Deep Desulfurization of Diesel using a Single-Phase Micro-reactor

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Abstract: This paper describes the benefits of computational fluid dynamics in the development of a microreactor used in the desulfurization of aromatic compounds. It is crucial to verify diffusion and extinction coefficients to ensure accurate simulation results prior to experiments.

Keywords: desulfurization, microreactor, dibenzothiophene

1. Introduction

Aromatic sulfur bearing compounds such as dibenzothiophene and alkylated dibenzothiophenes are difficult to remove from fossil hydrocarbon fuels. For example, the remaining sulfur in low sulfur diesel is mostly found in these aromatic compounds. An alternative to conventional hydrodesulfurization is oxidative desulfurization, where these molecules are oxidized using hydroxyl radicals to form polar molecules which can then be removed by liquid-liquid extraction. One way to implement this process is to photochemically activate the reaction using short wavelength UV light, to produce hydroxyl radicals from a precursor such as tert-butyl hydro peroxide (TBHP). Though the process could be implemented in a macroscale reactor, the high linear extinction coefficient of the aromatic species present towards the UV light employed leads to sluggish kinetics. Therefore, we are investigating the implementation of the process in a microreactor where the small thickness of the reactor will allow penetration of light through the bulk of the reacting fluid and thus a higher conversion rate. Experiments have shown that conversion stops at a given level instead of continuing to completion as predicted.[1] COMSOL multiphysics was used to model the behavior of all of the possible species present and reactions that may occur. This model will also help in comparing this process to previous processes in efficiency and degree of completion.

2. Use of COMSOL Multiphysics

The interplay between Computational Fluid Dynamics (CFD) and chemical kinetics plays an important role in experimentation. It allows an experiment to be designed, optimized, and varied before the experimental apparatus is even set up. This presents tremendous advantages such as determining branching points or revealing other useful experiments which may improve data collection or accuracy. Traditionally an experiment is conceived, drawn up, assembled, run, and results are collected. Sometimes the results are as expected and other times they cause the need for further thought and experimentation which can cause costly delays. This is particularly true in the chemical engineering world, where even simple measurements may take days to perform. Using a mathematical model to "run" the experiment beforehand allows us to see that it may be beneficial to conduct a few runs differently or to collect additional information prior to setting up our experiment.

One example of this is that when we ran our mathematical model the results revealed that it was crucial to experimentally verify the linear extinction and diffusion coefficients of the main chemical species present because they can be significantly different for our single phase system than for two-phase systems such as previously conducted. Diffusion coefficient experiments were set up and conducted using a Taylor Dispersion Apparatus as shown in Figure 1. A Beckman 112 solvent delivery pump was used to control flow rate at 0.277 (+/- .005) ml/min through a 25 ft (7.62 m) column with inside diameter of 0.02 inch (0.0005 m).

A 100 μL sample volume of an approx. 1.0 mM was used for each compound and data was collected by a Gilson model 111b UV Detector interfaced with a computer using a TracerDAQ 1008 analog to digital converter board. Diffusion coefficients were extracted from the correlation between the variance of the distribution of
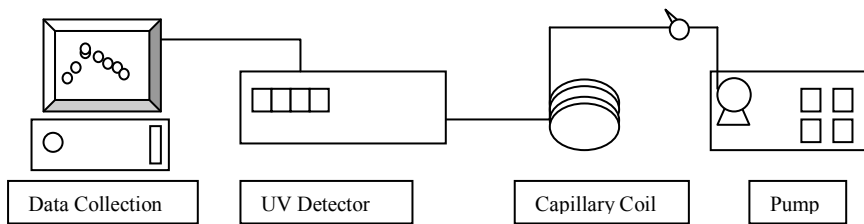
Figure 1: Taylor Dispersion setup

| Data Collection | UV Detector | Capillary Coil | Pump |

elution time to the second moment of the elution time as proposed by Taylor.[3,4,5] The first and second moments are correlated with the measurements using the refractive index through Equation 1

(1)
$$\frac{\sigma^2}{s^2} = \frac{\tau r^2}{24 D_{12}}$$

Where:
τ is the first moment of the elution time
σ is the second moment of the elution time
r is the inner radius of the capillary
and D_{12} is the diffusion coefficient.
The values obtained are similar to those predicted by Wilke-Chang as demonstrated in Table 1.

We also decided to collect extinction coefficients for each of the expected species by measuring their absorptivity. This is important because having just one product with a high absorptivity could effectively block the UV light and stop the reaction prematurely. Using an Avaspec 3648 spectrophotometer absorbance data was collected for Dibenzothiophene, Dibenzothiophene Sulfoxide, Dibenzothiophene Sulfone, and Tert-Butyl Hydro Peroxide shown in Figures 2 – 5.
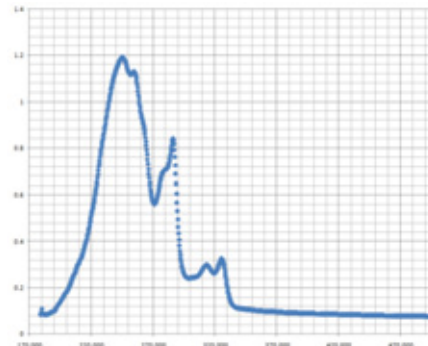

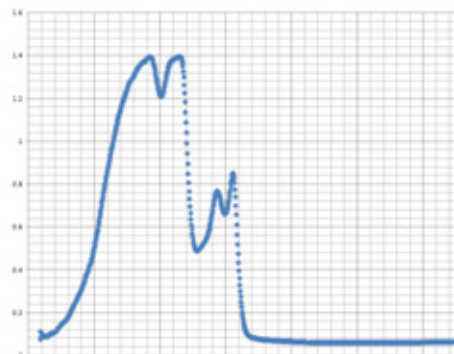Figure 2: absorbance peak for DBTS (0.109 mM)

Figure 3: absorbance peak for DBTSO (0.05 mM)

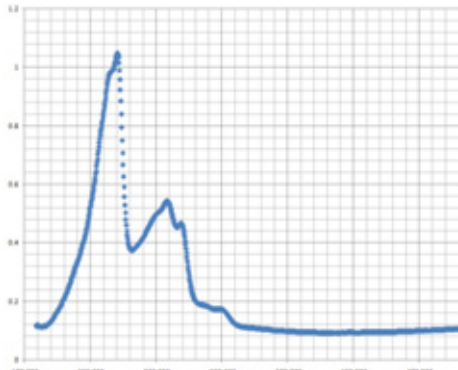| Table 1: Experimental and Empirical Diffusion Coefficients Comparison				
	DBTS	DBTSO	DBTSOO	TBHP
Taylor Dispersion	1.49E-09	2.07E-09	1.27E-09	2.39E-09
Wilke - Chang	1.14E-09	1.22E-09	1.19E-09	1.68E-09

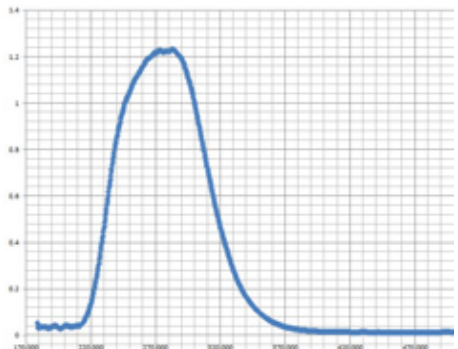Figure 4: absorbance peak for DBTSOO (0.04 mM)

Figure 5: absorbance peak for TBHP (0.1442 M)

The extinction coefficient is correlated to the absorbance using Beer's Law (Equation 2).

$$(2) \qquad \varepsilon = \frac{A}{cL}$$

Where:
A is absorbance
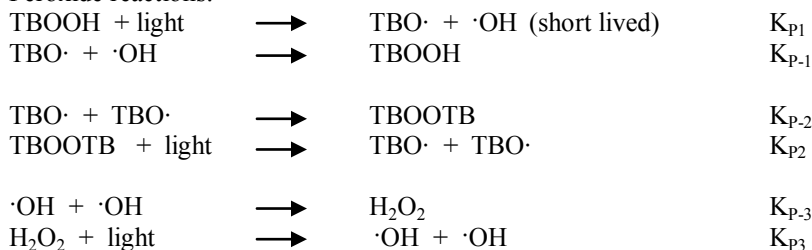c is concentration (M)
L is length (cm)
and ε is extinction coefficient

Clearly, the extinction coefficients of the various species vary drastically. For example, for DBTS the absorbance measurement of a 1.09×10^{-4} M solution at a wavelength of 254 nm gave an absorbance of 1.129, which gives an extinction coefficient of 1.04×10^4 M^{-1}cm^{-1}. Similarly for DBTSO, using a 0.000050 M solution gave an absorbance of 1.349 and an extinction coefficient of 2.7×10^4 M^{-1}cm^{-1} and for DBTSOO using a 0.000040 M solution gave an absorbance of 0.382 and an extinction coefficient of 955 M^{-1}cm^{-1}. TBHP at 0.1442 M and an absorbance of 1.06 gives an extinction coefficient of 7.35 M^{-1}cm^{-1}. and its influence in the light extinction system is therefore negligible. These values are summarized in Table 2.
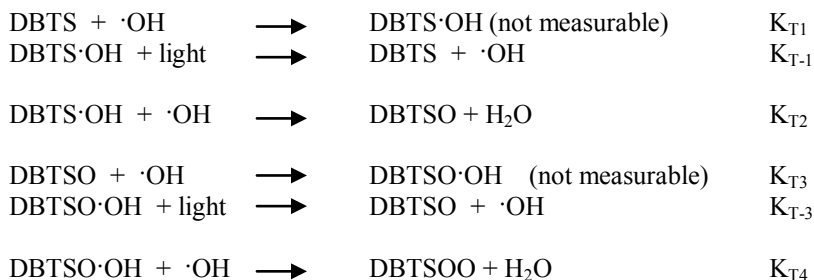
Our COMSOL model utilizes the Steady-state Incompressible Navier Stokes Laminar Momentum Transport as well as the Steady-state Convection and Diffusion Mass Transport module. The model tracks 11 species and 18 possible reactions. These reactions are grouped into three categories: peroxide reactions, thiophene reactions, and side reactions. The peroxide reactions include the interaction between the UV light and the TBHP to form a hydroxyl radical and the reverse reaction. The thiophene reactions track the progress of Dibenzothiophene (DBTS) as it is oxidized by this radical to form the polar molecule Dibenzothiophene Sulfone (DBTSOO) as well as the reverse reactions. The side reactions include all of the unwanted reactions which form various other products as well as their reverse reactions. Some of these reactions will be combined for ease of tracking and the inability to measure some of the intermediate species. Others can be eliminated based on the conditions of the reactor or based on the physical nature of the species involved. Once experiments are complete the product stream will be analyzed by gas chromatography. Based on the products found in this analysis other reactions can be ignored as well.

Table 2: extinction coefficients				
	DBTS	DBTSO	DBTSOO	TBHP
Concentration	0.000109	0.000050	0.000040	0.144
Absorbance	1.129	1.349	0.382	1.06
extinction coefficient	10400	27000	955	7.35

Peroxide reactions:

TBOOH + light	$\longrightarrow$	TBO· + ·OH (short lived)	K_{P1}
TBO· + ·OH	$\longrightarrow$	TBOOH	K_{P-1}
TBO· + TBO·	$\longrightarrow$	TBOOTB	K_{P-2}
TBOOTB + light	$\longrightarrow$	TBO· + TBO·	K_{P2}
·OH + ·OH	$\longrightarrow$	H_2O_2	K_{P-3}
H_2O_2 + light	$\longrightarrow$	·OH + ·OH	K_{P3}

Thiophene reactions:

DBTS + ·OH	$\longrightarrow$	DBTS·OH (not measurable)	K_{T1}
DBTS·OH + light	$\longrightarrow$	DBTS + ·OH	K_{T-1}
DBTS·OH + ·OH	$\longrightarrow$	DBTSO + H_2O	K_{T2}
DBTSO + ·OH	$\longrightarrow$	DBTSO·OH (not measurable)	K_{T3}
DBTSO·OH + light	$\longrightarrow$	DBTSO + ·OH	K_{T-3}
DBTSO·OH + ·OH	$\longrightarrow$	DBTSOO + H_2O	K_{T4}

Side reactions:

~~DBTS + TBO·~~	$\longrightarrow$	~~DBTS·OTB~~ (unstable)	K_{S1}
~~DBTS·OTB + light~~	$\longrightarrow$	~~DBTS + TBO·~~	K_{S-1}
DBTS·OTB + ·OH	$\longrightarrow$	DBTSO + TBOH	K_{S2}
DBTSO + TBO·	$\longrightarrow$	DBTSO·OTB	K_{S3}
DBTSO·OTB + light	$\longrightarrow$	DBTSO + TBO·	K_{S-3}
DBTSO·OTB + ·OH	$\longrightarrow$	DBTSOO + TBOH	K_{S4}
~~DBTS·OH + DBTS·OH~~	$\longrightarrow$	~~DBTSOSDBT + H_2O~~ (stearically hindered)	K_{S5}

A scheme of the microreactor employed is shown in Figure 6. A major issue with the model development is dealing appropriately with the intensity of the light present as a function of the path through the reactor. In our case, the UV light was tracked as a concentration flowing orthogonally to the bulk flow. Although the UV light is required for the reaction it is not used up by the reaction in the same sense as typical reactants. It is not used up by the amount of reactant that it reacts with but rather the amount of reactants or products that it encounters as it passes through the reactor. Therefore it shows up as a reactant in each of the applicable reactor kinetics equations to ensure the reaction does not go forward unless there is sufficient light present but the reaction rate equation for light itself is entirely different. The reaction rate for light follows the correlation in equation 3.
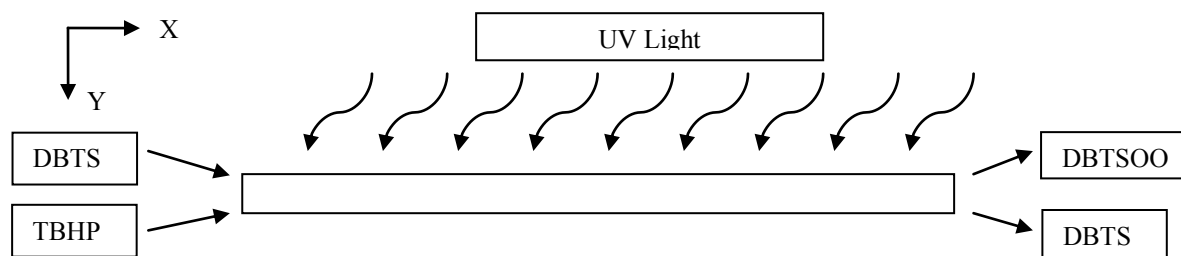
Figure 6. Micro reactor sketch

(3) $\qquad C_I = C_I^0 * \sum \varepsilon_i C_i$

Where:
C_I^0 is the initial concentration of light at the boundary
ε_i is the extinction coefficient for each species
C_i is the concentration of each species
and C_I represents the concentration of light at a given point.

The reactor was scaled by a factor of 100 in the x-direction to allow higher resolution and meshing. Diffusion coefficients and velocities were also scaled appropriately. The products will help determine the reaction rates based on the reaction equations and their stoichiometry.

3. Results

In prior experimental work a high conversion rate (80% conversion for 30 second residence time) of DBTS for the given conditions was observed, and higher conversion is expected with a multistage reactor. Results from use of the COMSOL model developed matching the experimental observation is presented in Fig. 7 below. The optimization of parameters for this set of conditions allows us to extract relevant reactor kinetics parameters. Developing the model will help tremendously in setting up future experiments which can be used to further fine tune the parameters used in the COMSOL model. In future work we intend to examine further the effect of other experimental parameters such as residence time and reaction temperature for better process optimization. This model can be ultimately used to determine conditions under which deep desulfurization through oxidation of aromatic sulfur containing compounds is more effective than conventional alternatives.
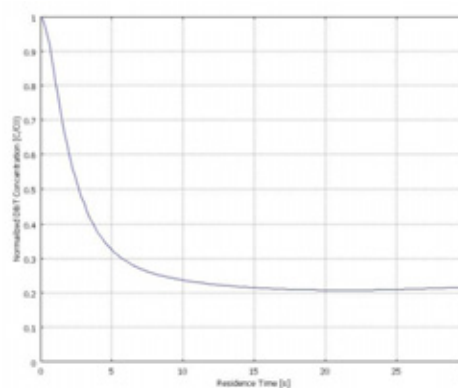

Figure 7. Normalized Concentration of DBTS showing nearly 80% conversion of DBTS

4. Conclusions

A comprehensive model of the reactive system under investigation has been developed. Computational work with the model allowed understanding that in this system this reaction is quenched by equilibrium rather than limited by mass transfer.

Further, rapid, inexpensive experimentation *in silico* allows prior optimization of reactant concentrations and residence times to achieve high dibenzothiophene oxidation with low tert-butylhydroperoxide inputs at high fluid volumetric flowrate.

5. References

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