

# Ultrasound Assisted Oxidative Desulfurization of Dibenzothiophene Using Htmab as a Phase Transfer Agent

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**Abstract:** Increase in energy demand and consumption has been accompanied by a corresponding increase in sulfur emissions. These pollutants have both health and economic consequences. Furthermore, it significantly reduces the efficiency of advanced emission control systems of diesel engines, thereby indirectly causing more harm to the environment. This resulted in stringent sulfur emission limit down to about 15 ppm or less and in turn served as an incentive for research into alternative sulfur reduction technologies. Although feasible improvements to hydrodesulfurization are currently under investigation, adsorptive, extractive, oxidative and biodesulfurization have also been studied in recent years. Oxidative desulfurization appears to be one of the most promising desulfurization technologies due to mild operating condition. This paper attempts to discern the physical and chemical effect ultrasound on the oxidative desulfurization process using HTMAB as a phase transfer agent (PTA). With different experimental protocols, an attempt is made to deduce individual beneficial effects of PTA and ultrasound on the oxidative desulfurization system, and also identify the synergy between the effects of PTA and ultrasound. In present study, dibenzothiophene (DBT) is used as a model sulfur compound and toluene used as a model solvent (20 mL) with an initial DBT concentration of 100 ppm has been used in all experiments. This paper reports investigation in the mechanistic features of phase transfer agent (PTA) enhanced oxidative desulfurization for two systems, viz. mechanically stirred system and ultrasound irradiated system. The beneficial effect of PTA is more marked for the former system than latter, as intense emulsification due to ultrasound enhances the reaction, and this relatively reduce the beneficial effect of PTA. On the other hand, faster interphase transport of oxidizing species by PTA also reduces beneficial effect of higher static pressure in case of ultrasound irradiated system. PTA also reduces scavenging effect of  $H_2O_2$  due to complexation with the oxidant species and its effective transfer to organic phase. The oxidant performic acid is found to have higher oxidation yield than peracetic acid, which is attributed to higher diffusivity of performic acid-PTC complex across interphase.

**Keywords:** Ultrasound, Cavitation Desulfurization, Phase transfer agent, HTMAB, Dibenzothiophene

## 1. Introduction

The environmental pollution generated by vehicular emission is one of the biggest global concerns, as the total oil consumption of world (mostly as liquid transportation fuel) crosses 90 million barrel a day. Emission of sulfur oxides or SO<sub>x</sub> gases from engine exhaust makes primary contribution to the pollution, and as a consequence, the sulfur content regulations in transportation fuels like diesel and gasoline are becoming more and more stringent. The Euro-IV norms have already put a limit of 100 ppmw on the sulfur content of fuel. However, in near future, zero sulfur level requirements may be imposed, and this makes development of advanced desulfurization technologies a major challenge before scientific community. In view of this, recent past has witnessed enormous research activity in the area of deep desulfurization of diesel and gasoline. Most of the petroleum refineries worldwide implement the technology of catalytic hydro-desulfurization (HDS), which is based on removal of sulfur molecules from fuel by converting them to H<sub>2</sub>S. However, this technology is not suitable for deep desulfurization of fuel (10 ppm level). Moreover, this technology is highly energy intensive and requires expensive hydrogen and catalyst. Moreover, this technique is not effective in removal of refractory sulfur compounds like dibenzothiophene and its alkylated derivatives, as these compounds have limited reactivity with HDS catalyst due to steric hindrance.

The alternate oxidative desulfurization technology emerged in past few years has high promises in this regard. This

technology is not only far less energy and cost intensive than HDS, but also has the distinct advantage of effective removal of refractory sulfur compounds mentioned earlier. In oxidative desulfurization, the sulfur compounds undergo chemical oxidation to respective sulfones, which have higher polarity. These oxidized products can then be removed by extraction with common polar solvents like methanol and/or acetonitrile. The chemical oxidation of sulfur compounds is achieved using common oxidants like organic peroxyacids, hydrogen peroxide and ozone. The oxidative desulfurization reaction system is essentially a liquid-liquid heterogeneous system, i.e. the oxidant is in aqueous phase, while the substrate or sulfur compounds on which it acts is in organic phase. These systems are well known to be limited by mass transfer, as the rate of reaction is determined by the interfacial area between the two phases, and the rate of transfer of reactants across this interface. The emulsification of the reaction mixture, which governs the interfacial area generated between phases, therefore plays a crucial role in determination of overall kinetics of oxidative desulfurization. The emulsification itself, in turn, is a function of the convection present in the system.

Ultrasound irradiation of the reaction mixture has already been attempted by several researchers to enhance the kinetics of oxidative desulfurization through enhanced emulsification. In our earlier papers [1,2], we have investigated the mechanistic issues of sonochemical or ultrasonic oxidative desulfurization. Another means of enhancing kinetics of a liquid-liquid heterogeneous reaction system is phase transfer catalyst (PTC). Quaternary

ammonium salts, which have been used as surfactant, have unique capability of dissolving in both aqueous and organic phases. These salts can form a complex with the oxidant in the aqueous phase, and transport it across interface to the organic phase, where reaction takes place effectively converting sulfur compound like DBT to corresponding sulfone. The reduced species that dissociates with phase transfer agent returns to the aqueous phase, and this gives a catalytic cycle. Although, the gross emulsification and interfacial area is a function of convection in medium, the transport of the complex between oxidant and PTC is still a function of intrinsic diffusivity. Several papers have appeared in recent past that have reported beneficial effects of PTC on the oxidative desulfurization system. [3,4]

In this paper, we have investigated the hybrid technique of simultaneous application of both PTC and ultrasound for oxidative desulfurization. Particularly, we have tried to discern the role of quaternary ammonium salts or the PTC in formation of complex with the oxidant, the transport of the complex across interface, and the reaction of oxidant with sulfur compound in the organic phase. Moreover, we have also tried to distinguish between the physical and chemical effects of ultrasound and cavitation. Comparative assessment for oxidation achieved with different experimental protocols has helped in identification of the individual roles and contributions of mass transfer characteristics and intrinsic kinetics in the oxidative desulfurization process. Essentially, our analysis provides a mechanistic insight into the process by linking physics and chemistry of the oxidative desulfurization system.

## 2. Materials, Methods and Mathematical Model

### 2.1 Chemicals

Dibenzothiophene (abbreviated as DBT, 98%, Sigma Aldrich) used as model sulfur compound; Toluene (Synthesis grade, Merck) and n- decane used as the model liquid fuel; 30% v/v  $H_2O_2$  (AR Grade, Merck), Acetic acid (99–100%, AR Grade, Merck), Formic acid (~ 86%, AR Grade, Lobachem), Phosphotungstic acid. Hexadecyltrimethylammonium bromide (HTMAB, Sigma Aldrich) used as a phase transfer catalyst, Acetonitrile (HPLC grade, Merck) used as a mobile phase for HPLC analysis. All the chemicals were used as received without further any pre-treatment.

### 2.2 Experimental setup

Experimental A schematic diagram of experimental setup for ultrasound and mechanical stirred system are shown in Figure 1(a) and (b) respectively. For the experiments conduct in ultrasound system, an ultrasonic bath (Make: Jeio-Tech, Model: UC02, Capacity: 2 L) was used for sonication of the reaction mixture. This bath had transducers attached to the bottom of the bath that operated at frequency 35 kHz with maximum theoretical power dissipation of 70 W. The bath was filled with water that acted as media for propagation of ultrasound waves. The actual power dissipated in the bath was determined calorimetrically and on that basis, the acoustic pressure amplitude generated in

the bath was calculated as 150 kPa. Oxidative desulfurization reactions were carried out in a round bottom flask (50 mL, borosilicate glass). The round bottom flask was placed in the center of the bath. As the ultrasound intensity in the bath shows significant spatial variations, the position of the round bottom flask inside bath was carefully maintained the same in all experiments. The experiments were carried out with different temperature for that, the spherical coil placed inside the sonication bath. Water bath was used to maintain the required temperature and circulate the water inside the coil. Same experiments were done with mechanical stirred system.



Figure 1a: Experimental setup of ultrasound

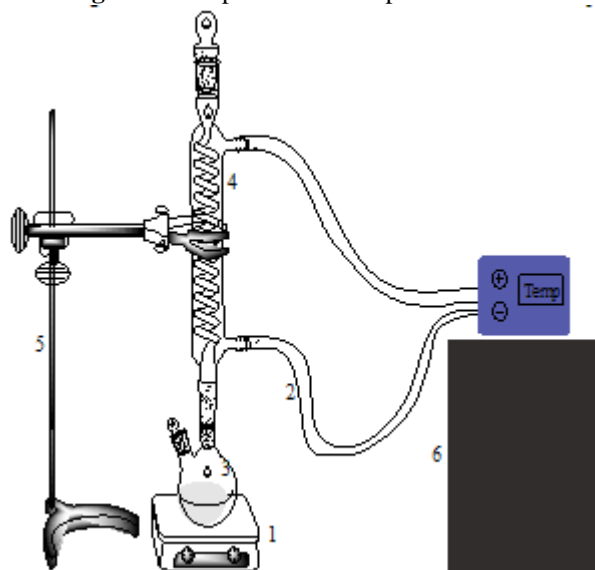


Figure 1b: Experimental setup for mechanical stirring

**Legends:** 1 – Magnetic stirrer, 2 – Silicon pipe, 3 – Round bottom flask containing reaction mixture, 4 – Condenser, 5 – Holding stand, 6 – Temperature controllers

### 2.3 Analysis

The residual concentration of DBT in the aliquots of reaction mixture was analyzed using Shimadzu High Performance Liquid Chromatography (HPLC, Model: SPD-20A) equipped with a reverse phase C-18 column (5  $\mu$ m, 4.6 mm  $\times$  250 mm) and UV detector at 287 nm. The mobile phase was a mixture of acetonitrile and water (80:20 v/v)

with a flow rate of 1 mL/min. The formation of sulfone in oxidative desulfurization was confirmed using FTIR analysis after completion of reaction. To identify the intermediates during DBT oxidation, GC–MS analysis of the same reaction sample was performed using Varian 240– GC equipped with VF–5ms column (30 m × 0.25 mm ID, DF = 0.25). 1 µL sample was injected in the GC with a split ratio of 10:1. The temperature program was as follows: injection temperature – 250°C, column temperature – 100°C for zero min and increased to 300°C at a ramping rate of 70°C/min. The scanned mass range was from 50 – 1000 m/z and helium gas was used as a carrier gas.

## 2.4 Mathematical model for cavitation bubble dynamics

Most of the physical and chemical effects of ultrasound are attributed to phenomenon of cavitation. Cavitation is essentially nucleation, growth and implosive transient collapse of gas bubbles driven by bulk pressure variation induced by ultrasound wave. The nuclei for cavitation are contributed by tiny gas bubbles already suspended in liquid or the gas pockets trapped in the crevices of the solid boundaries in the medium such as reactor wall or sonicator probe surface. The transient collapse of the cavitation bubble is an extremely energetic event that causes immense energy concentration on extremely short spatial and temporal scale. The velocity of the bubble wall (or gas–liquid interface) can reach or even exceed the sonic speed in liquid medium. The compression of the bubble is adiabatic, and temperatures and pressures in the bubble (compressed to 1/100th of its original size or size of ~ 0.05 microns at the moment of minimum radius during radial motion) reach extreme, i.e. ~ 5000 K, and ~ 500 bar. However, these conditions last only for an extremely short duration of time of collapse, ~ 50 ns or so. The bubble then rebounds for another expansion. The radial motion of the bubble also gives rise to strong convection in the medium through two principal physical effects, viz. microturbulence and acoustic (or shock) waves. The general description of these effects can be found in popular books on cavitation [5-7] and also in our previous paper [8]. In the context of the present study, both of these effects are of relevance as these effects can enhance the interfacial area between oxidant and organic phase. A direct measurement of the magnitude of these effects is beyond the capabilities of the instrumentation used in this study, and hence, we rely on numerical simulations of radial motion of the cavitation bubbles to estimate magnitude of microturbulence and acoustic waves under different experimental conditions.

$$R \frac{d^2 R}{dt^2} + \frac{3}{2} \left( \frac{dR}{dt} \right)^2 = \frac{1}{\rho} (p(R, t) - P_0 - P(t)) + \frac{R}{\rho c} \frac{d}{dt} [I] \quad (1)$$

Two solvents or liquid media have been considered in this study, viz. toluene and n–decane. The physical properties of these solvents used in the simulations are as follows:

Sr. No.	Property	Solvent	
		Toluene	n–Decane
1.	Density (kg/m <sup>3</sup> )	867	730
2.	Surface tension (N/m)	0.0285	0.0238
3.	Viscosity (Pa–s)	$5.89 \times 10^{-4}$	$9.2 \times 10^{-4}$
4.	Sonic velocity (m/s)	1275	1234

Various notations are as follows: R = radius of the bubble at any time; dR/dt = velocity of bubble wall; P<sub>0</sub> = ambient or static pressure in bulk liquid; ρ = density of bulk liquid; c = sonic speed in bulk liquid; μ = viscosity of the bulk liquid; σ = surface tension of bulk liquid. p(R, t) and P(t) are the pressures inside the cavitation bubble and the time variant pressure of the acoustic wave, respectively; and are written as:

$$p(R, t) = \left( P_0 + \frac{2\sigma}{R_0} - P_v \right) \left( \frac{R_0^3 - h^3}{R^3 - h^3} \right)^{\gamma} + P_v \quad (2)$$

$$P(t) = P_A \cos(2\pi ft) = P_A \cos(\omega t) \quad (3)$$

Various notations are as follows: R<sub>0</sub> = initial or equilibrium radius of the bubble; P<sub>0</sub> = vapor pressure of bulk liquid; h = van der Waal's hard core radius; γ = polytropic constant of bubble content; P<sub>A</sub> = pressure amplitude of ultrasound wave; f = frequency of ultrasound wave; ω = angular frequency of ultrasound waves. Equations A.1-1.3 can be easily transformed into two simultaneous ODEs which can be solved using Runge–Kutta adaptive step size method [9]. The numerical solution yields time series of R and dR/dt, and the magnitude of the convective effects, viz. velocity of the microturbulence μ(r, t) and pressure amplitude of the shock waves P<sub>s</sub>(r, t) can be calculated from this solution as follows:

$$u(r, t) = \frac{R^2}{r^2} \left( \frac{dR}{dt} \right) \quad (4)$$

$$P_s(r, t) = \rho \frac{R}{r} \left[ 2 \left( \frac{dR}{dt} \right)^2 + R \frac{d^2 R}{dt^2} \right] \quad (5)$$

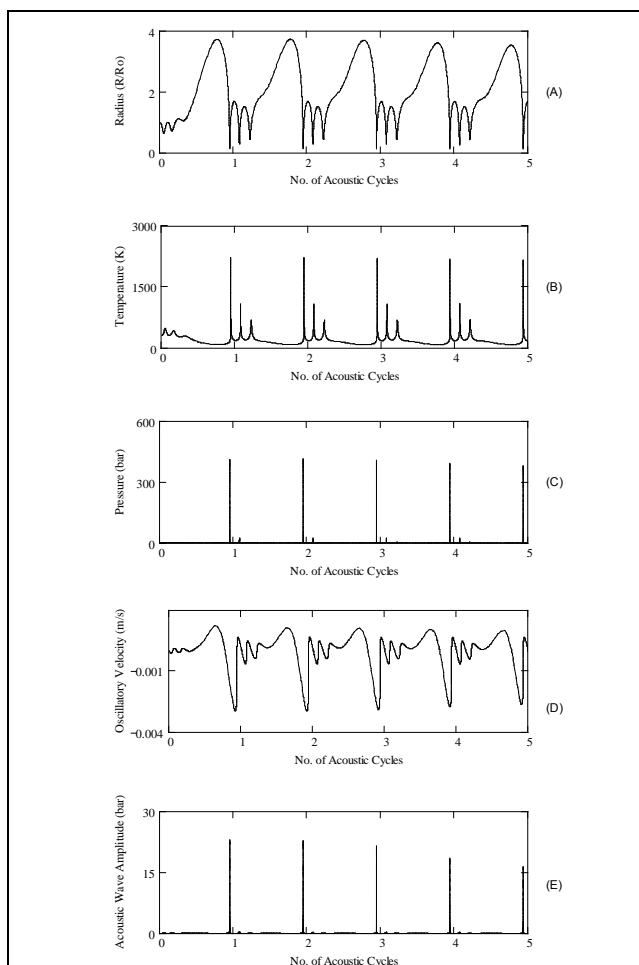
where r is the distance from bubble centre.

## Simulation Parameters

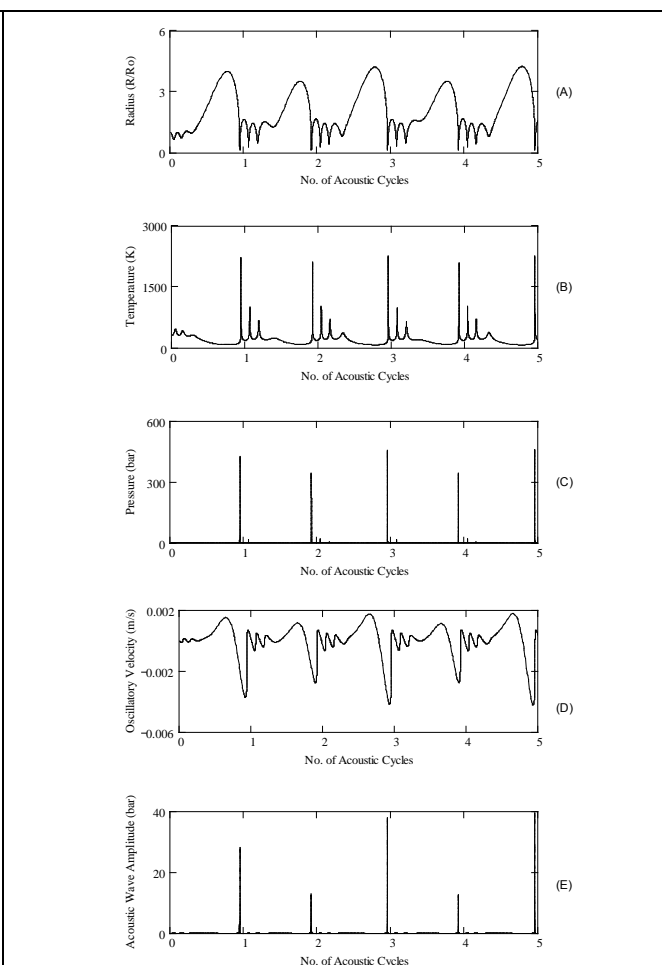
The process parameters for simulations are as follows:

Frequency of the ultrasound waves (f) = 35 kHz (same as the frequency of the ultrasound bath); pressure amplitude of the ultrasound waves (P<sub>A</sub>) = 1.5 bar (estimated using calorimetric techniques as described by Sivasankar et al., 2007); initial radius of cavitation bubble (R<sub>0</sub>) = 5 µm (taken as representative value; Mettin et al., 1997); polytropic constant of an air bubble, γ = 1/3; h = R<sub>0</sub>/8.86 (van der Waal's hard core radius); r = 1 mm (taken as representative value).

5.	Vapor pressure (bar) (NIST Data Gateway, 2014)	$\log_{10} P_v = 4.08245 - \frac{1346.382}{T_o - 53.508}$	$\log_{10} P_v = 0.21021 - \frac{440.616}{T_o - 156.896}$
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**Figure 2a.** Simulations of radial motion of a 5 micron air bubble in toluene at atmospheric static pressure. Time history of (A) radius of the bubble; (B) temperature inside the bubble; (C) pressure inside the bubble; (D) microturbulence generated by the bubble; (E) acoustic waves emitted by the bubble.

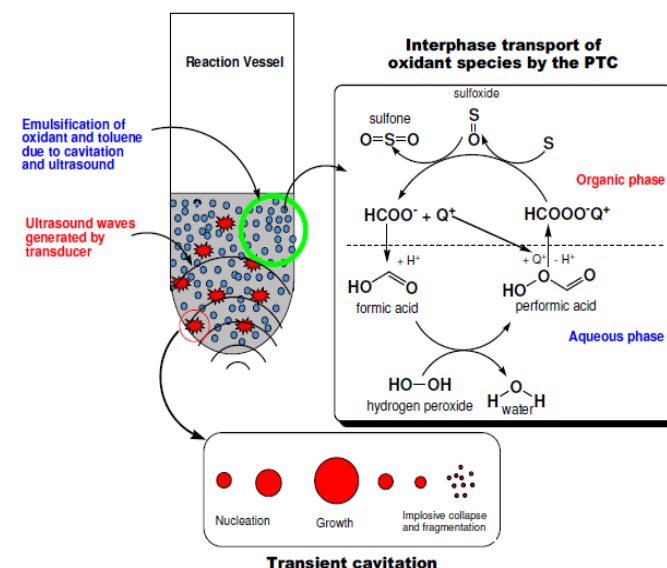


**Figure 2b.** Simulations of radial motion of a 5 micron air bubble in n-decane at atmospheric static pressure. Time history of (A) radius of the bubble; (B) temperature inside the bubble; (C) pressure inside the bubble; (D) microturbulence generated by the bubble; (E) acoustic waves emitted by the bubble.

### 3. Cycling mode of desulfurization of DBT by PTC

In cycling mode of desulfurization of DBT, we give herewith a brief discussion about the individual mechanisms of effect of ultrasound and PTC on oxidative desulfurization reaction system. The mechanism of action of PTC is explained in Scheme-1. Either formic acid or acetic acid reacts with H<sub>2</sub>O<sub>2</sub> to form peracids, which then dissociates. PTC forms a complex with the anion of the oxidant species (either HCOO<sup>-</sup> or CH<sub>3</sub>COO<sup>-</sup>) and transports it to the organic phase, where it can induce the oxidation reaction of sulfur compound to sulfone. This transport is, of course, dependent on the interfacial area between the organic and aqueous phase, which in turn depends on the convection present the system. After oxidation reaction both species, i.e. the anion of acid (HCOO<sup>-</sup> or CH<sub>3</sub>COO<sup>-</sup>) and the cation of PTC (Q<sup>+</sup>) returns to aqueous phase and the cycle continues. PTC thus assists faster transport of oxidant species across interface, and helps overcome the mass transfer limitations

of the process that result in enhancement of kinetics of oxidation [4].



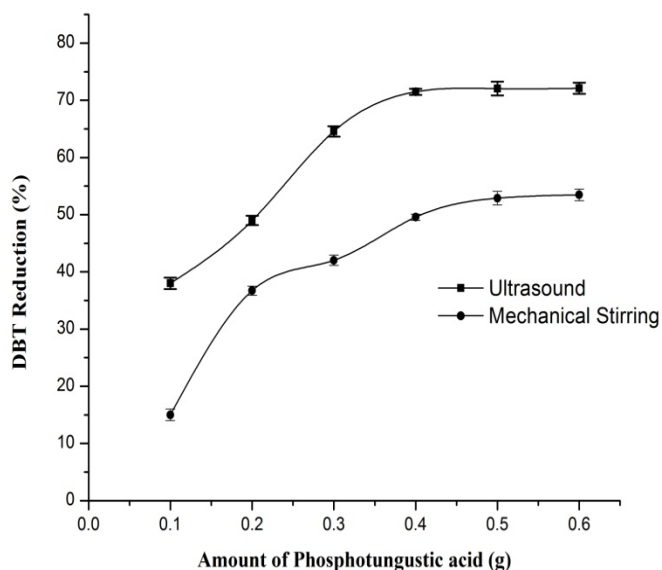


**Scheme 1:** The cyclic mechanism of phase transfer catalyst (PTC) during oxidative desulfurization with perorganic acid.

## Result and Discussion:

### 4.1 Effect of phosphotungstic acid dose

The results of effect of phosphotungstic acid concentration on DBT reduction are shown in figure 4. Phosphotungstic acid was used as an oxidant promoter agent in reaction system instead of formic acid and acetic acid. The amount of phosphotungstic acid added to reaction solution was varied in the range of 0.1–0.6 g. Figure 4, shows direct variation of DBT reduction with phosphotungstic dosage due to increasing concentration of catalytically active species  $[W(Q_2)_n-Q^+]$  in reaction system. The % DBT reduction in ultrasonic process was higher than mechanical stirred system. However, the DBT reduction levelled off after phosphotungstic acid loading of 0.4 g/20 mL of diesel in both ultrasound and mechanical stirring. Further increase in concentration of phosphotungstic acid has negligible effect on augmentation of DBT reduction. Results revealed efficient oxidation of sulfur compound – with more than 78% DBT reduction – using  $H_2O_2$ /phosphotungstic acid/TOAB reaction system. The catalyst molecules act as emulsification agent and get uniformly distributed in the interface of aqueous and organic phase (water–oil interface) and form a thin film around the dispersed water droplets.



**Figure 3:** DBT reduction in presence of TOAB with different dosage of phosphotungstic acid

### 4.2 Discussion

#### Category A: DBT + Toluene (100 ppm)

In the present study the experiments were carried out in two category viz. Category (A): DBT + Toluene (100 ppm), and Category (B): DBT + (toluene + n-decane) (100 ppm). All 2 experimental categories conducted with three different types of oxidant system ( $H_2O_2/CH_3COOH$ ,  $H_2O_2/HCOOH$  and  $H_2O_2$ /phosphotungstic acid). In category A, experiments were conducted with hexadecyl trimethyl ammonium bromide (HTMAB) used as a phase transfer agent and the oxidant systems were  $H_2O_2/CH_3COOH$ ,  $H_2O_2/Formic$  acid

and  $H_2O_2$ /Phosphotungstic acid. The results of the experiments are depicted in Fig.4 and 5. Figs. 4 and 5 show the results of time history of DBT reduction with HTMAB using ultrasound and mechanical stirred system, respectively. Table 1 give the summary of the results on DBT reduction in category A along with 1st order kinetic constant fitted to the experimental data (justification for fitting 1st order kinetic model has been given earlier with a simple mathematical model).

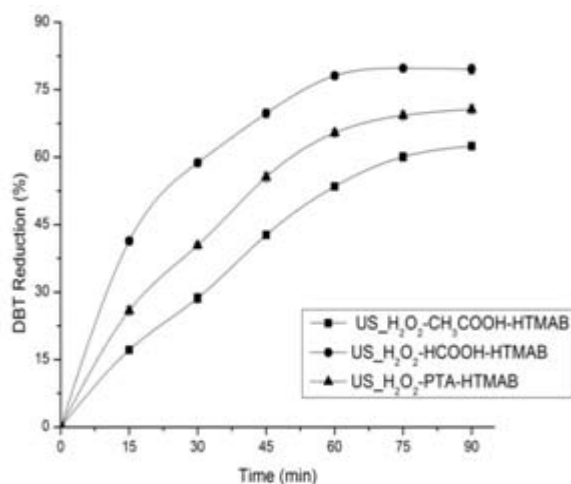
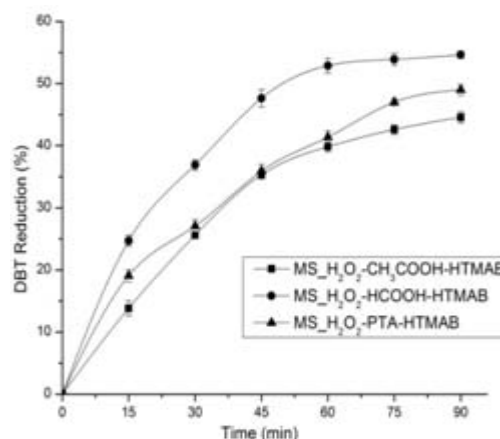
(1) From Figs. 4 and 5, it is clearly observed that, ultrasound gives higher DBT reduction compared to mechanically stirred system. The ultrasound assisted oxidation experiments have been carried out at  $40^\circ C$  and mechanical stirring experiments have been carried out at  $60^\circ C$ . Maximum DBT reduction has been observed for  $H_2O_2-HCOOH-HTMAB$  oxidant system in both cases (US and MS). Comparing between all three oxidant systems,  $H_2O_2-HCOOH-TOAB$  oxidant system enhances the oxidation rate by  $\sim 47\%$  and  $\sim 13\%$ , as compared to  $H_2O_2-CH_3COOH-HTMAB$  and  $H_2O_2-PTA-HTMAB$  systems, respectively. Major reason underlying enhancement of oxidation with formic acid (as compared to acetic acid) is probably higher intrinsic diffusivity of formic acid-PTC complex due to smaller size. Higher oxidation potential and reactivity of performic acid as compared to peracetic acid has also been reported in several published papers in the area of disinfectants. The relative influences of ultrasound on enhancement of oxidation are evident. Replacement of stirring with ultrasound causes about  $\sim 17\%$  enhancement in oxidation of DBT.

(2) Table 2 shows the summary of experimental results for HTMAB as phase transfer catalyst with different oxidant systems for ultrasound and mechanical stirred system in category B. Figs. 6 and 7 show the time history of DBT reduction in ultrasound and mechanical stirring system.  $H_2O_2-HCOOH$  oxidant system gives higher oxidation of DBT as compared to other systems for ultrasound assisted process.  $H_2O_2-HCOOH-HTMAB$  gives 27% and 13% enhanced DBT oxidation as compared to  $H_2O_2-CH_3COOH-HTMAB$  and  $H_2O_2-PTA-HTMAB$  oxidant system. In mechanical stirring, the enhancement in DBT oxidation with  $H_2O_2-HCOOH-HTMAB$  oxidant system was 22% as compared to  $H_2O_2-CH_3COOH-HTMAB$  system and 12% as compared to  $H_2O_2-PTA-HTMAB$  system.

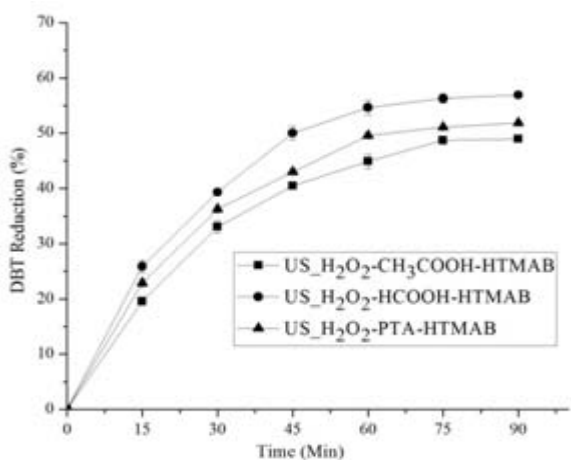
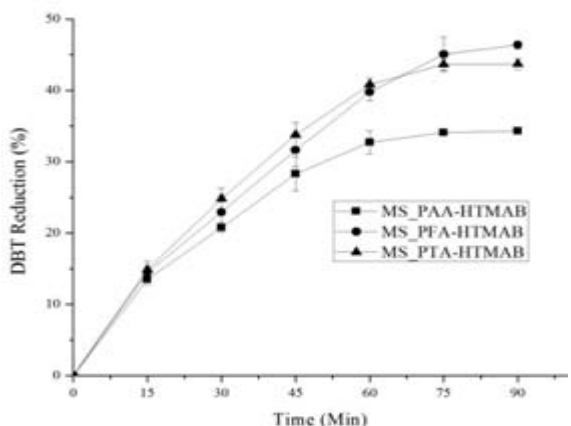
(3) Comparing the results of categories A and B, one can conclude that model solvent (toluene + n-decane) used for oxidation of DBT shows lower oxidation efficiency, while only toluene used as a model solvent gives maximum oxidation. This interesting result is attributed to the difference in physical properties of toluene and toluene-decane mixture, which essentially gets manifested in intensities of physical and chemical effects of cavitation bubbles and ultrasound. Further investigation in this matter we carried out simulations of cavitation bubble dynamics for both solvent used in present study. The simulation results of cavitation bubble dynamics depicted in Figs. 2a-2b.

**Table 1:** DBT reduction using HTMAB as a phase transfer catalyst with different oxidant system for category A

Oxidant system	Ultrasound			Mechanical Stirring		
	$\eta$ %	$k(\text{min}^{-1})$	$R^2$		$k(\text{min}^{-1})$	$R^2$
$\text{H}_2\text{O}_2$ - $\text{CH}_3\text{COOH}$ -HTMAB	$62.46 \pm 0.86$	0.0115	0.9863	$44.57 \pm 0.92$	0.0067	0.9395
$\text{H}_2\text{O}_2$ - $\text{HCOOH}$ -HTMAB	$79.57 \pm 1.1$	0.0179	0.9085	$54.64 \pm 0.56$	0.0087	0.9138
$\text{H}_2\text{O}_2$ -PTA-HTMAB	$70.62 \pm 0.96$	0.0142	0.9622	$48.98 \pm 0.87$	0.0076	0.9642

**Figure 4:** DBT reduction for HTMAB with ultrasound**Figure 5:** DBT reduction for HTMAB with mechanical stirring**Table 2:** DBT reduction using HTMAB as a phase transfer catalyst with different oxidant system for category B

Oxidant system	Ultrasound at 40°C			Mechanical stirring at 60°C		
	$\eta$ %	$k(\text{min}^{-1})$	$R^2$	$\eta$ %	$k(\text{min}^{-1})$	$R^2$
$\text{H}_2\text{O}_2$ - $\text{CH}_3\text{COOH}$ -HTMAB	$48.9 \pm 0.5$	0.0074	0.90	$34.3 \pm 0.27$	0.0047	0.9
$\text{H}_2\text{O}_2$ - $\text{HCOOH}$ -HTMAB	$56.9 \pm 0.6$	0.0092	0.88	$46.4 \pm 0.53$	0.0071	0.94
$\text{H}_2\text{O}_2$ -PTA-HTMAB	$51.8 \pm 0.4$	0.0079	0.89	$43.72 \pm 0.75$	0.0066	0.94

**Figure 6:** DBT reduction for HTMAB with ultrasound**Figure 7:** DBT reduction for HTMAB with mechanical stirring

## 5. Conclusion

In the present study, we have attempted to deduce the physical or mechanistic features of the oxidative desulfurization process simultaneous assisted by ultrasound and PTC. The relative role of ultrasound and PTC in enhancement of oxidation has been verified with different experimental protocols. The results have been compared on the basis of oxidative desulfurization achieved with mechanical stirring. Three oxidizing agents, viz. peracetic acid, performic acid or phosphotungstic acid and two different model solvent have been employed and comparative assessment has been made. The results of this study have highlighted several interesting facets of the oxidative desulfurization process as follows:

- 1) Both ultrasound and PTC influence each other's individual beneficial effects on the reaction system.
- 2) Ultrasound can significantly improve the reaction efficiency under phase transfer condition.
- 3) Despite assistance of the oxidative desulfurization process by PTC and ultrasound, the intrinsic factors and properties such as polarity (and hence partition coefficient) and diffusivity have a crucial effect on the extent of oxidation. The intrinsic reactivity of the oxidant also plays a vital role, as seen from the extent of oxidation achieved with performic acid and peracetic acid.
- 4) The process of oxidative desulfurization, especially under sonication, is influenced by the physical properties of the solvent used as model fuel. This essentially is a manifestation of the effect of these physical properties on the ultrasound wave phenomena and cavitation bubble

dynamics, and the physical and chemical effects associated therewith.

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