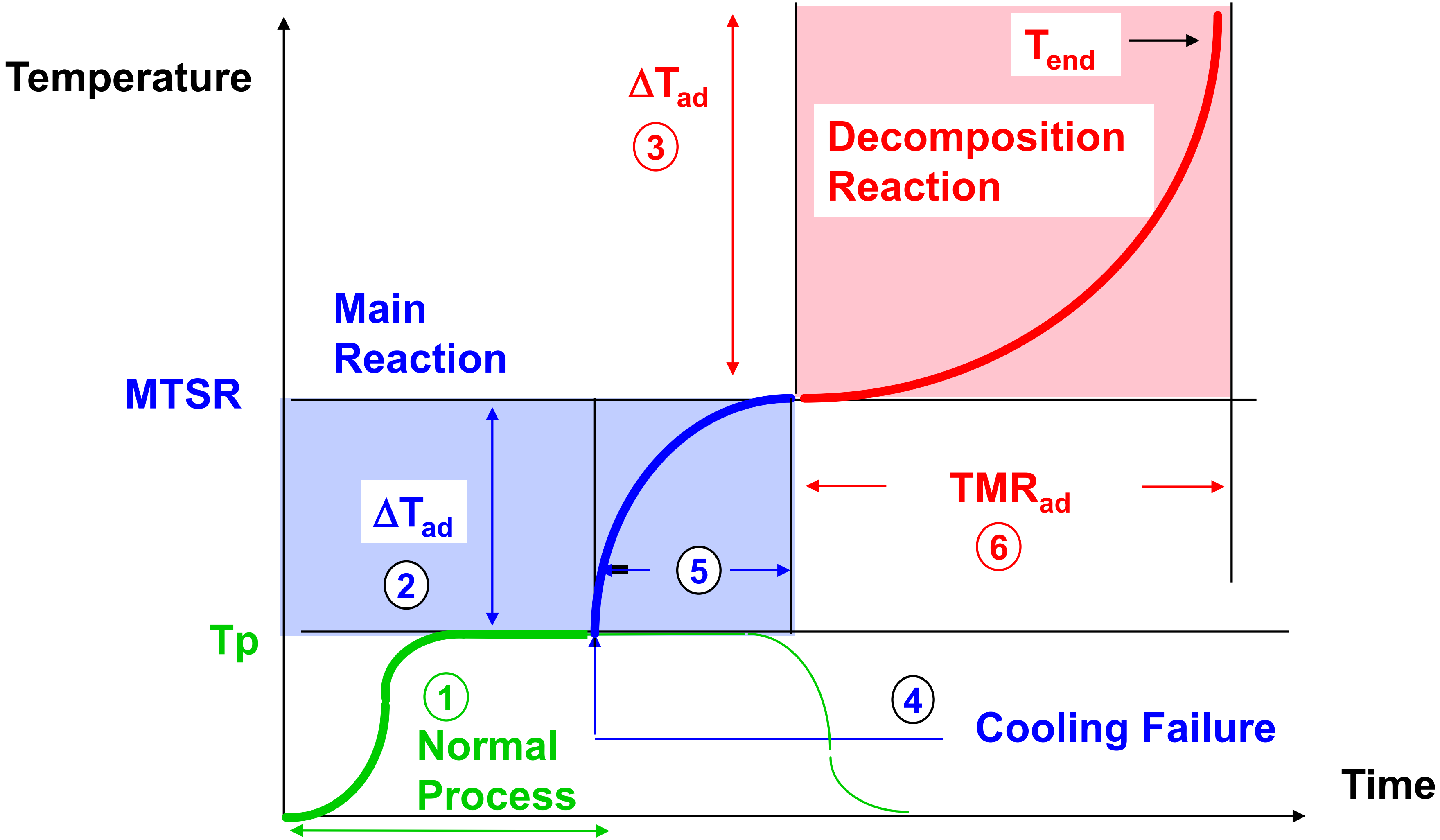
# Reactors
# Synthesis reaction

Module 5
ENG 431: Safety Chemical Processes

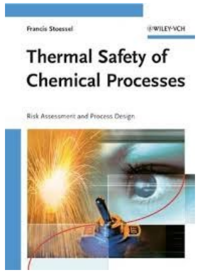
Annik Nanchen

# Cooling Failure Scenario

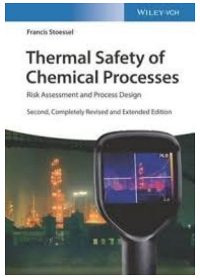


# Chemical Reactor Safety

- Calorimetric methods
- Heat balance on reactors
- Stability criteria
- Ideal reactors
  - Batch Reactor
  - Semi-Batch Reactor
  - Continuous Stirred Tank Reactor
  - Plug Flow Reactor

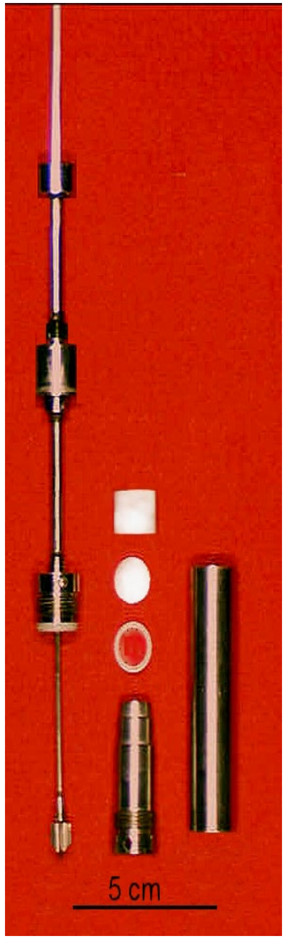



Chapters 6, 7, 8

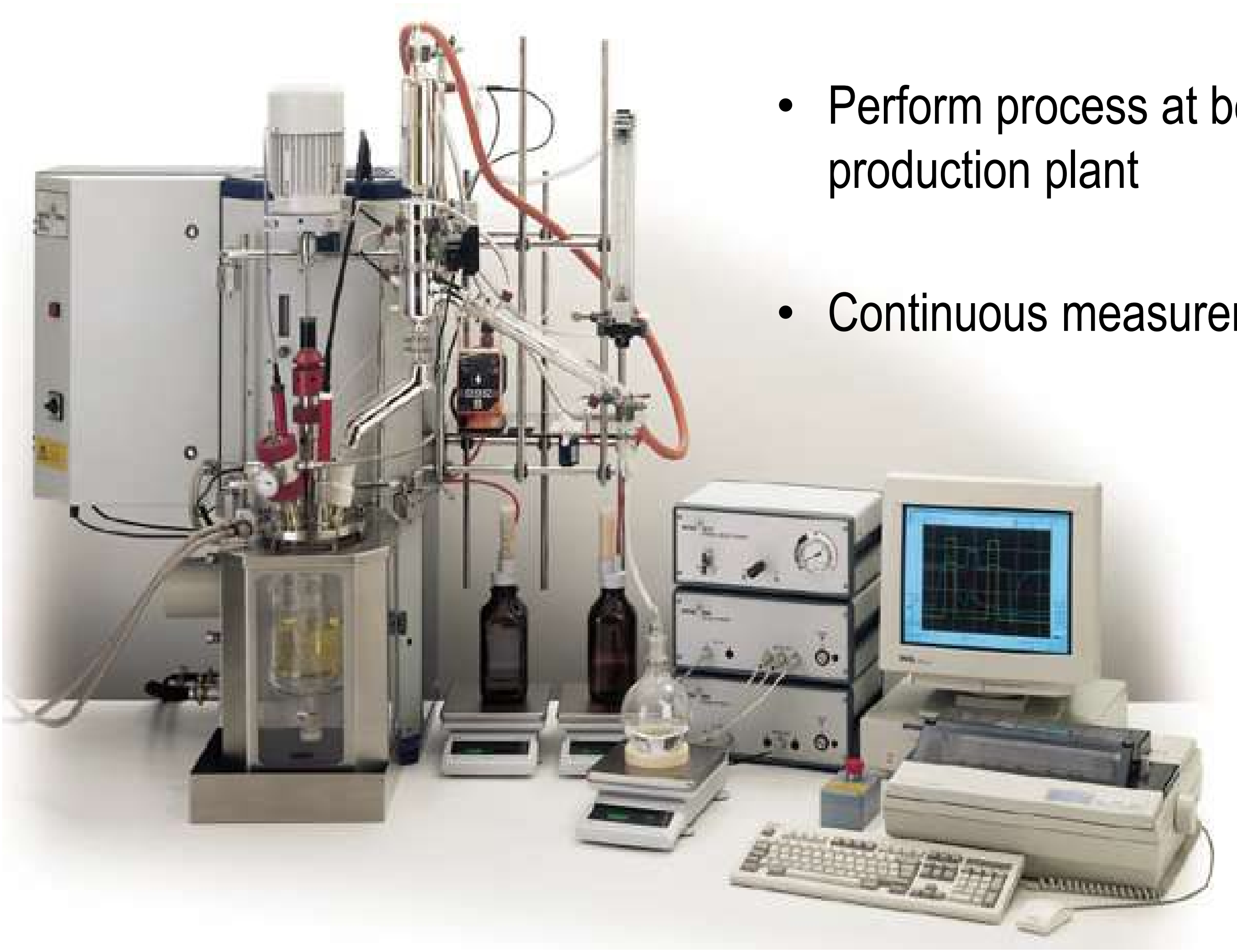



Chapters 7, 8, 9

# Calvet Calorimeter SETARAM C80




# Reaction Calorimetry



- Perform process at bench scale as in production plant
- Continuous measurement of heat flow

# Chemical Reactor Safety

- Calorimetric methods
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# Heat balance on reactors

- Heat release rate by reaction
- Convective heat exchange at wall
- Convective exchange by flow (sensible heat)
- Accumulation
- Evaporation
- Agitation
- Heat losses

**Convention:**
**All contributions that increase reactor temperature are counted for positive.**

# Heat release rate of reaction

$$q_{RX} = r \cdot V \cdot \left(-\Delta H_R\right)$$

$$\left[W\right] = \left[\frac{mol}{m^3 \cdot s} \cdot m^3 \cdot \frac{J}{mol}\right]$$

$$r = k_\infty \cdot e^{-Ea/RT_R} \cdot C_{A0}^n \cdot \left(1 - X_A\right)^n$$

# Convective exchange across the wall

$$q_{ex} = U \cdot A \cdot (T_R - T_c)$$

| | | |
|---|---|---|
| ex: | exchange | |
| q: | heat production | W |
| U: | heat transfer coefficient | $W \cdot m^{-2} \cdot K^{-1}$ |
| A: | heat exchange area | $m^2$ |
| $T_R$: | Temperature reactor | K or °C |
| $T_c$: | Temperature heating/ cooling media | K or °C |

| Scale | V $m^3$ | A $m^2$ | A/V $m^{-1}$ | Typical cooling capacity[a] $W \cdot kg^{-1}$ |
|---|---|---|---|---|
| Research | 100 ml | 0.01 | 100 | 1500 |
| Bench | 1 l | 0.03 | 30 | 450 |
| Pilot | 100 l | 1 | 10 | 150 |
| Pilot/Prod | 1 $m^3$ | 3 | 3 | 45 |
| Production | 10 $m^3$ | 13.5 | 1.35 | 20 |

[a] Cooling capacity calculated based on $U=300\ W \cdot m^{-2} \cdot K^{-1}$ and $T_R$-$T_C$ = 50 K, reactor filled to nominal value and density of 1000 $kg \cdot m^{-3}$

# Accumulation

**Mass units**

$$q_{AC} = \left( \sum_i M_i \cdot c'_{pi} \right) \cdot \frac{dT_R}{dt}$$

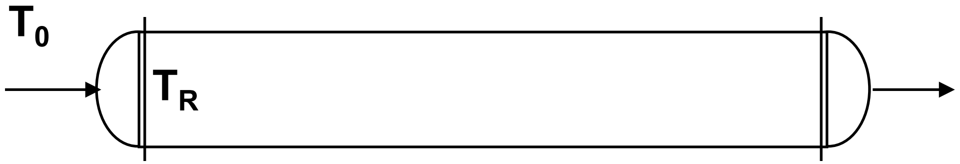
$$[W] = \left[ kg \cdot \frac{J}{kg \cdot K} \cdot \frac{K}{s} \right]$$

**Volume units**

$$q_{AC} = \left( \sum_i \rho_i \cdot V_i \cdot c'_{pi} \right) \cdot \frac{dT_R}{dt}$$

$$[W] = \left[ \frac{kg}{m^3} \cdot m^3 \cdot \frac{J}{kg \cdot K} \cdot \frac{K}{s} \right]$$

# Convective exchange: sensible heat




**Mass units**

$$q_{CS} = \dot{m} \cdot c'_p \cdot \Delta T = \dot{m} \cdot c'_p \cdot \left(T_0 - T_R\right)$$

$$[W] = \left[\frac{kg}{s} \cdot \frac{J}{kg \cdot K} \cdot K\right] \qquad [W]$$

**Volume units**

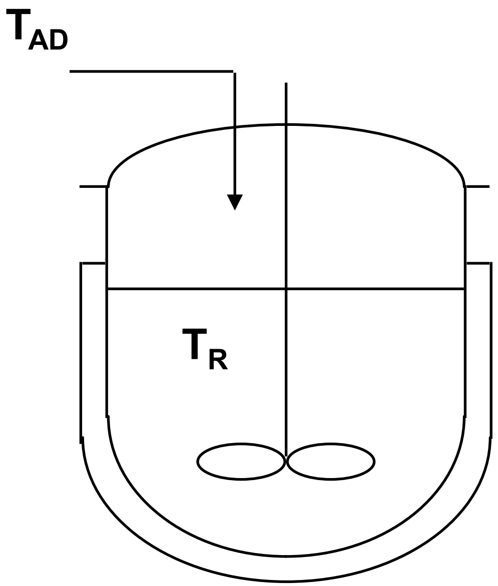
$$q_{CS} = \rho \cdot \dot{v} \cdot c'_p \cdot \Delta T = \rho \cdot \dot{v} \cdot c'_p \cdot \left(T_0 - T_R\right)$$

$$[W] = \left[\frac{kg}{m^3} \cdot \frac{m^3}{s} \cdot \frac{J}{kg \cdot K} \cdot K\right]$$

# Convective exchange: sensible heat (SBR)

$$q_{AD} = \dot{m}_{AD} \cdot c'_p \cdot \left(T_{AD} - T_R\right)$$

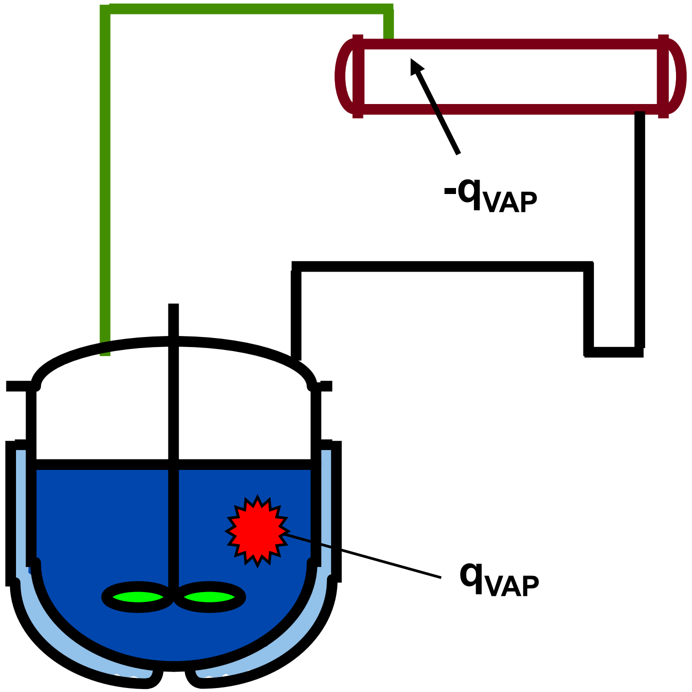
$$[W] = \left[\frac{kg}{s} \cdot \frac{J}{kg \cdot K} \cdot K\right]$$



# Evaporation

$$q_{VP} = \dot{m}_{VP} \cdot (-\Delta H_V)$$

$$[W] = [kg \cdot s^{-1}][J \cdot kg^{-1}]$$




$$q_{RX} + q_{EX} = q_{VP} \Rightarrow \dot{m}_{VP} = \frac{q_{RX} + q_{EX}}{(-\Delta H_V)}$$

# Agitation

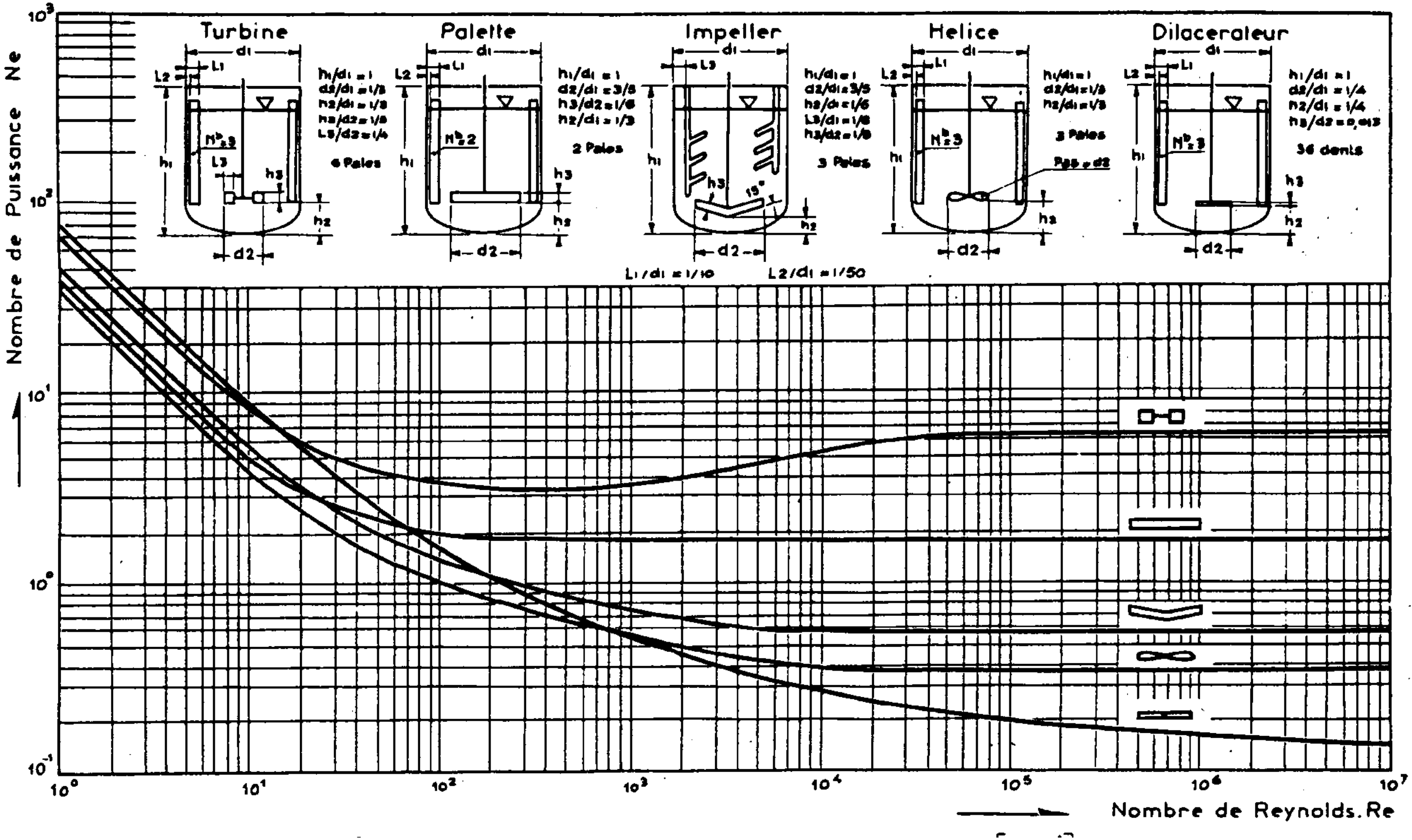
$$q_{AG} = \mathrm{N}_P \cdot \rho \cdot N^3 \cdot d_s^5$$

$$[W] = [-]\left[kg \cdot m^{-3}\right]\left[s^{-3}\right]\left[m^5\right] = \left[kg \cdot m^2 \cdot s^{-3}\right]$$

| | |
|---|---|
| $\mathrm{N}_P$ | **Newton criterium (Ne)**<br>**Or power number** |

| | |
|---|---|
| $N \cdot d_s^3$ | $\left[s^{-1}\right]\left[m^3\right] = \left[m^3 \cdot s^{-1}\right]$ |
| $\rho \cdot N^2 \cdot d_s^2$ | $\left[kg \cdot m^{-3}\right]\left[s^{-2}\right]\left[m^2\right] = \left[kg \cdot m^{-1} \cdot s^{-2}\right]$ |

# Ne = f (Re)



Turbine
Palette
Impeller
Helice
Dilaceraleur
h1/d1 = 1
d2/d1 = 1/3
h2/d1 = 1/3
h3/d2 = 1/5
L3/d2 = 1/4
6 Pales
d2/d1 = 3/5
h3/d2 = 1/6
h2/d1 = 1/3
2 Pales
h2/d1 = 1/6
L3/d1 = 1/8
h3/d2 = 1/8
3 Pales
3 Pales
Pas = d2
d2/d1 = 1/4
h2/d1 = 1/4
36 dents
L1/d1 = 1/10
L2/d1 = 1/50
Nombre de Puissance Ne
Nombre de Reynolds. Re

# Heat losses

$$q_{LOSS} = \alpha \cdot \left(T_{amb} - T_R\right)$$

$$[W] = \left[W \cdot K^{-1}\right][K]$$

| | |
|---|---|
| **10 ml:** | **5,91 W/(kg.K)** |
| **100 ml:** | **3,68** |
| **Dewar 1l:** | **0,018** |
| **Reactor 2,5 m3** | **0,054** |
| **Reactor 10 m3** | **0,02** |

# Heat balance

$$q_{AC} = q_{RX} + q_{EX} + q_{CS} + q_{VP} + q_{AG} + q_{Loss}$$

**Simplified**

$$q_{AC} = q_{RX} + q_{EX} \Leftrightarrow \rho \cdot V \cdot c'_p \cdot \frac{dT_R}{dt} = \left(-r_A\right) \cdot V \cdot \left(-\Delta H_R\right) - U \cdot A \cdot (T_R - T_C)$$

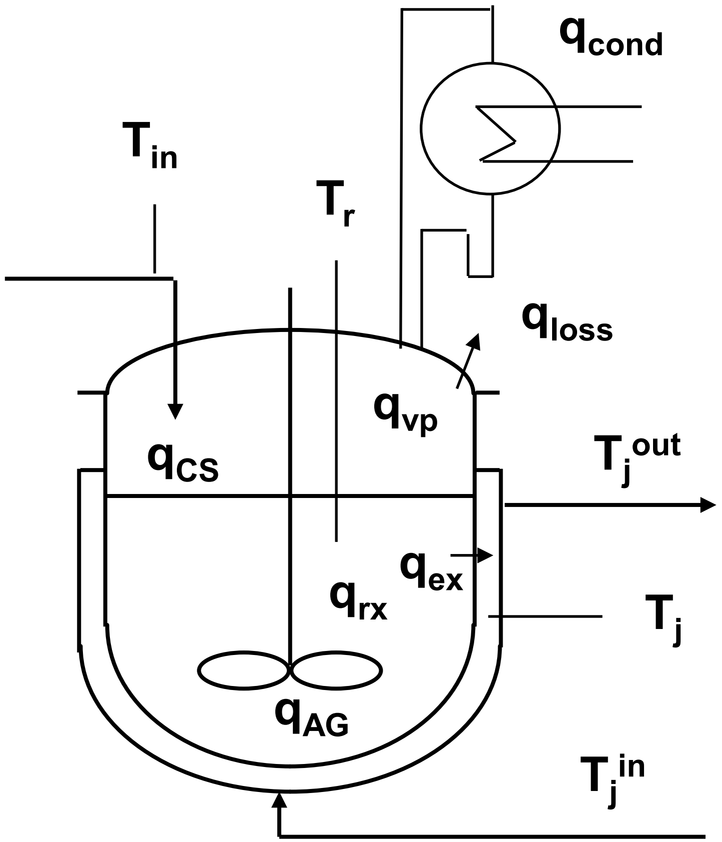
$$\Delta T_{ad} = \frac{c \cdot \Delta H_r}{\rho \cdot c'_p}$$

$$\frac{dT_R}{dt} = \Delta T_{ad} \cdot \frac{-r_A}{C_{A0}} - \frac{U \cdot A}{\rho \cdot V \cdot c'_p} \cdot \left(T_R - T_C\right)$$

**Thermal time constant of agitated vessel:** $\tau = \frac{\rho \cdot V \cdot c'_p}{U \cdot A}$

# Heat balance on stirred tank reactor

$$q_{AC} = q_{RX} + q_{EX} + q_{CS} + q_{VP} + q_{AG} + q_{Loss}$$



# Chemical Reactor Safety

- Calorimetric methods
- Heat balance on reactors
- Stability criteria
- Ideal reactors
  - Batch Reactor
  - Semi-Batch Reactor
  - Continuous Stirred Tank Reactor
  - Plug Flow Reactor

# Stability criteria: Safety Constraints

| Normal Operating Condition | In Case of Failure |
| --- | --- |
| Cooling Capacity | Accumulation |
| $q_{rx} < q_{ex}$ | $MTSR < T_{D24}$ |

# Stability Criteria

- Adiabatic temperature rise

$$\Delta T_{ad} = \frac{(-\Delta H_R) \cdot C_{A0} \cdot X_A}{\rho \cdot c'_p} = \frac{Q'_R \cdot X_A}{c'_p}$$

- Non critical for ΔTad < 50 K as far as no pressure

- Critical for ΔTad > 200 K

# Stability Criteria

- Reaction number B: sensitivity of the reaction rate towards temperature

$$r = k_{\infty} \cdot e^{-\frac{E}{RT}} \cdot C_0 \cdot (1 - X)$$

Temperature sensitivity

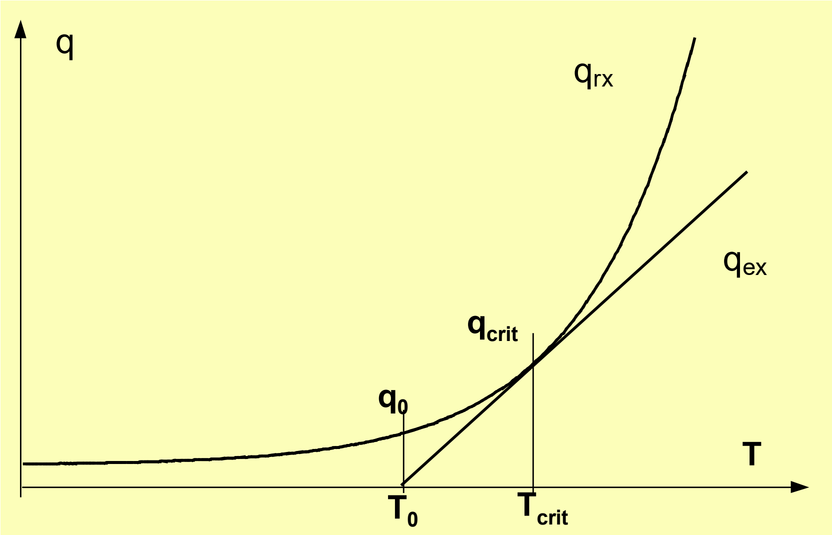
$$\frac{dr}{dT} = k_{\infty} \cdot e^{-\frac{E}{RT}} \cdot C_0 \cdot (1 - X) \cdot \frac{E}{RT^2} = r \cdot \frac{E}{RT^2}$$

$$B = \frac{\Delta T_{ad} \cdot E}{R \cdot T^2}$$

**Batch reactor critical if B> 5**

But does not take heat removal into account

# Heat Balance Semenov




$$q_{rx} = q_{ex} = Q_r \cdot k_0 \cdot exp\left[\frac{-E}{RT_{crit}}\right] = \mathrm{U} \cdot A \cdot (T_{crit} - T_0)$$

$$\frac{dq_{rx}}{dT} = \frac{dq_{ex}}{dT} = Q_r \cdot k_0 \cdot exp\left[\frac{-E}{RT_{crit}}\right] \cdot \frac{E}{RT_{crit}^2} = \mathrm{U} \cdot A$$

Divide one side by the other, obtain the Semenov Criterion

$$Se = \frac{k_0 \cdot e^{\frac{-E}{RT_{crit}}}}{UART_{crit}^2} Q_r \cdot E = \frac{q_{crit}E}{UART_{crit}^2}$$

At Tcrit, Se =1, and Se>1 depicts a critical situation

If replace with cooling Temperature $T_0$ (and assumption $T_o T_{crit} = T^2_{crit}$)

$$Se = \frac{q_0 E}{UART_0^2} < \frac{1}{e} \cong 0.368$$

For 0 order reaction, but can be extended to other reaction kinetics

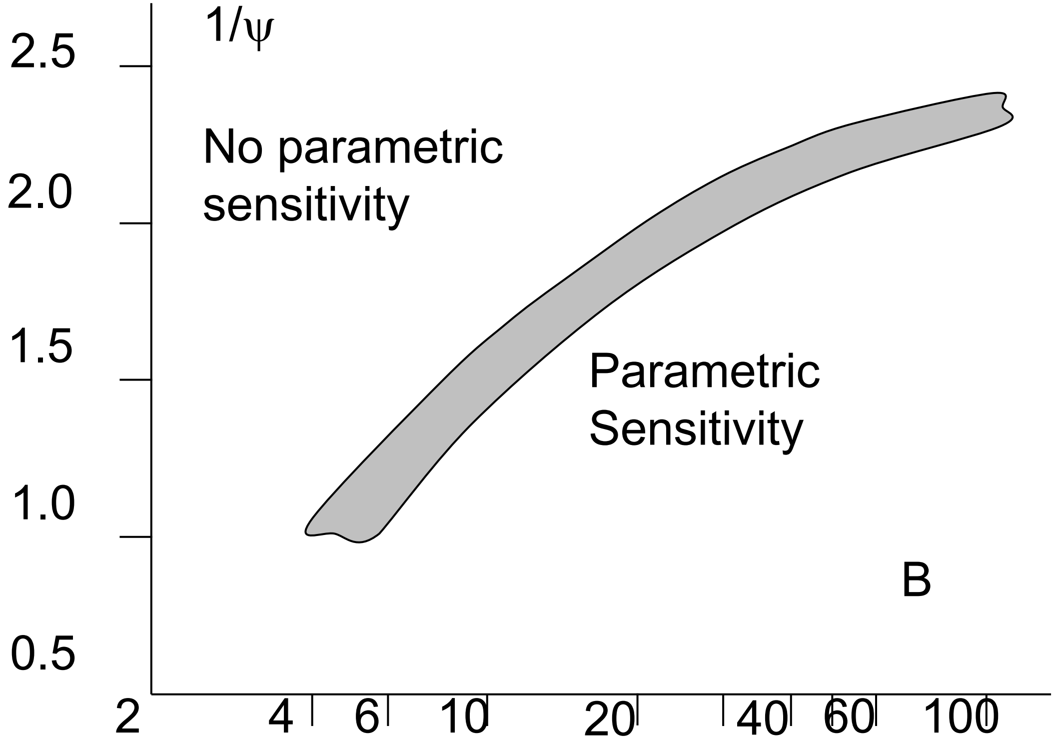
Hugo, P (2016), Chemie Ingenieur Technik 88 (11) 1643-1649

# Parametric sensitivity

Inverse Semenov criterion

$$\frac{1}{\psi} = \frac{UART_0^{\ 2}}{q_0 E}$$

$$\begin{cases} \dfrac{dT}{dt} = \Delta T_{ad} \cdot \dfrac{dX}{dt} - \dfrac{U \cdot A}{M \cdot c_p'}\left(T - T_C\right) \\ \dfrac{dX}{dt} = k_0 \cdot e^{\frac{-E}{RT}} \cdot f\left(X\right) \end{cases}$$




$$B = \frac{\Delta T_{ad} \cdot E}{RT^2}$$

# Stability criteria

$$\begin{cases} \dfrac{dX}{dt} = k_\infty \cdot e^{-\frac{E}{RT}} \cdot (1 - X) \\ \dfrac{dT}{dt} = \dfrac{U \cdot A}{M_R \cdot c'_p} \cdot (T_C - T) + \Delta T_{ad} \cdot \dfrac{dX}{dt} \end{cases}$$

Material balance

Heat balance

$$St = \frac{U \cdot A \cdot \tau_r}{M_R \cdot c'_p} = \frac{U \cdot A \cdot \tau_r}{V_R \cdot \rho \cdot c'_p} = \frac{\tau_r}{\tau_c}$$

$$Da = k \cdot C_{A0}^{n-1} \cdot \tau_r$$

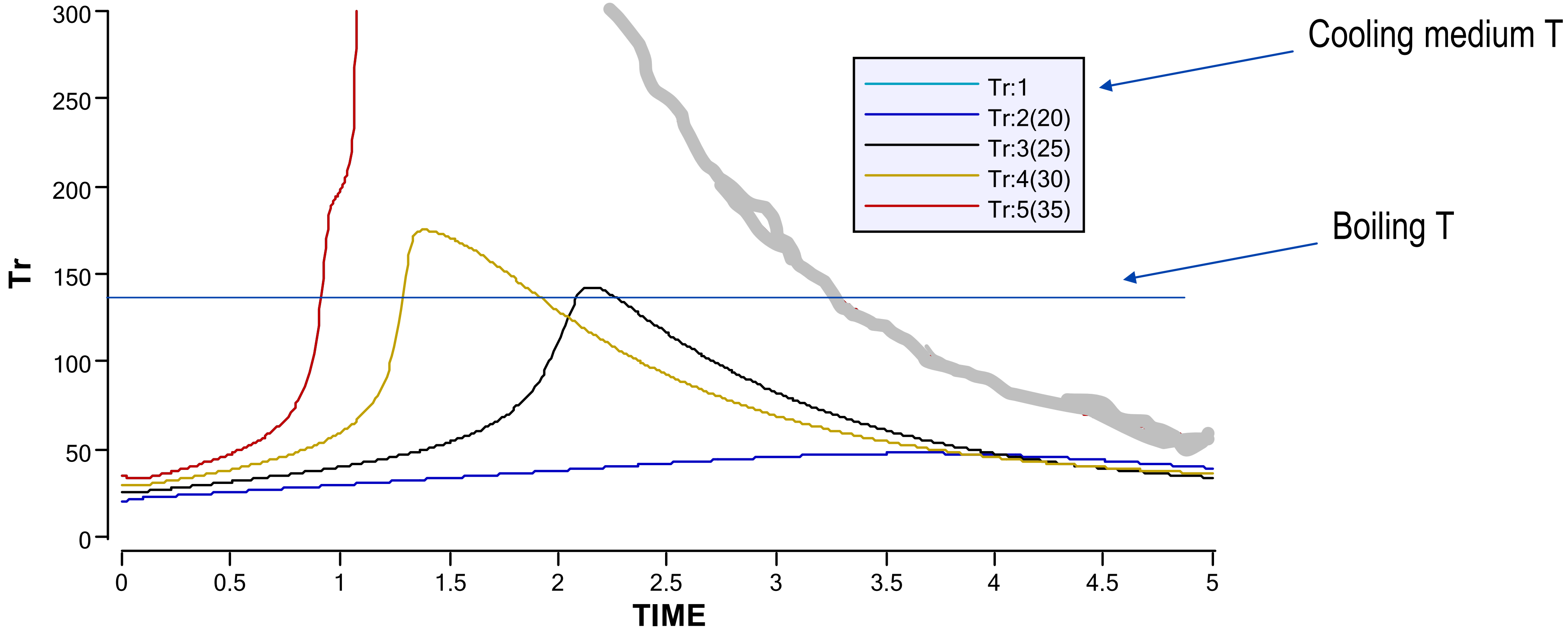
$$\frac{Da}{St} = \frac{k \cdot C_{A0}^{n-1} \cdot \rho \cdot V \cdot c'_p}{U \cdot A}$$

Reaction time defined at cooling T: $\tau_r = \frac{1}{k_{(T_C)} \cdot c_0^{n-1}}$

Cooling time: $\tau_c = \frac{\rho V c'_p}{UA}$

**Batch reactor stable if Da/St << 1**

# Isoperibolic Reactor, parametric sensitivity



# Chemical Reactor Safety

- Calorimetric methods
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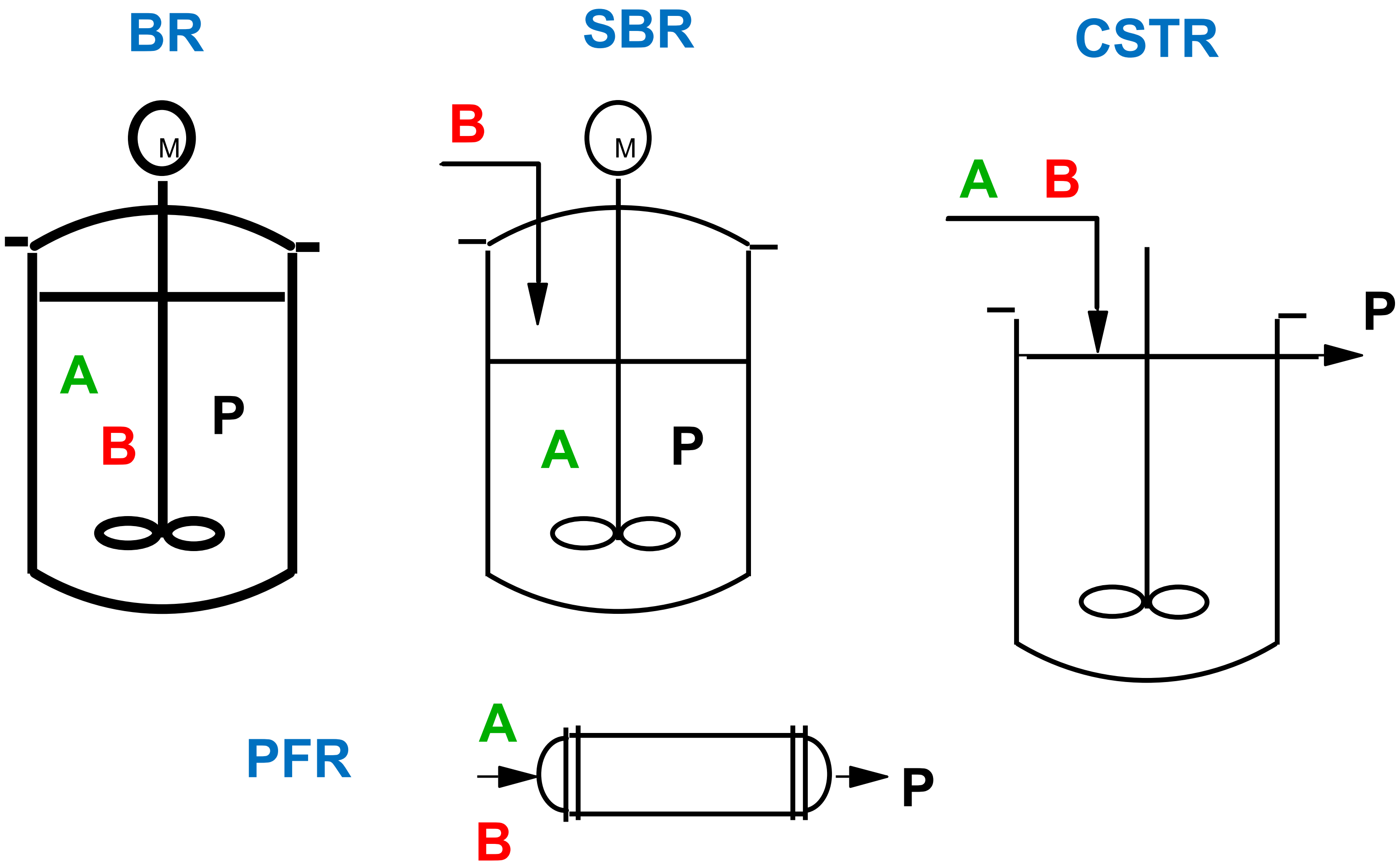
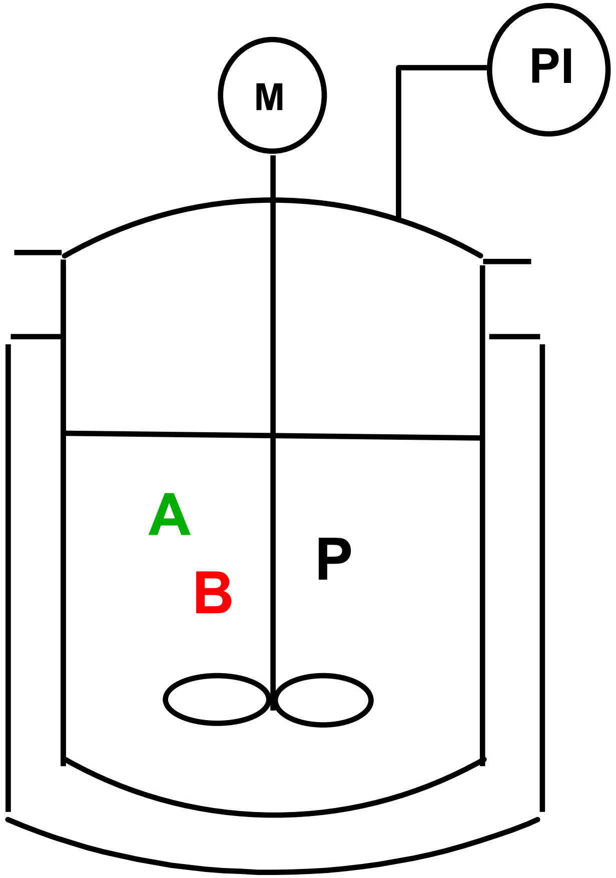
# Ideal Reactors (CRE)



# Batch Reactor

$$A + B \longrightarrow P$$

$$-r_A = k \cdot C_A \cdot C_B$$



# Adiabatic Reaction

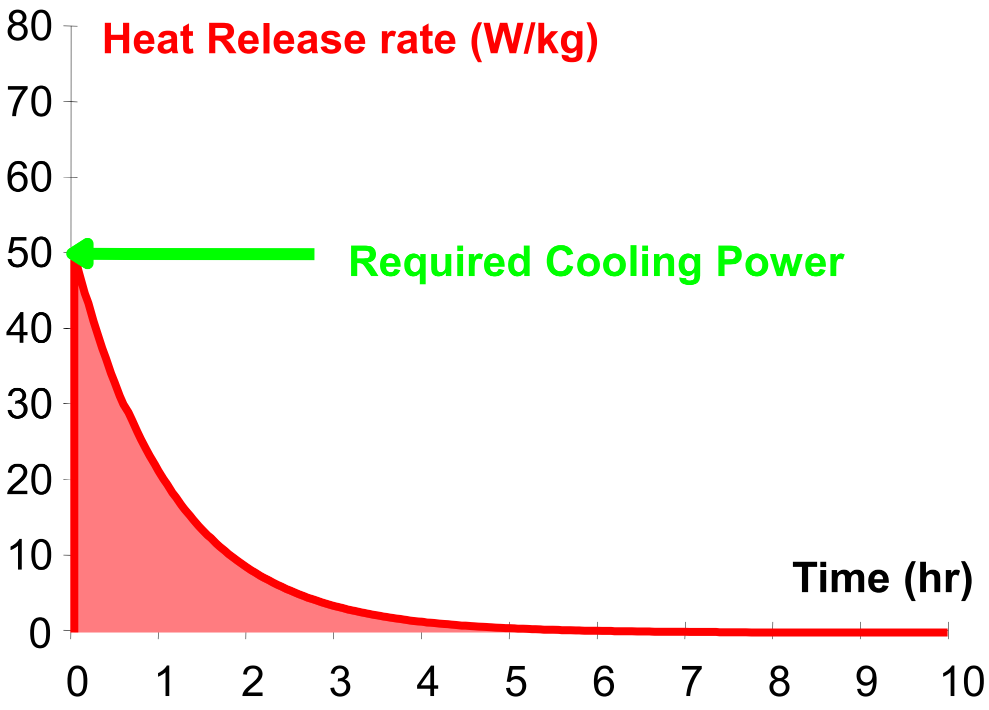
**Heat accumulation** = **Heat production**

$$\Delta T_{ad} = \frac{Q'_R}{C'p} \quad \frac{[kJ/kg]}{[kJ/kg/K]} = \frac{C_{A_0}\,(-\Delta H_R)\,X_A}{\rho\, C'_P}$$

$$T_{final} = T_{initial} + \Delta T_{ad}$$

# Isothermal Reaction

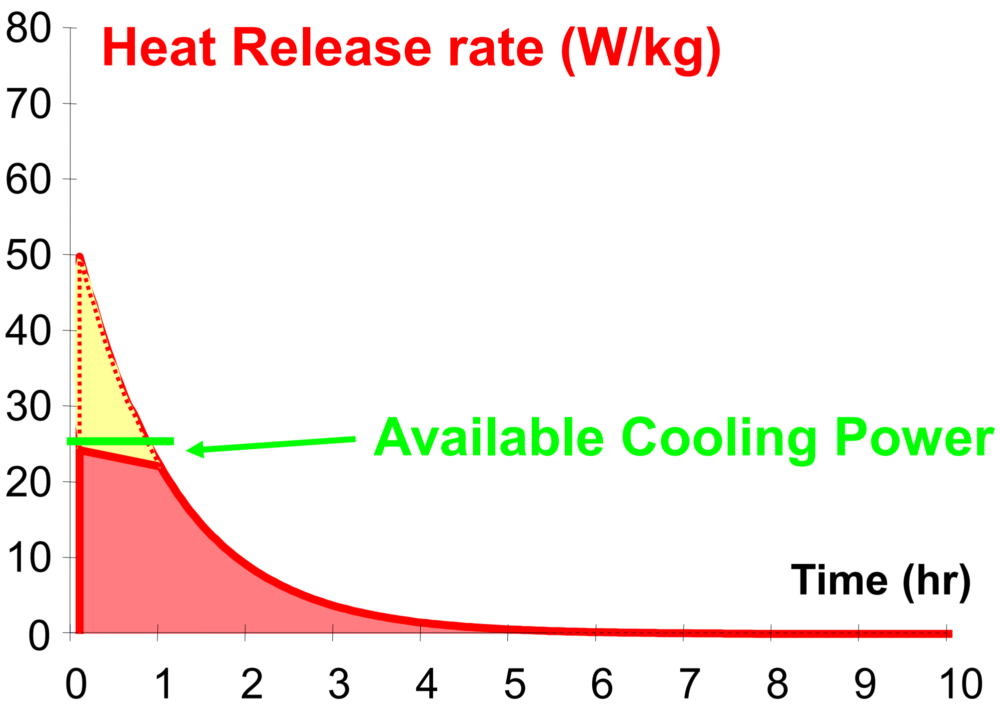
**Heat production** = **Heat exchange**




$$q_{rx} = q_{ex}$$

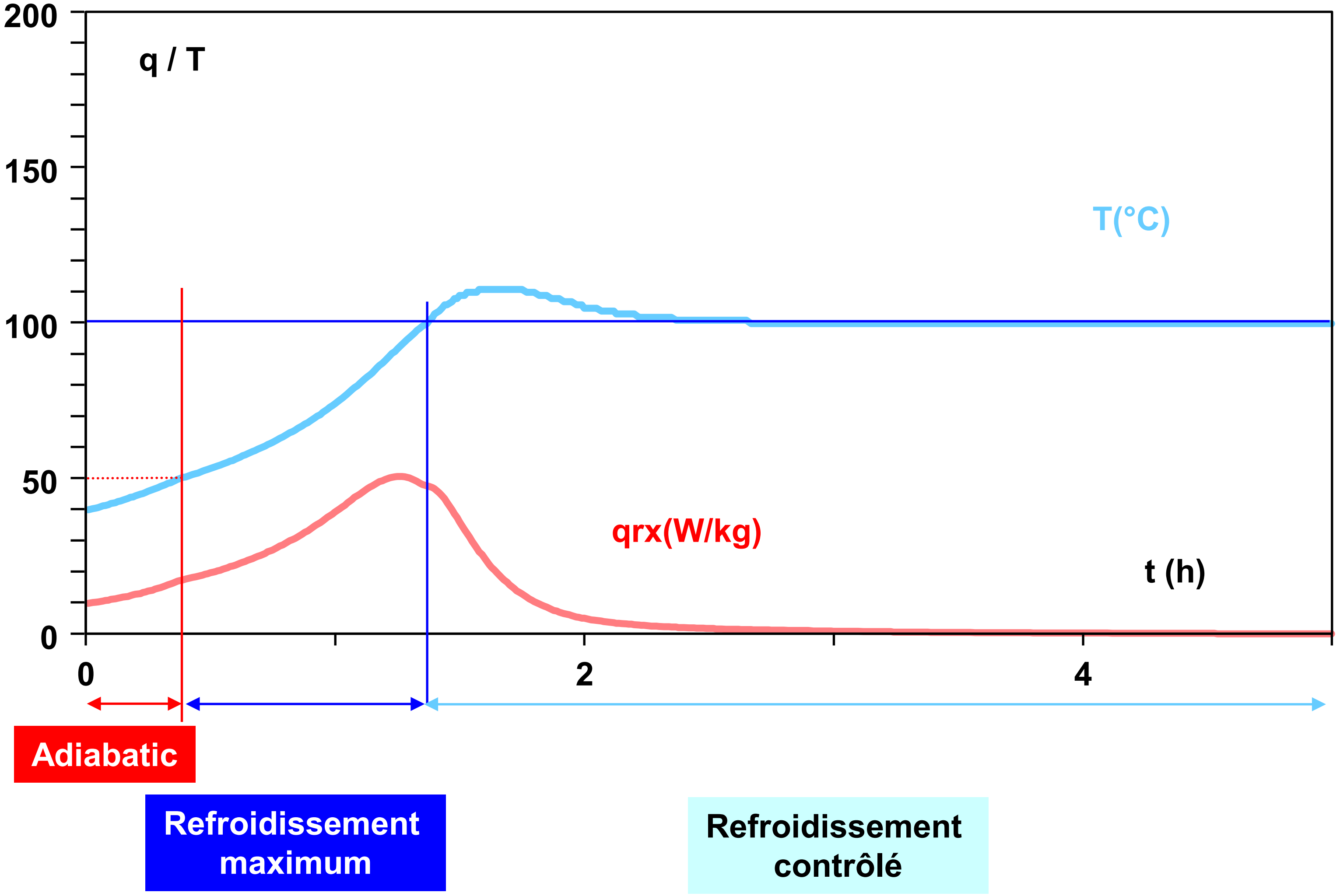
# Isothermal Reaction

**Heat production** = **Heat exchange**



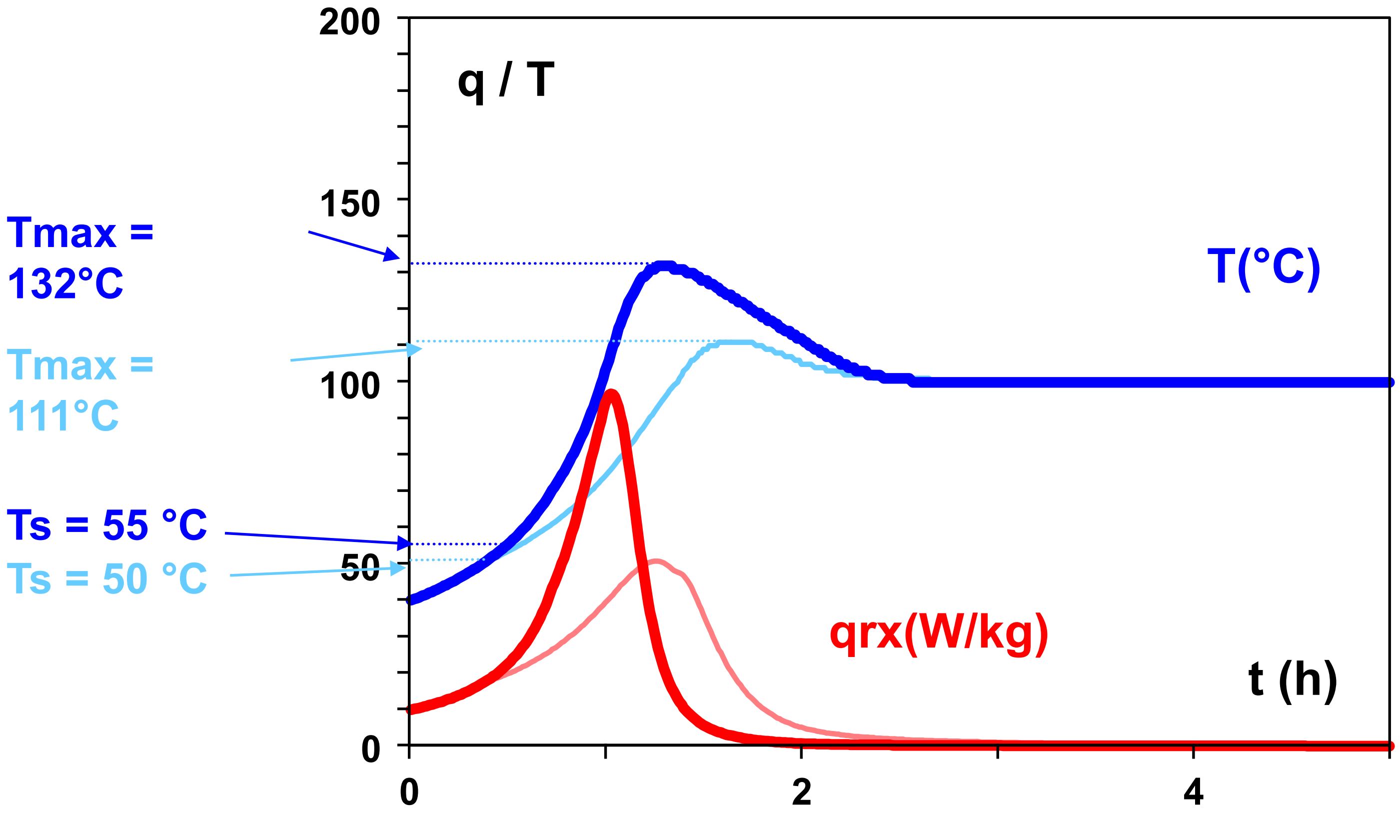

$q_{rx} = q_{ex}$

# Polytropic reactor

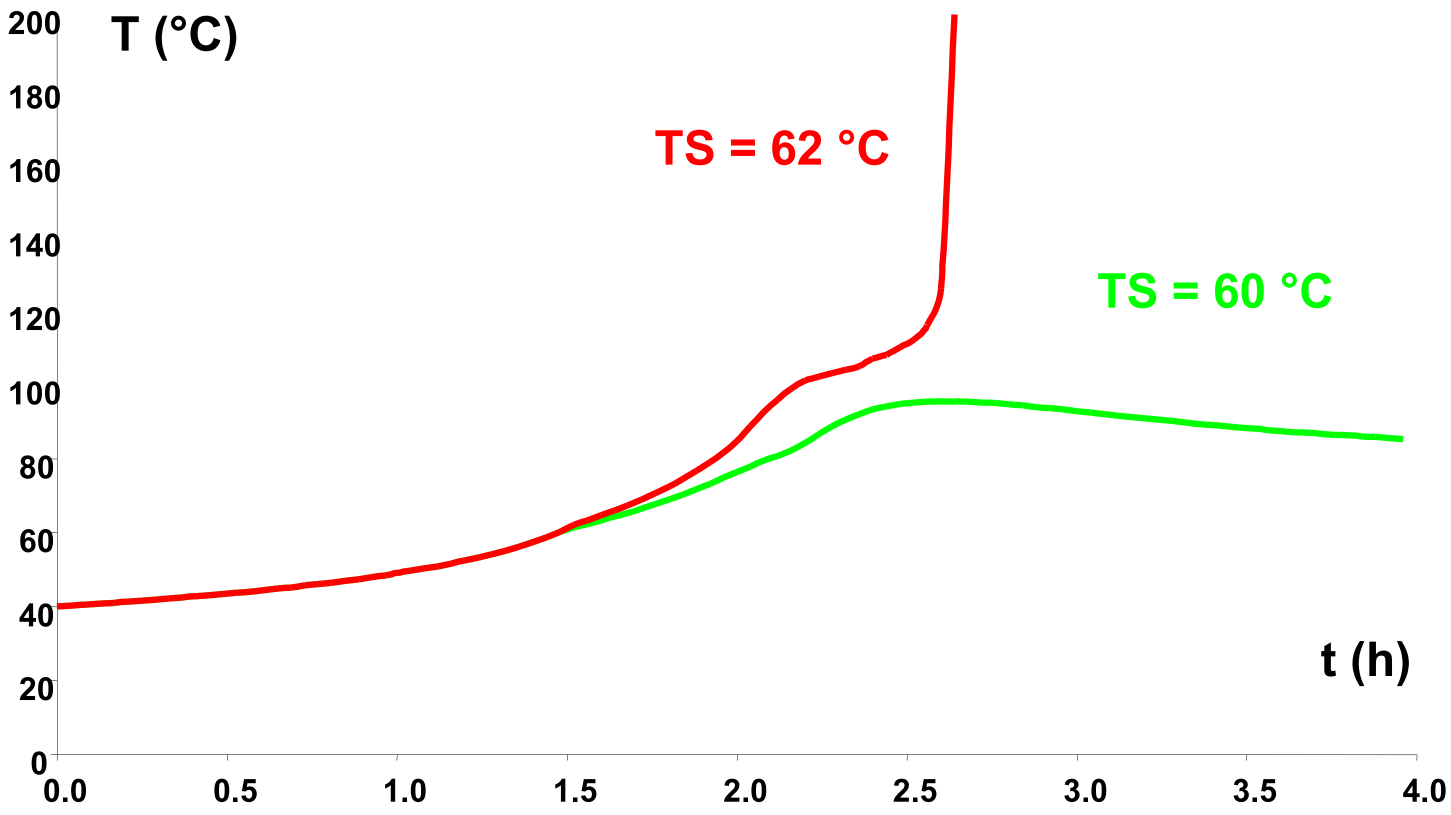


# Polytropic Reaction

## Effect of starting cooling at different $T_s$

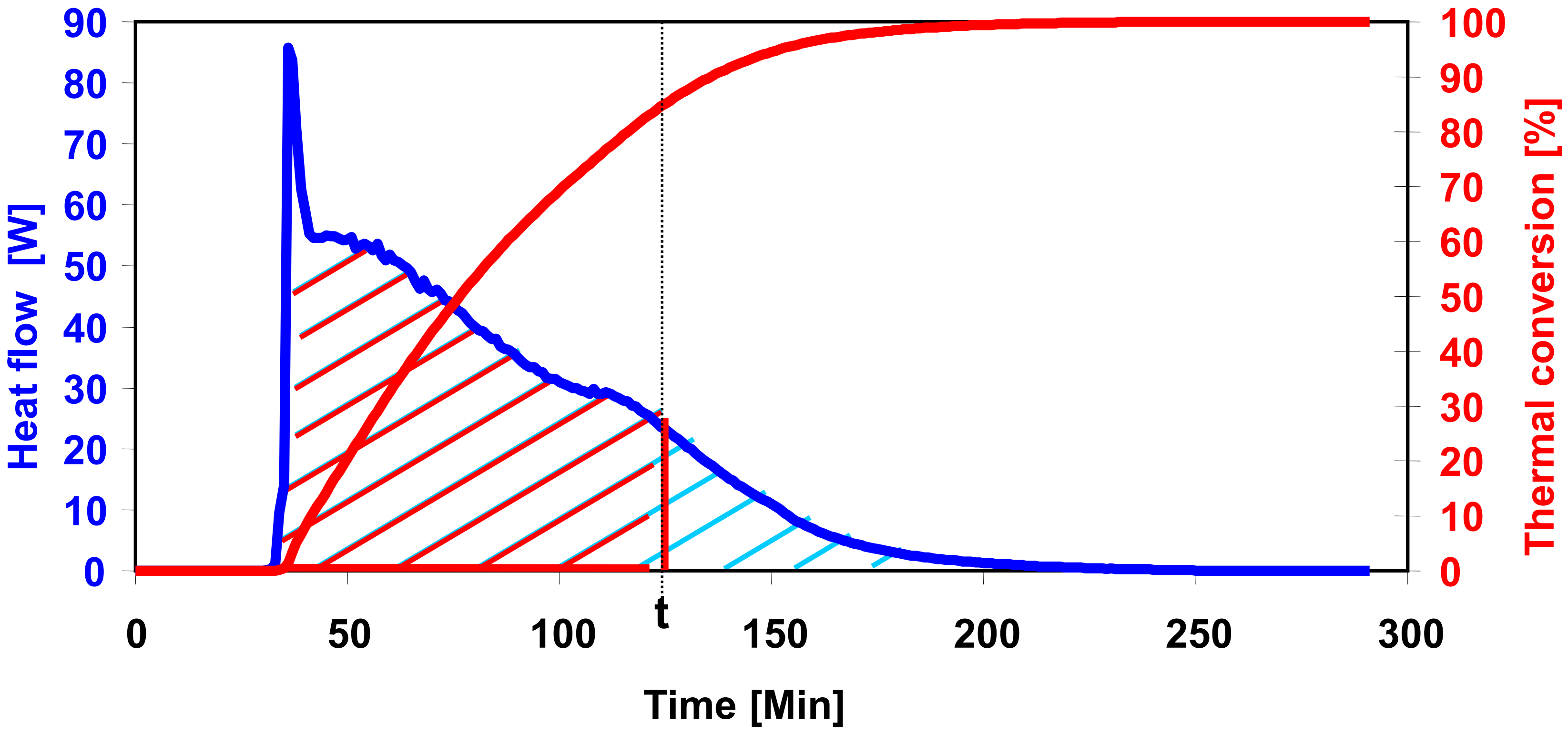


# Polytropic Reactor: Sensitivity

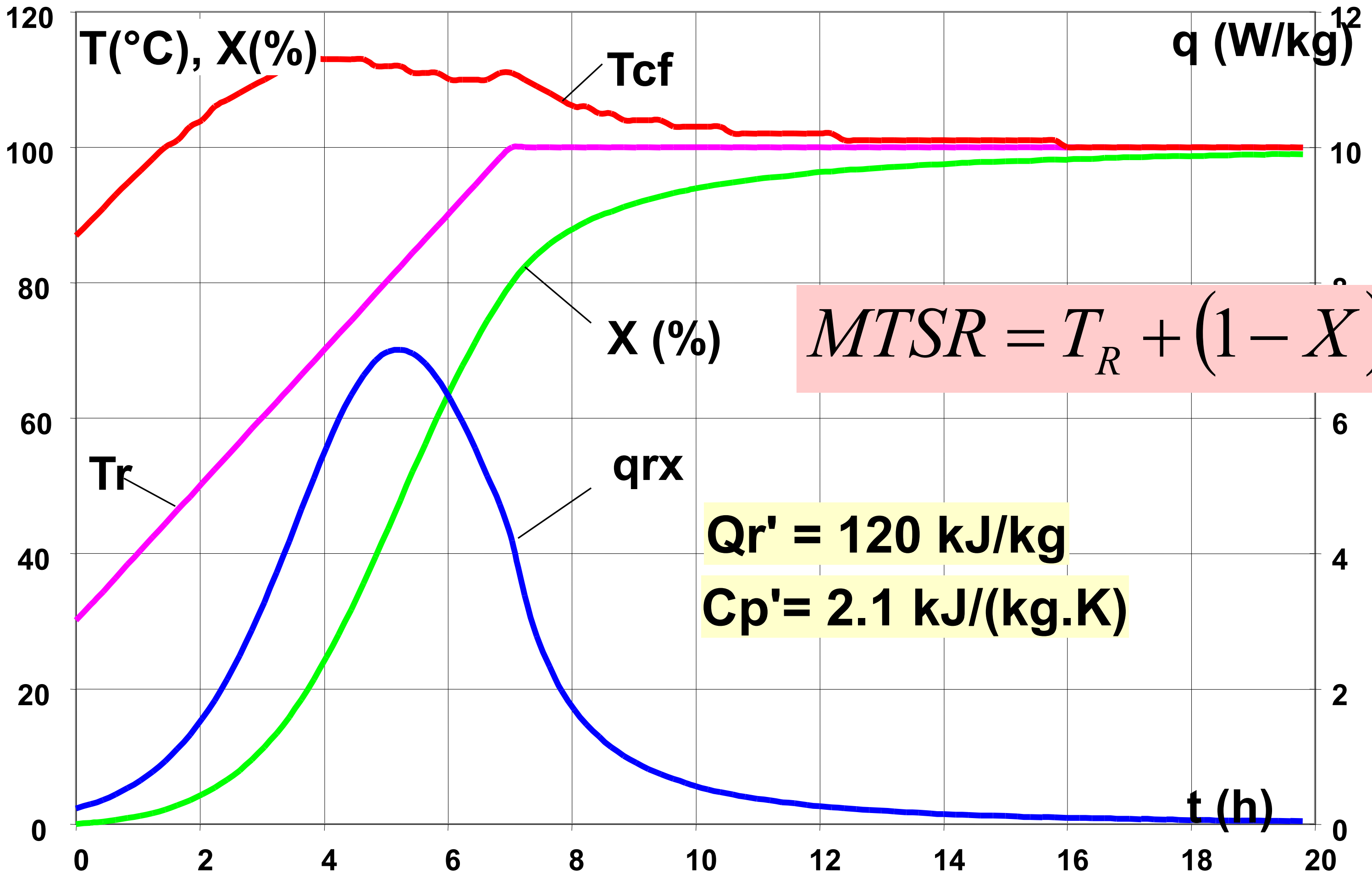


# Batch Reactor: Determination of MTSR

$$\text{Thermal conversion} = 100\% \times \frac{(-\Delta H_r)_t}{-\Delta H_r}$$



# Batch Reactor: Determination of MTSR

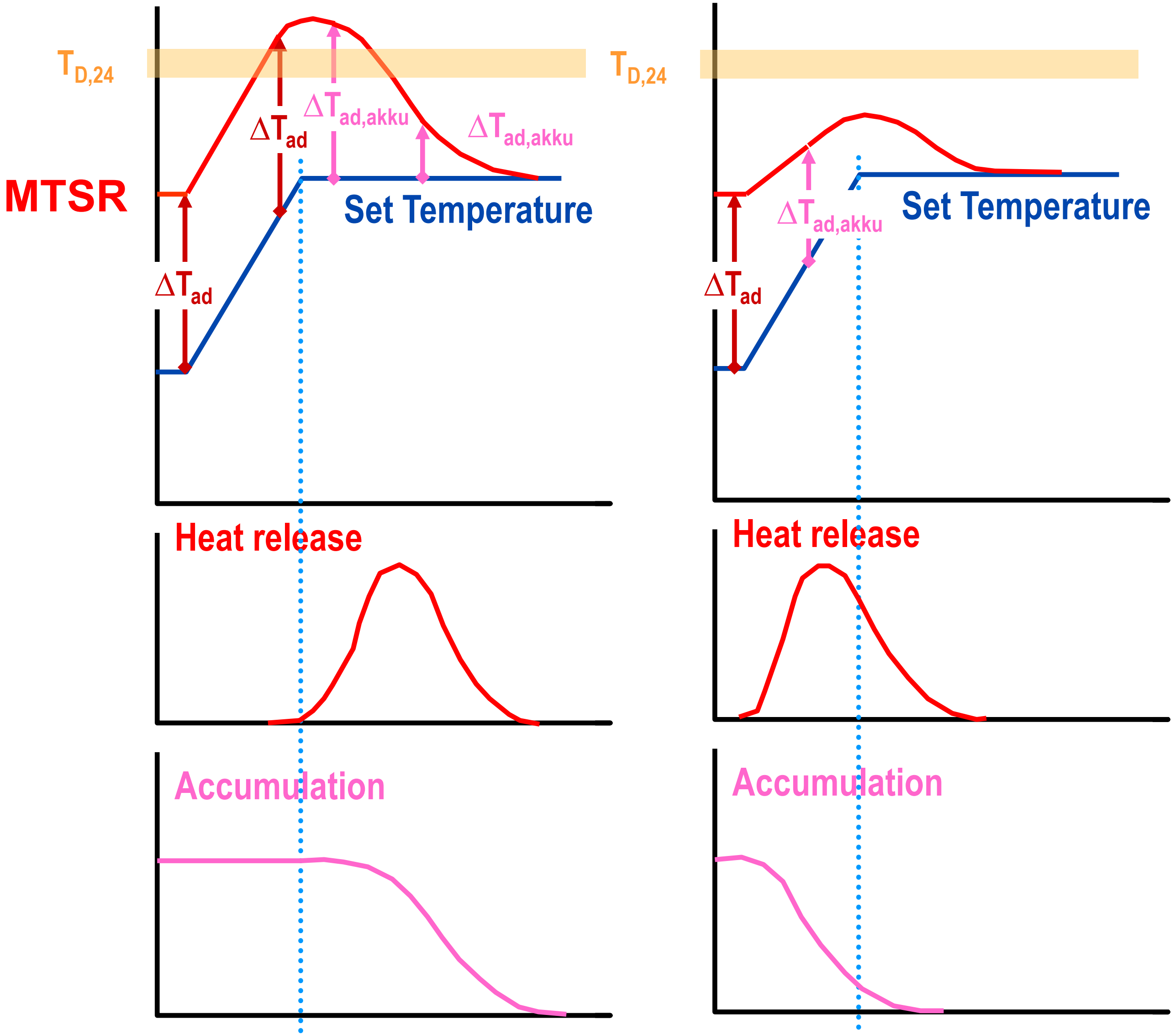



$$MTSR = T_R + (1 - X)\Delta T_{ad}$$

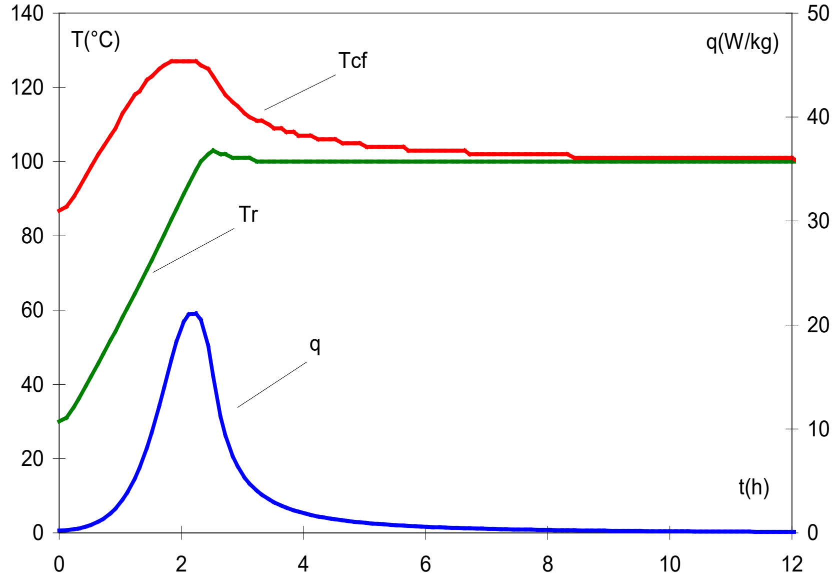
**Qr' = 120 kJ/kg**

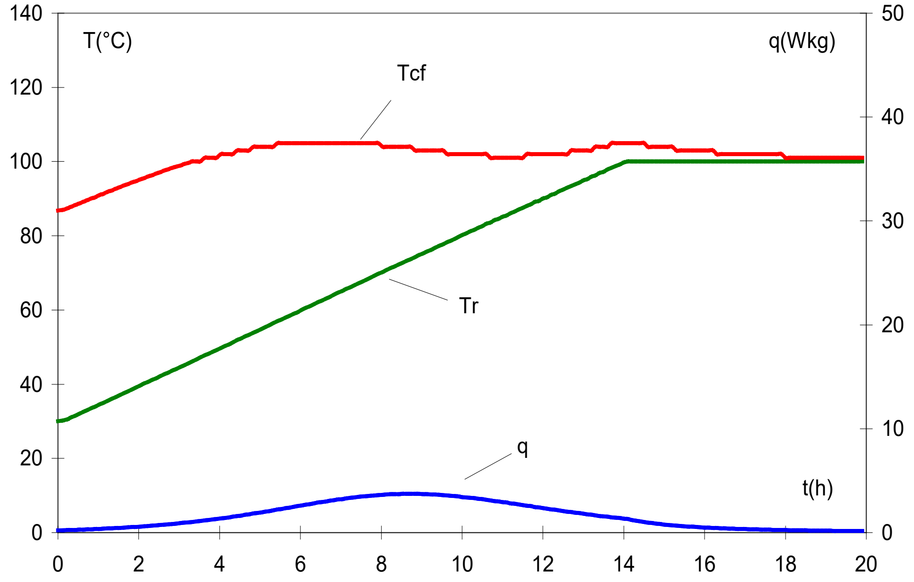
**Cp'= 2.1 kJ/(kg.K)**

# MTSR for batch reactor: slow and fast reaction



# Batch reactor with thermal initiation




Fast heating ramp

Large overshoot for MTSR

Slow heating ramp

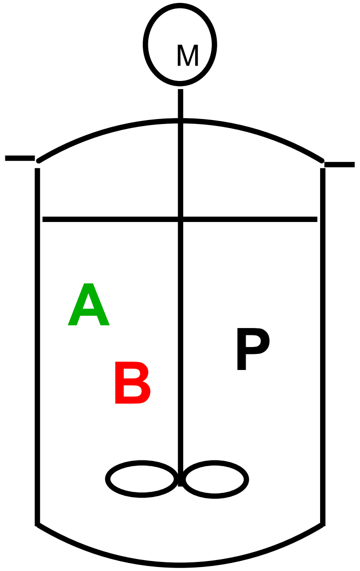
No significant overshoot

# Batch Reactor: Golden Rules

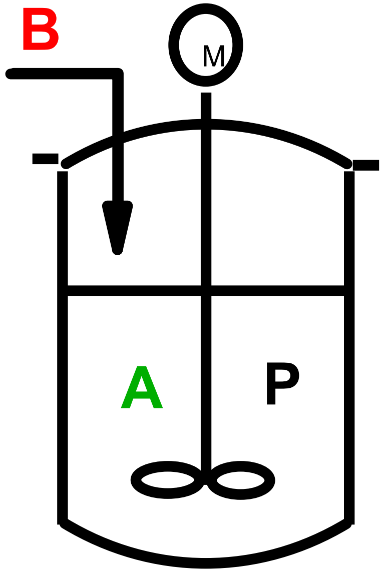
- Temperature as low *as possible*
- Charge must be guaranteed
  - Energy Potential
  - Identity and Quality of reactants
- Temperature Control must be adequate
  - Heating rate
  - Maximum temperature of heating system
- Emergency measures must be provided
  - In case of cooling failure or deviation from normal operating conditions

# Ideal Reactors

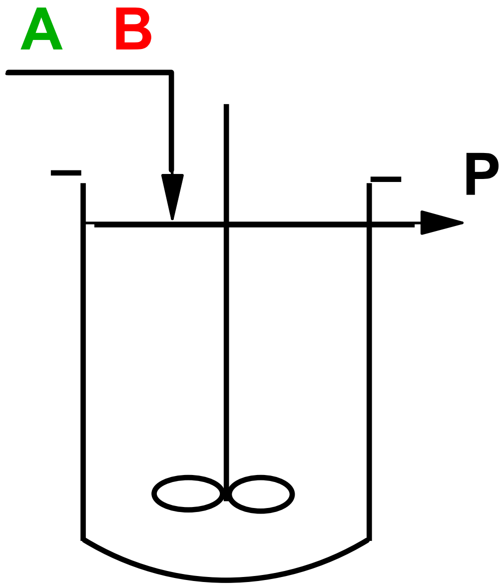
BR



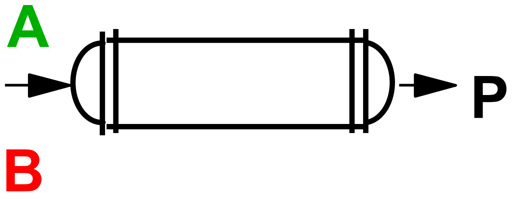

SBR




CSTR




PFR

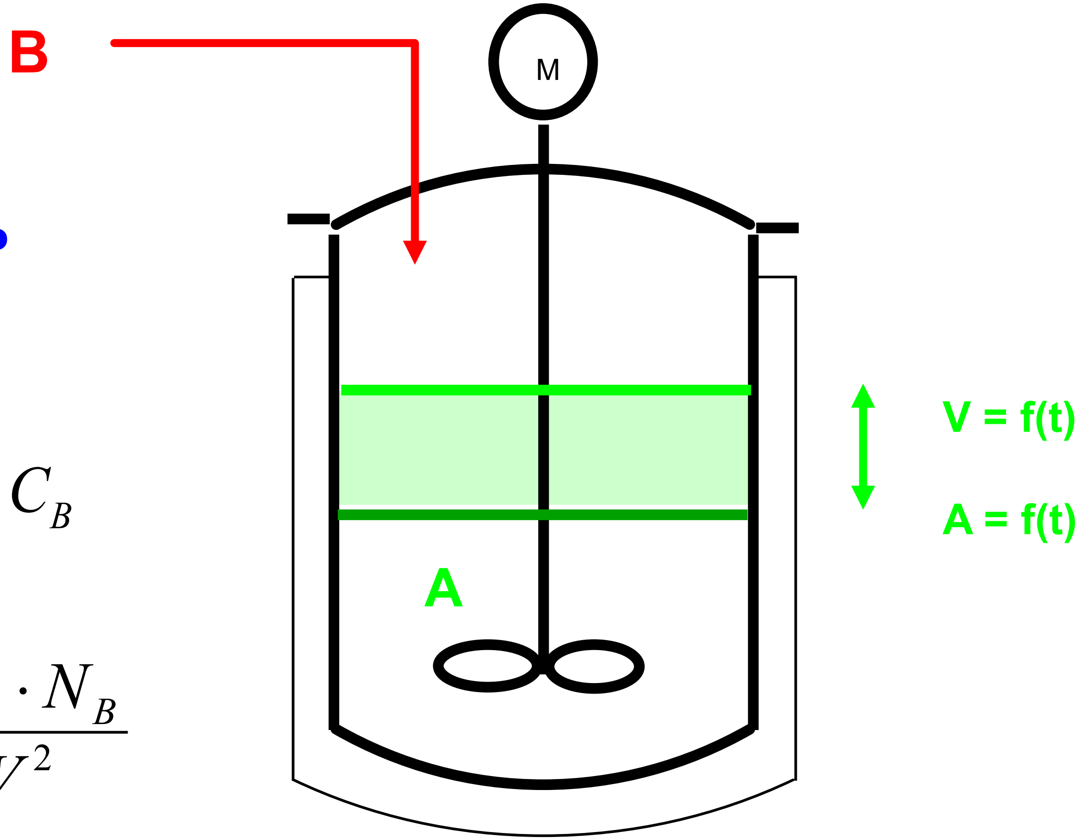


# Semi-Batch Reactor

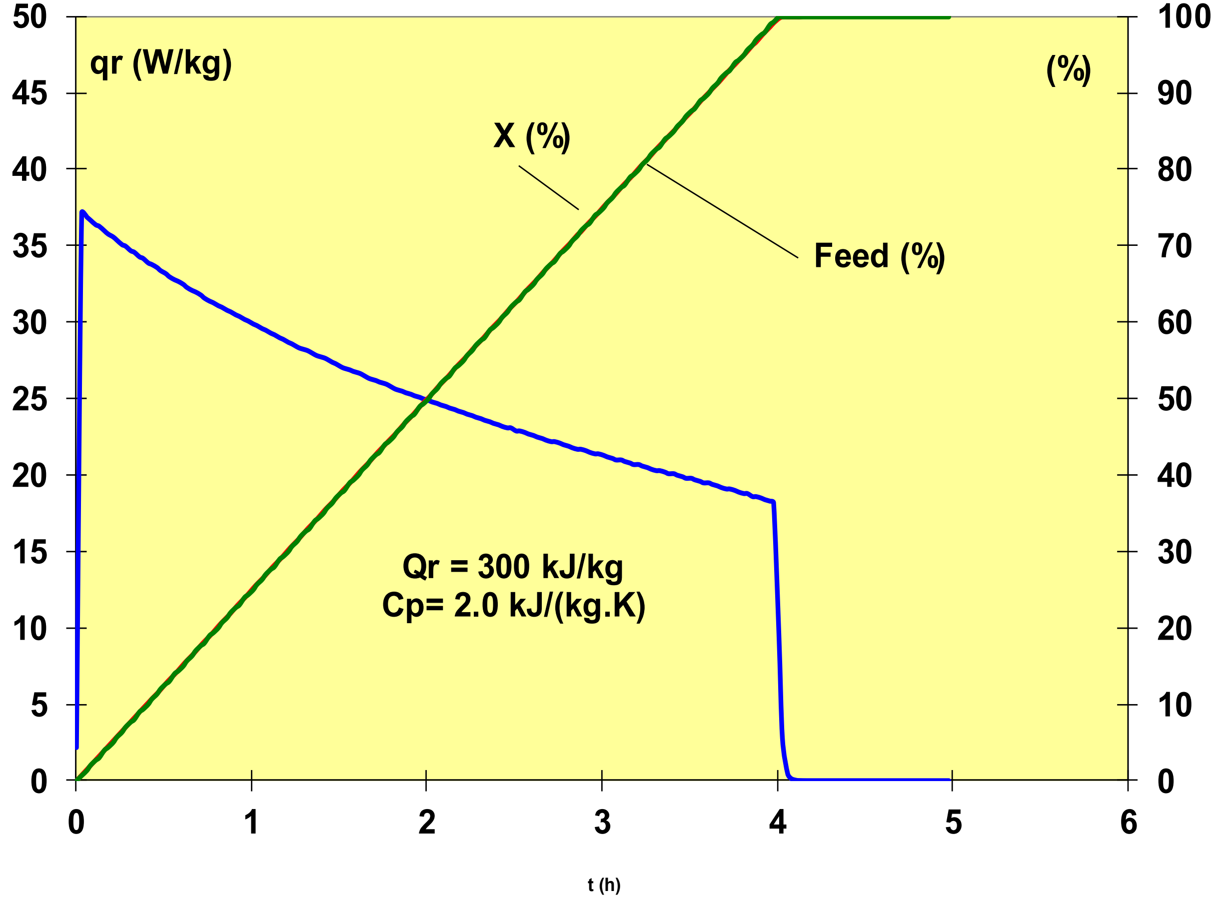
A + B $\rightarrow$ P

$$-r_A = k \cdot C_A \cdot C_B$$

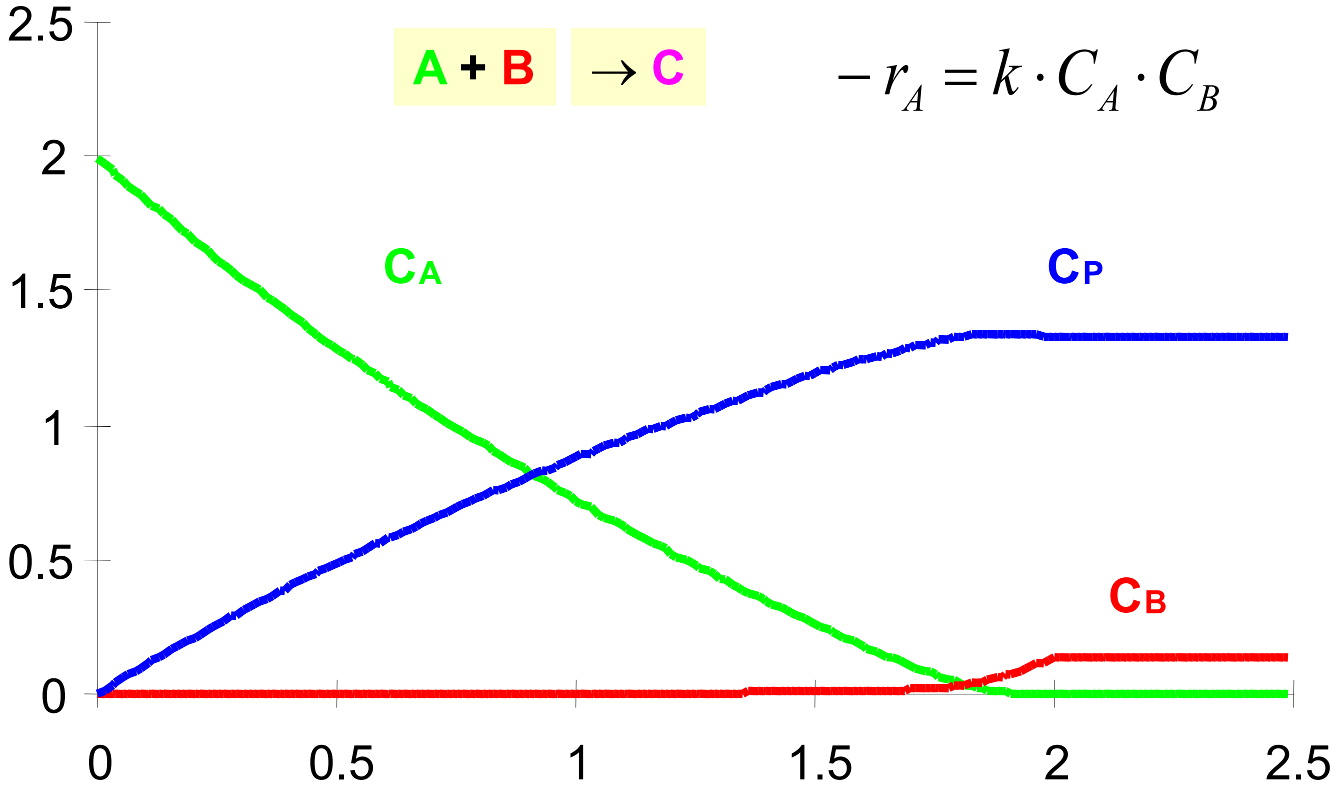
$$-r_A = k \cdot \frac{N_A \cdot N_B}{V^2}$$



# SBR: Fast Reaction



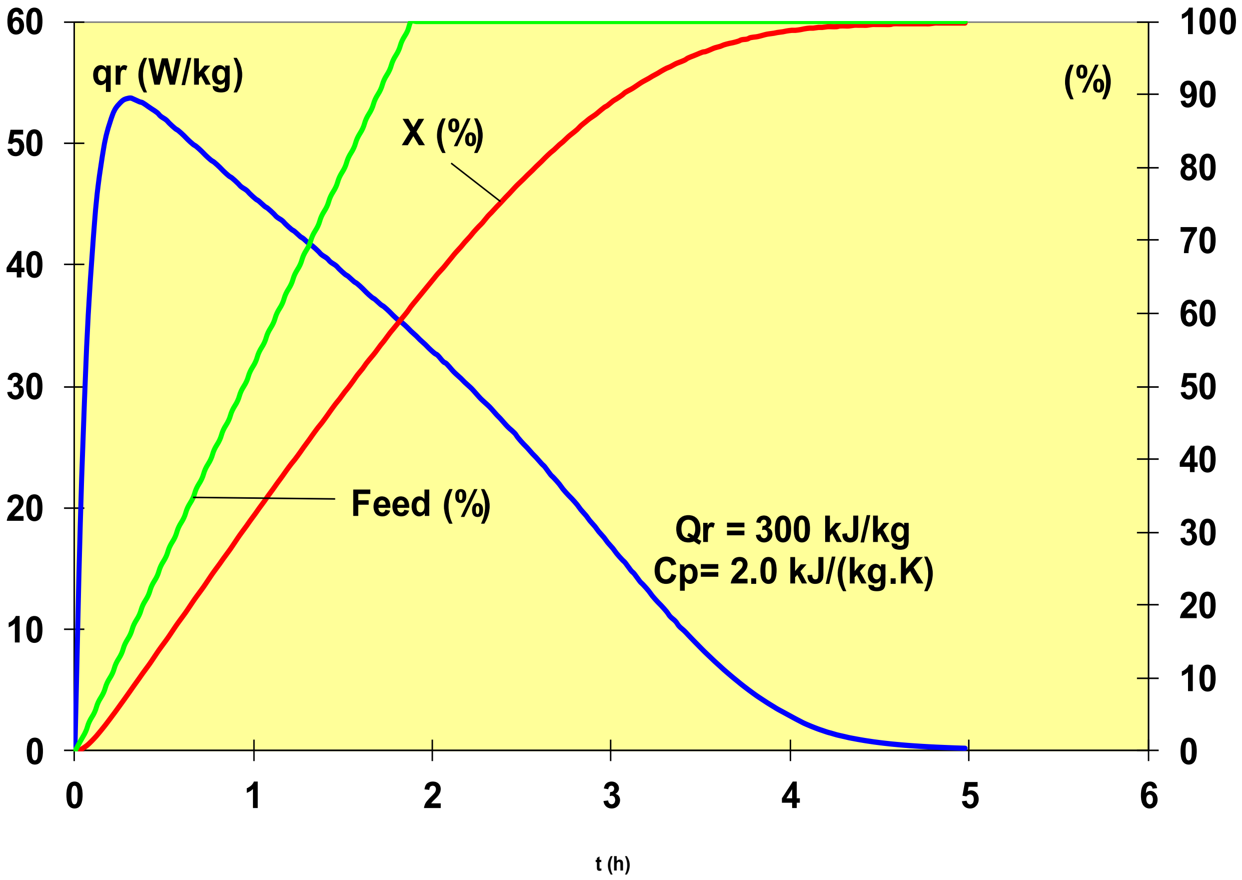
# SBR: Fast Reaction



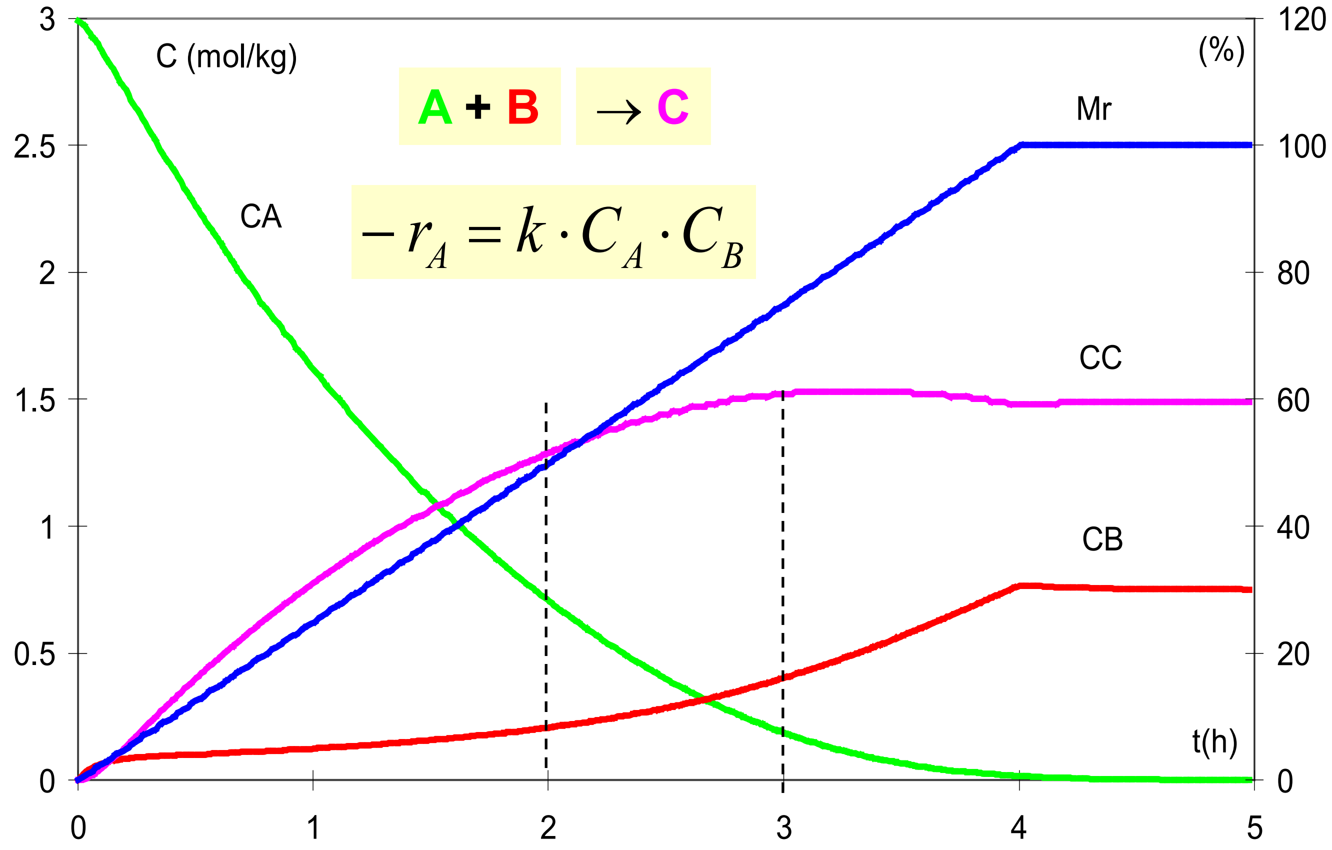
# SBR: Slow Reaction

**A + B → C**

$$-r_A = k \cdot C_A \cdot C_B$$

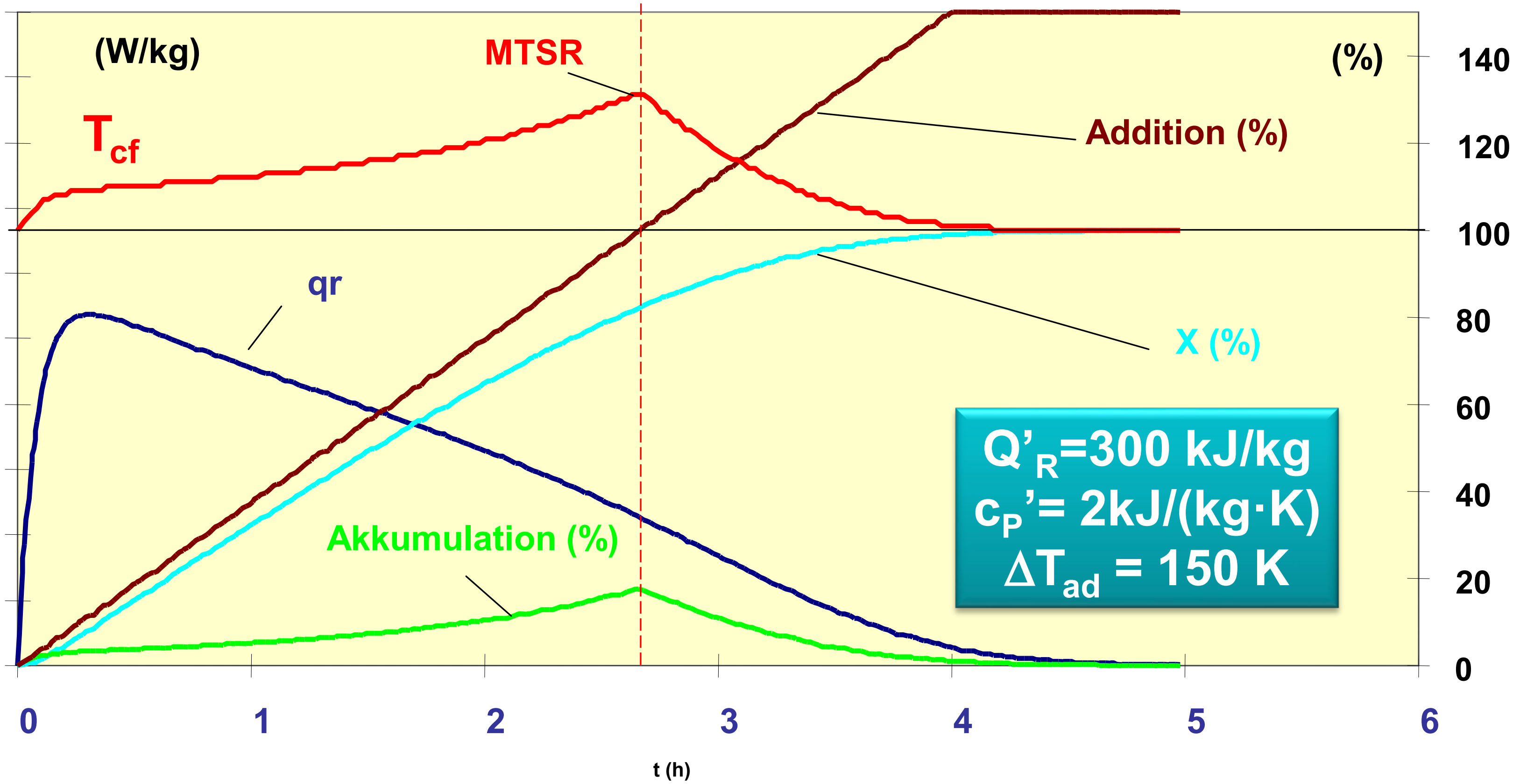


# SBR: Slow Reaction



# Semi-Batch Reactor
## Determination of MTSR

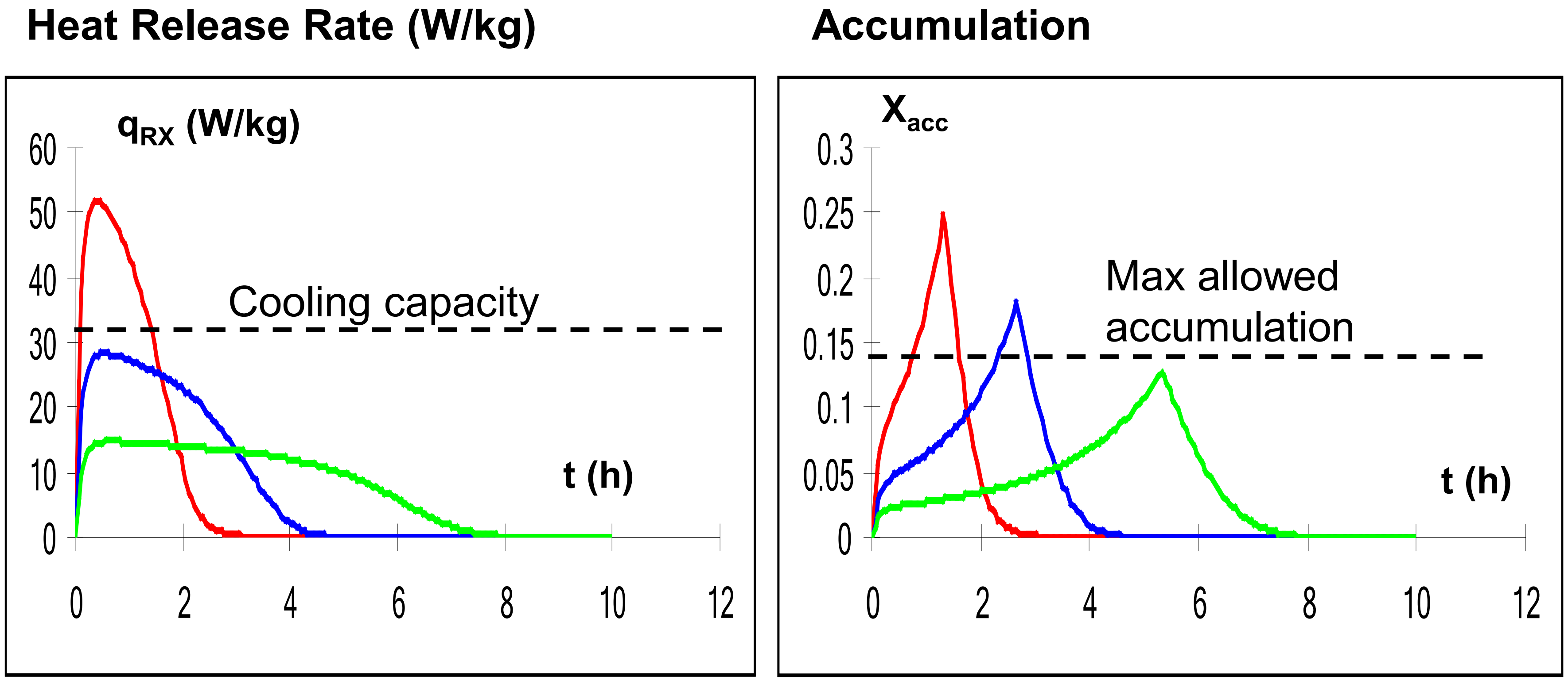
$$MTSR = T_p + (1 - X_{st}) \cdot \Delta T_{ad} \cdot \frac{m_f}{m_{st}}$$



# Stability criteria: Safety Constraints

| Normal Operating Condition | In Case of Failure |
| --- | --- |
| Cooling Capacity | Accumulation |
| $q_{rx} < q_{ex}$ | $MTSR < T_{D24}$ |

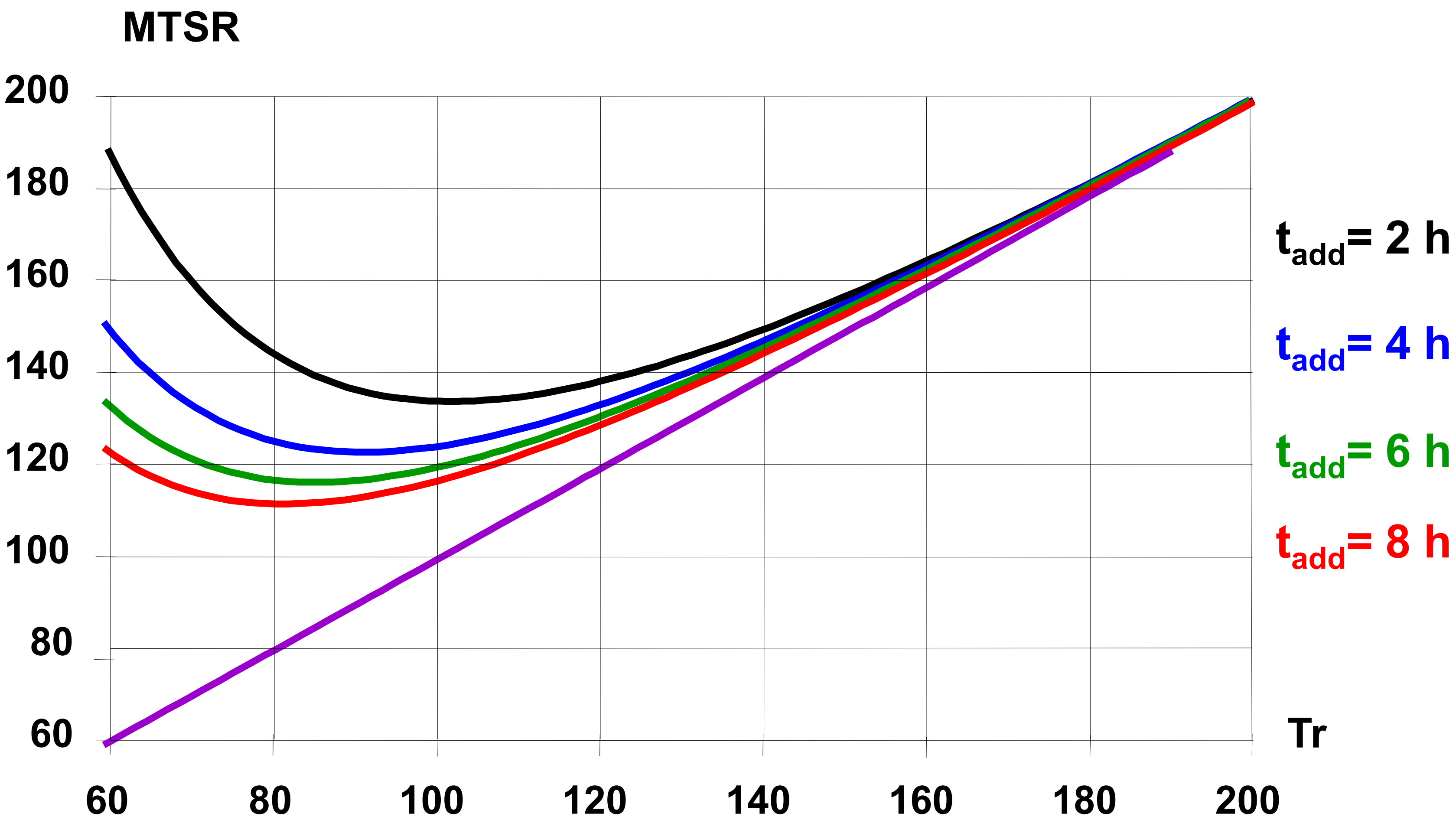
# SBR: Different Feed Rates




**Feed 110% during 2, 4, 6 hrs**

# SBR: Optimisation of MTSR

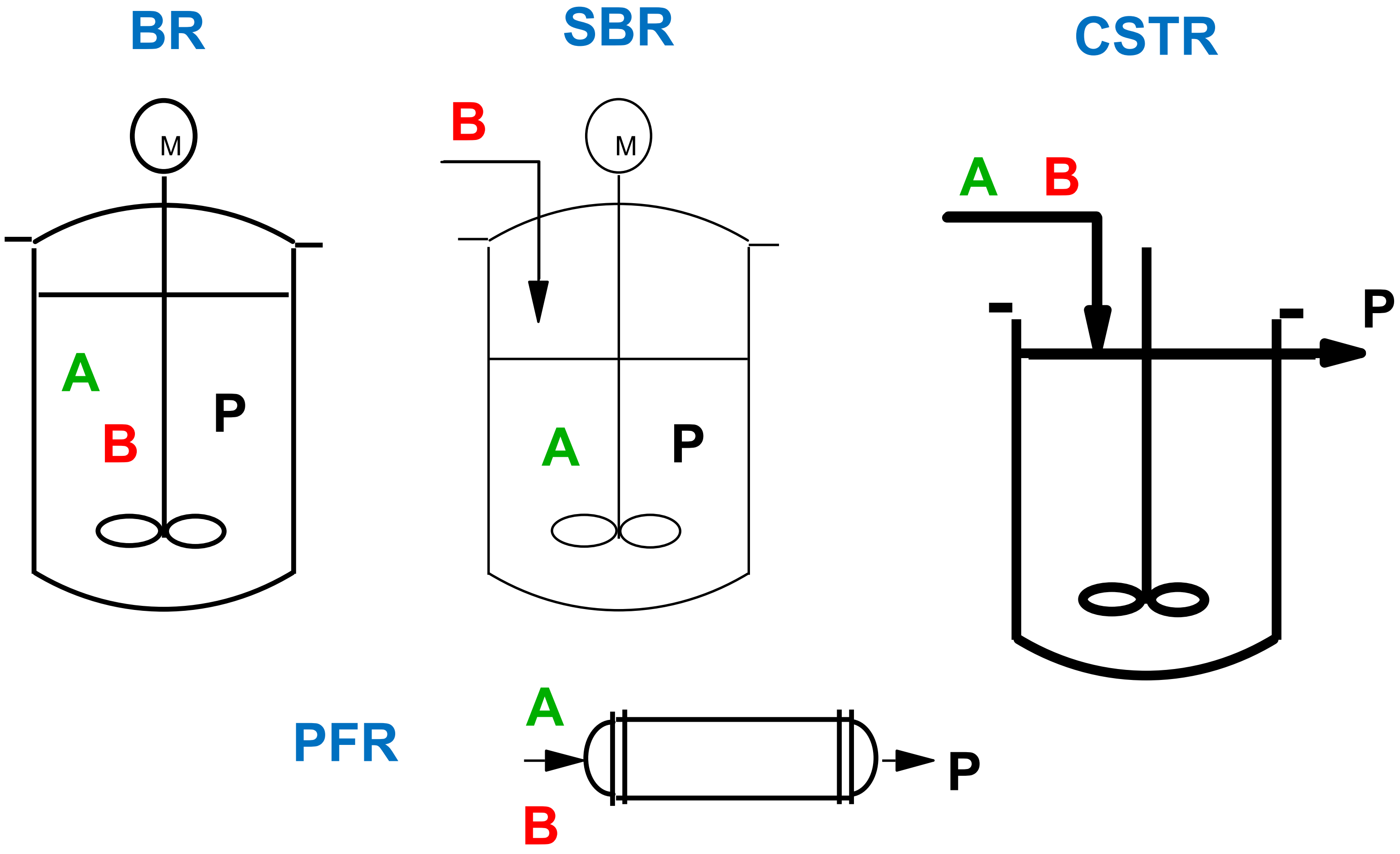
p.171-172



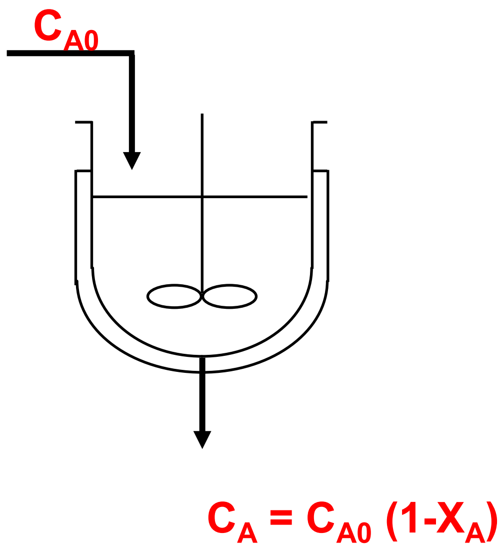
# Semi Batch Reactor: Golden Rules

- Temperature as high *as possible*
- Feed rate must be limited
  - Adapted to cooling capacity
  - Adapted to maximum tolerable accumulation
- Temperature control
  - Maximum level switches off feed
  - Minimum level switches off feed
- Stirrer control
  - ensures good mixing, avoids accumulation
  - interlock with feed in case of malfunction

# Ideal Reactors



# CSTR: Heat Balance




$$q_{RX} = \dot{m} \cdot \left(C_0' - C_f'\right) \cdot \left(-\Delta H_R\right)$$

$$[W] = \left[\frac{kg}{s} \times \frac{mol}{kg} \times \frac{J}{mol}\right]$$

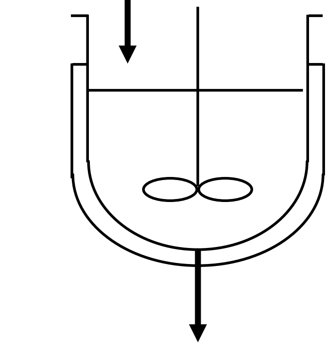
$$q_{EX} = U \cdot A \cdot \left(T_R - T_C\right)$$

$$[W] = \left[\frac{W}{m^2 \cdot K} \cdot m^2 \cdot K\right]$$

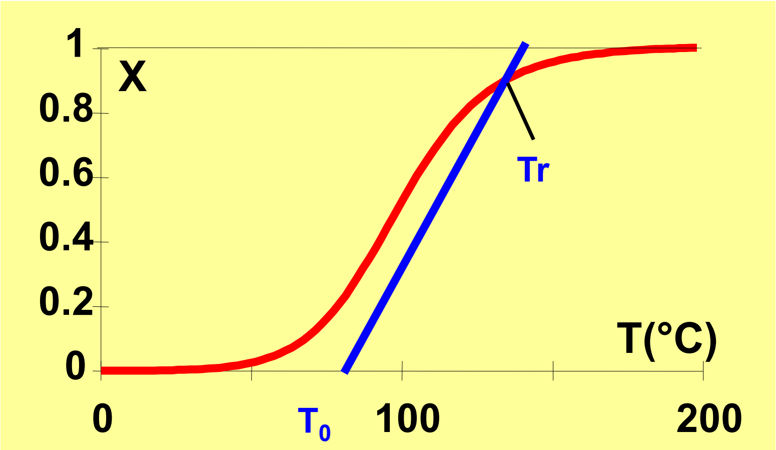
$$q_{AC} = \dot{m} \cdot Cp' \cdot \left(T_R - T_0\right)$$

$$[W] = \left[\frac{kg}{s} \cdot \frac{J}{kg \cdot K} \cdot K\right]$$

# CSTR




$C_A = C_{A0}\,(1\text{-}X_A)$




- Mass balance: $$\tau = \frac{C_{A0}.\,X_A}{-r_A}$$

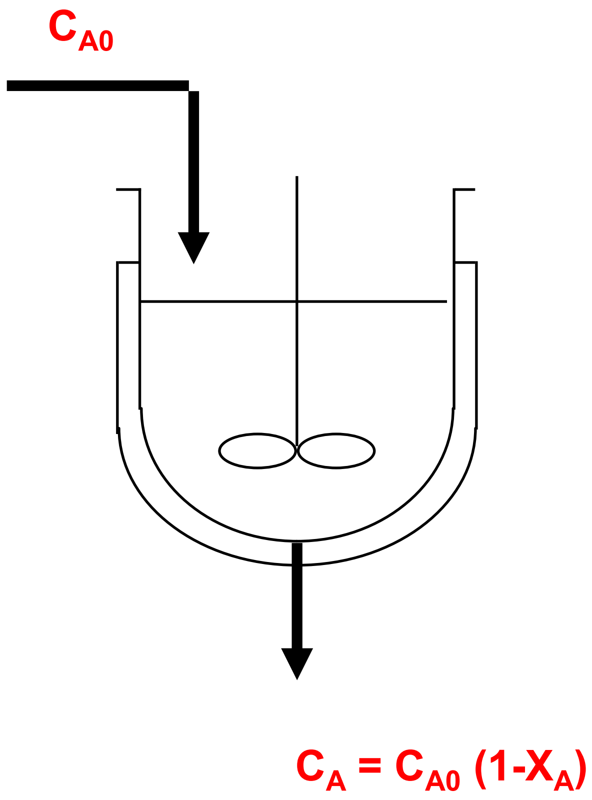
- Energy Balance adiabatic CSTR

$$q_{RX} = -r_A \cdot V \cdot (-\Delta H_R) = F_{A0} \cdot Cp \cdot (T_R - T_0)$$

- Adiabatic CSTR

$$X_A = \frac{c_p}{-\Delta H_R} \cdot (T_R - T_0) = \frac{1}{\Delta T_{ad}} \cdot (T_R - T_0)$$

# CSTR: Safety Aspects

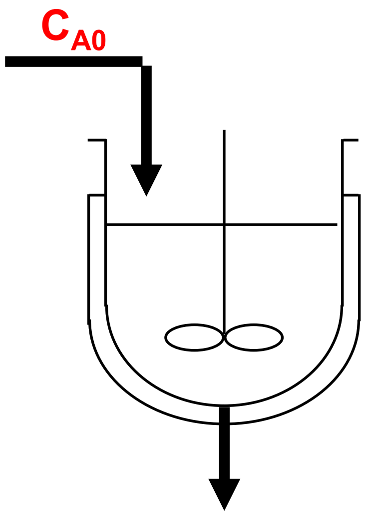



- Low adiabatic rise if operated at high conversion

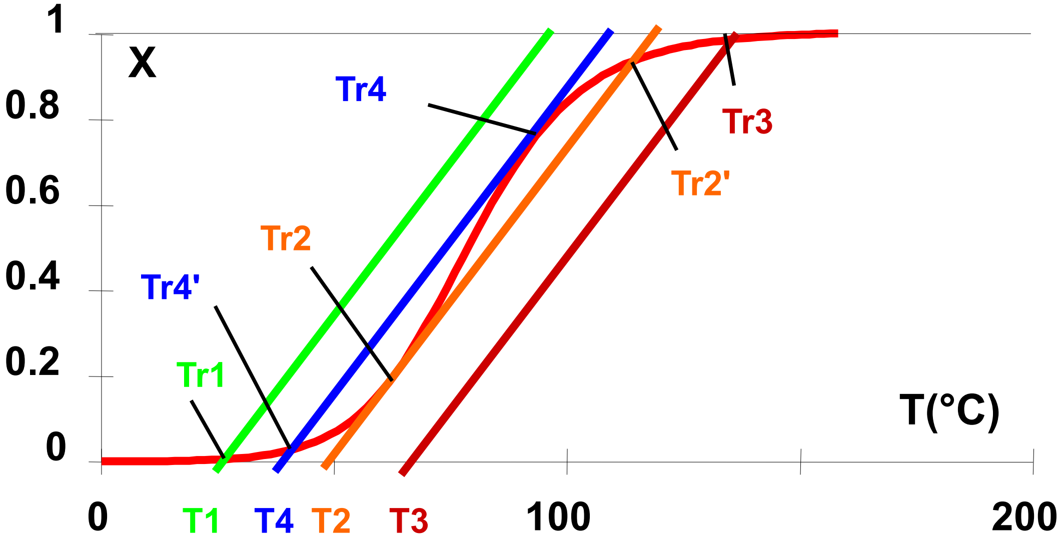
$$T_{cf} = T_r + (1 - X_A)\Delta T_{ad}$$

- Equivalent to batch reactor at start-up
- Critical choice of operating temperature: Optimisation for low MTSR

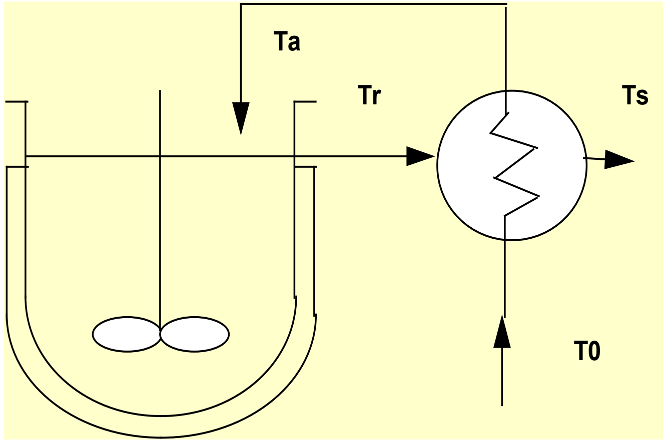
# CSTR: Dynamic Control

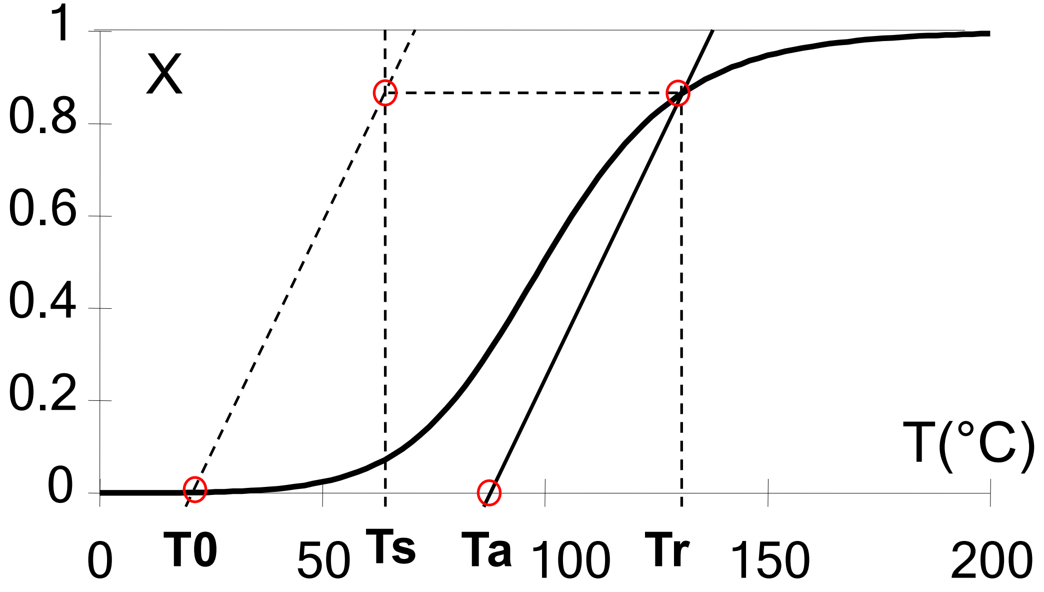



- Easy control at steady state
- Hysteresis at start-up / shut down

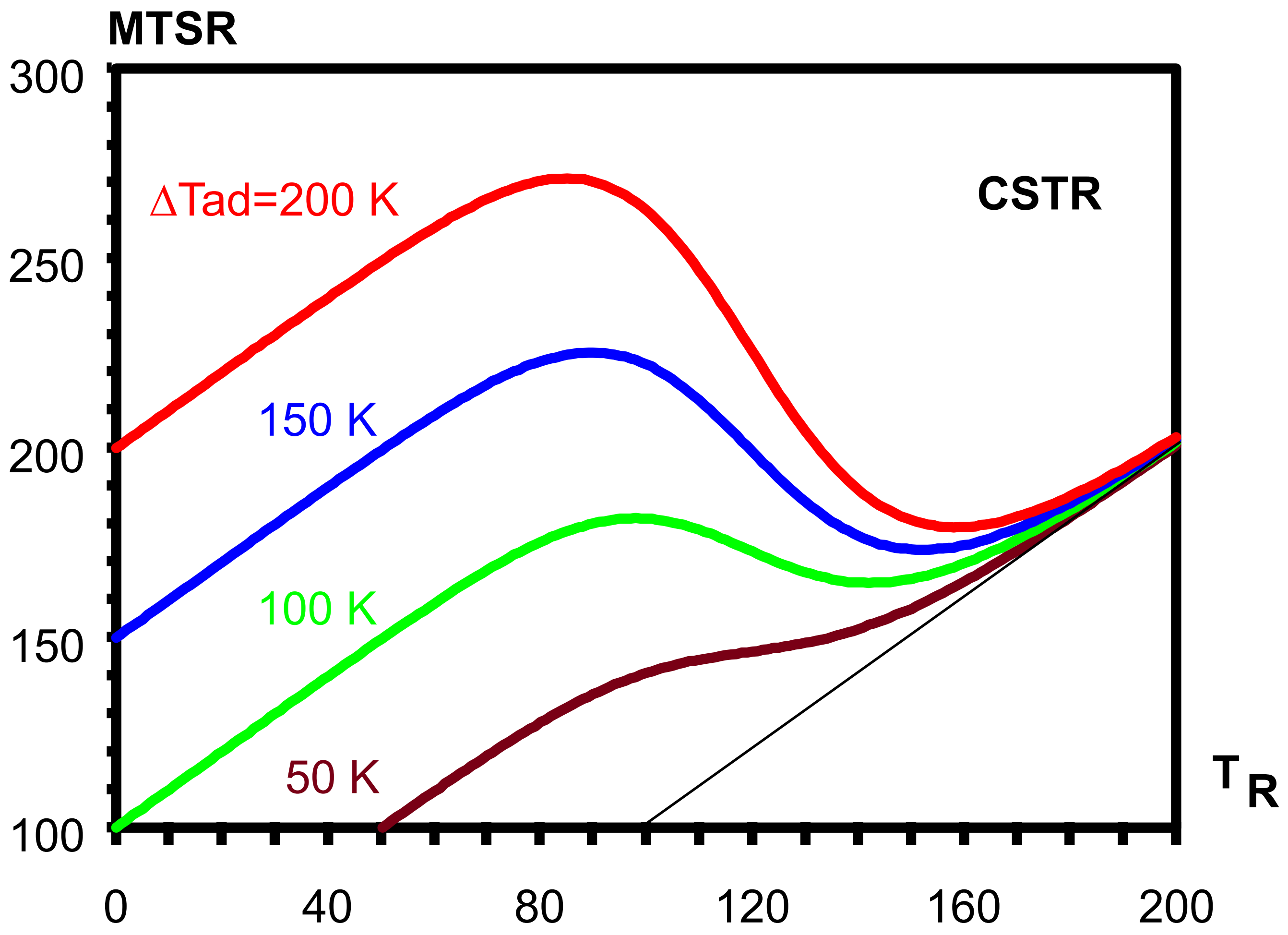


# CSTR: Autothermic

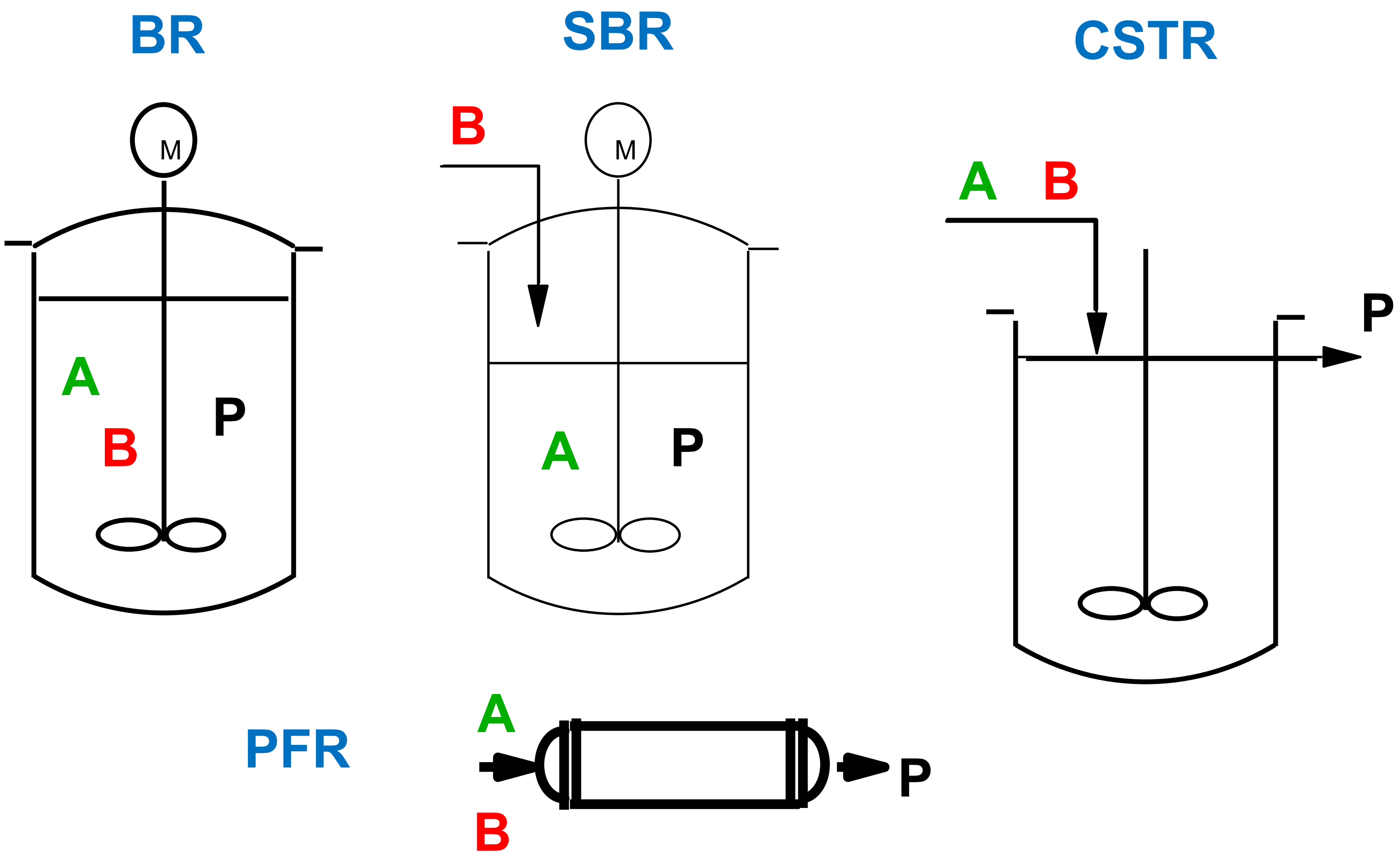


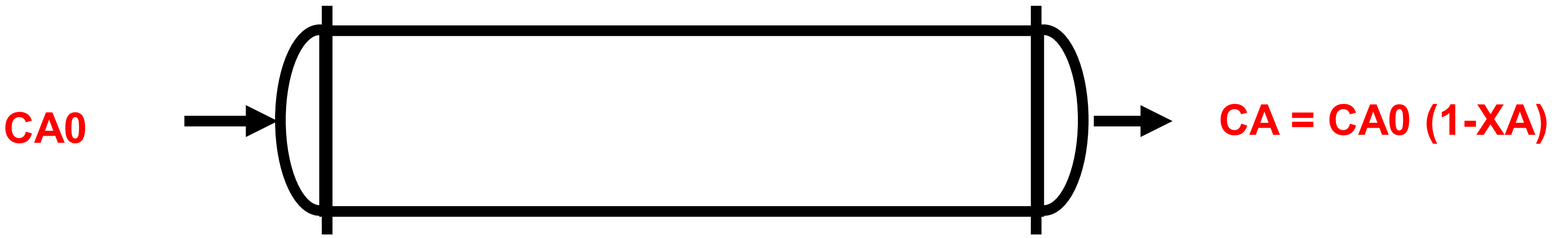
# Optimisation of CSTR



# Ideal Reactors



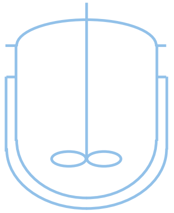
# PFR: Tubular reactor
## Engineering Characteristics




- Small volume
- High productivity
- Concentration / temperature profile
- High specific heat exchange area

# Heat Removal and Geometry

(U=1000 W/($m^2$.K)), $\Delta T$ = 10 K

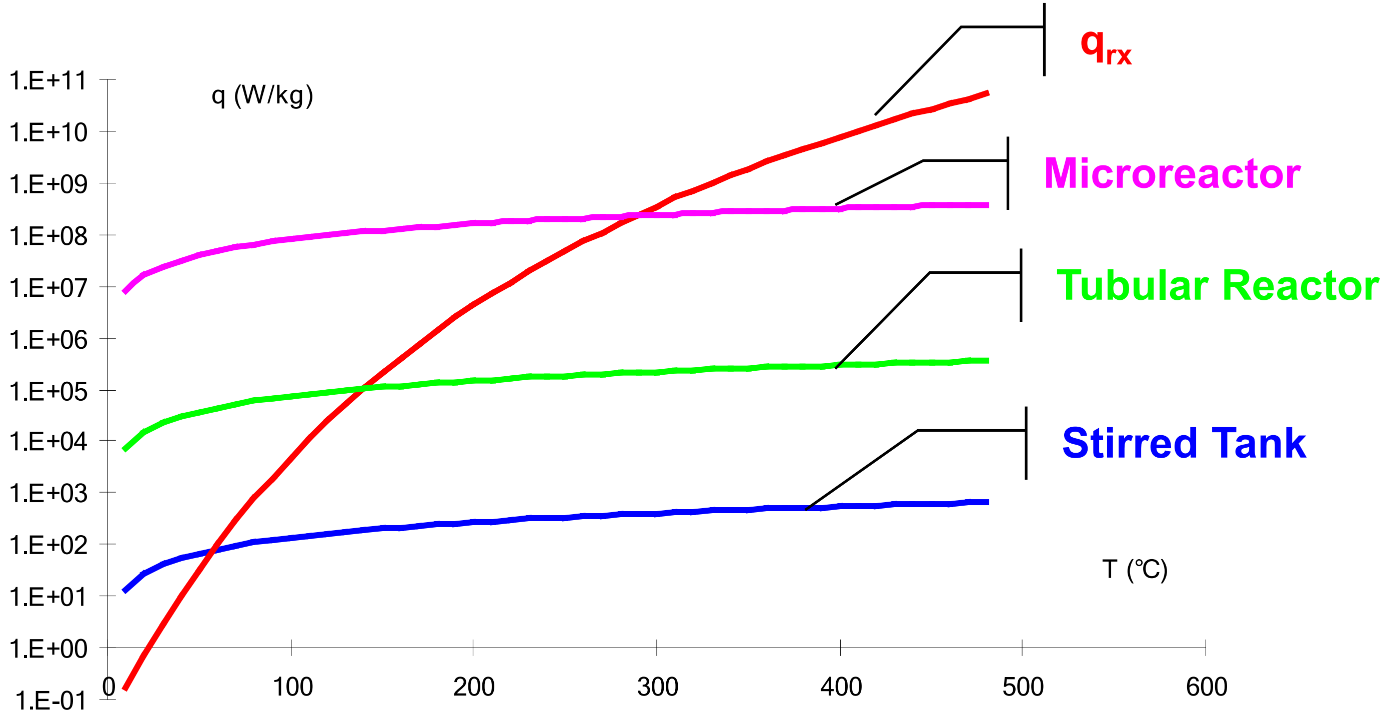


kW/$m^3$

| | | A/V $m^2/m^3$ | $q_{ex}$ |
|---|---|---|---|
| Laboratory | 0.1 l | 100 | 1000 |
| Bench Scale: | 2.0 l | 40 | 400 |
| Pilot plant | 100 l | 10 | 100 |
| Production | 1 $m^3$ | 4 | 40 |
| Production | 25 $m^3$ | 1 | 10 |
| Tube-Diameter | 100 mm | 40 | 400 |
| Tube-Diameter | 10 mm | 400 | 4000 |
| Tube-Diameter | 1 mm | 4000 | 40000 |
| Tube-Diameter | 0.1 mm | 40000 | 400000 |

# Comparison 10m³ / tubular / micro : Temperature Control

Reaction with 100W/kg at 60°C and Ea = 100 kJ/mol



# Construction of the microchannel

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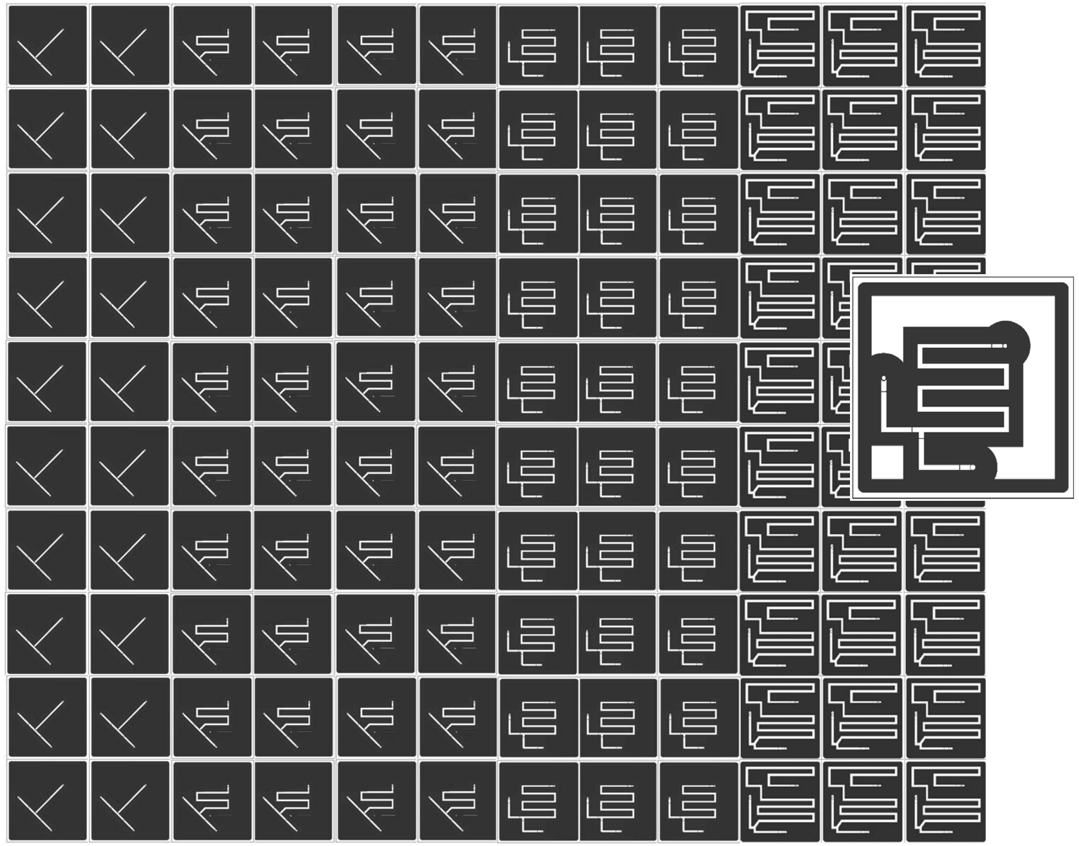
- Find a precise, flexible technique to build microchannel at low cost
  - Silk-screen printing of a thick-film dielectric



**d = 250µm**
**e = 100µm**
**L = 18.75mm**

# PFR: Safety aspects


- High specific heat exchange area
- Short distance center to wall
  avoids heat accumulation conditions
- "Thermal dilution"
- Hot spot

# PFR: X and T Profiles

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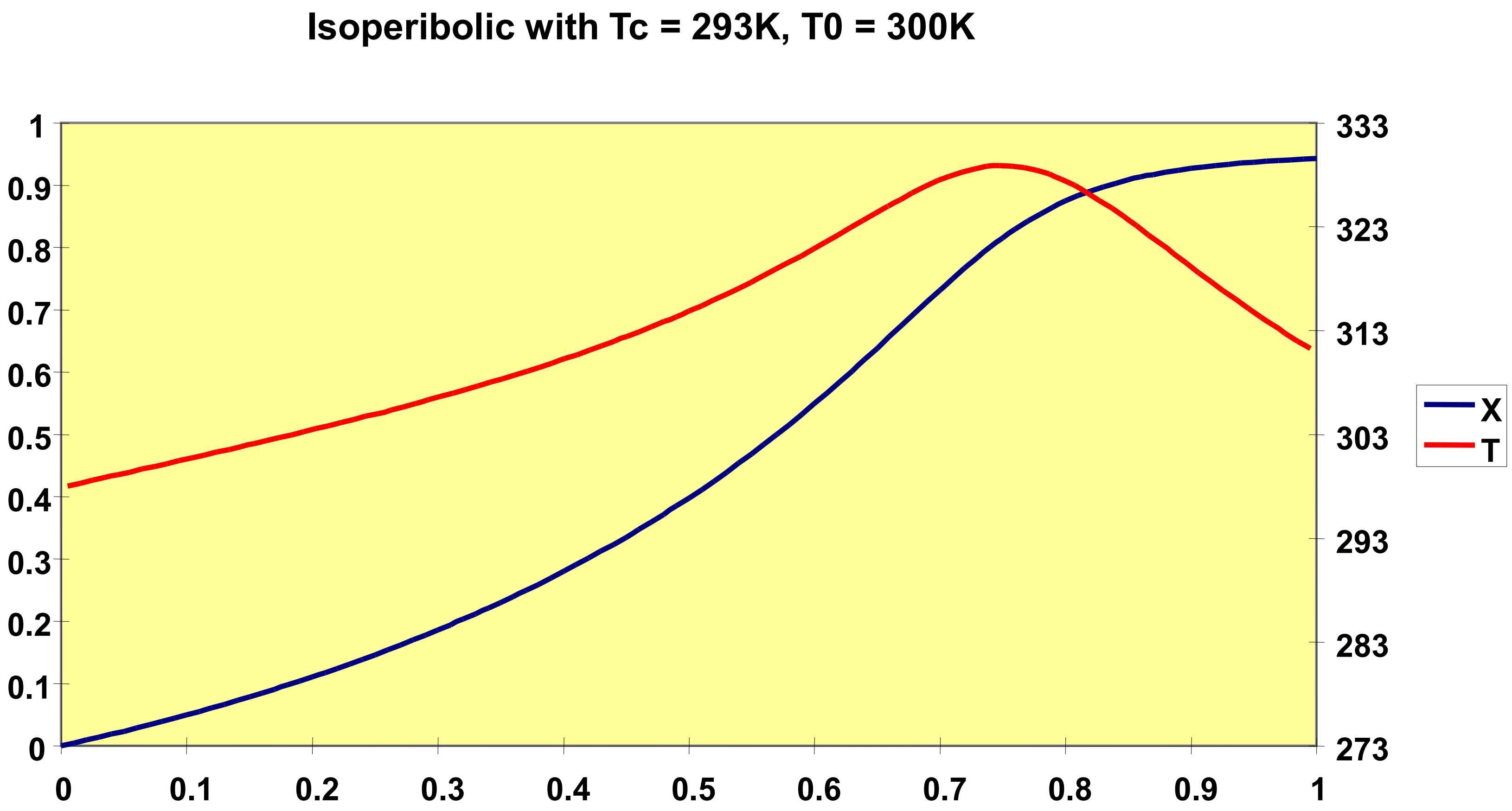
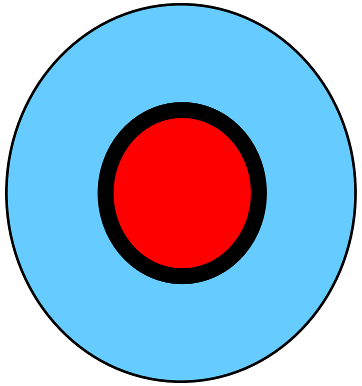


# PFR: Thermal Dilution

- Heat Capacity of the Reactor itself

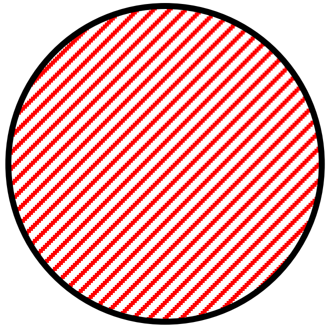


| | |
|---|---|
| Reaction mass: | 0.06 kJ/K |
| Wall: | 0.17 kJ/K |
| Water: | 28.2 kJ/K |

$\Phi = 473$

# PFR: Cooling Failure

- Heat Accumulation:



$$r = \sqrt{\frac{\delta_{crit} \cdot \lambda \cdot RT^2}{\rho \cdot q \cdot Ea}}$$

r: critical radius [m]
$\lambda$: Thermal conductivity [W/(K·m)]
$\delta_{crit}$: form factor
Ea: activation energy [J/mol]
q: heat release rate [W/kg]