Desalination and Water Treatment
www.deswater.com

47 (2012) 96–104
September

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doi: 10.1080/19443994.2012.696802

Ultrasound-assisted oxidative desulfurization (UAOD) using phosphotungstic acid: effect of process parameters on sulfur removal

Meng-Wei Wan[a], Luisa Cyd Charisse Biel[b], Ming-Chun Lu[c,*], Rizalinda de Leon[d], Susan Arco[e]

[a]*Department of Environment Engineering and Science, Chia-Nan University of Pharmacy and Science, Tainan 71710, Taiwan, ROC*
[b]*Environmental Engineering Graduate Program, University of Philippines-Diliman, Quezon City 1800, Philippines*
[c]*Department of Environmental Resources Management, Chia-Nan University of Pharmacy and Science, Tainan 71710, Taiwan, ROC*
Tel. +886 6 266 7323; email: mmclu@mail.chna.edu.tw
[d]*Department of Chemical Engineering, University of Philippines-Diliman, Quezon City 1800, Philippines*
[e]*Institute of Chemistry, University of Philippines-Diliman, Quezon City 1800, Philippines*

Received 26 August 2011; Accepted 6 March 2012

ABSTRACT

The oxidation of dibenzothiophene (DBT) and benzothiophene (BT) from a model diesel fuel, using hydrogen peroxide (H_2O_2) as an oxidant, was carried out in the presence of phosphotungstic acid and phase transfer agent (PTA) at 50–80˚C. The desulfurization efficiency and selectivity for the various compounds were examined and compared on the basis of the amount of sulfur converted to polar sulfone. The effect of process parameters (temperature, amount of catalyst, amount of PTA, and H_2O_2 concentration) were investigated to determine the highest reaction rate on the conversion of BT and DBT. The results indicate that using $[PW_{12}O_{40}]^{3-}$ as a catalyst accelerates the reaction rate on the conversion of BT and DBT to their corresponding polar sulfones. High conversion (>99%) was achieved as the temperature was increased from 50 to 80˚C. The activity of BT also increased markedly when the amount of oxidant increased. For DBT, as low as 0.02 M of H_2O_2 was enough to lower the concentration from 500 to 10 ppm at 80˚C. The Arrhenius equation was appropriately applied to describe the data by using the pseudo-first-order reaction kinetic equation. The apparent activation energies for BT and DBT were determined to be 60.52 and 45.01 kJ/mol, respectively.

Keywords: Phase transfer agent; Phosphotungstic acid; Ultrasound-assisted oxidative desulfurization

1. Introduction

The importance of deep desulfurization technologies to be adopted in the referring processes is ever increasing in the refining industry. With stringent environmental regulations and fuel specifications for environmental purposes, the refiners are tasked to bring down sulfur concentrations to the prescribed levels [1].

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*Corresponding author.

Challenges in Environmental Science and Engineering, CESE 2011 25–30 September 2011, Tainan City, Taiwan

In most of the countries, such as Taiwan, the sulfur content had been gradually shifted from 500 to 50 ppm in 2007. By 2011, the sulfur limit in any fuel was reduced to 10 ppm [2]. But in some countries a more stringent regulations were implemented. Refineries in the US were required to produce only 20% low sulfur diesel (500 ppm) in 2007, while 80% of their annual output is devoted to producing ultra low sulfur diesel (<15 ppm). Then in 2010, the United States Environmental Protection Agency (USEPA) issued a revised requirement for producing diesel fuel, mandating only the production of an ultra low sulfur diesel [3].

To produce a low-sulfur diesel fuel, the conventional technology that is being adopted in industries is hydrodesulfurization (HDS). This process involves mixing the heated oil with hydrogen in a reactor packed with a catalyst such as Co–Mo/Al_2O_3 or Ni–Mo/Al_2O_3 [4,5]. When the C–S bond breaks down, hydrogen sulfide (H_2S) and sulfur-free hydrocarbons are generated in the reactor. The generated H_2S is removed and the hydrogen and desulfurized products are recovered at the end of the process [6].

Although the HDS is capable of producing an ultra low sulfur diesel, there are several disadvantages connected to its usage. First, the HDS method is limited to treating refractory sulfur compounds only, namely the benzothiophenes (BTs) and dibenzothiophenes (DBTs), and alkyl-DBT with alkyl substitutions at four- and/or six positions due to steric hindrance [7]. The C–S bond energy of these compounds is almost equal to that of the C–H bond energy, which makes it difficult for them to be desulfurized by the hydrotreatment. Second, to achieve ultra low levels the HDS needs to be operated at a higher temperature (300–400℃) and higher hydrogen pressure (13–30 atm). The use of highly active catalysts is also required to enhance the process [8]. Consequently, it is not preferred to utilize the HDS for achieving an ultra low fuel owing to the high operational cost connected to its usage. Therefore, the necessity of introducing newer and effective technologies for producing an ultra low fuel has become inevitable to complement the conventional technique [9,10].

In the past few decades, alternative desulfurization techniques were extensively developed. The various techniques include extractive desulfurization [11], oxidative desulfurization [9], adsorptive desulfurization [12], biodesulfurization [13], and a combination of these technologies [14]. Among the various desulfurization methods employed, oxidative desulfurization is the most extensively used as it can be operated at low temperature and pressure, is a non-hydrogen consuming technology, and is very effective in the removal of refractory sulfur [15–17]. Furthermore, the system can be enhanced with the use of an ultrasonicator to minimize the mass transfer resistance [18].

To date, there are various oxidative desulfurization technologies that are available. A typical process consists of making the hydrocarbon streams containing the refractory sulfur compounds to come into contact with an oxidant such as hydrogen peroxide [9,18,19], ferrate [20], Fenton's reagent [21], and other reagents as oxidizers. Among those mentioned above, the most promising is hydrogen peroxide (H_2O_2) due to its low cost, high removal rates, and formation of water only as the by-product [22].

In recent studies, selective oxidation of sulfur compounds to sulfoxides and sulfones was achieved with the use of a H_2O_2—catalyst system in conjunction with a phase transfer agent (PTA) to enhance the mass transfer [18]. Various transition-metal-based catalysts such as Mo, Ti, W, V, and Cu were found to meet substantially these requirements in the presence of H_2O_2. Giuseppe et al. [23] reported on the homogeneous and heterogenous oxidation of dibenzothiophene by heteropoly compounds to their corresponding sulfoxides and sulfones in the presence of hydrogen peroxide. In their study, a high yield of sulfones was achieved. Jose et al. [24]reported on the oxidation of thiophene catalyzed by transition metal substituted silicates like titanium silicates in the presence of hydrogen peroxide. At an optimized condition, as high as 93% conversion of thiophene was attained in their study. However, among the different types of catalysts the use of tungstate catalyst was found to be effective in achieving polar sulfur compounds with H_2O_2 as an oxidant [8,22,23].

Despite of all the above-mentioned studies on the desulfurization techniques adopted, much less information is available on the influence of process parameters on the conversion of sulfur compounds, namely BT and DBT, to polar sulfones utilizing an ultrasonic processor. Furthermore, differences in the reaction kinetics for DBT and BT over phosphotungstic acid have not been reported.

Consequently, the objective of the present study was to determine the effects of process parameters on desulfurization efficiency that include the concentrations of hydrogen peroxide, a catalyst, and the PTA. Moreover, the aim of the present paper is to investigate both the reactivity and selectivity of BT and DBT at various reaction temperatures which are observed in the reaction medium. A kinetic model will also be proposed and its relative importance evaluated.

2. Materials and method

2.1. Materials

All the reagents used were of analytical grade and were used as received without further purification. Tetraoctylammonium bromide and phosphotungstic acid were purchased from Sigma Aldrich with quoted purities of 0.99 mass fractions. Dibenzothiophene and benzothiophene were supplied from Alfa Aesar and Acro, respectively. The toluene, as a solvent, was purchased from Merck with quoted purities of 0.99 mass fractions. Hydrogen peroxide (30 wt.% H_2O_2, Merck) was used in excess amount as an oxidant. Its utilization was not monitored during the reaction process.

The initial concentrations of the stock solutions for model fuels (BT and DBT) were regulated to a concentration of approximately 500 μg/mL. This solution was prepared by mixing an appropriate amount of BT and DBT in toluene.

2.2. Experimental and analytical method

In a glass reactor, the experiments were conducted in batch with a 20 kHz ultrasonic processor (Sonic) equipped with a tapered titanium probe transducer. A specific amount of model fuel (BT or DBT) with an initial concentration of 500 μg/mL was added to the reactor. Hydrogen peroxide (30%) was then added along with tetraoctylammonium bromide and phosphotungstic acid. To maintain the reactors at the required temperature, a water bath was employed. After the selected temperature had stabilized, the mixture was irradiated with an ultrasonicator for 15 min. The reactor was removed from the water bath and allowed to cool down. On cooling, the emulsified mixture was centrifuged for 10 min to break down the emulsion. The organic phase was separated by decantation and the samples were taken for further analysis. The results of the above-mentioned analysis were recorded to determine the percentage conversion of the sulfur compounds.

To determine the amount of sulfur in an oxidized solution, the Agilent Technologies 7890A gas chromatography (GC) System equipped with a fused-silica capillary HP-5 ms column (30 m) having a thickness of 0.25 mm film (J&W Scientific, Folsom, CA, USA) was employed. The GC was connected to a Sulfur Chemiluminescence Detector (SCD) for higher selectivity and sensitivity toward an ultralow sulfur concentration [12] The GC temperature was initially set at 100° C for 3 min and ramped to 300℃ at an increasing rate of 20℃/min.

3. Result and discussion

3.1. Catalytic oxidation in the UAOD process

Catalytic oxidation of the sulfur compounds with H_2O_2 in the UAOD system can be explained by the following steps (refer to Fig. 1). Step (1): in the presence of excess amount of H_2O_2, the catalyst was peroxidized to polyperoxometalate $\{PO_4[WO(O_2)_2]_4\}^{3-}$, a peroxometal complex bearing an active oxygen. Step (2): the resulting peroxo-compound underwent an ion exchange with the PTA and subsequently transferred to an organic phase. Step (3): the sulfur compounds were oxidized by the peroxometal complex in the organic phase to their corresponding sulfones. Step (4): the reduced peroxo-compound exchanged an ion with the PTA and transferred back to the aqueous phase where it was regenerated with the H_2O_2. Step (5): ultrasound increased desulfurization efficiency by allowing for an effective mass transfer between the biphasic layers.

After catalytic oxidation, the total ion chromatogram generated from the analysis showed dibenzothiophene sulfone (DBTO) as the only product formed. For benzothiophene also, a similar result was observed. The oxidation reaction was monitored minute wise for 15 min and the result showed that only polar sulfones were detected. Generally, the oxidation of sulfur compounds is considered to be a chain reaction (i.e. sulfur-containing compounds sulfoxides and sulfones). Therefore, in the present study, no sulfoxide was detected, and the sulfone formation was considered to dominate the reaction rate.

3.2. Selectivity and reactivity of the sulfur compounds

Owing to water insolubility property of the sulfur compounds, the aqueous-organic biphasic catalysis for oxidation of the sulfur compounds was successfully established. In this way, biphasic operation minimizes the production of intermediates, for example into dihydroxydibenzothiophene [25], by reducing the opportunity of contact between BT and DBT in the bulk organic phase and the oxidant in the aqueous phase. As such, H_2O_2 from the aqueous phase and sulfur compounds from the organic phase may interact with the catalyst to generate the product benzothiophene sulfone (BTO) and DBTO. These more polar sulfur compounds were produced rapidly and diffused into the bulk of the organic phase, as such compounds are more soluble in organic phase than in water. This resulted in a highly selective oxidation of BT and DBT to polar sulfones.

For a UAOD system, as high as 99 and 96% selectivity was achieved toward DBTO and BTO,

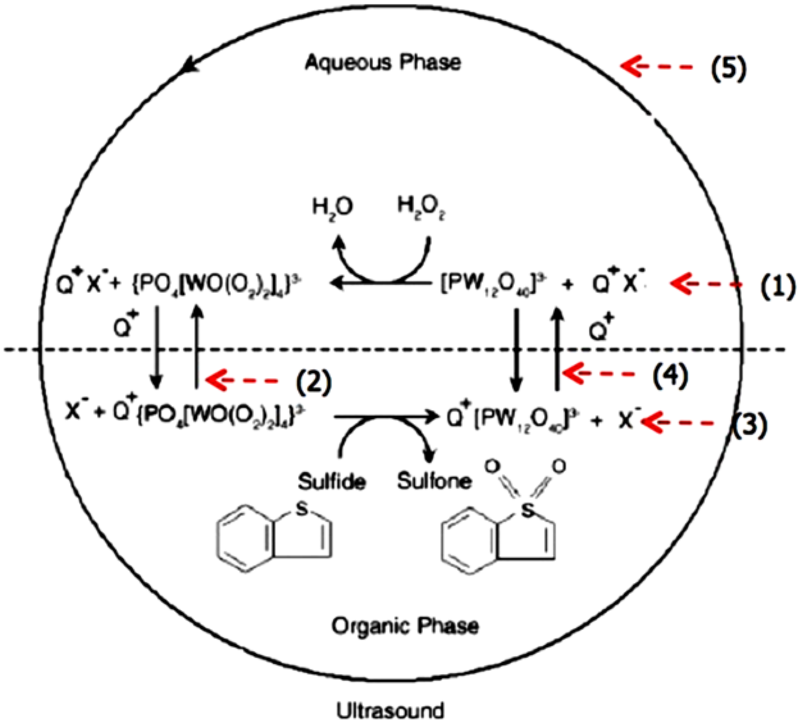

Fig. 1. The reaction mechanism for catalytic oxidation in a UAOD process.

respectively. This is equally important to ensure that no adverse effects on the composition of the diesel fuel would result post-treatment. Attaining a high selectivity value is ideal to ensure a higher percentage removal of the sulfur compounds from the fuel through extraction or adsorption at the end of the process. As presented in Fig. 2, almost all of the DBTs were converted to DBTO. The same result was also obtained for BT. Thus, it clearly indicate the effectiveness of the UAOD system for desulfurization of the sulfur compounds.

With regard to the reactivity of sulfur compounds, the use of phosphotungstic acid and PTA demonstrated high catalytic activity as presented in Table 1. The UAOD system exhibited a nearly 100 and 50% conversion for DBT and BT, respectively. The conversion of model sulfur compounds was determined by conducting an experiment under the same reaction condition (30% H_2O_2, 0.2 g catalyst, 0.1 g PTA, 50˚C, and 15 min). Based on the result, oxidation reactivity decreased in the order of DBT > BT. This reaction process is explained in the study conducted by Otsuki et al. [26]. In their study, difference in the reactivity of a sulfur compound to an oxidant can be attributed to electron density. The higher the electron density, the easier it can be oxidized [26]. For this study, dibenzothiophene having an electron density of 5.756 exhibited the highest reactivity. While BT having an electron density value of 5.739 resulted in low oxidation reactivity. Therefore, reactivity of the UAOD system was governed by the electron density value. The results obtained in this work correspond to those reported for a formic acid/H_2O_2 system [27].

3.3. Effect of amount of oxidant

The amount of H_2O_2 used in this system is an important factor influencing the oxidation of the sulfur

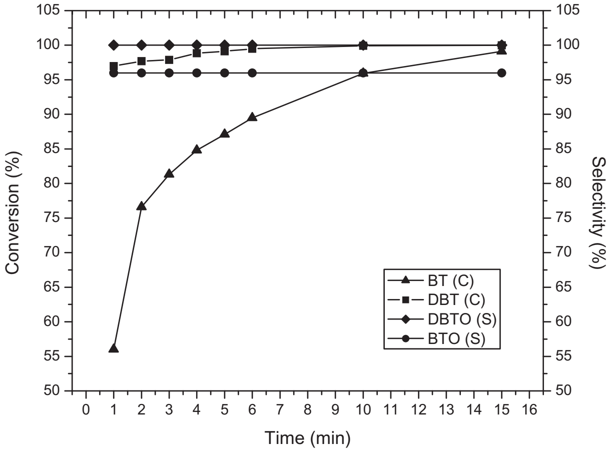

Fig. 2. The conversion of BT and DBT and selectivity to BTO and DBTO at fixed reaction temperatures. Reaction conditions: 15 min, 80˚C, 0.65 M H_2O_2, catalyst 0.2 g, and 0.1 g PTA.

Table 1
Reactivity of refractory sulfur compounds

Sulfur compound	Sonication time (min)	Temperature (℃)	Sulfur concentration (ppm)		Sulfur conversion (%)
			Original	After oxidation	
DBT	15	50	489	6.41	98.69
BT	15	50	467	241.86	48.23

compounds. To investigate the effect of the oxidant, three different initial concentrations of the oxidant (i.e. 0.02, 0.33, and 0.65 M) were tested, keeping the remaining operating parameters, such as catalyst concentration, PTA, and temperature, constant at 0.2 g, 0.1 g, and 80℃, respectively. Table 2 shows the desulfurization efficiency in terms of percentage conversion of the sulfur compounds using H_2O_2 as an oxidant. Based on the table, the conversion increased with an increasing molar concentration of the oxidant. As high as 99.9% conversion of DBT and yield of DBTO were obtained for as low as 0.02 M of H_2O_2. For BT, the desulfurization efficiency of 99% was reached only when the concentration of H_2O_2 was increased to 0.65 M.

In the oxidation of sulfur compounds, the high percentage conversion of BT and DBT to corresponding sulfones can be explained as follows: in the presence of a catalyst, the sulfur compound reacts with a peroxometal intermediate formed by the reaction of the catalyst with the oxidant. With an increase in H_2O_2 concentration in the mixture, more active oxygen is available in the system to produce $\{PO_4[WO(O_2)_2]_4\}^{3-}$ as presented in Fig. 1. This compound is a more active oxidant leading to a faster conversion of the sulfur compounds. Therefore, desulfurization (%) increased as the concentration of H_2O_2 increased from 0.02 to 0.65 M. Furthermore, the conversion levels of DBT were very high for all H_2O_2 concentrations, as compared to BT. As previously discussed, the electron density of the sulfur compounds dictates how fast it can be oxidized. This finding clearly indicates that the hydrogen peroxide concentration affects the conversion of sulfur compounds to polar sulfones to a large extent.

Table 2
Desulfurization efficiency of refractory sulfur compounds with varying concentrations of an oxidant

Concentration (M)	Desulfurization efficiency (%)	
	DBT	BT
0.02	99.1	55.5
0.33	99.3	75.6
0.65	99.9	99.0

3.4. Effect of amount of catalyst

The desulfurization efficiency of the UAOD system was significantly influenced by the amount of catalyst. The effect of the amount of catalyst on the oxidation of BT and DBT was studied by varying its amount from 0.05 to 0.20 g, as presented in Table 3. The results indicated that the conversion of the sulfur compounds increased with increasing the amount of catalyst. Maximum conversion (99%) was obtained when using 0.2 g of catalyst at 50℃. Increasing the amount of the catalyst resulted in an increase in the amount of the peroxometal complex, which was being transferred by the PTA from the aqueous to the organic phase and acted as an oxidant. In addition, the use of phosphotungic acid minimizes the decomposition of H_2O_2 [28]. Thus, this leads to a higher conversion of the sulfur compounds.

The conversion of BT and DBT, as well as the selectivity, toward polar sulfones using phosphotungstic acid as a catalyst at different reaction times is shown in Fig. 2. From the figure, initial conversion of the refractory sulfur compounds increased as the reaction progressed and reached maximal conversion of 99.9% (DBT) and 99.0% (BT) after 15 min. In addition, the selectivity toward BTO and DBTO within the reaction span of 15 min remained in the range of 96–99%.

3.5. Effect of amount of PTA

The effect of the amount of PTA on desulfurization efficiency is presented in Fig. 3. One notable conclusion

Table 3
Desulfurization efficiency of refractory sulfur compounds with varying concentrations of PTA

Catalyst (g)	Desulfurization efficiency (%)	
	DBT	BT
0	62.1	0
0.05	97.1	63.0
0.12	98.0	88.5
0.20	98.9	90.6

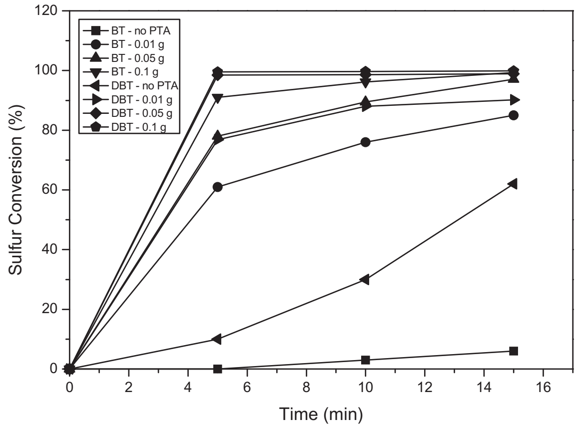

Fig. 3. The effect of tetraoctylammonium bromide on the conversion of sulfur compounds to polar sulfones. Reaction conditions: 15 min, 80˚C, 0.65 M H_2O_2, and catalyst 0.2 g.

that can be drawn from the figure is that an increase in the amount of PTA from 0.05 to 0.10 g led to a remarkable increase in the conversion of BT. For DBT, the amount of 0.05 g was adequate enough to achieve 99% conversion at shorter treatment time. As mentioned previously, DBT was easier to oxidize than BT; thus, the system only required a small amount of PTA to allow the transfer of oxidant from the polar to the organic phase. Moreover, in the absence of PTA the maximum conversion of 6 and 62% was attained for BT and DBT, respectively. This clearly indicates the importance of PTA.

The mechanisms involved in the oxidation of DBT and BT by PTA can be explained in two steps. In the first step, the peroxometal complex forms a complex with the PTA. This resulted in a decrease in the polarity of the peroxometal complex, which enabled it to transfer from the polar phase to the organic phase. In principle, diffusional resistance (during the transfer of reactant and catalyst from one phase to the other) may be involved and requires an efficient stirring (>300 rpm) for an efficient mass transfer of the peroxometal complex [29]. But in the present study, diffusional resistance is negligible due to a highly effective mixing produced by the ultrasonicator. The main reaction of the transferred peroxometal complex with the organic substrate takes place in the organic phase. The second step is the oxidation of the sulfur compounds. In this step, the BT and DBT were oxidized to sulfones then the PTA disassociated and transferred back to the aqueous phase. The cycle continues until all the sulfur compounds have been converted.

3.6. Effect of temperature

It has been reported that the reaction temperature has a strong influence on the process of sulfur oxidation. The effect of temperature on the process of oxidation of the model fuel, specifically BT, was studied in the temperature range of 50–80˚C and the results are presented in Fig. 4. The results suggested that increasing the reaction temperature increases the system's desulfurization efficiency. As high as 99% conversion (<1 ppm) of the sulfur compounds, after 15 min of treatment, was achieved when the temperature was regulated at 80˚C. This process is due to an increase in the reaction rate as the temperature increases, leading to a higher percentage conversion of the sulfur compounds.

Zhao et al.'s study reported using coordinated IL $(C_4H_9)_4NBr\ 2C_6H1_1NO$ as a catalyst and H_2O_2, the highest sulfur conversion of up to 98.8% for 30 min of treatment was achieved at 40˚C [30]. When the temperature was increased to 50˚C, desulfurization (%) consequently decreased to 85.7%. According to their study, the reason attributed to this reaction process was the presence of an amide compound that caused a large decomposition of H_2O_2 at a high temperature. However, in the present study the use of phosphotungic acid minimizes the decomposition of H_2O_2 [28]. Therefore, temperature as high as 80˚C was viable for the system. Furthermore, the reaction time became shorter due to the use of an ultrasonicator, wherein 15 min of treatment was enough to achieve 99% conversion as compared to the 30 min of mixing in the study by Zhao et al. [30].

In addition, the effect of temperature on the selectivity of the system is presented in Fig. 4. The selectivity for the model sulfur compounds was almost

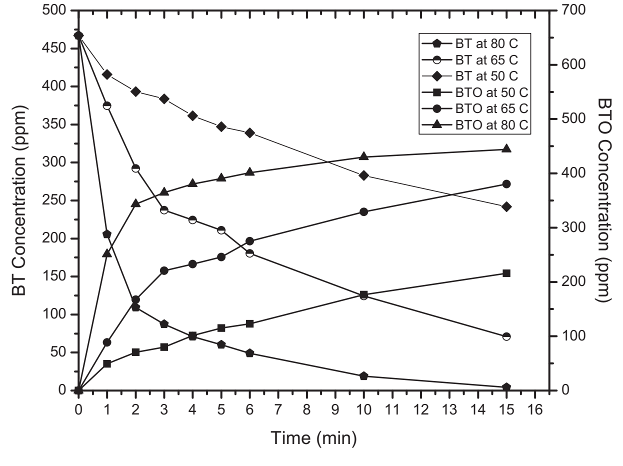

Fig. 4. Sulfur concentration as a function of the reaction time in a H_2O_2/catalyst system at varying temperatures.

unchanged, preserving as high as 96% in the whole range of reaction temperatures. This finding shows that increasing temperature can accelerate the reaction and has almost no impact on the selectivity toward BTO in the temperature range from 50 to 80°C. Moreover, the catalytic oxidation reaction is dominant when the reaction is conducted at a higher temperature, resulting in a high conversion of BT and a high selectivity for the polar compounds. The same result was observed for DBT.

3.7. Chemical reaction kinetics of the oxidation of BT and DBT over phosphotungstic acid

In determining the rate of reaction for a biphasic system using BT and DBT as model compounds, the same process as a single-phase system applies. The only difference was the fact that the concentration taken into consideration was not the total concentration of the whole system but the concentration of the reactants and products in the phase where the reaction took place [31]. For simplification, the amount of H_2O_2 was taken in excess that the change in concentration of H_2O_2 compared to BT or DBT was negligible. The catalytic oxidation of the sulfur compounds is a pseudo-first-order reaction, yielding

$$-\frac{dC}{dt} = k'C \tag{1}$$

where C is the concentration of the sulfur compounds and k' is the apparent rate constant of BT and DBT under catalytic oxidation.

In terms of conversion of BT and DBT (X, $X = (C_{\text{in}} - C)/C_{\text{in}}$), Eq. (1) becomes

$$\frac{\mathrm{d}X}{\mathrm{d}t} = -\frac{\mathrm{d}(C/C_{\text{in}})}{\mathrm{d}t} = k'(1 - X) \tag{2}$$

Illustrated in Fig. 5(a) is the plot of $\ln(1 - X)$ vs. t at various reaction temperatures for the catalytic oxidation of DBT with the correlation coefficient, R^2, in the range of 0.988–0.991. As the data presented here are average values, R^2 is thus estimated according to these values. The results indicate a straight-line relationship between $\ln(1 - X)$ and t, supporting the assumption of pseudo-first-order reaction. Table 4 summarizes the kinetic parameters obtained from the analysis.

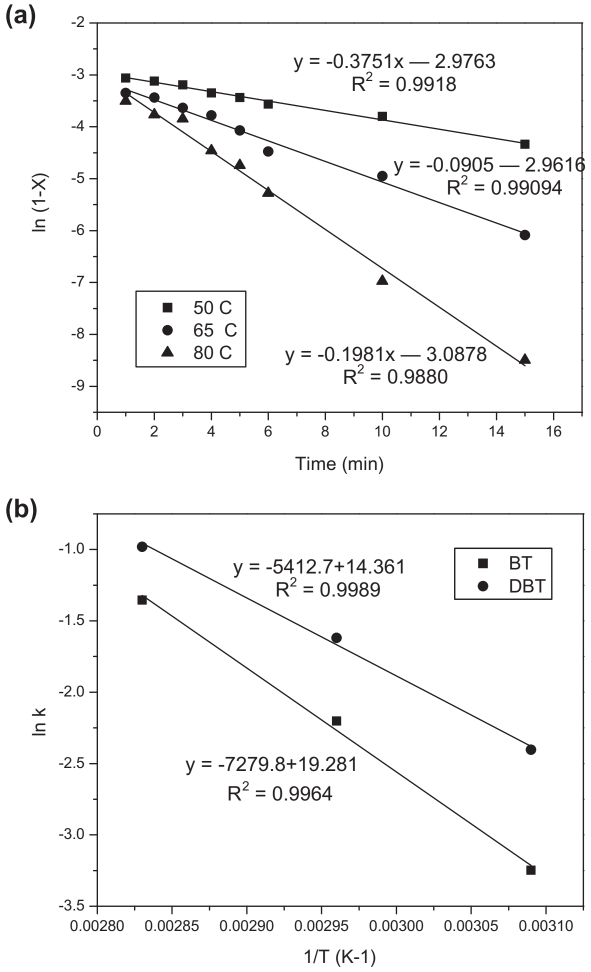

Fig. 5. (a) Pseudo-first-order oxidation reactions of DBT in the UAOD system and (b) Arrhenius activation energies for BT and DBT under catalytic oxidation.

Table 4
BT and DBT rate constants at various temperatures

Substrate	Reaction temperature (°C)	Rate constant (min^{-1})	Correlation coefficient (R^2)
BT	50	0.0389	0.995
	65	0.1106	0.982
	80	0.2582	0.987
DBT	50	0.0905	0.991
	65	0.1981	0.988
	80	0.3750	0.992

Fig. 5(b) presents the Arrhenius plots for the catalytic oxidation of the sulfur compounds over the catalyst. A linear plot was obtained with the correlation coefficient (R^2) of 0.996 for BT and 0.999 for DBT. The activation energies were 45.01 and 60.52 kJ/mol for DBT and BT, respectively. Komitacharat and Trankarnpruk [32] pointed out that the activation energies for BT and DBT were 62.73 and 52.83 kJ/mol, respectively. It is apparent that the oxidation of BT and DBT over the catalyst employed in this process is faster, which is attributed to a decrease in the activation energy brought about by the phosphotungstic acid. Further studies will be helpful to develop the reaction rates in terms of coverage, structure of the molecule, and molecular weight.

4. Conclusion

Oxidative desulfurization of DBT and BT using hydrogen peroxide, catalyst, and PTA was investigated. It was found that the oxidation reaction proceeds very rapidly to give the corresponding sulfones at low temperature and atmospheric pressure. With regard to the process parameters such as temperature, the increase in reaction temperature led to a remarkable increase in desulfurization efficiency. The reaction time to reach 99.0% conversion of BT was achieved in 15 min as the temperature was elevated to 80°C. For the amount of catalyst, amount of PTA, and amount of hydrogen peroxide, they are directly proportional to the percentage conversion of the refractory sulfur compounds.

The hydrogen peroxide concentration exerts a strong influence on the rate of sulfur conversion. Interestingly, in case of an amount of excess oxidant, an almost complete conversion of BT and DBT occurs at 15 min of reaction time. Using the PTA and phosphotungstic acid, a hydrophilic–liphophilic catalyst was formed in the system which demonstrated high reactivity and selectivity toward the oxidation of BT and DBT. The results of the kinetic study indicate that the Arrhenius equation can be applied to describe the experimental data by using the pseudo-first-order reaction kinetic equation. The activation energies of 45.01 kJ/mol (DBT) and 60.52 kJ/mol (BT) were obtained. This work demonstrates that deep desulfurization of DBT and BT was achieved under very mild reaction conditions, namely atmospheric pressure and temperatures close to ambient (50–80°C). Furthermore, high reactivity and selectivity make the UAOD system promising for a deep desulfurization of the fuel.

Acknowledgment

This research was supported by the National Science Council, Taiwan (Grant No.: NSC 100-2221-E-041-005).

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