Enhanced Oxidative Desulfurization in a Film-shear Reactor

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ABSTRACT

A film-shear reactor was used to significantly enhance the oxidative desulfurization (ODS) of model fuels using hydrogen peroxide as the oxidant. Significant increases in the amount of sulfur removed were seen in comparison to conventionally stirred ODS reactions. For example, up to 50% desulfurization occurred in a single pass of the model fuel through the film-shear reactor at 10 °C. The desulfurization reactions were very fast in the reactor, occurring on the time scale of seconds to minutes. Desulfurization was studied under a variety of conditions, and a statistical design of experiment (DOE) showed that the fuel to oxidant ratio was the only statistically significant parameter to impact the extent of desulfurization: a larger amount of oxidant led to higher desulfurization. A variety of benzothiophene contaminants (benzothiophene, 2-methylbenzothiophene, 5-methylbenzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene) were examined, and the film-shear reactor was effective in removing all of these contaminants. The film-shear reactor was effective at both low (0.5 – 2.0 mL/min) and high (100 – 300 mL/min) flow rates. Experiments showed that oxygen in air was not an effective oxidant for ODS in the film-shear reactor. Experiments using Mo(CO)_6 as a molecular thermometer showed that “hot spots” are not forming in the film-shear reactor, and thus the increase in the ODS rate cannot be attributed to intense thermal activation occurring within the film-shear reactor. It is suggested that superb mixing of the aqueous and fuel phases is responsible for the increased rate of ODS in the reactor.

Keywords Oxidative desulfurization, film-shear reactor, sulfur heterocycles, recalcitrant thiophenes, biphasic reaction

1. Introduction

The effect of high shear and superb mixing on reaction rates is an active area of process intensification research [1–8]. One method of increasing shear and mixing is to use a film-shear reactor (Figure 1) [9]. A film-shear reactor is a device with a rotating disk (the rotor) placed at an adjustable distance 20-300 μm from a stationary disk (the stator). The rotor spins at speeds up to 10^4 rpm, and two solution streams containing the reactants are introduced between the two disks. Contact of the fluids within the narrow gap results in intense shear with consequent intimate mixing of the two solutions.

Figure 1 here

In a previous communication [10], we reported significant enhancement of a biphasic oxidative desulfurization (ODS) reaction using a film-shear reactor with hydrogen peroxide as the oxidant. For example, up to 55% of the benzothiophene in a model fuel was oxidized in the few seconds required for a single pass of the model fuel through the reactor at room temperature or lower temperatures; further desulfurization was achieved when the model fuel was recirculated through the reactor. In comparison, negligible oxidation of the benzothiophene occurred under these conditions using conventional stirring. In this report, we expand on the use of a film-shear reactor for ODS. Specifically, we extend the ODS process to thiophene contaminants other than benzothiophene, and we investigate the effect of much higher flow rates through the reactor on the efficiency of ODS. We also report the results of experiments using molecular oxygen rather than hydrogen peroxide as the oxidant in the ODS process. Finally, we

report the results of a mechanistic investigation into whether the film-shear reactor can thermally activate molecules.

2. Experimental

For this investigation, a 0.5% solution of the indicated thiophene in decane was employed as a model fuel. A 5% solution of formic acid in 30% H₂O₂ mixed with an equal volume of isopropanol (to enhance sulfone solubility) was used as the oxidant stream. The aqueous and decane phases separated readily upon exiting the reactor, facilitating quantitative analysis by ¹H NMR spectroscopy of the remaining sulfur in the decane layer. Specifically, analysis of the signal intensity in the aromatic region relative to 1,1,2,2-tetrachloroethane as an internal standard allowed calculation of the remaining thiophene (Figures S1-S5).

2.1. Reagents

Benzothiophene (BT; 99%), 2-methylbenzothiophene (2-MeBT; 97%), and 4,6-dimethyldibenzothiophene (4,6-DMDBT; 97%), dibenzothiophene sulfone (97%) and γ -butyrolactone were obtained from Sigma-Aldrich. Dibenzothiophene (DBT; 98%) was obtained from Fluka. 5-methylbenzothiophene (5-MeBT; 98%) and benzothiophene sulfone (98%) were obtained from Alfa Aesar. Decane (99%) and 1,1,2,2-tetrachloroethane were obtained from TCI. Hydrogen peroxide (30-32%) and isopropanol were obtained from Mallinckrodt. Deuterated cyclohexane was obtained from Cambridge Isotope Laboratories. All reagents were used without further purification.

2.2. Film-shear reactor trials

All film-shear reactor trials were carried out in a KinetiChem, Inc. SynthetronTM film-shear reactor. The bulk temperature in the reaction zone was controlled using a recirculating

temperature bath with a heat exchanger. The system was allowed to equilibrate at the indicated temperature for 2 or more hours prior to setting the rotor-stator gap. Reagents were delivered through Teflon tubing using independent SYR-2200 dual programmable syringe pumps obtained from J-Kem Scientific. Upon reaching indicated reaction conditions, a minimum of 2 full reaction volumes was allowed to flow through the reactor prior to sample collection in order to ensure steady conditions.

For the desulfurization studies using H_2O_2 , the fuel and oxidant feeds were introduced at room temperature using independent syringe pumps. The feeds encountered each other in the reaction zone (defined as the space within the rotor-stator gap). For the oxidation-by-air trials, the γ -butyrolactone and model fuel phases were allowed to mix in a t-joint in the absence of air prior to encountering the air in the reactor. Air flow was provided from a tank of Grade D breathing air (19.5-23.5% oxygen) and delivery was controlled using a flow meter.

2.3. Sample preparation and analysis

For both types of oxidation, the model fuel phase separated from the other phase immediately upon exiting the reactor. 0.3 mL of the decane layer was combined in an NMR tube with 0.3mL deuterated cyclohexane containing 1,1,2,2- tetrachloroethane (10-100mM) as an internal standard. Relative integrals of the aromatic region (compared to that of a sample of the starting solution prepared in exactly the same way with the same internal standard solution) were used to calculate the percent of the initial thiophene remaining. ^1H NMR spectra were recorded a Varian 600 spectrometer at an operating frequency of 599.98 MHz.

For analysis of the γ -butyrolactone layer, 0.3 mL of the sample was combined in an NMR tube with 0.3 mL deuterated methanol for locking. The ^1H NMR spectrum was obtained of this

sample, which was then spiked with authentic thiophene. ^1H NMR spectra of the thiophenes in γ -butyrolactone are shown in Figure S6.

2.4. Conventional mixing controls

For the control desulfurization studies (with H_2O_2 as the oxidant) using conventional laboratory stirring, 10 mL of each reactor feed was placed in a 50 mL 2-neck round bottom flask equipped with a magnetic stir bar and reflux condenser. The apparatus was placed in an oil bath preheated to 80 °C and stirred vigorously. A sample (1 mL) was withdrawn from each phase at the indicated time (in order to maintain equal volumes), and the decane layer was analyzed in the manner reported for the reactor trials. (These results are illustrated in Figure 3 in the Results and Discussion section.)

For desulfurization studies using air as the oxidant, 15 mL of each feed was placed in a 3-neck round bottom flask equipped with a reflux condenser and stir bar. The second and third necks were sealed with septa, and air was introduced into the solutions using a needle and penetrating into the lower γ -butyrolactone phase. Air flow was maintained at 1 mL/min using a flow meter. This apparatus was placed in a preheated oil bath (100 °C). At the indicated time, 1 mL was withdrawn from each phase (in order to maintain equal volumes), and the decane and γ -butyrolactone layers were both analyzed in the manner described above for the film-shear reactor trials. No oxidation was observed.

2.5. Checking for thermal “hot spots”

The reaction of $\text{Mo}(\text{CO})_6$ with PPh_3 was used to check for thermal “hot spots.” A recirculating THF solution of $\text{Mo}(\text{CO})_6$ was reacted with a THF solution of PPh_3 in the film-shear reactor at a (bulk) temperature of 23 °C. One experiment was carried out for 5 hours and another for 33 hours. A strong absorption band in the infrared spectrum at 2072 cm^{-1} was used to quantify the

amount of $\text{Mo}(\text{CO})_5\text{PPh}_3$ that formed in the reaction system. For comparison, a conventionally stirred reaction solution that did not pass through the reactor was put aside in the dark. For both the 5-hour and the 33-hour experiments, the absorbances of the 2072 cm^{-1} band for the reaction and control solutions was identical, indicating that an equal concentration of $\text{Mo}(\text{CO})_5\text{PPh}_3$ formed in the two solutions.

3. Results and Discussion

3.1. Brief overview of oxidative desulfurization (ODS)

Oxidative desulfurization (ODS) [11–17] is a complementary alternative to current hydrodesulfurization (HDS) technologies [18–22]. In the ODS reaction, an aqueous oxidant (typically hydrogen peroxide with catalytic amounts of an acid) reacts with the sulfur contaminant in the fuel phase. In current practice, ODS is used after HDS to remove sterically hindered polycyclic aromatics, the so-called “recalcitrant thiophenes” [23–30]. The thiophene contaminants are oxidized to sulfones (Scheme 1), which are easily removed from the fuel because they are not soluble in the fuel phase [11–13]. ODS is appealing because the sulfur contaminants that are most resistant to HDS, the recalcitrant thiophenes, are the most reactive under ODS conditions [31–33]. However, because an aqueous oxidant (e.g., H_2O_2) must react with the sulfur-containing contaminant in the fuel (organic) phase, hours of stirring at elevated temperatures are generally required to carry out the ODS process. It was hypothesized that the film-shear reactor could increase the rate of the biphasic ODS reaction by enhancing the mixing of the fuel and aqueous phases. This was indeed the case, as we reported earlier for benzothiophene [10].

Scheme 1 here

3.2. Extending the ODS process to contaminants other than benzothiophene

Experiments were carried out to determine if the results with benzothiophene (BT) could be extended to other benzothiophene contaminants. For this study, 0.5% dibenzothiophene (DBT), 5-methylbenzothiophene (5-MeBT), 2-methylbenzothiophene (2-MeBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), and BT were investigated (Figure 2). The model fuel consisted of one of these thiophenes in decane, and the oxidant solution was 30% H₂O₂, mixed 1:1 with isopropanol. The catalyst, formic acid, was included in the oxidant solution. The purpose of the isopropanol was to prevent the sulfone from clogging the reactor because the sulfone is poorly soluble in water [34]. To ensure a fair comparison of the results obtained with the film-shear reactor to those obtained with conventional stirring, all of the control reactions with conventional stirring also had isopropanol in the oxidant solution. Note that, among the common organic solvents, acetonitrile would have been an excellent choice for extracting the sulfone products [35]; however, control experiments showed that this solvent reacted in the film-shear reactor; it was therefore unsuitable for these experiments.

Figure 2 here

The fuel and oxidant feeds were introduced into the reactor separately by independent syringe pumps. Upon exiting the reactor, the phases separated readily, and the thiophene remaining in the decane layer was quantitatively analyzed by ¹H NMR relative to 1,1,2,2-

tetrachloroethane as an internal standard. Sulfone products were identified by TLC by comparison to authentic samples.

The results of the various trials are found in Table S1 and are summarized as follows: The film-shear reactor can be used to carry out ODS of all the benzothiophenes shown in Figure 2; in some cases, over 50% of the sulfur contaminant was removed with only short residence times in the reactor (seconds to minutes, see Table S1). In contrast, the results for ODS by conventional stirring are shown in Figure 3. In these experiments, desulfurization occurred on the time scale of hours. Based on these comparisons, it is concluded that, compared to conventional stirring, the film-shear reactor provides a significant enhancement of the ODS process for a variety of benzothiophene contaminants.

Figure 3 here

3.3. Factors affecting the efficiency of ODS in the film-shear reactor

In order to elucidate the experimental and instrumental parameters that affect the extent of desulfurization, a balanced DOE (statistical design of experiment) analysis was carried out using BT as the sulfur-containing contaminant. (Details of the DOE analysis are found in the Supporting Information.) The six parameters investigated in the DOE are shown in Table 1, and the results are summarized as follows. Of the six parameters, only the fuel to oxidant ratio (“ratio” in Table S2) is statistically significant. The effect of the ratio on the extent of sulfur removal is logical: increasing the fuel to oxidant ratio results in less sulfur removal. Restated, more oxidant leads to more oxidation of the BT and consequently more sulfur removal.

Table 1 here

200
201 3.4. *Are the conditions for the ODS of benzothiophene also useful for other benzothiophenes?*

202 As discussed above, if the film-shear reactor were ever to become practical for the ODS
203 process, it would have to remove a variety of benzothiophenes, not just BT, from fuels. It is
204 interesting to ask, therefore, if the reaction conditions that remove substantial amounts of BT will
205 also remove substantial amounts of the other benzothiophenes. To explore this question, the
206 oxidations of DBT, 5-MeBT, 2-MeBT, and 4,6-DMDBT were examined using the conditions
207 and parameters shown in Table 2. These conditions were selected for the trials because they
208 were among the best conditions for benzothiophene removal. Removal of the thiophenes was
209 monitored by ¹H NMR spectroscopy in the aromatic region, relative to 1,1,2,2-tetrachloroethane
210 as an internal standard. Representative spectra for each of the thiophene contaminants are found
211 in the Supporting Information, Figures S1-S5.

212
213 Table 2 here

214
215 Table 3 here

216
217 While the three sets of conditions gave nearly identical results for benzothiophene (Table
218 3), the results for some of the thiophenes were strikingly different from those of benzothiophene.
219 For example, there was essentially no desulfurization of 5-MeBT, 2-MeBT, and 4,6-DMDBT
220 under conditions A and B, which worked well for benzothiophene and to some extent for DBT.
221 This result was surprising because 5-MeBT, 2-MeBT, and 4,6-DMDBT were expected to be
222 more reactive than benzothiophene. [31–33,35] The third set of conditions (set C in Table 2)
223 was markedly better than the others, and provided especially effective desulfurization in the case

of 4,6-DMDBT. A straightforward conclusion is that one set of conditions will probably not be effective in removing all types of thiophenes. For practical applications, the best set of reaction conditions would need to be determined for each contaminant.

It is not clear why a set of conditions that is so effective in removing one thiophene, say benzothiophene under “condition A” or “condition B”, is so ineffective at removing the other thiophenes, especially when those thiophenes are expected to be more reactive than BT. These results suggest that the function of the film-shear reactor is to provide more than superb mixing and that some other experimental parameters are also affecting the reactivity. Studies delving into what those other parameters might be are currently underway in our laboratory.

3.5. High Combined Flow Rate

In an attempt to increase the throughput of the ODS process in the film-shear reactor, a set of experiments at high flow rates was conducted using benzothiophene as the contaminant. For these experiments, the flow rate was varied between 100-300 mL/min, which represents an increase of approximately 2 orders of magnitude over the experiments described previously. The experimental results and the conditions are outlined in Table 4. Hydrogen peroxide and formic acid concentrations were held constant for these experiments at 30% and 5%, respectively. Desulfurization ranged from 2 - 25%, with values between 10-20% being typical. While these yields are slightly lower than for the slower flow rates in Table S1 (0.2 – 2.0 ml/min), it is interesting to point out that, at these high flow rates, the residence times range from 0.1-2.4 sec. In addition, because it has already been shown that recirculation of the fuel results in further desulfurization [10], one could imagine a set of film-shear reactors in series operating at these high flow rates as a highly effective approach to desulfurization.

Table 4 here

3.6. *Using oxygen in air as the oxidant*

In an attempt to eliminate the need for hydrogen peroxide, ODS was carried out in the film-shear reactor using O₂ as the oxidant. If successful, this desulfurization system would be ideal for portable applications where access to hydrogen peroxide might be limited. These attempts were based on the method of Makee, et al., who were able to effectively remove thiophene contaminants from fuels using oxygen in air as an oxidant when γ -butyrolactone was used as a cosolvent [36].

The necessary reagents were introduced into the reactor as illustrated in Figure 4, and the sulfur remaining in the fuel layer after the reaction was quantified by ¹H NMR spectroscopy as in the preceding experiments (Figure S6). Experiments were run at temperatures up to 80 °C. In these experiments, up to 98% of the thiophenes were removed, but the removal was found to be simply due to extraction of the thiophene into the γ -butyrolactone layer. (The presence and identity of the thiophene in the γ -butyrolactone layer was confirmed by spiking the sample with a sample of authentic thiophene for each trial.) Each of the thiophenes listed in Figure 2 was examined in this manner, and no sulfone formation was observed under any of the experimental conditions. The inability to use oxygen in air as an oxidant is consistent with the results of control reactions using conventional stirring, which found that no detectable oxidation occurred after stirring overnight at 100 °C in the presence of oxygen in air. It is noted that, in their original report, Makee et al. reported that 140 °C was necessary for the ODS reaction to occur

with oxygen in air. For technical reasons, this temperature was not achievable in the film-shear reactor.

Figure 4 here

3.7. Does the film-shear reactor thermally activate molecules?

For biphasic reactions, it is generally assumed that superb mixing is one of the factors responsible for the increased rates of reactivity in the film-shear reactor. Another possible reason for the enhanced activity is that high shear rates may thermally activate molecules due to the high frictional forces on the solvent molecules. Thermal activation could potentially arise from either bulk warming of the reaction solution or from the presence of localized thermal “hot spots.” Bulk warming of the solutions was straightforwardly ruled out: our temperature measurements of the reaction solution as it emerged from the reactor indicated only a slight warming of the solution by several degrees, certainly not enough of a temperature increase to cause an increase in the ODS rates by a factor of 10^2 - 10^3 as reported here.

The possibility of localized thermal hot spots was probed by using molecules with well-defined reaction rates as “molecular thermometers” [37,38]. Specifically, the substitution reaction of the Mo(CO)_6 complex by PPh_3 (eq 1) was selected as a suitable molecular thermometer because the rates and activation parameters for the reaction are well known [39,40]. The procedure was to react Mo(CO)_6 with PPh_3 in the reactor (the metal complex in one feed tube and PPh_3 in the other) and to monitor the concentration of Mo(CO)_6 and $\text{Mo(CO)}_5\text{PPh}_3$ as a function of time as the reaction solution was repeatedly recirculated through the reactor. From this data, the rate constant for the reaction can be obtained. Using the rate constant and the

known values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$, the Eyring equation can then be used to back-calculate the effective temperature in the reaction zone.

equation 1 here

The reaction of Mo(CO)_6 with PPh_3 was carried out in the film-shear reactor for 5 hours at a (bulk) temperature of 23 °C. As a control, a conventionally stirred reaction solution that did not pass through the reactor was put aside in the dark. Infrared spectroscopy was used to quantify the amount of $\text{Mo(CO)}_5\text{PPh}_3$ that formed in each reaction system. (The product has a strong absorption band at 2072 cm^{-1} [41,42].) The spectra showed that an equal concentration of $\text{Mo(CO)}_5\text{PPh}_3$ formed in the two solutions. The reaction was repeated with a longer reaction time (33 hours), but again the two solutions had equal concentrations of $\text{Mo(CO)}_5\text{PPh}_3$. From these results, it is concluded that localized hotspots are not forming in the film-shear reactor.

4. Summary and conclusions

The film-shear reactor provides a significant enhancement of the ODS process compared to conventional stirring for a variety of benzothiophene contaminants. A concern expressed by some about our prior communication was that the flow rates of the fuel through the reactor were quite small, certainly not large enough for any practical application. However, the work reported here demonstrates that the increased efficiency of the ODS process in the reactor is maintained even for flow rates as high as 300 mL/min. (At these flow rates, the residence times of the fuel in the reactor are less than 1 second.) Another possible concern is that one would like to replace H_2O_2 by oxygen in the air. As discussed, ODS reactions using oxygen in air as the oxidant have

been reported at 140 °C using γ -butyrolactone as the solvent [36]. However, for technical reasons this temperature is not feasible with the film-shear reactor, and no ODS occurred with oxygen in air using the film-shear reactor at lower temperatures (10-80 °C). Experiments to carry out the ODS process using oxygen rather than H₂O₂ are continuing in our laboratory. Finally, the results reported here show that the film-shear reactor is not enhancing the rate of the ODS process by thermally exciting the reactants in “hot spots” created by the high shear rates. Superb mixing of the two immiscible phases is likely the primary reason for the increased rates, but investigation of other reasons for the dramatically increased rates are also continuing in our laboratory.

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Appendix A. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at doi:

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Table, Figure, and Scheme Captions

Table captions

Table 1. Parameters included in the DOE and the range over which they were surveyed. ^aThe voltage is used to adjust the rpm of the rotor. ^bRefers to the volumetric ratio of the fuel phase to the oxidant phase. ^cReported as the percent formic acid in hydrogen peroxide used for the oxidant phase. ^dFlow rate of the 2 phases combined.

Table 2. The three sets of experimental conditions used to probe the oxidation of the thiophenes. All of the trials used 5% formic acid in 30% H₂O₂ (1:1 with *i*-PrOH).

Table 3. Extent of thiophene removal under the three conditions detailed in Table 2.

Table 4. High flow rate experiments and the extent of desulfurization.

Figure captions

Figure 1. Diagram of the film-shear reactor (not to scale).

Figure 2. The five thiophenes examined in this study

Figure 3. The fraction of thiophene remaining as a function of time during ODS carried out with conventional stirring. Note that the desulfurization occurred on the time scale of hours.

Figure 4. Schematic of the reactor setup for oxidation by oxygen in the air. Air delivery was controlled by way of a flow meter, and independent syringe pumps delivered the liquid components to a t-joint for mixing in the absence of oxygen prior to entry into the reactor.

Table 1. Parameters included in the DOE and the range over which they were surveyed. ^aThe voltage is used to adjust the rpm of the rotor. ^bRefers to the volumetric ratio of the fuel phase to the oxidant phase. ^cReported as the percent formic acid in hydrogen peroxide used for the oxidant phase ^dFlow rate of the 2 phases combined.

Parameter	Low Value	High Value
Temperature (°C)	10	70
Gap (µm)	250	1500
Voltage ^a (V)	4	16
Ratio ^b	1	10
Composition ^c (% formic acid)	2.5	5
Combined Flow Rate ^d (mL/min)	0.5	2

Table 2. The three sets of experimental conditions used to probe the oxidation of the thiophenes.
All of the trials used 5% formic acid in 30% H₂O₂ (1:1 with *i*-PrOH).

Parameter	Reaction Conditions		
	A	B	C
Gap size (um)	250	1500	250
Temperature (° C)	10	70	70
Ratio (fuel:ox)	10	1	1
CFR (mL/min)	0.5	2	0.5
Average RPM	6300	1500	1500
Residence time (sec)	80	120	80
Average max shear rate (sec ⁻¹)	84000	3500	19000

Table 3. Extent of thiophene removal under the three conditions detailed in Table 2.

Thiophene	% Thiophene Removal		
	A	B	C
Benzothiophene	44	51	55
Dibenzothiophene	7	17	27
5-Methylbenzothiophene	0	0	13
5-Methylbenzothiophene (series B)	0	0	21
2-Methylbenzothiophene	0	0	13
4,6-Dimethylbenzothiophene	0	0	45

Table 4. High flow rate experiments and the extent of desulfurization.

Combined Flow Rate (mL/min)	Rotation Speed (RPM)	Gap (μm)	Temp. (°C)	Percent Sulfur Removed
300	6300	250	70	15
300	6300	250	10	2
300	1600	1500	10	3
300	1600	250	10	16
100	6300	250	10	7
100	1600	1500	70	13
100	6398	1500	70	11
200	3965	875	40	14
100	1586	250	10	12
300	6300	1500	70	18
100	1537	1500	10	11
100	6344	250	70	16
100	6260	1500	10	15
200	3919	875	40	15
300	6300	1500	10	16
300	1600	250	70	19
300	1600	1500	70	29
200	4031	875	40	24
100	1600	250	70	25
200	3930	875	40	19

Figure

Figure

benzothiophene

4,6-dimethyldibenzothiophene

dibenzothiophene

2-methylbenzothiophene

5-methylbenzothiophene

Figure

Figure

Figure

Graphical abstract