Process Intensification and Green Chemistry

Heat transfer in microreactors

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Master of Science in Chemical Engineering and Biotechnology
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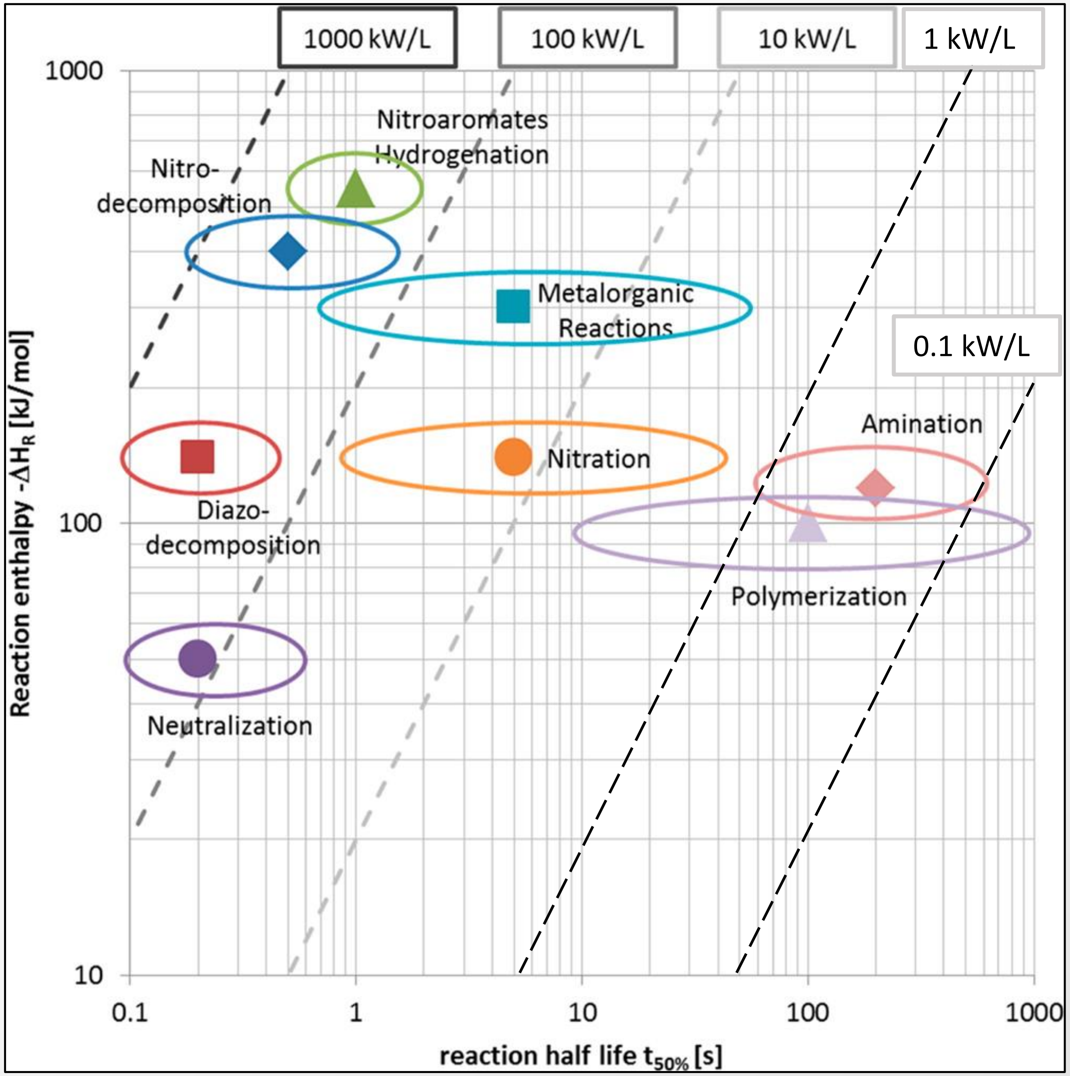
  - Estimation of reactor design for safe operation
- Multi-injection microreactors
  - Hot spot reduction for fast exothermic reactions by multi-injection.

1. Introduction

Reaction classes and heat production for fast exothermic reactions



Assumptions:

- 1^{st} order reaction
- initial reactant concentration: 1 mol/l
- estimated volumetric heat production rate:

$$\dot{q}_r = -\Delta H_r r_0 \cong -\boldsymbol{\Delta H_r} \frac{c_{1,0}}{2} \frac{1}{\boldsymbol{t_{1/2}}} \left[\frac{W}{m^3}\right]$$

adapted from: T. Westermann; L. Mleczko; Org. Process Res. Dev. 2016, 20, 487-494

Reaction classification

- **Type A**
  - Very fast ($t_r < 1s$)
  - Mostly influenced or completely controlled by the mixing process
  - Reaction and the heat production take place near the entrance in the mixing zone
  - Intensity of mixing controls the heat production
- **Type B**
  - Fast ($1s < t_r < 10\ min$)
  - Mainly kinetically controlled
  - Temperature control critical for systems with high reaction enthalpy
- **Type C**
  - Slow ($t_r > 10\ min$)
  - Normally carried out in batch
  - Microreactors may be advantageous if safety or product quality are important

Roberge (2004) Org. Process Res. Dev., 8 (6), 1049–1053.

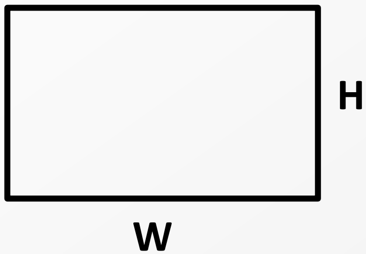
Heat management for Type A reactions

- Heat evacuation may be critical even for high volumetric heat transfer coefficient U_V
- Heat production maximal in mixing zone → hot spot formation due to limited cooling even for typical microchannel size (~500 µm)
- Strategies to reduce hot spot formation:
  1. Reduce channel diameter → increase specific interfacial area ($a \propto 1/d_h$)
     - Beware of clogging and increased Δp
  2. Use active heat exchange or mixing elements (e.g., fins or static mixers) to increase U
     - Beware of technical complexity
  3. Use high heat conducting material for microreactors to distribute heat along reactor
  4. Multi-injection: distribute reactant (thus heat production) along the channel to distribute heat along reactor

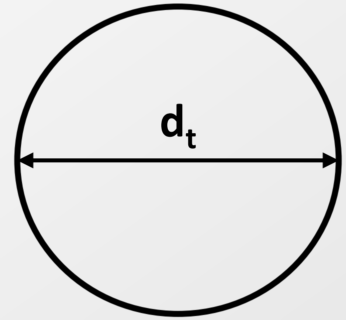
2. Heat transfer in microchannels for homogeneous systems

Heat transfer in straight micro-channels

Square



Circular



Hydraulic diameter

$$\boldsymbol{d_h} = 4\frac{\text{cross−sectional area}}{\text{wetted perimeter}} = \mathbf{2}\frac{\boldsymbol{HW}}{(\boldsymbol{H}+\boldsymbol{W})}$$

$$\boldsymbol{d_h} = 4\frac{\frac{\pi d_t^2}{4}}{\pi d_t} = \boldsymbol{d_t}$$

Specific exchange area

$$\boldsymbol{a} = \frac{2(H+W)L}{HWL} = \frac{\mathbf{4}}{\boldsymbol{d_h}}$$

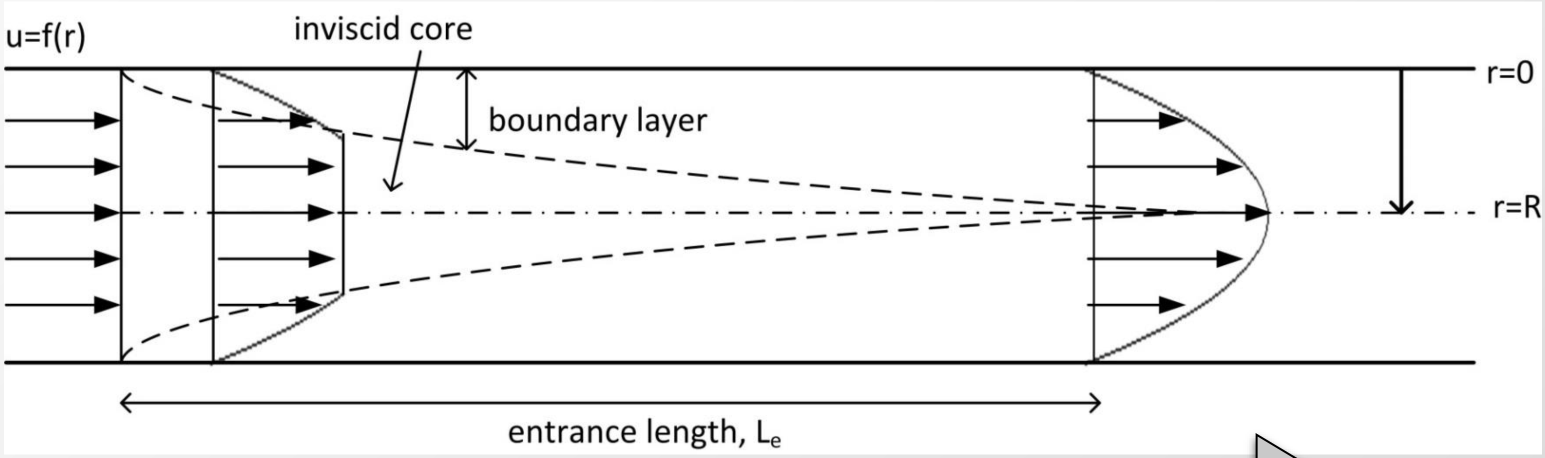
$$\boldsymbol{a} = \frac{\pi d_t L}{\frac{\pi d_t^2}{4}L} = \frac{\mathbf{4}}{\boldsymbol{d_t}}$$

Heat transfer in straight micro-channels
(Constant wall temperature)

- Convection (shell-side) characterized by Nusselt number: $Nu = \frac{h d_h}{\lambda_f}$
- The Nusselt number varies with position in the tube
- The mean Nusselt number is a function of Reynolds number, Prandtl number and geometry:

$$Nu_m = f\left(Re \cdot Pr \cdot \frac{d_h}{L}\right)$$

$$\begin{cases} Pr = \frac{\nu}{\alpha} = \frac{\mu c_p}{\lambda} \\ Re = \frac{\bar{u} d_h}{\nu} \end{cases}$$



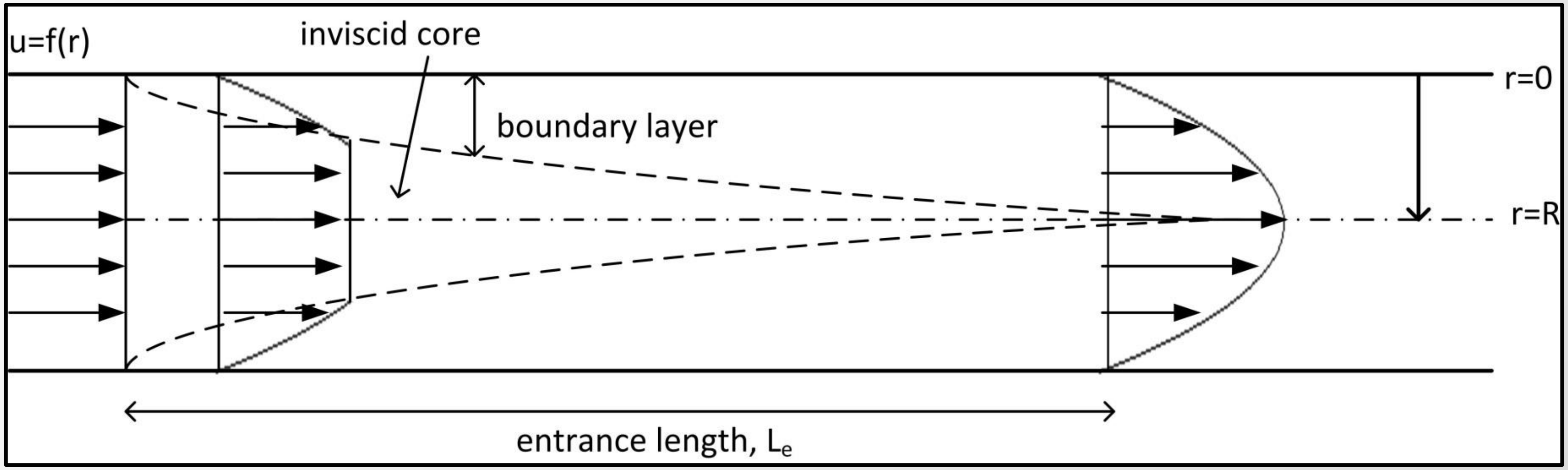
Increasing thickness of boundary layer → decreasing heat transfer rate

Heat transfer in straight micro-channels
(Constant wall temperature)

- Correlation for mean Nusselt number:

$$Nu_m = [Nu_\infty^3 + 0.7^3 + (Nu_2 - 0.7)^3 Nu_3^3]^{1/3}$$

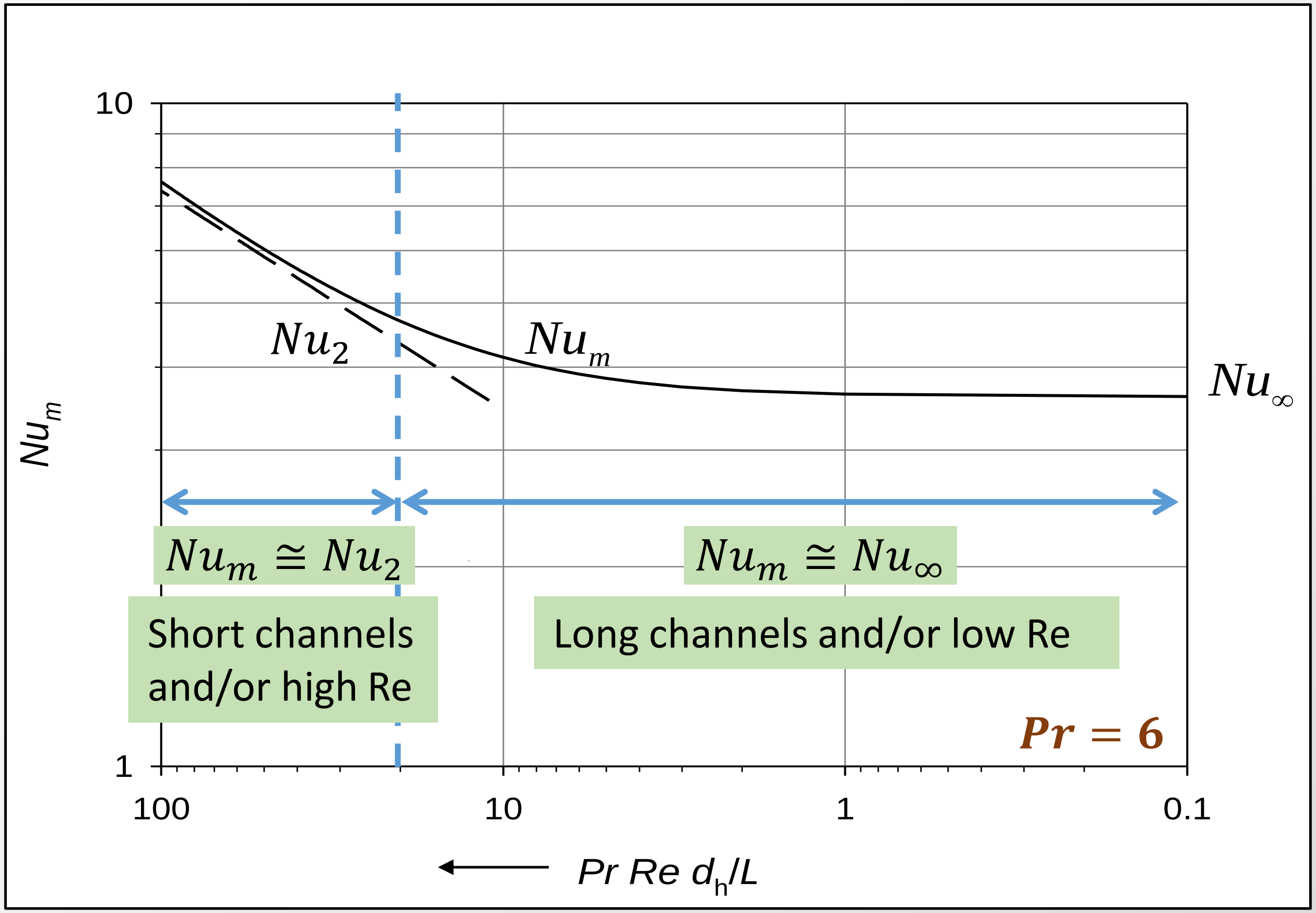
$$Nu_2 = 1.615\left(Re \cdot Pr \cdot \frac{d_h}{L}\right)^{1/3} \qquad Nu_3 = \left(\frac{2}{1 + 22\,\boldsymbol{Pr}}\right)^{1/6}\left(Re \cdot Pr \cdot \frac{d_h}{L}\right)^{1/2}$$



Development of laminar velocity profile

Nu_m as function of $Re \cdot Pr \cdot \frac{d_h}{L_c}$

$$Nu_m = [Nu_\infty^3 + 0.7^3 + (Nu_2 - 0.7)^3 Nu_3^3]^{1/3}$$



Asymptotic Nusselt number Nu_∞ for different geometries at constant wall temperature

Geometry	Nu_∞ or Sh_∞
Circular	3.66
Ellipse (width/height =2)	3.74
Parallel plates	7.54
Rectangle (height / width =0.25)	4.44
Rectangle (height / width =0.5)	3.39
Square	2.98
Equilateral triangle	2.47
Sinusoidal	2.47
Hexagonal	3.66

Cybulski, A. and J.A. Moulijn,. Catal. Rev. - Sci. Eng., 1994

Heat transfer in straight micro-channels

- Overall heat transfer coefficient:

$$\frac{1}{U} = \frac{1}{h_r} + \frac{e}{\lambda_{wall}} + \frac{1}{h_c}$$

- Assuming reactor channel is main heat transfer resistance:

$$U \cong h_r = \frac{Nu_\infty \cdot \lambda_f}{d_h} \left[\frac{W}{m^2 K}\right]$$

Long channels and/or low Re $\rightarrow Nu_m \cong Nu_\infty$

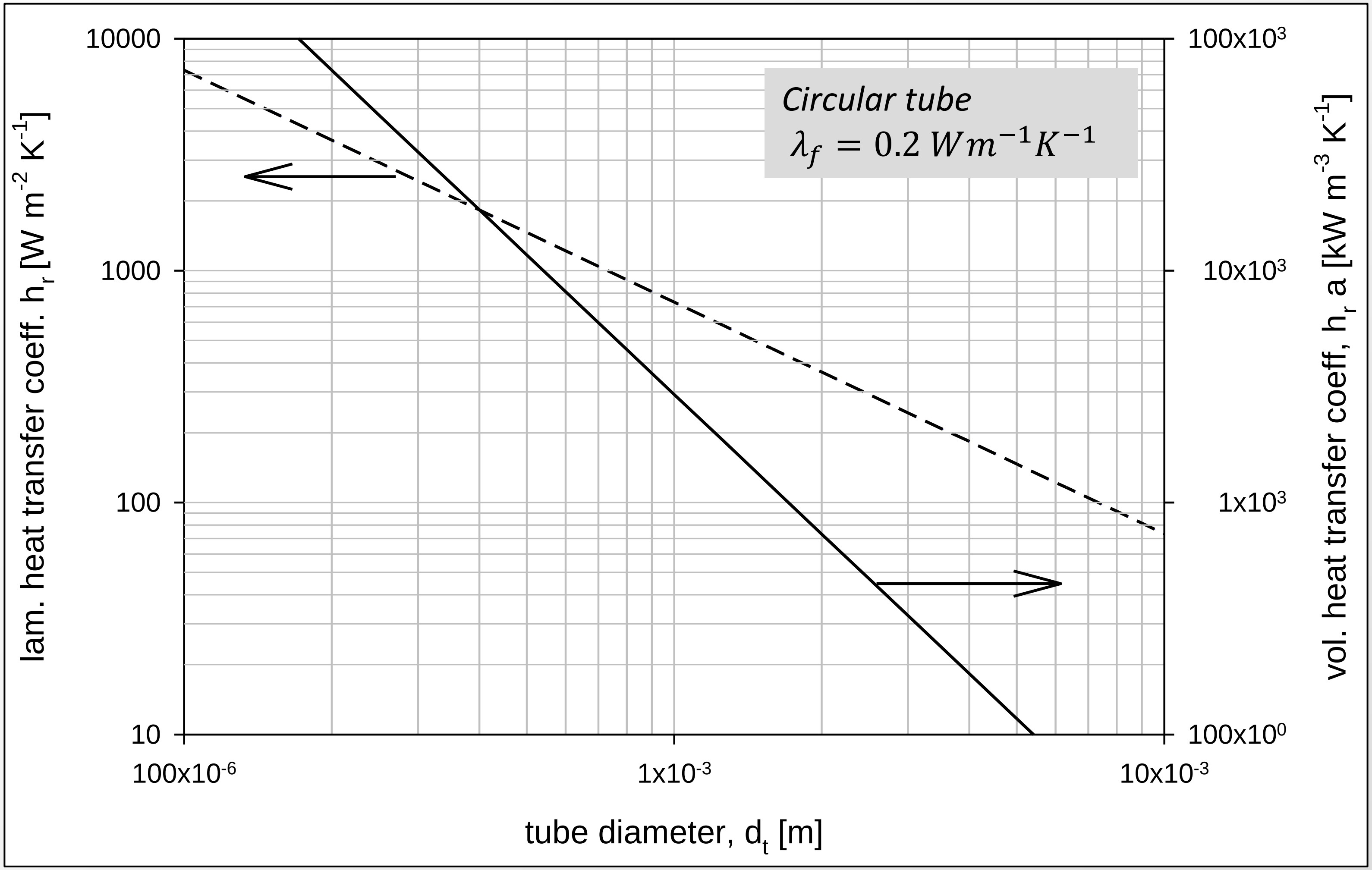
- For circular tubes with fully developed laminar profile:

$$Nu_\infty = 3.66$$

- Volumetric heat transfer coefficient:

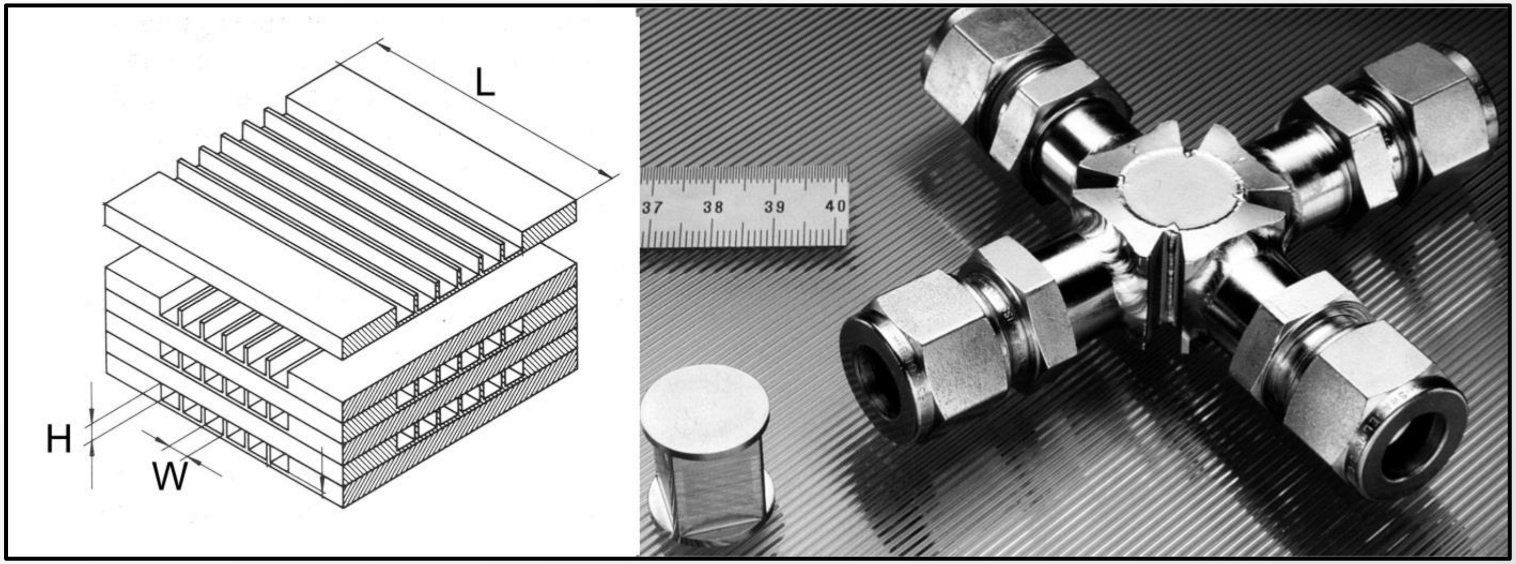
$$\boldsymbol{U_V} = Ua = U\frac{A}{V} = h_r\frac{A}{V} = \frac{Nu_\infty \cdot \lambda_f}{d_t}\frac{4}{d_t} = 14.6\frac{\lambda_f}{\boldsymbol{d_t^2}}\left[\frac{W}{m^3 K}\right]$$

Heat transfer in straight micro-channels



Heat transfer in straight micro-channels

Crosscurrent arrangement of reaction and cooling channels

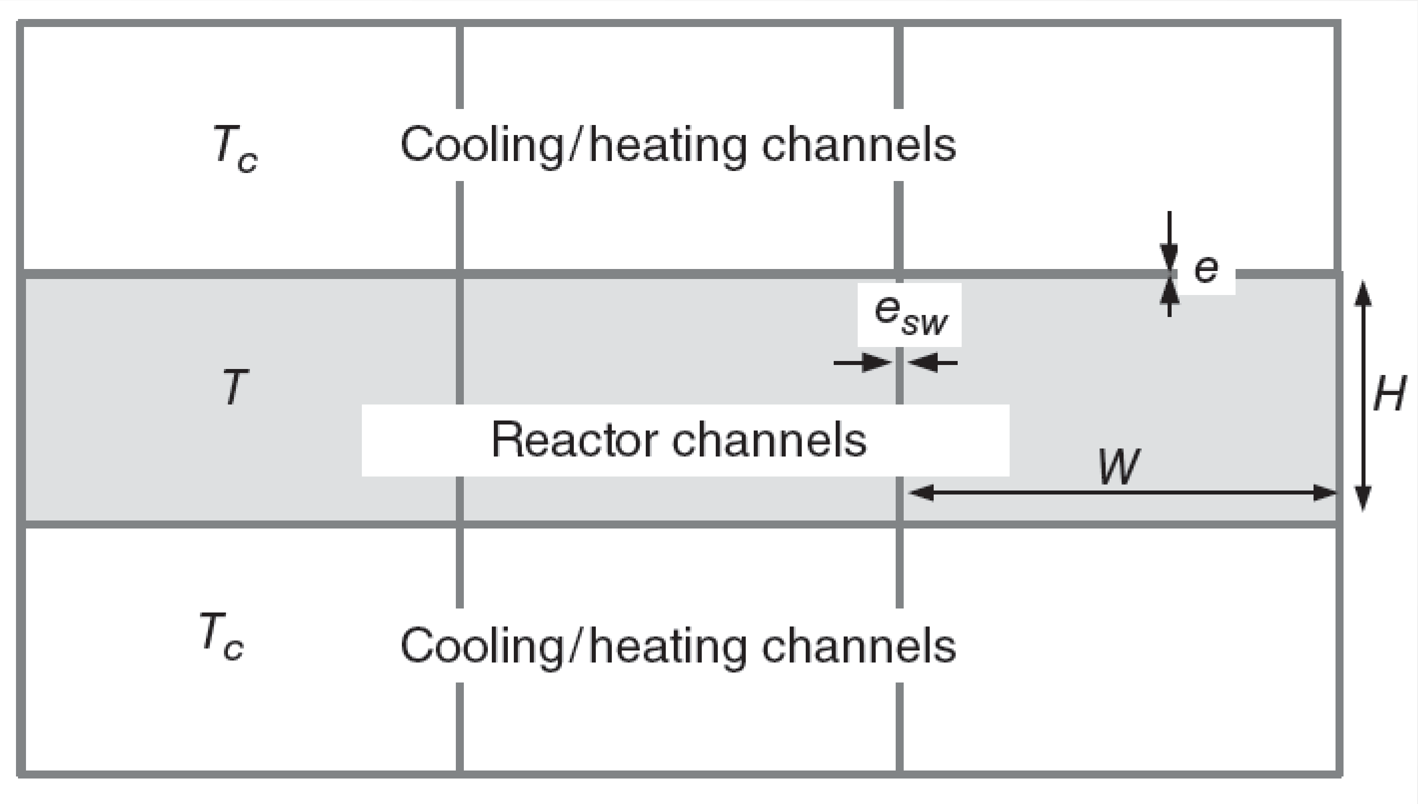


Microstructured heat exchanger/reactor (Karlsruher Institut für Technologie)

Bier, W., et al., Chemical Engineering and Processing, 1993. **32**(1): p. 33-43.

Heat transfer in straight micro-channels

Alternate arrangement of reaction and cooling channels



Heat transfer in straight micro-channels

Thin walls

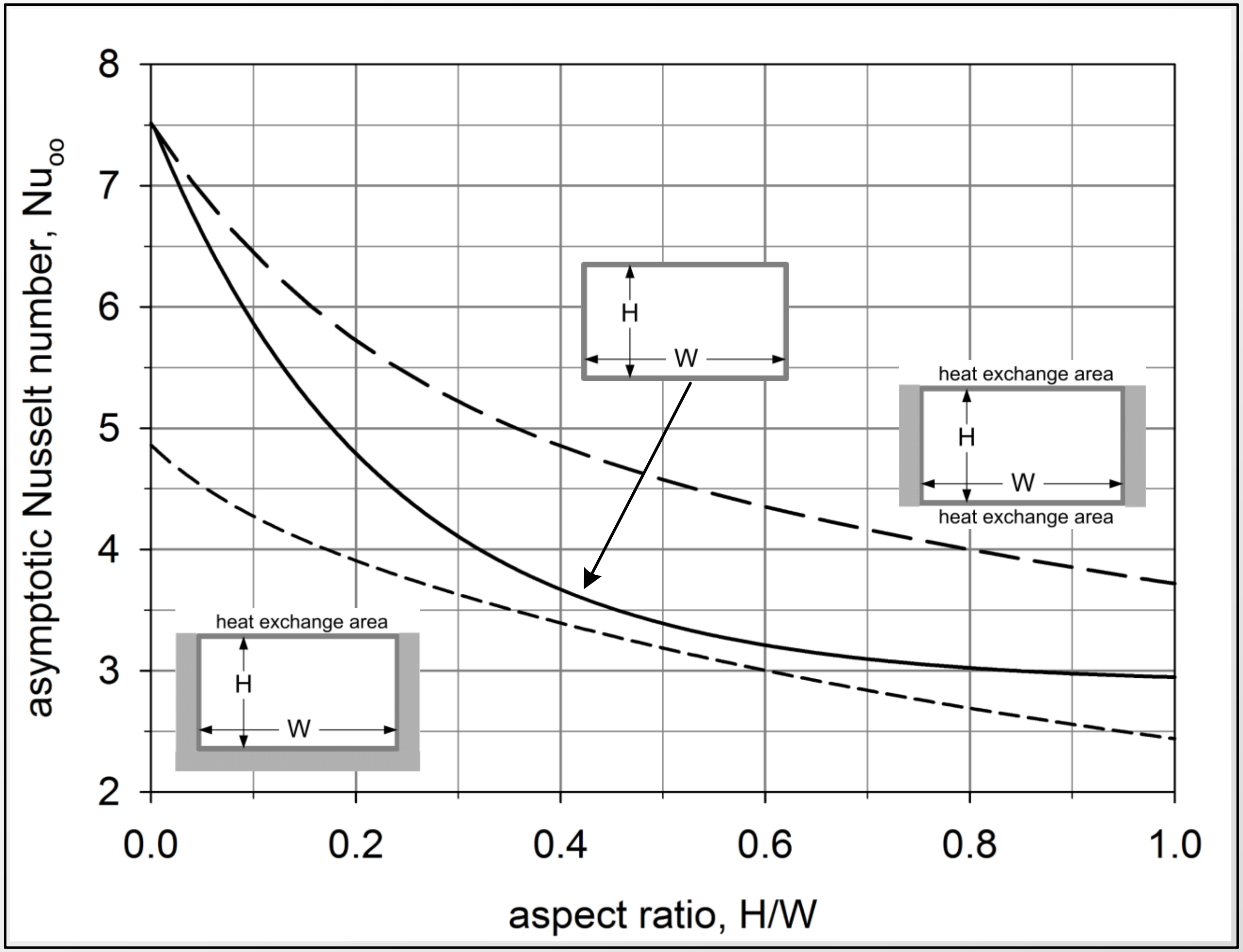
- Alternate arrangement of heating and cooling channels
  - **Thin walls** between reaction channels ($e_{sw} \ll H \text{ and } W$) → no heat evacuation through walls separating reaction channels

$A_{HEX} = 2 \cdot N \cdot W \cdot L$(cooling on two sides)

$A_{HEX} = N \cdot W \cdot L$(cooling on one side)

Nu_∞ in rectangular channels as a function of aspect ratio 1, 2 and 4 thin cooled or heated walls with constant wall temperature

Slit channel: H/W → 0



Values taken from: Hartnett, J.P. and M. Kostic, Advances in heat transfer, 1989.

Heat transfer in straight micro-channels

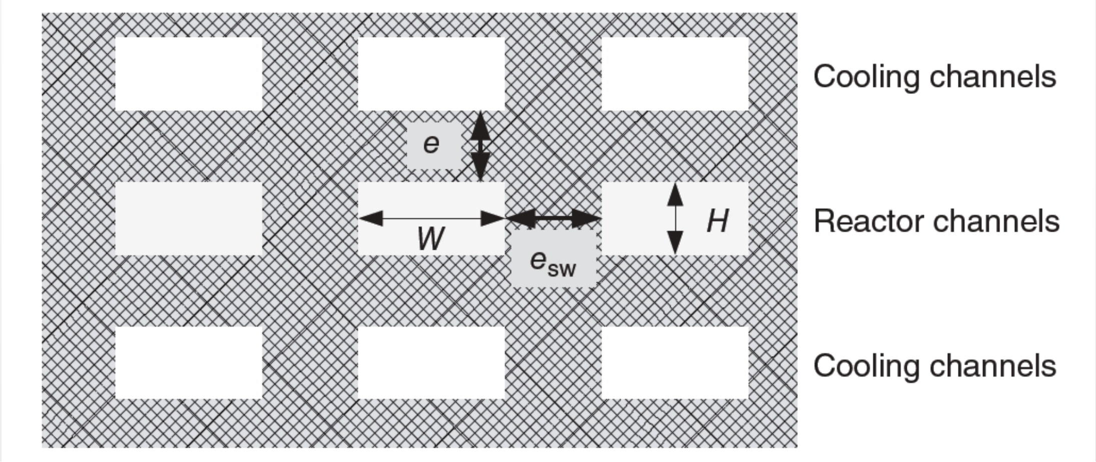
Optional

Thick walls: approach 1

- Very thick channel walls → adiabatic behavior between two channels not valid
- Inter-channel walls contribute to heat exchange → included in heat exchange area
- Effective exchange area A_{eff} estimated by including the heat conductivity λ_{wall} into the side walls of thickness e_{SW}
- In general $0.8 < \eta_{SW} < 1$

$$\eta_{SW} = \frac{tanh\left(H/2\sqrt{2h_r/(\lambda_{wall}\, e_{SW})}\right)}{H/2\sqrt{2h_r/(\lambda_{wall}\, e_{SW})}}$$

$$A_{eff} = (W + H\,\eta_{SW})L$$



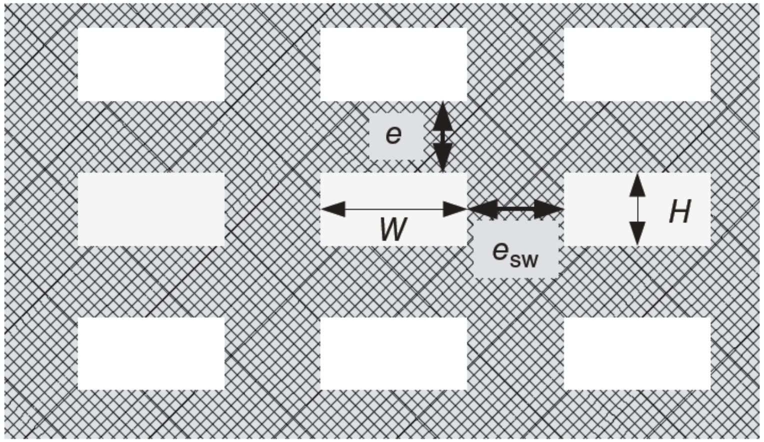
Heat transfer in straight micro-channels

Optional

Thick walls: approach 2

- Alternate arrangement of heating and cooling channels
  - **Thick walls** ($e_{sw} \approx H\ and\ W$) → some heat evacuation through walls separating reaction channels → increased heat exchange area

$$A_{HEX} \cong N(e_{sw} + W)L \text{ (cooling on one side)}$$

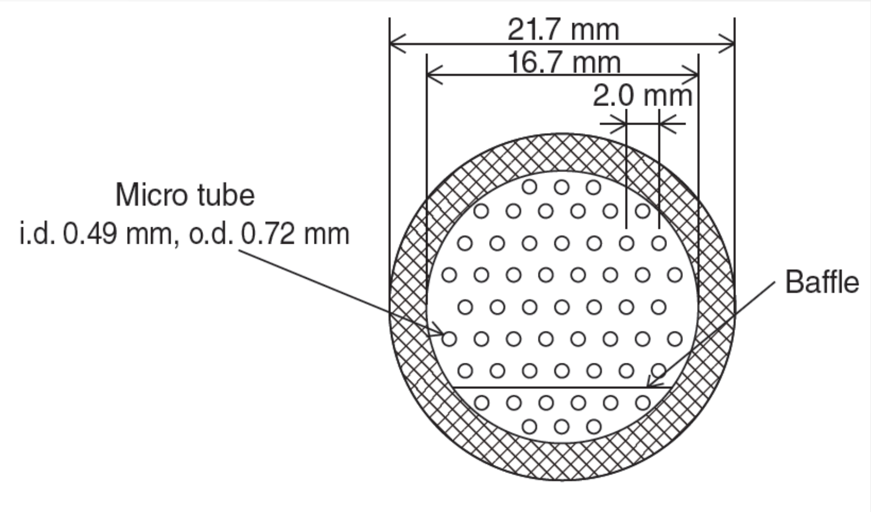


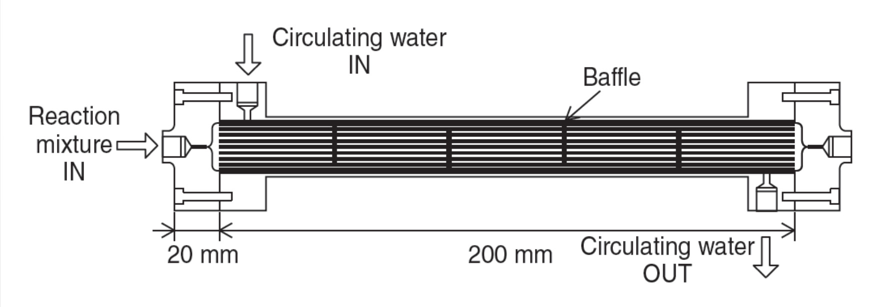
Shell-and-tube micro heat exchangers

- Internal heat transfer coefficient (short microchannels):

$$Nu \cong Nu_2 = 1.615\left(Re \cdot Pr \cdot \frac{d_h}{L}\right)^{1/3}$$

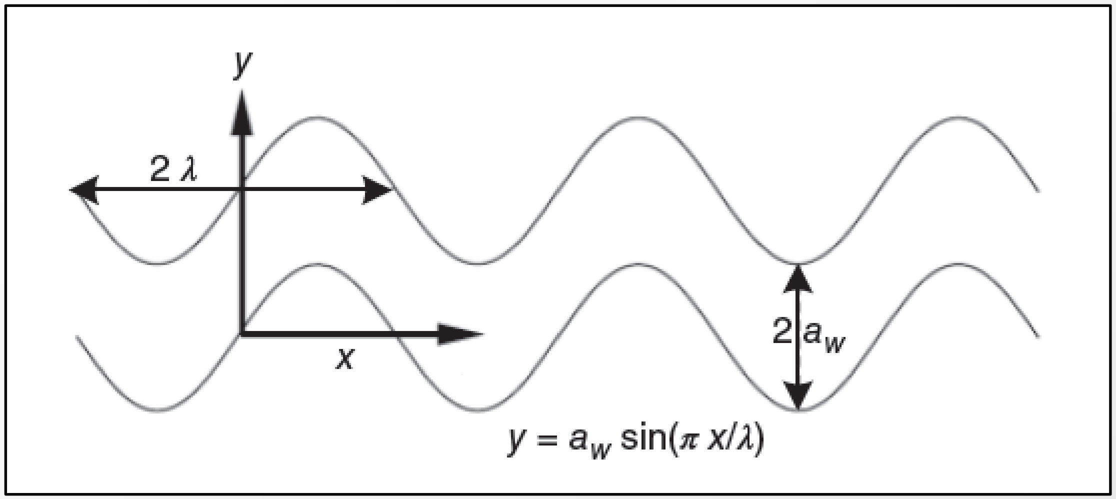
- $h_{external} = f(flow\ regime, tube\ arrangement, baffles)$
- Small-scale systems: capillaries submerged in constant temperature baths often used → usually external heat transfer limitation





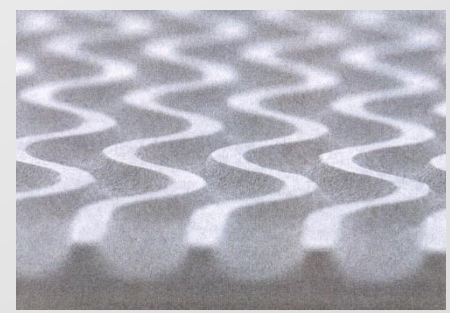
Curved channel geometry

- Heat transfer can be substantially improved by using zig-zag or curved microchannels
- Example for sinusoidal corrugated-plate channels*:



Parallel-plate channel with sinusoidal wall waviness

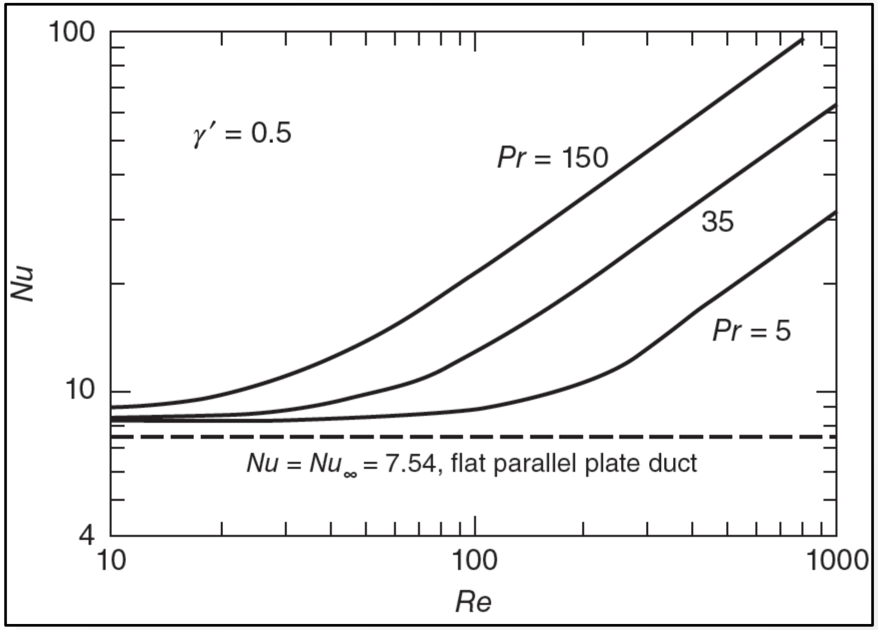
- Wall corrugation aspect ratio $\gamma' = 4\frac{a_w}{\lambda''}$
- Wall waviness a_w
- Corrugation wave length λ''



Example: Sinusoidal channels etched in stainless steel (160 µm wide, 60 µm deep)

**Metwally and Manglik (2004) Int. J. Heat Mass Transfer, 47 (10–11), 2283–2292.*

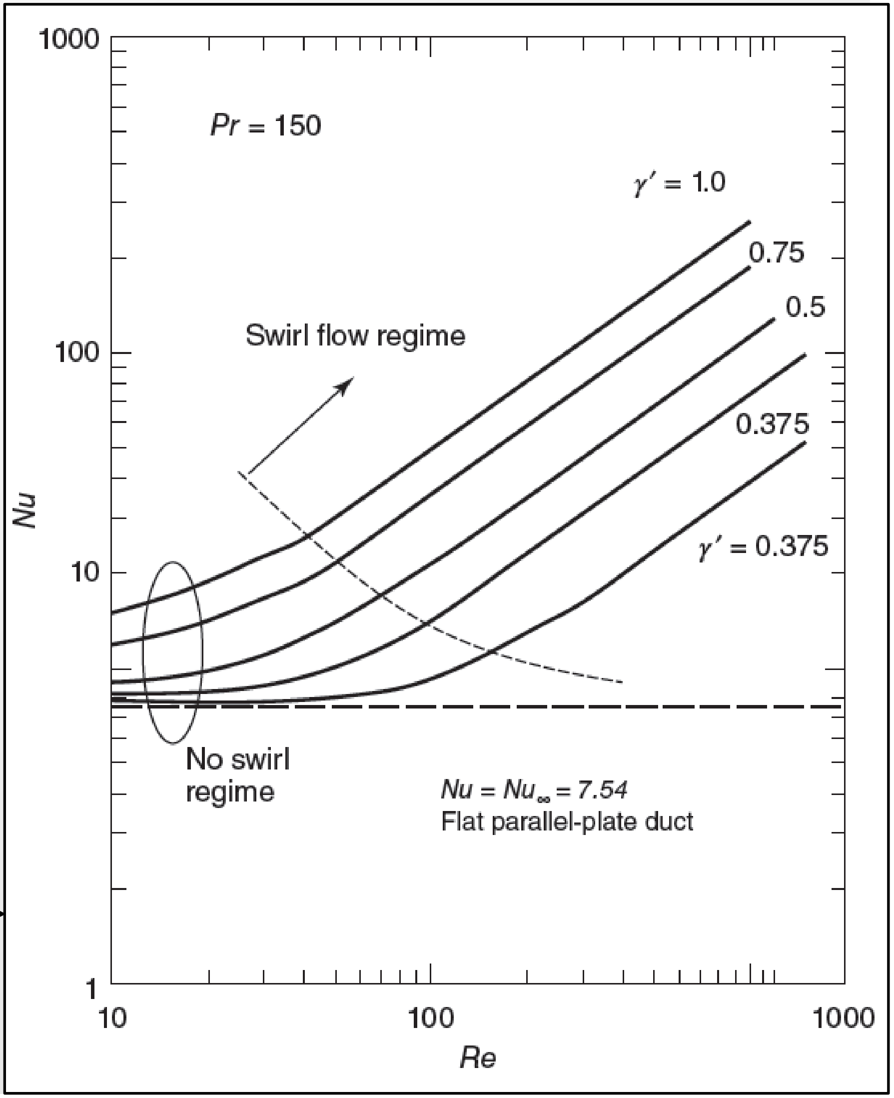
Curved channel geometry



Viscous liquids ($\mathrm{Pr} = 150$) → ~ one order of magnitude heat transfer performance increase *vs* slit channel

Significant performance increase for $Re >$ ~ 100 (swirl flow regime)

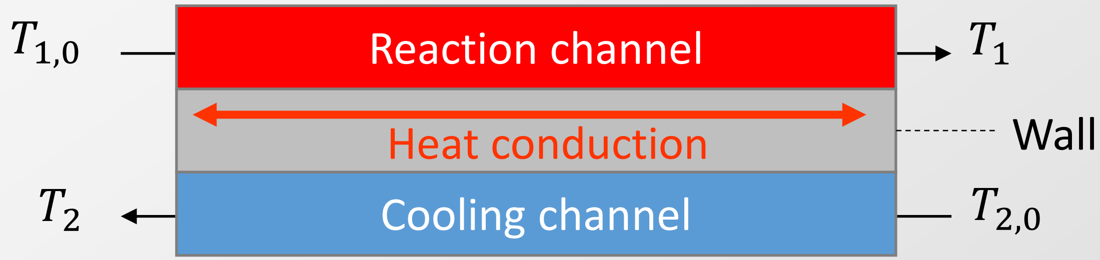
Metwally and Manglik (2004) Int. J. Heat Mass Transfer, 47 (10–11), 2283–2292.



Micro heat exchangers for gas-gas systems

- Microreactors: thickness of channel walls often close to channel size → axial heat conduction along channel walls cannot be neglected
- Particularly important for (but not limited to) gas-gas heat exchange
- Heat exchanger efficiency:

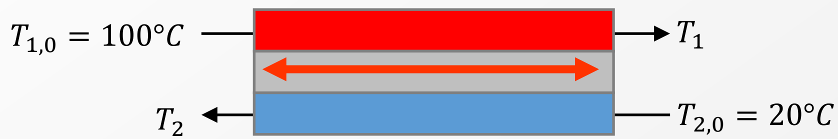
$$\eta_{HEX} = \frac{T_{1,0} - T_1}{T_{1,0} - T_{2,0}} = \frac{T_{2,0} - T_2}{T_{1,0} - T_{2,0}}$$

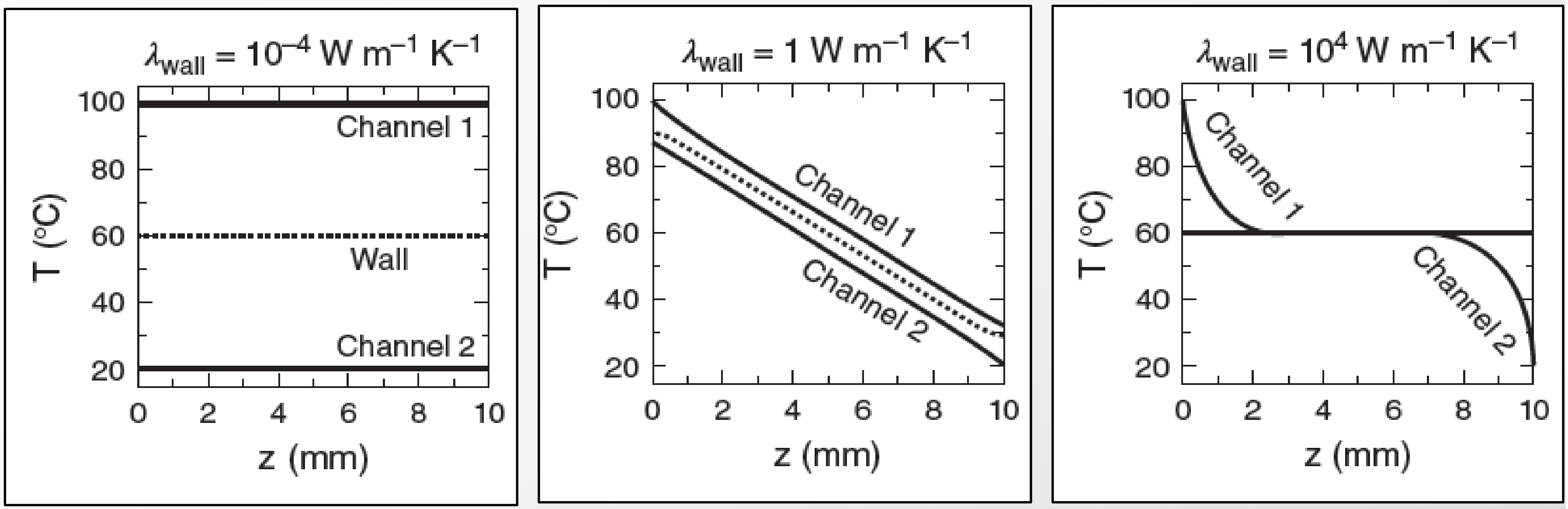


Stief et al, (1999) Chem. Eng. Technol., ***22*** *(4), 297–303*

Micro heat exchangers for gas-gas systems

Temperature profiles as a function of wall thermal conductivity





Low λ_{wall}: no heat exchange → temperature stays constant in channels

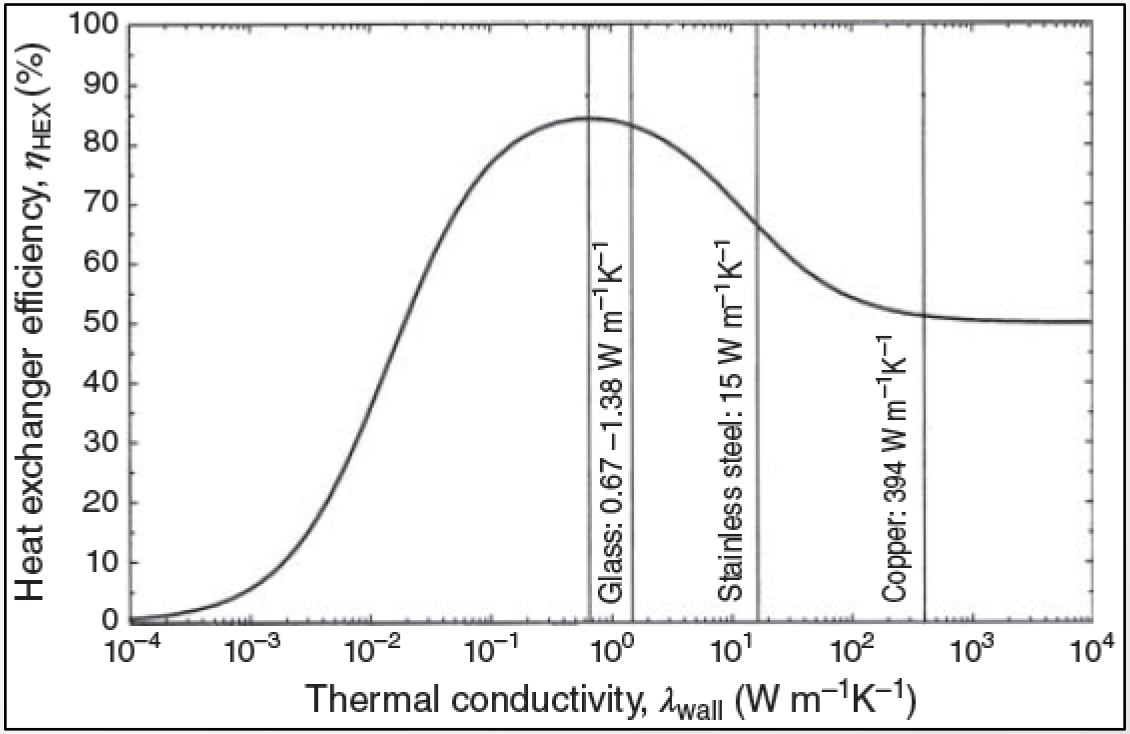
Medium λ_{wall} → almost linear temperature profiles

High λ_{wall}: constant wall temperature → fast temperature change at channels entrance

*Stief et al, (1999) Chem. Eng. Technol., **22** (4), 297–303*

Micro heat exchangers for gas-gas systems

Temperature profiles as a function of wall thermal conductivity

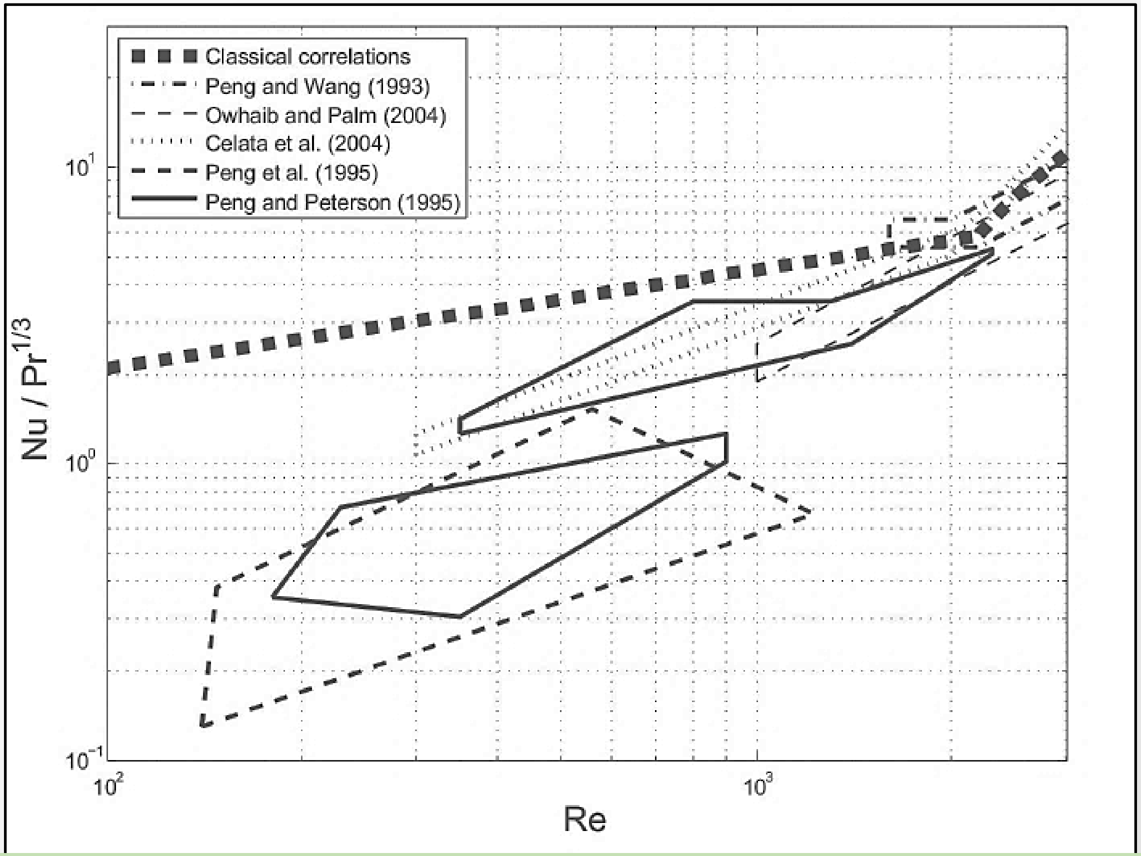


High λ_{wall} → constant wall material temperature → same efficiency as co-current heat exchanger ($\eta_{HEX} = 50\%$ at equal volumetric flowrates of the same fluid in both channels)

Gas-to-gas micro heat exchangers: use materials with low λ_{wall} (e.g., glass or polymers) to maximize heat transfer efficiency

Stief et al, (1999) Chem. Eng. Technol., 22 (4), 297–303

Predicted vs measured Nu in microchannels under laminar conditions for liquid systems



$Nu_{obs} < Nu_{pred}$: potentially due to longitudinal heat conduction in the channel walls, which decreases thermal gradients and artificially reduces the values of the observed Nu

Aubin et al., "Process Intensification by Miniaturization", in Poux, M. (Ed.), Cognet, P. (Ed.), Gourdon, C. (Ed.). (2015). Green Process Engineering. Boca Raton: CRC Press.

General approach for complex geometries

- Use of an overall volumetric heat transfer coefficient U_V

$$\dot{Q} = U_V V_R (T_c - T)$$

- U_V determined experimentally using a non-reactive system
- $U_V \geq 10^6 W m^{-3} K^{-1}$ for type A reactions

Kockmann and Roberge (2009) Chem. Eng. Technol., 32 (11), 1682–1694.

Characteristic times for convectional heat transfer
Microreactor *vs* jacketed stirred tank

$$t_{heat} = \frac{\rho c_p}{h}\left(\frac{V}{A}\right) = \frac{\rho c_p}{\lambda}\frac{R^2}{Nu}$$

Microreactor		Jacketed stirred tank	
$\boldsymbol{R}$	$\boldsymbol{t_{heat}}$	$\boldsymbol{V}$	$\boldsymbol{t_{heat}}$
$100\ \mu m$	$19\ ms$	$0.1\ m^3$	$38\ min$
$1\ mm$	$1.9\ s$	$1\ m^3$	$1.4\ h$
$10\ mm$	$190\ s$	$6\ m^3$	$2.5\ h$

Physical properties: $\lambda = 0.6\ W\ m^{-1}K^{-1}$ $\quad c_p = 4.186\ J\ kg^{-1}K^{-1}$

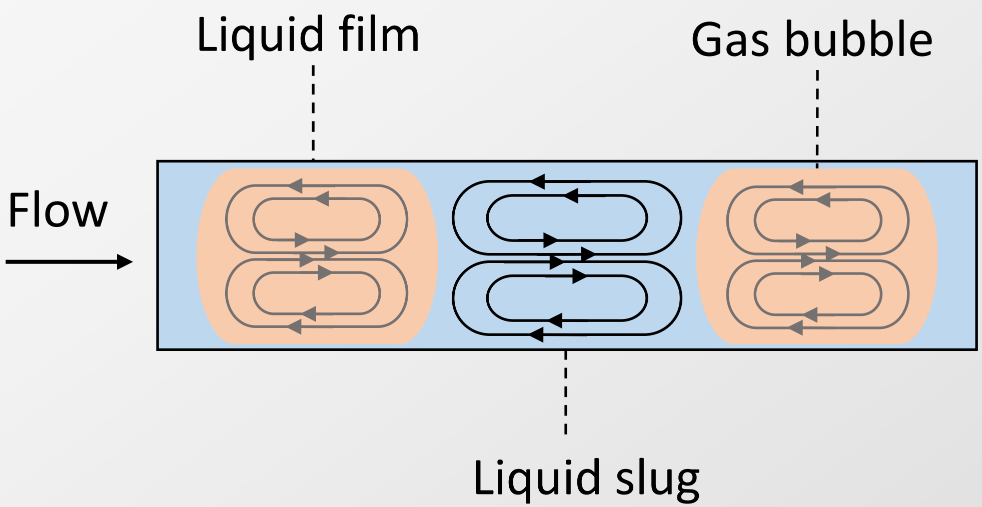
Tank: $\frac{A}{V} = 4.3V^{-1/3}$ $\quad U = 200\ Wm^{-2}K^{-1}$

Microreactor: $Nu = 3.66$

3. Heat transfer in microchannels with segmented flow

Heat transfer in segmented flow (gas-liquid)

- Heat transfer significantly faster for segmented gas/liquid flow *vs* single-phase flow
- Nusselt number increases due to:
  - ✓ Internal flow circulation within liquid slugs
  - ✓ Constant fluid layer renewal at wall / bubble interface



Heat transfer in segmented flow (gas-liquid)

Optional

- A correlation for Nusselt number in gas-liquid segmented flow*

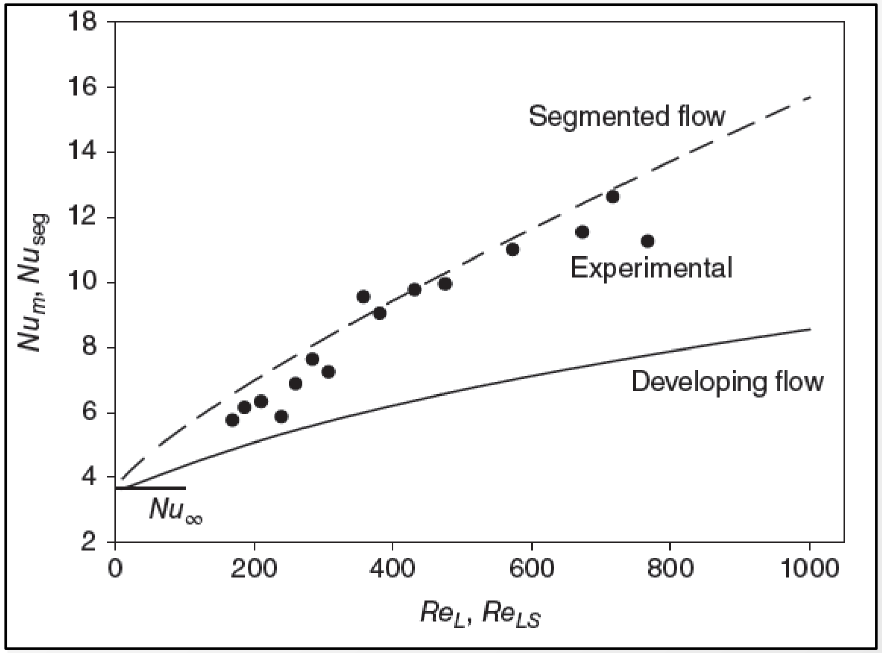
$$Nu_{seg} \cong Nu_{\infty} + 0.022 \cdot Pr_L^{0.4} \cdot Re_{LS}^{0.8}$$

$$Re_{LS} = \frac{u_b d_h}{\nu_L \, L_b/\left(L_b + L_{slug}\right)}$$

**Lakehal et al. (2008), Microfluid. Nanofluid., 4 (4), 261–271.*

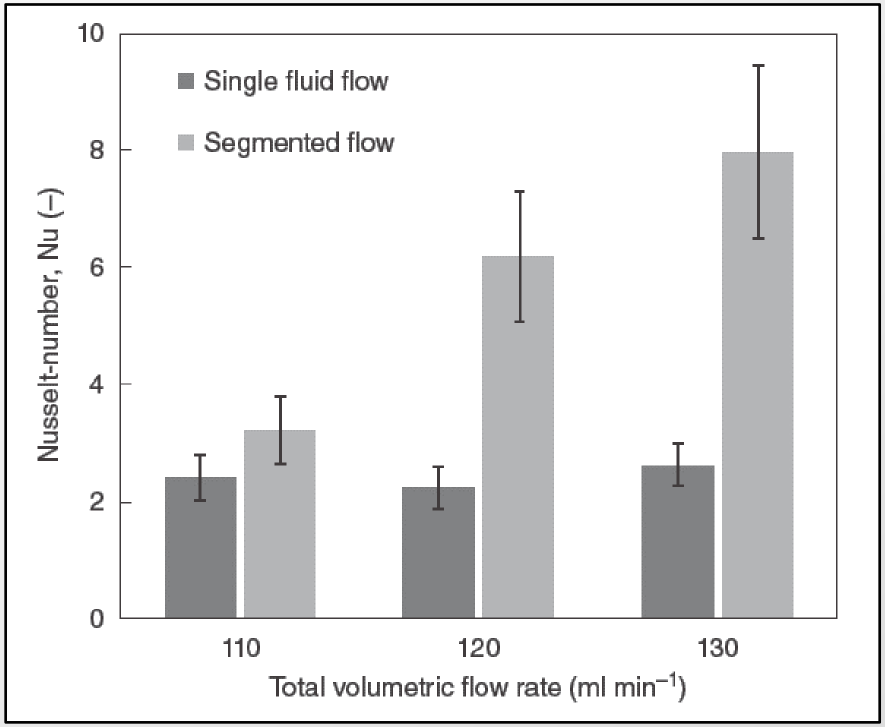
Heat transfer in segmented flow (liquid-liquid)

✓ Faster heat transfer observed for segmented liquid-liquid flow in microchannels *vs* single-phase flow



Corr: Lakehal et al. (2008), Microfluid. Nanofluid., 4 (4), 261–271.

Exp: Betz and Attinger (2010), Int. J. Heat Mass Transfer, 53 (19-20), 3683–3691



Asthana et al., (2011) Int. J. Heat Mass Transfer, 54 (7-8), 1456–1464

Heat transfer in segmented flow

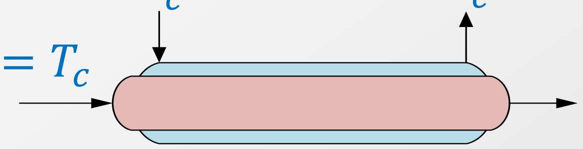
- Heat transfer for liquid-liquid systems is faster than for gas–liquid (higher heat capacity and thermal conductivity of liquids relative to gases)
- Larger viscosity of liquids→ higher pressure drop for liquid-liquid vs gas-liquid systems
- Huge variability (> 500%) in Nu values obtained from reported correlations* attributed to insufficient description and consideration of the flow conditions

**Bandara et al., Chemical Engineering Science 126 (2015) 283–295*

4. Thermal sensitivity in microchannels

Thermal sensitivity analysis

(Plug flow reactor at steady-state, reaction of apparent order n)



- Mass balance:

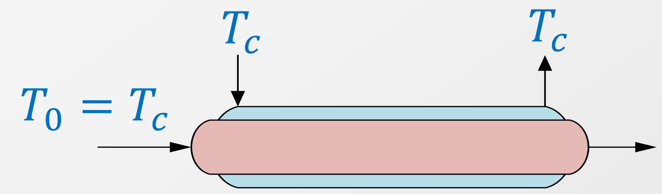
$$\frac{dc}{d\tau} = -k_0 \exp\left[-\frac{E}{RT}\right] c^n$$

- Heat balance:

$$\frac{dT}{d\tau} = \frac{Ua(T_c - T) + k_0 \exp[-E/(RT)]c^n(-\Delta H_r)}{\rho c_p}$$

Thermal sensitivity analysis

(Plug flow reactor at steady-state, reaction of apparent order n)



- Dimensionless mass balance:

$$\frac{dX}{dZ} = \tau_R' exp\left(\frac{\Delta T'}{1+\frac{\Delta T'}{\gamma}}\right)(1-X)^n \cong \tau_R' exp(\Delta T')(1-X)^n$$

In general $\gamma > 20 \rightarrow \frac{\Delta T'}{\gamma} \ll 1$

- Dimensionless heat balance:

$$\frac{d\Delta T'}{dZ} = \tau_R' S' exp\left(\frac{\Delta T'}{1+\frac{\Delta T'}{\gamma}}\right)(1-X)^n - \tau_R' N' \Delta T' \cong$$

$$\tau_R' S' exp(\Delta T')(1-X)^n - \tau_R' N' \Delta T'$$

Thermal sensitivity analysis
(Plug flow reactor at steady-state, reaction of apparent order n)

- Ratio of reaction and cooling characteristic times:

$$N' = \frac{t_r}{t_c} = \frac{Ua}{\rho c_p} \frac{1}{k(T_c) c_{1,0}^{n-1}}$$

- Heat production potential:

$$S' = \Delta T_{ad} \frac{E}{R T_c^2}$$

- Arrhenius number:

$$\gamma = \frac{E}{R T_c}$$

Thermal sensitivity analysis

(Plug flow reactor at steady-state, reaction of apparent order n)

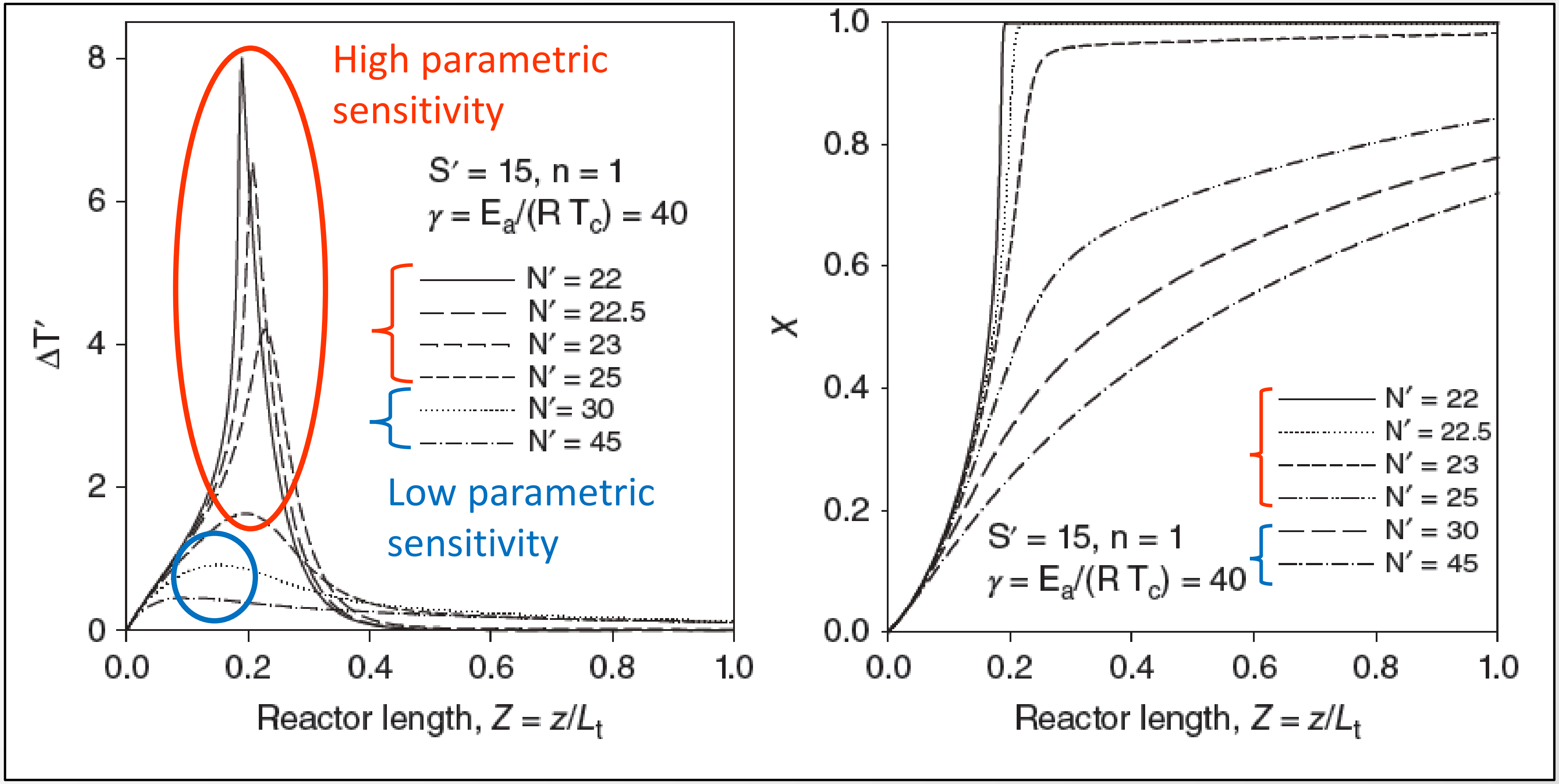
- Dimensionless temperature increase:

$$\Delta T' = \frac{T - T_c}{T_c}\gamma$$

- Dimensionless space-time:

$$\tau'_R = \frac{\tau_{PR}}{t_r(T_c)} = DaI(T_c) = \tau_{PR}\, k_0\, exp\left(\frac{-E}{RT_c}\right) c_{1,0}^{n-1}$$

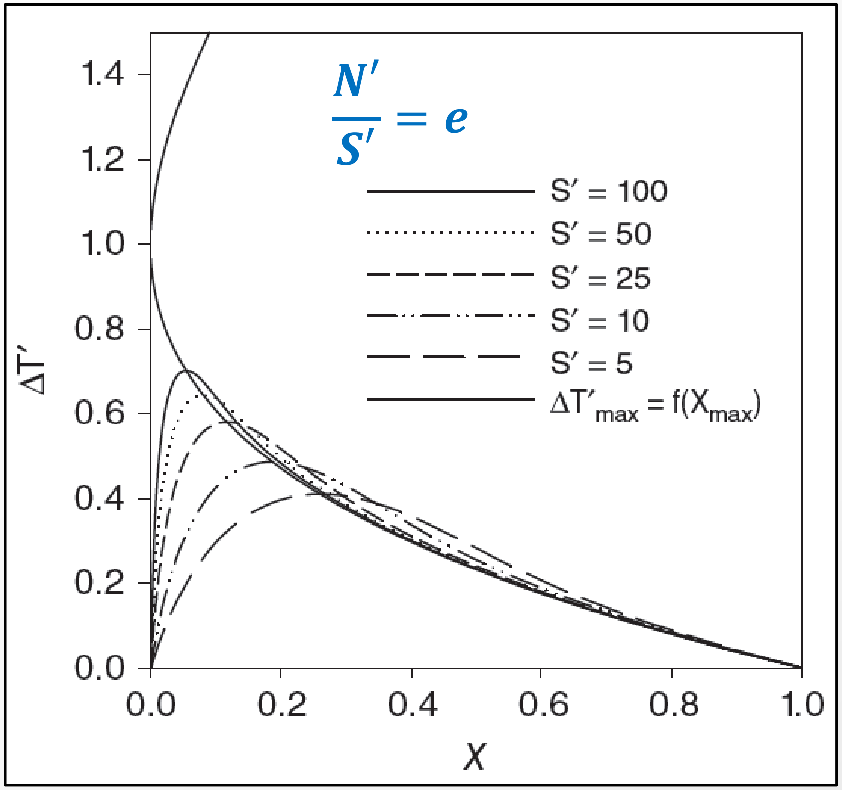
Thermal sensitivity analysis
(Plug flow reactor, first order reaction)

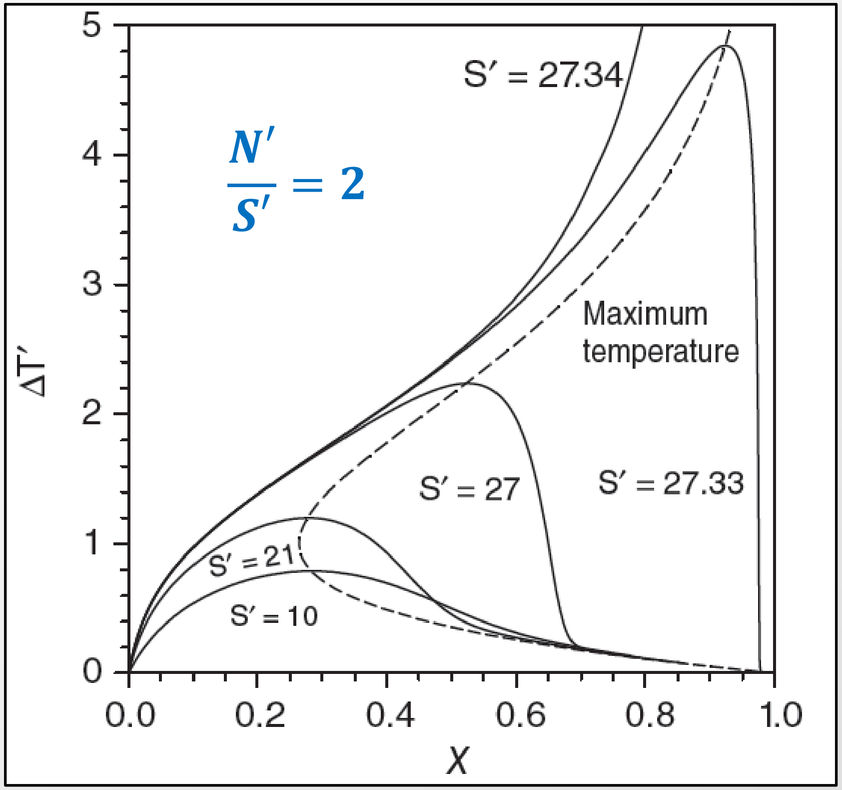


Below a critical value of $\frac{N'}{S'} = \frac{1}{Se}$ → a small change in N' generates a big increase in $\Delta T'$

Semenov number

Thermal sensitivity analysis
(Plug flow reactor, first order reaction)





Low parametric sensitivity

High parametric sensitivity

$\frac{N'}{S'} \geq e \rightarrow$ stable reactor for $n \geq 0\ \forall S'$

$\frac{N'}{S'} < e \rightarrow$ unstable region exists for $n \geq 0$

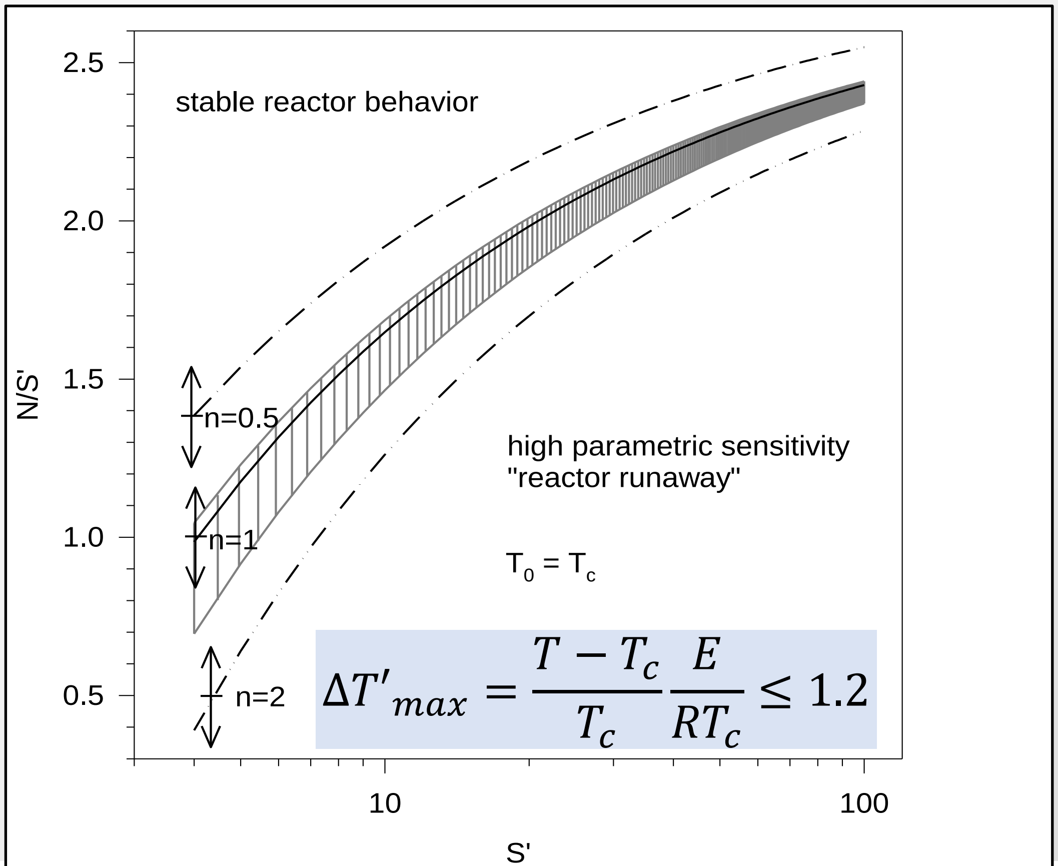
Thermal sensitivity analysis

Plug flow reactor, reaction of apparent order n, max temperature peak $\Delta T' \leq 1.2$: correlation for $\frac{N'}{S'}$

$$\frac{N'}{S'} = 2.72 - \frac{B}{\sqrt{S'}}$$

n	0	0.5	1	2
B	0	2.60	3.37	4.57

$$N'_{min} = 2.72\, S' - B\sqrt{S'}$$



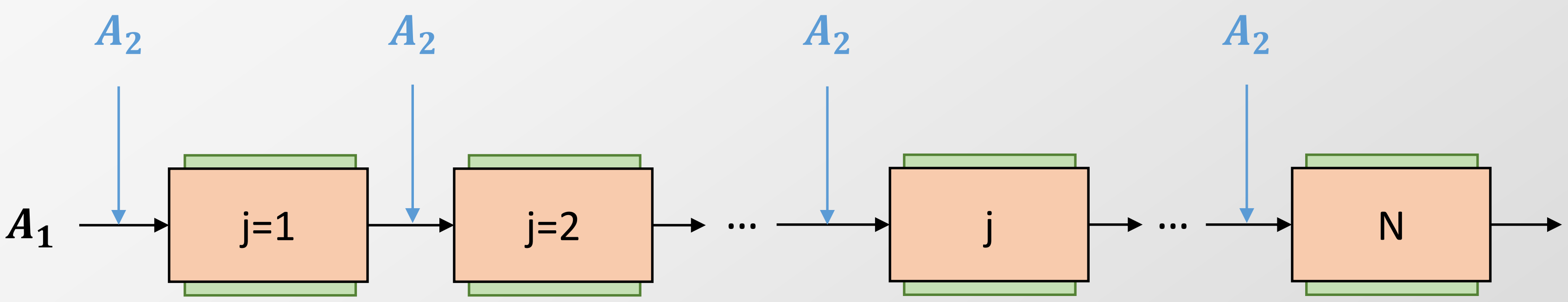
5. Multi-injection microreactors

Multi-injection microreactors

- Exothermic quasi-instantaneous reactions (Type A): channel sizes below $100\ \mu m$ may be needed to handle the heat production, which may not be operable on an industrial scale because of high Δp and risk of clogging

➢ Use multi-injection microchannel reactor to distribute the heat of reaction along the reactor and reduce magnitude of hot spots (analogy with semi-batch reactor)

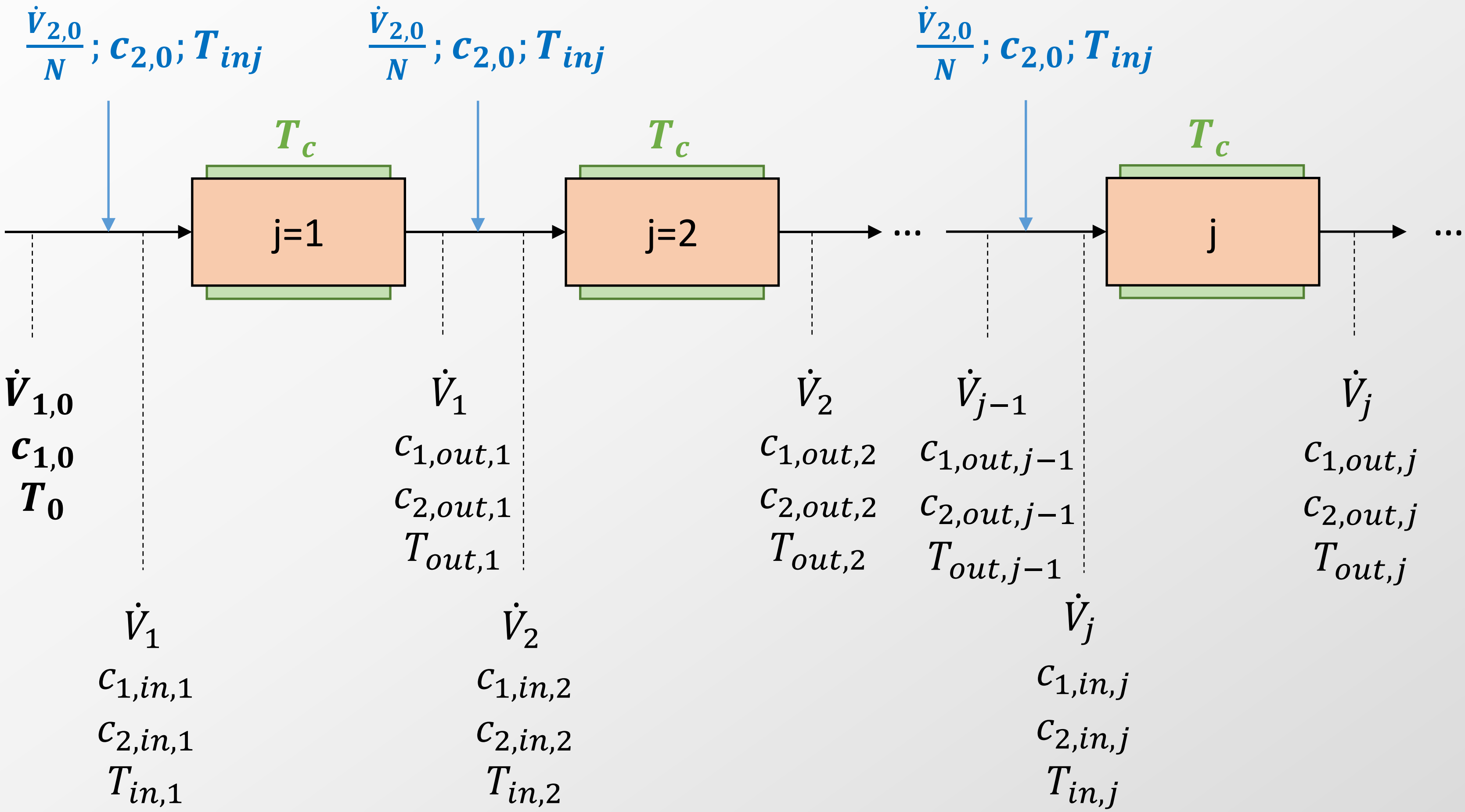
$$\boldsymbol{A_1 + A_2 \xrightarrow{k} P}$$



Modeling multi-injection microreactor

Equal flow partition

Cascade of plug flow reactors



Multi-injection microreactors

Mass and heat balances, section 1

$$A_1 + A_2 \xrightarrow{k} P$$

$$r = k_0 \exp[-E/(RT)] c_1 c_2$$

$$0 < z \leq Z/N$$

System of ordinary differential equations

$$\frac{dc_1}{dz} = -k(T) c_1 c_2 \frac{S}{\dot{V}_{10} + \dot{V}_{20}/N}$$

$$\frac{dc_2}{dz} = -k(T) c_1 c_2 \frac{S}{\dot{V}_{10} + \dot{V}_{20}/N}$$

$$\frac{dT}{dz} = \frac{U\pi D(T_c - T) + k(T) c_1 c_2 (-\Delta H_r) S}{\left(\dot{V}_{10} + \dot{V}_{20}/N\right)\rho c_p}$$

Inlet conditions (z = 0)

$$c_{1,in,1} = \frac{\dot{V}_{10} c_{1,0}}{\dot{V}_{10} + \dot{V}_{20}/N}$$

$$c_{2,in,1} = \frac{\left(\dot{V}_{20}/N\right) c_{2,0}}{\dot{V}_{10} + \dot{V}_{20}/N}$$

$$T_{in,1} = T_0$$

Multi-injection microreactors

Mass and heat balances, section 2

$$\boldsymbol{A_1} + \boldsymbol{A_2} \xrightarrow{\boldsymbol{k}} \boldsymbol{P}$$

$$r = k_0 \exp[-E/(RT)] c_1 c_2$$

$$Z/N < z \leq 2\,Z/N$$

System of ordinary differential equations

$$\frac{d\boldsymbol{c_1}}{dz} = -k(\boldsymbol{T})\boldsymbol{c_1}\boldsymbol{c_2}\frac{S}{\dot{V}_{10} + \boldsymbol{2}\,\dot{V}_{20}/N}$$

$$\frac{d\boldsymbol{c_2}}{dz} = -k(\boldsymbol{T})\boldsymbol{c_1}\boldsymbol{c_2}\frac{S}{\dot{V}_{10} + 2\,\dot{V}_{20}/N}$$

$$\frac{d\boldsymbol{T}}{dz} = \frac{U\pi D(T_c - \boldsymbol{T}) + k(\boldsymbol{T})\boldsymbol{c_1}\boldsymbol{c_2}(-\Delta H_r)S}{\left(\dot{V}_{10} + 2\,\dot{V}_{20}/N\right)\rho c_p}$$

Inlet conditions (z = Z/N)

$$c_{1,in,2} = \frac{\left(\dot{V}_{10} + \dot{V}_{20}/N\right)c_{1,out,1}}{\dot{V}_{10} + 2\,\dot{V}_{20}/N}$$

$$c_{2,in,2} = \frac{\left(\dot{V}_{10} + \dot{V}_{20}/N\right)c_{2,out,1} + \left(\dot{V}_{20}/N\right)c_{2,0}}{\dot{V}_{10} + 2\,\dot{V}_{20}/N}$$

$$T_{in,2} = \frac{T_0\frac{\dot{V}_{20}}{N} + T_{out,1}\left(\dot{V}_{10} + \dot{V}_{20}/N\right)}{\dot{V}_{10} + 2\,\dot{V}_{20}/N}$$

Multi-injection microreactors

Mass and heat balances, section j

$$\boldsymbol{A_1} + \boldsymbol{A_2} \xrightarrow{\boldsymbol{k}} \boldsymbol{P}$$

$$r = k_0 \exp[-E/(RT)] c_1 c_2$$

$$(j-1)\, Z/N < z \leq j\, Z/N$$

System of ordinary differential equations

$$\frac{d\boldsymbol{c_1}}{dz} = -k(\boldsymbol{T})\boldsymbol{c_1} c_2 \frac{S}{\dot{V}_{10} + j\,\dot{V}_{20}/N}$$

$$\frac{d c_2}{dz} = -k(\boldsymbol{T})\boldsymbol{c_1} c_2 \frac{S}{\dot{V}_{10} + j\,\dot{V}_{20}/N}$$

$$\frac{d\boldsymbol{T}}{dz} = \frac{U\pi D(T_c - \boldsymbol{T}) + k(\boldsymbol{T})\boldsymbol{c_1}\boldsymbol{c_2}(-\Delta H_r)S}{\left(\dot{V}_{10} + j\,\dot{V}_{20}/N\right)\rho c_p}$$

Inlet conditions (z = (j-1) · Z/N)

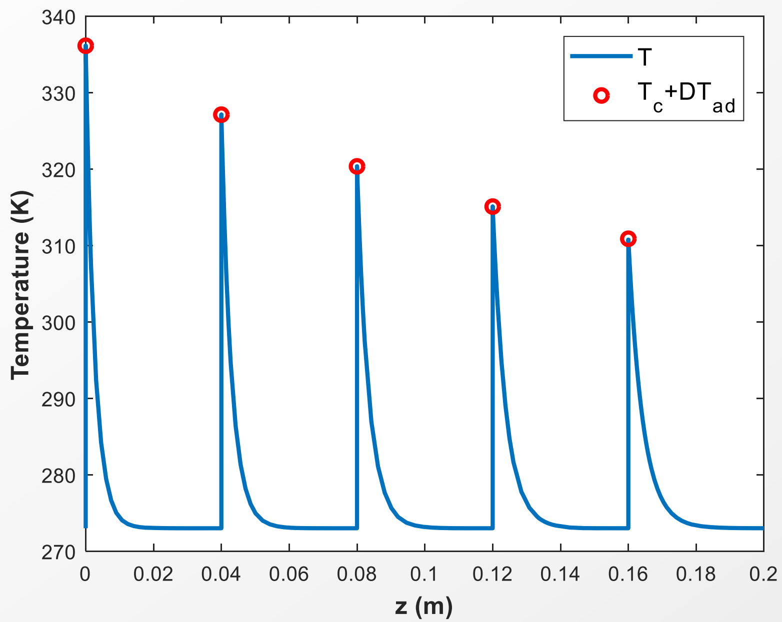
$$c_{1,in,j} = \frac{\left(\dot{V}_{10} + (j-1)\,\dot{V}_{20}/N\right) c_{1,out,j-1}}{\dot{V}_{10} + j\,\dot{V}_{20}/N}$$

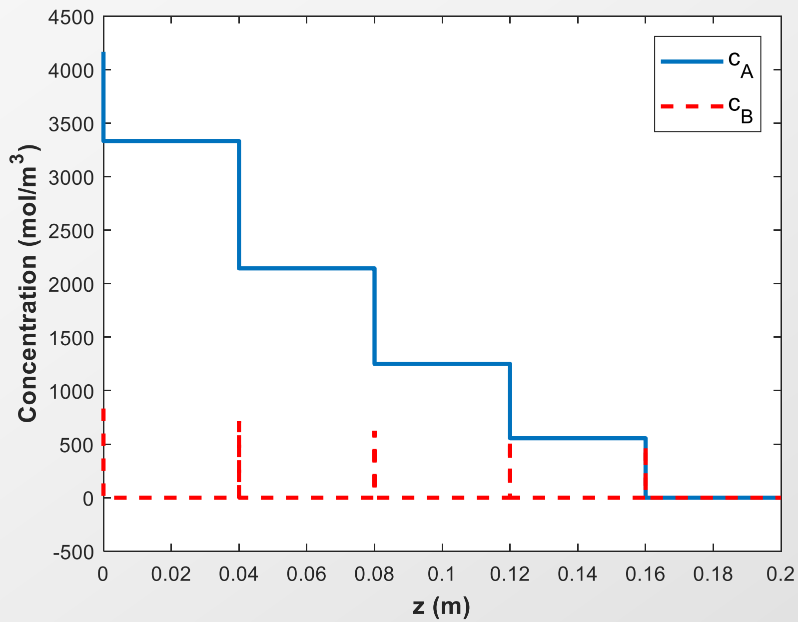
$$c_{2,in,j} = \frac{\left(\dot{V}_{10} + (j-1)\,\dot{V}_{20}/N\right) c_{2,out,j-1} + \left(\dot{V}_{20}/N\right) c_{2,0}}{\dot{V}_{10} + j\,\dot{V}_{20}/N}$$

$$T_{in,j} = \frac{T_0 \frac{\dot{V}_{20}}{N} + T_{out,j-1}\left(\dot{V}_{10} + (j-1)\,\dot{V}_{20}/N\right)}{\dot{V}_{10} + j\,\dot{V}_{20}/N}$$

Multi-injection microreactors

Instantaneous reaction, five-point injection





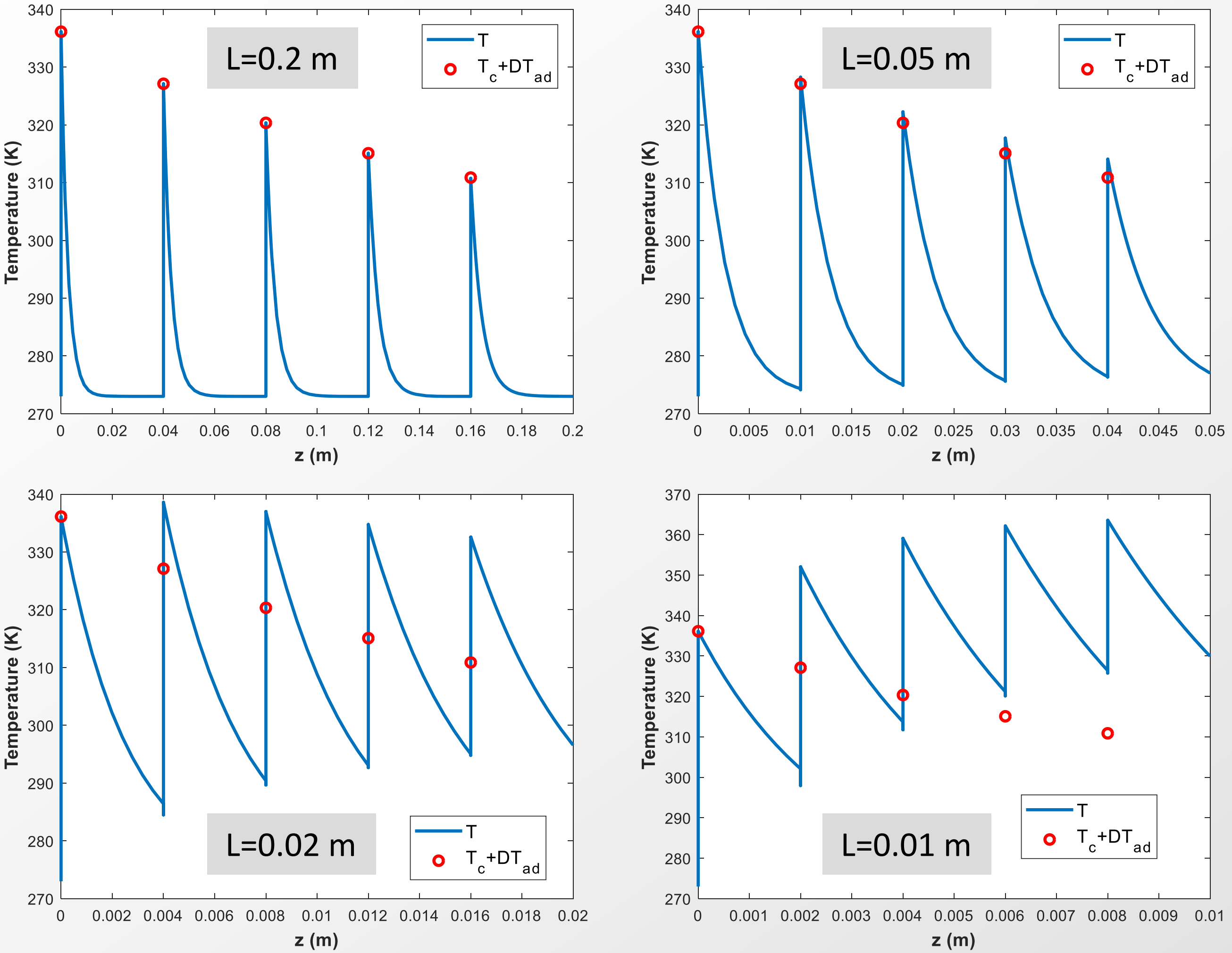
- Reaction occurs entirely at injection points
- Reactor only serves to cool down before the next injection
- Adiabatic temperature rise reached at each injection

$D = 10^{-3}\ m;\ L = 2 \cdot 10^{-1}\ m;\ \ \rho = 900\ kg\ m^{-3};\ \ c_p = 2200\ J\ kg^{-1}K^{-1};\ \ k_0 = 10^{14}\ m^3mol^{-1}s^{-1};\ E_a = 50\ kJ\ mol^{-1};\ \Delta H_r = 15\ kJ\ mol^{-1}$

$Nu = 3.66;\ \ \mu = 10^{-3}Pa \cdot s;\ \lambda_f = 0.2\ W\ m^{-1}K^{-1};\ \ c_{A,0} = c_{B,0} = 5 \cdot 10^3\ mol\ m^{-3};\ \ \dot{V}_{A,0} = \dot{V}_{A,0} = 10^{-8}m^3s^{-1}; T_c = 273\ K$

Multi-injection microreactors

Instantaneous reaction, effect of reactor length

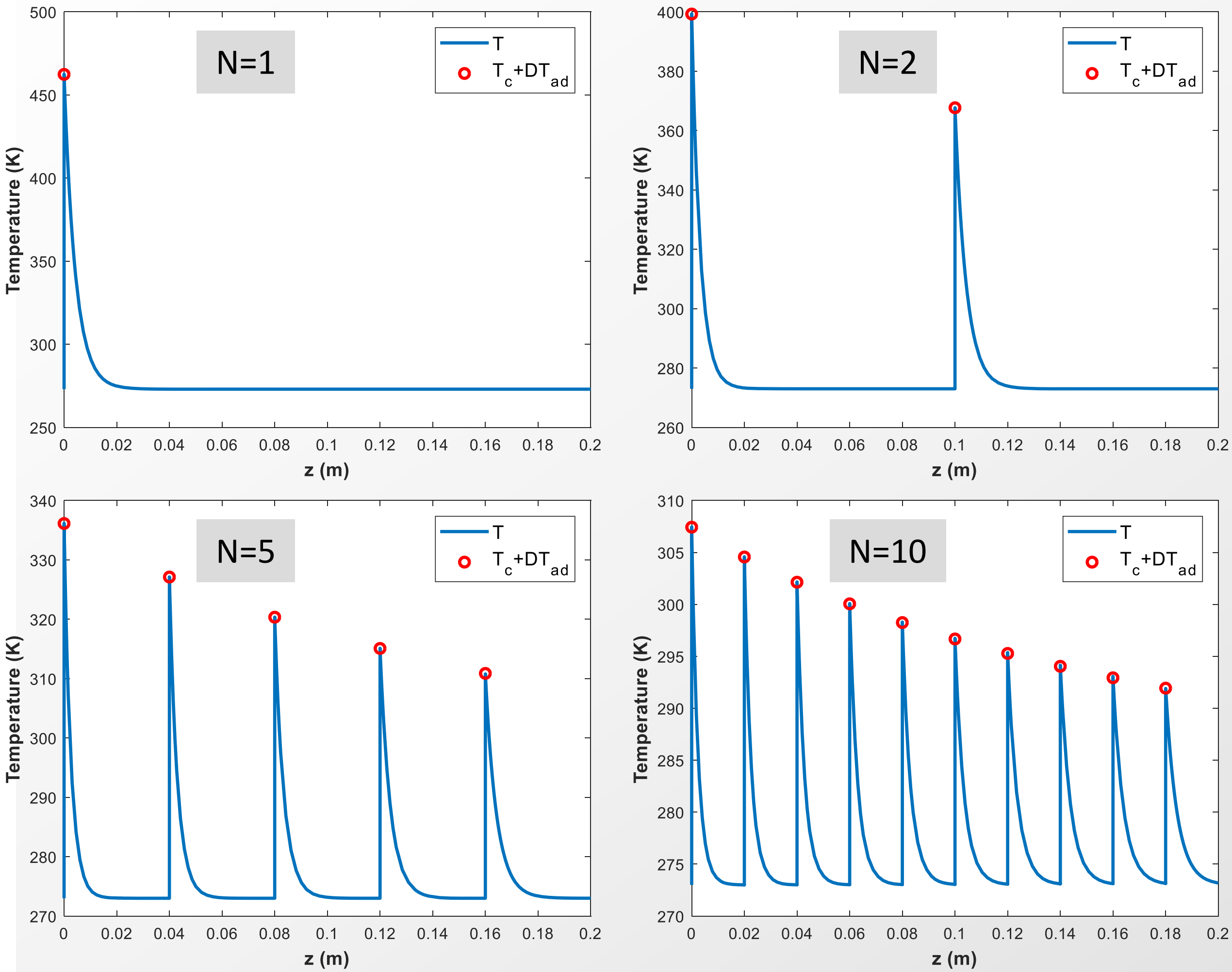


<u>Decrease L:</u>
→ Lower time for cooling
→ Higher temperature before next injection
→ Higher hot spot (heat accumulation)

$D = 10^{-3}\ m;\ \rho = 900\ kg\ m^{-3};\ \ c_p = 2200\ J\ kg^{-1}K^{-1};\ \ k_0 = 10^{14}\ m^3 mol^{-1}s^{-1};\ E_a = 50\ kJ\ mol^{-1};\ \Delta H_r = 15\ kJ\ mol^{-1}$
$Nu = 3.66;\ \ \mu = 10^{-3} Pa\cdot s;\ \lambda_f = 0.2\ W\ m^{-1}K^{-1};\ \ c_{A,0} = c_{B,0} = 5\cdot 10^3\ mol\ m^{-3};\ \ \dot{V}_{A,0} = \dot{V}_{A,0} = 10^{-8} m^3 s^{-1}; T_c = 273\ K$

Multi-injection microreactors

Instantaneous reaction, effect of number of injections



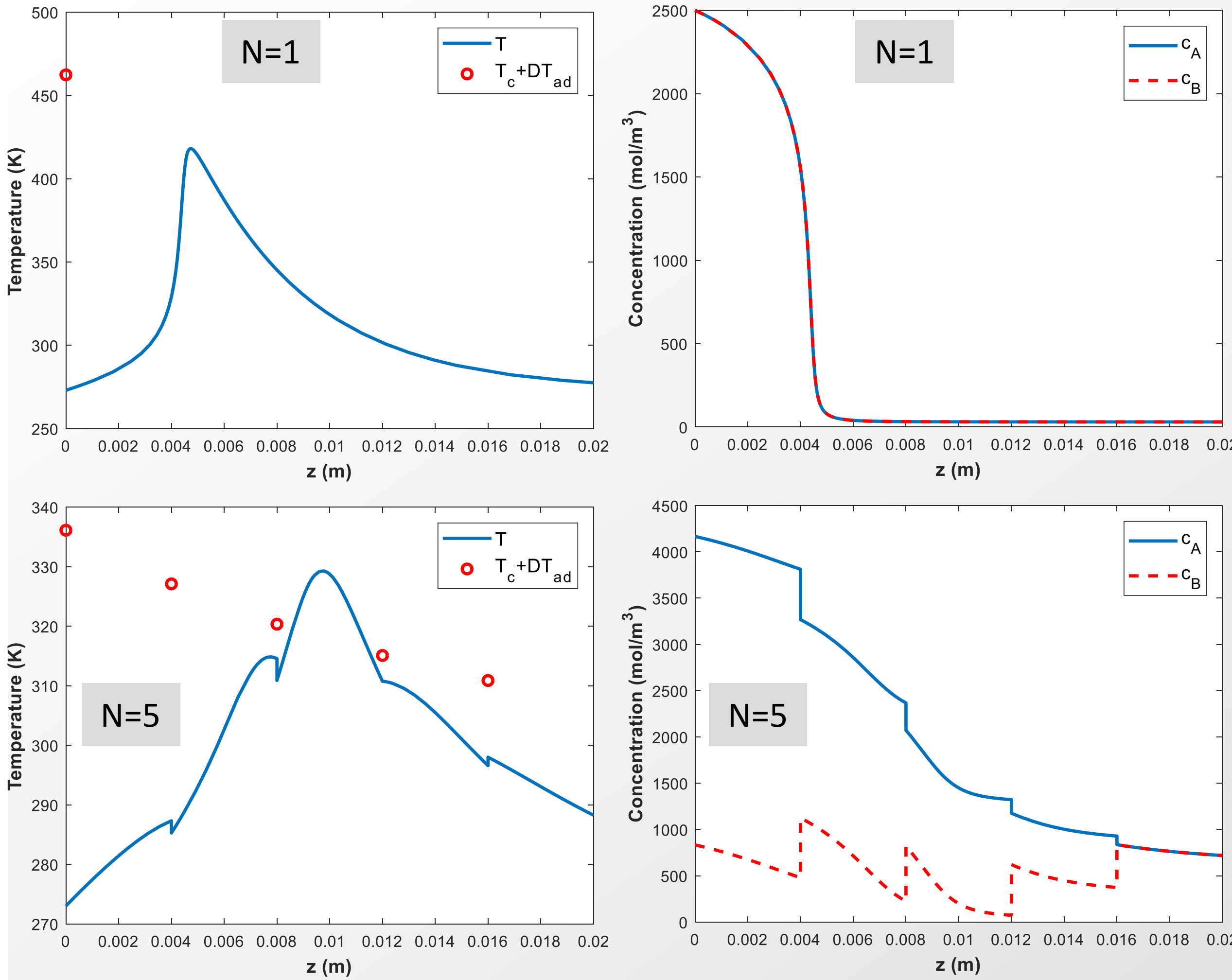
Increase N:
→ Lower hot spots

$D = 10^{-3}\ m;\ L = 2 \cdot 10^{-1}\ m;\ \rho = 900\ kg\ m^{-3};\ c_p = 2200\ J\ kg^{-1}K^{-1};\ k_0 = 10^{14}\ m^3 mol^{-1} s^{-1};\ E_a = 50\ kJ\ mol^{-1};\ \Delta H_r = 15\ kJ\ mol^{-1}$

$Nu = 3.66;\ \mu = 10^{-3} Pa \cdot s;\ \lambda_f = 0.2\ W\ m^{-1}K^{-1};\ c_{A,0} = c_{B,0} = 5 \cdot 10^3\ mol\ m^{-3};\ \dot{V}_{A,0} = \dot{V}_{A,0} = 10^{-8} m^3 s^{-1}; T_c = 273\ K$

Multi-injection microreactors

Fast reaction, effect of number of injections



- Hotspot not located at entrance
- Increase N $\rightarrow$ lower hot spots

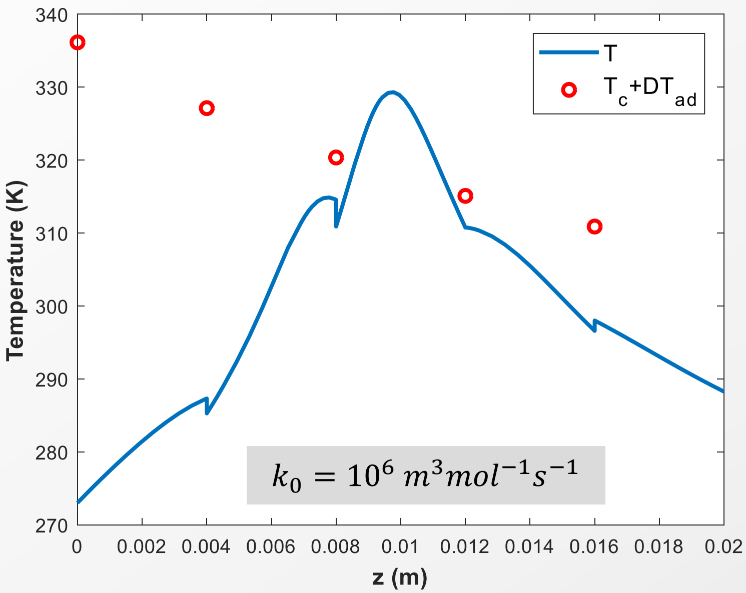
$D = 10^{-3}\ m;\ L = 2 \cdot 10^{-2}\ m;\ \rho = 900\ kg\ m^{-3};\ c_p = 2200\ J\ kg^{-1}K^{-1};\ k_0 = 10^6\ m^3mol^{-1}s^{-1};\ E_a = 50\ kJ\ mol^{-1};\ \Delta H_r = 15\ kJ\ mol^{-1}$

$Nu = 3.66;\ \mu = 10^{-3}Pa \cdot s;\ \lambda_f = 0.2\ W\ m^{-1}K^{-1};\ c_{A,0} = c_{B,0} = 5 \cdot 10^3\ mol\ m^{-3};\ \dot{V}_{A,0} = \dot{V}_{A,0} = 10^{-8}m^3s^{-1}; T_c = 273\ K$

Multi-injection microreactors

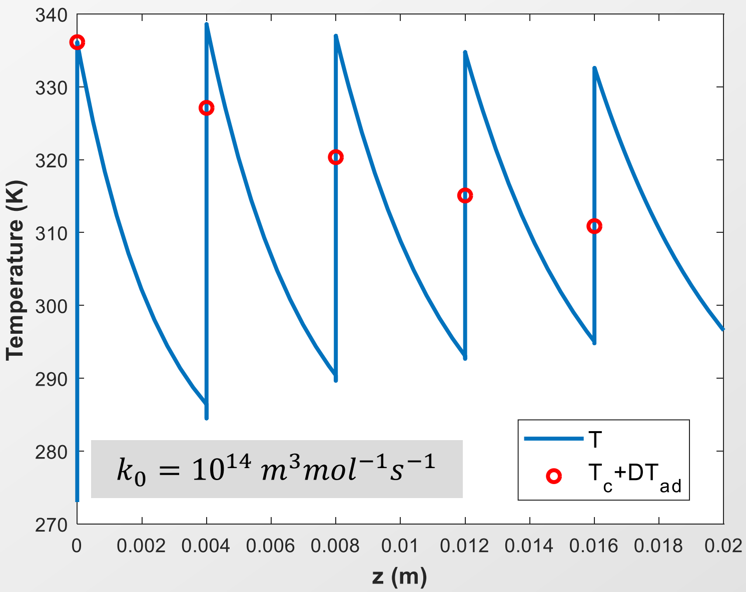
Fast vs instantaneous reactions, effect of number of injections

Fast reaction



Insufficient cooling length → heat accumulation $T > T_c + \Delta T_{ad}$

Instantaneous reaction



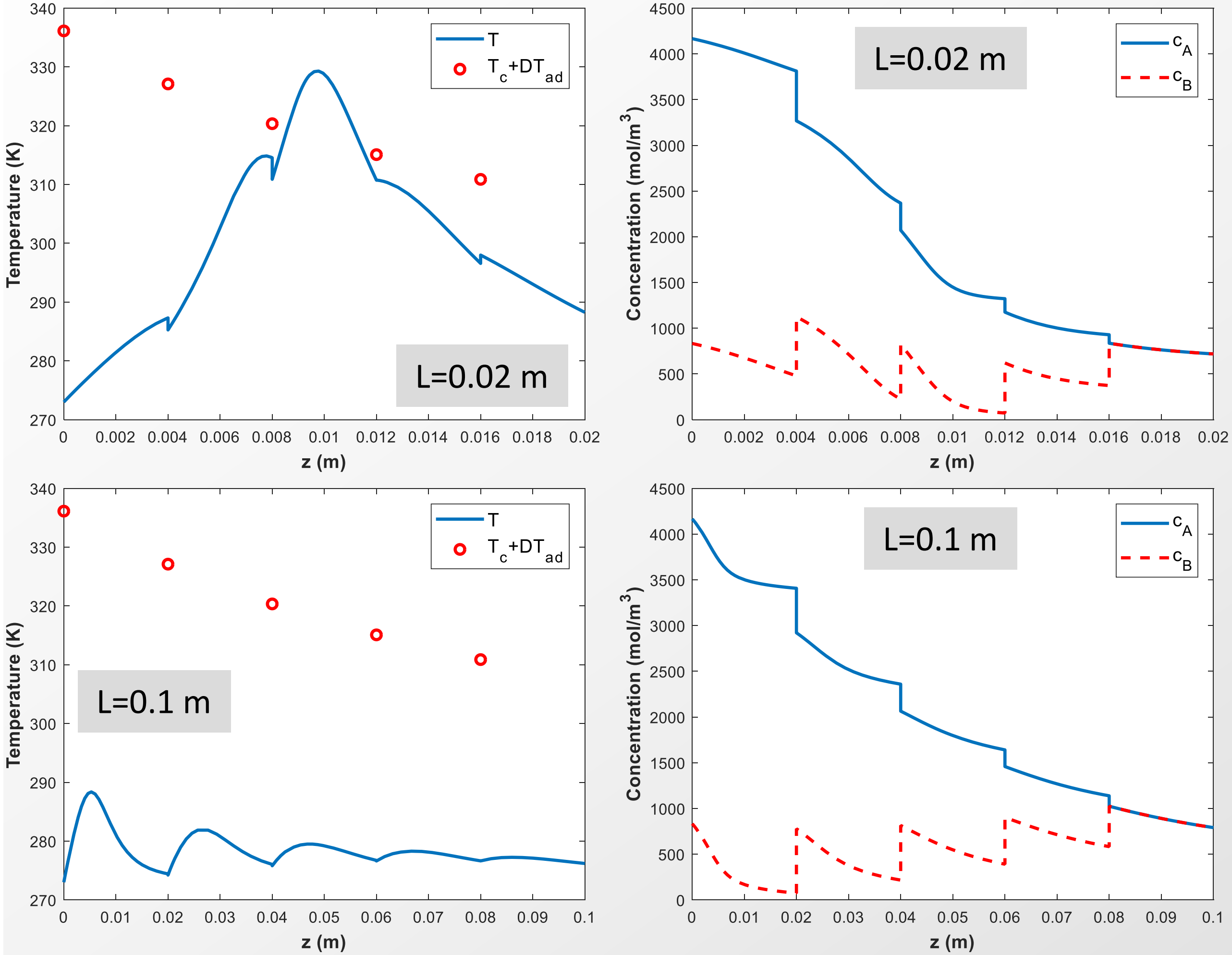
Insufficient cooling length → heat accumulation $T > T_c + \Delta T_{ad}$

$D = 10^{-3}\ m;\ L = 2 \cdot 10^{-2}\ m;\ \rho = 900\ kg\ m^{-3};\ c_p = 2200\ J\ kg^{-1} K^{-1};\ E_a = 50\ kJ\ mol^{-1};\ \Delta H_r = 15\ kJ\ mol^{-1}$

$Nu = 3.66;\ \mu = 10^{-3} Pa \cdot s;\ \lambda_f = 0.2\ W\ m^{-1} K^{-1};\ c_{A,0} = c_{B,0} = 5 \cdot 10^3\ mol\ m^{-3};\ \dot{V}_{A,0} = \dot{V}_{A,0} = 10^{-8} m^3 s^{-1}; T_c = 273\ K$

Multi-injection microreactors

Fast reaction, effect of reactor length



<u>Increase L:</u>

→ More heat exchange area

→ Lower temperature before next injection

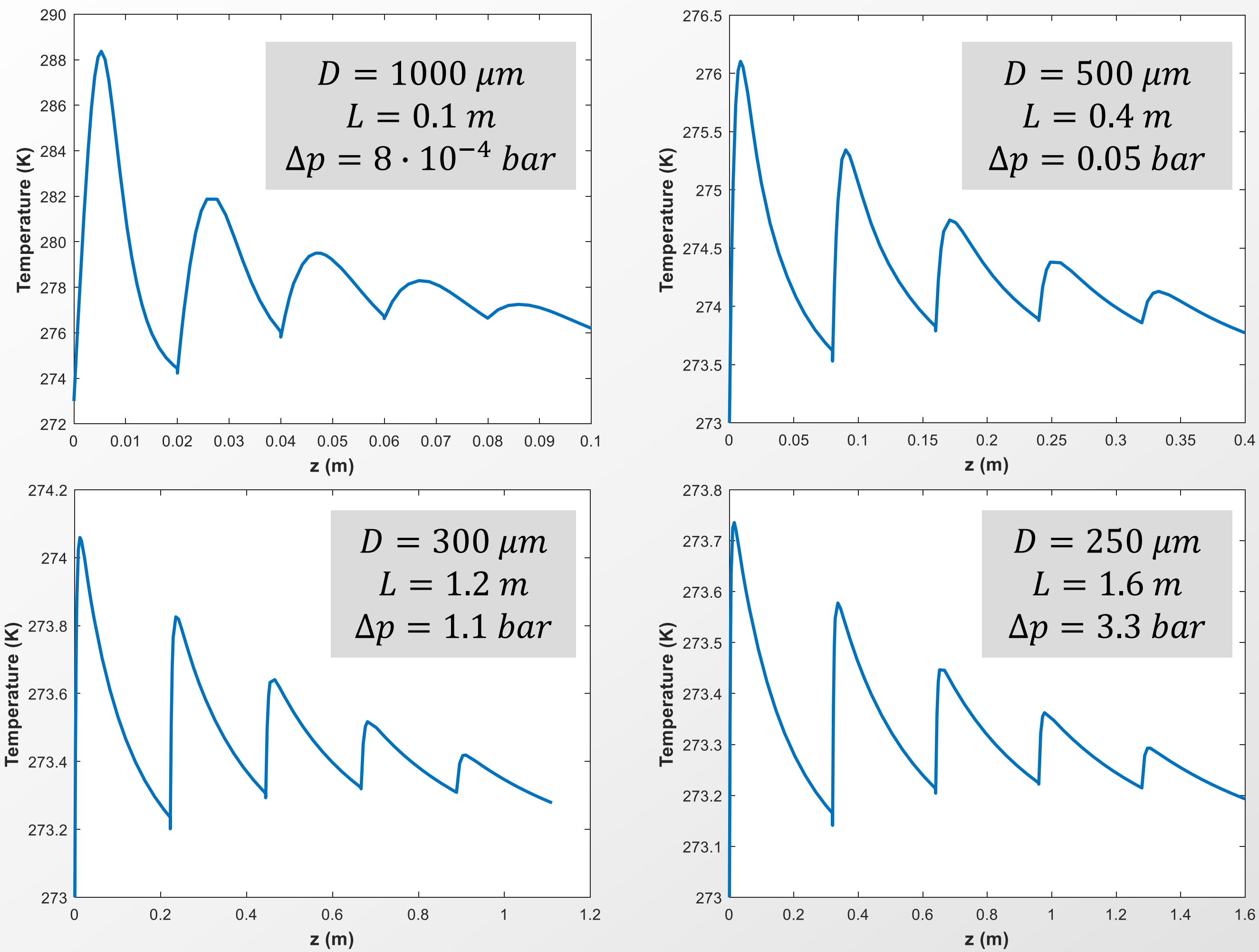
→ Lower hot spots

$D = 10^{-3}\ m;\ \ \rho = 900\ kg\ m^{-3};\ \ c_p = 2200\ J\ kg^{-1}K^{-1};\ \ k_0 = 10^6\ m^3mol^{-1}s^{-1};\ \ E_a = 50\ kJ\ mol^{-1};\ \Delta H_r = 15\ kJ\ mol^{-1}$

$Nu = 3.66;\ \ \mu = 10^{-3}Pa\cdot s;\ \lambda_f = 0.2\ W\ m^{-1}K^{-1};\ \ c_{A,0} = c_{B,0} = 5\cdot 10^3\ mol\ m^{-3};\ \ \dot{V}_{A,0} = \dot{V}_{A,0} = 10^{-8}m^3s^{-1}; T_c = 273\ K$

Multi-injection microreactors

Fast reaction, effect of reactor diameter (constant volume)



<u>Decrease D (constant V):</u>
→ Higher $U \cdot A/V$
→ Higher L
→ Higher Δp

$V = 7.85 \cdot 10^{-8} m^3$; $\rho = 900\ kg\ m^{-3}$; $c_p = 2200\ J\ kg^{-1} K^{-1}$; $k_0 = 10^6\ m^3 mol^{-1} s^{-1}$; $E_a = 50\ kJ\ mol^{-1}$; $\Delta H_r = 15\ kJ\ mol^{-1}$

$Nu = 3.66$; $\mu = 10^{-3} Pa \cdot s$; $\lambda_f = 0.2\ W\ m^{-1} K^{-1}$; $c_{A,0} = c_{B,0} = 5 \cdot 10^3\ mol\ m^{-3}$; $\dot{V}_{A,0} = \dot{V}_{A,0} = 10^{-8} m^3 s^{-1}$; $T_c = 273\ K$

Multi-injection microreactors

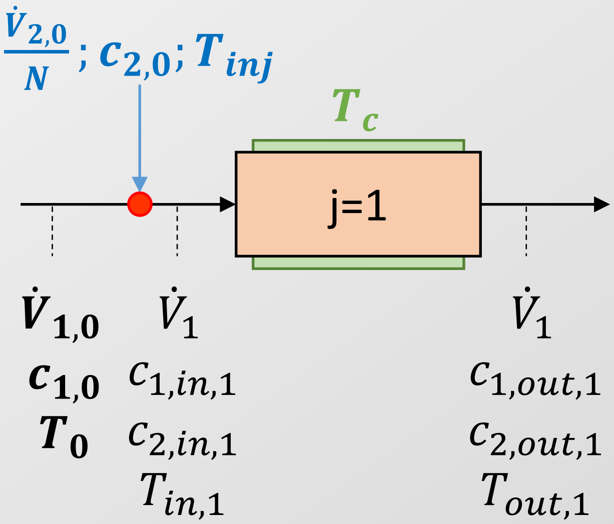
Estimation of ΔT_{ad} for equal flow partition

- Segment 1 inlet temperature ($T_c = T_{inj} = T_0$, constant c_p)

$$T_{in,1} = T_0 + \Delta T_{ad,1} = T_c + \Delta T_{ad,1}$$

$$\Delta T_{ad,1} = \frac{(\dot{n}_{2,0}/N)(-\Delta H_r)}{(\rho \dot{V}_1)c_p} \; ; \; \dot{V}_1 = \dot{V}_{1,0} + \frac{\dot{V}_{2,0}}{N}$$

- $t_{rx} \ll t_{heat}$ → mixing & reaction occur entirely at mixture point ●
- Microchannel only serves to cool down to $T_{out,1}$ before the next injection (no more reaction going on in microchannel)



Multi-injection microreactors

Estimation of ΔT_{ad} for equal flow partition

- Segment 2 inlet temperature ($T_c = T_{inj} = T_0$, constant c_p)

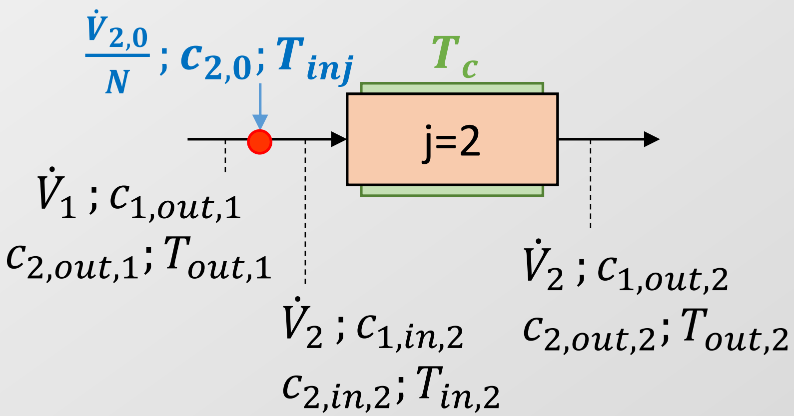
$$T_{in,2} = \frac{\dot{V}_1}{\dot{V}_2} T_{out,1} + \frac{\dot{V}_{2,0}/N}{\dot{V}_2} T_c + \Delta T_{ad,2}$$

$$\Delta T_{ad,2} = \frac{(\dot{n}_{2,0}/N)(-\Delta H_r)}{(\rho \dot{V}_2) c_p}; \quad \dot{V}_1 = \dot{V}_{1,0} + \frac{\dot{V}_{2,0}}{N}; \quad \dot{V}_2 = \dot{V}_{1,0} + 2\frac{\dot{V}_{2,0}}{N}$$

- $T_{out,1}$ estimated e.g. assuming 90% heat removal[(1)] in segment 1: $T_{out,1} = T_c + 0.1(T_{in,1} - T_c)$

▪ $t_{rx} \ll t_{heat} \rightarrow$ mixing & reaction occur entirely at mixture point ●

▪ Microchannel only serves to cool down to $T_{out,2}$ before the next injection (no more reaction going on in microchannel)



(1) $\frac{T_{in,1} - T_{out,1}}{T_{in,1} - T_c} = 0.9$

Multi-injection microreactors

Estimation of ΔT_{ad} for equal flow partition

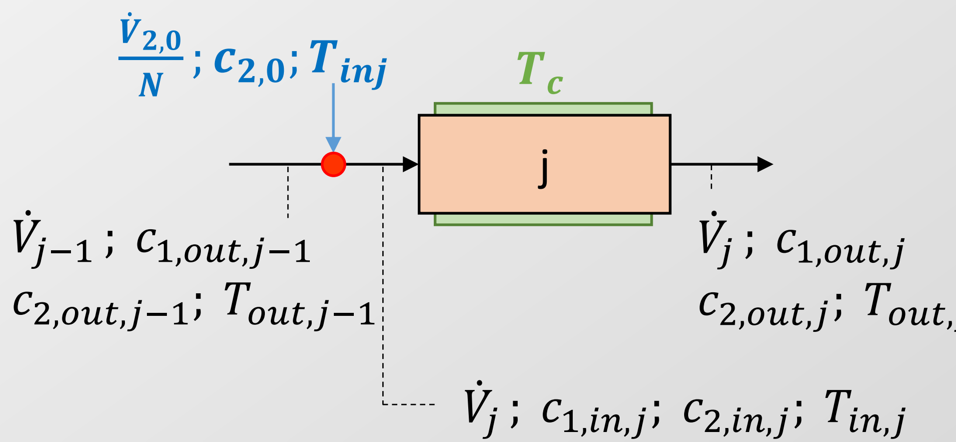
- Segment *j* inlet temperature ($T_c = T_{inj} = T_0$, constant c_p)

$$T_{in,j} = \frac{\dot{V}_{j-1}}{\dot{V}_j} T_{out,j-1} + \frac{\dot{V}_{2,0}/N}{\dot{V}_j} T_c + \Delta T_{ad,j}$$

$$\Delta T_{ad,j} = \frac{(\dot{n}_{2,0}/N)(-\Delta H_r)}{(\rho \dot{V}_j) c_p}; \quad \dot{V}_{j-1} = \dot{V}_{1,0} + (j-1)\frac{\dot{V}_{2,0}}{N}; \quad \dot{V}_j = \dot{V}_{1,0} + j\frac{\dot{V}_{2,0}}{N}$$

- $T_{out,j-1}$ estimated e.g. by assuming 90% heat removal in segment 1 (infinite length required for $T_{out,j-1} = T_c$): $T_{out,j-1} = T_c + 0.1\left(T_{in,j-1} - T_c\right)$

- $t_{rx} \ll t_{heat} \rightarrow$ mixing & reaction occur entirely at mixture point ●
- Microchannel only serves to cool down to $T_{out,j}$ before the next injection (no more reaction going on in microchannel)



Multi-injection microreactors

- Instantaneous mixing and reaction ($t_{mx}, t_{rx} \ll t_{heat}$) → heat produced only at reactor inlet. Heat balance for plug-flow microchannel:

$$\frac{dT}{d\tau} = \frac{U_V}{\rho c_p}(T_c - T)$$

➢ Required residence time in segment *j* to cool from $T_{in,j}$ to $T_{out,j}$

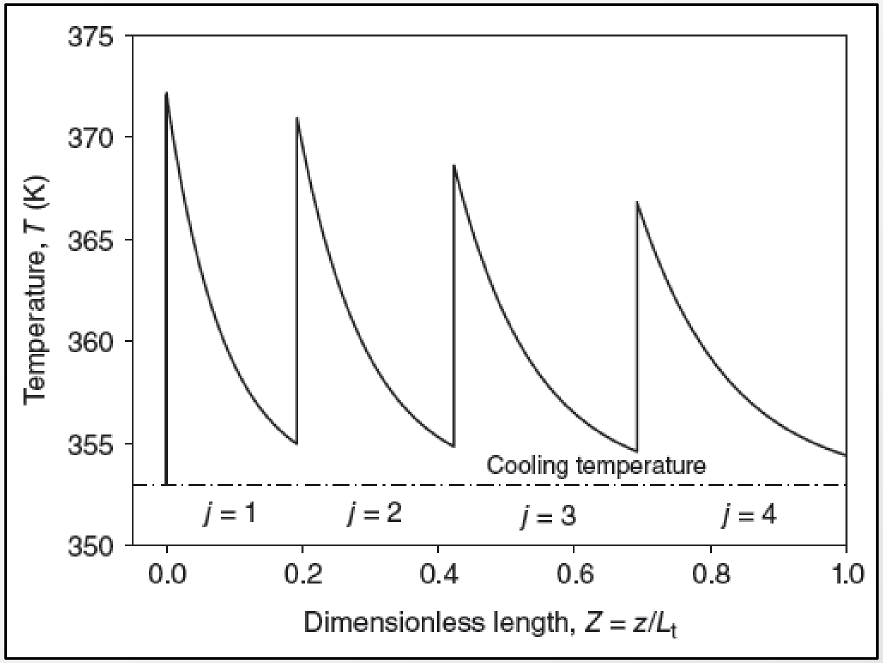
$$\tau_j = \frac{\rho c_p}{U_{V,j}} ln\left(\frac{T_{in,j} - T_c}{T_{out,j} - T_c}\right)$$

➢ Required length of segment *j* to cool from $T_{in,j}$ to $T_{out,j}$

$$L_j = \frac{\rho c_p u_j}{U_{V,j}} ln\left(\frac{T_{in,j} - T_c}{T_{out,j} - T_c}\right)$$

Multi-injection microreactors

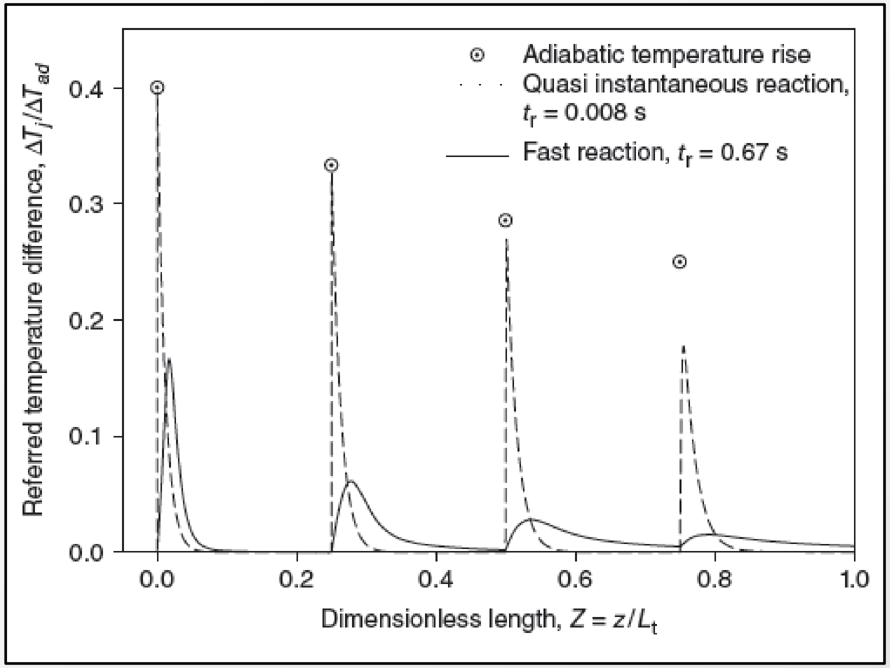
- Typical temperature profile for multi-point injection microreactor ($N = 4$) with 90% heat removal in each segment:



- Segment length increases due to the increased volumetric flowrate

Multi-injection microreactors

- Temperature profile for multi-point injection microreactor ($N = 4$) with different characteristic reaction times ($T_c = T_{inj} = T_0$):



- For quasi-instantaneous reactions, hot spot in first two segments almost equal to the predicted ΔT_{ad}
- Predicted temperature at 4th injection point underestimated because of decreasing reaction rate (increased $\dot{V}$ and decreased c_1) allowing some heat to be removed simultaneously to reaction at segment inlet ($t_{rx} \cong t_{heat}$)

Hot Spot Reduction

Optional

Instantaneous mixing and reaction, equal flow partition

- Overall adiabatic temperature rise ($j = n = 1$):

$$\Delta T_{ad} = \frac{\dot{V}_{2,0} \cdot c_{2,0}(-\Delta H_r)}{(\dot{V}_{1,0} + \dot{V}_{2,0})\bar{\rho}\bar{c}_p}$$

- Adiabatic temperature rise at injection point *j*:

$$\Delta T_{ad,j} = \frac{(\dot{V}_{2,0}/N)}{\dot{V}_{1,0}+j(\dot{V}_{2,0}/N)} \frac{c_{2,0}(-\Delta H_r)}{\bar{\rho}\bar{c}_p} = \frac{1}{N\frac{\dot{V}_{1,0}}{\dot{V}_{2,0}}+j} \frac{c_{2,0}(-\Delta H_r)}{\bar{\rho}\bar{c}_p}$$

→ Maximum temperature rise occurs at first injection point ($j = 1$)

Hot Spot Reduction

Optional

Instantaneous mixing and reaction, equal flow partition

- Ratio of adiabatic temperature rises:

$$\frac{\Delta T_{ad,j}}{\Delta T_{ad}} = \frac{\dot{V}_{1,0}/\dot{V}_{2,0}+1}{N \cdot \dot{V}_{1,0}/\dot{V}_{2,0}+j} = f\left(N, \dot{V}_{1,0}/\dot{V}_{2,0}\right)$$

→ Ratio can be controlled with number of injection points (N) and ratio of flowrates ($\dot{V}_{1,0}/\dot{V}_{2,0}$)

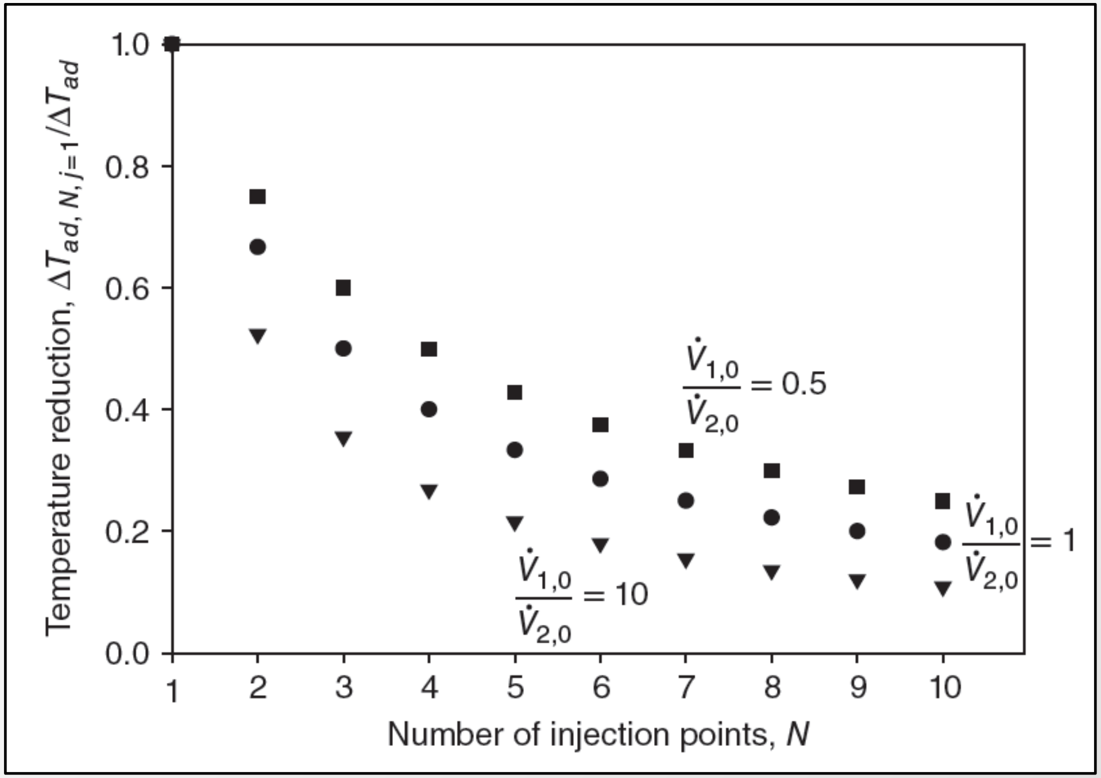
- Number of injection points required for temperature reduction at first injection point $\frac{\Delta T_{ad,N,j=1}}{\Delta T_{ad}}$

$$N = (1 + \mathrm{F})\frac{\Delta T_{ad}}{\Delta T_{ad,N,j=1}} - F \qquad \text{with } F = \frac{\dot{V}_{2,0}}{\dot{V}_{1,0}}$$

Hot Spot Reduction

Instantaneous mixing and reaction, equal flow partition

Reduction of temperature rise at the first injection point ($j = 1$)



Need to choose the residence time in microchannels τ_j carefully to avoid accumulation of heat in the reactor!

Hot Spot Reduction

Optional

Instantaneous mixing and reaction, unequal flow partition

- Use microreactor with equal adiabatic temperature rises at each injection point, by increasing the injected flowrate along the reactor

$$\Delta T_{ad,1} = \Delta T_{ad,2} = \cdots = \Delta T_{ad,N} \quad (N-1) \text{ equations}$$

$$F_j = \dot{V}_{2,j} / \dot{V}_{1,0} \qquad \text{N unknown flowrates}$$

→ Flowrate for injection number j as a function of F_1

$$F_j = F_1 (F_1 + 1)^{j-1} \qquad (N-1) \text{ equations}$$

- Constant density: $F = \sum_{j=1}^{N} F_j$ $\qquad + 1$ equation

= N equations

Hot Spot Reduction

Optional

Instantaneous mixing and reaction, unequal flow partition

- Relative adiabatic temperature rise:

$$\frac{\Delta T_{ad,N,j}}{\Delta T_{ad}} = \frac{\Delta T_{ad,N,1}}{\Delta T_{ad}} = \frac{\dot{V}_{2,1}}{\dot{V}_{1,0} + \dot{V}_{2,1}} \frac{\dot{V}_{1,0} + \dot{V}_{2,1}}{\dot{V}_{2,0}}$$

$$= \frac{F_1}{1 + F_1} \frac{1 + F}{F} \qquad \begin{cases} F_1 = \dot{V}_{2,1}/\dot{V}_{1,0} \\ F = \dot{V}_{2,0}/\dot{V}_{1,0} \end{cases}$$

→ 20% reduction in temperature rise at $j = 1$ with $N = 4$ compared to an equally distributed multi-injection reactor.