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Photo-Catalyzed Reactions I

Photochemical Reaction Process

In Affiliation With:

MBI

Microproducts Breakthrough Institute

PTT - LOA

PTT - Laboratories Of America

Goals and Objectives

GOAL:

To investigate phenomena pertinent to oxidative desulfurization of fuels, and to demonstrate that desulfurization is feasible in a single-phase UV-assisted microreactor.

OBJECTIVES:

To design, manufacture, and build a microreactor system;

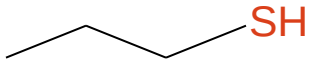
To perform experiments;

To build mathematical model of the desulfurization process;

To analyze data using mathematical model.

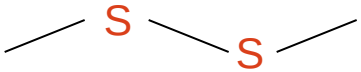
Origin of sulfur in fuels

Common sulfur compounds in crude oil:

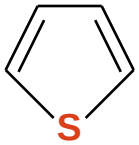


Thiols

Sulfides



Disulfides



Thiophene

- **Diesel engines emit particulate matter (PM) in the sub-micron range;**
- **The extent of PM is directly related to the sulfur content of diesel fuel;**
- **Sulfur poisons the catalyst in fuel cell and other applications;**
- **SO_2 and SO_3 gases are main source of acid rain and air pollution.**

Sulfur content in fuels - Regulations

Region / Country	Year	Regulation By	Maximum S (ppm)	Application
USA	1993	EPA	500	On-road engines
	2006	EPA	15	On-road engines
	2006	EPA	500	Off-road engines
Canada	1998	Canadian Environmental Protection Act	500	On-road engines
	2006	Canadian Environmental Protection Act	15	On-road engines
	Future	Canadian Environmental Protection Act	400	Off-road engines
European Union	1989	Council of Ministers	3000	On/off-road engines
	1994	Council of Ministers	2000	On/off-road engines
	1996	Council of Ministers	500	On/off-road engines
	2000	Council of Ministers	350	On/off-road engines
	2005	Council of Ministers	50	On/off-road engines

*** Control of Air Pollution from New Motor Vehicles: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements, EPA, January 18, 2001.**

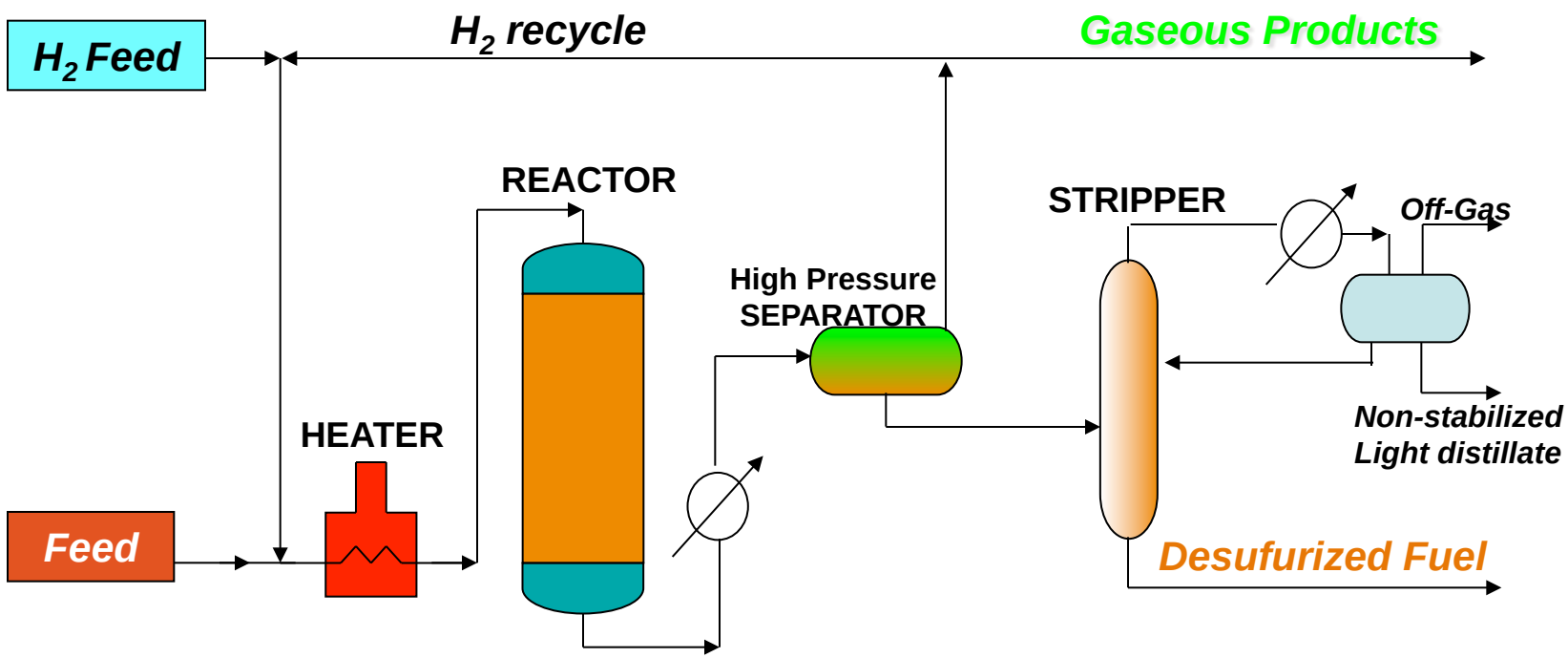
*** Final Report of the Government Working Group on Sulfur in Gasoline and Diesel Fuel, July, 1998.**

*** Dieselnet, July 30, 1999.**

Hydrodesulfurization (HDS) is currently predominant method of sulfur removal from fuels

Hydrodesulfuriztaion reaction:

$$RSR' + 2H_2 \xrightarrow{Co-Mo/Ni-Mo} RH + R'H + H_2S$$



Hydrodesulfurization (HDS)

Challenges with HDS process:

Reaction conditions: elevated T and P, and H_2 safety

Operating cost is high: H_2 + catalyst;

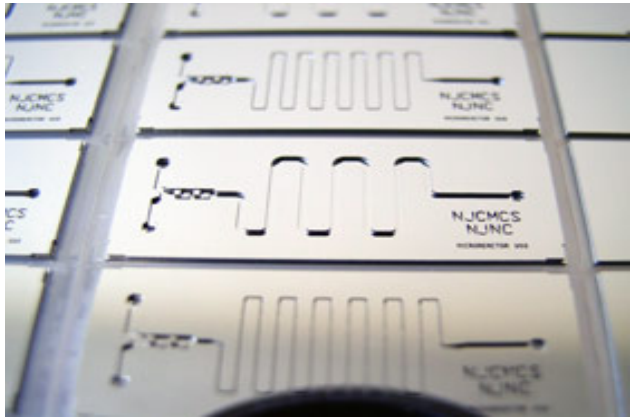
Does not effectively remove all thiophenes.

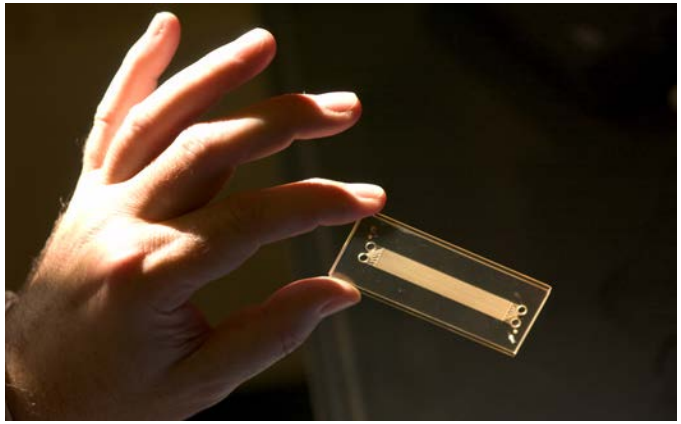
We propose *oxidative desulfurization* in microscale technology

Concept: **Sulfur atom in thiophenes is oxidized, and obtained sulfoxides and/or sulfones are later extracted with a polar immiscible solution.**

Advantages:

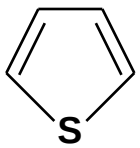
- **Catalyst is not needed;**
- **Process is easy to control;**
- **Reaction occurs at mild temperature and atmospheric pressure;**
- **Lower operating cost and capital investment**



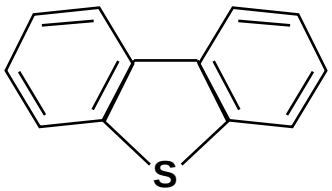


Reactants

We will concentrate our attention to *Thiophenes* because they are the most difficult to remove from petroleum products like diesel and gasoline.

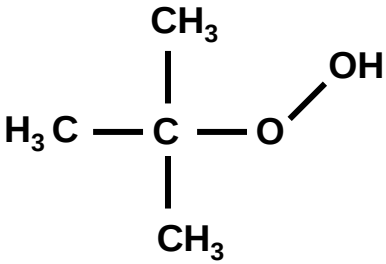


Thiophene

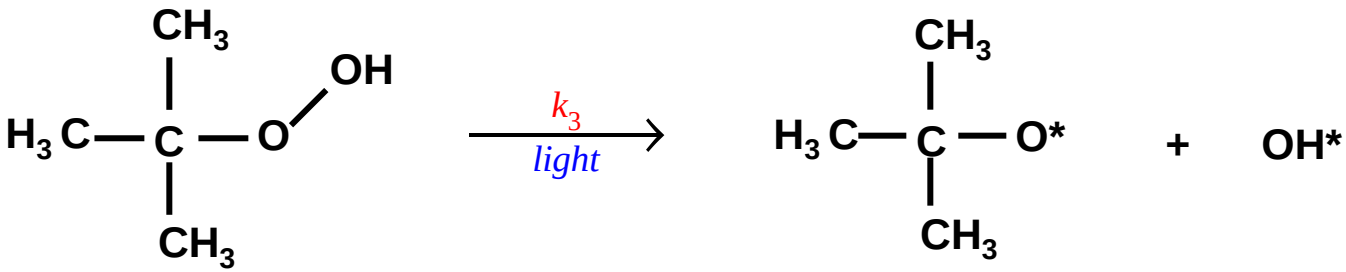


Dibenzothiophene

As a model organic peroxide we will use *Tert-Butyl Hydro Peroxide* (TBHP)



Peroxide (TBHP) reactions



Tert-Butyl Hydro Peroxide Tert-Butoxyl Radical Hydroxyl Radical

$$\left(CH_3\right)_3 COOH + Light \xrightarrow{k_3} \left(CH_3\right)_3 CO^* + OH^*$$

$$OH^* \xrightarrow{k_4} products$$

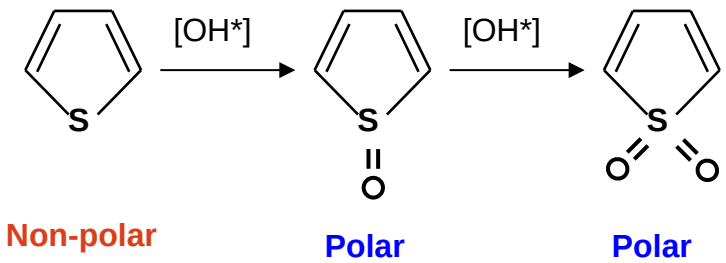
Kinetic expressions:

$$r_{TBHP} = -k_3\, C_{TBHP} \left[I \right] \qquad r_{TBR} = k_3\, C_{TBHP} \left[I \right]$$

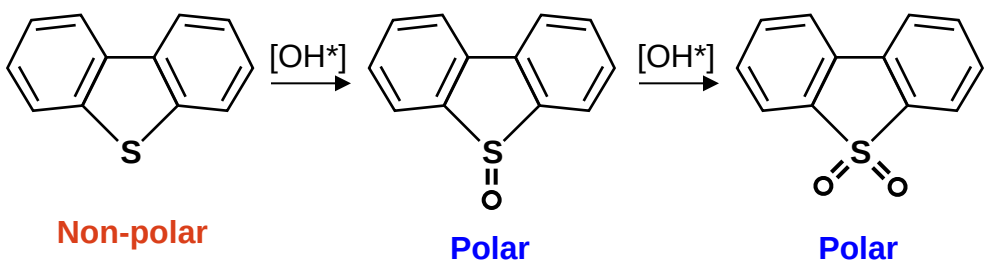
$$r_{OH^*} = k_3\, C_{TBHP} \left[I \right] - k_4\, C_{OH^*}$$

Oxidative desulfurization reactions

Thiophene



Dibenzothiophene



Dibenzothiophene Oxidation reactions

$$C_{12}H_8S + OH^* \xrightarrow[k_1]{\textit{slow}} C_{12}H_8SO + OH^* \xrightarrow[k_2]{\textit{fast}} C_{12}H_8SO_2$$

Dibenzothiophene	Dibenzosulfoxide	Dibenzosulfone
DBT	DBSO	DBSF

Kinetic expressions:

$$r_{DBT} = -k_1\, C_{DBT}\, C_{OH^*} \quad \Leftarrow \quad \textit{Slow reaction}$$

$$r_{DBSO} = k_1\, C_{DBT}\, C_{OH^*} - k_2\, C_{DBSO}\, C_{OH^*}$$

$$\frac{k_2}{k_1} >>> 1$$

$$r_{DBSF} = k_2\, C_{DBSO}\, C_{OH^*} \quad \Leftarrow \quad \textit{Fast reaction}$$

Reaction in series - sum of resistances (1/*k*)

The previous set of kinetic expressions can be simplified since first reaction is much faster than second reaction;

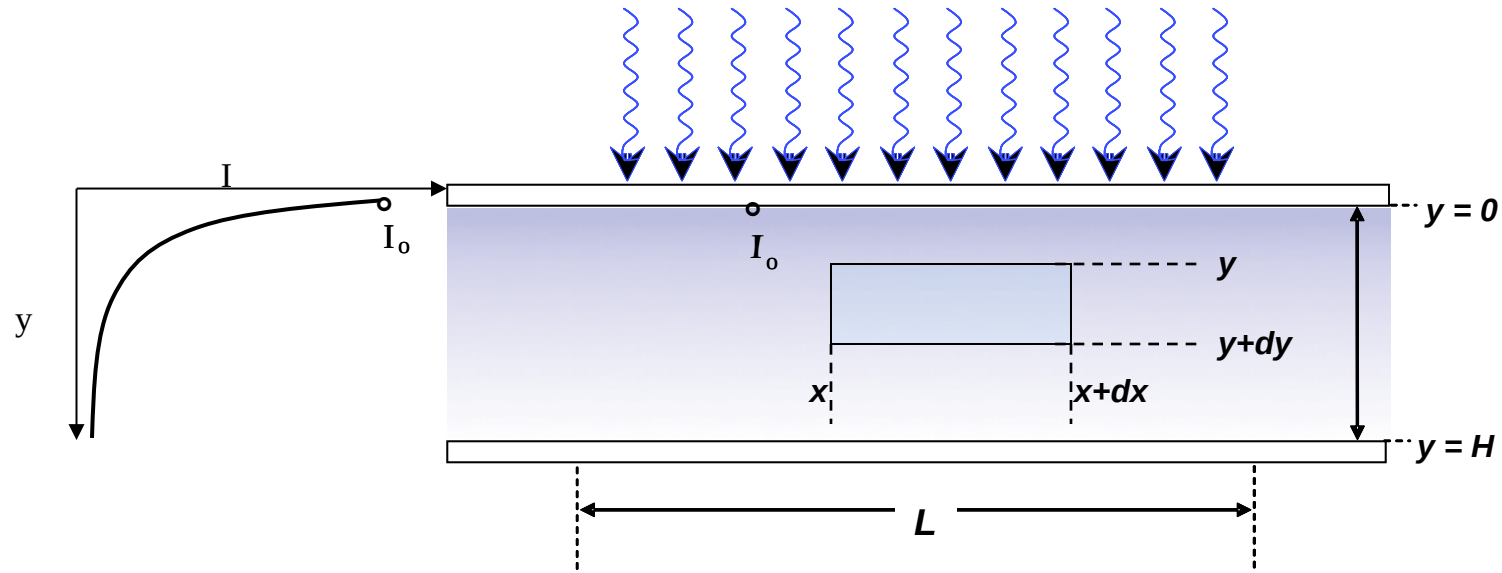
$$\frac{1}{K} = \frac{1}{k_1} + \frac{1}{k_2} \quad \Rightarrow \quad \frac{1}{K} = \frac{k_2}{k_1 k_2} + \frac{k_1}{k_1 k_2} \quad \Rightarrow \quad \frac{1}{K} = \frac{k_2}{k_1 k_2} + 0$$

$$\Rightarrow \quad \frac{1}{K} = \frac{\cancel{k_2}}{k_1 \cancel{k_2}} = \frac{1}{k_1}$$

Therefore slow step governs kinetics:

$$r_{DBT} = -k_1 \, C_{DBT} \, C_{OH^*} \qquad\qquad r_{DBSF} = k_1 \, C_{DBT} \, C_{OH^*}$$

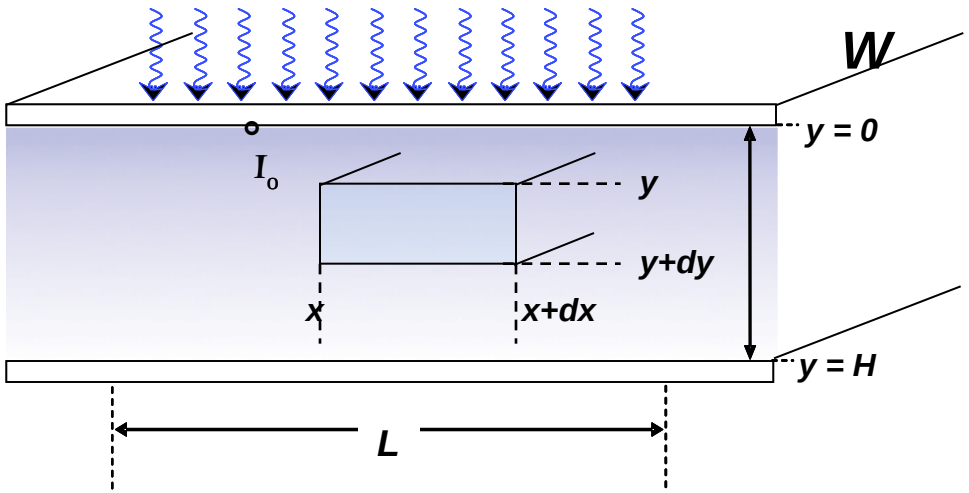
Light Intensity



$$I \;-\; irradiation \left[\frac{J}{m^2 s}\right] \; or \; light \;\; Intensity$$

$$\varepsilon \;-\; molar \;\; absoptivity \left[\frac{m^3}{mol \cdot m}\right] or \left[\frac{L}{mol \cdot cm}\right] \; or \;\; extinction \;\; coefficient$$

Light Intensity



$$I = I_o \cdot 10^{\left(-\bar{\varepsilon}\, C\, y\right)}$$

Beer-Lambert Law

After Integration

$$I\big|_y \left(Wdx\right)\Delta t - I\big|_{y+dy}\left(Wdx\right)\Delta t - I\varepsilon_i\left(Wdxdy\right)C_i\Delta t = 0$$

$$\frac{I\big|_y - I\big|_{y+dy}}{dy} - I\varepsilon_i C_i = 0 \quad \Rightarrow \quad \boxed{\frac{dI}{I} = -\varepsilon_i C_i dy} \quad \Rightarrow \quad \boxed{\frac{dI}{dy} + I\varepsilon_i C_i = 0}$$

Extinction Coefficient

The molar extinction coefficient, also known as molar absorptivity, is a measure of how strongly a chemical specy absorbs light at a given wavelength. It is an intrinsic property of chemical species; the actual absorbance, *A*, of a sample is dependent on the pathlength *l* and the concentration *C* of the species via the Beer-Lambert law, $A = \varepsilon C l$. The units of ε are usually in [L /(mol cm)].

$$\bar{\varepsilon} C_{total} = \left[\varepsilon_{TBHP} C_{TBHP} + \varepsilon_{DBT} C_{DBT} + \varepsilon_{DBSO} C_{DBSO} + \ldots \right] = \sum_{i=1}^{N} \varepsilon_i C_i$$

Therefore:

$$\frac{dI}{dy} + I \bar{\varepsilon} C_{total} = \frac{dI}{dy} + I \sum_{i=1}^{N} \varepsilon_i C_i$$

Final reaction model equations

$$r_{TBHP} = -k_3\, C_{TBHP}\, [I]$$

$$r_{DBT} = -k_1\, C_{DBT}\, C_{OH^*}$$

$$r_{DBSF} = k_1\, C_{DBT}\, C_{OH^*}$$

$$r_{OH^*} = k_3\, C_{TBHP}\, [I] - k_4\, C_{OH^*} - 2k_1\, C_{DBT}\, C_{OH*}$$

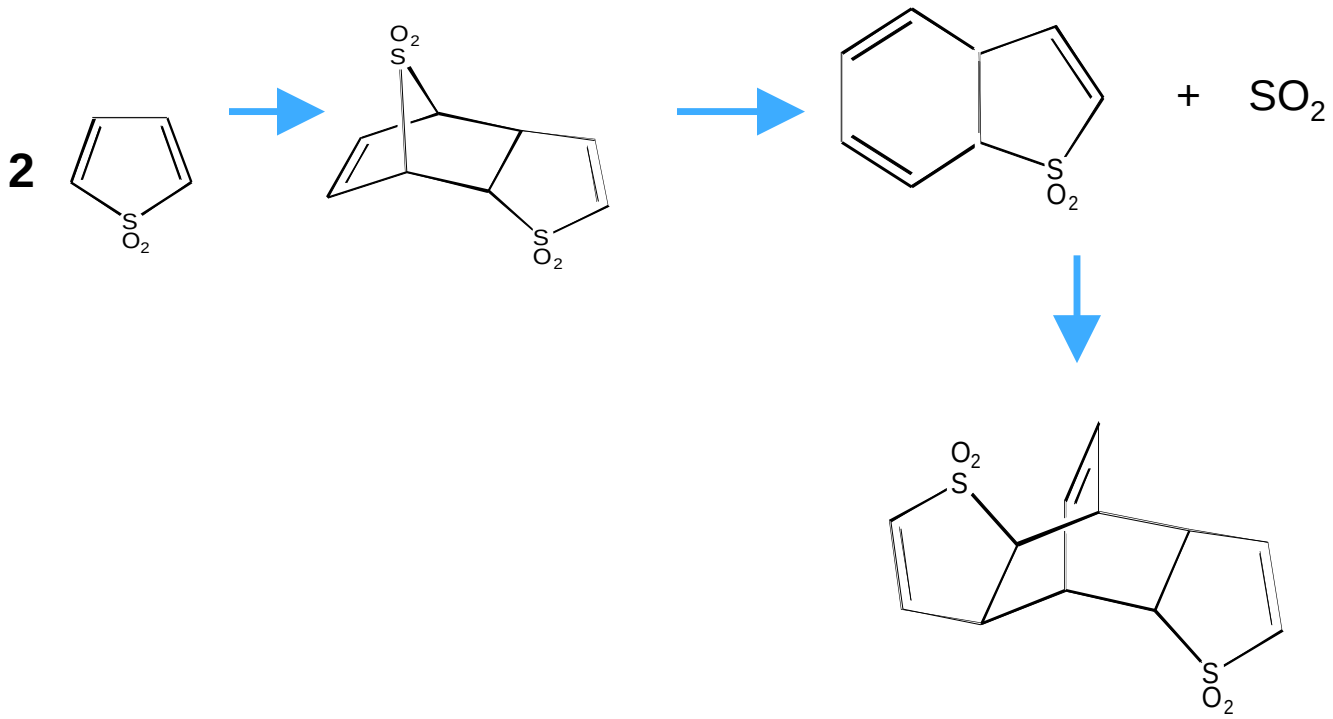
$$0 = \frac{dI}{dy} + I \sum_{i=1}^{N} \varepsilon_i C_i$$

$$where \quad C_i \Rightarrow C_{DBT}; C_{DBSF}; C_{OH^*}; C_{TBHP}; C_{TBR}$$

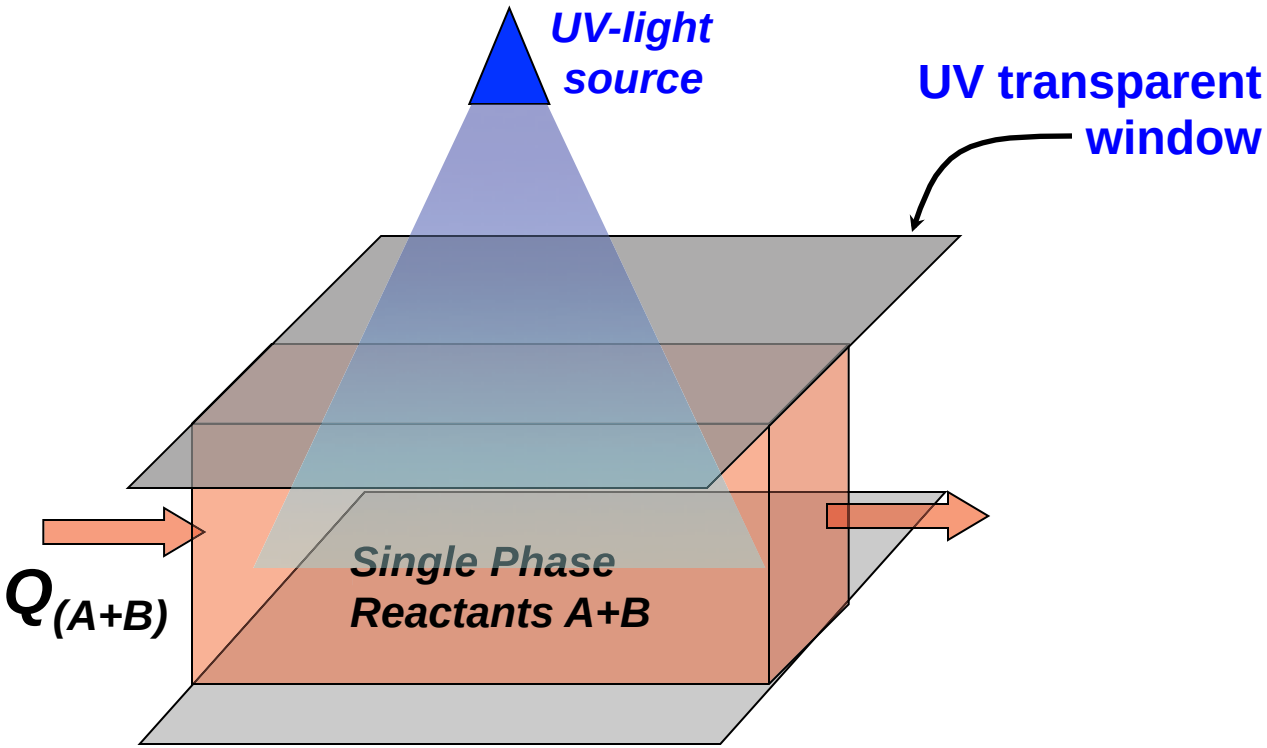
$$and \quad C_{total} = C_{DBT} + C_{DBSF} + C_{OH^*} + C_{TBHP} + C_{TBR}$$

Oxidative desulfurization - Reaction kinetics

Diels-Alder Reactions

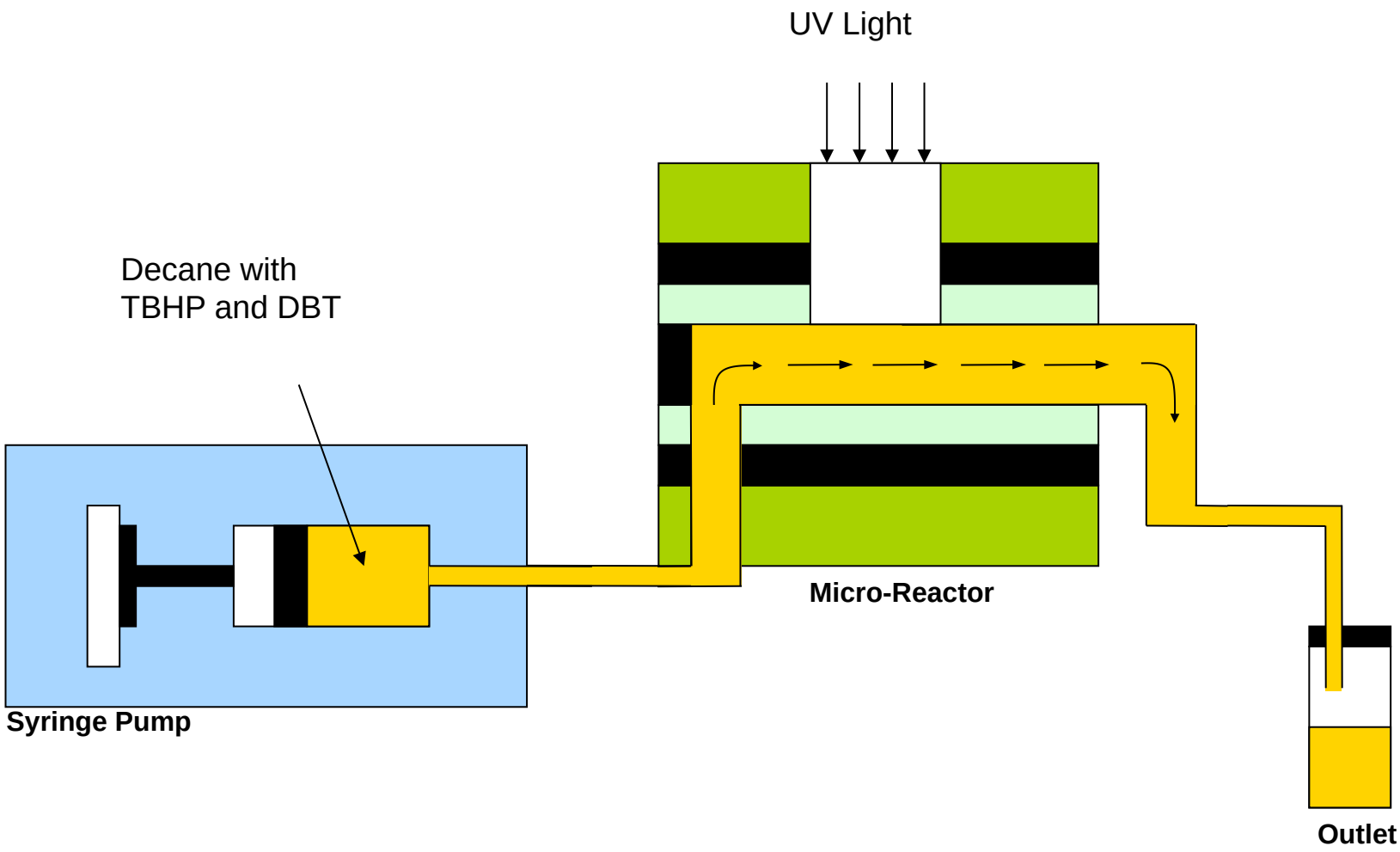


Problem Statement - single-phase case

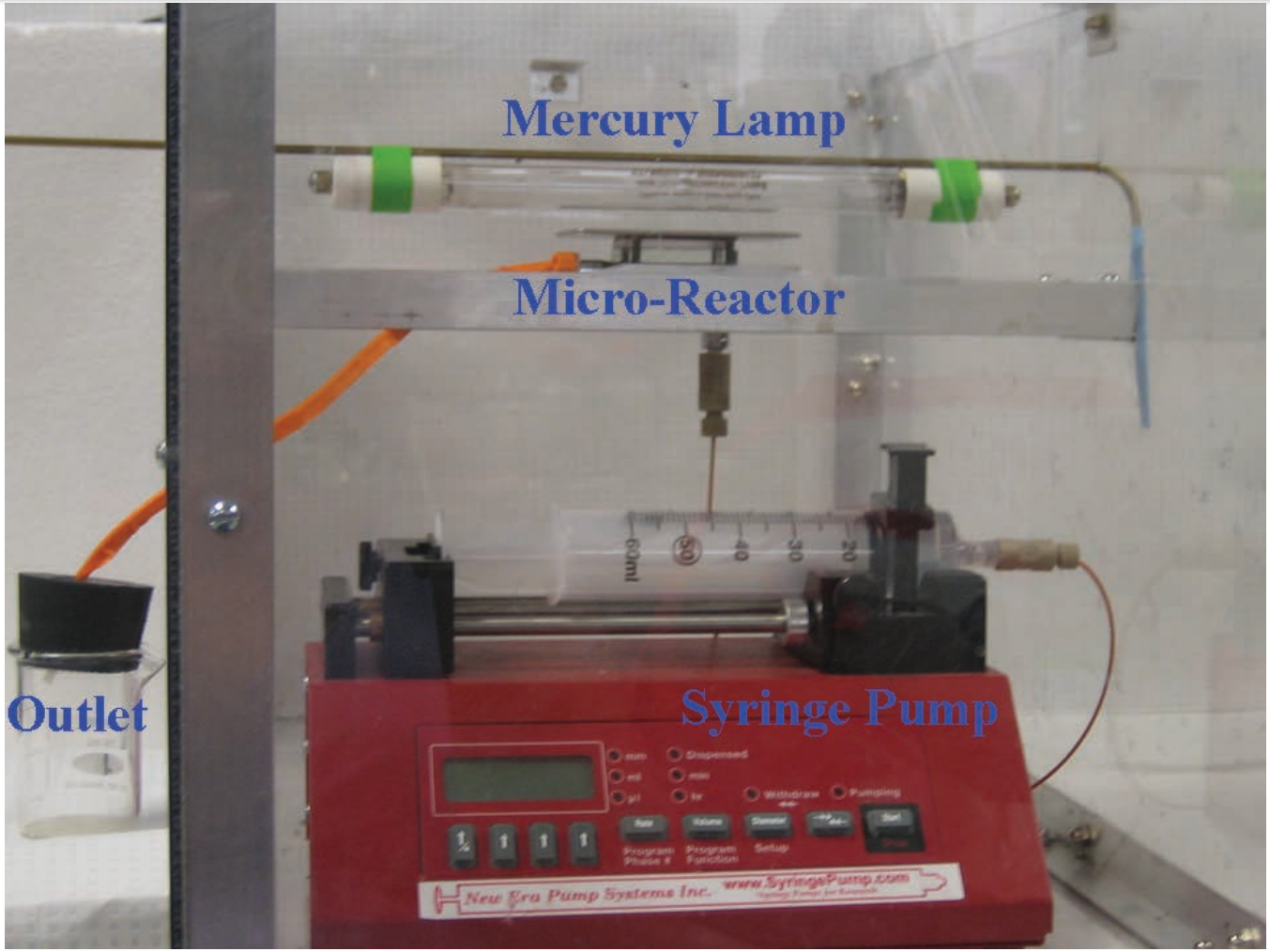


- **Two reactants enter micro-channel together in a single phase.**

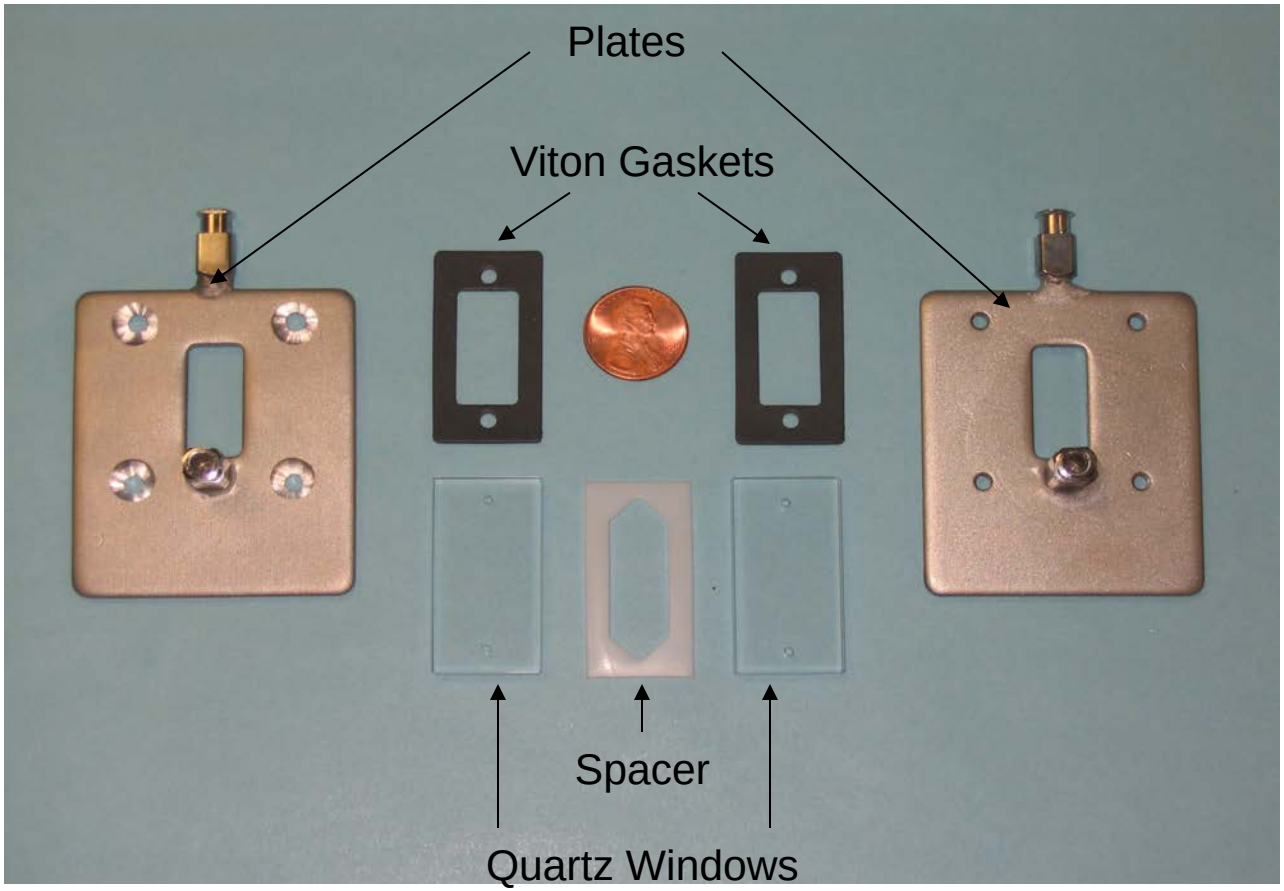
Experimental Set-up



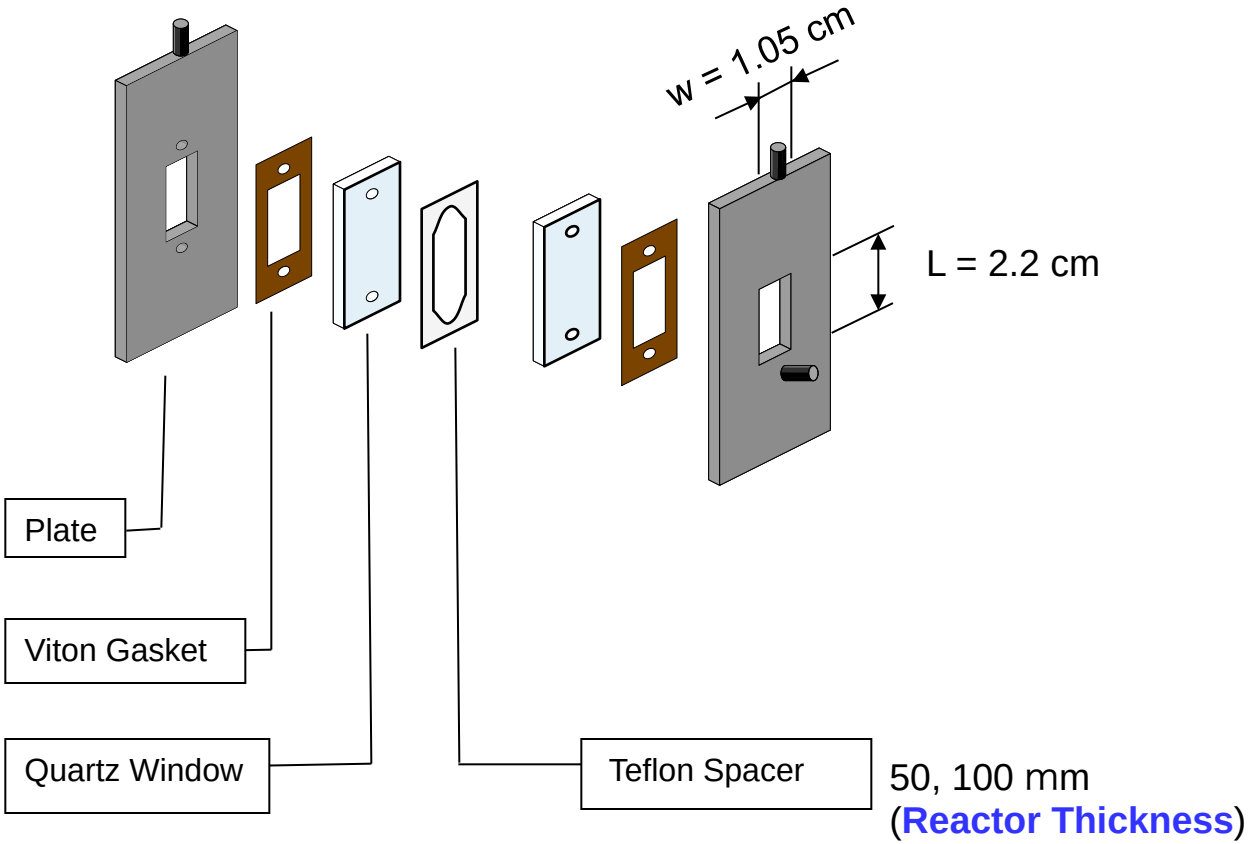
Experimental Set-up



Experimental Set-up



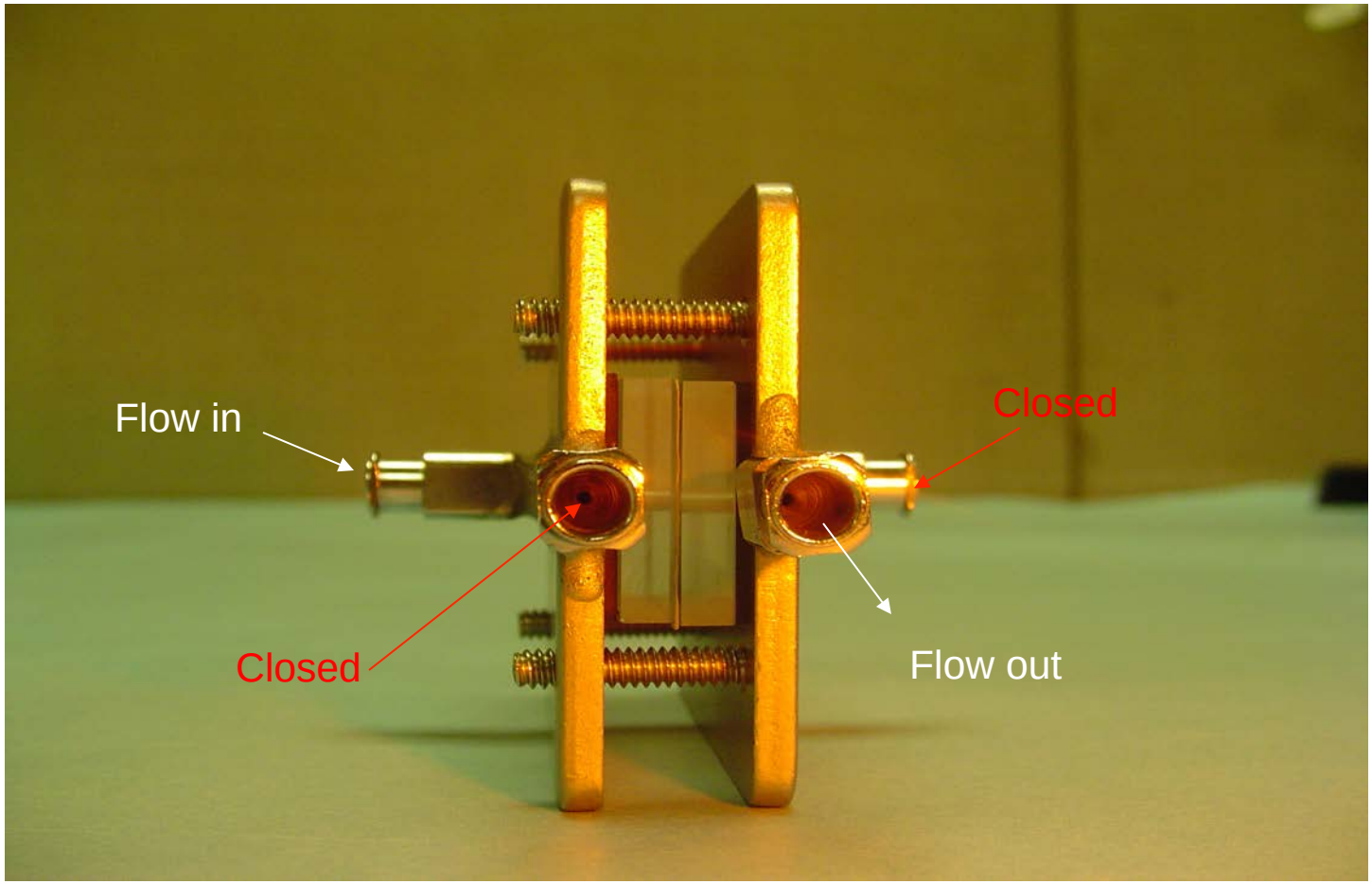
Experimental Set-up



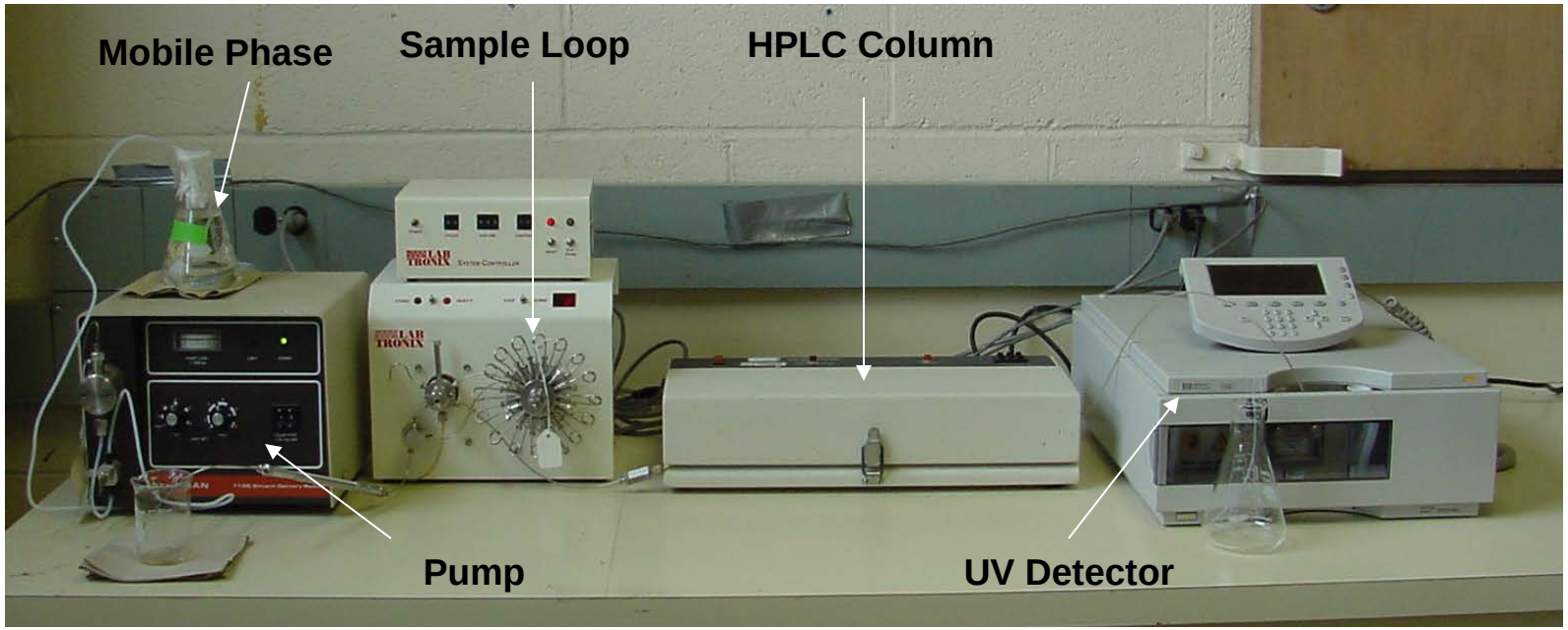
Experimental Set-up

Experimental Set-up

μ-reactor



Analytical-HPLC Set-up

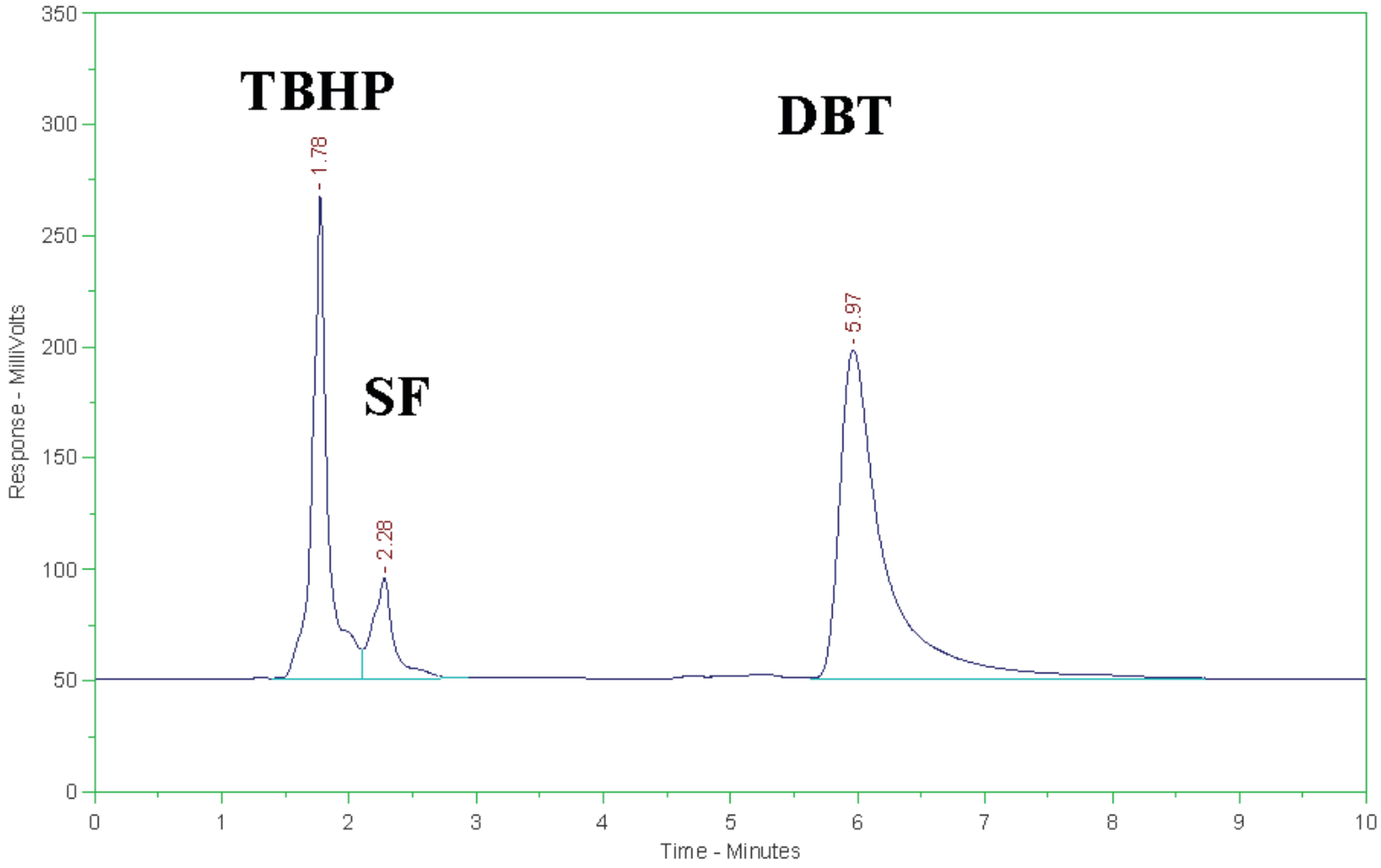


Experimental Parameters

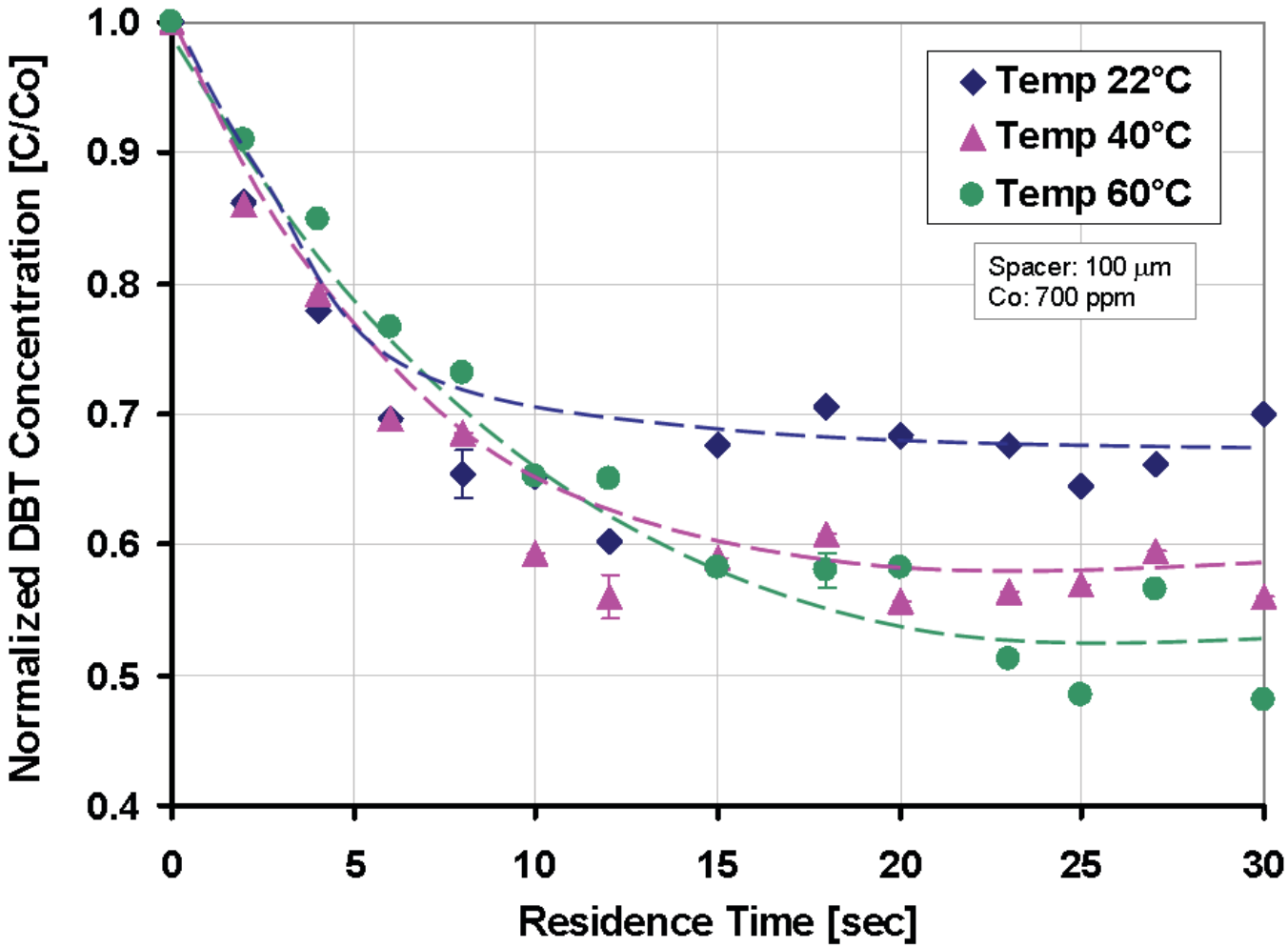
- **Micro-Reactor Thickness**
  - **100 μm and 50 μm**

- **System Temperature**
  - **22 ^{o}C, 40 ^{o}C, and 60 ^{o}C**

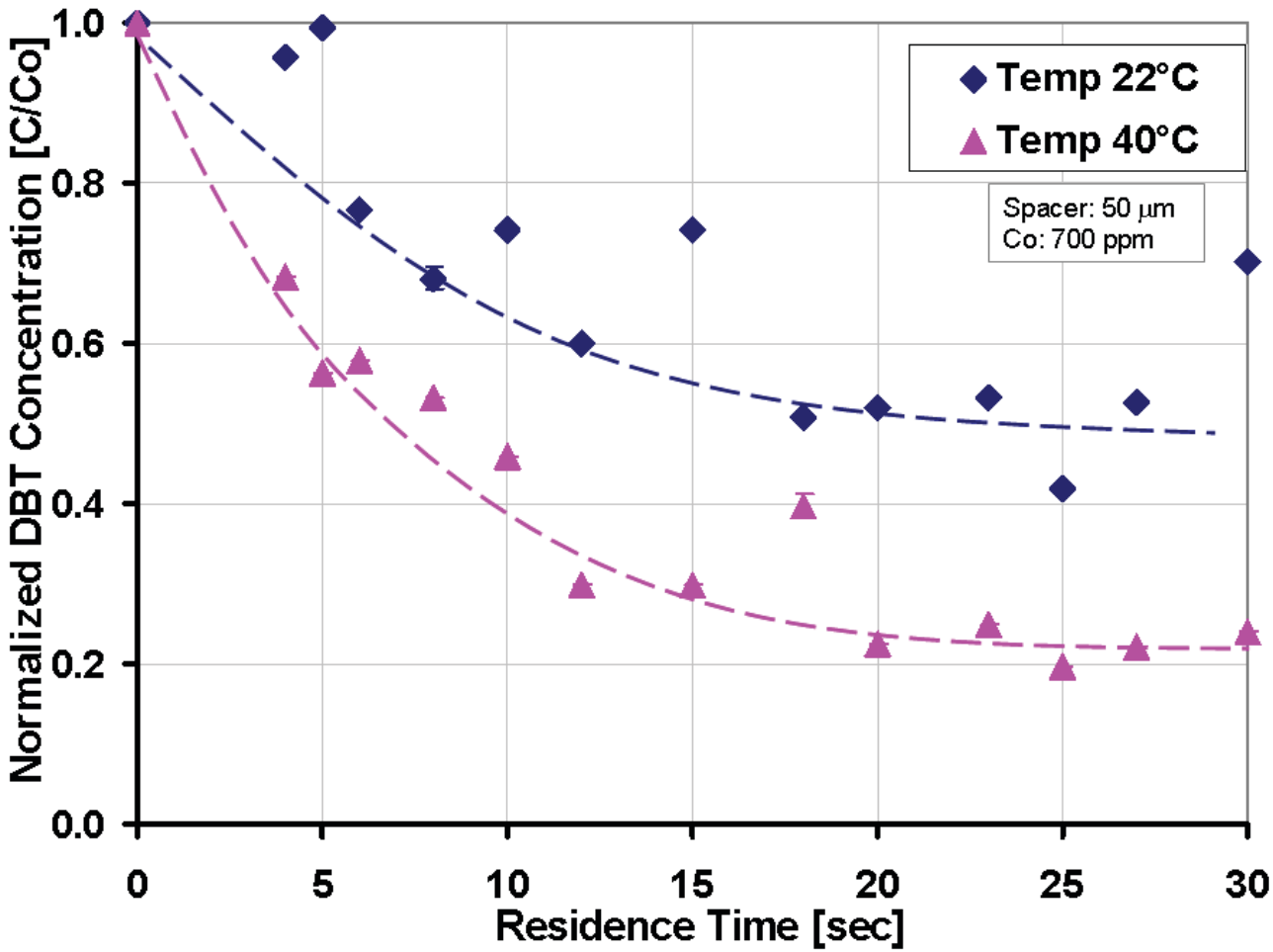
HPLC output


TBHP
SF
DBT
1.78
2.28
5.97
Response - MilliVolts
Time - Minutes
350
300
250
200
150
100
50
0
0
1
2
3
4
5
6
7
8
9
10

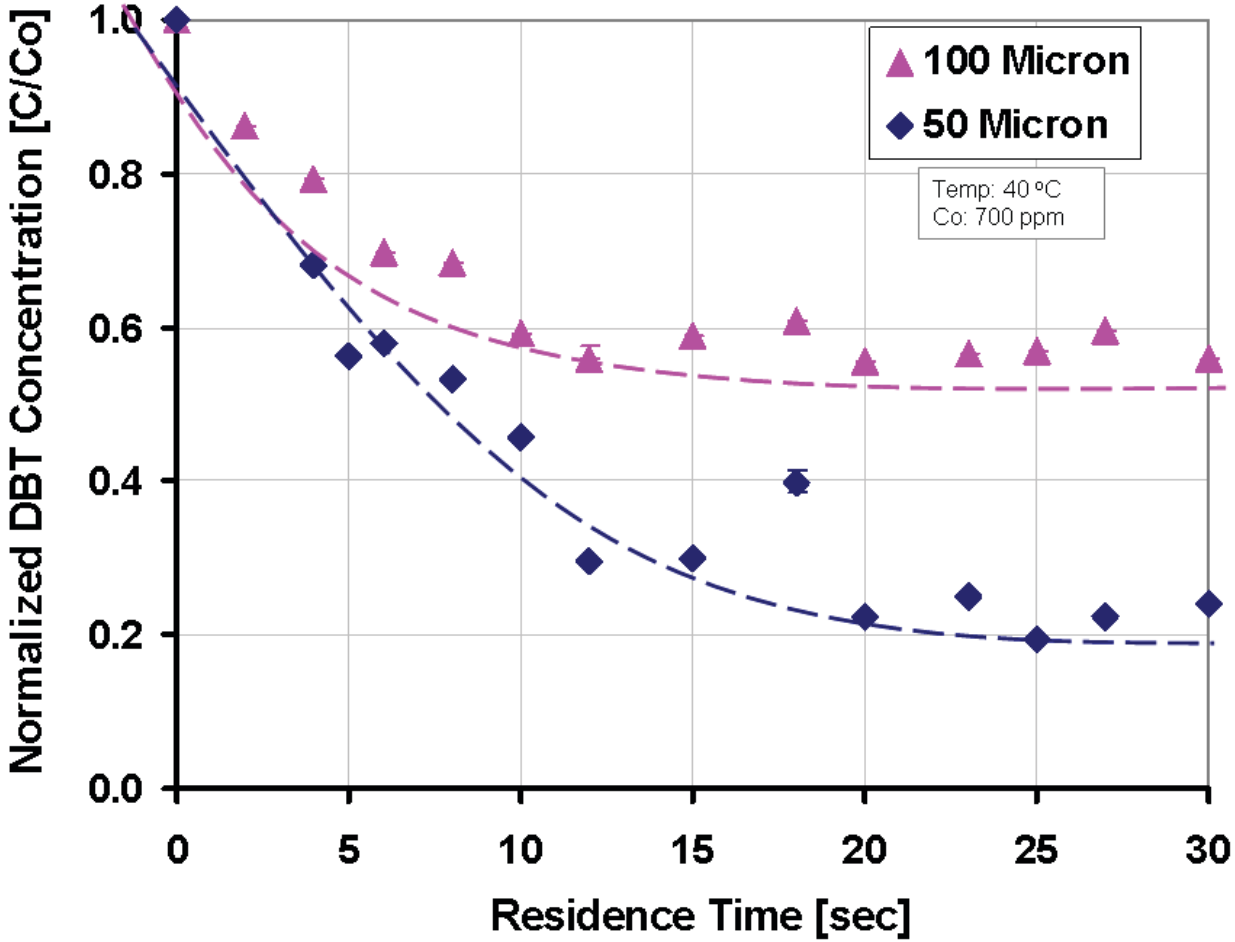
Dibenzothiophene conversion at 100µm



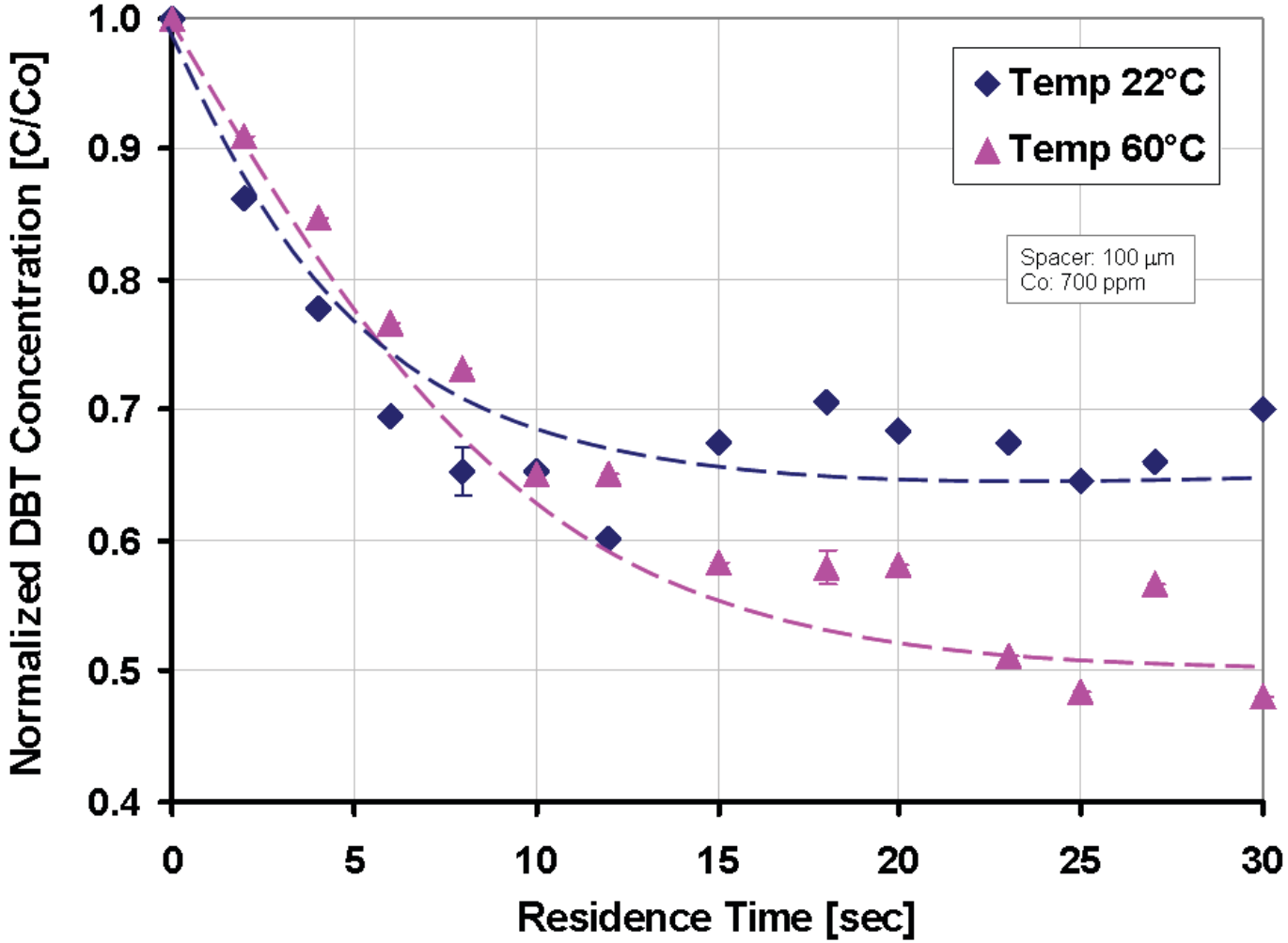
Dibenzothiophene conversion at 50µm



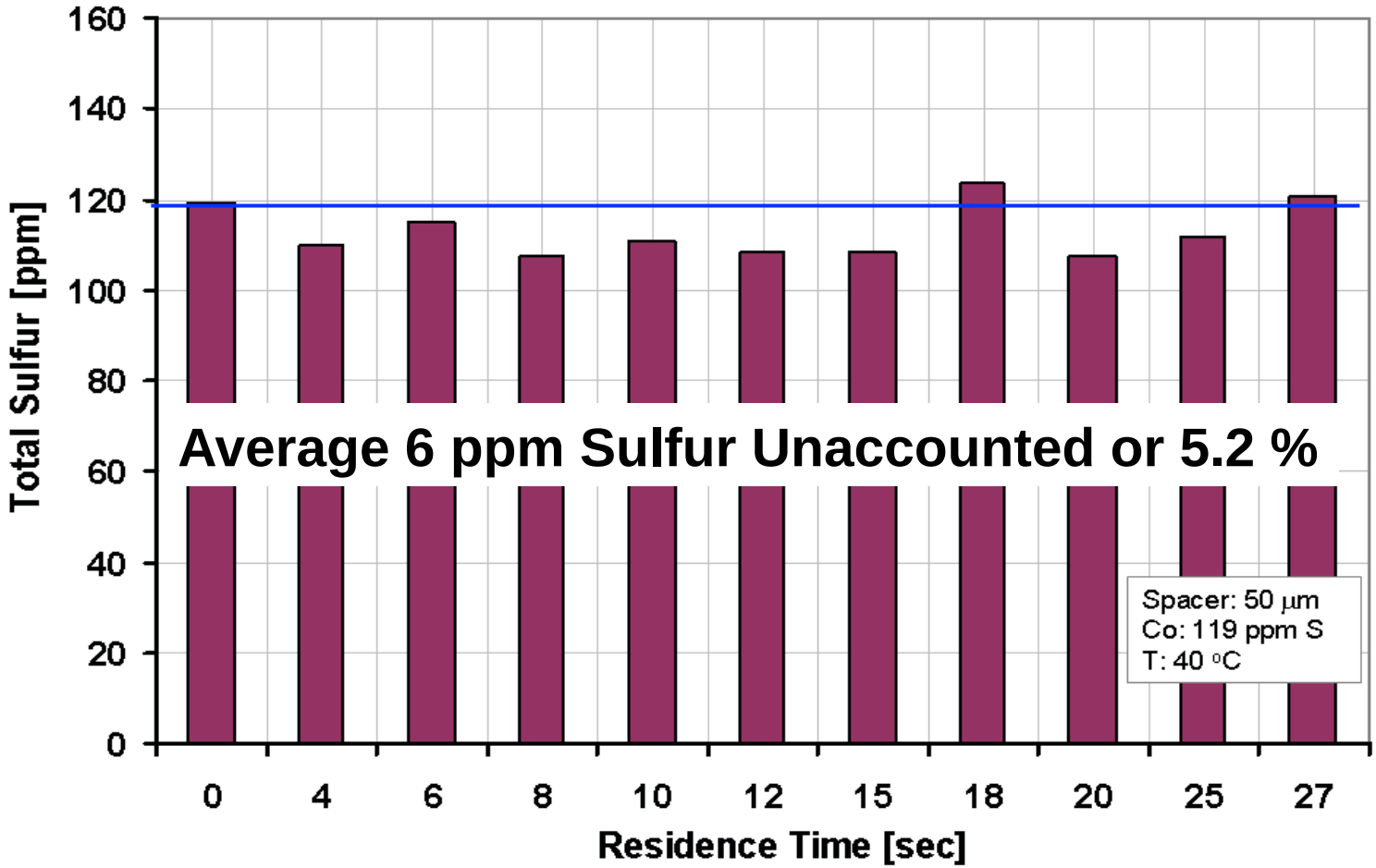
Exp-results effect of spacer thickness



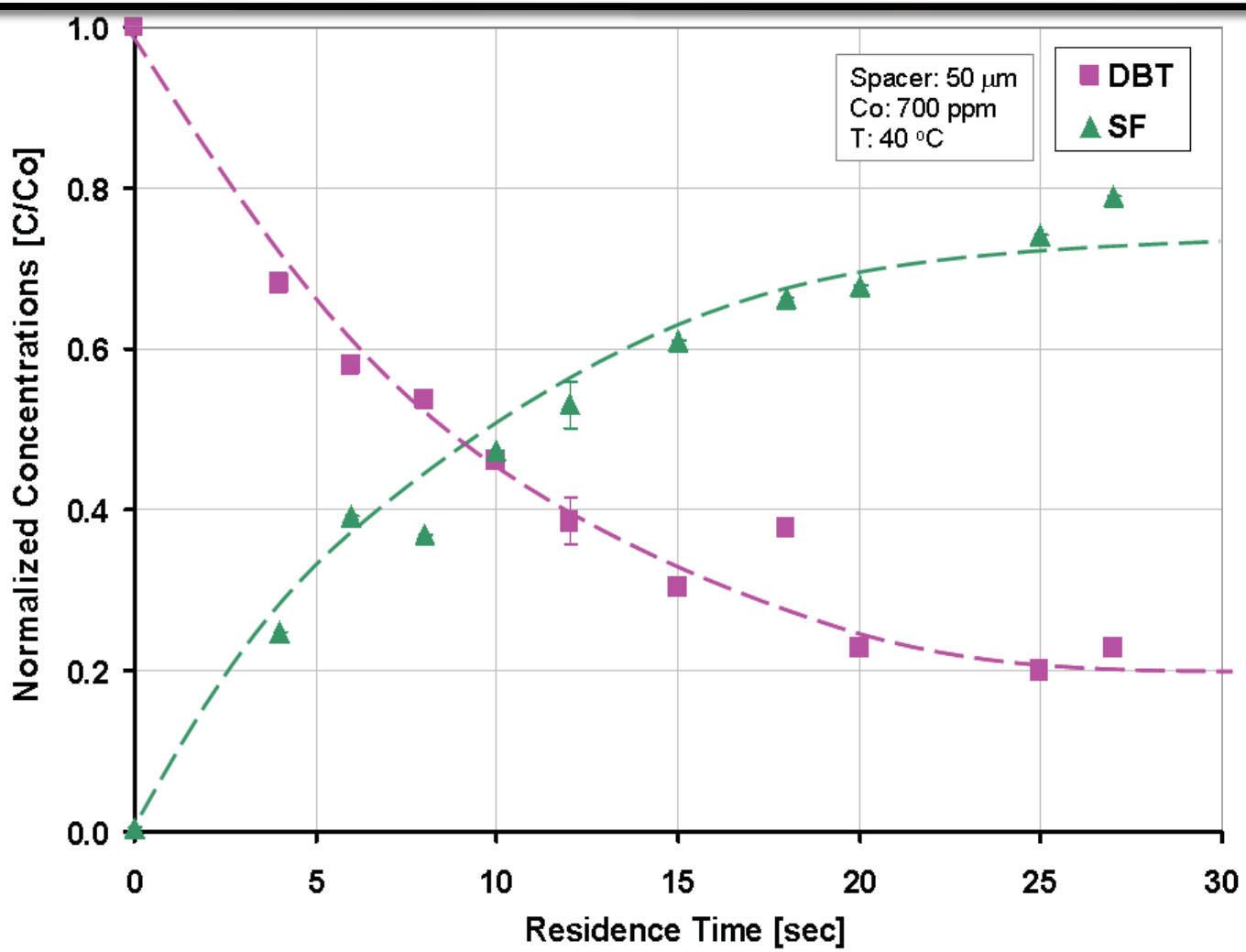
Experimental results effect of temperature



Material Balance at 50 [μm] and 40 [°C]



Material Balance at 50 [μm] and 40 [°C]



Model and velocity profile

Assumptions:

1. The system is at steady state condition;
2. The system is at uniform and constant room temperature;
3. Constant physical properties such as D, ρ, and μ;
4. Laminar flow profile inside the reactor;
5. Ignore gravity effects, $g_x = g_y = g_z = 0$.
6. No velocities in y and z directions $U_y = U_z = 0$.
7. Velocity U_x is only function of y, $U_x = U(y)$;
8. Newtonian fluid;
9. Consider rectangular coordinate system.

Velocity profile

Continuity Equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}\left(\rho U_x\right) + \frac{\partial}{\partial y}\left(\rho U_y\right) + \frac{\partial}{\partial z}\left(\rho U_z\right) = 0$$

$$\frac{\partial U_x}{\partial x} = 0 \quad \Rightarrow \quad U_x = f\left(y\right) \neq f\left(x\right)$$

Velocity profile

Momentum Equations:

$$\rho\left(\frac{\partial U_x}{\partial t}+U_x\frac{\partial U_x}{\partial x}+U_y\frac{\partial U_x}{\partial y}+U_z\frac{\partial U_x}{\partial z}\right)=-\frac{\partial P}{\partial x}+\rho g_x+\mu\left(\frac{\partial^2 U_x}{\partial x^2}+\frac{\partial^2 U_x}{\partial y^2}+\frac{\partial^2 U_x}{\partial z^2}\right)$$

$$0=-\frac{\partial P}{\partial x}+\mu\frac{\partial^2 U}{\partial y^2}$$

$$\rho\left(\frac{\partial U_y}{\partial t}+U_x\frac{\partial U_y}{\partial x}+U_y\frac{\partial U_y}{\partial y}+U_z\frac{\partial U_y}{\partial z}\right)=-\frac{\partial P}{\partial y}+\rho g_y+\mu\left(\frac{\partial^2 U_y}{\partial x^2}+\frac{\partial^2 U_y}{\partial y^2}+\frac{\partial^2 U_y}{\partial z^2}\right)$$

$$0=-\frac{\partial P}{\partial y}$$

$$\rho\left(\frac{\partial U_z}{\partial t}+U_x\frac{\partial U_z}{\partial x}+U_y\frac{\partial U_z}{\partial y}+U_z\frac{\partial U_z}{\partial z}\right)=-\frac{\partial P}{\partial z}+\rho g_z+\mu\left(\frac{\partial^2 U_z}{\partial x^2}+\frac{\partial^2 U_z}{\partial y^2}+\frac{\partial^2 U_z}{\partial z^2}\right)$$

$$0=-\frac{\partial P}{\partial z}$$

Velocity profile

Integrate momentum equation to obtain:

$$U_x = -\frac{\Delta P}{2\mu L} y^2 + C_1 y + C_2$$

With BCs:

$$U_x = 0 \quad @ \quad y = 0$$

$$U_x = 0 \quad @ \quad y = H$$

$$\frac{\partial U_x}{\partial y} = 0 \quad @ \quad y = \frac{H}{2}$$

Then:

$$\mathrm{U_x} = \frac{\Delta \mathrm{P}}{2\mu \mathrm{L}} y\left(H - y\right)$$

Mass Transfer Equations

$$D_{DBT/DEC}\frac{\partial^2 C_{DBT}}{\partial y^2} + D_{DBT/DEC}\frac{\partial^2 C_{DBT}}{\partial x^2} - U_x\frac{\partial C_{DBT}}{\partial x} - \left[k_1\, C_{DBT}\, C_{OH*}\right] = 0$$

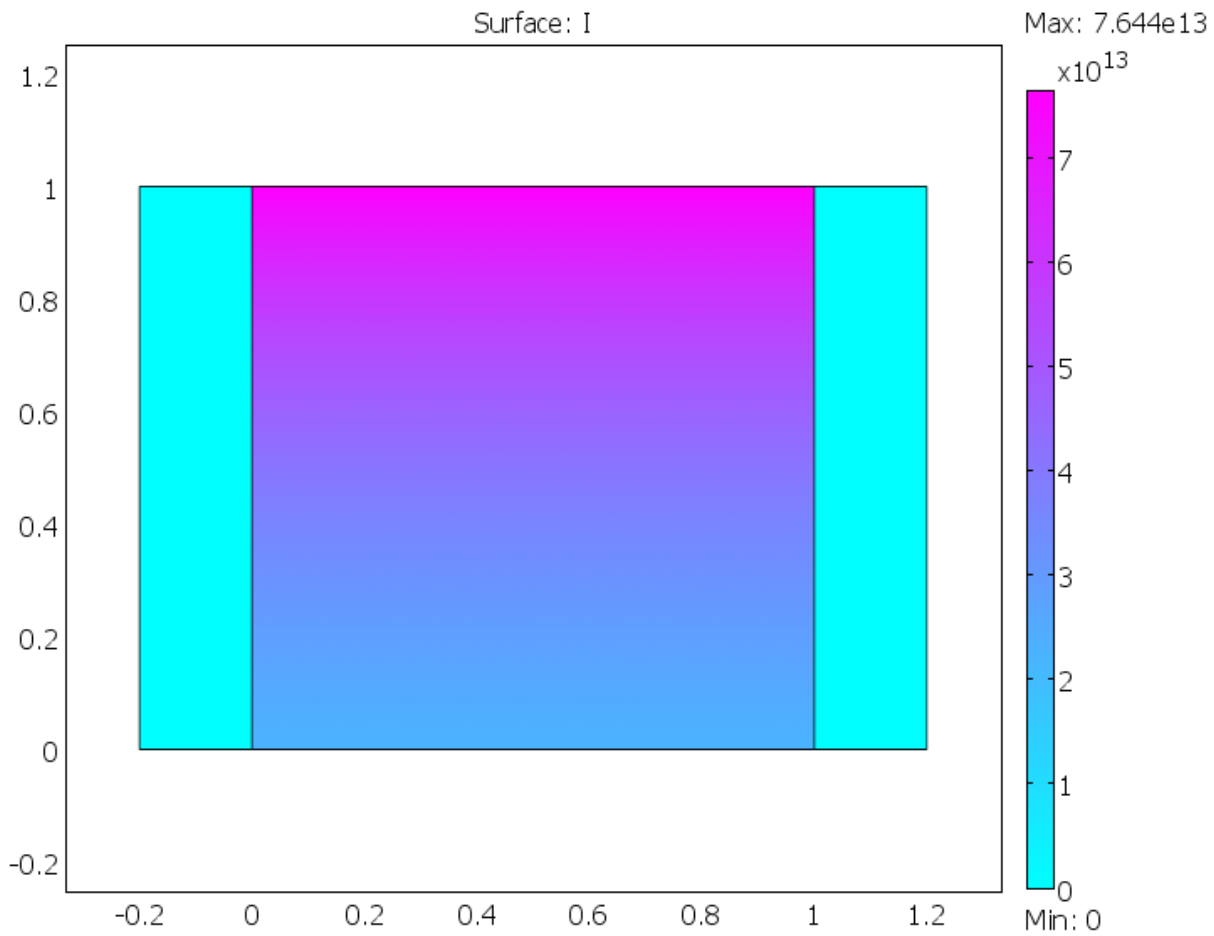
$$D_{TBHP/DEC}\frac{\partial^2 C_{TBHP}}{\partial y^2} + D_{TBHP/DEC}\frac{\partial^2 C_{TBHP}}{\partial x^2} - U_x\frac{\partial C_{TBHP}}{\partial x} - \left[k_3\, C_{TBHP}\,[I]\right] = 0$$

$$D_{OH^*/DEC}\frac{\partial^2 C_{OH^*}}{\partial y^2} + D_{OH^*/DEC}\frac{\partial^2 C_{OH^*}}{\partial x^2} - U_x\frac{\partial C_{OH^*}}{\partial x} - 2k_1\, C_{DBT} C_{OH^*}\,[I] +$$

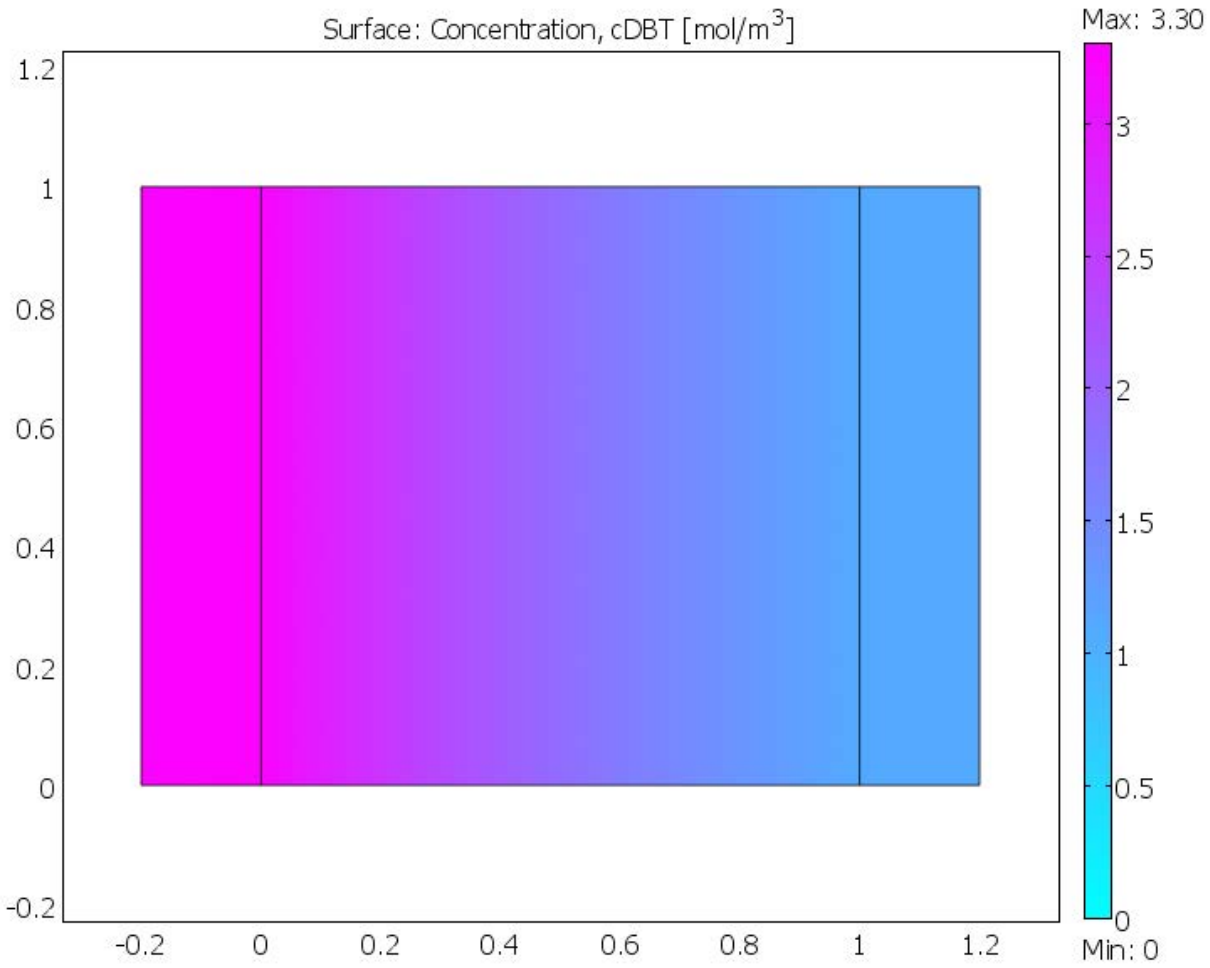
$$+k_3 C_{TBHP}\,[I] - k_4 C_{OH^*} = 0$$

$$D_{DBSF/DEC}\frac{\partial^2 C_{DBSF}}{\partial y^2} + D_{DBSF/DEC}\frac{\partial^2 C_{DBSF}}{\partial x^2} - U_x\frac{\partial C_{DBSF}}{\partial x} + \left[k_1\, C_{DBT}\, C_{OH*}\right] = 0$$

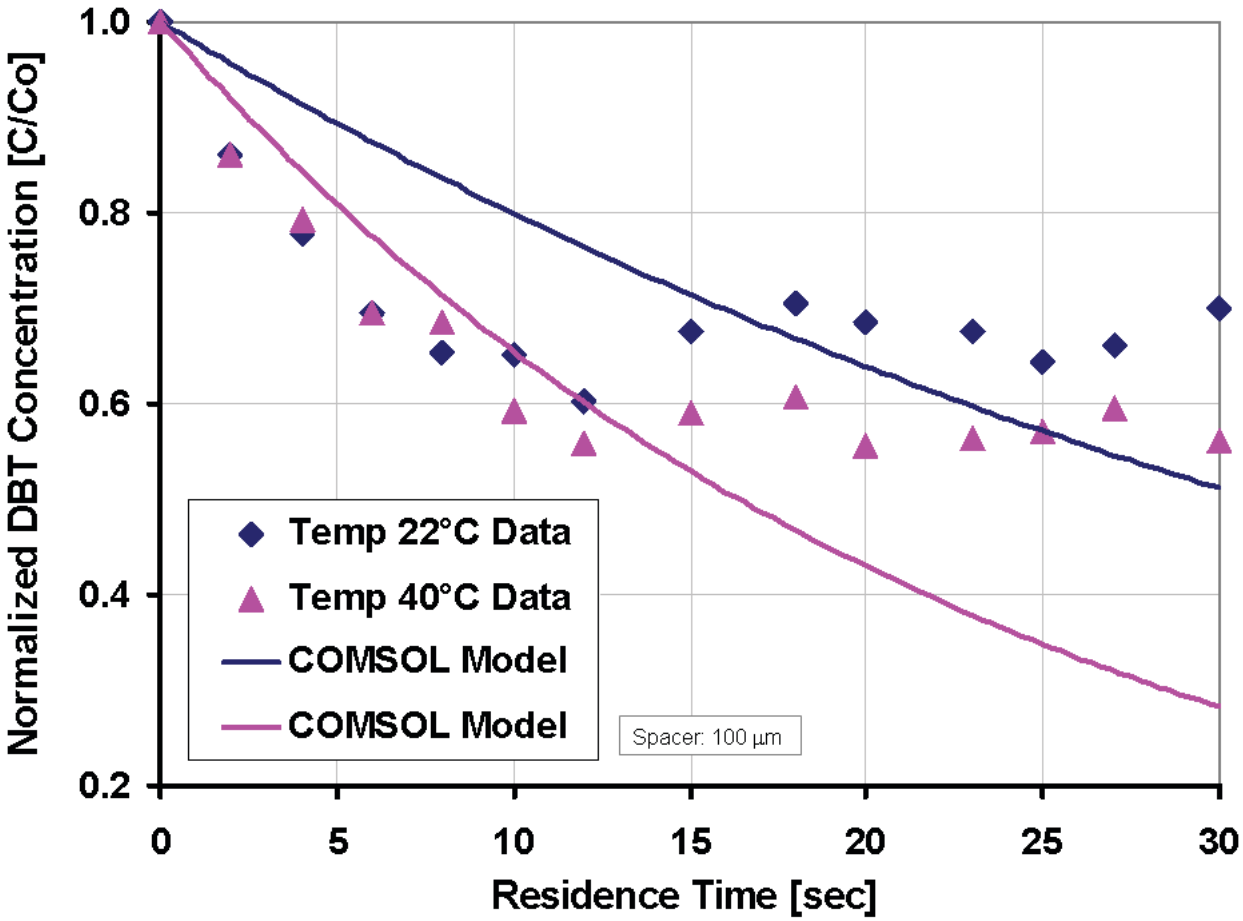
DBT Concentration - COMSOL Simulation



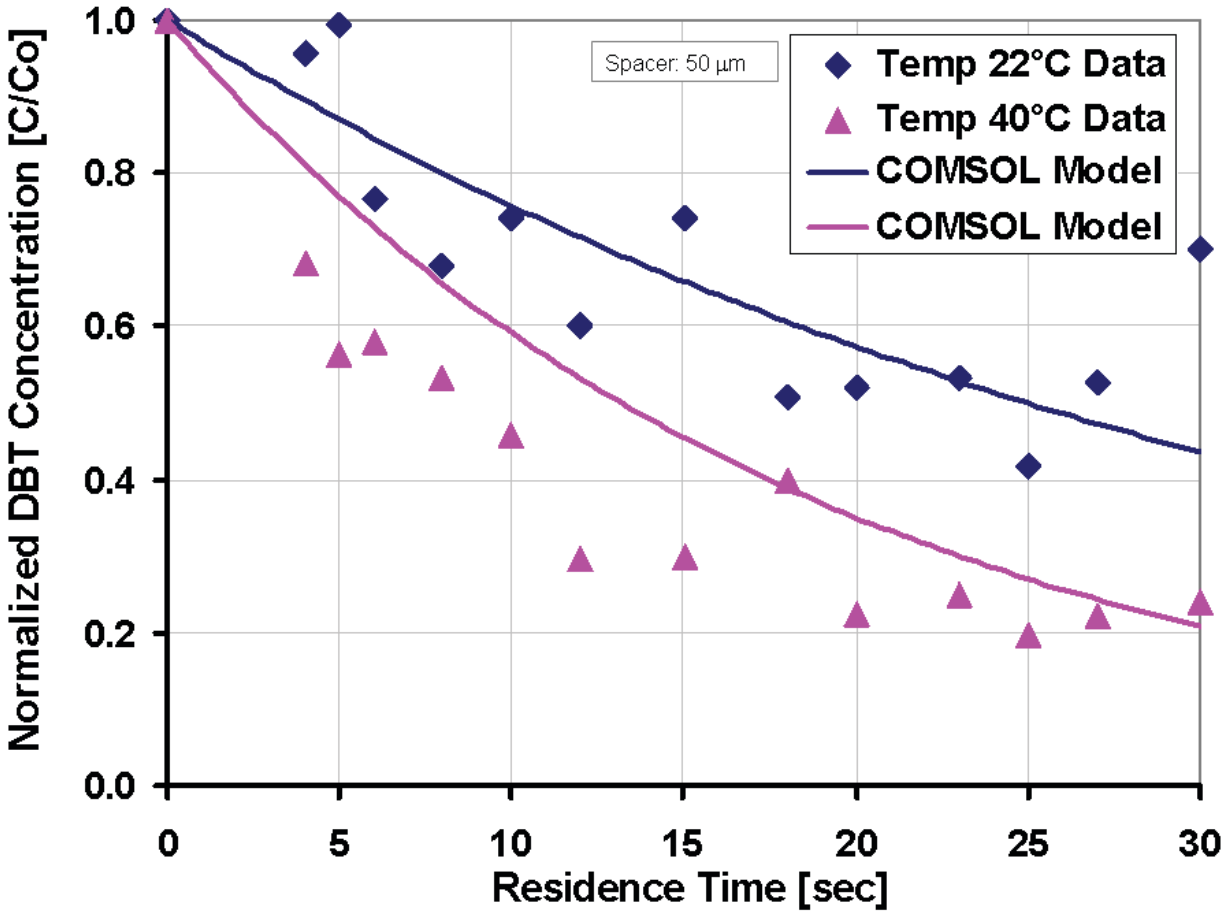
Light Intensity - COMSOL Simulation



COMSOL fit for 100 [µm]

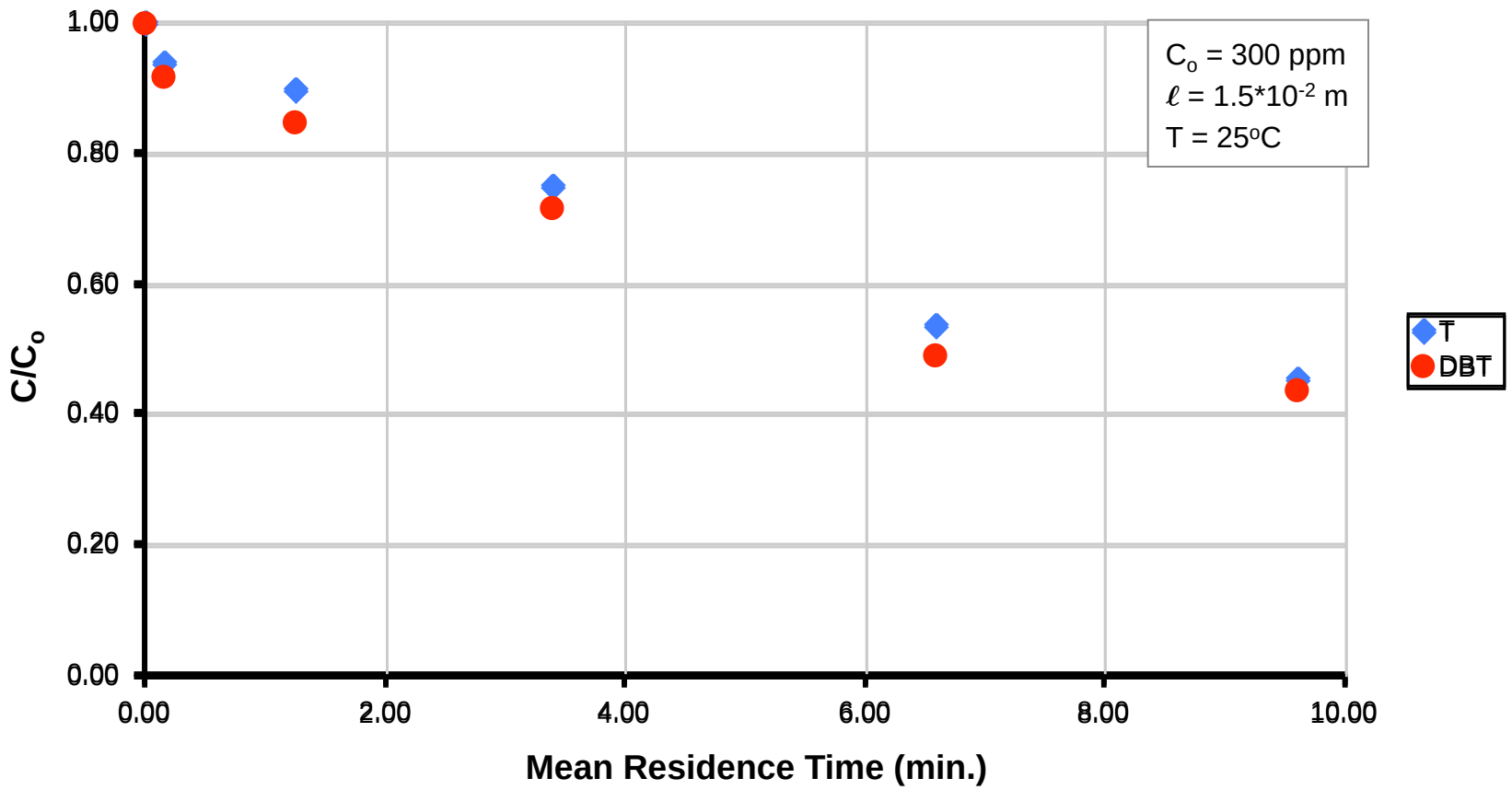


COMSOL fit for 50 [μm]

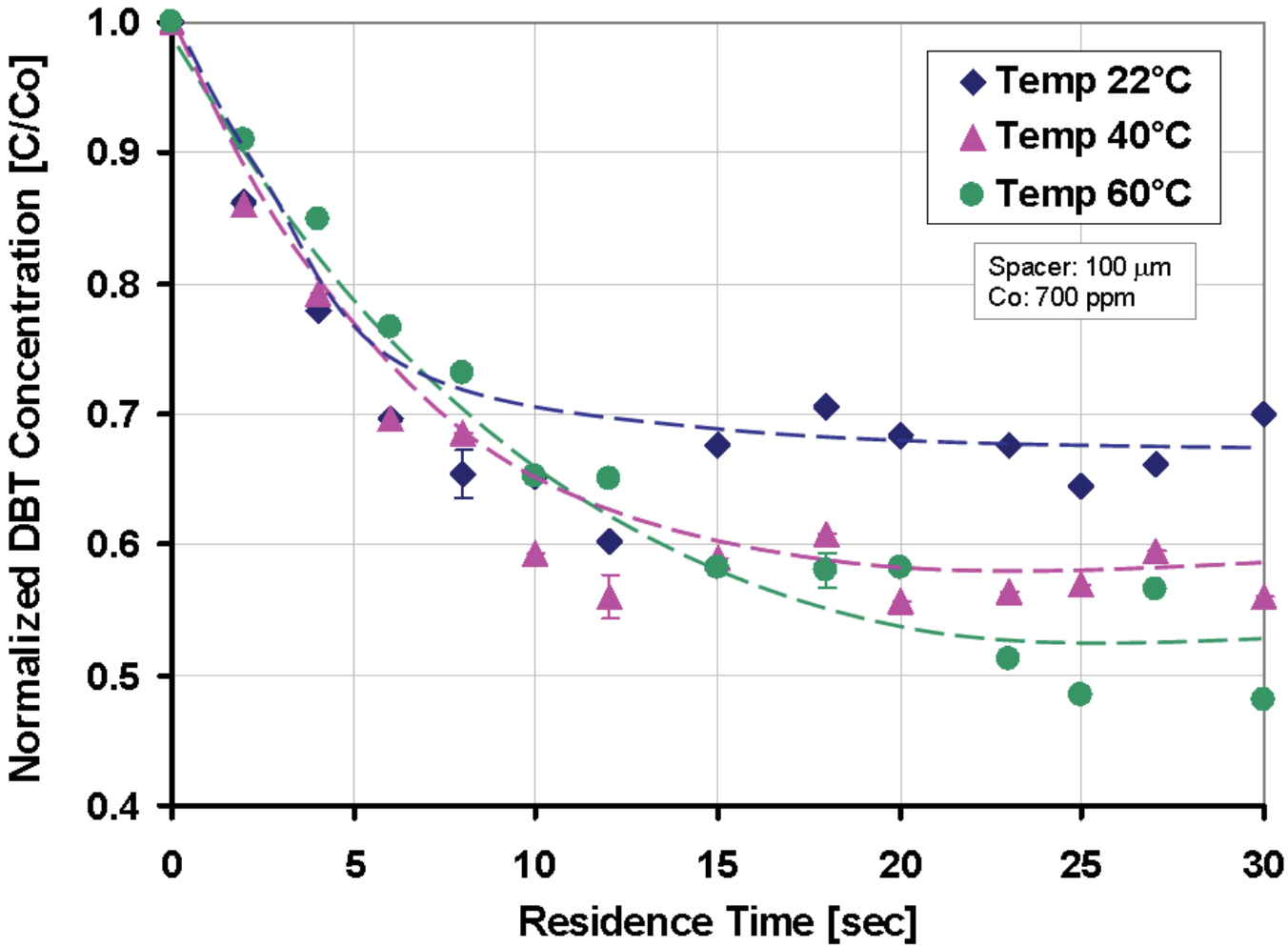


Experimental Results - Two Phase Model

Conversion of Thiophene and Dibenzothiophene at spacer thickness=100 μm



Experimental results - Single Phase Model



Summary

UV plays a major role in the desulfurization process of thiophene and dibenzothiophene; no reaction takes place in the absence of UV light.

Distance between the UV source and the microreactor substantially influences the conversion of thiophenes.

Conversion in microreactor increases as the residence time in the microreactor increases.

Developed mathematical model predicts fairly well conversion in the microreactor.

Summary

A decrease in the spacer thickness of the microreactor resultes in a higher conversion.

Microreactor is much more efficient in the desulfurization of thiophene and dibenzothiophene than all (batch) reactors reported in open literature.

Single-phase microreactor model is more efficient than two-phase microreactor model.

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Thank you for your attention!

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