



## Enhanced oxidative desulfurization in a film-shear reactor



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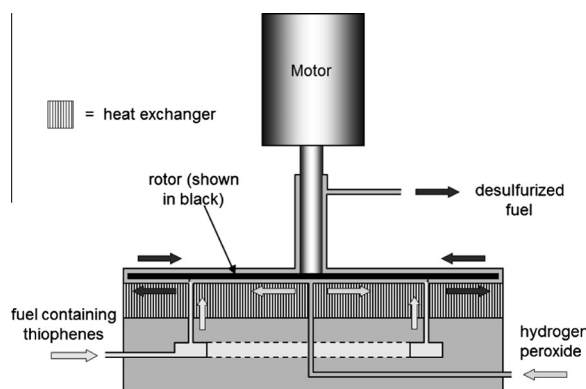
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### HIGHLIGHTS

- A film-shear reactor was used to enhance oxidative desulfurization (ODS).
- Recalcitrant thiophenes are oxidized within seconds to sulfones in the reactor.
- Desulfurization using hydrogen peroxide occurs within seconds at high flow rates.
- Molecular thermometers showed the absence of thermal hot spots in the reactor.
- The fast ODS reaction is attributed to superb mixing of the nonmiscible phases.

### GRAPHICAL ABSTRACT



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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)<sub>6</sub> 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.

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## 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 (Fig. 1) [9]. A film-shear reactor is a device with a rotating disk (the rotor) placed at an adjustable distance 20–300  $\mu\text{m}$  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.

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%  $\text{H}_2\text{O}_2$  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  $^1\text{H}$  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 (Figs. 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  $\gamma$ -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. Synthetron™ 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  $\text{H}_2\text{O}_2$ , 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  $\gamma$ -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 0.3 mL deuterated cyclohexane containing 1,1,2,2-tetrachloroethane (10–100 mM) as

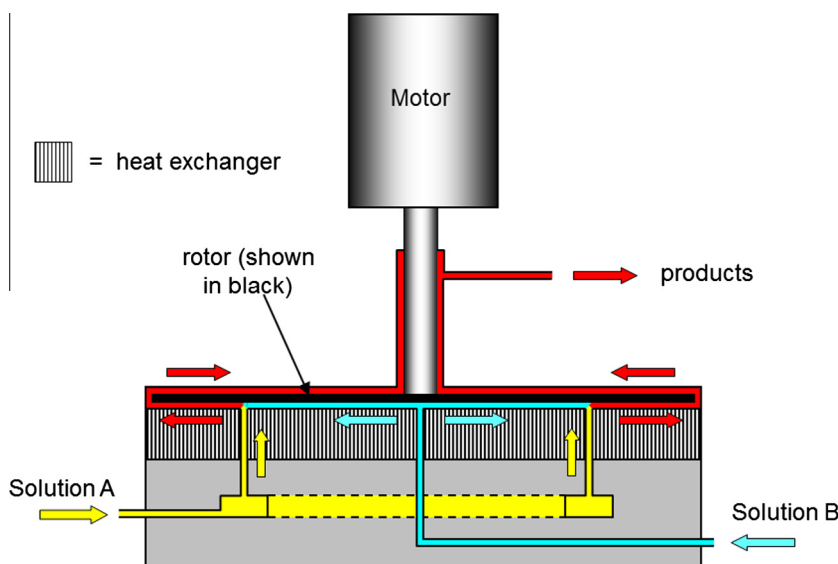


Fig. 1. Diagram of the film-shear reactor (not to scale).

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