Microreactor Engineering

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Photo-Catalyzed Reactions II

Photochemical Reaction Process

In Affiliation With:

MBI

Microproducts Breakthrough Institute

PTT - LOA

PTT - Laboratories Of America

Purpose of Study

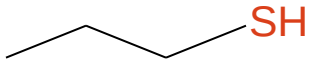
Investigate phenomena pertinent to oxidative desulfurization of fuels including convection, diffusion, and reaction kinetics in two-phase microreactor system.

Develop two-dimensional velocity, and diffusion-reaction model for the desulfurization reaction process in microreactors.

Consider two options when the reacting fluids are either completely miscible or immiscible.

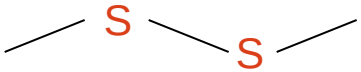
Origin of sulfur in fuels

Common sulfur compounds in crude oil:

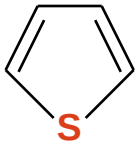


Thiols

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

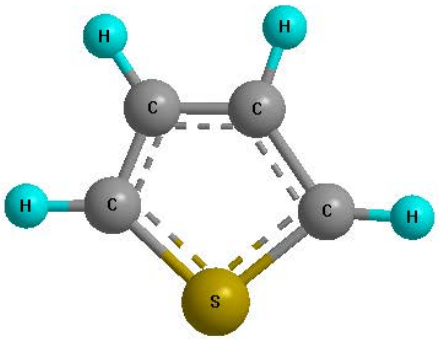
*** Control of Air Pollution from New Motor Vehicles: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements, EPA, January 18, 2001.**

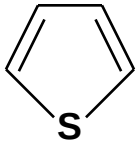
*** Final Report of the Government Working Group on Sulfur in Gasoline and Diesel Fuel, July, 1998.**

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

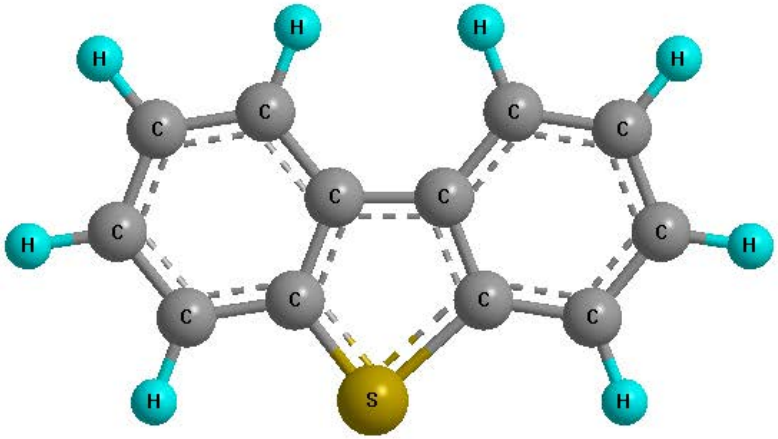
Problem Consideration - two-phase case

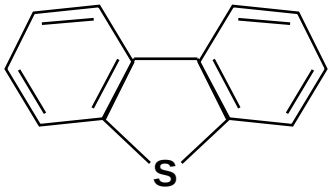
We will concentrate our attention to *Thiophenes* because they are the most difficult to remove from petroleum products like diesel and gasoline.





Thiophene



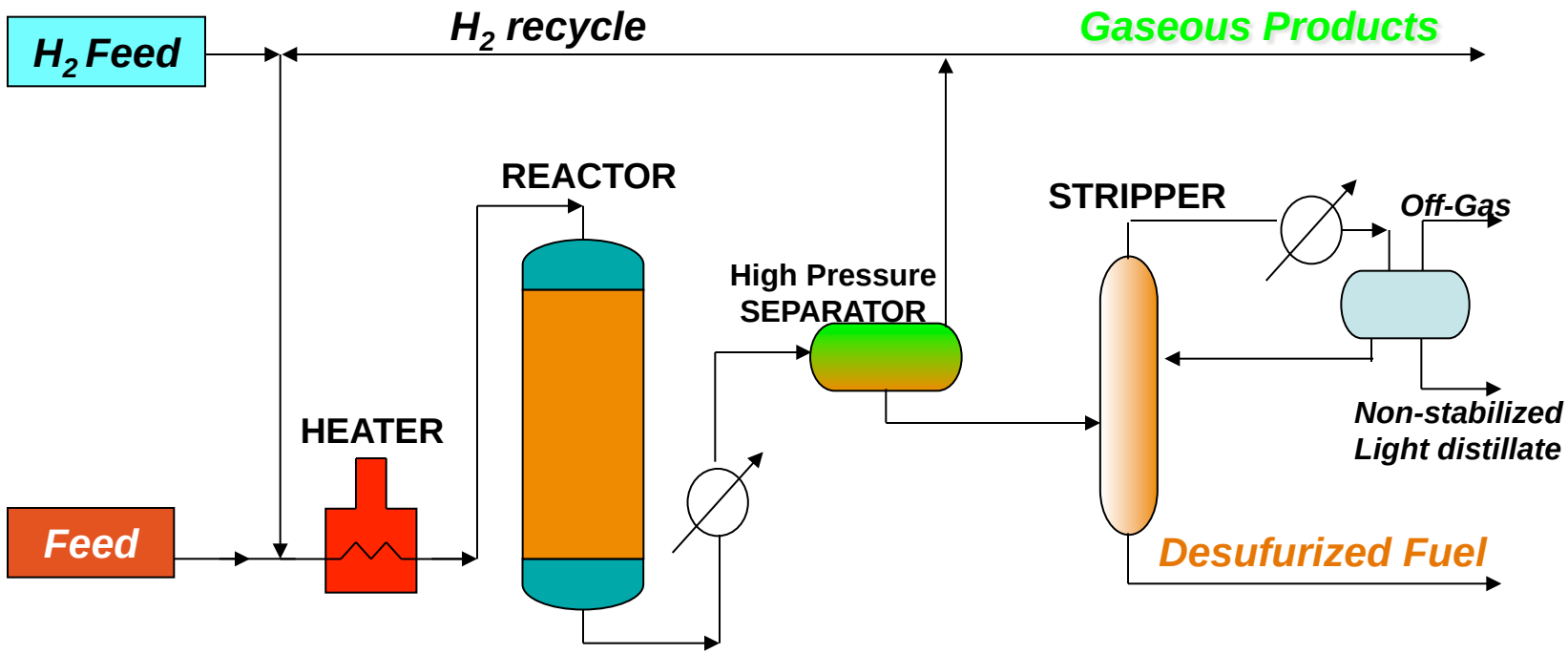


Dibenzothiophene

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)

Disadvantages of HDS process:

Reaction conditions: elevated T and P, and H_2 safety

Operating cost is high: H_2 + catalyst;

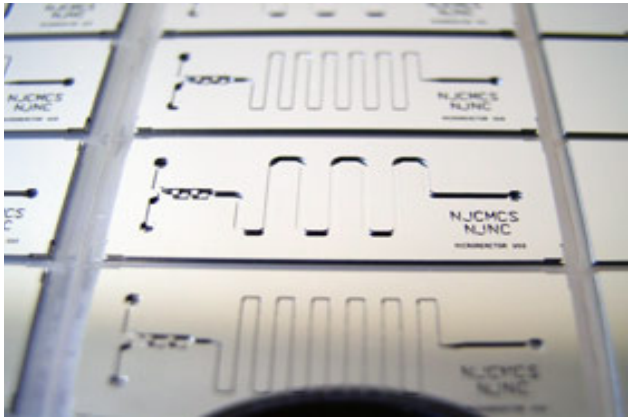
Does not effectively remove all thiophenes.

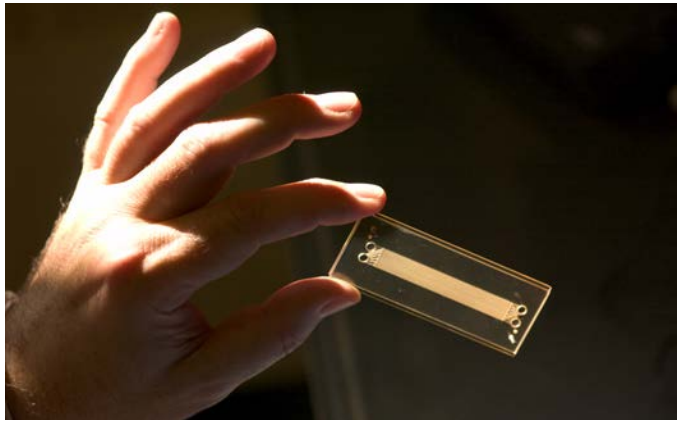
We propose *oxidative desulfurization* in microscale technology

Concept: **Sulfur molecules are oxidized, and as polar compounds extracted with an aqueous solution.**

Advantages:

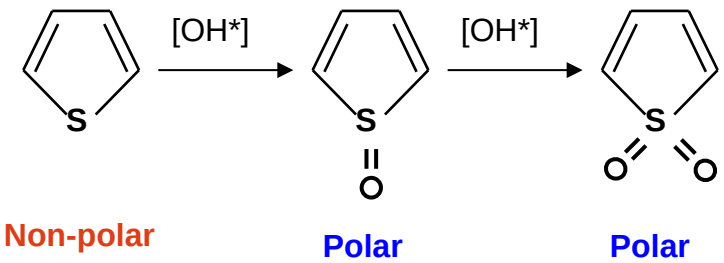
- **Catalyst is not needed;**
- **Process is easy to control;**
- **Reaction occurs at room temperature and atmospheric pressure;**
- **Lower operating cost and capital investment**



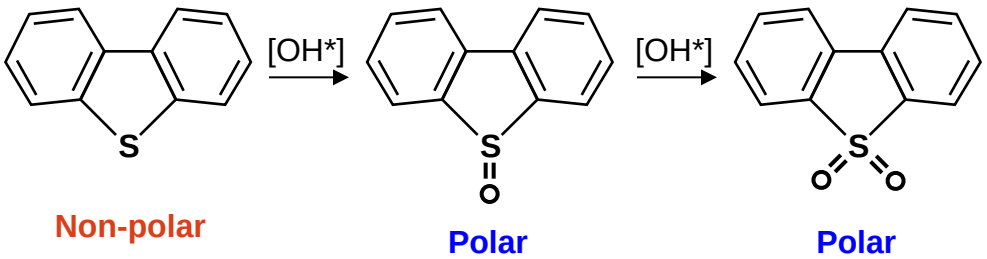


Oxidative desulfurization - Reaction kinetics

Thiophene



Dibenzothiophene



Oxidative desulfurization - Reaction kinetics

The desulfurization reaction kinetics is approximated with a pseudo 1st order rate model. The pseudo 1st order approximation is associated with the overall degradation reaction of thiophene which consist of the following steps:

$$T \xrightarrow{h\nu,\ k_1} T^*$$ ***Activation of thiophene***

$$H_2O_2 \xrightarrow{h\nu,\ k_2} H_2O_2^*$$ ***Activation of oxidant***

$$T^* \xrightarrow{k_{-1}} T$$ ***Deactivation of thiophene***

$$T^* \xrightarrow{k_3} \text{product}$$ ***Activated thiophene conversion***

$$T + H_2O_2^* \xrightarrow{k_4} \text{products}$$ ***Thiophene conversion with activated oxidant***

Oxidative desulfurization - Reaction kinetics

Under UV radiation the following reactions takes place with hydrogen peroxide:

$$H_2O_2 + h\nu \rightarrow 2\,OH^*$$

$$OH^* + H_2O_2 \rightarrow H_2O + HO_2^*$$

$$2HO_2^* \rightarrow O_2 + H_2O_2$$

$$HO_2^* \Leftrightarrow H^+ + O_2^{-*}$$

$$HO_2^* + O_2^{-*} + H_2O \rightarrow H_2O_2 + O_2 + OH^-$$

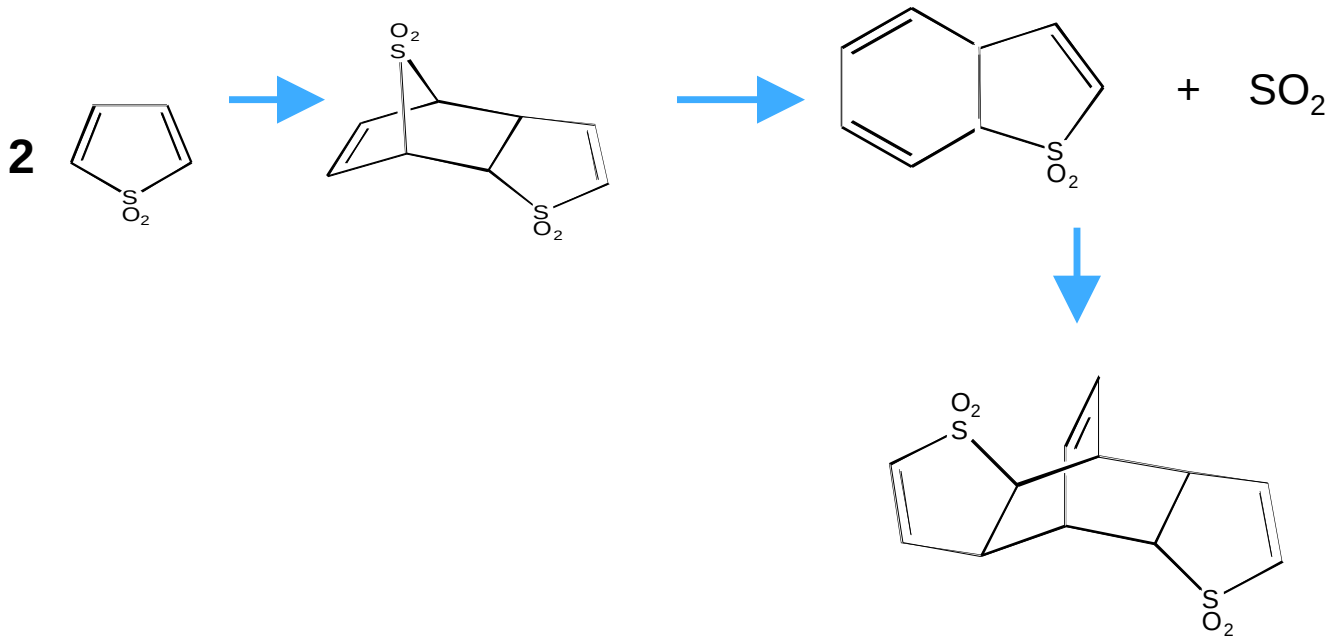
In the above degradation pathway, all the radicals formed by the collision of one photon and one molecule of H_2O_2 are included in the terms H_2O_2*

The perhydroxyl radical (HO_2*) is a relatively weak and short-lived oxidizing agent

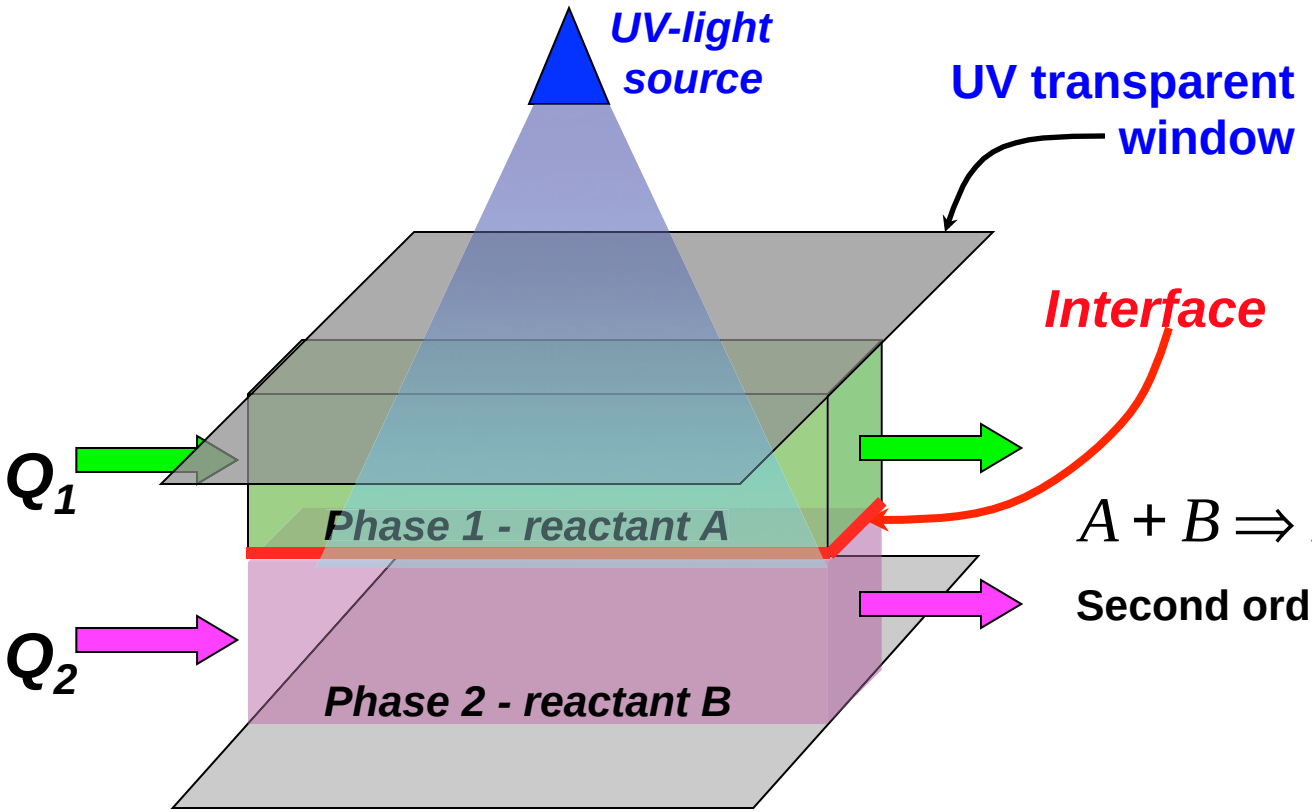
The hydroxyl free radical (OH*) is an extremely reactive and strong oxidizing agent capable of sulfur/hydrogen abstraction from hydrocarbons.

Oxidative desulfurization - Reaction kinetics

Diels-Alder Reactions



Problem Statement - two-phase case

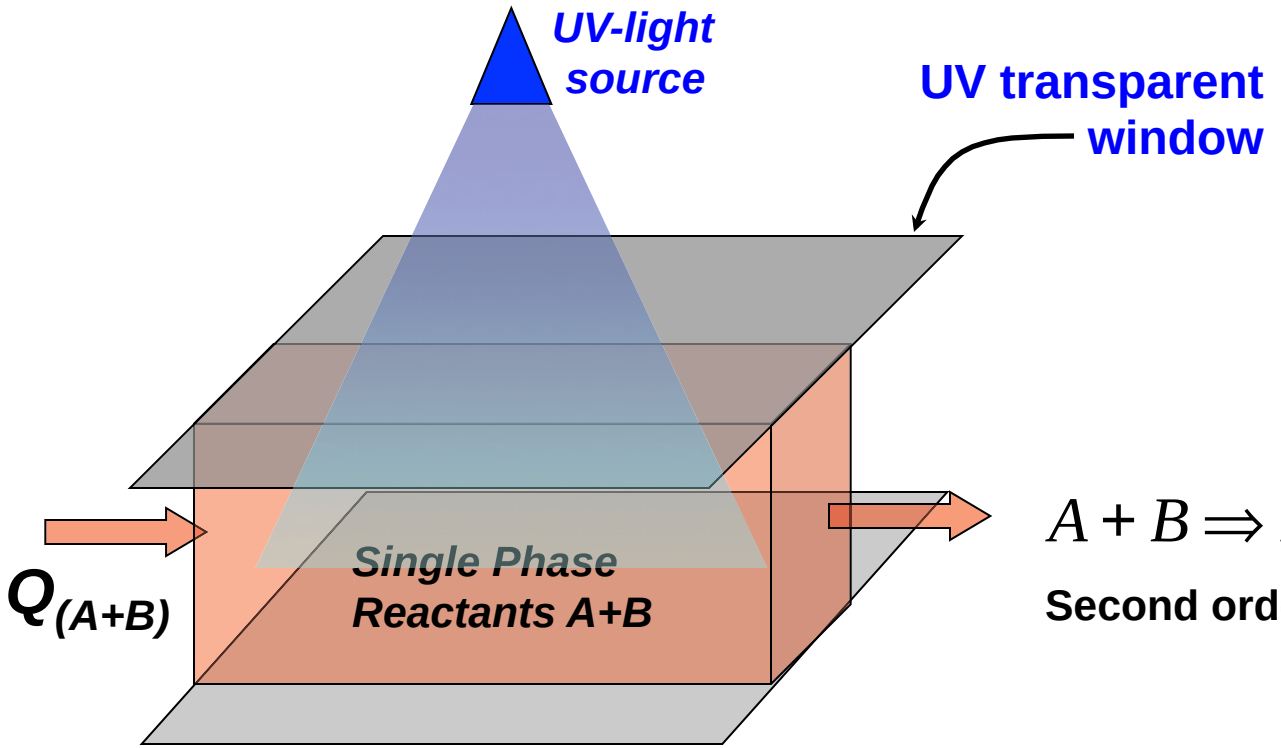


$$A + B \Rightarrow R \qquad -r_A = kC_AC_B$$

Second order chemical reaction;

- **Two reactants enter micro-channel separately with flow rates Q_1 and Q_2;**
- **Two phases have different properties (D,ρ,μ,σ)**

Problem Statement - single-phase case



$$A + B \Rightarrow R \qquad -r_A = kC_A C_B$$

Second order chemical reaction;

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

Problem Consideration - two-phase case

The two fluids may have substantially different properties, which may create variety of reaction (process) cases:

***V*iscosity ratio $m_{12}=\mu_1/\mu_2$ influences velocity distribution and fluid residence time inside micro channels;**

Diffusion coefficients of reactants *A and B* determine the scope and form of the governing differential equation and location of the reaction zone;

Different fluid densities may influence the orientation of micro devices with respect to gravity;

large surface tension may cause flow maldistribution.

Problem Consideration

There are additional elements to be considered that may play important role in 'constructing' governing model equations for reaction processes in microreactors:

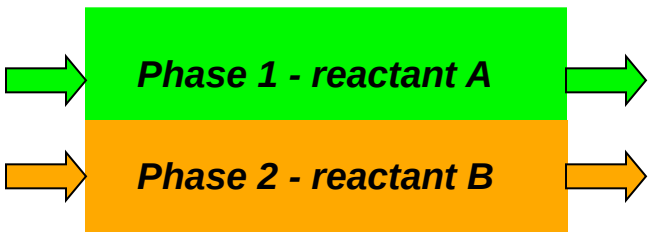
Reaction kinetics;

Thermodynamic equilibrium;

Phase changes during the process;

Problem Consideration - two-phase case

In order to consider different reaction situations that arise from different reactant diffusivities in the two-phase case (immiscible phases) we have to learn more about our particular reaction system. There are four possible cases for reactant diffusivities in the two immiscible phases:



$$A + B \Rightarrow R \qquad -r_A = kC_A C_B$$

Reactant *A* diffuses into Phase 2,
Reactant *B* does not diffuse into Phase 1.

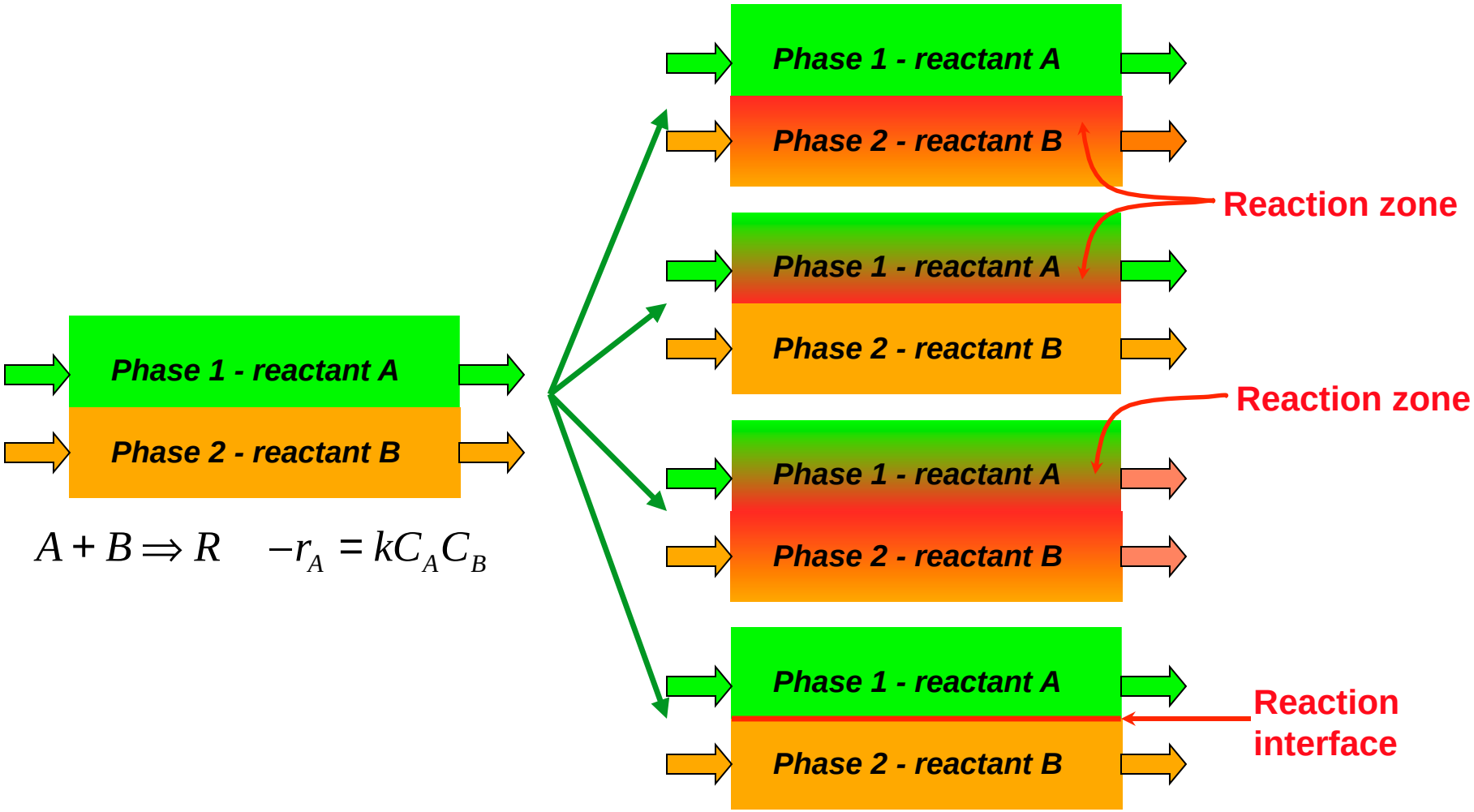
Reactant *A* does not diffuse into Phase 2,
Reactant *B* diffuses into Phase 1.

Reactant *A* diffuse into Phase 2, and
Reactant *B* diffuse into Phase 1.

Reactant *B* does not diffuse into Phase 1,
Reactant *A* does not diffuse into Phase 2.

Problem Consideration - two-phase case

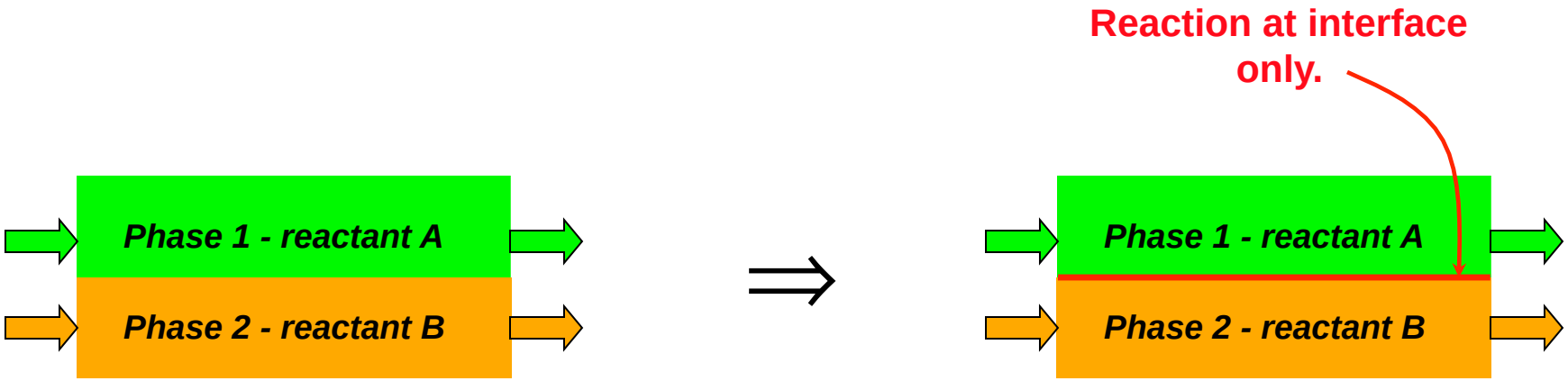
Graphically these four cases could be shown as:



$$A + B \Rightarrow R \qquad -r_A = kC_A C_B$$

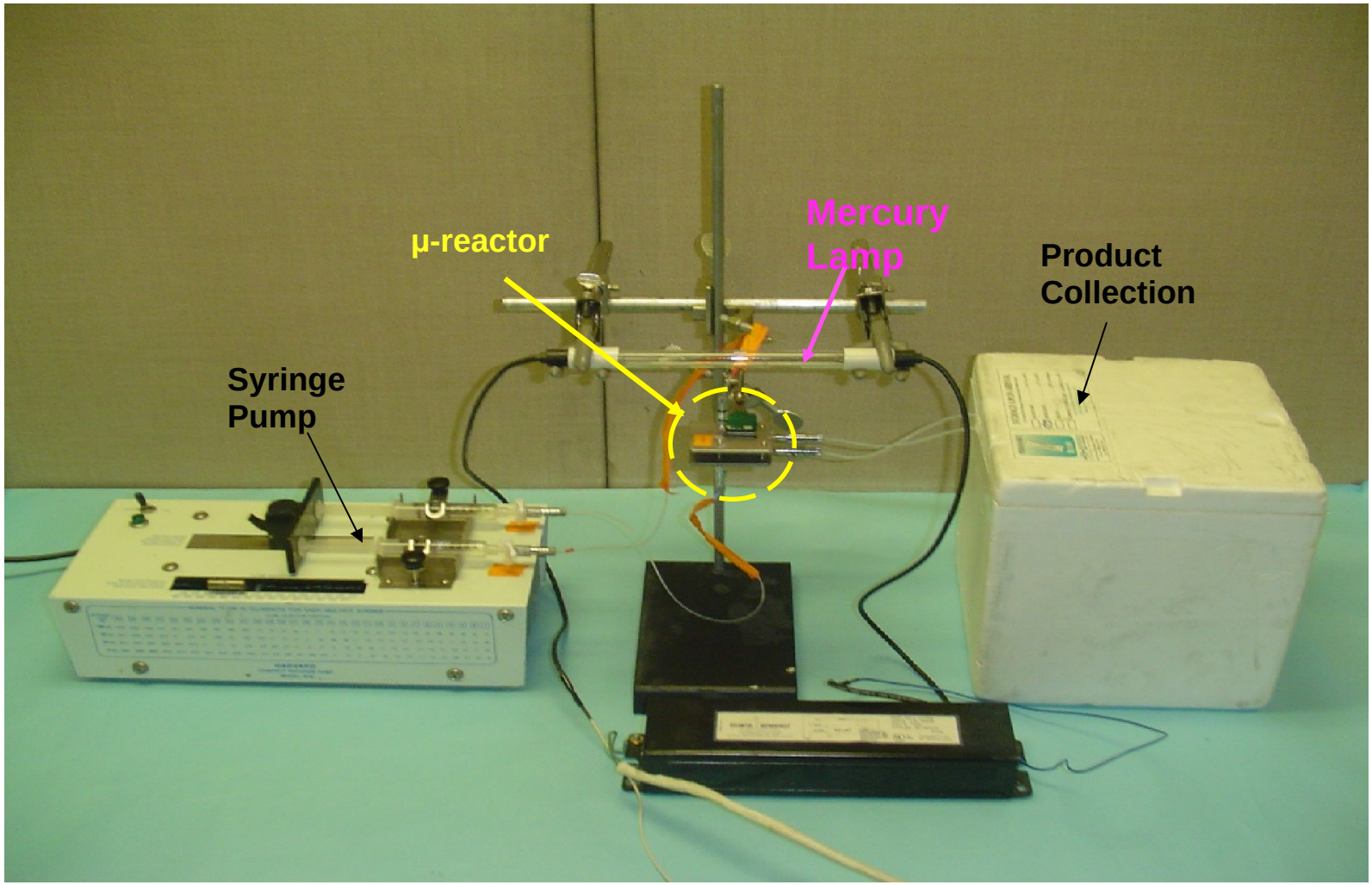
Problem Consideration - two-phase case

By examining the nature of the two phases, (H_2O and Hexane), and solubility of each reactant (H_2O_2, Dibenzothiophene) into opposite phase one can conclud that the best approximation for this two phase reaction process is:

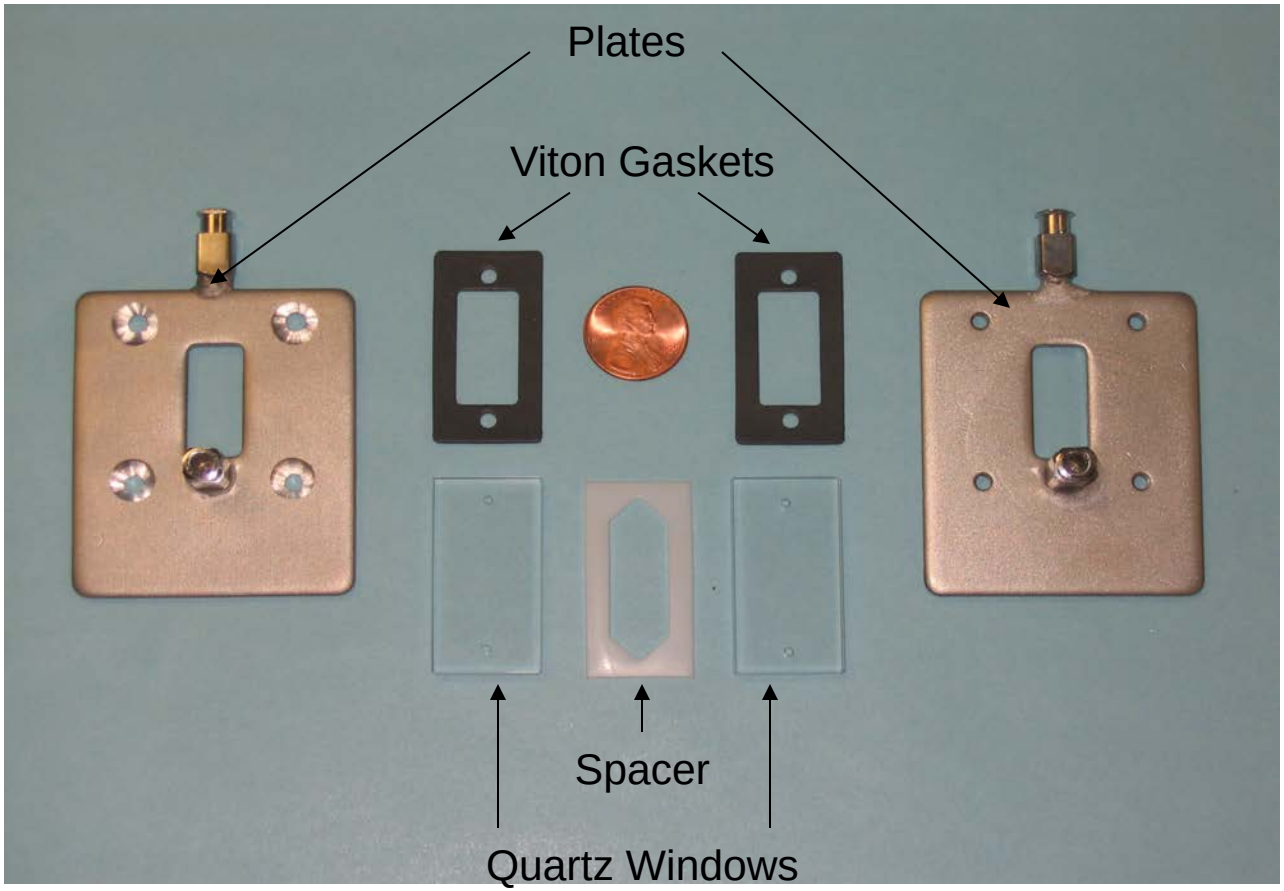


Reactant *B* does not diffuse into Phase 1, and Reactant *A* does not diffuse into Phase 2.

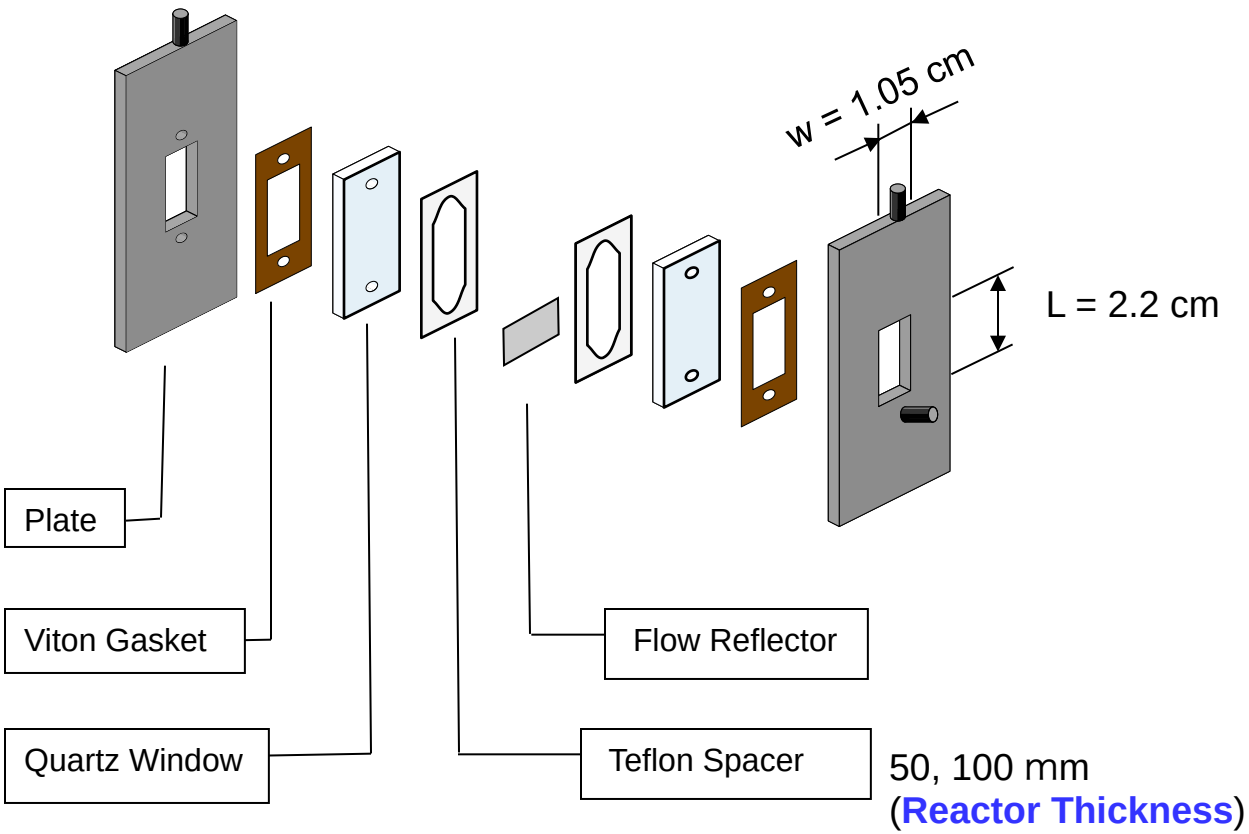
Experimental Set-up



Experimental Set-up



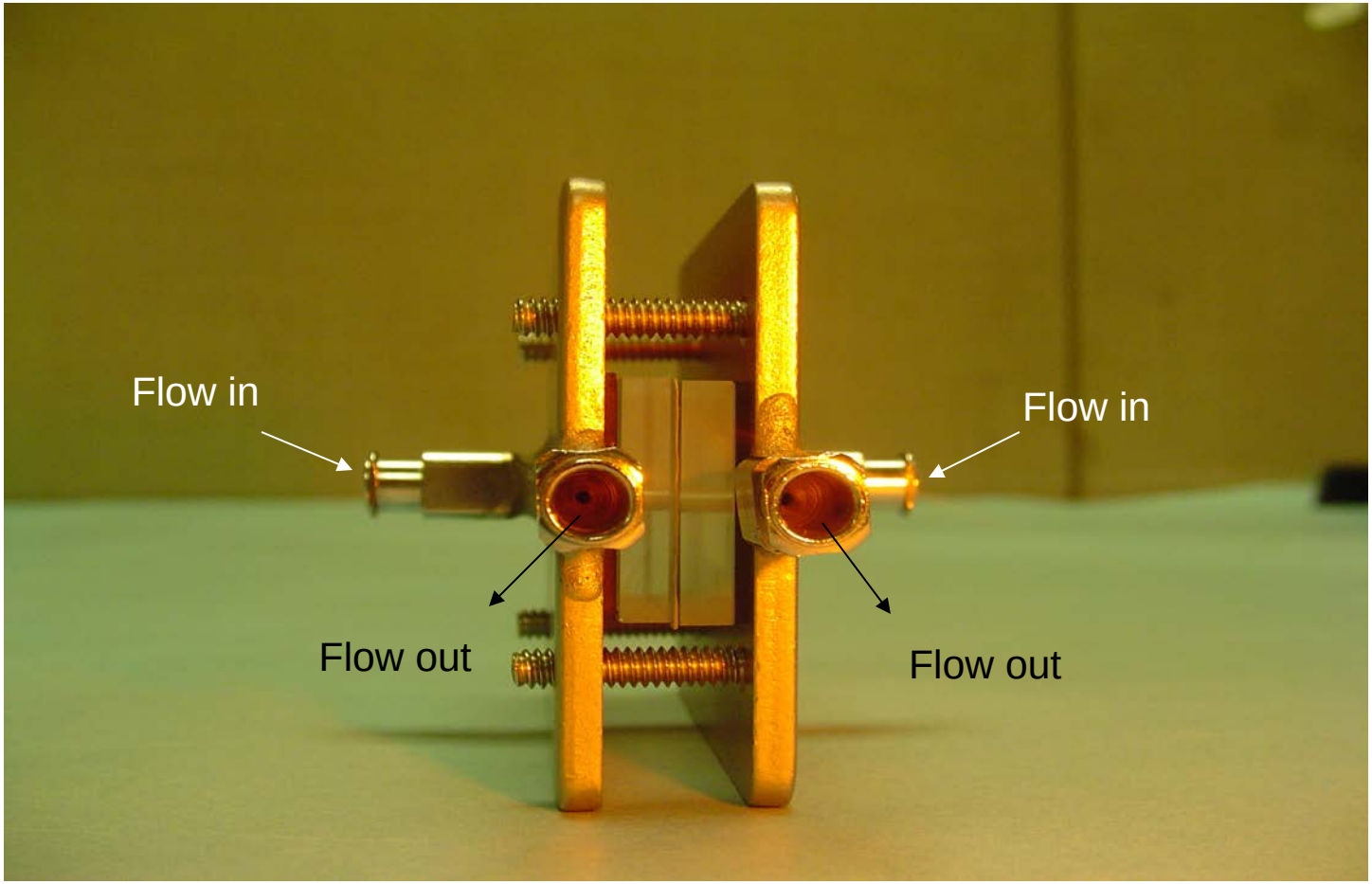
Experimental Set-up



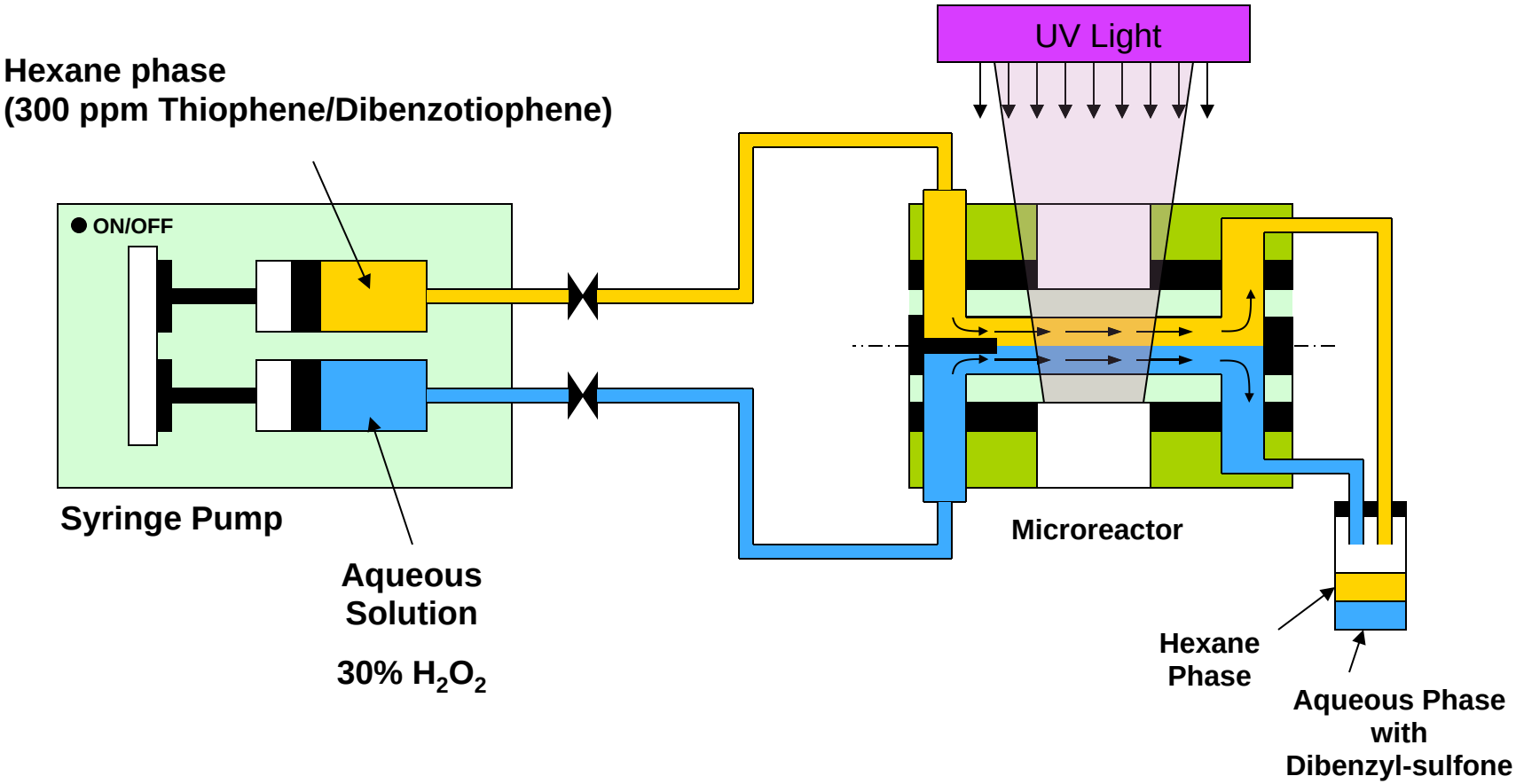
Experimental Set-up

Experimental Set-up

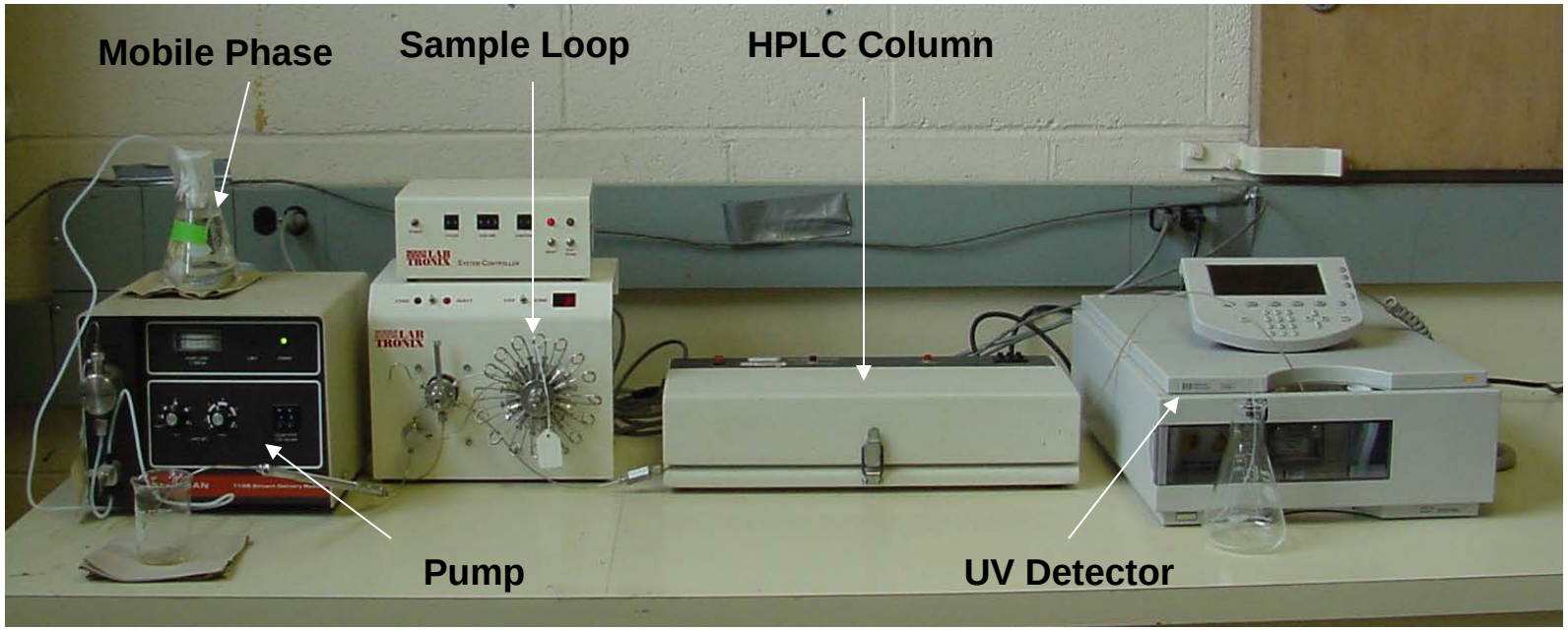
μ-reactor



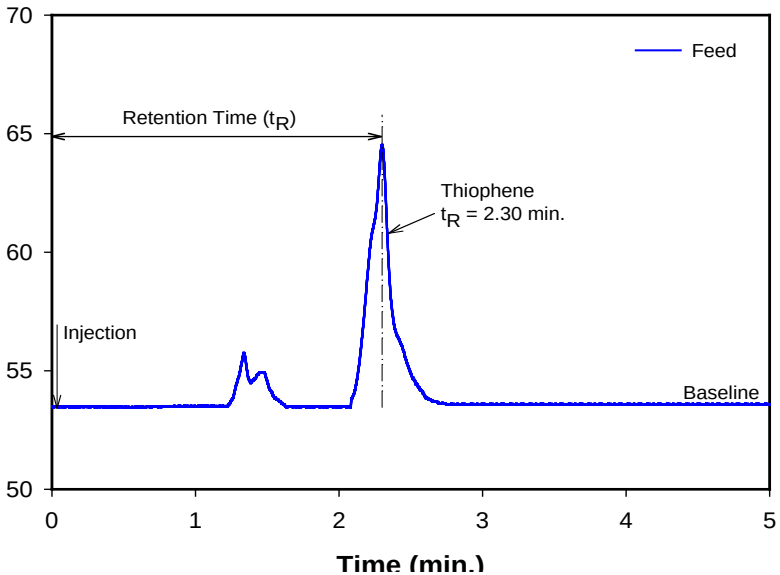
Experimental Set-up

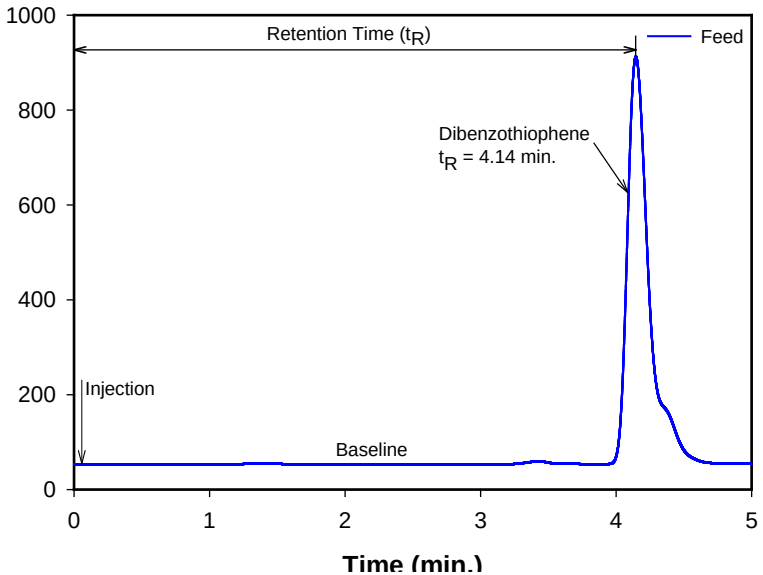


Analytical-HPLC Set-up

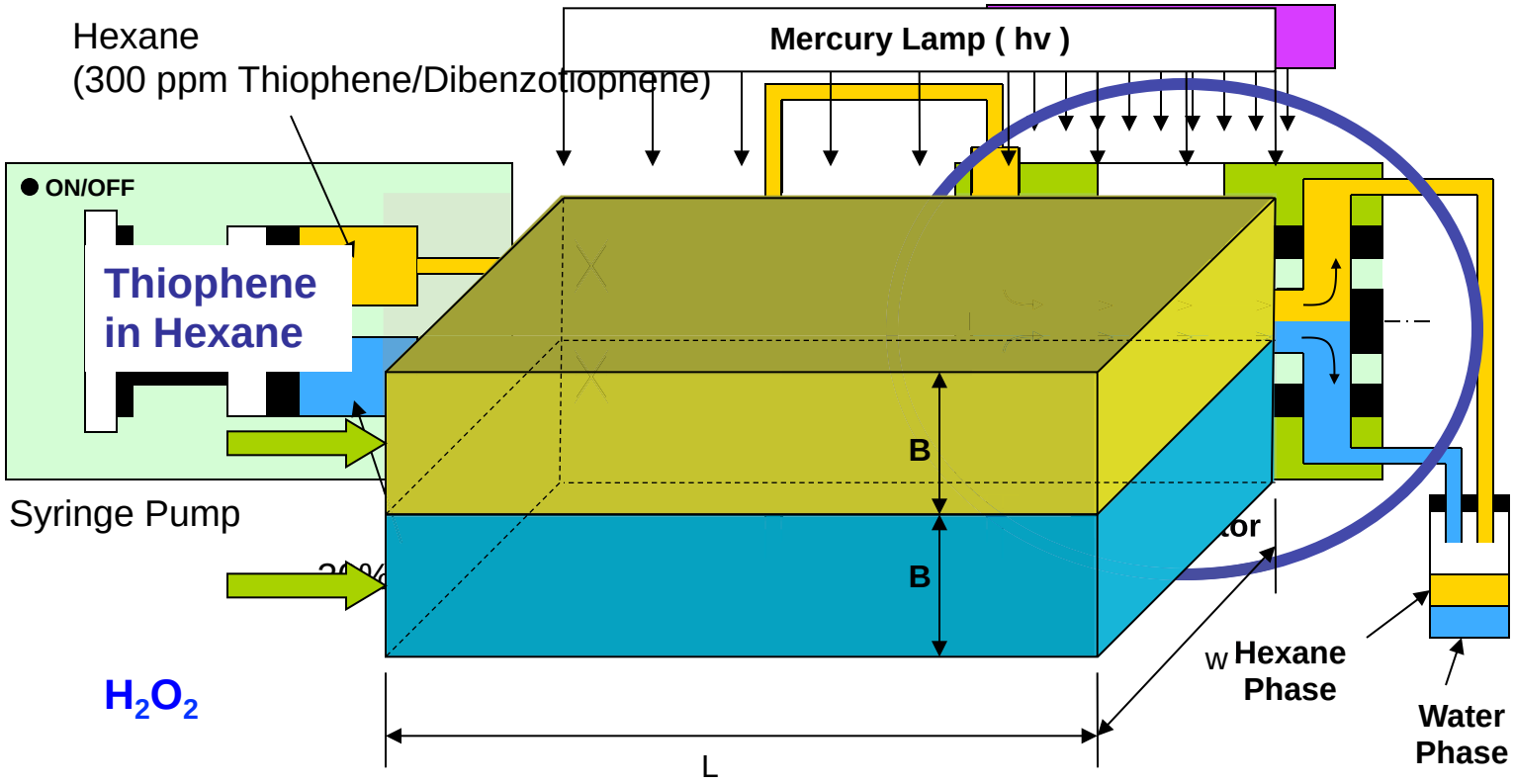


Experimental Set-up; HPLC output

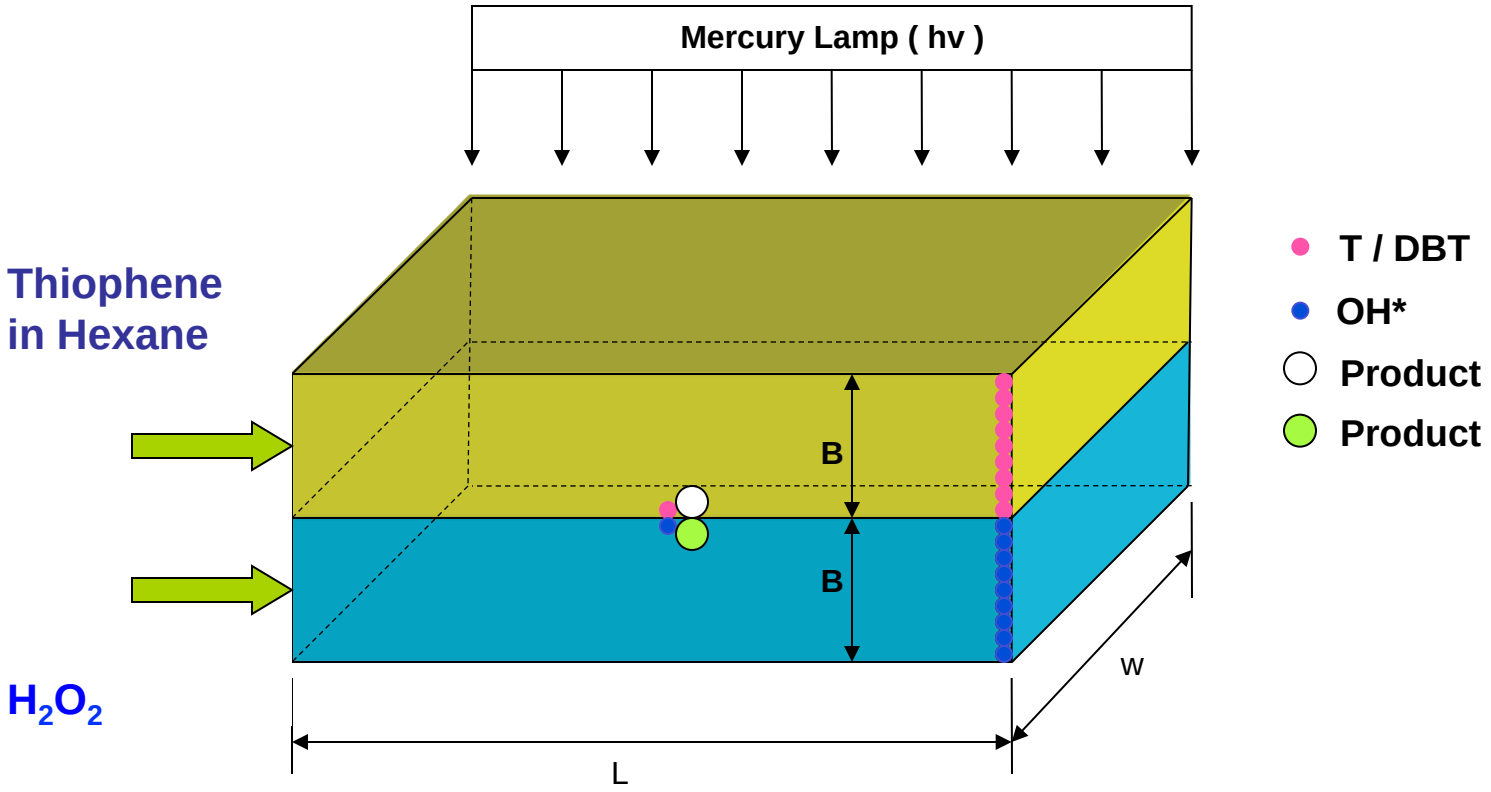




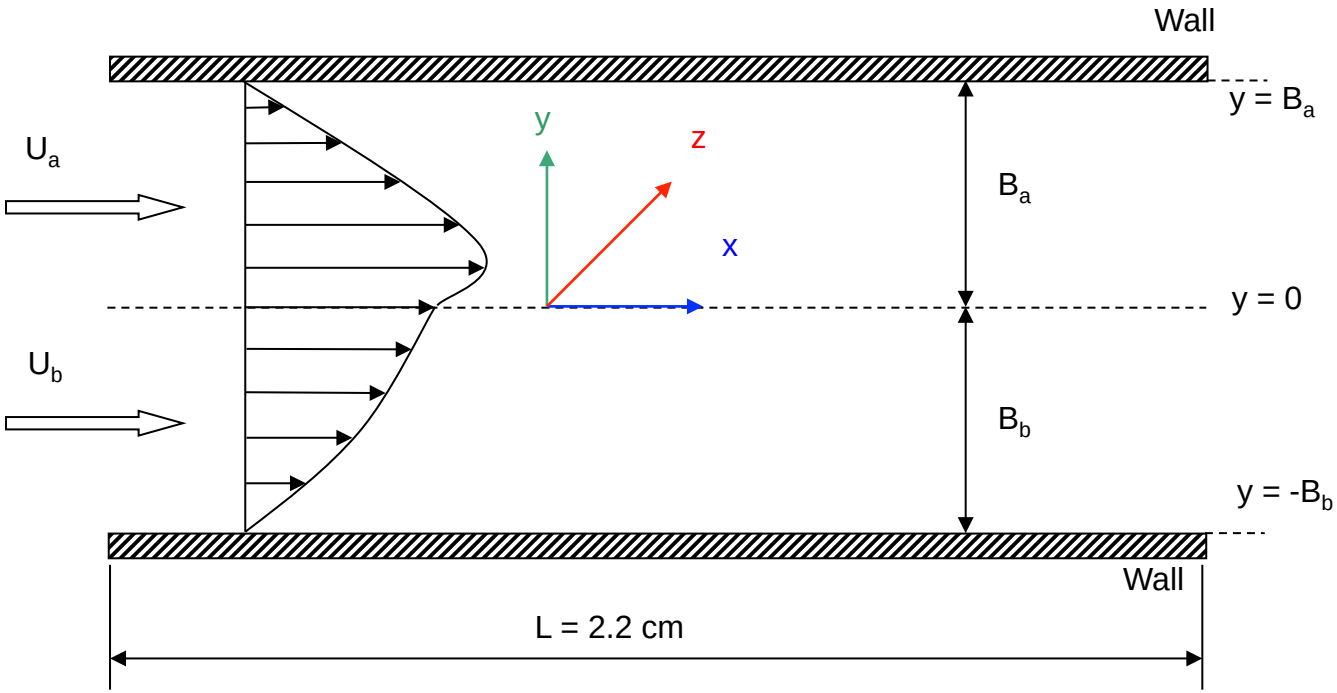
Model and velocity profile



Model and velocity profile



Model and velocity profile



- **The flow behavior of the two fluids through the micro channels has an effect on the reaction conversion;**
- **One must to determine the velocity profile through the channels by solving the continuity equation, and the equations of motion for the rectangular coordinate system**

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. Both layers are immiscible.
6. Ignore gravity effects, $g_x = g_y = g_z = 0$.
7. Negligible velocities in the directions of y and z, $U_y = U_z = 0$.
8. Consider velocity to be a function of y direction, $U_x = U(y) \neq 0$.
9. Newtonian fluids.
10. Consider rectangular coordinate system.

Model and velocity profile

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

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

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

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

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

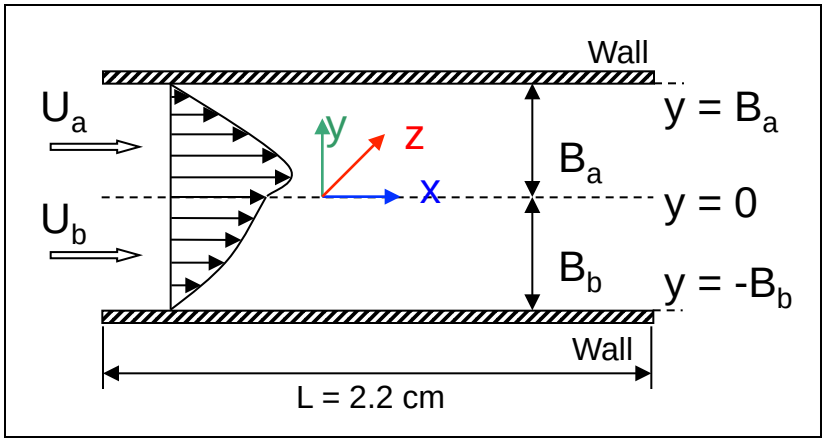
$$\rho\left(\frac{\partial U_z}{\partial t}+U_x\frac{\partial U_z}{\partial x}+U_y\frac{\partial U_z}{\partial y}+U_z\frac{\partial U_z}{\partial z}\right)=-\frac{\partial P}{\partial z}+\rho g_z+\mu\left(\frac{\partial^2 U_z}{\partial x^2}+\frac{\partial^2 U_z}{\partial y^2}+\frac{\partial^2 U_z}{\partial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

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

Model and velocity profile

Therefore, equation of motion becomes:

$$\mu \frac{\partial^2 U}{\partial y^2} = -\frac{dP}{dx} = \frac{-\Delta P}{L}$$



The boundary conditions are:

@ $y = +B_a$ $\qquad U_a = 0$

@ $y = -B_b$ $\qquad U_b = 0$

@ $y = 0$ $\qquad \mu_a \frac{\partial U_a}{\partial y} = \mu_b \frac{\partial U_b}{\partial y}$

@ $y = 0$ $\qquad U_a = U_b$

Model and velocity profile

Integrate momentum equation to obtain:

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

Then,

$$U_a = -\frac{\Delta P}{2\mu_a L} y^2 + C_1 y + C_2 \qquad U_b = -\frac{\Delta P}{2\mu_b L} y^2 + C_3 y + C_4$$

Model and velocity profile

Introduce the boundary conditions to obtain:

$$U_a = M\left[1 + \frac{1}{A\,B_a}\left(\frac{B^2 - A}{B + 1}\right)y - \frac{1}{A\,B_a B_b}\left(\frac{A + B}{B + 1}\right)y^2\right]$$

$$U_b = M\left[1 + \frac{1}{B_a}\left(\frac{B^2 - A}{B + 1}\right)y - \frac{1}{B_a B_b}\left(\frac{A + B}{B + 1}\right)y^2\right]$$

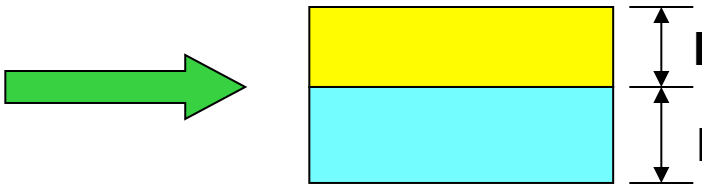
Where,

$$M = \frac{\Delta P\, B_a\, B_b}{2\,\mu_b\, L}\left(\frac{B+1}{A+B}\right) \qquad A = \frac{\mu_a}{\mu_b} \qquad B = \frac{B_a}{B_b}$$

Model and velocity profile

$$\frac{Q_a}{Q_b} = 1 = B\frac{\left[1 + \frac{1}{2A}\left(\frac{B^2 - A}{B + 1}\right) - \frac{B}{3A}\left(\frac{A + B}{B + 1}\right)\right]}{\left[1 - \frac{1}{2B}\left(\frac{B^2 - A}{B + 1}\right) - \frac{1}{3B}\left(\frac{A + B}{B + 1}\right)\right]}$$

Solution, B = 0.84



Then substitute B into equations for the velocity profile.

Model and velocity profile

The final forms of the velocity profiles are:

At spacer thickness 100 mm

$$U_a = \Delta P \left[0.000382 + 2.098\, y - 68799.2\, y^2 \right]$$

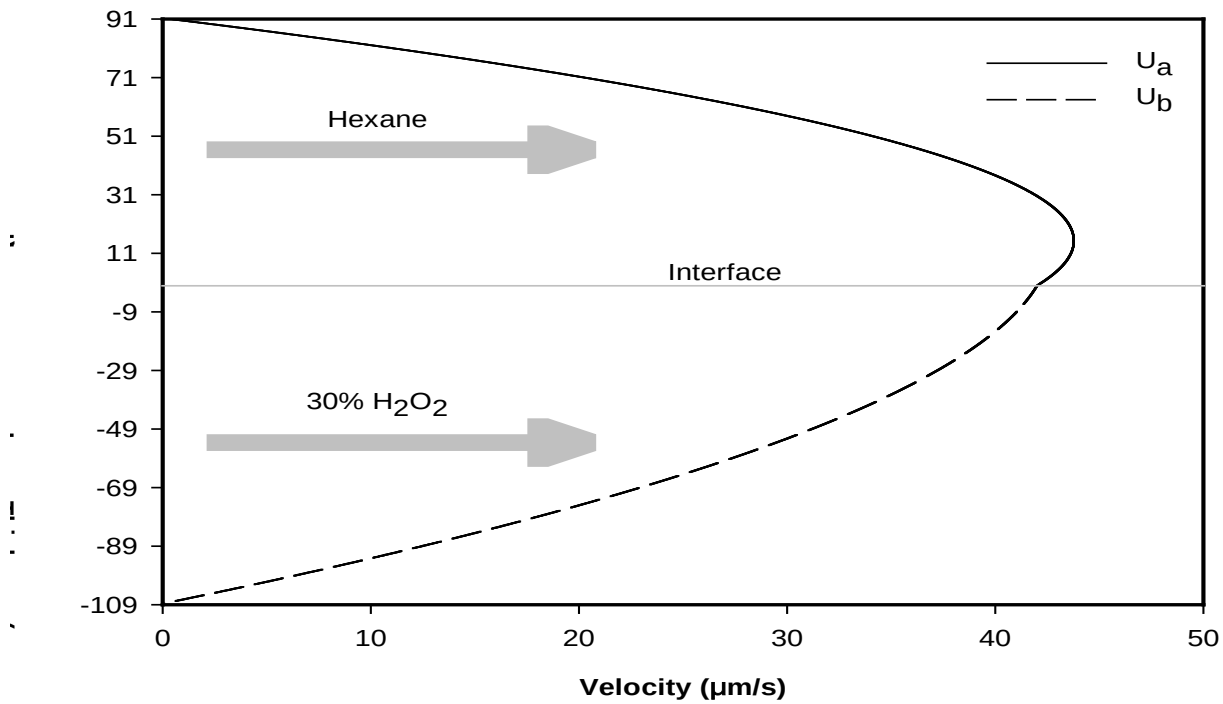
$$U_b = \Delta P \left[0.000382 + 0.770\, y - 25249.3\, y^2 \right]$$

At spacer thickness 50 mm

$$U_a = \Delta P \left[0.000096 + 1.054\, y - 69159.4\, y^2 \right]$$

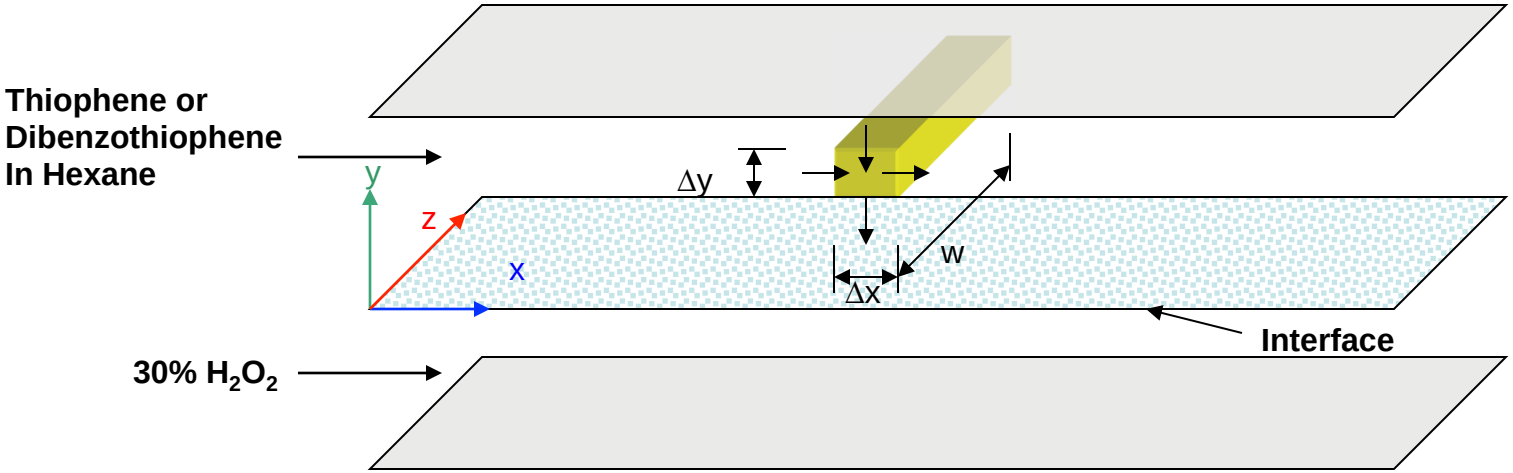
$$U_b = \Delta P \left[0.000096 + 0.387\, y - 25381.5\, y^2 \right]$$

Model and velocity profile



Actual velocity profile inside the microreactor. (B_a=91.304 [µm], B_b=108.696 [µm], RT=5.02 [min], $\mu_a=3.3*10^{-4}$ [Pa.s], $\mu_b=9.0*10^{-4}$ [Pa.s])

Model - convection, diffusion



Constant concentration of H_2O_2 in Phase II (1st order reaction)

Consider a control volume of (Δx Δy w) in phase I

Input:

$$U_a A_1 C\Big|_x + \left(-DA_1 \frac{\partial C}{\partial x}\Big|_x \right) + \left(+DA_2 \frac{\partial C}{\partial y}\Big|_{y+\Delta y} \right)$$

Output:

$$U_a A_1 C\Big|_{x+\Delta x} + \left(-DA_1 \frac{\partial C}{\partial x}\Big|_{x+\Delta x} \right) + \left(+DA_2 \frac{\partial C}{\partial y}\Big|_{y} \right)$$

Model - convection, diffusion

Input – Output + Generation = Acc.

Generation: 0 **(No reaction inside the control volume)**
Accumulation: 0 **(Steady State)**

$$\left\{U_a A_1 C\Big|_x + \left(-DA_1 \frac{\partial C}{\partial x}\Big|_x\right) + \left(+DA_2 \frac{\partial C}{\partial y}\Big|_{y+\Delta y}\right)\right\} - \left\{U_a A_1 C\Big|_{x+\Delta x} + \left(-DA_1 \frac{\partial C}{\partial x}\Big|_{x+\Delta x}\right) + \left(+DA_2 \frac{\partial C}{\partial y}\Big|_y\right)\right\} = 0$$

$$A_1 = w\Delta y$$

$$U_a w\Delta y C\Big|_x - Dw\Delta y \frac{\partial C}{\partial x}\Big|_x + Dw\Delta x \frac{\partial C}{\partial y}\Big|_{y+\Delta y} - U_a w\Delta y C\Big|_{x+\Delta x} + Dw\Delta y \frac{\partial C}{\partial x}\Big|_{x+\Delta x} - Dw\Delta x \frac{\partial C}{\partial y}\Big|_y = 0$$

Model - convection, diffusion

Governing Equation:

$$- U_a \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} + D \frac{\partial^2 C}{\partial y^2} = 0$$

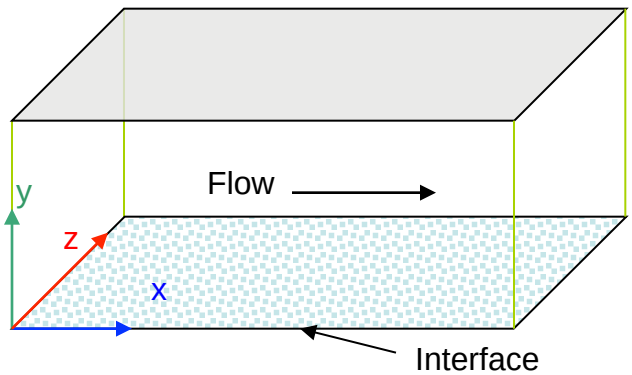
Boundary conditions:

$$C(0,y) = C_o \qquad 0 \le y \le B_a$$

$$\frac{\partial C}{\partial x}(L,y) = 0 \qquad 0 \le y \le B_a$$

$$\frac{\partial C}{\partial y}(x,0) = \frac{-kC}{D} \qquad 0 \le x \le L$$

$$\frac{\partial C}{\partial y}(x,B_a) = 0 \qquad 0 \le x \le L$$



Model - in dimensionless form

$$\eta = \frac{y}{B_a}; \quad \zeta = \frac{x}{L}; \quad \theta = \frac{C}{C_o}$$

Dimensionless PDE:

$$\left[1 + 0.501\,\eta - 1.501\,\eta^2\right]\frac{\partial\theta}{\partial\zeta} = \frac{D}{L\,M}\frac{\partial^2\theta}{\partial\zeta^2} + \frac{D\,L}{B_a^{\,2}\,M}\frac{\partial^2\theta}{\partial\eta^2}$$

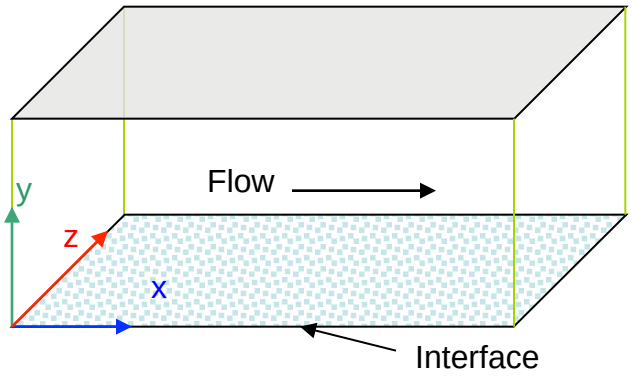
Boundary Conditions:

$$\theta(0,\eta) = 1 \qquad 0 \le \eta \le 1$$

$$\frac{\partial\theta}{\partial\zeta}(1,\eta) = 0 \qquad 0 \le \eta \le 1$$

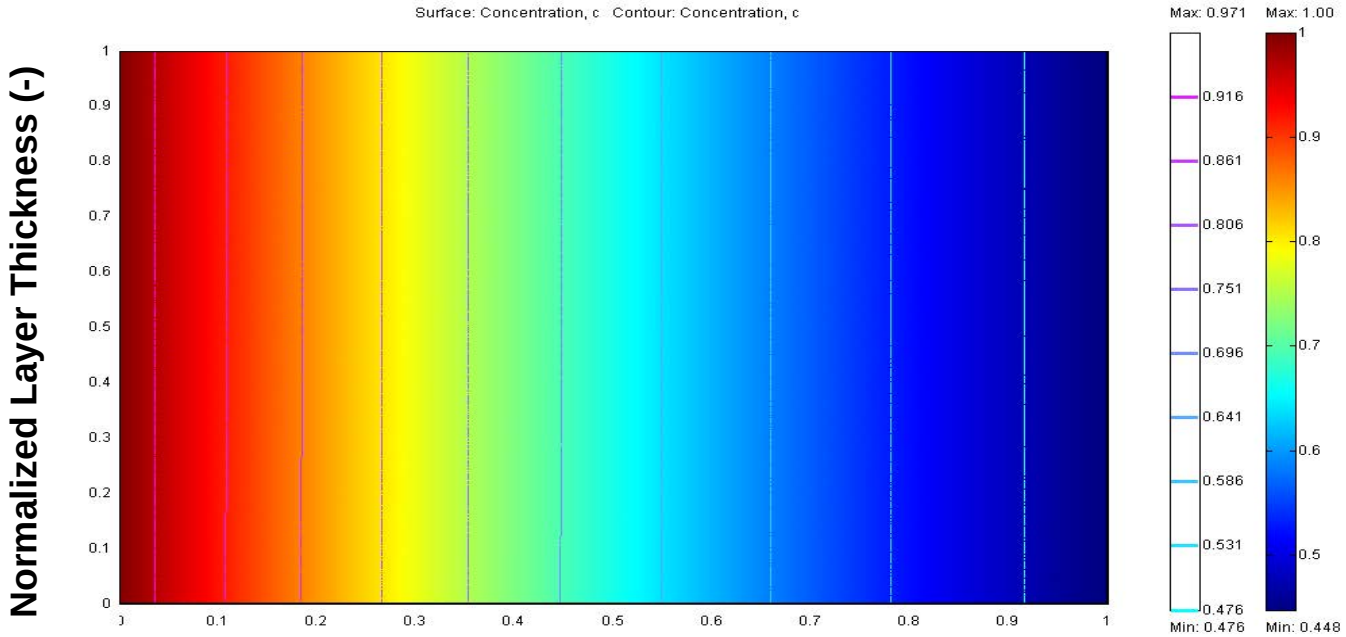
$$\frac{\partial\theta}{\partial\eta}(\zeta,0) = \frac{-k\,B_a\,\theta}{D} \qquad 0 \le \zeta \le 1$$

$$\frac{\partial\theta}{\partial\eta}(\zeta,1) = 0 \qquad 0 \le \zeta \le 1$$



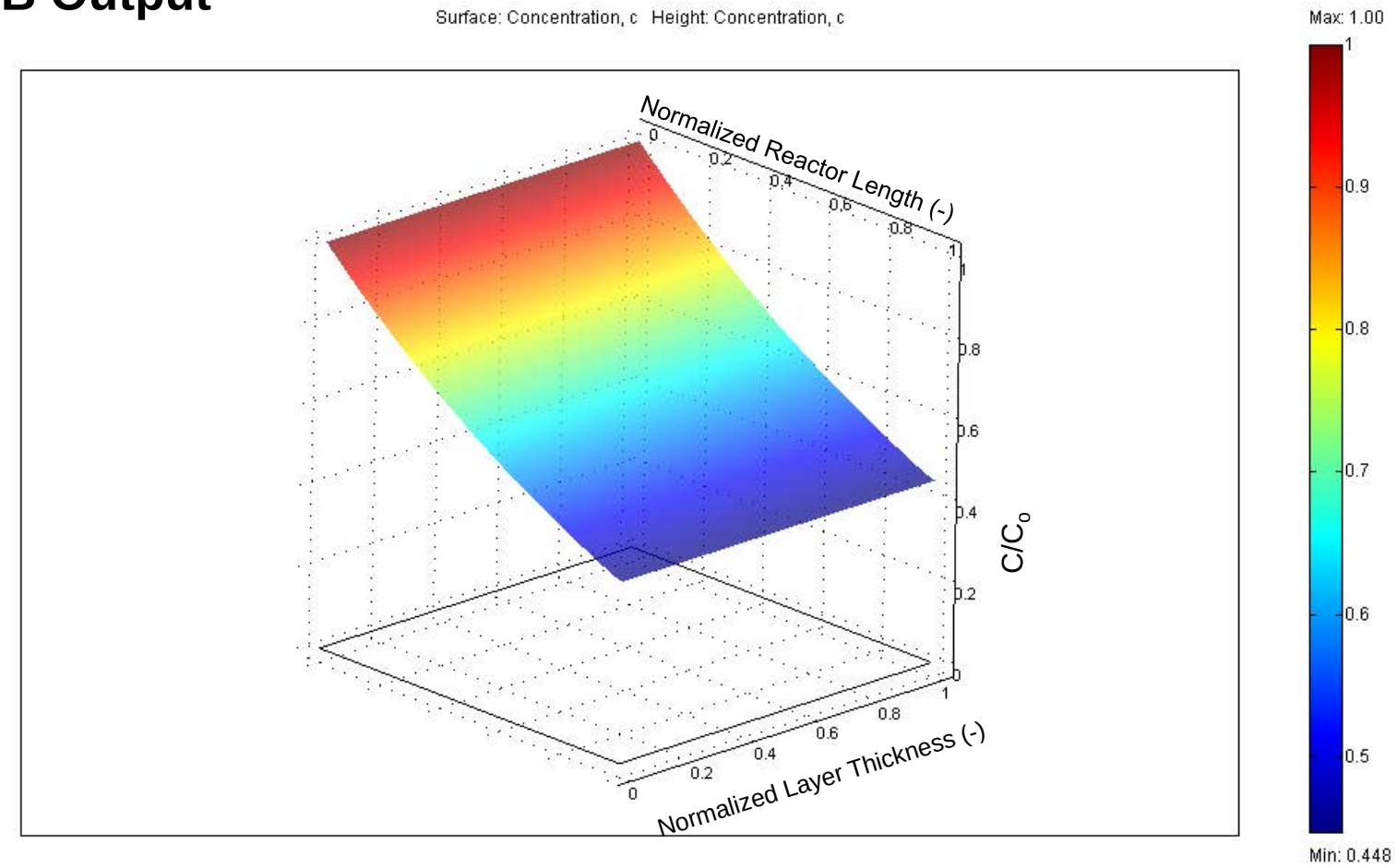
Model simulation

FEMLAB Output



Model simulation

FEMLAB Output



Model simulation

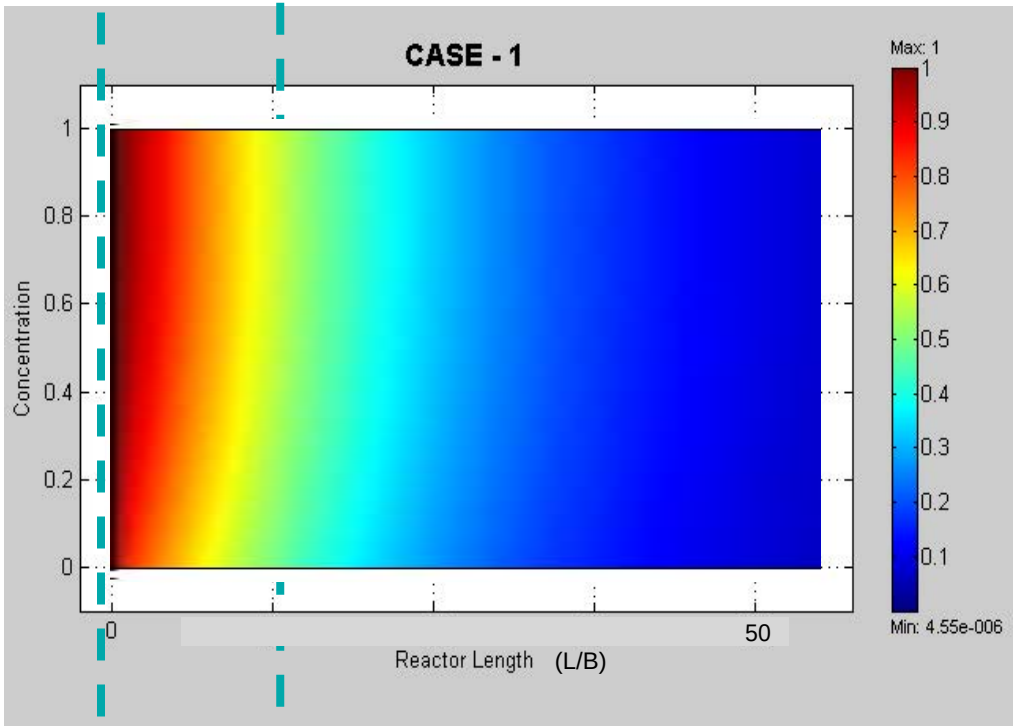
Numerical Solutions:

- **Effect of the Fluid Velocity**

  k=0.000023 1/s
  B=0.0001 m
  U_m=0.000476 m/s

The outlet concentration is 5.2001e-6

EXPAND



Model simulation

Numerical Solutions:

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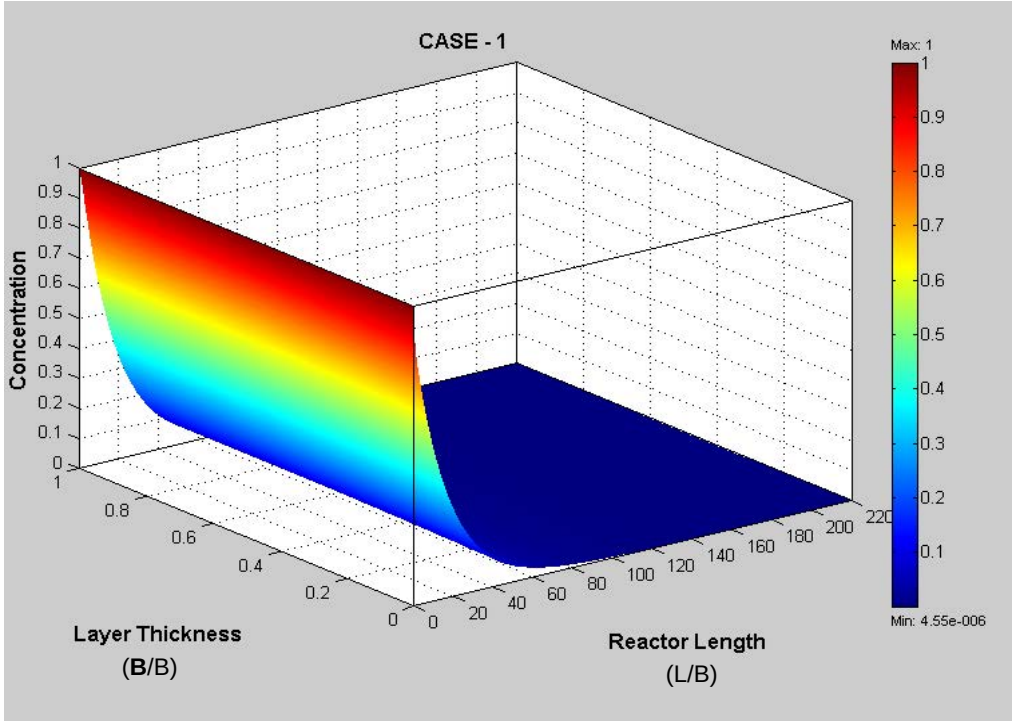
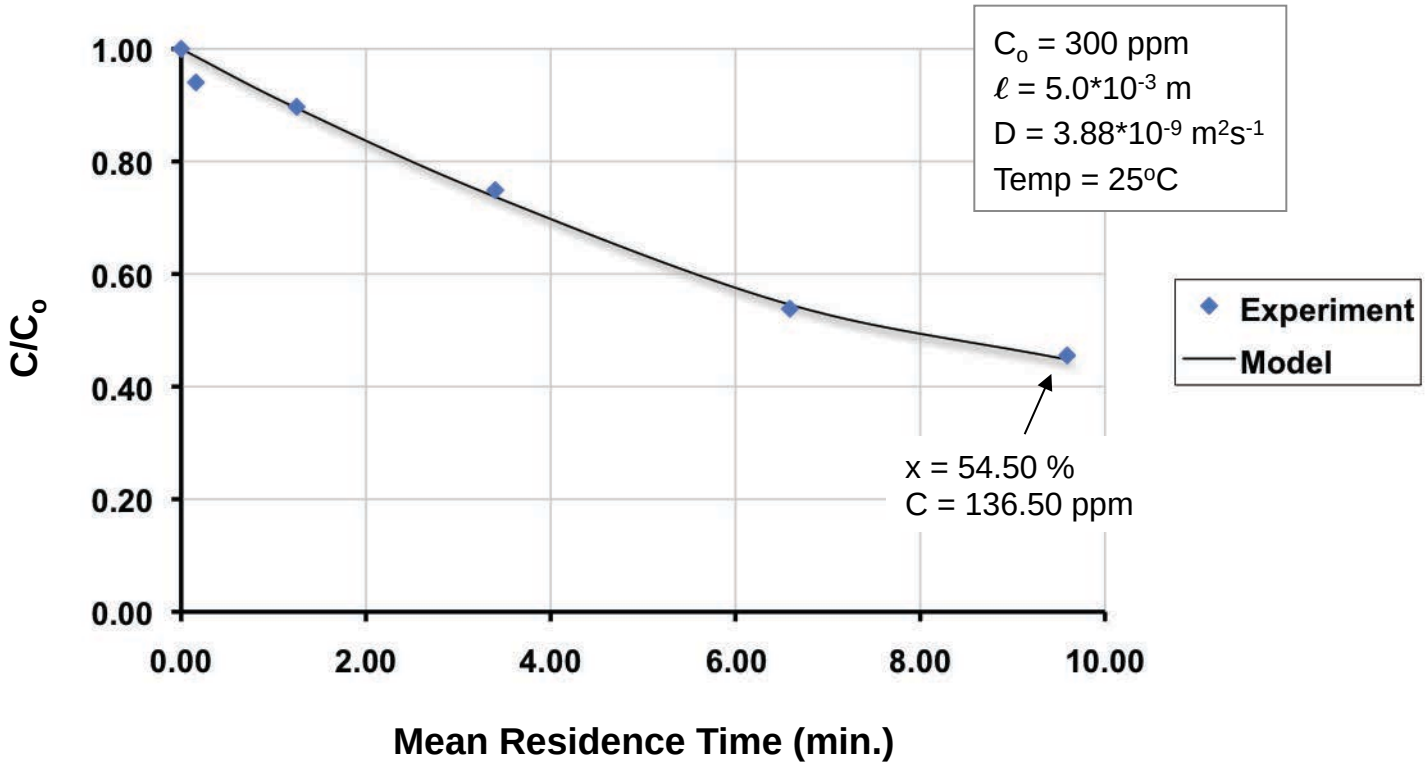


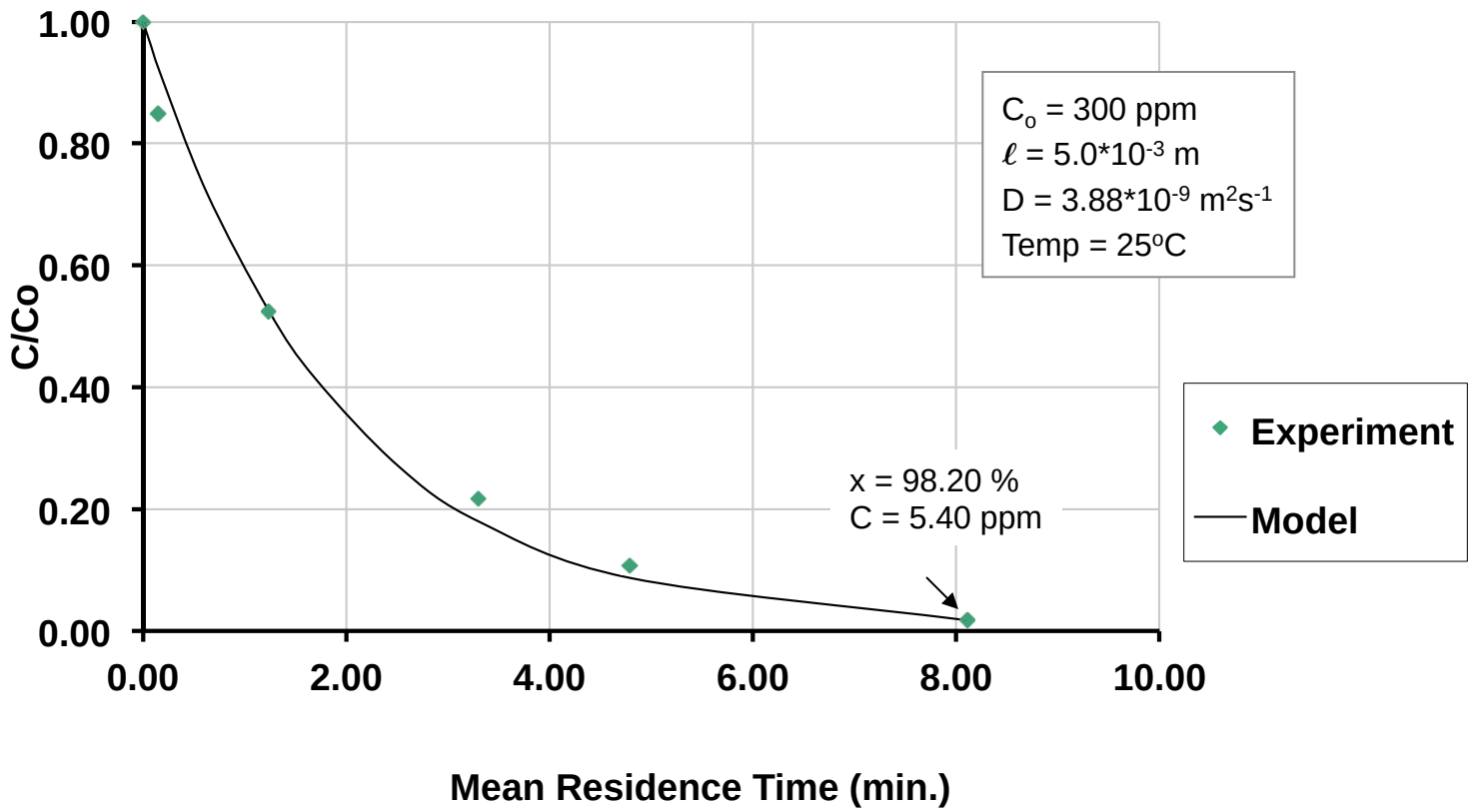
Experimental Results and Model Simulation

Thiophene concentration at spacer thickness = 100 µm



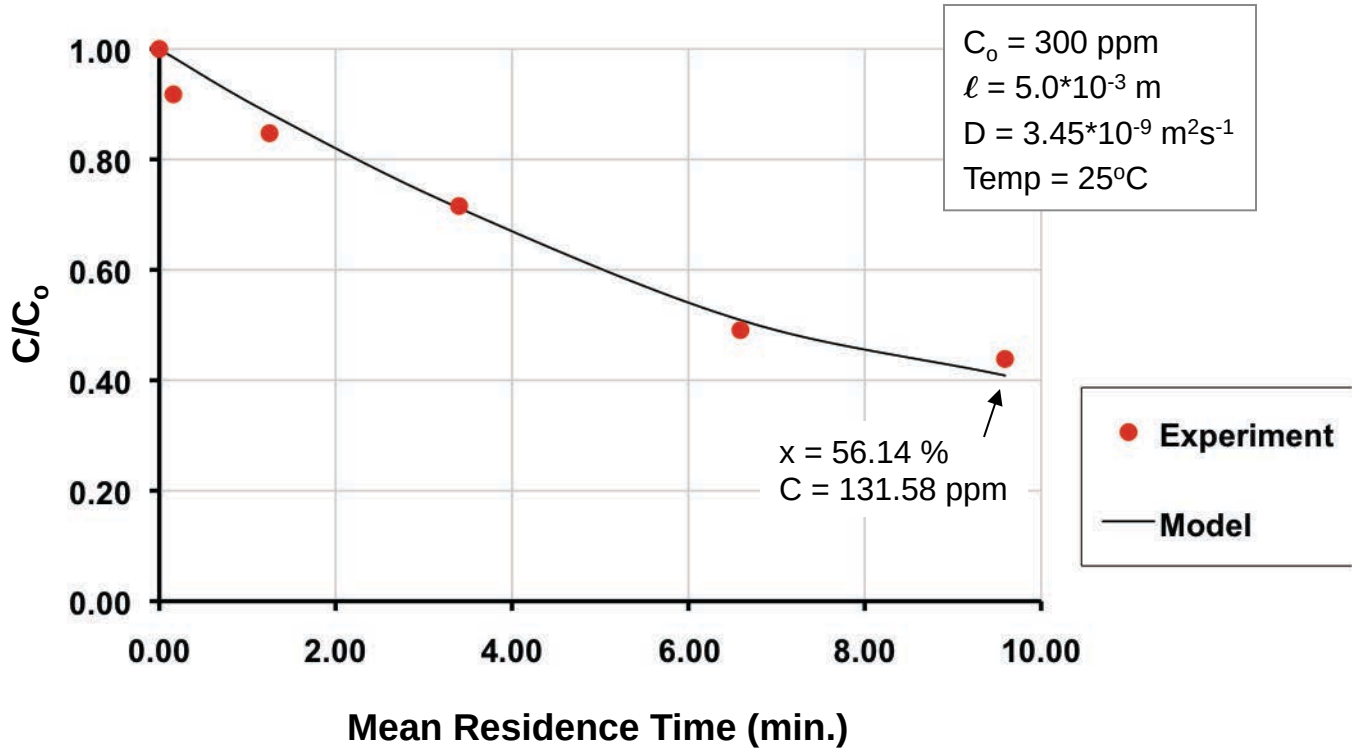
Experimental Results and Model Simulation

Thiophene concentration at spacer thickness = 50 µm



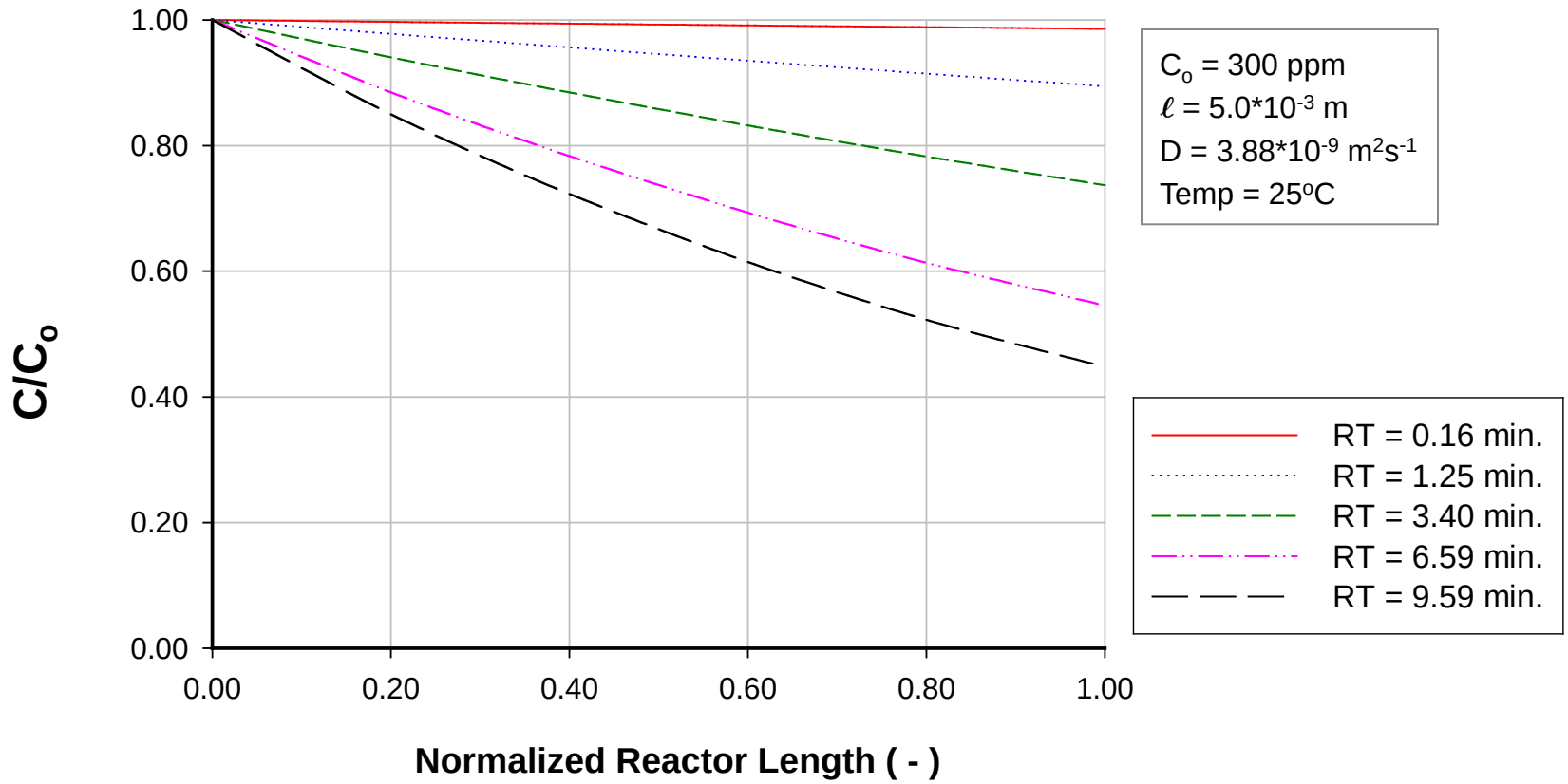
Experimental Results and Model Simulation

Dibenzothiophene concentration at spacer thickness = 100 μm



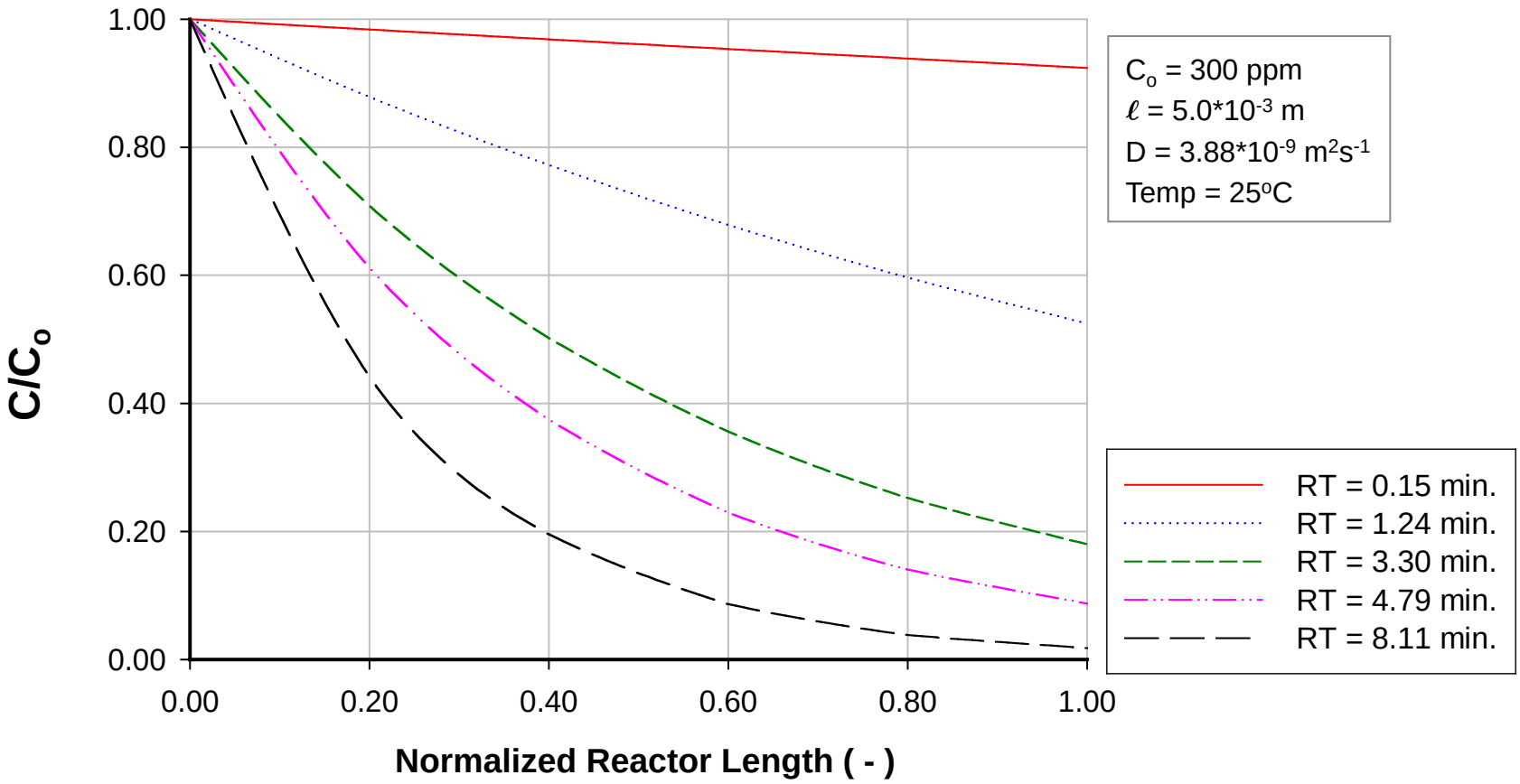
Experimental Results and Model Simulation

Model (Thiophene concentration profile at 100 μm)



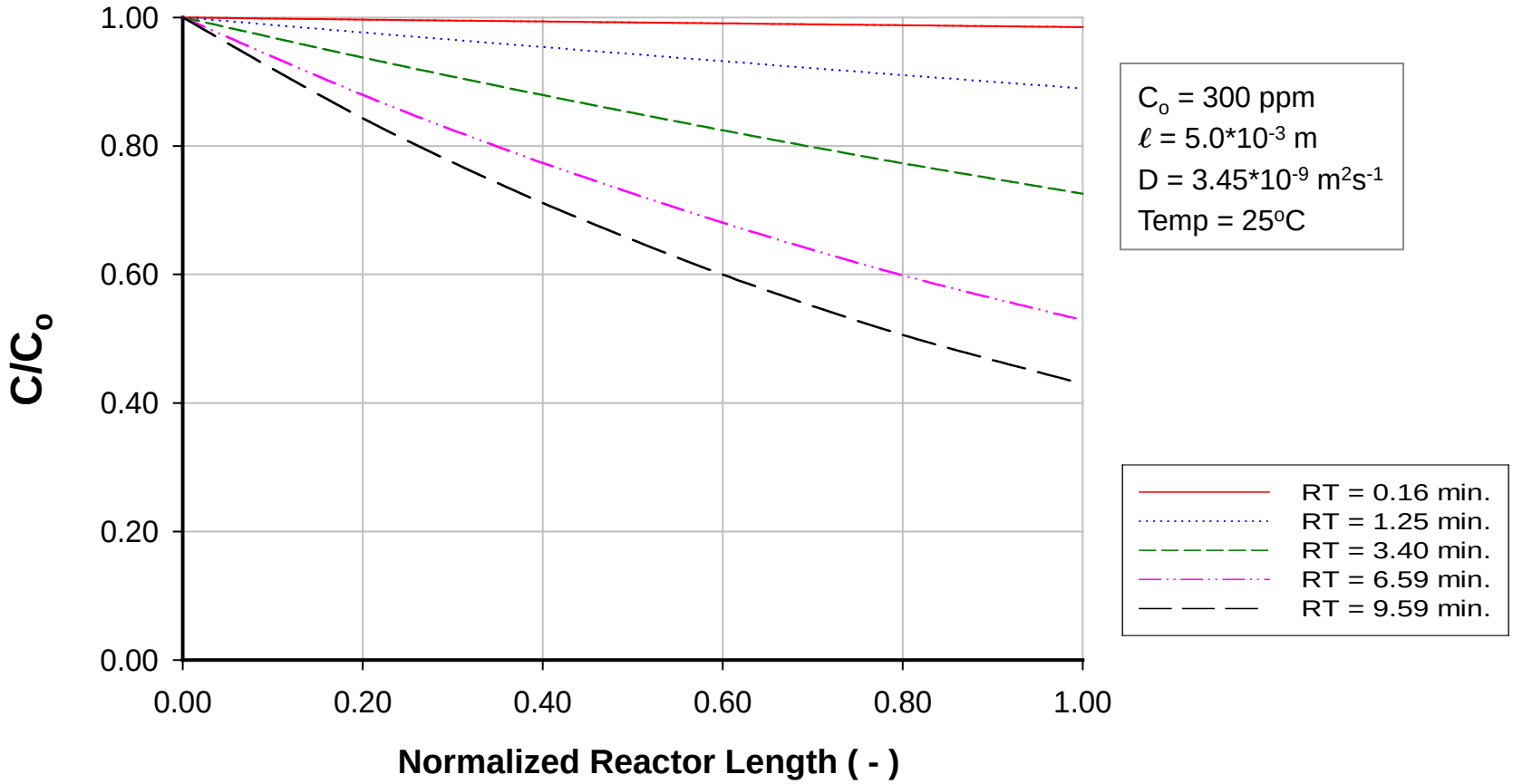
Experimental Results and Model Simulation

Model (Thiophene concentration profile at 50 μm)



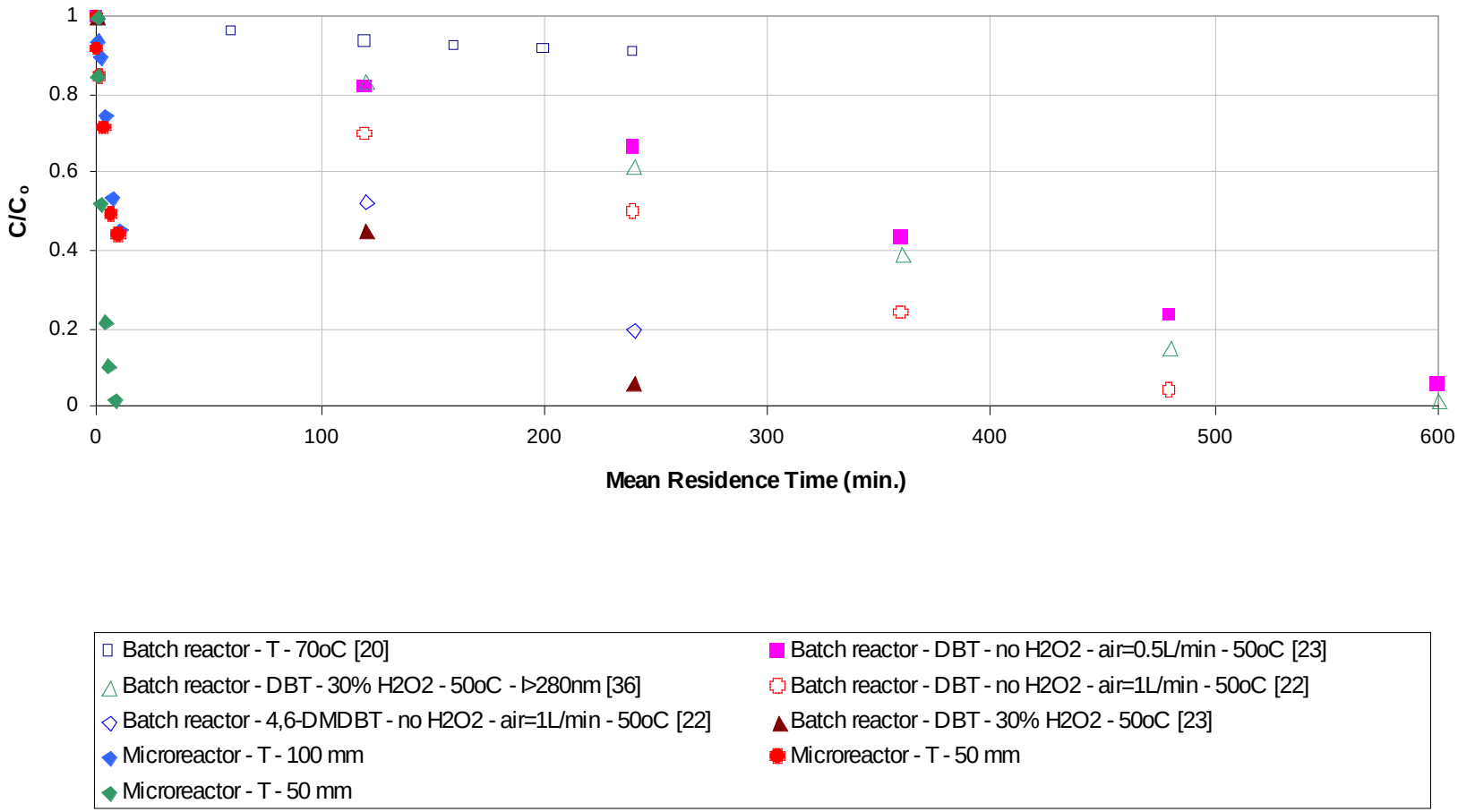
Experimental Results and Model Simulation

Model (Dibenzothiophene concentration profile at 100 μm)



Experimental Results and Model Simulation

Comparison with other researchers!



Conclusion

- **UV plays a major role in the desulfurization process of thiophene and dibenzothiophene;**
  - **No reaction is detected in the absence of UV light;**
  - **Change in the distance between UV source and microreactor substantially influences the conversion of thiophenes;**
- **Exit concentration decreases as the residence time in the microreactor increases;**
- **Mathematical model successfully predicts exit concentration of thiophene and dibenzothiophene;**
  - **Results of the mathematical model (for a first order reaction kinetics) are inline with the experimental profile of thiophene and dibenzothiophene.**

Conclusion

Dibenzothiophene is more reactive than thiophene;

The decrease in the spacer thickness of the microreactor results in better conversion;

Continuous flow *microreactor* is much more effective in desulfurization of thiophene and dibenzothiophene than a batch reactor process.

In summery:

Desulfurization of thiophene and dibenzothiophene can be realized in the microreactor by exposing thiophene and hydrogen peroxide to UV irradiation at room temperature;

The mathematical model proposed and the analytical solution obtained are accurate enough to predict the concentration in the microreactor.