

EFFECT OF TEMPERATURE & PRESSURE ON OXIDATIVE DESULFURIZATION

Manohar Kumar Bolla*,
Chemical Engineering
BVRIT

Venkat Sai Bolla
Chemical Engineering
BVRIT

Likhitha Rekkabu
Chemical Engineering
BVRIT

ABSTRACT -- Several technologies has been developed to removal of sulfur compounds from liquid fuels is oxidative desulfurization, hydro desulfurization, catalytic hydro desulfurization, bio desulfurization etc.. Although several studies have reported enhancement effect of ultrasound irradiation on oxidative desulfurization, exact mechanism underlying this enhancement is not known yet. In this study, we have addressed this issue with dual approach with how pressure and temperature effect the desulfurization mechanism. Results of this study have given interesting revelation of interaction between mechanism of ultrasound, cavitation and oxidation system. Isolation of cavitation phenomenon helps to increase the extent of oxidation. This effect is attributed to formation of hydrogen and carbon monoxide during transient collapse of cavitation bubbles due to thermal dissociation of hexane vapor entrapped in the bubble, which hamper action of O species generated from oxidation system. Transient cavitation itself does not give rise to radical formation due to rather low temperature peaks reached during collapse. Therefore, cavitation does not enhance the oxidation process, but in fact, has adverse effect on it. Current study has established that beneficial effect of ultrasound on oxidative desulfurization system is merely of physical nature (i.e. emulsification due to intense micro-mixing) with no involvement of sonochemical effect.

Keywords: Cavitation, Sonochemistry, Bubble Dynamics, Desulfurization

1. INTRODUCTION

Crude oil contains numerous sulfur compounds, mainly in the form of aromatic hydrocarbons such as sulfides, thiophenes, benzothiophene, dibenzothiophene and their substituted derivatives. During distillation and refining of crude oil, these compounds end up in the gasoline and diesel fractions. Combustion of these compounds in vehicle engines results in generation of SO₂ and particulate matter emission. Growing concerns over air pollution created by these emissions have led to stringent restrictions on the sulfur content of the liquid fuels. To meet these specifications, quest is on for technologies for deep desulfurization that could give ultra-low sulfur diesel (ULSD). Conventional technique for the desulfurization of diesel and petrol practiced by petroleum industry is hydrotreating or catalytic hydrodesulfurization, in which the sulfur in the hydrocarbons is removed as H₂S. However, this technique has poor economics and requires harsh conditions of temperatures (> 300°C) and pressures (> 30 bar). Moreover, there are other limitations such as negligible removal of substituted benzothiophenes and dibenzothiophenes due to their low reactivity.

There are several disadvantages by different desulfurization process. Out of all techniques we are choosen the oxidative desulfurization process. The main assest by using this process is it is carried out at optimum temperature and pressure. The technology of oxidative desulfurization has several merits over the conventional hydrotreating in that it does not require use of expensive hydrogen, the treatment conditions (i.e. temperature and pressure) are almost ambient and effective oxidation (and hence removal by liquid extraction) of the substituted sulphur aromatics (which are recalcitrant to hydrotreating). The oxidants commonly employed are peroxy organic acids, hydroperoxides, nitrogen oxides, peroxy salts and ozone. These oxidants donate oxygen atoms to the sulfur in the aromatic hydrocarbons. Being simple and effective, this technique has high potential for implementation on large scale. More recently, the oxidative desulfurization has been coupled with ultrasound irradiation.¹⁻⁶ This new technique is reported to enhance kinetics as well as yield of oxidative desulfurization process. Most of the studies published earlier have emphasized on the results of ultrasonic oxidative desulfurization, and little attempt is dedicated to explore the exact mechanism underlying the beneficial actions of ultrasound on the reaction system, which is essentially a biphasic liquid-liquid heterogeneous system and studying the effect of temperature on desulfurization mechanism.. In this paper, we have addressed the matter of discerning the mechanism of ultrasound-enhanced oxidative desulfurization. Our approach is to couple experimental results (with model sulfur compounds and oxidants) with different temperatures and different pressures. Before proceeding to the main components of the study, we outline briefly the physical and chemical effects of ultrasound and cavitation on a process. The principal chemical effect of cavitation bubbles is generation of radicals through dissociation of vapor molecules entrapped in the bubble at the extreme conditions of temperature and pressure (~ 5000 K and ~ 500 bar) generated in the bubble at transient collapse. The physical effect of ultrasound is creation convection in the medium through small amplitude oscillatory motion of fluid elements around a mean position, known as micro-streaming. Cavitation also generates convection in the medium, however; there are several mechanism associated with the convection generated by cavitation such as microturbulence (which is oscillatory liquid velocity generated by bubble), shock waves and high-speed microjets (generated due to asymmetric collapse of bubble in the vicinity of a phase boundary with magnitude 120-150 m/s). For greater on these mechanisms, we refer the reader to our earlier paper⁷. This greatly enhances the interfacial area and obviates need for additional agents for mass transfer enhancement such as phase transfer catalysts.

2. MATERIALS AND METHODS

2.1 Materials

Following chemicals were used in the experiments: benzothiophene, 30% hydrogen peroxide, hexane and acetic acid (or per acetic acid). benzothiophene, thiophene, 30% hydrogen peroxide, acetonitrile and water. All chemicals were procured from Merck (analytical grade) and were used as received without any pretreatment.

2.2 Methods

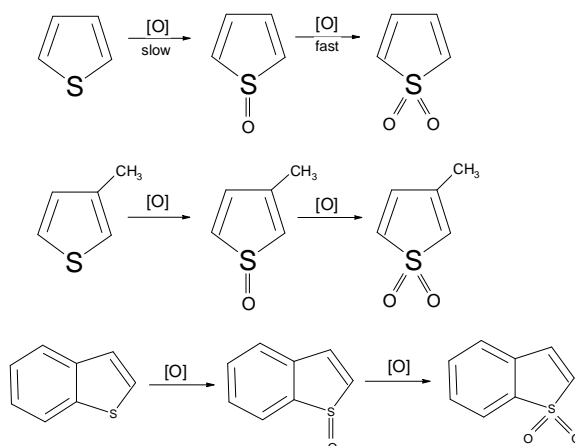
The major parameter varied in the experiments of the present study was system pressure. We conducted our experiments under two static pressures, viz. atmospheric (1 bar) and elevated to 1.5 bar gauge (or an absolute pressure of 2.5 bar) and at different temperatures 30, 35 and 40°C. The rationale underlying this technique will be discussed in the next section. An ultrasound bath which operates at a frequency of 35 kHz and power of 35 W was used for sonication of the medium. The power rating of the ultrasound bath (35 W) corresponds to theoretical (or maximum) ultrasound intensity. The actual ultrasound power delivered to the medium was determined using calorimetric technique.⁸ Per calorimetric measurements, for a theoretical intensity of 35 W, the ultrasound bath produced an acoustic wave of 1.5 atm pressure amplitude. However, the ultrasound wave undergoes attenuation as it passes through the medium and hence the actual pressure amplitude sensed by the cavitation bubble is lesser than 1.5 atm.

2.3 Calibration experiments

Prior to main experiments calibration charts were prepared using known quantities of 3 model sulfur compounds, viz. benzothiophene, thiophene dissolved in n-hexane, which was the model petrol. The charts showed an excellent linearity for thiophene (concn. range 0–1000 mg/dm³), benzothiophene (concn. range 0–1000 mg/dm³) and 3-methyl thiophene (concn. range 0–1000 mg/dm³). The analysis was performed using HPLC with a Hibar-Purospher-STAR RP-18 column (Merck) and UV detector at $\lambda = 271$ nm. The mobile phase constituted of acetonitrile and water in 4:1 volumetric ratio, at a flow rate of 0.7 cm³/s.

2.4 Oxidation experiments

2 model oxidants used in this study were: (1) CH₃COOH + H₂O₂ (peracetic acid), (2) CH₃COOH + H₂O + H₂O₂ (diluted peracetic acid). Oxidation of the two model sulfur compounds used in this study (viz. thiophene, and benzothiophene) is represented by following reactions:



The schematic diagram of the experimental set up is given in supplementary material (Figure A.1). In a typical experiment, initially solution of a particular model sulfur compound in n-hexane (25 mL) was prepared in desired concentration (either 100 or 300 or 500 ppm) in a conical flask of 100 mL volume. 25 mL of the desired oxidant was added to this solution that resulted heterogeneous liquid mixture with volumetric ratio of 1:1. The initial temperature of solution was 298 K (25°C). In each experiment, 2/3rd of the bath was filled with water. The conical flask was placed at the center of the ultrasound bath for all the experiment. The intensity of the ultrasound field in the bath shows significant spatial variation. Therefore, to avoid the change of intensity of the ultrasound field to which the flask is exposed, the position of the flask in the bath was carefully maintained constant during all experiment with the help of a burette stand and clamp. A simple arrangement was used for raising the static pressure in the conical flask. The mouth of the flask was sealed using a rubber cork with a central tube pierced in it. The outer end of the tube was connected to a Nitrogen gas cylinder with a double stage regulator. The water in the bath was replaced every 10 min to maintain the constant temperature of reaction mixture during sonication. The average temperature of the bath, and the reaction mixture in conical flask, varied by less than 2°C due to this procedure. In order to monitor the kinetics of degradation, samples of the reaction solution (5 mL) were withdrawn every 15 min for HPLC analysis.

2.5 Estimation of sonochemical effect (radical generation by cavitation bubbles)

Using the numerical solution of bubble dynamics model, one can estimate the composition of the bubble contents at the collapse. While calculating the composition of the bubble at the time of collapse, we assume that thermodynamic equilibrium is attained.⁹ The equilibrium mole fraction of the various species in the bubble at the conditions of temperature and pressure at first the compression of the bubble can be calculated using Gibbs free-energy minimization technique.¹⁸

3. RESULTS AND DISCUSSION

As noted in section 3, we have conducted our experiments under atmospheric, elevated static pressure and at different temperatures. Before proceeding to the main results and discussion section, we would like to discuss the rationale underlying the application of elevated pressure. Irradiation of a liquid medium with ultrasound (which is essentially a longitudinal wave) leads to occurrence of two phenomena: (1) high velocity oscillation of fluid elements around their mean position, giving alternate compression and rarefaction cycles, and (2) the phenomenon of cavitation, which is nucleation growth and transient collapse of the gas/vapor bubbles driven by bulk pressure variation due to the ultrasound wave. The first phenomenon creates intense micro-mixing in the medium, while the second phenomenon, which is of secondary nature, can give rise to two effects: (1) the physical effect of micro-mixing or micro turbulence due to liquid set into motion by volume oscillations of bubble, and (2) generation of radical species due to dissociation of the solvent vapor entrapped in the bubble at the moment of transient collapse. The intensity of the collapse of the bubble depends on its expansion during the rarefaction cycle of ultrasound where the bulk pressure in the system falls below atmospheric. The greater the fall of the system pressure below ambient, the larger the expansion of the bubble, and more intense the ensuing collapse.

For distinguishing between the physical and chemical effects, the expansion of the bubble needs to be suppressed. This could be achieved by raising the ambient or static pressure in the system above the pressure amplitude of the ultrasound wave. As noted in section 3, the amplitude of the ultrasound generated by ultrasound bath used in this study was 1.5 atm. Therefore, raising the static pressure to 1.5 atm (gauge) or total absolute pressure of 2.5 atm, could suppress all transient cavitation in the system, and thus, help distinguish the influence of micro-mixing due to ultrasound itself. With this preamble, we first present the experimental results followed by the simulations results. Next, we correlate these results to deduce the exact mechanism of the ultrasound assisted oxidative desulfurization.

3.1 Experimental results

We have selected 2 model compounds, viz. benzothiophene and thiophene along with the 2 model oxidants, viz. peracetic acid ($\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2$), diluted peracetic acid ($\text{CH}_3\text{COOH} + \text{H}_2\text{O} + \text{H}_2\text{O}_2$). We have conducted our experiments in Ultrasound Sonicator operating under atmospheric pressure, and at different temperatures. Before proceeding to the main results and discussion section, we would like to discuss the rationale underlying the application of temperature. We are studying the effect of temperature on our process mechanism. The trends in oxidation of 2 model sulfur compounds at atmospheric, elevated static pressure and at different temperatures are shown in Figures 1, 2 and 3 for the oxidants peracetic acid, diluted peracetic acid respectively. In order to quantify the rate of oxidation, first order kinetics model has fitted to the reaction data. The entire summary of the results of oxidation experiments is presented in Tables 3. Also listed in these tables are the first order kinetic constants for the oxidation reaction of different compounds. An Excel file giving greater details of the reaction data for all experiments has been provided as supplementary material. From the results presented in Figures 1–3 and Tables 3, we can identify the following trends in the kinetics of oxidation of model sulfur compounds with different oxidants.

3.1.1 Oxidation system of peracetic acid

Extent of oxidation in 90 min of sonication with peracetic acid for atmospheric pressure at 30°C, 35°C and 40°C is in the order: benzothiophene > thiophene. For any particular compound, the percentage conversion remains the same, irrespective of the initial concentration. It must be noted, while increasing the temperature the percentage of degradation of sulfur compounds is very high and however, that the absolute amount of sulfur compound oxidized increases with initial concentration, which would essentially mean that in the oxidation mixture used in present experiments, sulfur compounds were the limiting reactant. The kinetic constants observed for these three initial concentrations are also almost same. Significant rise (~ 50% or higher) in the kinetics of oxidation as well as extent of oxidation achieved in 90 min of sonication is seen with rise in static pressure of the reaction mixture.

3.1.2 Oxidation system of diluted peracetic acid

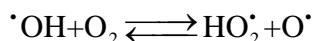
This system gives similar trends as seen for the peracetic acid; however, the extent of oxidation is reduced marginally for all three model compounds and both sonication systems. The absolute degradation increases with % degradation remaining the same for all three compounds shown that it is a kinetically limited system with sulfur compound as limiting reactant. Comparing among the 3 model compounds, we see exact same trend as seen for peracetic acid. Similarly, the kinetics of oxidation, and hence, the extent of oxidation in 90 min of sonication also rises with increase in static pressure of the reaction medium.

3.2 Analysis

Analysis of the experimental results reveals interesting features of ultrasound-assisted oxidative desulfurization, which are summarized below:

(1) Oxidation is found to follow 1st order kinetics for all three sulfur compounds. No generation of any radical species during transient collapse of cavitation bubbles of both sizes indicates that the influence of ultrasound and cavitation on the reaction system is of merely physical nature. Intense turbulence generated by ultrasound and cavitation generates fine emulsion of n-hexane (organic medium) with oxidation system (aqueous medium), due to which interfacial area increases drastically resulting in rise in the kinetics of oxidation.

(2) Higher degradation seen in case of peracetic acid with Fenton's reagent is essentially due to additional generation of the oxidant species by reaction of $\cdot\text{OH}$ radicals generated from Fenton's reactions with the dissolved oxygen in the system through reaction:



The dissolved oxygen content of the medium is relatively independent of the static pressure of the medium, and hence, the above effect is present in experiments at both atmospheric as well as raised static pressure.

(3) The most interesting experimental result, which is consistent for all three oxidation systems employed, is the rise in oxidation of all three sulfur compounds with application higher pressure to the reaction system. A plausible reason for this effect could be given by analysis results and simulation. As noted previous section, the predominant species generated from thermal dissociation of n-hexane during transient collapse of cavitation bubbles in the reaction system at atmospheric pressure are hydrogen and carbon monoxide. These species can competitively consume the $\text{O}\cdot$ species generated by the oxidation system. Thus, the utilization of the $\text{O}\cdot$ species towards oxidation of sulfur compounds is limited, which reduces the extent of oxidation.

(4) With application of elevated pressure, the transient cavitation in the system is eliminated. The cavitation bubbles undergo stable oscillatory motion, with very small generation of H_2 and practically no generation of CO . The intensity of microturbulence as well as shock waves generated by bubbles also decreases with rise in static pressure. However, as stated in section 4.3, the convection generated in the reaction mixture during sonication is mostly contributed by ultrasound waves, which is not affected by rise in static pressure. Hence, the extent of emulsification and interfacial area for reaction is not influenced by the rise in static pressure.

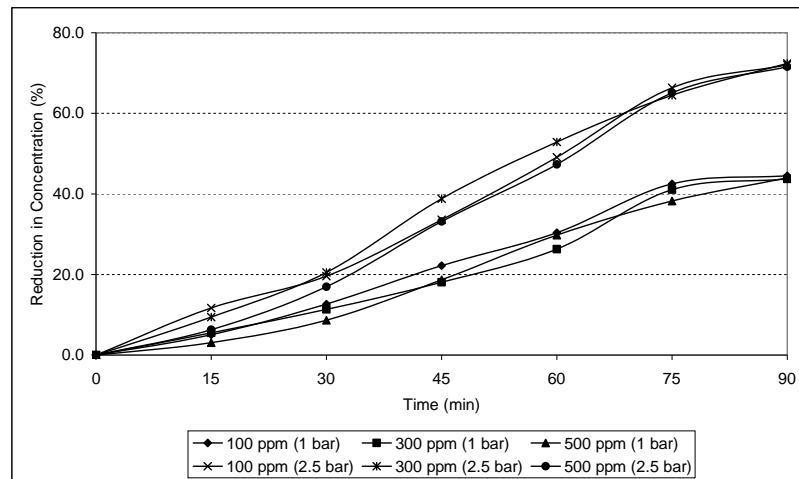
Table 1. Summary of experimental results at different pressures

Sulfur Compound	P_o	C_o (ppm)	Oxidation System			
			Peracetic Acid $\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2$		Diluted Peracetic Acid $\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$	
			k_1 (min^{-1})	η (%)	k_1 (min^{-1})	η (%)
Benzothiophene	Atmospheric	100	10×10^{-3}	63.5	9×10^{-3}	58.7
		300	9×10^{-3}	62.4	9×10^{-3}	59.01
		500	9×10^{-3}	62.8	10×10^{-3}	59.2
	2.5 bar	100	12×10^{-3}	72.0	12×10^{-3}	71.2
		300	13×10^{-3}	72.4	12×10^{-3}	72.5
		500	12×10^{-3}	71.5	11×10^{-3}	71.4
Thiophene	Atmospheric	100	10×10^{-3}	56.9	8×10^{-3}	53.3
		300	9×10^{-3}	56.2	8×10^{-3}	53.6
		500	10×10^{-3}	55.3	9×10^{-3}	54.02
	2.5 bar	100	12×10^{-3}	71.5	11×10^{-3}	69.4
		300	12×10^{-3}	71.1	11×10^{-3}	69.4
		500	13×10^{-3}	70.5	11×10^{-3}	68.5

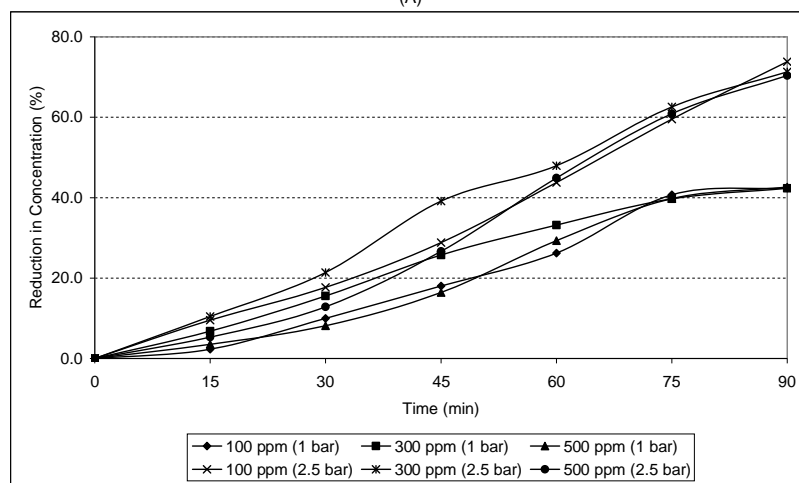
Table 2. Summary of experimental results at different temperatures

Sulfur Compound	T	C_o (ppm)	Oxidation System				
			Peracetic Acid $\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2$		Diluted Peracetic Acid $\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$		
			k_1 (min^{-1})	η (%)	k_1 (min^{-1})	η (%)	
Benzothiophene	30	100	10×10^{-3}	61.96	9×10^{-3}	58.72	
		35	11×10^{-3}	65.85	9×10^{-3}	59.56	
		40	11×10^{-3}	66.85	9×10^{-3}	60.45	
	35	100	9×10^{-3}	62.48	9×10^{-3}	59.06	
		300	11×10^{-3}	65.16	10×10^{-3}	62.25	
		500	11×10^{-3}	67.59	10×10^{-3}	64.96	
	Thiophene	30	100	10×10^{-3}	59.08	8×10^{-3}	53.38
			35	11×10^{-3}	63.07	9×10^{-3}	55.93
			40	12×10^{-3}	65.07	9×10^{-3}	56.96
35		100	9×10^{-3}	56.25	8×10^{-3}	53.69	
		300	9×10^{-3}	57.58	9×10^{-3}	54.33	
		40	10×10^{-3}	59.54	9×10^{-3}	54.59	

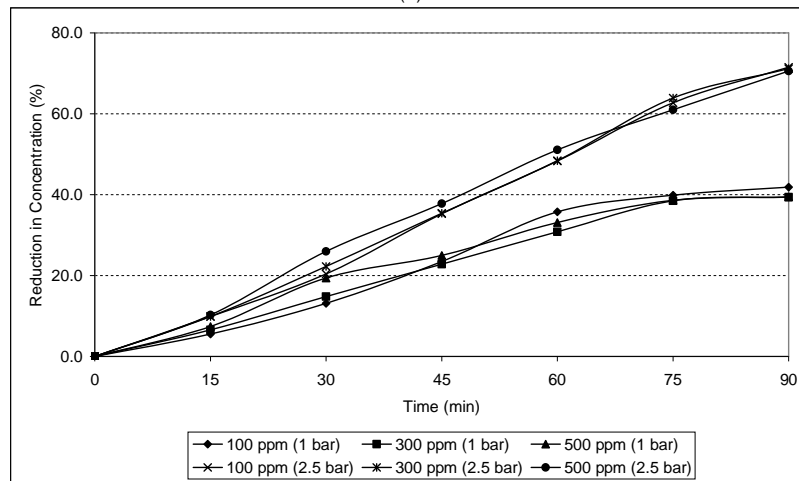
k_1 - 1st order kinetic constant; C_o – initial concentration of the sulfur compound in n-hexane; η - percentage oxidation of sulfur compound calculated as $[100 \times (\text{initial concn.} - \text{final concn.}) / \text{initial concn.}]$.



(A)

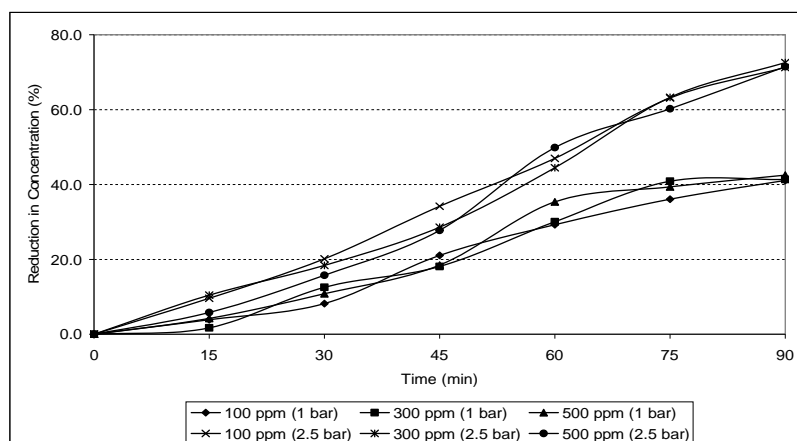


(B)

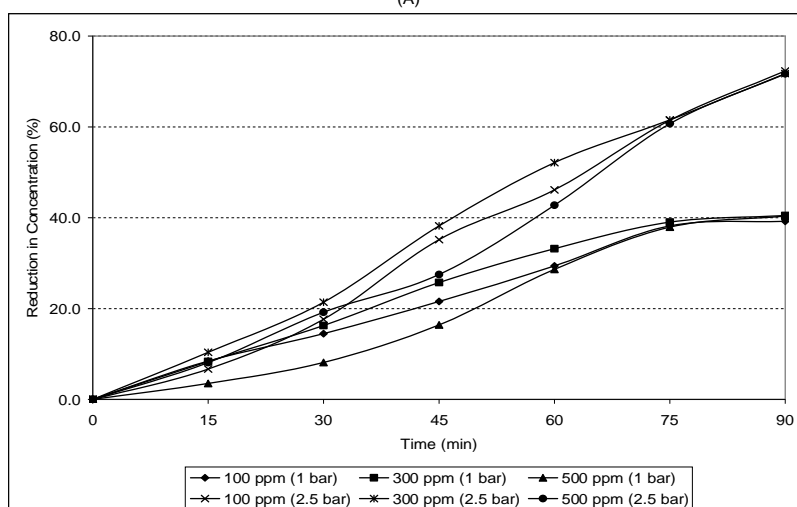


(C)

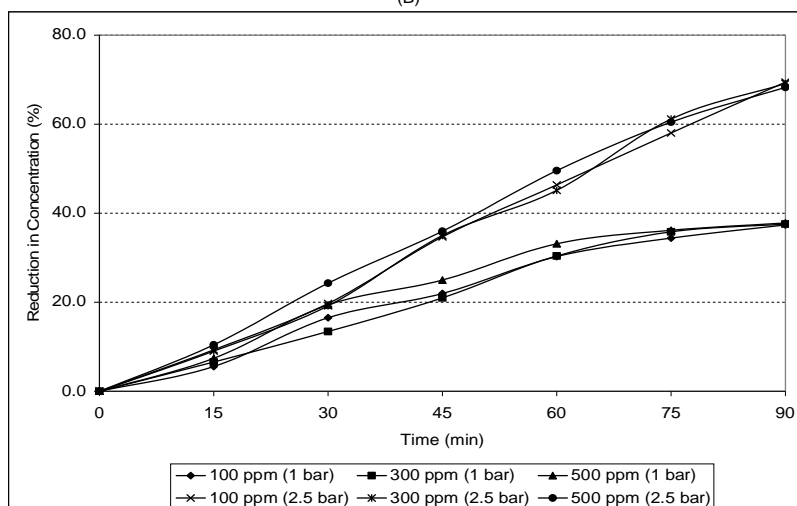
Figure 1. Trends in the oxidative desulfurization (represented as reduction in the concentration of the model sulfur compound) with oxidant peracetic acid ($\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2$). (A) oxidation of benzothiophene; (B) oxidation of 3-methyl thiophene (C) oxidation of thiophene.



(A)

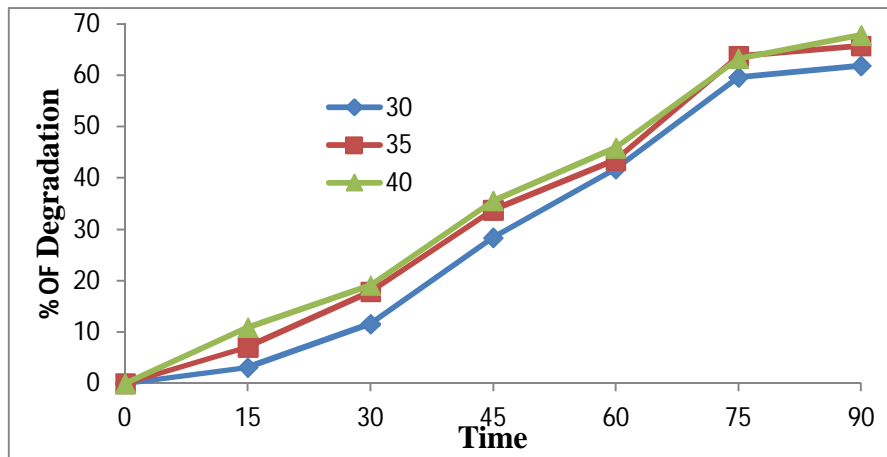


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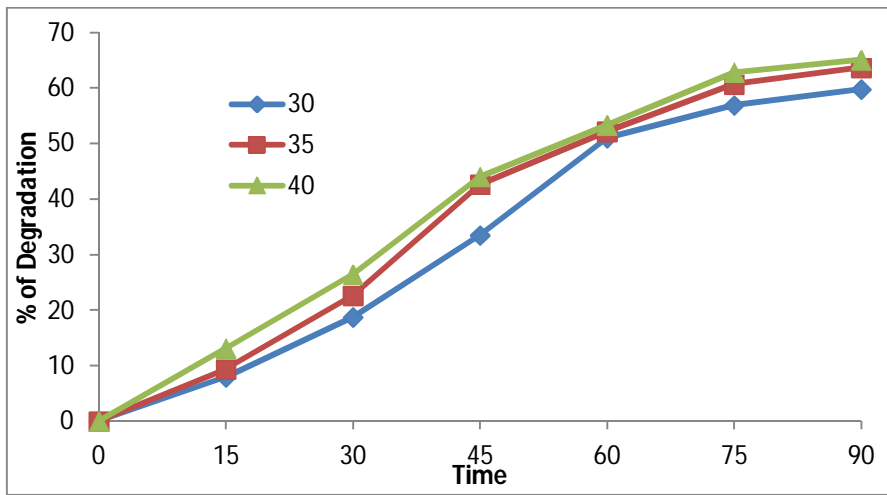


(C)

Figure 2. Trends in the oxidative desulfurization (represented as reduction in the concentration of the model sulfur compound) with oxidant diluted peracetic acid ($\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$). (A) oxidation of benzothiophene; (B) oxidation of 3-methyl thiophene (C) oxidation of thiophene.

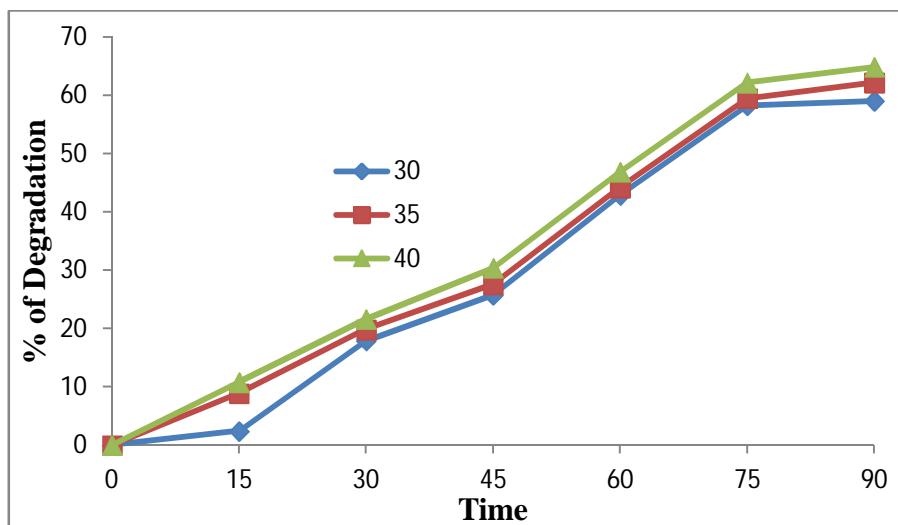


(A)



(B)

Figure 3 Percentage of Degradation with oxidant $\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2$. (A) 100 ppm of bezothiophene at temperature 30, 35, 40 degree centigrade; (B) 100 ppm of thiophene at temperature 30, 35, 40 degree centigrade.



(A)

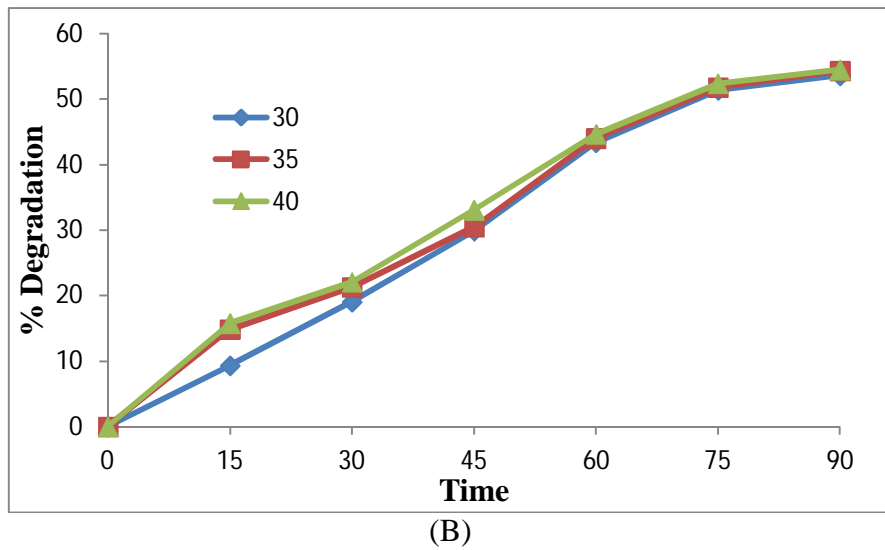


Figure 4 Percentage of Degradation with oxidant $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$. (A) 100 ppm of bezothiophene at temperature 30, 35, 40 degree centigrade; (B) 100 ppm of thiophene at temperature 30, 35, 40 degree centigrade.

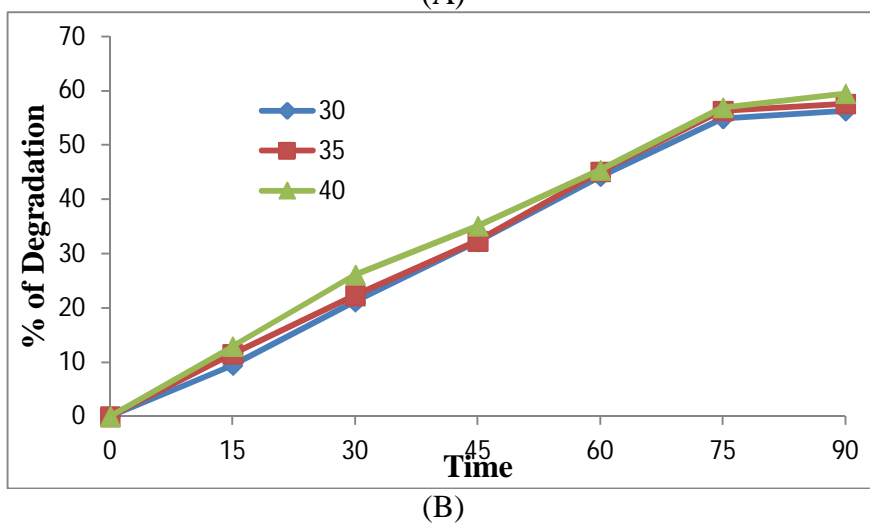
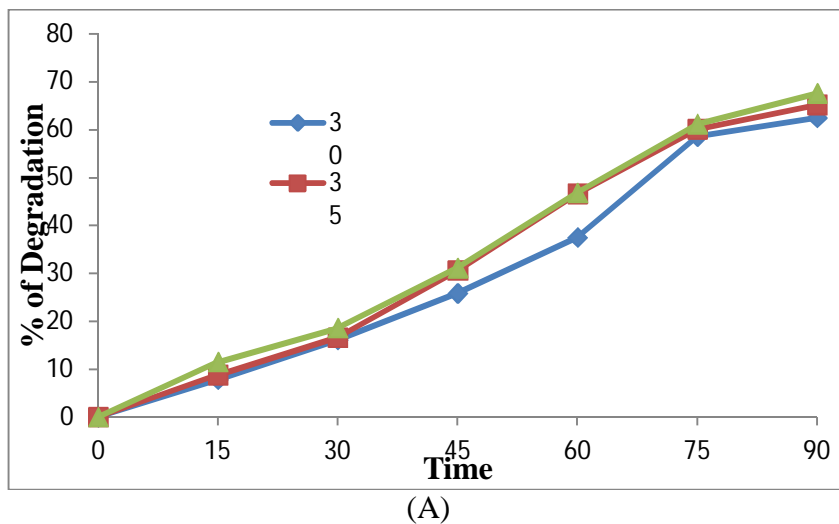
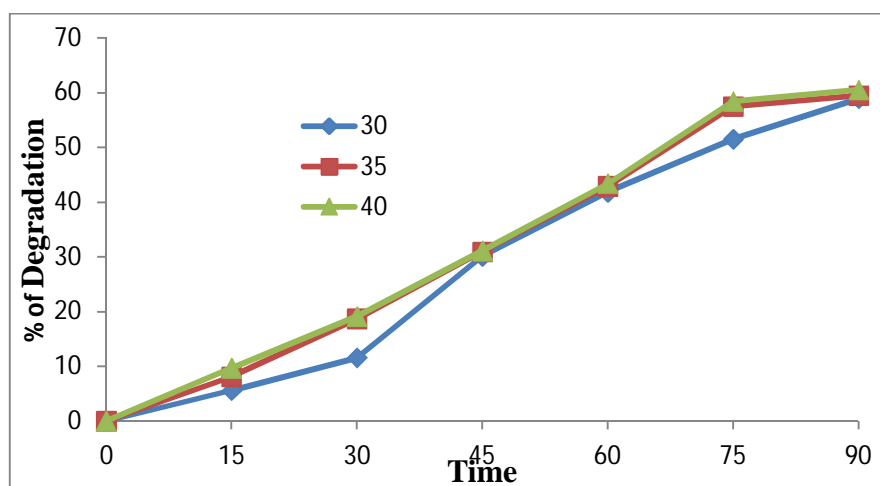
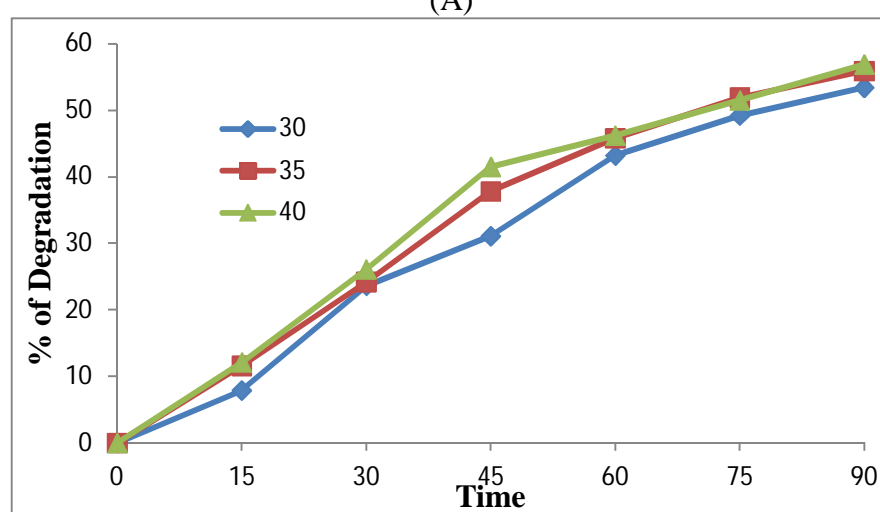


Figure 5 Percentage of Degradation with oxidant $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$. (A) 300 ppm of bezothiophene at temperature 30, 35, 40 degree centigrade; (B) 300 ppm of thiophene at temperature 30, 35, 40 degree centigrade.



(A)



(B)

Figure 6 Percentage of Degradation with oxidant $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$. (A) 300 ppm of bezothiophene at temperature 30, 35, 40 degree centigrade; (B) 300 ppm of thiophene at temperature 30, 35, 40 degree centigrade.

LIST OF CAPTIONS FOR FIGURES AND TABLES

Figure 1. Trends in the oxidative desulfurization (represented as reduction in the concentration of the model sulfur compound) with oxidant peracetic acid ($\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2$). (A) oxidation of benzothiophene; (B) oxidation of 3-methyl thiophene (C) oxidation of thiophene.

Figure 2. Trends in the oxidative desulfurization (represented as reduction in the concentration of the model sulfur compound) with oxidant diluted peracetic acid ($\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$). (A) oxidation of benzothiophene; (B) oxidation of 3-methyl thiophene (C) oxidation of thiophene.

Figure 3 Percentage of Degradation with oxidant $\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2$. (A) 100 ppm of bezothiophene at temperature 30, 35, 40 degree centigrade; (B) 100 ppm of thiophene at temperature 30, 35, 40 degree centigrade.

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Figure 5 Percentage of Degradation with oxidant $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$. (A) 300 ppm of bezothiophene at temperature 30, 35, 40 degree centigrade; (B) 300 ppm of thiophene at temperature 30, 35, 40 degree centigrade.

Figure 6 Percentage of Degradation with oxidant $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$. (A) 300 ppm of bezothiophene at temperature 30, 35, 40 degree centigrade; (B) 300 ppm of thiophene at temperature 30, 35, 40 degree centigrade.

Table 1. Summary of experimental results at different pressures

Table 2. Summary of experimental results at different temperatures

4. CONCLUSIONS

In this study, we have attempted to identify the mechanistic features of beneficial action of ultrasound irradiation on oxidative desulfurization reaction system, which essentially is a liquid-liquid heterogeneous system. Concurrent analysis of experimental and simulations results reveals that the beneficial action of ultrasound on oxidative desulfurization is merely by the physical effect of intense micro-convection generated in the system, which causes fine emulsification of fuel and oxidant, and generates high interfacial area between fuel and oxidant. An anomaly of the oxidative desulfurization system with conventional sonochemical systems is that occurrence of transient cavitation in the medium is revealed to affect the process adversely. This is a consequence of the generation of chemical species such as hydrogen and carbon monoxide that competitively consume the oxidant species, thus hindering the oxidation of sulfur compounds. Elimination of transient cavitation by a simple technique of raising static pressure of the system is found to give significant boost to the oxidation process due to efficient utilization of oxidizing species for oxidation for sulfur compounds.

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SUPPLEMENTARY MATERIAL

Following supplementary material has been provided with this paper: (1) Schematic diagram of the experimental set-up. (2) An Excel file listing all the kinetic data for the reactions, along with fitted data with first order kinetic model and the regression constants. (3) An Excel file listing all the kinetic data for the reactions along with the percentage degradation with two oxidants.

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