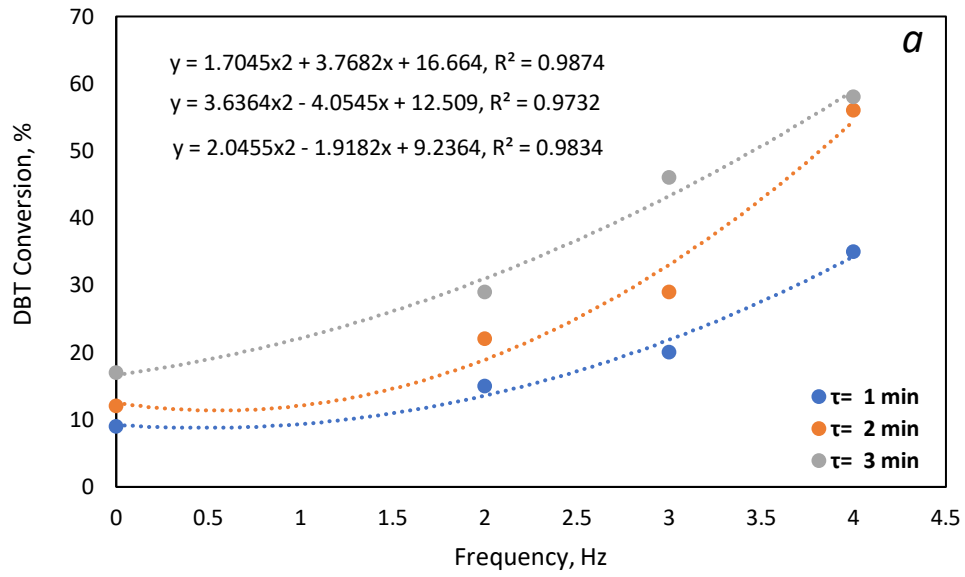
Item	Specifications
Type	Total sulfur analyzer for petroleum products by energy dispersive X-ray fluorescence method
Conforming standards	ISO 9454, ASTM D4294-03, etc.
Sample volume	3-5 ml
Measuring range	0 - 6.00 wt%
Operating temperature	10-30°C with a temperature drift within 10°C in a day.
C/H ratio compensation	Automatic with 0.003wt% max of compensation error when a 1wt% sample is tested.
Measuring time	10-990 s with a 10s increment.

3. Results and discussion

The degree of DBT removal from diesel fuel (D.F.) in the OBR was investigated at different process variables (temperature, residence time, oscillation frequency, and oscillation amplitude) in an attempt to elucidate the experimental and instrumental parameters that influence the extent of the ODS process.

3.1 Effect of the frequency of oscillation on DBT conversion

To establish satisfactory mixing conditions within the OBR, the conversion of DBT as a function of the oscillation frequency was studied at 0 Hz, 2 Hz, 3 Hz, and 4 Hz at the various reaction temperatures, residence times, and amplitudes of oscillation using acetic acid/H₂O₂ as catalyst/oxidant system as shown in Figure 3.



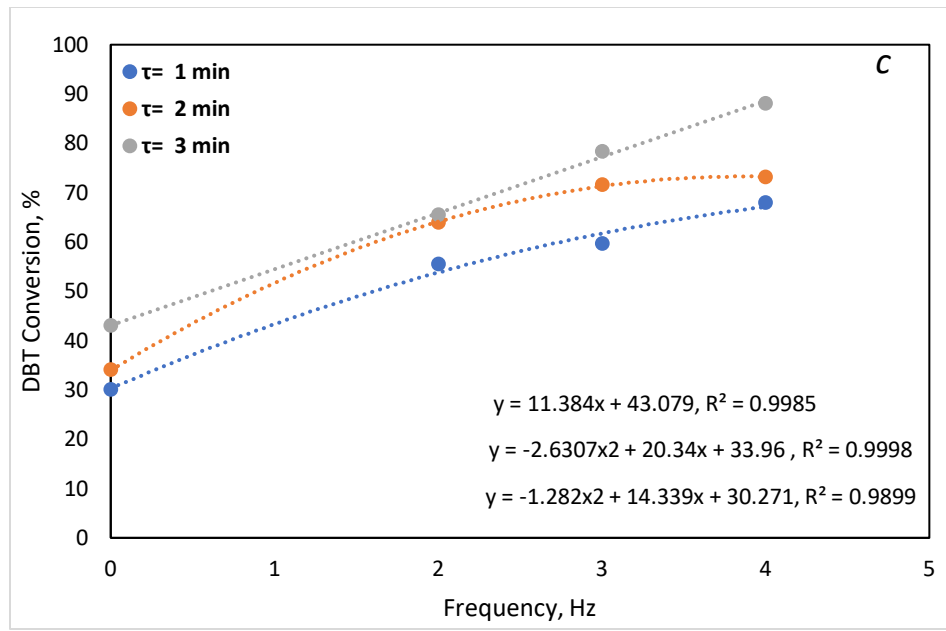


Figure 3. Effect of oscillation frequency on DBT conversion at **a)** $T = 60\text{ }^{\circ}\text{C}$, $x_o = 2\text{ mm}$, **b)** $T = 70\text{ }^{\circ}\text{C}$, $x_o = 2\text{ mm}$, **c)** $T = 80\text{ }^{\circ}\text{C}$, $x_o = 2\text{ mm}$.

Figure 3 shows that the conversion of DBT increased with increasing oscillation frequency. For example, the conversion increased from 9% to 15% to 35% as the oscillation frequency increased from 0 Hz to 2 Hz to 4 Hz at $T = 60\text{ }^{\circ}\text{C}$, $x_o = 2\text{ mm}$, and $\tau = 1\text{ min}$. This is a consequence of the increasing local intensity of mixing generated in the reactor as the oscillation frequency increases. These intensities concentrated at the baffled areas along the tubular reactor and indicated that the reaction was still in the mixing-limited regime at these conditions (McDonough, 2019). The overall mass transfer coefficient (k_{La}) in the OBR increases significantly with the increase of oscillation frequency (Hewgill, 1993) (increasing the mass transfer rate of the acetic acid/ H_2O_2 system in the diesel fuel). This increase leads to an increase in the dispersion of the H_2O_2 molecules through the fuel (diesel fuel) phase and the generation of emulsions of the H_2O_2 and fuel phases due to the micro-mixing generated by oscillation. Then, under the temperature and the controlled and uniform mixing produced by the oscillation conditions fine emulsion was generated between the oxidant and the diesel fuel. The emulsion increases the interfacial area that assists the effective

transfer of HO₂ radicals that attack sulfur in the DBT ring and convert it to sulfone. Thus, the net utilization of these radicals towards oxidation becomes high which results in greater oxidation of DBT(Bhasarkar, 2013).

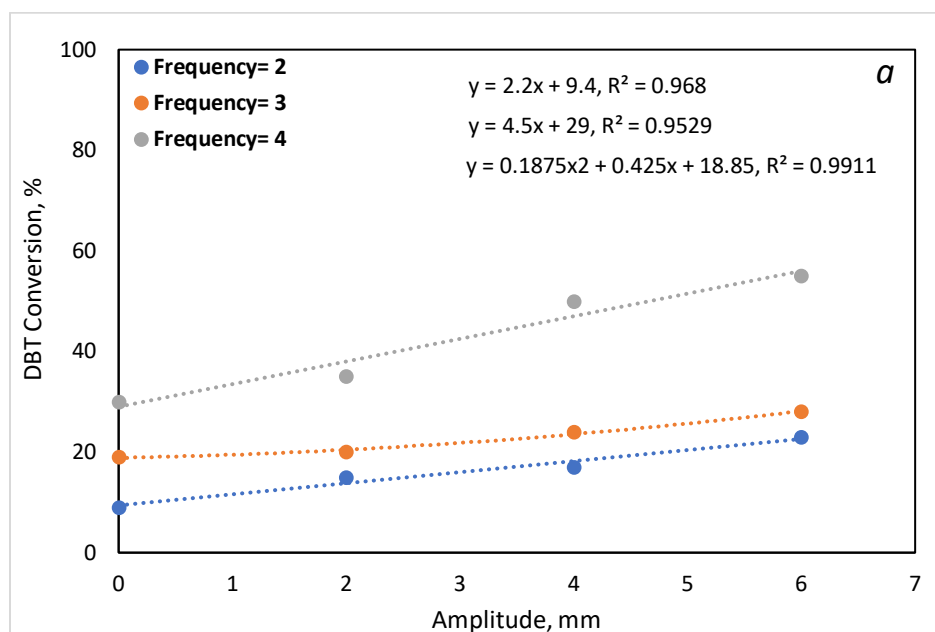
The conversion increased from 50% to 72% as the oscillation frequency increased from 2 Hz to 4 Hz at T=70 °C, $x_o = 4$ mm, and $\tau = 2$ min (Figure 3.b). Increasing the oscillation frequency also increased the conversion, e.g. increasing the oscillation frequency from 2 Hz to 3 Hz at T=80 °C, $x_o = 6$ mm, and $\tau = 3$ min, increased the conversion from 66% to 79% ((Figure 3.c). The maximum conversion was achieved at 4 Hz, T= 80°C and 3 min residence time which led to improving DBT removal from 79% to 94%.

In the first stage of the ODS reaction, it is essential to provide a satisfactory level of hydrogen peroxide dispersion in the diesel fuel phase to selectively oxidize the organic sulfur-containing molecules to their corresponding sulfoxides or sulfones. Without efficient mixing, the transfer of the hydrogen peroxide into the nonpolar organic fuel phase is very limited. Therefore, a low reaction rate and a slow conversion of organosulfur were obtained in this two-phase system, as shown in Figure 3 at e.g., 0 Hz. As the oscillation frequency was increased the fuel phase and the peroxide phase formed an emulsion. The diesel fuel was the continuous phase, and the hydrogen peroxide plus acetic acid catalyst formed the dispersed phase. In there and at the second stage, as mixing continues with a high oscillation frequency, the back mixing produced high hydraulic shear. It broke the aqueous phase of the peroxide into sub-micron and nanosize droplets(G. X. Yu, et al. 2014). Also, it was shown that an increase in either the oscillation amplitude or frequency decreased the Sauter mean droplet size, with gradients of -0.76 and -1.12 respectively. This suggests that the oscillation frequency had a more prominent effect on the droplet size than the oscillation amplitude. Increasing the oscillation frequency caused a greater break-up of the droplets, increasing the interfacial surface area, which increased the observed rate of the ODS

reaction. Also, working at higher levels of oscillation frequency promoted the disproportionation of hydrogen peroxide into the active free radicals, suggesting that they remained stable and active oxidants throughout the time of the DBT oxidation reaction(Haw et al., 2010). It has previously been reported that the OBR is advantageous when applied to reactions with mass-transfer limitations (Phan et al., 2011), and these results seem to be further evidence to support this observation.

3.2 Effect of the amplitude of oscillation on DBT conversion

Vortex propagation increases with amplitude (X Ni, 1998; Xiongwei Ni and Gough, 1997; Xiongwei Ni et al., 2003). Small amplitudes give poor vortex propagation. The influence of amplitude on the conversion of DBT via oxidation reaction in OBR was studied at 0, 2, 4, and 6 mm at the various reaction temperatures, residence time, and frequencies of oscillation using acetic acid/H₂O₂ as catalyst/oxidant system. Figure 4 shows DBT conversion as a function of the amplitude of oscillation.



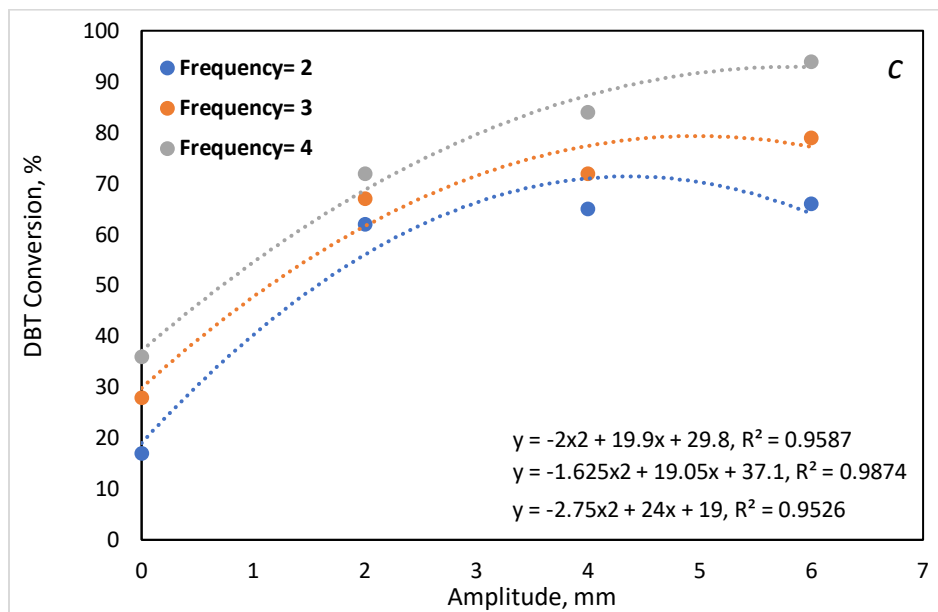
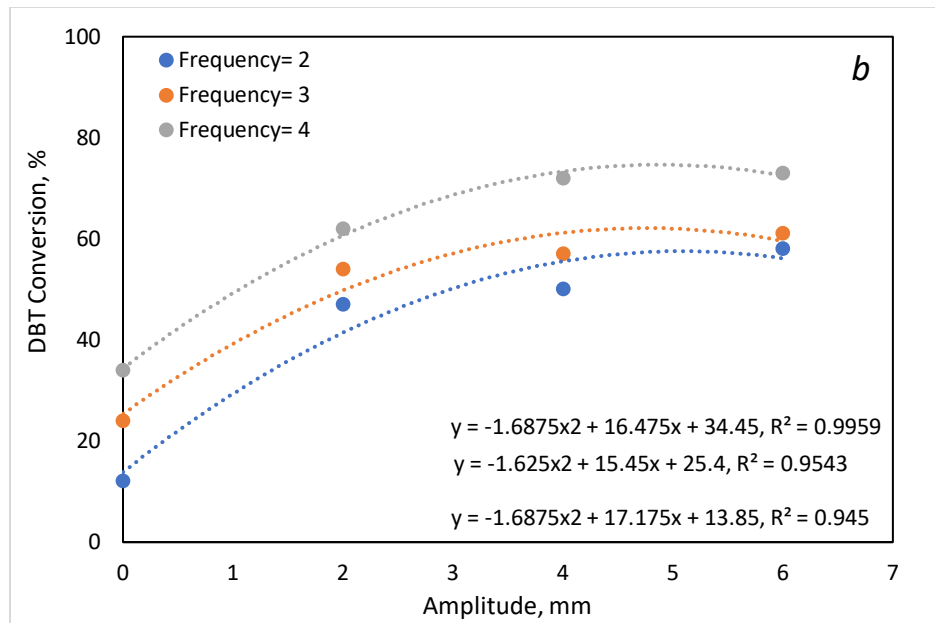


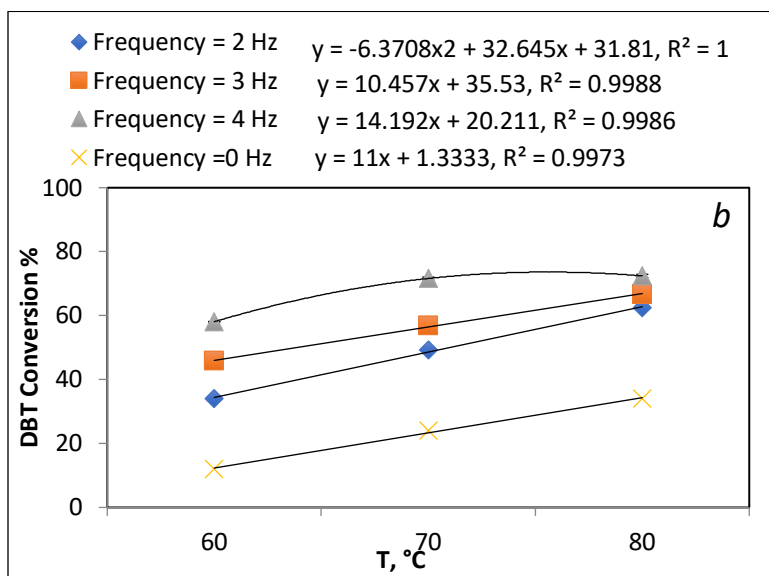
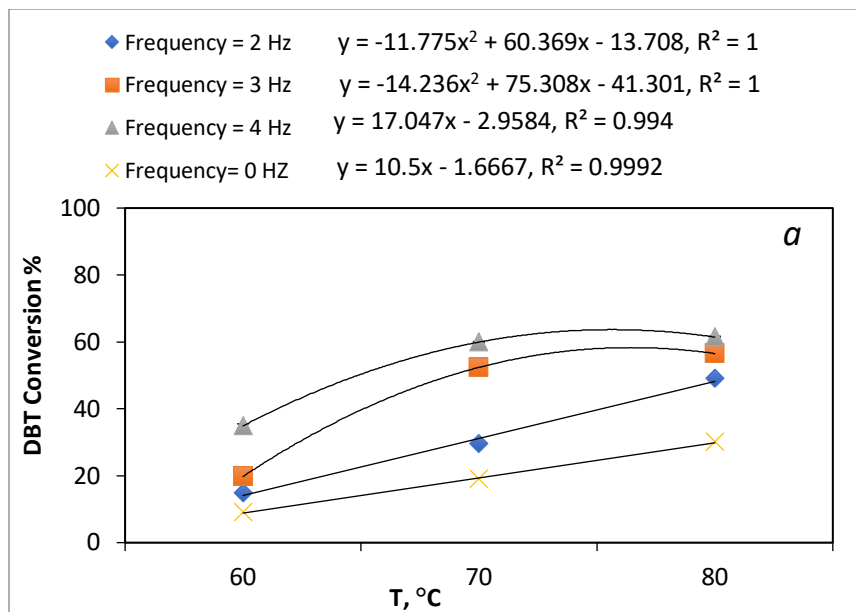
Figure 4. Effect of amplitude of oscillation on DBT conversion at **a)** $T = 60\text{ }^{\circ}\text{C}$, $\tau = 1\text{ min}$, **b)** $T = 70\text{ }^{\circ}\text{C}$, $\tau = 2\text{ min}$, **c)** $T = 80\text{ }^{\circ}\text{C}$, $\tau = 3\text{ min}$.

The experimental results indicated that increasing the amplitude of oscillation leads to an increase in DBT removal from diesel fuel. These results indicated that increasing the amplitude of oscillation from 0 to 2 mm then to 6 mm leads to an increase DBT removal from 9%, 15% then

to 23% at $T=60^{\circ}\text{C}$, $f=2\text{ Hz}$, and $\tau=1\text{ min}$ (Figure 4.a). The DBT oxidation was upgraded from 58% to 61% with increasing the amplitude of oscillation at $T=70^{\circ}\text{C}$, $f=3\text{ Hz}$, and $\tau=2\text{ min}$ (Figure 4.b). Also, the results showed that the DBT removal increases from 72% to 84% with increasing oscillation amplitude from 2 mm to 4 mm at $T=80^{\circ}\text{C}$, $f=4\text{ Hz}$, and $\tau=3\text{ min}$. However, it was observed that a small increase to 94% was observed as the oscillation amplitude was raised from 4 to 6 mm, as shown (Figure 4.c). As described in section 3.3, the DBT reacted at the interphase. The products, sulfoxides, and sulfones accumulated at the aqueous droplet surface and block other sulfur compounds from interacting at the aqueous phase. The hydraulic shear caused by the eddies generated by the oscillations resulted in eddy flow and material transport from and to droplet surfaces in each baffle zone. It led to the repeated coalescence and subsequent formation of new droplets. As the ODS progresses over time, increasing the amplitude with time maximizes the exposure and interaction of the reactants. However, as the amplitude directly relates to the length of eddies propagated inside each baffled cavity so that the increase in oscillation amplitude increased the size of eddies generated. Therefore, the small droplets collided and coalesced into larger droplets, which in turn enlarge the specific surface area of the interphase and lower the rate of ODS reaction.

3.3 Effect of reaction temperature on DBT conversion

The Effect of different reaction temperatures (60°C , 70°C , and 80°C) on DBT conversion in the OBR was investigated at atmospheric pressure and other operating variables, as shown in Table 4. Figure 5 shows the effect of conducting the ODS of the diesel fuel at different reaction temperatures in the OBR unit with and without mixing effect.



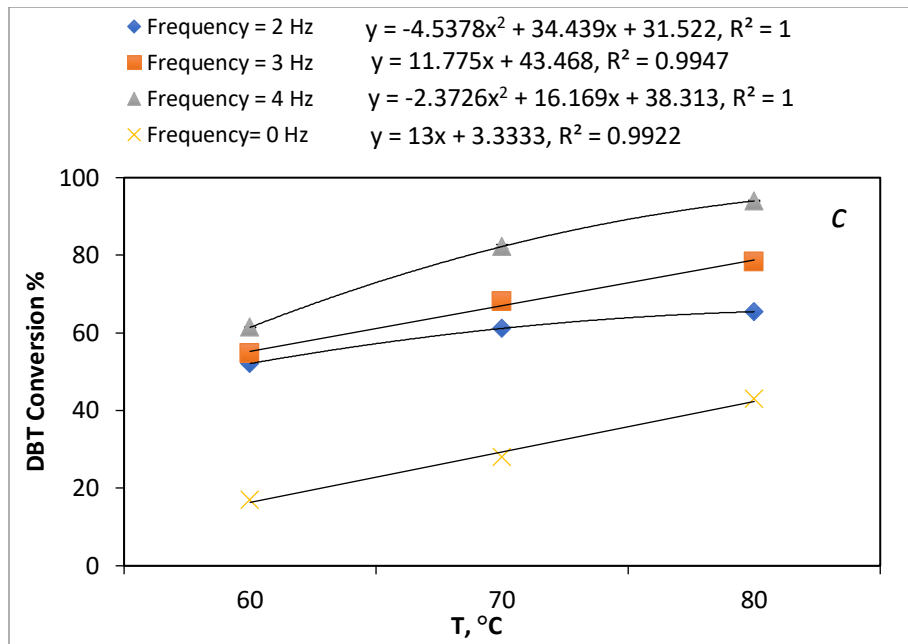


Figure 5. Effect of ODS temperature on DBT conversion at **a)** $\tau = 1$ min, $x_o = 2$ mm, **b)** $\tau = 2$ min, $x_o = 4$ mm, **c)** $\tau = 3$ min, $x_o = 6$ mm

Basically, it was observed that the ODS of DBT in the OBR is mass transfer limited as the tests revealed that the DBT conversion was significantly improved due to running the experiments in the presence of mixing compared to the conversion achieved at no mixing condition. The Figure shows that at all mixing conditions (low (2 mm), moderate (2 and 3 Hz, 4 mm), and high 4 Hz, 6 mm), the conversion of DBT was much higher than the conversion achieved at the same temperature and residence time at no mixing condition. For example, it was shown that conversion of only 36% was achieved without mixing versus 62%, 72%, and 94% achieved in the OBR at 3 min residence time, 80 °C and low, moderate, and high mixing conditions, respectively.

It can be observed from Figure 5.a that as the temperature increases from 60 °C to 70 °C at low flow and oscillation conditions ($\tau = 1$ min, $x_o = 2$ mm, and $f = 2$ Hz), DBT removal increases from 15% to 30%. At 80 °C the conversion of DBT increases from 30% to 50%. At moderate oscillation conditions ($x_o = 2$ mm and $f = 3$ Hz), increasing temperature from 60 °C to 70 °C led to a sharp

increase, from 20% to 53% DBT removal. As the temperature was raised to 80 °C, the increase in DBT conversion was much less (53% to 62%). This reduction in the increase of DBT conversion as temperature increases may attribute to the fact that at 80 °C the hydrogen peroxide began to decompose (Otaibi et al., 2015); thus, the strength of oxidation became less. The enhancement of DBT conversion by raising the temperature from 70 to 80°C at 4 Hz was limited, which indicates that the reaction has reached mixing independence. Figure 5.b shows the DBT conversion profiles versus reaction temperature for a residence time of 2 min. Extending reaction time made the conversion much higher even at the lowest temperature of 60°C and oscillation conditions (34%) compared to Figure 5. where the time was 1 min. The same behavior of steeper increase in DBT conversion with temperature up to 70°C was observed at all oscillation conditions and the same limited enhancement from 70 to 80°C was also noted. The highest conversion is shown in Figure 5.b was 73% at 80°C, 2 min, 4 mm amplitude, and 4 Hz. As the conditions were changed to severe ($\tau = 3$ min, $x_o = 6$ mm, and $f = 4$ Hz), the increase in reaction temperature from 60 to 80°C led to enhancing DBT removal from 62% to 94% as shown in Figure 5.c. In general, the experimental results obtained indicated that at 80°C the conversion of DBT by the ODS process was higher than the conversion at 60°C and 70°C. The vortices generated between periodically reversing the flow and regularly spaced constrictions significantly improve mixing in the baffle cavities by improving the droplet breakup process and emulsion formation at the start of the reaction between diesel fuel (continuous phase) and hydrogen peroxide catalyst (dispersed phase)(Phan et al., 2011). Thus, the increase in reaction temperature promoted DBT oxidation. Compared to previous studies, Sinhmar et al.(Sinhmar and Gogate, 2020) found that rising temperature from room temperature to 60 °C of ODS of DBT in diesel fuel using H₂O₂ and acetic acid by ultrasound-assisted oxidative desulfurization (UAOD) process (20 kHz and 18-120 min residence time) led to an increase from 10% to 50%. They explained that the increase in the oxidation reaction rate of DBT was due to the

strong dependence of the reaction rates on the reaction temperature(Yazu et al., 2004). Much less reaction time was required in the present study to achieve 94%. Also, Al Otaibi1 et al. (Otaibi et al., 2015) showed that the conversion of sulfur compounds in a crude oil desulfurized in H₂O₂/acetic acid batch reactor system increased from 14% to 35% as the temperature raised from 40 to 70 °C, and declined from to 33% as the temperature was increased to 80°C due to H₂O₂ decomposition. However, different extents of enhancement by temperature were observed at different oscillation conditions.

The results of the present study can be explained as follows:

- **Physical properties of the reactants**

Increasing temperature will contribute to increases in diffusivity and decreases in viscosity and surface tension, all of which will increase the rate of transport between phases. The increase in temperatures will raise the diffusion rate of the oxidant radicals to the DBT molecules in the fuel and the rate of mass transfer of aqueous peroxide to the acetic acid catalyst, which facilitated the rapid rate of DBT conversion (Jiang, 2011; G. Yu, 2005).

- **Thermal decomposition of hydrogen peroxide**

Hydrogen peroxide is a chemically unstable substance, resulting in the decomposition of H₂O₂ aqueous solution (H₂O_{2(aq)})(Zapata et al., 2005). The increase in the reaction temperature strongly affects the behavior of this decomposition. The reaction of decomposition of hydrogen peroxide is very slow at moderate temperatures and can be sped up by increasing the temperature, which triggers thermal decomposition. The nature of hydrogen peroxide decomposition affects significantly DBT conversion depending on the products of this degrading. There are two competitive pathways for H₂O₂ decomposition that may affect the oxidation rate of the DBT:

1- The decomposition of H_2O_2 to produce hydroxyl radicals (desirable reaction). These radicals combined with acetic acid to form peracetic acid, the strong oxidizing agent. It is reported in the literature that the oxidation reaction of sulfur compounds can be promoted by increasing peracetic acid, which is formed in situ by acetic acid and H_2O_2 [43].

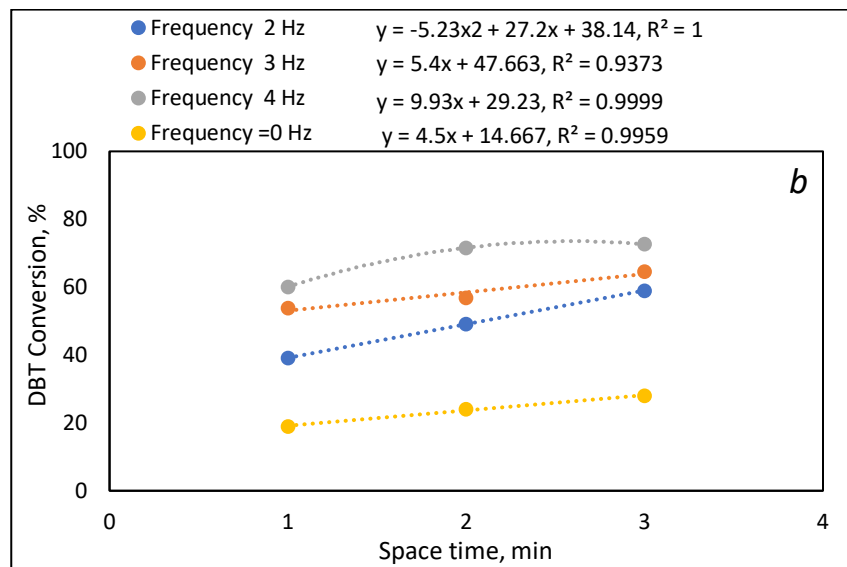
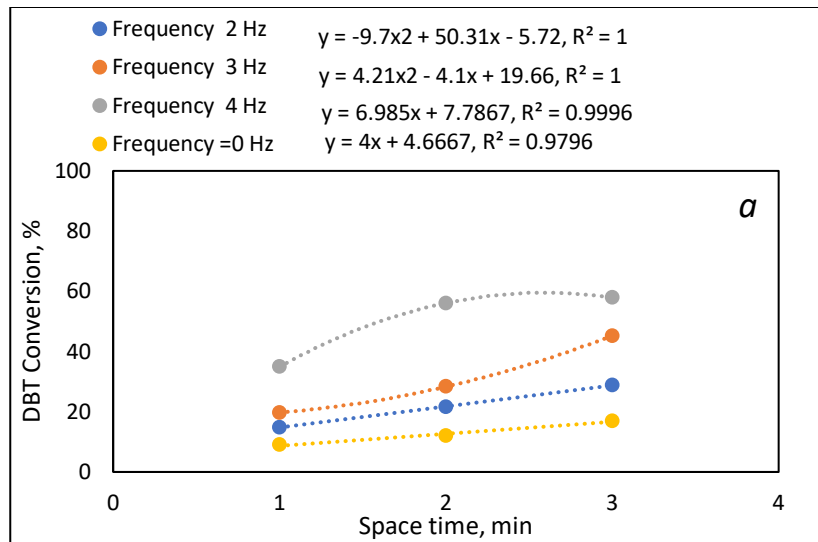
2- The decomposition of H_2O_2 to produce water and oxygen (undesirable reaction). The boiling point of these mixtures is $114\text{ }^\circ\text{C}$ (Eul, 2000; Hess, 2000) i.e. less oxidation strength which in turn limits the increase of the oxidation reaction rate of DBT(Sobati, 2010; Zhao, 2008).

This unwanted decomposition negatively affects the DBT removal performance of the fuel by oxidation. In the present study, the effect of the change in temperature of the oxidation process on DBT removal in the OBR was examined up to $80\text{ }^\circ\text{C}$ to avoid the unwanted decomposition of the H_2O_2 at higher temperatures which is highly influential. The H_2O_2 begins to decompose to unwanted products at $80\text{ }^\circ\text{C}$. However, the reaction time (3 min) was very short and not sufficient for the production of the unwanted products of decomposition. Significant unwanted decomposition of H_2O_2 needs more time according to the literature [50].

The increase in the reaction temperature strongly influences the mechanism of this decomposition. Also, the mechanism of $\text{H}_2\text{O}_2(\text{aq})$ decomposition influences the DBT conversion significantly, as the products of this decomposition are different for each mechanism.

3.4 Effect of the residence time of reactants on DBT conversion

To examine the effect of residence time on the effectiveness of the ODS process, several oxidation experiments were conducted and investigated at different residence times (1, 2, and 3 min), reaction temperatures, amplitudes, and frequencies using acetic acid as catalyst and H_2O_2 as oxidant at atmospheric pressure. The profiles of the DBT conversion versus residence time at different conditions are presented in Figure 6.



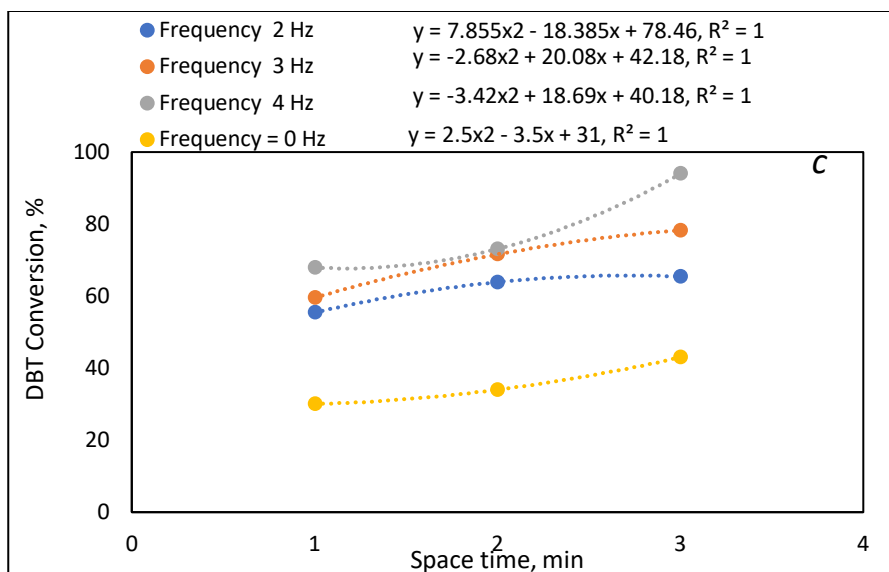


Figure 6. Effect of residence time on DBT conversion at

a) $T = 60\text{ }^{\circ}\text{C}$, $x_o = 2\text{ mm}$ **b)** $T = 70\text{ }^{\circ}\text{C}$, $x_o = 4\text{ mm}$, **c)** $T = 80\text{ }^{\circ}\text{C}$, $x_o = 6\text{ mm}$

Again, the effect of mixing on the ODS of DBT in the OBR of the emulsified mixture is obvious as the DBT conversion was significantly increased due to increasing the extent of mixing compared to the conversion achieved at no mixing conditions (without oscillation). It is also observed that the DBT conversion in the OBR was significantly enhanced by extending residence times as the conversion of DBT increased from 14.85% to 21.62% with extending the time of reaction from 1 min to 2 min at $T=60\text{ }^{\circ}\text{C}$, $x_o = 2\text{ mm}$, and $f = 2\text{ Hz}$. Further increase of reaction time to 3 min leads to an increase of DBT conversion to 28.82%. At $T=70\text{ }^{\circ}\text{C}$, $x_o = 4\text{ mm}$, and $f = 3\text{ Hz}$ as the time of reaction was increased from 1 min to 3 min, the DBT conversion increased from 54% to 65 % (Figure 6.b) and the increase of reaction time from 1 min to 3 min at $T=80\text{ }^{\circ}\text{C}$, $x_o = 6\text{ mm}$, and $f = 4\text{ Hz}$, led to increasing the DBT removal conversion from 68% to 94% (Figure 6.c). At the time of experimentation, the reactor was left to run for more residence time, but no higher conversion was achieved as the reaction was likely to approach the equilibrium. Increasing the time of reaction increased the contact time between the reactants (oxidizing agent and the DBT) as time proceeds. Hydrogen peroxide and acetic acid can interact with DBT to produce

sulfones, and the undesirable fluctuation of flow was decreased by increasing residence time (Phan et al., 2011). Also, the rate of oxidation reaction, like any other reaction, needs enough time to raise and is promoted as time goes on. Mamaghani et al. (Mamaghani et al., 2013) showed that the ODS reaction of DBT in simulated diesel fuel (n-octane) in the presence of H_2O_2 as oxidant and formic acid as catalyst in a batch reactor was improved by increasing the time of the reaction to a certain extent then slightly decreased as the time of reaction increased. They observed that the sulfur conversion dropped from 97% to 60% with increasing reaction time from 50 min to 70 min due to the relatively long residence time of reaction that resulted in excessive decomposition of H_2O_2 and performic acid (Mamaghani et al., 2013). In contrast, the present study proved that the enhancement of DBT conversion in the OBR with the time of reaction did not interrupt as the time was increased because the maximum time used was short enough to prevent excessive decomposition of the strong oxidants. The good mixing achieved in the OBR in a short time was enough to oxidize the DBT with the $H_2O_{2(aq)}$ without significant decomposition that weakens the strength of the oxidants. The finding of the present study agrees with Ghaeli and Vakili (Ghaeli and Vakili, 2020). They observed that the oxidation of sulfur compounds in a light fuel oil using the H_2O_2 / acetic acid system as an oxidant/catalyst in the ultrasonic bath batch reactor was increased from 35% to 49% as the time of reaction increases from 10 min to 40 min (Ghaeli and Vakili). Table 6 compares the findings of the present study of ODS in the OBR with previous studies conducted in different types of reactors at different residence times. It can be concluded from this comparison that with the OBR, reaction time can be reduced significantly due to the uniform and efficient mixing provided by the motion of oscillatory fluid interacts at the baffles in the tube of the OBR and this promotes mass transfer and reaction rate in a very short time, hence increases conversion (Kefas et al., 2019; Syam et al., 2012).

Table 6. Summary of reaction time required for the ODS process and sulfur conversion in the present study and some previous studies.

Feedstock/ sulfur compounds	Oxidant/ catalyst system	Type of reactor	Reaction time	Separation stage	Sulfur removal efficiency	Reference
Kerosene/ different sulfur compounds	H ₂ O ₂ / formic acid	four-impinging- jets reactor	60 min	Extraction	92%	(Sobati et al., 2010)
Gasoil/different sulfur compounds	H ₂ O ₂ /formic acid	Ultrasonic reactor	29.2 min	-	20%	(Aghaei, Shahhosseini, and Sobati, 2020)
Diesel fuel/DBT	H ₂ O ₂ /acetic acid	Batch reactor	30 min	Extraction	98.25%	(Palaić, Sertić- Bionda, Margeta, and Podolski, 2015)
Diesel fuel/DBT	H ₂ O ₂ /acetic acid	Batch reactor	180 min	-	60%	(Haw et al., 2010)
Naphtha/ benzothiophene	H ₂ O ₂ /acetic acid	Batch reactor	120 min	Adsorption	80%	(Yazu, 2010)
Iso- octane/DBT	H ₂ O ₂ /(Cr/sulfated zirconium)	Batch reactor	360 min	-	79.26%	(Kumar, Srivastava, and Badoni, 2012)
Mixed octanes/DBT	H ₂ O ₂ /acetic acid	Batch reactor	80 min	-	93.41%	(Joskic et al., 2014)
Diesel fuel/DBT	H ₂ O ₂ /acetic acid	Continuous- OBR	3 min	-	94%	Present work

4. Conclusions

The oxidative desulfurization of dibenzothiophene (DBT) in diesel fuel was conducted at laboratory scale in a mesoscale oscillatory baffled reactor (meso-OBR) at various temperatures (60, 70, 80°C), residence times (1, 2, 3 min), oscillation frequencies (2, 3, 4 Hz), and oscillation amplitudes (2, 4, 6 mm), employing acetic acid (CH_3COOH) as a catalyst and hydrogen peroxide (H_2O_2) as oxidant, at atmospheric pressure to obtain the highest possible conversion of DBT at short residence time.

Higher conversions of DBT were achieved in just one pass than in various comparable studies conducted using the same oxidant and catalyst and required extraction step to obtain high DBT conversion. The combination of the oscillatory motion and the helical baffle design provided sufficient mixing of the reactants to accelerate the reaction to the necessary degree. Within this parameter space, the DBT conversion was increased by increasing the temperature, residence time, oscillation frequency, and oscillation amplitude: the maximum DBT conversion (94%) was achieved at 80 °C, the residence time of 3 min, the oscillation frequency of 4 Hz, and oscillation amplitude of 6 mm, which were the maximum levels of each in this parametric study. It is, therefore, likely that further increases would result in even higher conversions. However, a further increase in temperature is critically limited by the decomposition of hydrogen peroxide and would lead to undesirable and hazardous H_2O_2 decomposition. Temperature control was enhanced in the OBR, due to the large surface area to volume ratio and the radial transport of material within the reactor. This allowed a closer approach to the decomposition temperature. This is one of the advantages of using a tubular flow reactor for this application.

Clearly, a homogeneous ODS reaction can be operated continuously using this mesoscale oscillatory baffle design, and perhaps using similar plug flow reactor designs. The helical baffle with central rod design provided sufficient mixing to produce a homogeneous mixture even at low

net flow rates, resulting in high conversions in short residence times of 3 min, which should be contrasted with the residence times of an hour or longer time in batch and other conventional types of reactors.

Nomenclatures

Symbol	Definition	Unit
x_o	Oscillation amplitude	mm
D	Internal tube diameter	mm
D_0	Baffle diameter	mm
f	Oscillation frequency	Hz
L	The characteristic length of the reactor	(-)
l	Baffle spacing	mm
Re_n	Net flow Reynold's number	(-)
Re_o	Oscillatory Reynold's number	(-)
St	Strouhal number	(-)
X_{DBT}	Conversion of DBT	(-)
δ	Baffle thickness	mm
ρ	Fluid density	kg/ m ³
μ	Fluid viscosity	Pa. s
Ψ	Velocity ratio	(-)
τ	Space-time	min

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