Microreactor Engineering

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Dechlorination of Chlorinated Hydrocarbons

(Solid Catalyzed Reactions-Analytical Solution)

In Affiliation With:

MBI

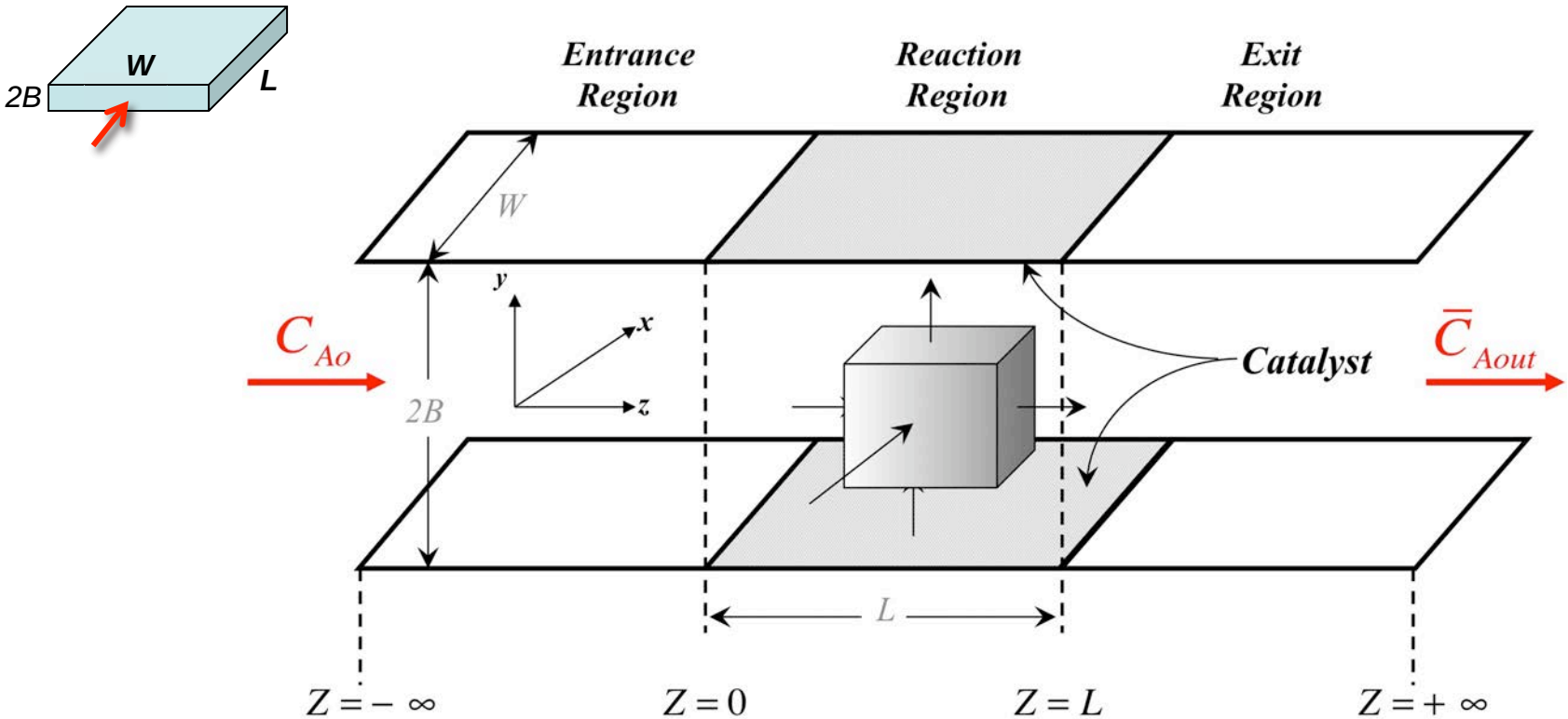
Microproducts Breakthrough Institute

PTT - LOA

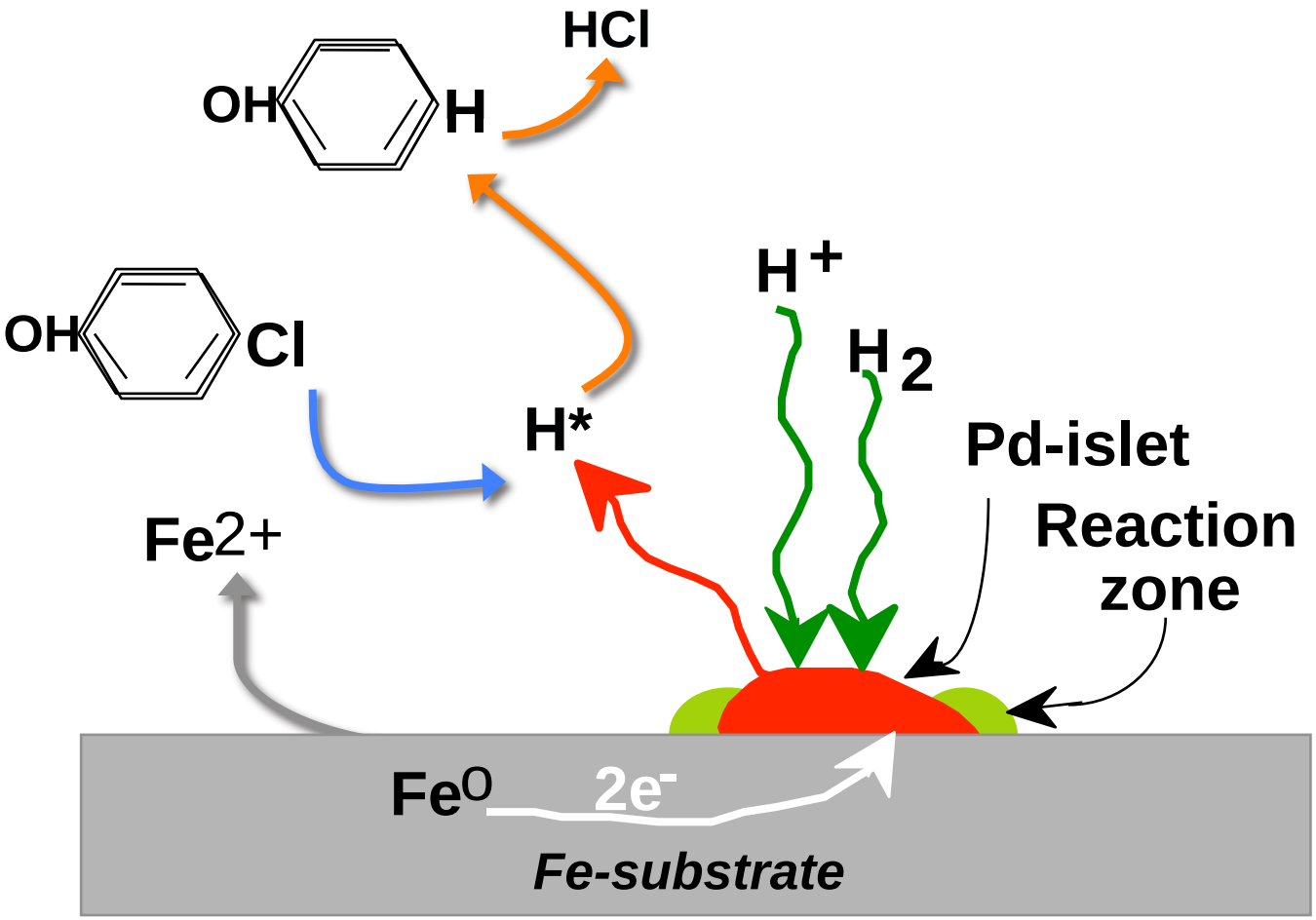
PTT - Laboratories Of America

Parallel Plate Microreactor

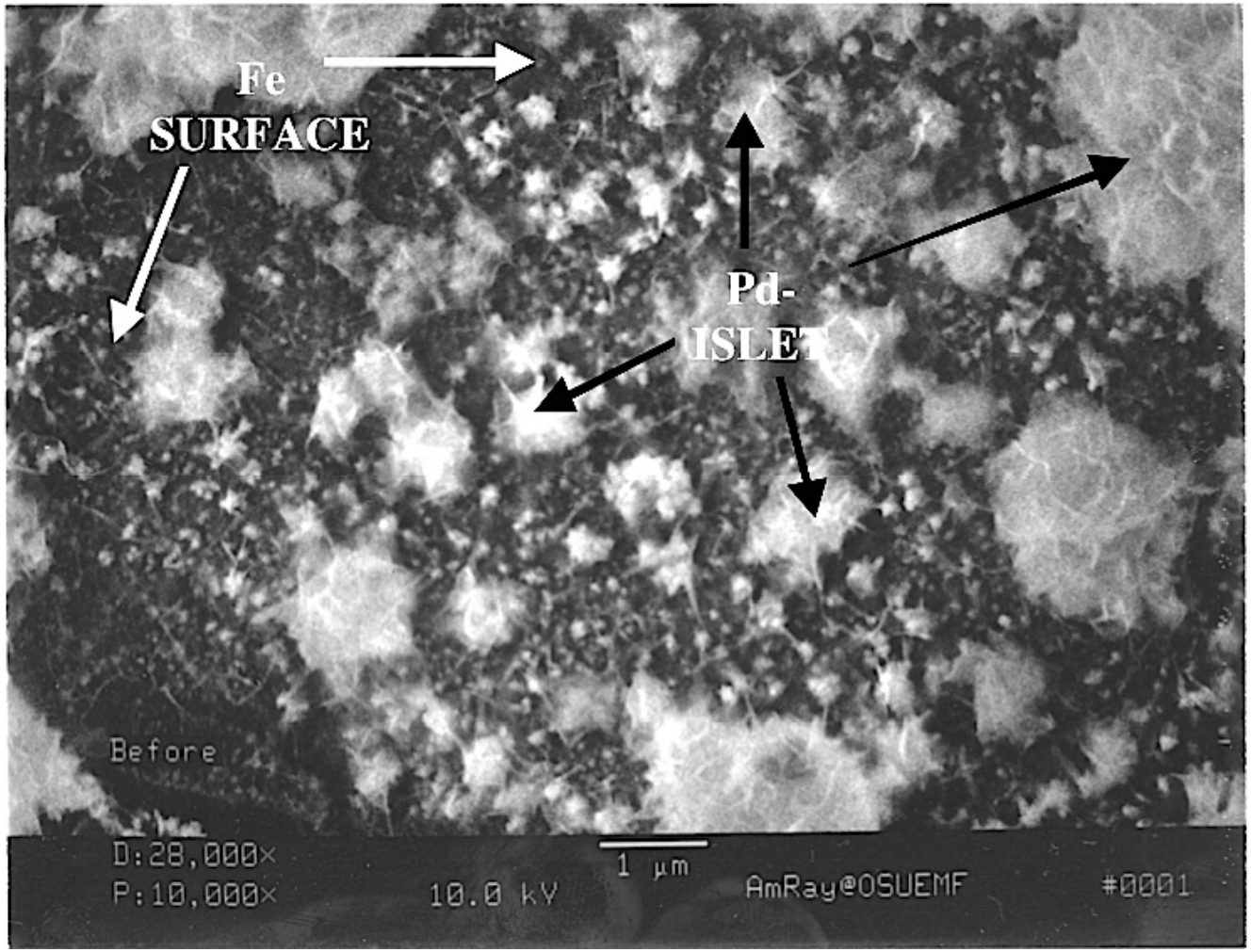
Consider a square-cross section microchannel vessel with characteristic dimensions W (width), 2B (height of approximately ≈100 μm), and length *L*; where, W>>2B and *L>>>2B.* In addition consider that a catalytic chemical reaction of known kinetics takes place at the upper and bottom walls/plates of the microreactor vessel.



Reaction Scheme



Pd Catalyst on Fe Substrate



Chemical Reactions

***Dissociation Reactions*:**

$$Fe^{o} \rightarrow Fe^{2+} + 2e^{-}$$

$$2H_2O \leftrightarrow 2H^{+} + 2OH^{-}$$

$$2HCl \rightarrow 2H^{+} + 2Cl^{-}$$

Hydrogen Radicals-Reactions:

$$2H^{+} + 2e^{-} \xrightarrow{Fe} 2H^{*} \rightarrow H_{2(g)}$$

$$2H^{+} + 2e^{-} \xrightarrow{Pd} 2H^{*} \rightarrow H_{2(g)}$$

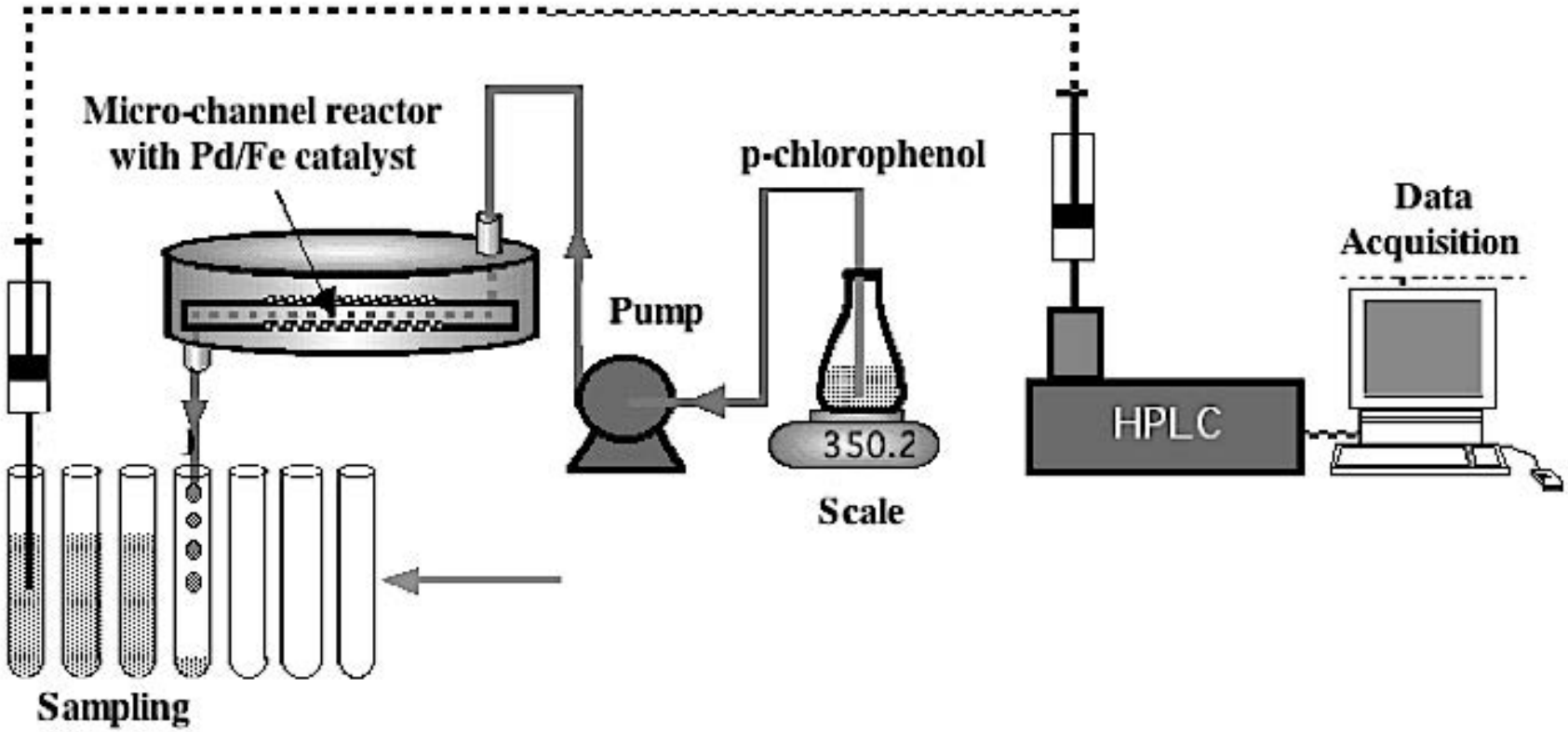
Dechlorination Reactions:

$$2H^{*} + R-Cl \longrightarrow R-H + HCl$$

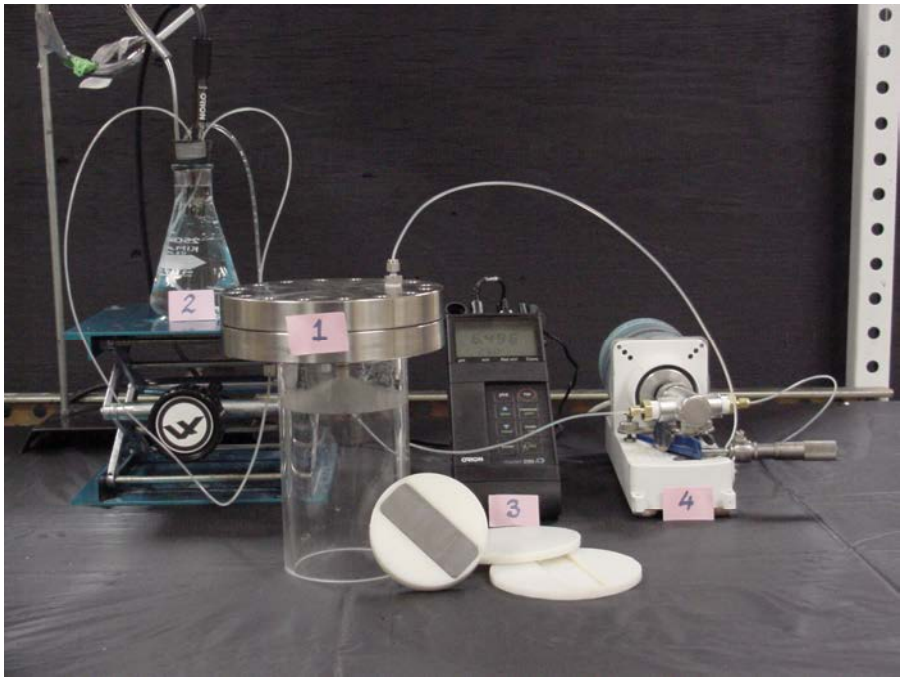
Overall Reactions:

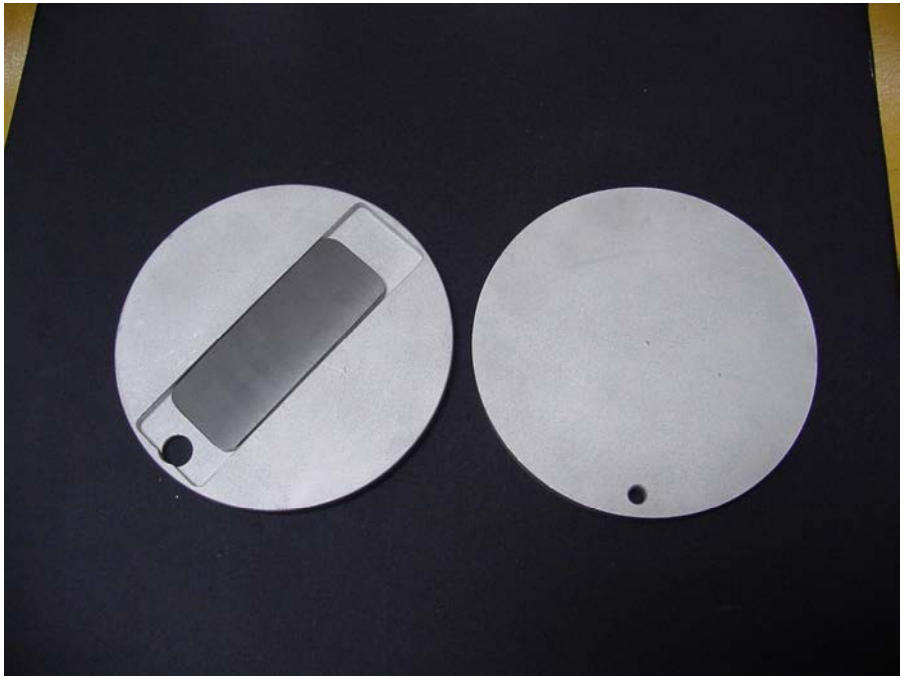
$$Fe^{o} + R-Cl + H^{+} \xrightarrow{Fe/Pd} R-H + Fe^{2+} + Cl^{-}$$

Experimental Apparatus-schematic

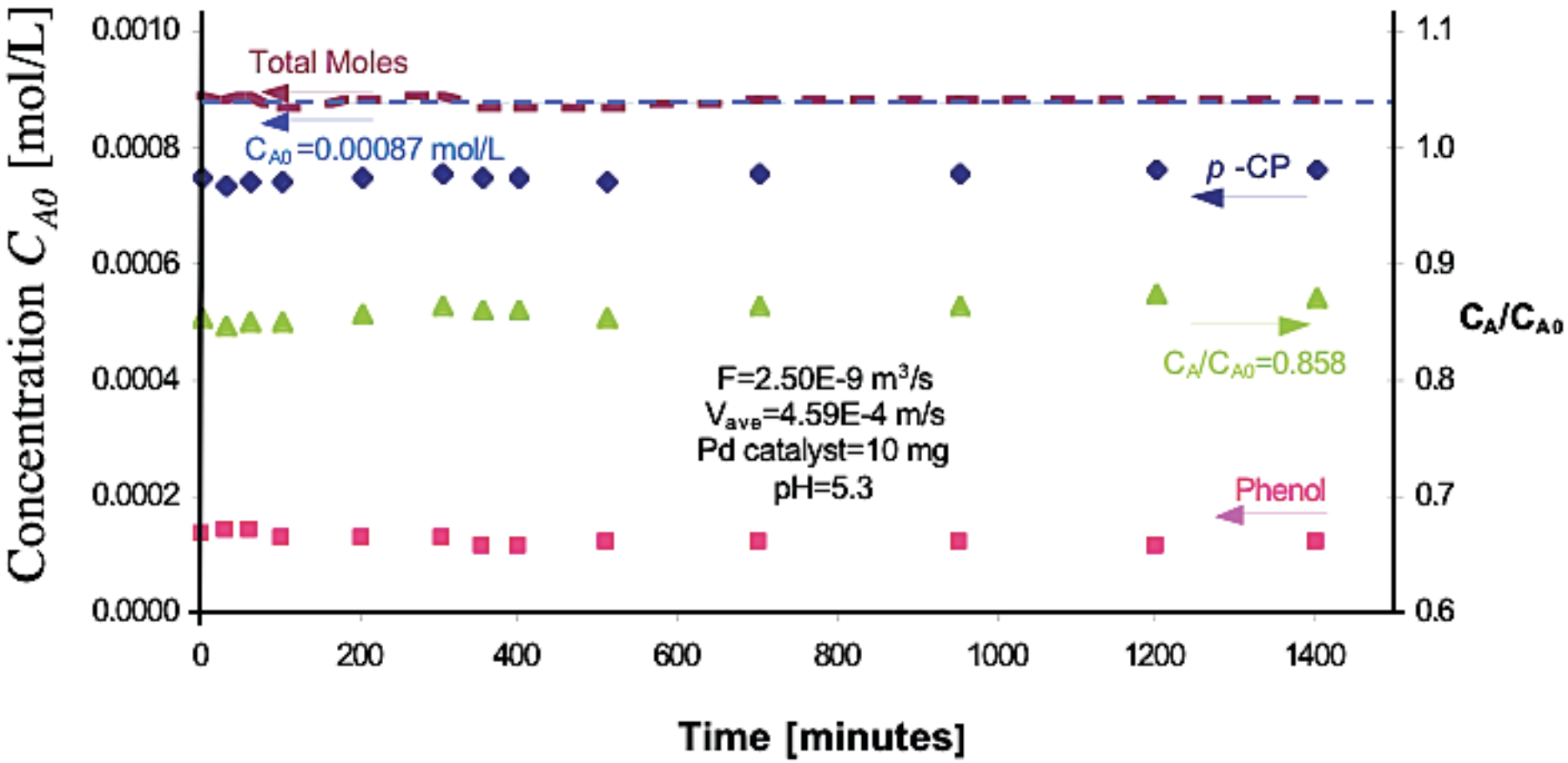


Experimental Apparatus





Experimental Data



Reaction Rate Expression

The rate of the catalytic reaction can be expressed by:

$$-r'' = -\frac{1}{S}\frac{dN}{dt} = k''C_A\left[\frac{moles\ A reacted}{m^2 cat - surface \cdot s}\right]$$

Based on catalyst Surface area

$$where\ k''\ is\ defined\ as:\ \ k''(=)\frac{m^3 reactor}{m^2 catalyst\ surface \cdot s}(=)\frac{m}{s}$$

Mathematical Model

The flow is laminar, i.e. $v_z(y) = v_m\,[1- (y/B)^2]$. The axial diffusion (in '*z*' direction) may substantially influence the axial transport of the reactant, and therefore (unlike in most macro-reactor applications), has to be added to the axial convection term in the convection/diffusion equation.

$$-v_z(y)\frac{\partial C_A}{\partial z} + D\frac{\partial^2 C_A}{\partial z^2} + D\frac{\partial^2 C_A}{\partial y^2} = 0$$

$$-V_m\left[1-\left(\frac{y}{B}\right)^2\right]\frac{\partial C_A}{\partial z} + D\frac{\partial^2 C_A}{\partial z^2} + D\frac{\partial^2 C_A}{\partial y^2} = 0$$

Scaling of Independent Variables

The reactor is divided into three regions:

Entrance region	$-\infty < z \leq 0$,
Reaction region	$0 < z < L$,
Exit region	$L \leq z < +\infty$

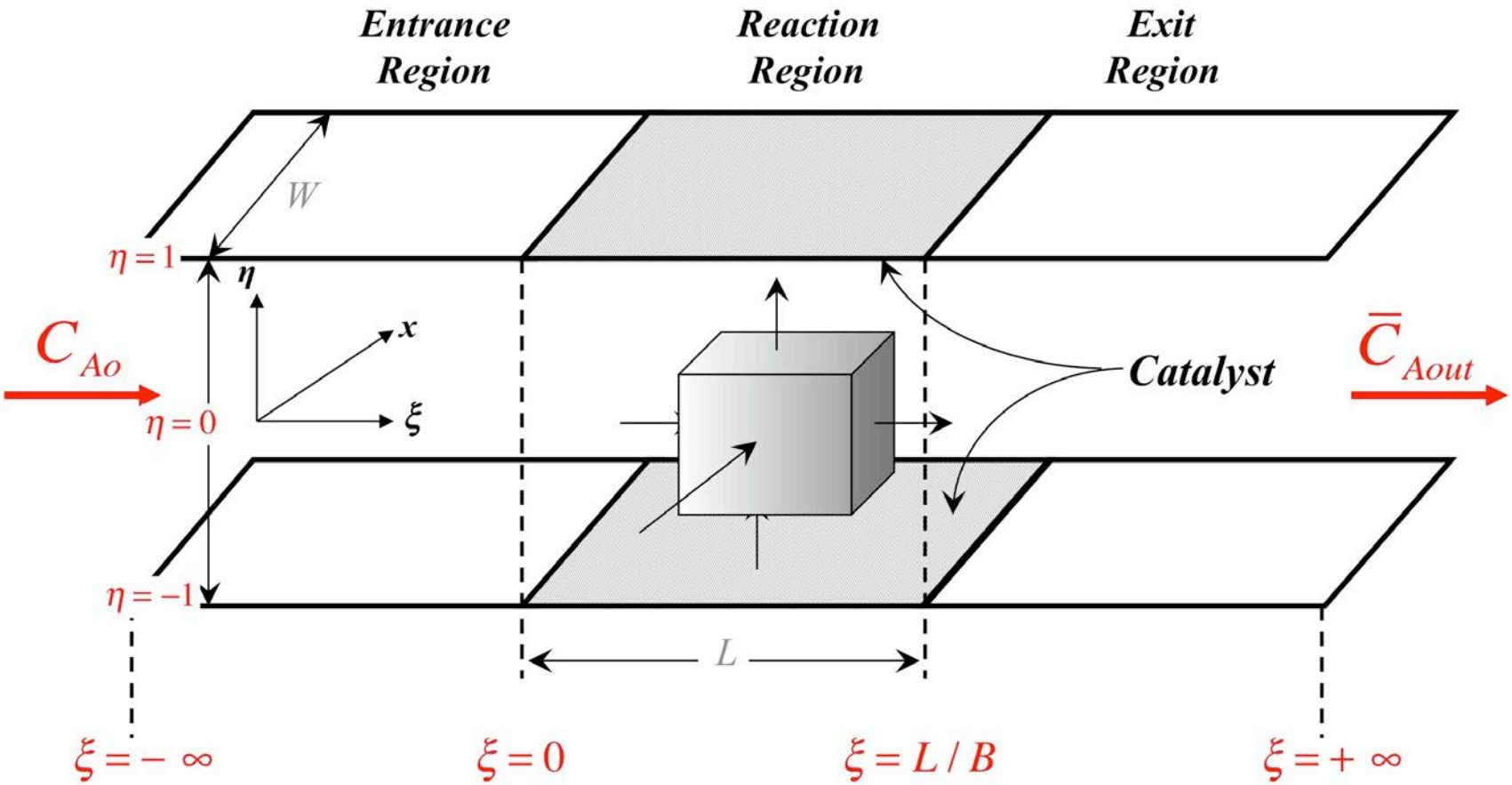
In the entrance and the exit regions only convection and diffusion take place.

However, in the reaction region convection and diffusion mass transfer is supplemented with chemical reaction, which takes place at the walls of the reactor.

It is convenient to scale axial and lateral dimensions with the characteristic length *B* of the microreactor, i.e.:

$$\eta = \frac{y}{B}; \quad \xi = \frac{z}{B}; \quad and \quad Pe = \frac{v_m B}{D}$$

Parallel Plate Microreactor-Scaled Dimensions



Scaled Concentrations

Entrance Region 1:

Define dimensionless concentration in the Entrance Region as:

$$\theta_1 = \frac{C_{Ao} - C_{A1}}{C_{Ao}} \quad in \quad \left(-\infty < z \le 0\right) \Leftrightarrow \left(-\infty < \xi \le 0\right)$$

Reaction Region 2:

Define dimensionless concentration in the Reaction Region as:

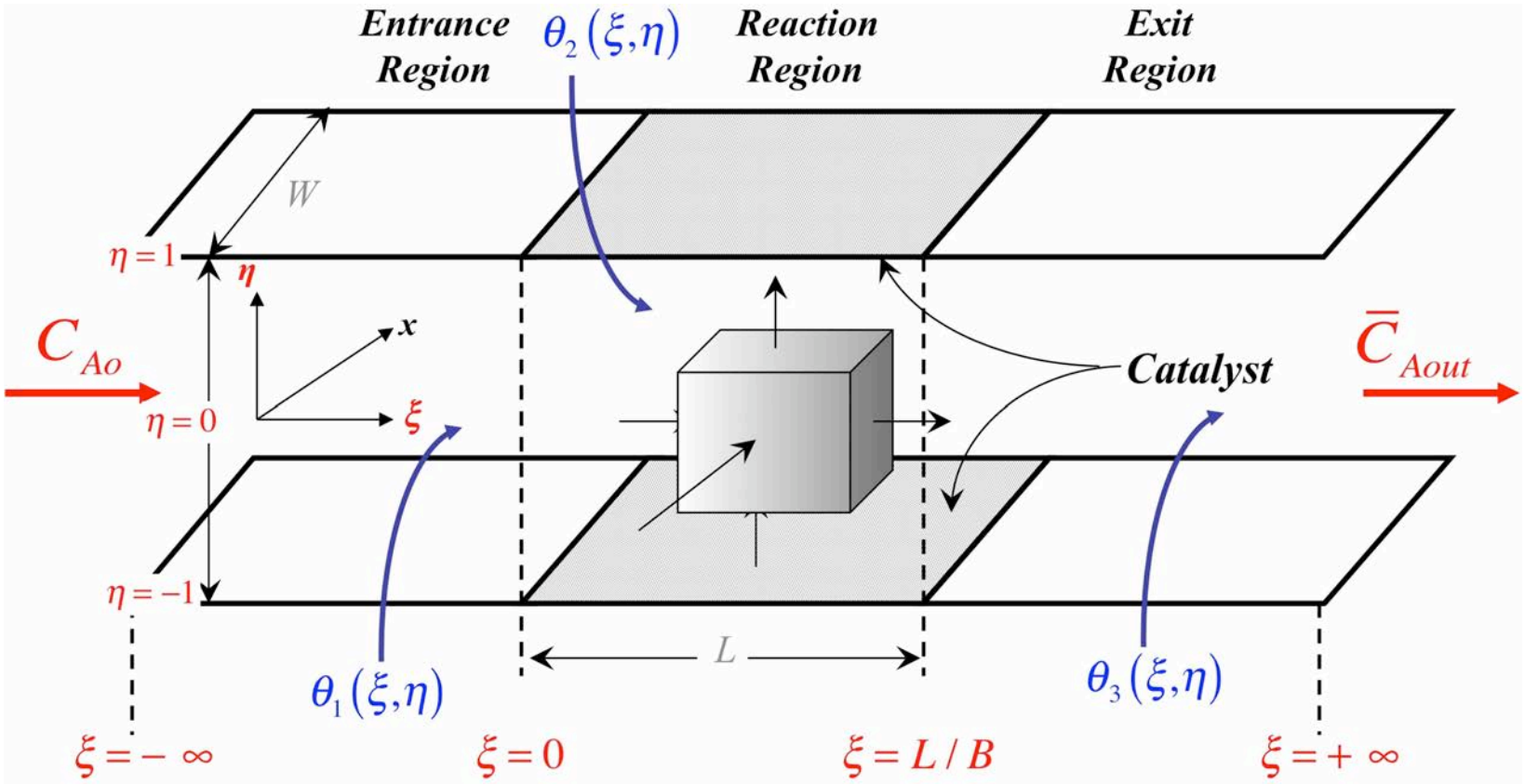
$$\theta_2 = \frac{C_{A2}}{C_{Ao}} \quad in \quad \left(0 < z < L\right) \Leftrightarrow \left(0 < \xi < L/B\right)$$

Exit Region 3:

Define dimensionless concentration in the Exit Region as:

$$\theta_3 = \frac{\bar{C}_{Aout} - C_{A3}}{C_{Ao}} \quad in \quad \left(L \le z < \infty\right) \Leftrightarrow \left(L/B \le \xi \le \infty\right)$$

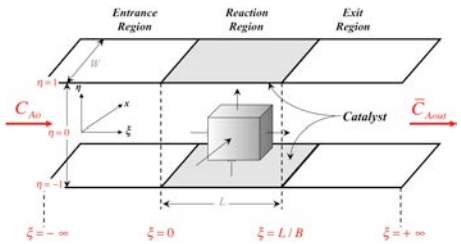
Scaled Concentrations



Entrance Region 1: $\theta_1 = \dfrac{C_{Ao} - C_{A1}}{C_{Ao}}$ in $(-\infty < z \le 0) \Leftrightarrow (-\infty < \xi \le 0)$

$$\left[1-\eta^2\right]\frac{\partial \theta_1}{\partial \xi} = \frac{1}{\mathrm{Pe}}\left[\frac{\partial^2 \theta_1}{\partial \xi^2} + \frac{\partial^2 \theta_1}{\partial \eta^2}\right] \Rightarrow \frac{L}{B}\underbrace{\left(\frac{v_m}{L}\right)}_{\frac{1}{\tau_L}}\left[1-\eta^2\right]\frac{\partial \theta_1}{\partial \xi} = \underbrace{\left(\frac{B^2}{D}\right)}_{\frac{1}{\tau_{D,B}}}\left[\frac{\partial^2 \theta_1}{\partial \xi^2} + \frac{\partial^2 \theta_1}{\partial \eta^2}\right]$$

Subject to the following boundary conditions:



Inlet condition: $C_{A1}(-\infty, y) = C_{A0} \Rightarrow \theta_1(-\infty, \eta) = 0$

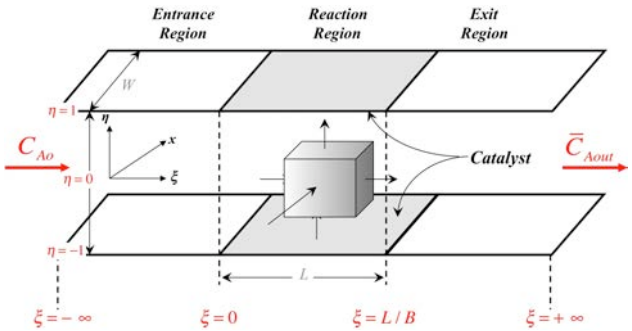
Symmetry: $\dfrac{\partial C_{A1}(z,0)}{\partial y} = 0 \Rightarrow \dfrac{\partial \theta_1(\xi,0)}{\partial \eta} = 0$

At the wall: $\dfrac{\partial C_{A1}(z, B)}{\partial y} = 0 \Rightarrow \dfrac{\partial \theta_1(\xi,1)}{\partial \eta} = 0$

Entrance Region 1: $\theta_1 = \dfrac{C_{Ao} - C_{A1}}{C_{Ao}}$ in $(-\infty < z \le 0) \Leftrightarrow (-\infty < \xi \le 0)$

Outlet condition:

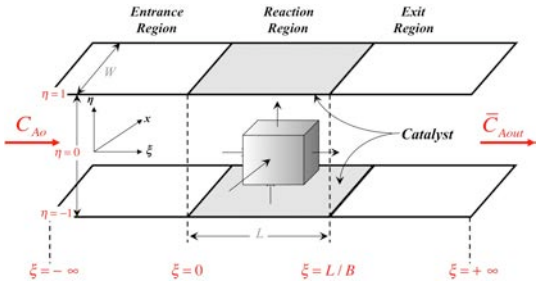
$$C_{A1}(0,y) = C_{A2}(0,y) \quad \Rightarrow \quad \theta_1(0,\eta) + \theta_2(0,\eta) = 1$$



$$\frac{\partial C_{A1}(0,y)}{\partial z} = \frac{\partial C_{A2}(0,y)}{\partial z} \quad \Rightarrow \quad \frac{\partial \theta_1}{\partial \xi}(0,\eta) + \frac{\partial \theta_2}{\partial \xi}(0,\eta) = 0$$

Reaction Region 2: $\theta_2 = \dfrac{C_{A2}}{C_{Ao}}$ in $(0 < z < L) \Leftrightarrow (0 < \xi < L/B)$

$$\left[1-\eta^2\right]\frac{\partial\theta_2}{\partial\xi} = \frac{1}{\mathrm{Pe}}\left[\frac{\partial^2\theta_2}{\partial\xi^2} + \frac{\partial^2\theta_2}{\partial\eta^2}\right]$$



Subject to the following boundary conditions:

Inlet condition:

$$C_{A1}(0,y) = C_{A2}(0,y) \quad \Rightarrow \quad \theta_1(0,\eta) + \theta_2(0,\eta) = 1$$

$$\frac{\partial C_{A1}(0,y)}{\partial z} = \frac{\partial C_{A2}(0,y)}{\partial z} \quad \Rightarrow \quad \frac{\partial\theta_1}{\partial\xi}(0,\eta) + \frac{\partial\theta_2}{\partial\xi}(0,\eta) = 0$$

Symmetry:

$$\frac{\partial C_{A2}(z,0)}{\partial y} = 0 \quad \Rightarrow \quad \frac{\partial\theta_2(\xi,0)}{\partial\eta} = 0$$

At the wall:

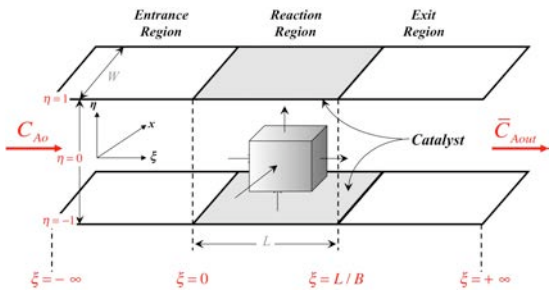
$$-D\frac{\partial C_{A2}(z,B)}{\partial y} = k'' C_{A2}(z,B) \quad \Rightarrow \quad \frac{\partial\theta_2(\xi,1)}{\partial\eta} + \frac{k''B}{D}\theta_2(\xi,1) = 0$$

Reaction Region 2: $\theta_2 = \dfrac{C_{A2}}{C_{Ao}}$ in $(0 < z < L) \Leftrightarrow (0 < \xi < L/B)$

Outlet condition:

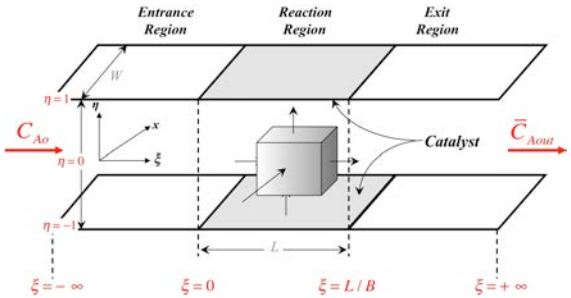
$$C_{A2}(L,y) = C_{A3}(L,y) \quad \Rightarrow \quad \theta_2\left(\frac{L}{B},\eta\right) + \theta_3\left(\frac{L}{B},\eta\right) = \frac{\bar{C}_{Aout}}{C_{A0}}$$

$$\frac{\partial C_{A2}(L,y)}{\partial z} = \frac{\partial C_{A3}(L,y)}{\partial z} \quad \Rightarrow \quad \frac{\partial \theta_2}{\partial \xi}\left(\frac{L}{B},\eta\right) + \frac{\partial \theta_3}{\partial \xi}\left(\frac{L}{B},\eta\right) = 0$$



Exit Region 3: $\theta_3 = \dfrac{\bar{C}_{Aout} - C_{A3}}{C_{Ao}}$ in $(L \le z < \infty) \Leftrightarrow (L/B \le \xi < \infty)$

$$\left[1-\eta^2\right]\frac{\partial \theta_3}{\partial \xi} = \frac{1}{\mathrm{Pe}}\left[\frac{\partial^2 \theta_3}{\partial \xi^2} + \frac{\partial^2 \theta_3}{\partial \eta^2}\right]$$



Subject to the following boundary conditions:

Inlet condition:

$$C_{A2}(L,y) = C_{A3}(L,y) \Rightarrow \theta_2\left(\frac{L}{B},\eta\right) + \theta_3\left(\frac{L}{B},\eta\right) = \frac{\bar{C}_{Aout}}{C_{A0}}$$

$$\frac{\partial C_{A2}(L,y)}{\partial z} = \frac{\partial C_{A3}(L,y)}{\partial z} \Rightarrow \frac{\partial \theta_2}{\partial \xi}\left(\frac{L}{B},\eta\right) + \frac{\partial \theta_3}{\partial \xi}\left(\frac{L}{B},\eta\right) = 0$$

Symmetry:

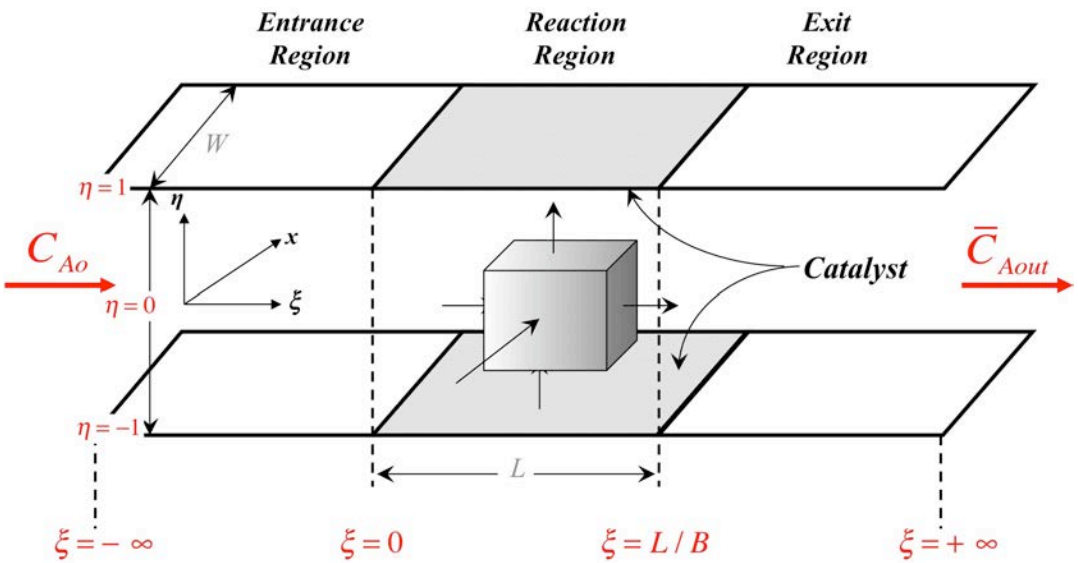
$$\frac{\partial C_{A3}(z,0)}{\partial y} = 0 \Rightarrow \frac{\partial \theta_3(\xi,0)}{\partial \eta} = 0$$

At the Wall:

$$\frac{\partial C_{A3}(z,\ B)}{\partial y} = 0 \Rightarrow \frac{\partial \theta_3(\xi,1)}{\partial \eta} = 0$$

Exit Region 3: $\theta_3 = \dfrac{\bar{C}_{Aout} - C_{A3}}{C_{Ao}}$ in $(L \le z < \infty) \Leftrightarrow (L/B \le \xi < \infty)$

Outlet condition: $C_{A3}(\infty, y) = \bar{C}_{Aout} \Rightarrow \theta_3(\infty, \eta) = 0$



Form of the Analytical Solution

Entrance Region:

$$\theta_1(\xi,\eta)=\sum_{n=1}^{\infty} A_n Y_n(\eta)\exp(\alpha_n \xi)$$

Reaction Region:

$$\theta_2(\xi,\eta)=\sum_{n=1}^{\infty} B_n X_n(\eta)\exp(-\beta_n \xi)$$

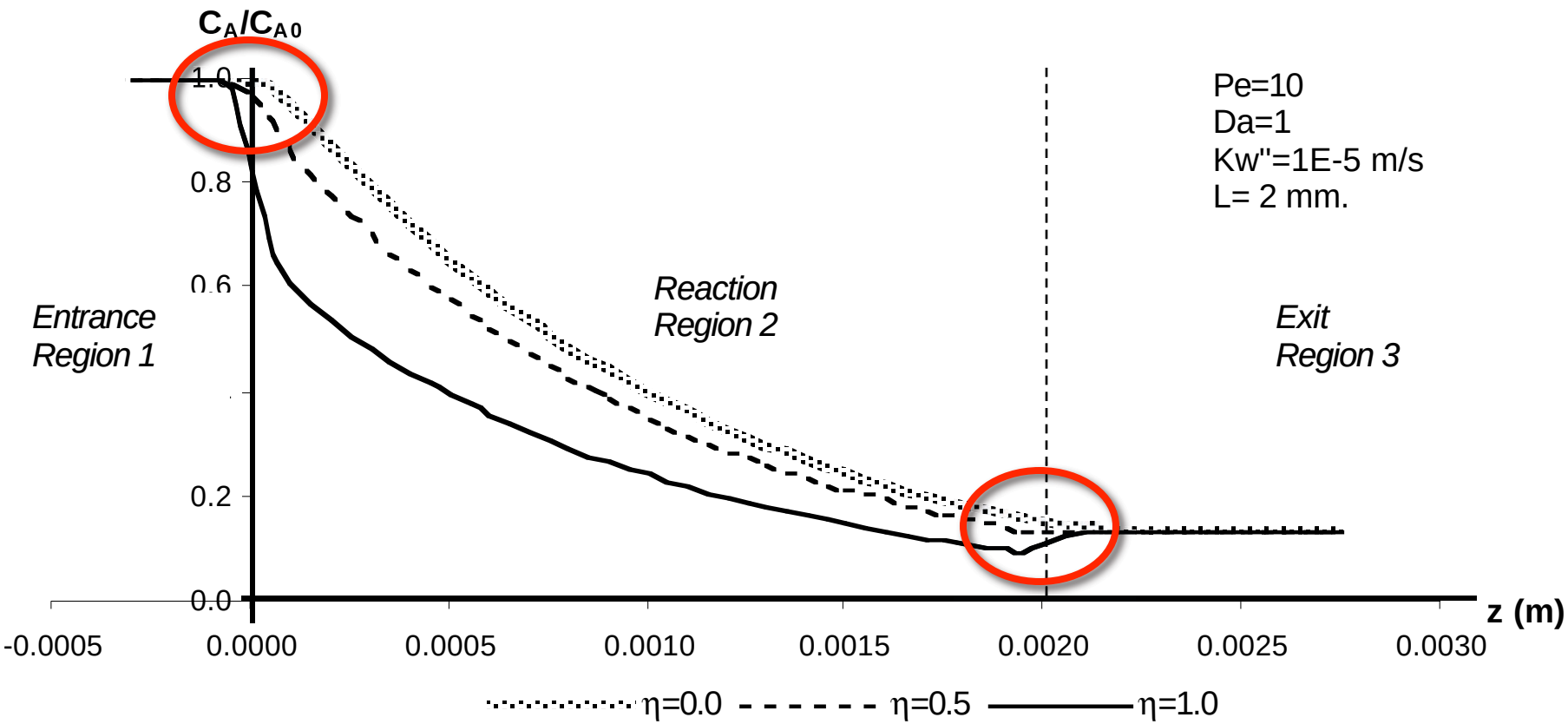
Exit Region:

$$\theta_3(\xi,\eta)=\sum_{n=1}^{\infty} C_n R_n(\eta)\exp(-\omega_n \xi)$$

$$\frac{\bar{C}_{Aout}}{C_{Ao}}=1+\frac{k''}{v_{ave}}\sum_{\mathrm{n}=1}^{2\mathrm{N}} B_{\mathrm{n}} X_{\mathrm{n}}(\eta)\Big|_{\eta=1}\left[\frac{1}{\beta_{\mathrm{n}}}\left(\exp\left(-\beta_{\mathrm{n}}\frac{L}{B}\right)-1\right)\right]$$

In all equations coefficients A_n, B_n, C_n, α_n, β_n, and ω_n are determined from boundary conditions; for details see reference (**1**) at the end of the lecture.

Analytical Solution



Evaluated reaction rate constant, *k*" values for variety of experimental conditions

Flow Rate *[ml/min]*	Half-Width *B [μm]*	Temp. *[°C]*	*k*"x10^7 *[m/s]*
0.10	100	20	3.15
0.15	100	20	3.07
0.63	100	20	3.23
0.10	100	20	3.31
0.10	50	20	3.26
0.10	100	40	7.86

References

Dechlorination of p-Chlorophenol on a Palladium Based Metal Support catalyst in a Microreactor; Experiment and Theory;
Sakrittichai, Ploenpun, *M.S. Thesis*, Oregon State University, Corvallis, Oregon, June 2001

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Goran N. Jovanovic, Polona Znidarsic–Plazl, Ploenpun Sakrittichai, Khaled AlKhaldi, *Ind. Eng. Chem. Research*, **44**(14) pp;5099-5106 (2005)

Dechlorination of p-Chlorophenol on Alginate Entrapped Bimetallic Pd/Fe Catalyst in a Magnetically Stabilized Fluidized Bed;
Lisa J. Graham, James Atwater and Goran N. Jovanovic, *AIChE Journal,* **52**(3), pp:1083-1093, (2006)