

Ultrasound-Assisted, Base-Catalyzed Oxidation of 4,6-Dimethyldibenzothiophene in a Biphasic Diesel–Acetonitrile System

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New stricter regulations are being imposed on diesel quality for sulfur content worldwide. Recalcitrant aromatic sulfur compounds such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) are resistant to removal by hydrodesulfurization, because of their low reactivity and sterically hindering structure. Oxidative desulfurization is one of the alternatives that are being investigated for this purpose. In this study, an oxidative system composed of sodium carbonate and hydrogen peroxide was investigated in a biphasic system of diesel and acetonitrile. Ultrasonic methods were applied for the intensive mixing of the biphasic system. The effects of different operating conditions—including temperature, amount of oxidant, and the base concentration—were investigated. Reduction of the DMDBT content by >90% was achieved in the diesel samples. The activation energy of pseudo-first-order reaction for DMDBT was determined to be 57 kJ/mol.

Introduction

Sulfur in fossil fuels is highly undesirable, because of its potential to cause pollution (i.e., SO_x gases and acidic rains). Sulfur also results in the corrosion of metals and poisoning of the precious metal catalyst in the petrochemical industries. The United States Environmental Protection Agency has recommended strict regulations for the sulfur content in the diesel fuel. According to these recommendations, the sulfur content in diesel fuel must be reduced from the current level of 500 ppm to 15 ppm by the year 2006.^{1–2} Presently, hydrodesulfurization (HDS) is commonly used for sulfur removal from hydrocarbon fuels. This process involves high temperature, elevated pressure, metal catalysts, and large reactors.^{3,4} Apart from being an energy-intensive process, HDS has some inherent problems in the treatment of aromatic hydrocarbon sulfur compounds, such as dibenzothiophene (DBT), and their methylated derivatives, such as 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene (4,6-DMDBT). These compounds cause steric hindrance as well, because their C–S bond energy is almost equal to the C–H bond energy, which makes them hard to be broken down by mere hydrotreatment.⁵ Kabe et al.⁶ also concluded that the most important factor for deep desulfurization

is the reactivity of aromatic sulfur compounds. Deep HDS may produce low-sulfur diesel but ultimately results in higher energy costs and the generation of CO₂, which is a greenhouse gas.

To overcome the limitations of HDS, other processes have been investigated in the literature. Sulfur removal by biological methods has been attempted for this purpose. Ambient temperature and pressure conditions make biological treatment an attractive alternative. Castorena et al.⁷ applied *Rhodococcus* bacteria to reduce the sulfur content in diesel by 60%. However, as noted by McFarland et al.,⁸ no naturally occurring species can effectively remove sulfur. Screening and genetic modification is necessary, which leads to complications in process design. Moreover, sulfur molecules are hydrophobic in nature; thus, in the presence of water, the rate of reaction is decreased, because of low solubility.⁹

Oxidative desulfurization is another promising method with several attractive features, such as lower temperature and pressure conditions and lower cost of operation. Oxidation of organosulfur compounds leads to the formation of their sulfoxides/sulfones, which are highly polar and thus can be quite easily removed by extraction into polar solvents or by adsorption. Attar et al.⁵ reported a decrease in the C–S bond energy after oxidation of 5.2 kcal/mol in aliphatic hydrocarbons and 11.8 kcal/mol in aromatic hydrocarbons. Several previous studies have investigated different methods of chemical oxidation for the conversion of HDS-resistant

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molecules to their sulfone forms. For example, Hirai et al.^{10,11} have reported on the photochemical oxidation of DBTs in light oil, followed by extraction of the sulfone. However, photochemical oxidation suffers from the quenching effect pronounced by the presence of aromatic compounds such as naphthalene.¹² The decrease in the rate of reaction was attributed to the selective absorption of radiation. Water (20%) in the solvent also has a tendency to reduce the conversion of the hydrophobic sulfur compounds.¹² Oxidation of sulfur compounds such as DBT has been previously studied by Gilman and Esmay¹³ and Heimlich and Wallace¹⁴ in the presence of 30% hydrogen peroxide (H₂O₂). Other oxidative systems investigated include polyoxometalate/H₂O₂ and formic acid/H₂O₂,^{4,15} heteropolyanion catalysis with H₂O₂,¹⁶ NO₂ oxidation,^{17,18} 12-tungstophosphoric acid/H₂O₂,¹⁹ and TAML activators/H₂O₂.²⁰ The oxidized compound must be extracted from the oil phase. The best performance of extracting sulfones from the oils was observed with dimethylformamide (DMF),^{15,21} but oil recovery was lesser as well. In regard to oil recovery, acetonitrile is better than DMF, as observed by other researchers.^{12,19} Previously, sodium carbonate (Na₂CO₃) has been applied in the photochemical oxidation of DBT in wastewater.²² The authors proposed that the carbonium radical (*CO₃⁻) was responsible for the oxidation process. The oxidation was performed in the presence of H₂O₂. In this study, we report on the oxidation of the highly recalcitrant compound 4,6-DMDBT in a biphasic system of diesel and acetonitrile using H₂O₂/Na₂CO₃ in the presence of ultrasonics.

Experimental Section

Materials. 4,6-DMDBT (97% pure) was purchased from Sigma–Aldrich (St. Louis, MO). The properties of the model sulfur compound are given in Table 1. Ultralow sulfur diesel was kindly provided by Imperial Oil Research Centre (Sarnia, Canada). The solvent for the experiments—99.5% pure acetonitrile (MeCN)—was purchased from MERCK, KgaA (Darmstadt, Germany). Na₂CO₃ was obtained from Caledon Laboratories, Ltd. (Georgetown (ON), Canada). The principal oxidizing agent, 30% H₂O₂, was also purchased from MERCK, KgaA. All other chemicals and reagents were of analytical grade.

Analytical Methods. Gas chromatography (GC) was used to analyze the sulfur compounds in the diesel and acetonitrile

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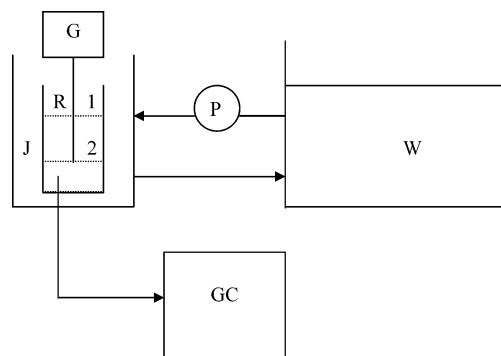


Figure 1. Experimental setup for an ultrasound-assisted oxidation system. Legend is as follows: G, ultrasonic pulse generator (frequency of 23 kHz); R, reactor containing the solvent–fuel system (1 denotes the solvent phase, 2 denotes the diesel phase); P, pump with a heating element; W, constant-temperature water bath; J, jacket for maintaining the temperature of the reactor; and GC, gas chromatograph equipped with a flame photometric detector (FPD).

Table 1. Properties of the Model Sulfur Compound, 4,6-Dimethyldibenzothiophene (4,6-DMDBT)

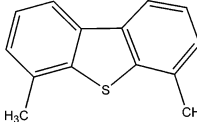
property	value/comment
chemical formula	C ₁₄ H ₁₂
molecular weight	212.3
melting point	153–157 °C
physical appearance	crystalline solid
boiling point	366 °C
chemical structure	

Table 2. Operating Parameters Used with Gas Chromatography (GC)

parameter	value
temperature	Inlet 300 °C
pressure	25 psi
split ratio	40:1
lit offset	22.0
H ₂ flow rate	Detector (FPD) 50 mL/min
air flow rate	60 mL/min
N ₂ flow rate	55 mL/min
initial temperature	Oven 95 °C
heating conditions	ramp I: 10 °C/min, up to 325 °C, and then held for 5 min

phases. The gas chromatograph was equipped with a sulfur-specific flame photometric detector (FPD). A Hewlett–Packard model HP-5 (cross-linked 5% PH ME siloxane) capillary column (30 m × 0.32 mm × 0.25 μm film thickness) was used. The sample was injected in the GC apparatus, using a 0–5 μL needle injector. Table 2 describes the various parameters that have been used for the GC analysis. The total time of analysis was 28.4 min. The retention times of DMDBT and its corresponding sulfone were 10.3–10.5 min and 10.7–10.9 min, respectively. Gas chromatography–mass spectroscopy (GC–MS) analysis was also performed, to confirm the formation of sulfone.

Experimental Methods. Figure 1 shows the experimental setup used to conduct oxidative reactions with 4,6-DMDBT spiked diesel and (acetonitrile) MeCN. The reactor was a 50-mL glass vessel that contained a biphasic system of the diesel and the MeCN with the oxidant 30% H₂O₂. The temperature

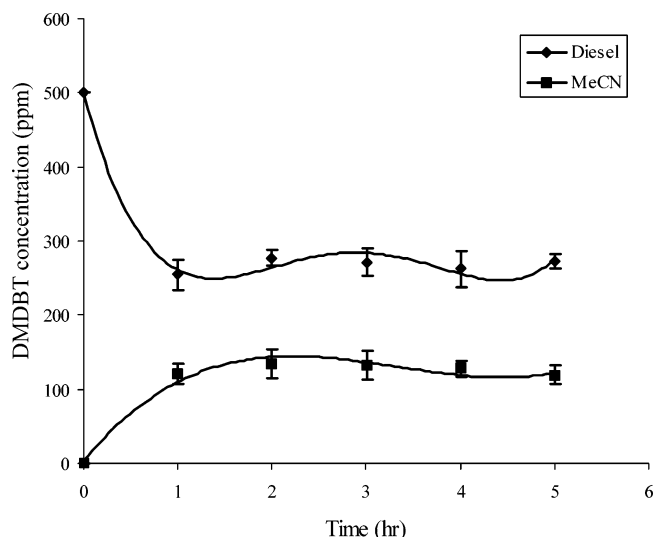


Figure 2. Extraction of dimethyldibenzothiophene (DMDBT) with acetonitrile (MeCN).

of the reactor was controlled using a constant-temperature glass jacket by supplying water from a, J. The continuous supply of constant-temperature water was provided from a water bath (W in Figure 1) with a pump (P in Figure 1). The accuracy of the temperature control was ± 1 °C and confirmed by the thermometer. The ultrasound pulse generator (G in Figure 1) transmitted the pulse at a constant frequency of 23 kHz. The cycle time and the amplitude ratio could be varied. The metallic probe, with a conical shape, tapering at the bottom, was dipped in the reaction mixture. The position of the horn (probe) could be altered.

Ultralow-sulfur diesel obtained from Imperial Oil was spiked with 500 ppm of 4,6-DMDBT. The diesel was mixed with acetonitrile (MeCN) in a volumetric ratio of 1:2. An excess of 30% H_2O_2 with a concentration of 0.8 M in the solvent (MeCN) phase was used for the oxidative reaction between the organosulfur compound and the oxidant. The solvent layer carrying 30% H_2O_2 was the lighter part of the biphasic system, because of its lower density. Solid Na_2CO_3 was added to the reaction mixture, and it dissolved in the solvent phase. The ultrasound probe (horn) was dipped inside the mixture, transmitting the ultrasonic pulse at a frequency of 23 kHz. The maximum reaction temperature was 60 °C, to avoid evaporation loss of MeCN (boiling point of BP = 72 °C). However, temperatures such as 30, 40, and 50 °C were also used to study the effect of temperature on the reaction. A constant-temperature water bath was used to control the temperature of the reactor. Analysis for the sulfur content was conducted occasionally. Only 1 μL of sample was used for the GC analysis of the sample. This did not cause any appreciable loss of fuel or solvent.

Results and Discussion

Extraction of 4,6-DMDBT by MeCN. Organosulfur compounds are polar in nature, because of the presence of the electronegative S atom. Extraction, which is a well-known process that is used in the petroleum industry, can be used to extract sulfur compounds. The polarity of the compound and solvent is the key factor. Figure 2 describes the process of extraction of DMDBT from diesel into the solvent phase. The final DMDBT content after 5 h was ~ 260 ppm. The process reached equilibrium within the first hour, and, thereafter, no appreciable change in the concentration of DMDBT was observed in either of the phases. The liquid-liquid extraction process could remove $\sim 50\%$ of the sulfur

compound from the oil phase at room temperature. However, an appreciable amount of DMDBT remained in the diesel phase. This remaining amount is much greater than the imminent regulatory limits for sulfur in diesel. Higher volumes of acetonitrile could extract more organosulfur compound from the diesel phase. However, the use of large amounts of the polar solvent is not desirable, given the economical constraints. In addition, fuel loss may be incurred with higher solvent-to-diesel volumetric ratios. The extraction efficiency could be enhanced if the sulfur compound in diesel was converted to a more-polar compound, to increase its affinity for polar solvents such as acetonitrile. Organosulfur compounds can be oxidized to more-polar sulfoxides and sulfones, which can enhance their removal from a nonpolar diesel phase into the polar solvent.

The oxidation of 4,6-DMDBT was performed in the diesel-acetonitrile biphasic system. The principal oxidizing agent used is a 30% aqueous solution of H_2O_2 . This oxidizing agent is soluble in acetonitrile but is insoluble in the fuel phase. Therefore, the system remained biphasic, even after the addition of H_2O_2 . Initially, experiments were conducted to determine a set of conditions to maximize the oxidation rate, which could lead to lower residence times and, hence, lower reactor volumes.

Effect of Mixing. The oxidation of the sulfur compound, which can occur at the interface or in the bulk of the solvent phase, requires good dispersion of the solvent and fuel phases. The effect of dispersion was investigated by comparing mechanical stirring with ultrasonic-pulse-induced dispersion. It was observed that the ultrasonic pulse created very fine droplets, leading to an emulsion-like dispersion of the two phases. The ultrasonic pulse used had a frequency of 23 kHz. Better emulsification was observed in the case of sonication: the entire reaction mixture became white. Mei et al.¹ have reported similar observations regarding the application of ultrasonics in a biphasic system that contained one viscous liquid. This is attributable to the cavitation effect that is caused by ultrasonic procedures.²³ Figure 3 indicates that a considerable difference (~ 80 ppm) exists in the level of reduction of 4,6-DMDBT with sonication, compared to stirring with mechanical means using a magnetic stirrer. After the sonication was stopped, the two phases separated easily, because of density differences. It was also noticed that the temperature of the reaction mixture increased due to the application of ultrasonic procedures. A water bath was used to control the temperature of the reaction, with an accuracy of ± 1 °C. Because of the higher conversions achieved with sonication, subsequent experiments used this mode of dispersion of the two phases.

Role of Na_2CO_3 . The oxidation efficiency of H_2O_2 can be affected by several factors, including temperature, pH, and dissolved ions. A significant increase in the decomposition rate of H_2O_2 with temperature can be achieved in pH range of 6–8. However, the pH of the H_2O_2 solution in acetonitrile was measured to be ~ 5 . After an initial screening of the alkaline reagents, Na_2CO_3 was selected for further testing. In our system, H_2O_2 is the main oxidizing agent assisted by Na_2CO_3 .

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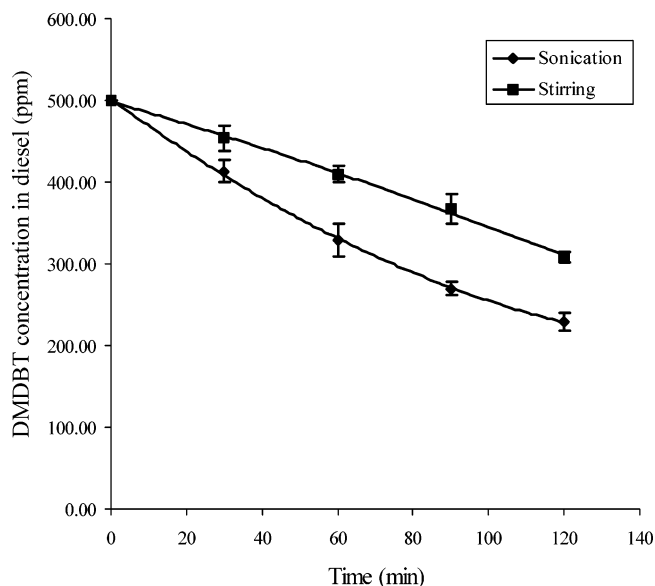
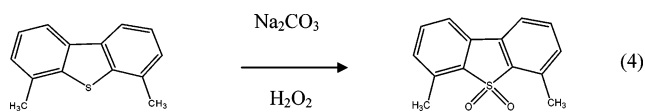
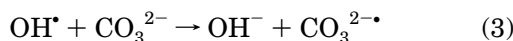


Figure 3. Comparison of sonication with stirring at 30 °C.

H_2O_2 can decompose to generate hydroxyl radicals (OH^\bullet) or O atoms by reactions 1 and 2.^{19,24} The main oxidation reaction is shown in eq 3.



H_2O_2 is the principal oxidizing agent; however, in the presence of Na_2CO_3 , carbonate radicals (CO_3^\bullet) are formed, which could help catalyze the oxidation reaction.²⁵ The carbonate radical is formed via a reaction between the hydroxyl radical (OH^\bullet) and CO_3 (reaction 2). Nascent oxygen (denoted as [O]) is contributed by H_2O_2 , as described by reaction 1.

Known weighed amounts of Na_2CO_3 were dissolved in a H_2O_2 solution to determine the optimum concentration for the oxidation of 4,6-DMDBT in a diesel-acetonitrile biphasic system. Figure 4 shows that increasing the concentration of Na_2CO_3 in the solvent phase significantly reduced the concentration of 4,6-DMDBT, because of improved conversion. However, Figure 4 also shows that there is an upper limit of Na_2CO_3 above which there was little effect on conversion. At concentrations of >30 mM, some precipitation was observed. It is likely that the solubility limits of the salt in the H_2O_2 -acetonitrile system were reached at these concentrations. Hence, further additions of salt will be ineffective.

Effect of Temperature. The concentration of 4,6-DMDBT in diesel decreased as the amount of oxidant increased. However, no significant difference was observed beyond a certain concentration (Figure 5). Oxidation reactions were performed using excess amounts

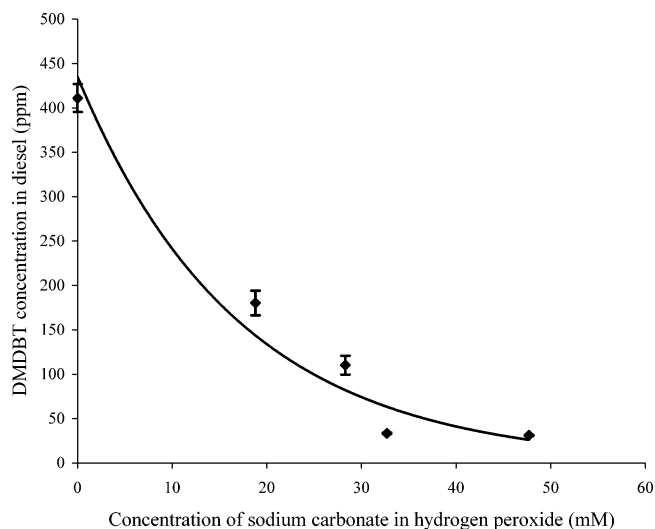


Figure 4. Effect of Na_2CO_3 on oxidative extraction of 4,6-dimethyldibenzothiophene (4,6-DMDBT).

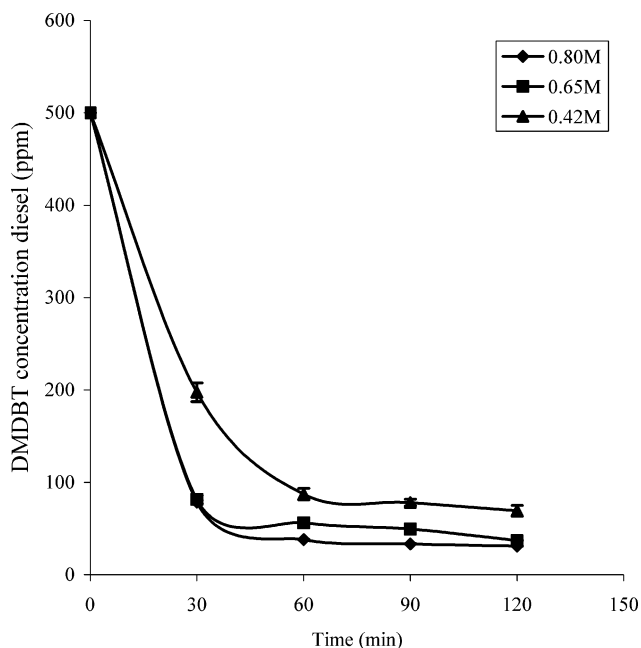


Figure 5. Effect of H_2O_2 concentration on the MeCN phase oxidative extraction of 4,6-DMDBT.

(0.8 M) of 30% H_2O_2 . The effect of temperature was investigated in the range of 30–60 °C. The upper limit for the temperature was determined by the BP (72 °C) of the more-volatile component in the biphasic system (i.e., the MeCN in the mixture). It was selected to be $\sim 10^\circ\text{C}$ lower, to avoid any appreciable loss of the solvent due to evaporation. The reactions in the biphasic system were performed at temperatures of 30, 40, 50, and 60 °C. The trends in Figure 6 clearly show that the reaction is faster at higher temperatures, such as 50 and 60 °C. An increase in conversion, which was followed by the disappearance of 4,6-DMDBT from the diesel phase, increased with temperature. The molar conversions of 4,6-DMDBT varied from 54% at 30 °C to $\sim 94\%$ at 60 °C (Figure 7). As the temperature of the reaction increases, the extent of the reaction increases, resulting in a lower final DMDBT content in the diesel phase after 2 h. At 60 °C, the final DMDBT content was ~ 30 ppm, which represents a reduction of $>90\%$ in the organo-

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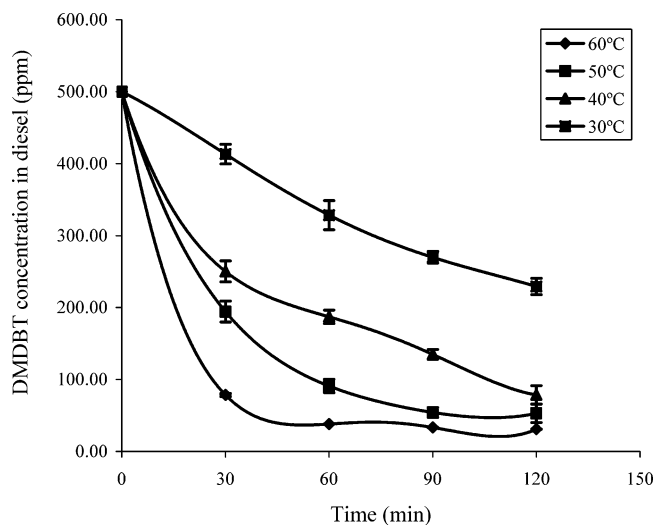


Figure 6. Effect of temperature on the oxidative reaction.

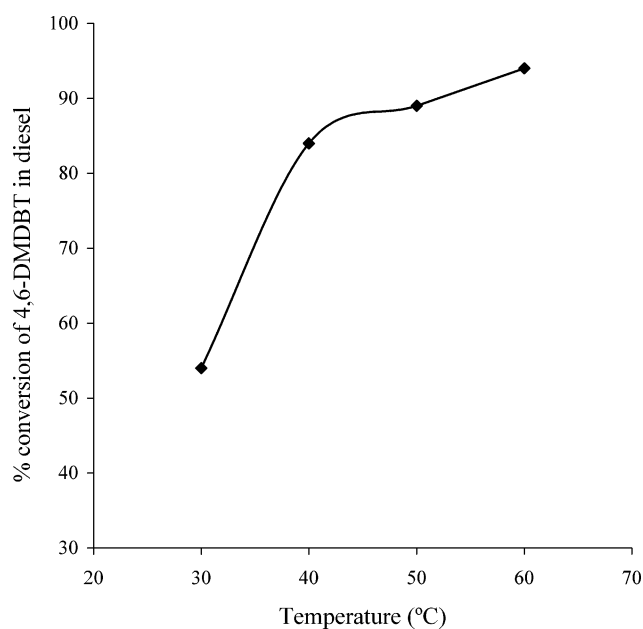


Figure 7. Conversion of 4,6-DMDBT in diesel.

sulfur compound (DMDBT). At temperatures of 40 and 50 °C, the final residual DMDBT concentrations in the diesel phase were 78 and 53 ppm, respectively. The effective temperature range seems to be 40–60 °C. This is similar to the range of 45–75 °C that was reported by Wallace et al.²⁶ for the base-catalyzed oxidation of organic sulfides with oxygen gas (O₂).

Figure 8 presents analysis of the acetonitrile (MeCN) phase after the reaction. As the temperature increases, the reaction rate (and the extent of reaction) increases. MeCN, which is a polar solvent, extracts the oxidized form of 4,6-DMDBT (i.e., sulfone). As the temperature increases, the concentration of sulfone in the solvent phase also increases, indicating successful removal after the oxidation. Figure 9 also shows the concentration of 4,6-DMDBT that is extracted by the solvent phase directly. The amount of 4,6-DMDBT in the solvent phase was much less, as compared to its sulfone.

Although most of sulfur is extracted by the solvent phase, analysis of the diesel phase also showed the

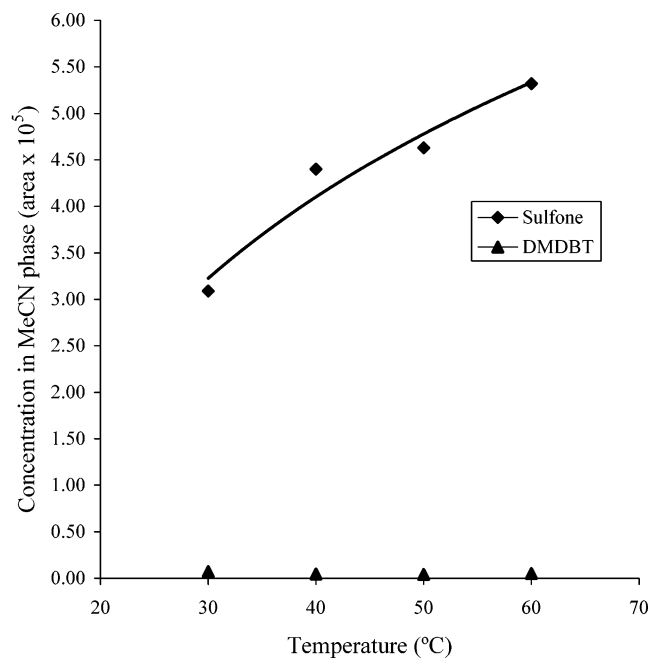


Figure 8. Analysis of the MeCN phase.

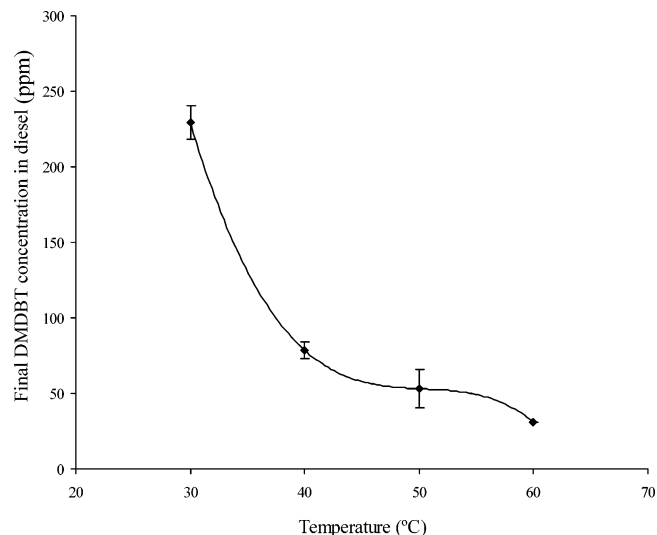


Figure 9. Final 4,6-DMDBT concentration in the diesel phase.

presence of sulfone and its concentration increased as the reaction temperature increased (Figure 10). This indicates the nonzero solubility of the polar sulfone in a nonpolar diesel phase. This is an important aspect of the reaction. Note that all these reactions were performed by single-stage extraction, because the solvent is neither removed nor added to the system during or after the reaction. This also suggests the need to study the balance between the extraction of sulfone and the rate of formation of sulfone.

Pseudo rate equations for the oxi-desulfurization reaction were developed to determine the reaction order and activation energy for the reaction system. The reaction system is heterogeneous, because of the presence of two phases. The reaction occurs in the solvent phase, which also has the oxidizing agent. The sulfur compound diffuses from the diesel phase into the solvent phase, where the reaction occurs in a 0.8 M H₂O₂ solution in MeCN. For the constant-volume batch reactor used in this study, we can write the following

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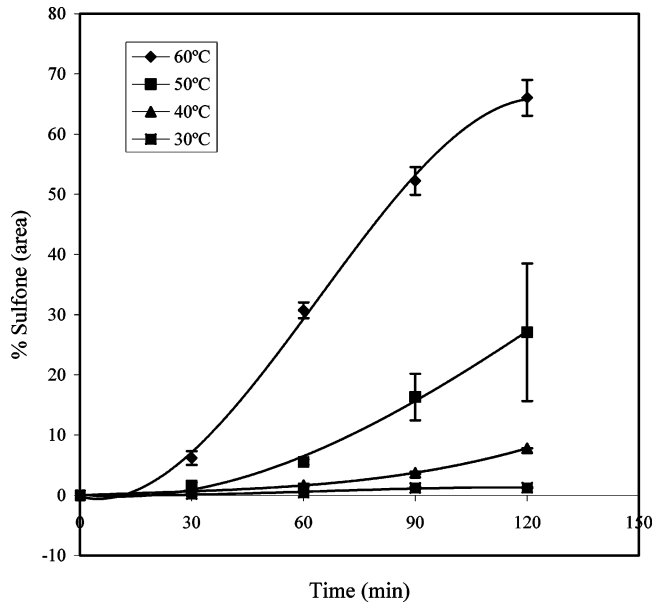


Figure 10. Sulfone content in the diesel phase after the reaction.

equation for the conversion rate of 4,6-DMDBT, assuming a pseudo reaction rate, which includes any physical effects.

$$(-r)V_R = -\left(\frac{dN_D}{dt}\right) \quad (5)$$

Here, N_D is the number of moles of DMDBT in the reaction mixture at time t and V_R is the total volume of the reaction mixture (in units of m^3). Equation 1 can be expressed in terms of fractional conversion ($X_D = (N_{DO} - N_D)/N_{DO}$):

$$(-r) = \left(\frac{N_{DO}}{V_R}\right) \left(\frac{dX_D}{dt}\right) \quad (6)$$

For a first-order reaction in DMDBT, we can write

$$\left(\frac{N_{DO}}{V_R}\right) \left(\frac{dX_D}{dt}\right) = k_1 C_D = k_1 C_{DO}(1 - X_D) \quad (7)$$

$$= k_1 \left(\frac{N_{DO}}{V_D}\right) (1 - X_D) \quad (8)$$

$$\left(\frac{dX_D}{dt}\right) = k_1 \left(\frac{V_R}{V_D}\right) (1 - X_D)^2 \quad (9)$$

A more-general form of eq 9 can be expressed to include the volume of diesel phase (V_D) and the ratio of solvent phase to diesel phase (R_{AD}):

$$V_R = V_D(1 + R_{AD}) \quad (10)$$

Integration of eq 9 gives

$$\ln(1 - X_D) = -k_1(1 + R_{AD})t \quad (11)$$

Reaction rate constant values were calculated graphically, as shown in Figure 11. The k_1 values are 0.0065, 0.015, and 0.025 min^{-1} at 30, 40, and 50 °C, respectively. The Arrhenius plot of the reaction kinetics is shown in

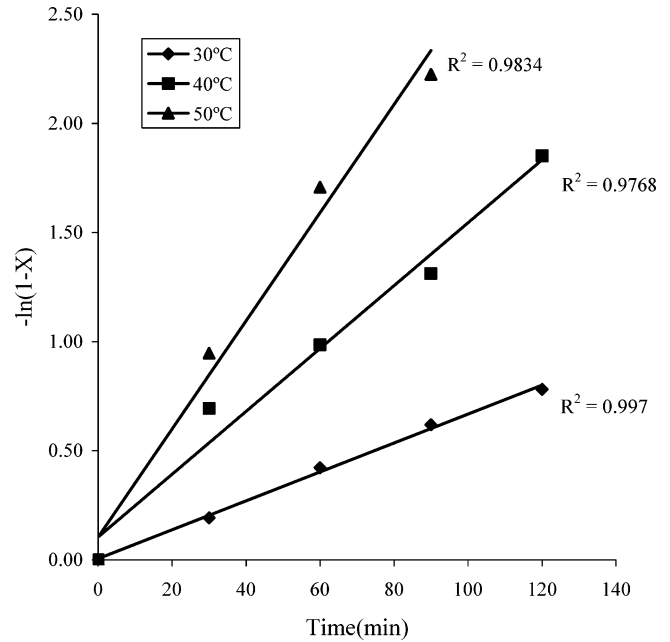


Figure 11. First-order reaction kinetics model.

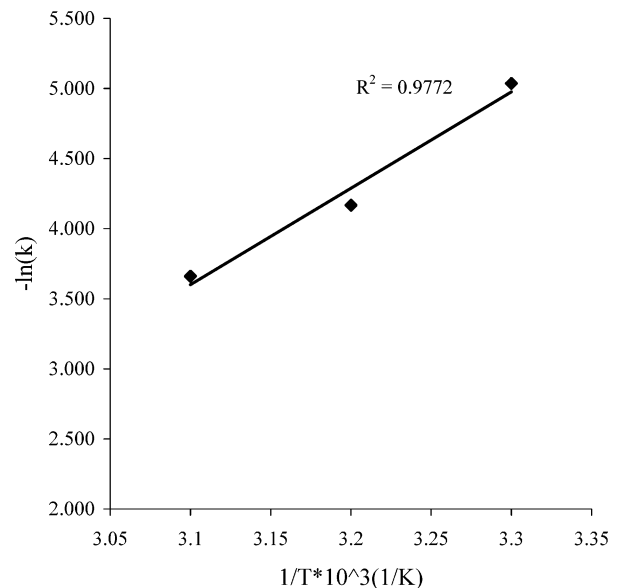


Figure 12. Determination of activation energy of the reaction.

Figure 12. The activation energy obtained is 57.12 kJ/mol. This is similar to the reported value of 58.7 kJ/mol in the literature.⁴ The small difference in the activation energy might be due to the different oxidative system.

Conclusions

The effectiveness of an oxidative desulfurization method with H_2O_2/Na_2CO_3 has been demonstrated in a diesel-acetonitrile (diesel-MeCN) biphasic system. This technique removed >90% of 4,6-dimethyldibenzothiophene (4,6-DMDBT) from the diesel phase by oxidation, using a H_2O_2/Na_2CO_3 system. Improvements due to the application of an ultrasonic pulse demonstrated the need for good contact between phases. The use of moderate temperature and the absence of hydrogen at higher pressure makes it an attractive process for further development. The balance between

the conversion of 4,6-DMDBT to its sulfone and extraction by the polar solvent MeCN seems to be the key to this problem. The reaction rate is low at low concentrations of 4,6-DMDBT, which shows agreement with earlier research work. This process of oxidative desulfurization can be well-integrated with the existing hydrodesulfurization process, which is resisted by the model sulfur compound 4,6-DMDBT.

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Notations

C_D = concentration of DMDBT in diesel phase at a given time (mol/m³)

C_{D0} = initial concentration of DMDBT in diesel phase (mol/m³)

k_1 = reaction rate constant for pseudo first-order reaction (s⁻¹)

N_D = number of moles of DMDBT at a given time in reactor (mol)

N_{D0} = initial number of moles of DMDBT in the reactor (mol)

r = reaction rate (mol m⁻³ s⁻¹)

R_{AD} = volume ratio of diesel to solvent phase

V_D = volume of diesel phase in reaction mixture (m³)

V_R = total volume of reaction mixture (m³)

X_D = fractional conversion of DMDBT

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