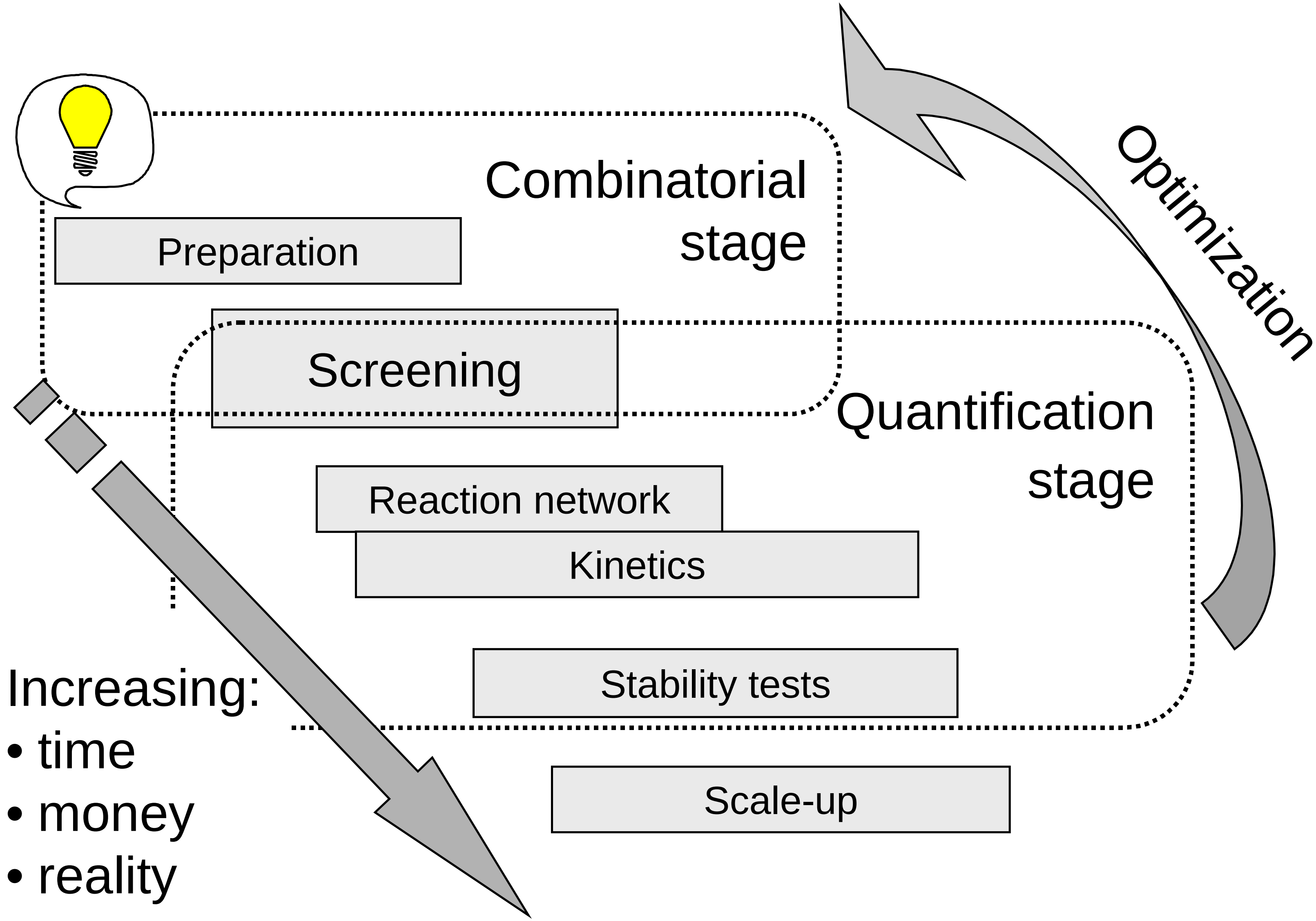
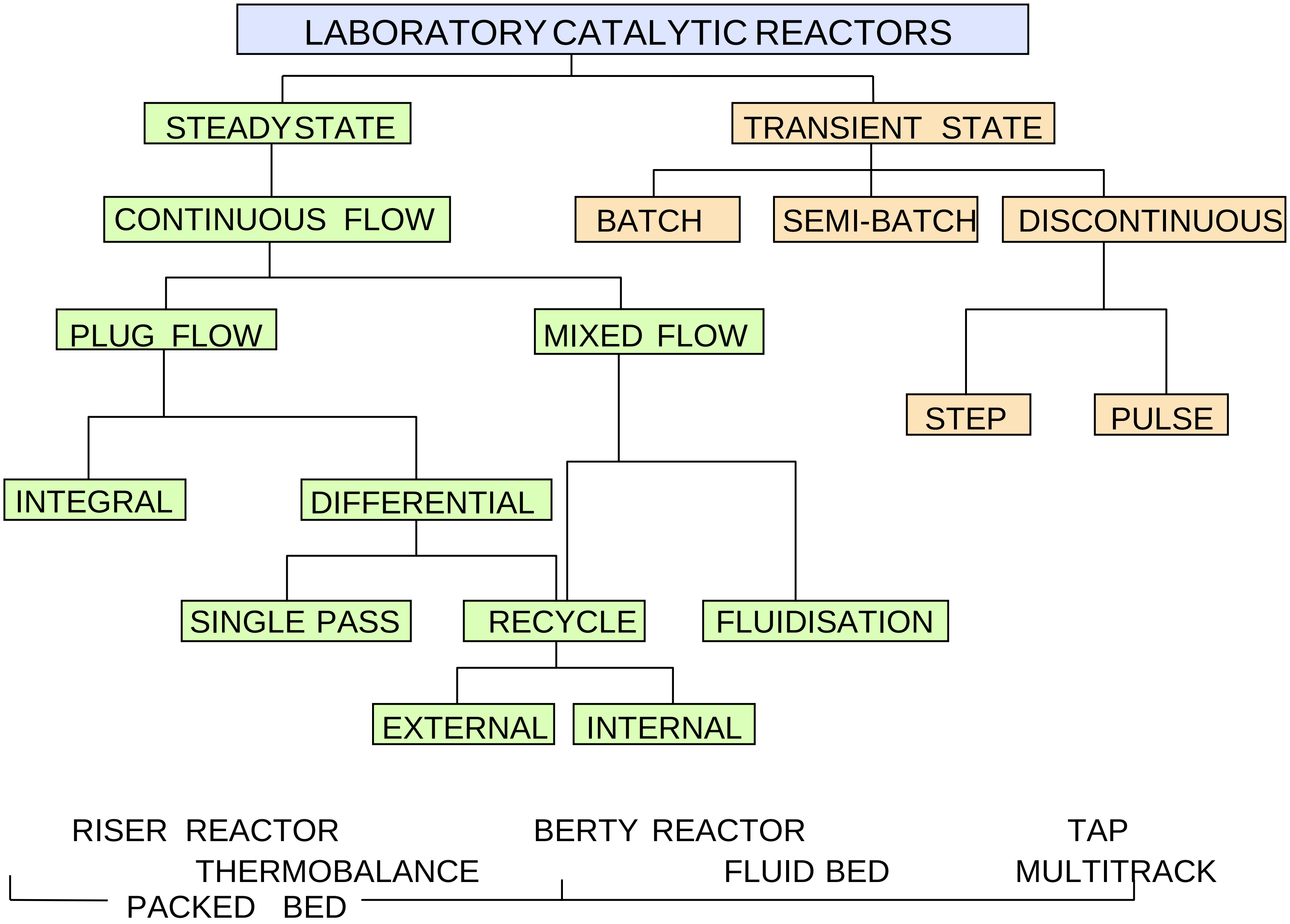

Combinatorial stage
Preparation
Screening
Quantification stage
Reaction network
Kinetics
Stability tests
Scale-up
Optimization
Increasing:
• time
• money
• reality


LABORATORY CATALYTIC REACTORS
STEADY STATE
TRANSIENT STATE
CONTINUOUS FLOW
BATCH
SEMI-BATCH
DISCONTINUOUS
PLUG FLOW
MIXED FLOW
STEP
PULSE
INTEGRAL
DIFFERENTIAL
SINGLE PASS
RECYCLE
FLUIDISATION
EXTERNAL
INTERNAL
RISER REACTOR
BERTY REACTOR
TAP
THERMOBALANCE
FLUID BED
MULTITRACK
PACKED BED

Catalyst testing & Kinetic studies

Information wanted

- ☞ Intrinsic reaction rate data
- ☞ Not obscured by parasitic phenomena
  - 👎 reactor characteristics
  - 👎 mass and heat transport phenomena
  - 👎 user manipulations
  - 👎 catalyst misbehaviour
    - 👎 deactivation/fouling

For

- Comparison activities and selectvities
- Kinetic modelling

Catalytic reactor design equation

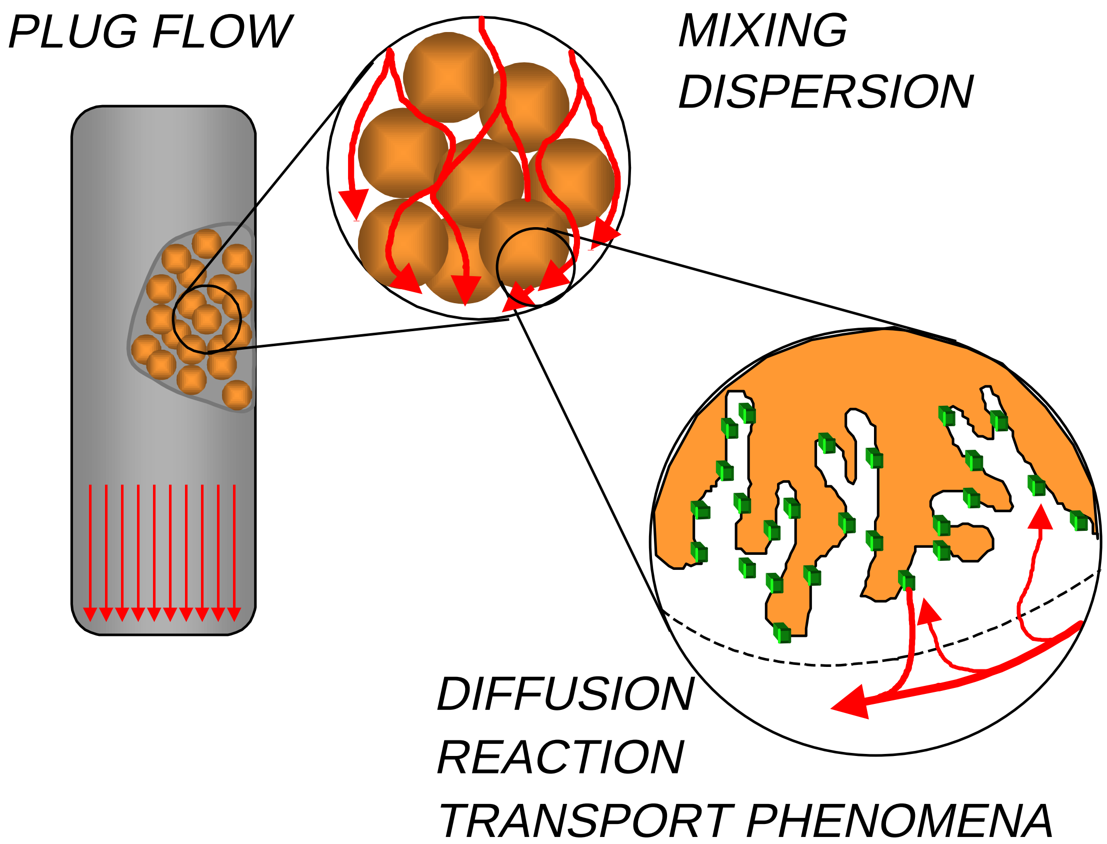
plug-flow, steady state

$$\frac{dx_i}{d\left(W/F_i\right)} = -\nu_i \cdot \eta \cdot r \cdot \Phi$$

- conversion i (dx_i)
- 'space time' ($d(W/F_i)$)
- stoichiometric coefficient i (ν_i)
- catalyst effectiveness (η)
- rate expression (r)
- deactivation function (Φ)

Eliminate deviations ideal reactor behaviour, low catalyst effectiveness and deactivation

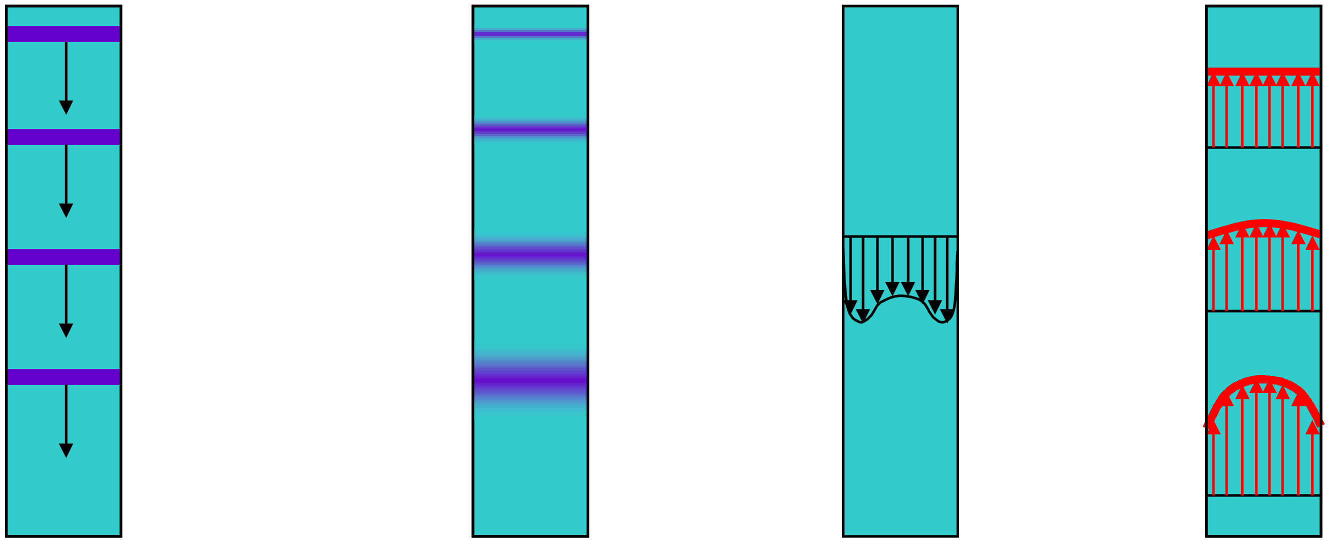
Phenomena in catalytic reactor
(two-phase: fluid-solid)



Packed bed reactor - assumptions

ideal

real life



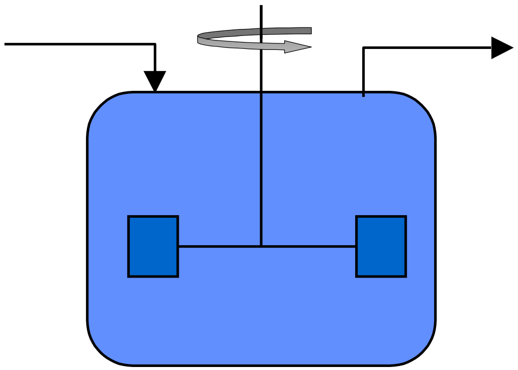
plug flow isothermal	axial dispersion	velocity profile	radial temperature gradient

equal τ, T — *τ varies* — *T varies*

impact on observed conversion levels

CSTR - assumptions

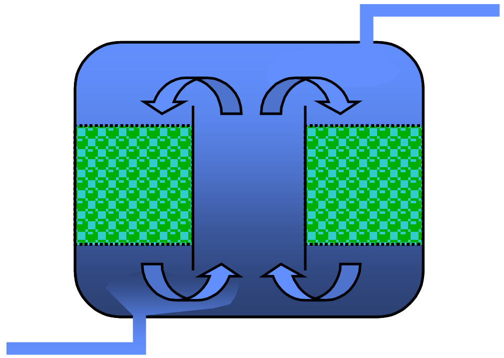
ideal



well mixed
isothermal

- *instantaneous mixing*
- *equal conditions*

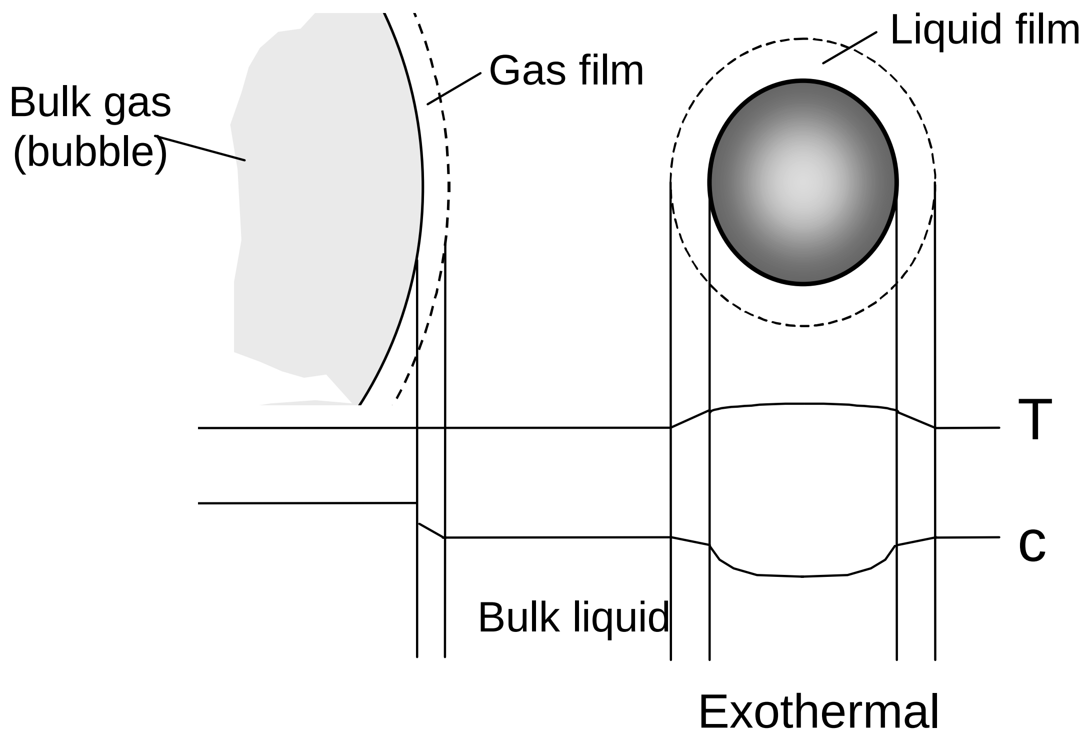
reality



recirculation

- *local concentration gradients*
- *conversion over bed*

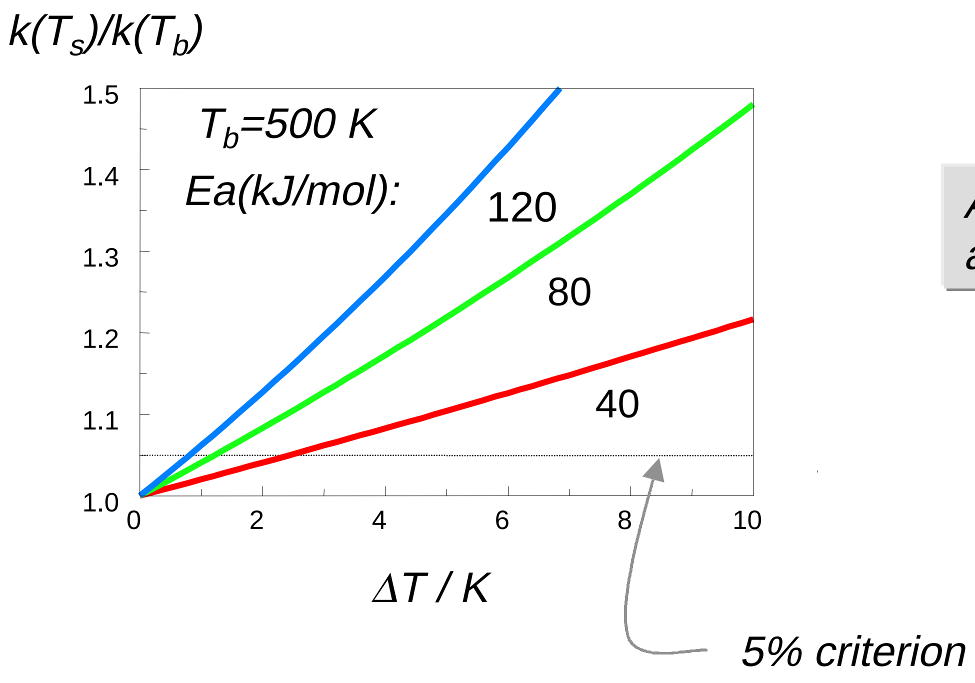
Gradients at Particle Scale
Gas/liquid/solid Slurry Reactor



Effect temperature rise

How much increases rate constant ?

$$\frac{k(T_s)}{k(T_b)} = \exp\left\{-\frac{E_a}{RT}\cdot\left(\frac{T_b}{T_s}-1\right)\right\} = \exp\left\{\gamma_b\left(\frac{\Delta T}{T_b+\Delta T}\right)\right\}$$



A few degrees already critical !

Criteria - experimental verification

Criterion: $$\frac{r_{v,obs}}{r_{v,chem}} = 1 \pm 0.05$$

5%deviation

observed rate

External transfer: $$Ca = \frac{r_{v,obs}}{a' k_f c_b} < \frac{0.05}{n}$$

reaction order

$$a' = \frac{S_p}{V_p}$$

mass transfer coefficient

particle properties

When mass transport limitations?

5%Criterion

Internal transfer: $\Phi = \eta\phi^2\left(\frac{n+1}{2}\right) < 0.15$

External transfer: $Ca < \frac{0.05}{n}$

$$\eta_i\phi_G^2 = \frac{r_{v,obs}}{a'^2 \cdot D_{eff} \cdot c_b}$$

$$Ca = \frac{r_{v,obs}}{a' k_f c_b}$$

Also: $\Phi = \frac{Bi_m}{s} \cdot Ca$

while Bi_m>~10
s=1,2,3 (geometry)

⇒ *Weisz-Prater more severe than Carberry criterion*

When temperature effects?

5%Criterion

Prater numbers

External transfer: $|\beta_e|\gamma_b Ca < 0.05$

$$\beta_e = \frac{(-\Delta H)k_f c_b}{hT_b}$$

$\frac{\beta_e}{\beta_i}$		
	$10\text{-}10^4$	gas-solid
	$10^{-4}\text{-}0.1$	liquid-solid

Internal transfer: $\frac{|\beta_i|\gamma_s\left(\eta_i\phi^2\right)}{2} < 0.05$

$$\beta_i = \frac{D_e(-\Delta H)c_s}{\lambda_e T_s}$$

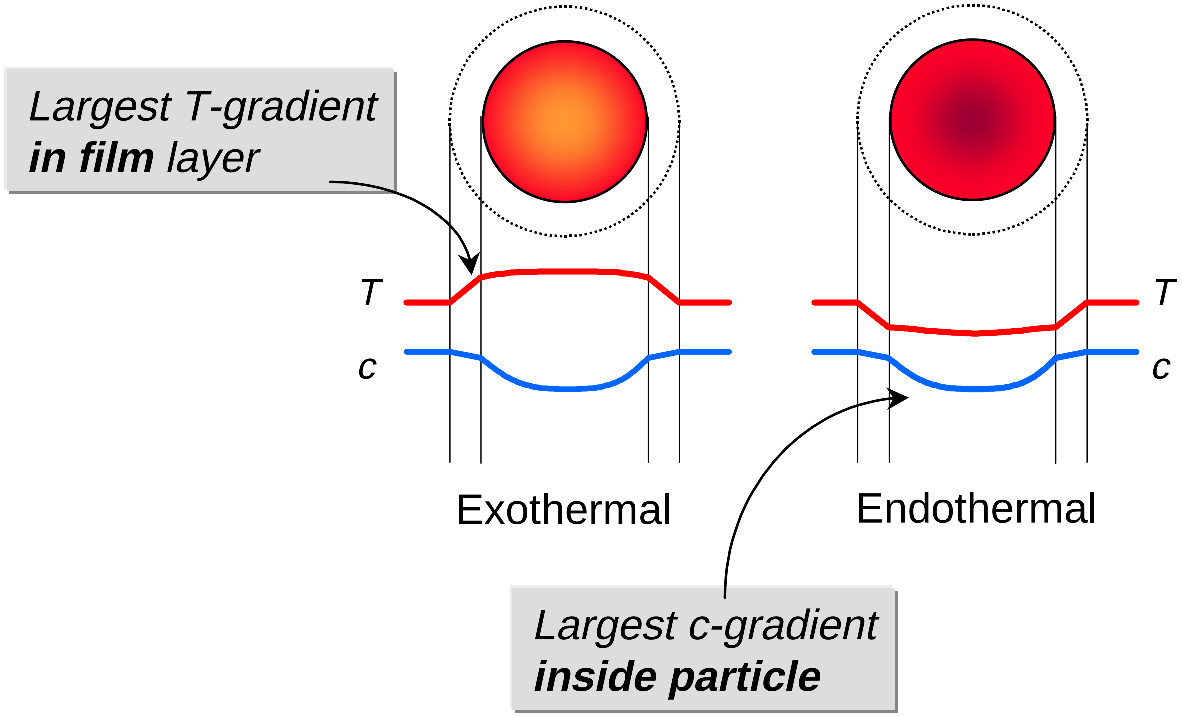
0-0.3 (exothermal)

$$\gamma_b = \frac{E_a}{RT_b}$$

10-20

External gradient criterion more severe than internal criterion

Temperature and concentration profiles



Temperature gradient in catalyst bed

$$\frac{E_a}{R\,T_w}\left|\frac{(-\Delta H_r)\,r_{v,obs}\;r_t^2}{\lambda_{eff,b}\;T_w}\right|(1-\varepsilon_b)\,(1-b)\left(\frac{1}{8}+\frac{1}{Bi_w}\frac{d_p}{d_t}\right)<0.05$$

$$\frac{\textit{criterion}\ \text{bed T - gradient}}{\textit{criterion}\ \text{film T - gradient particle}}\approx\left(\frac{r_t}{r_p}\right)^2\cdot\left(\frac{\lambda_{p,eff}}{\lambda_{b,eff}}\right)\cdot\left(\frac{s^2(1-\varepsilon_b)}{8}\right)>>1$$

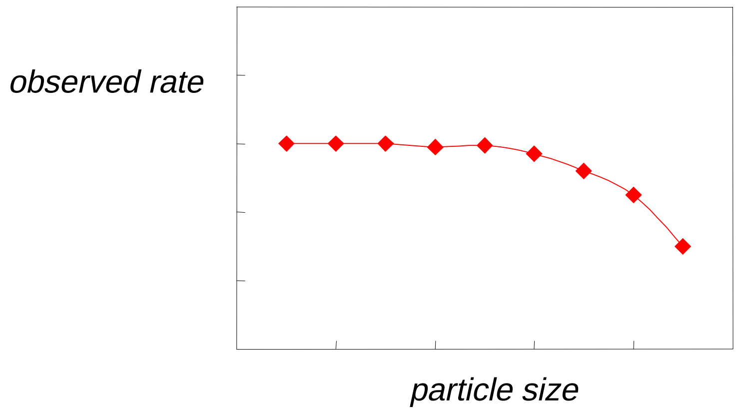
temperature gradient in bed always develops first !

Summary:

$$(T-grad)_{bed}>(T-grad)_{ext}>(c-grad)_{int},(T-grad)_{int}>(c-grad)_{ext}$$

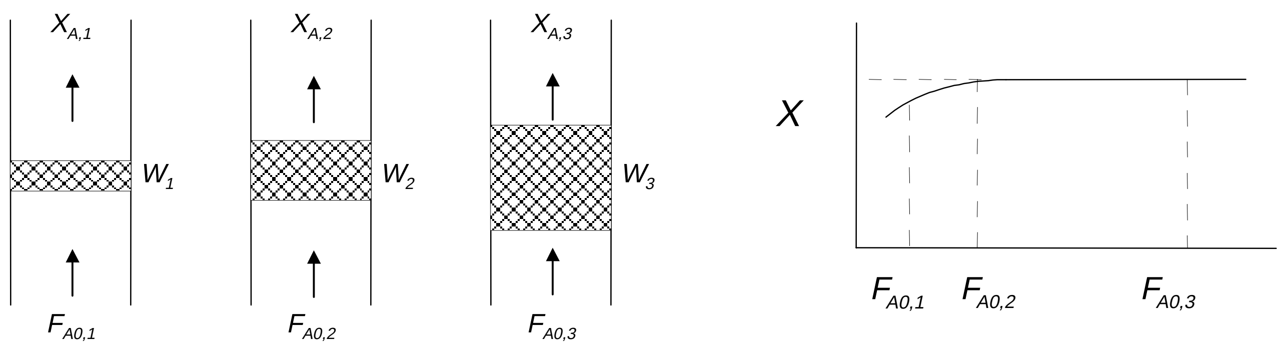
Diagnostic tests mass transport limitations

1. Particle size variation



egg-shell catalysts?

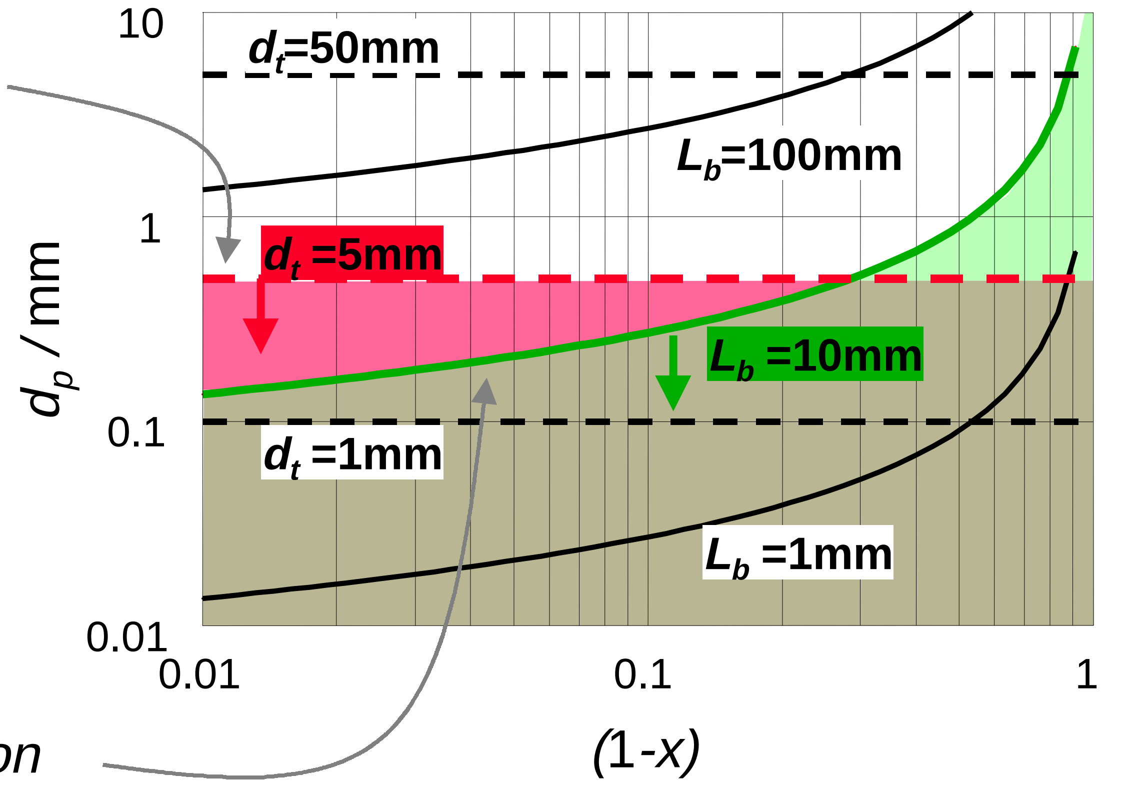
2. Flow rate variation at constant space time!



Nonideal reactor behaviour

$$\frac{d_t}{d_p} > 10$$

velocity profile



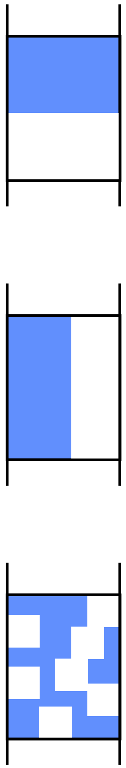
axial dispersion

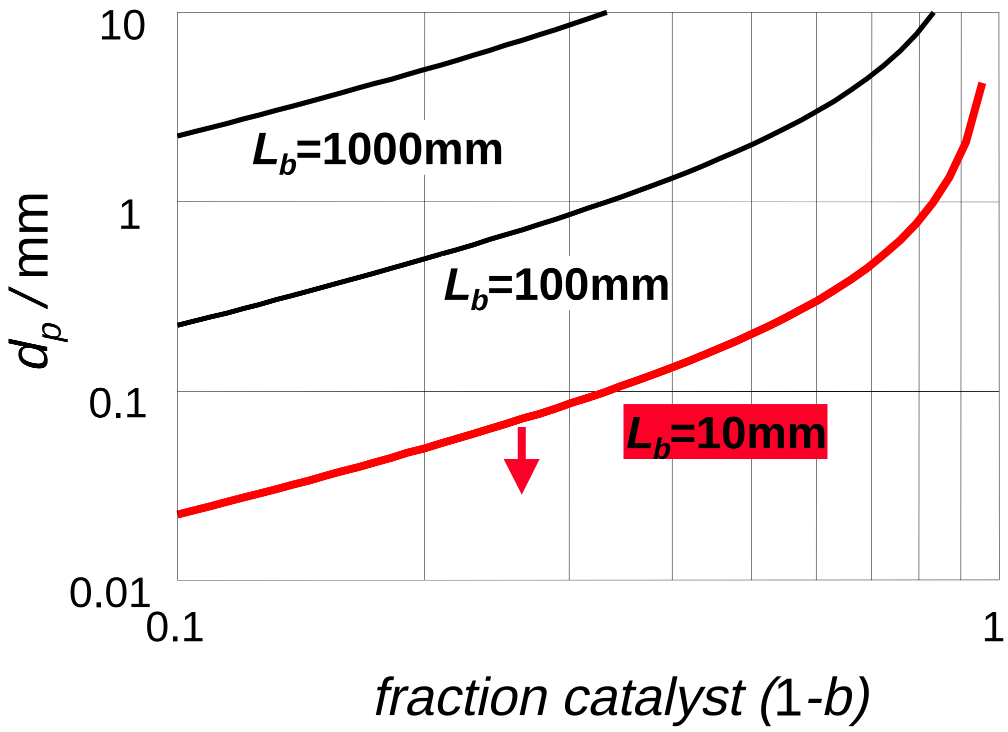
$$\frac{L_b}{d_p} > \frac{20\,n}{Bo}\ln\left(\frac{1}{1-x}\right)$$

Bed dilution

inhomogeneous distribution
catalyst by-passing

$$\frac{2.5\ b\ d_p}{(1-b)\ L_b} < 0.05$$



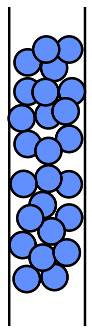


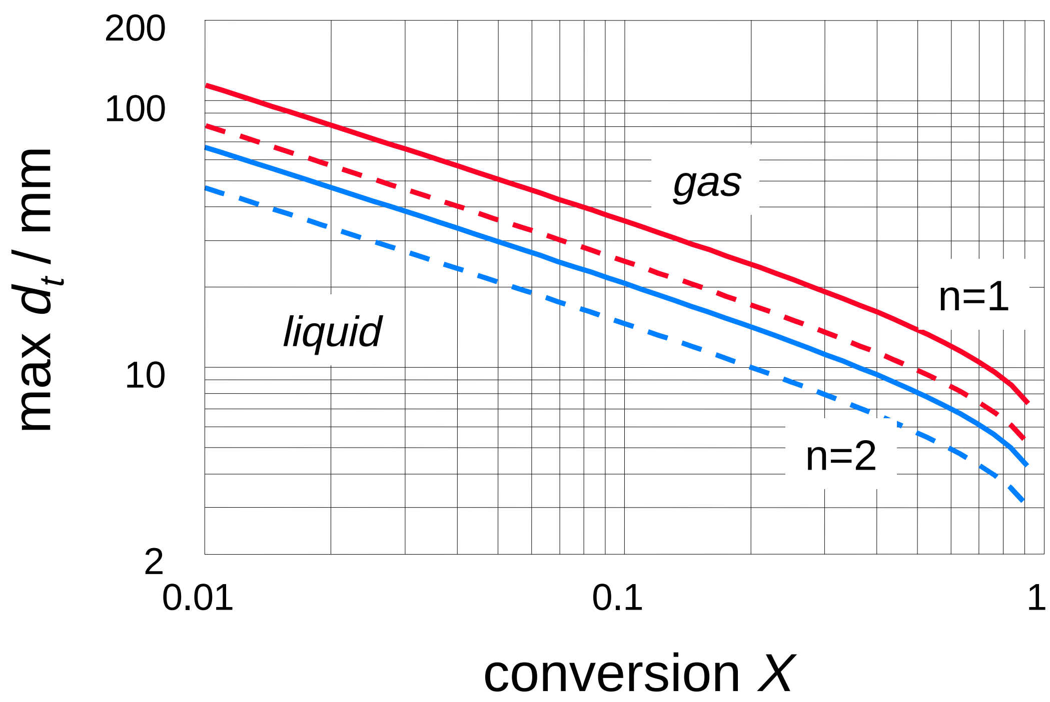
Small tube diameters

Sie 1996

$$\frac{L_b \cdot D_{rad}}{r_t^2 \cdot u} > 8 \cdot (\kappa/\varepsilon) \cdot n \cdot \ln\left(\frac{1}{1-x}\right)$$

SV(gas)= 10000 h^{-1}
SV(liquid)= 1 h^{-1}





d_t/d_p<5:
$\kappa = 0.04$
ε_b=0.4

$$d_t^2 < \frac{5 D_{rad}}{SV \cdot n \cdot \ln\left(\frac{1}{1-x}\right)}$$

maximum tube diameter !

Criteria recirculation reactors

rate over bed changes less than 5%

- Concentration effects $$\frac{x}{(1-x)(1+R_c)} < \frac{0.05}{n}$$

- Temperature effects

$$\frac{E_a}{RT_b} \cdot \left| \frac{r_{obs} \cdot (-\Delta H_r)}{\widetilde{C}_{pf} T_b} \right| \cdot \frac{W}{F_{tot}} = \gamma_b \cdot \left| \frac{(-\Delta H_r)}{\widetilde{C}_{pf} T_b} \right| \cdot \frac{y_0 \cdot x}{(R_c + 1)} < 0.05$$

Reaction order - Activation energy

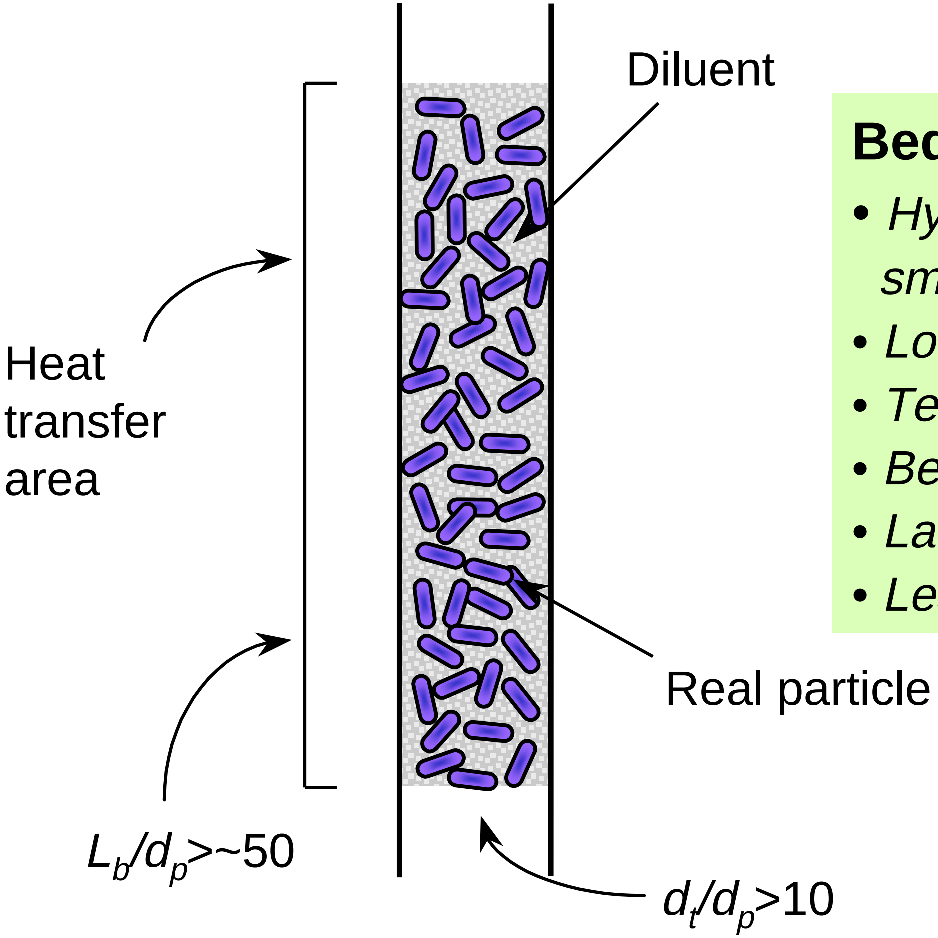
rate expression $r = \frac{k_2 N_T K_A p_A}{\left(1 + K_A p_A + K_B p_B\right)}$

Reaction order	$n_A = 1 - \theta_A$	0 - 1
	$n_B = -\theta_B$	(-1) - 0
Activation energy	$E_a^{obs} = E_{a2} + \left(1 - \theta_A\right)\Delta H_A - \theta_B \Delta H_B$	

depend strongly on occupancy!
vary during reaction

Catalyst testing - Bed dilution

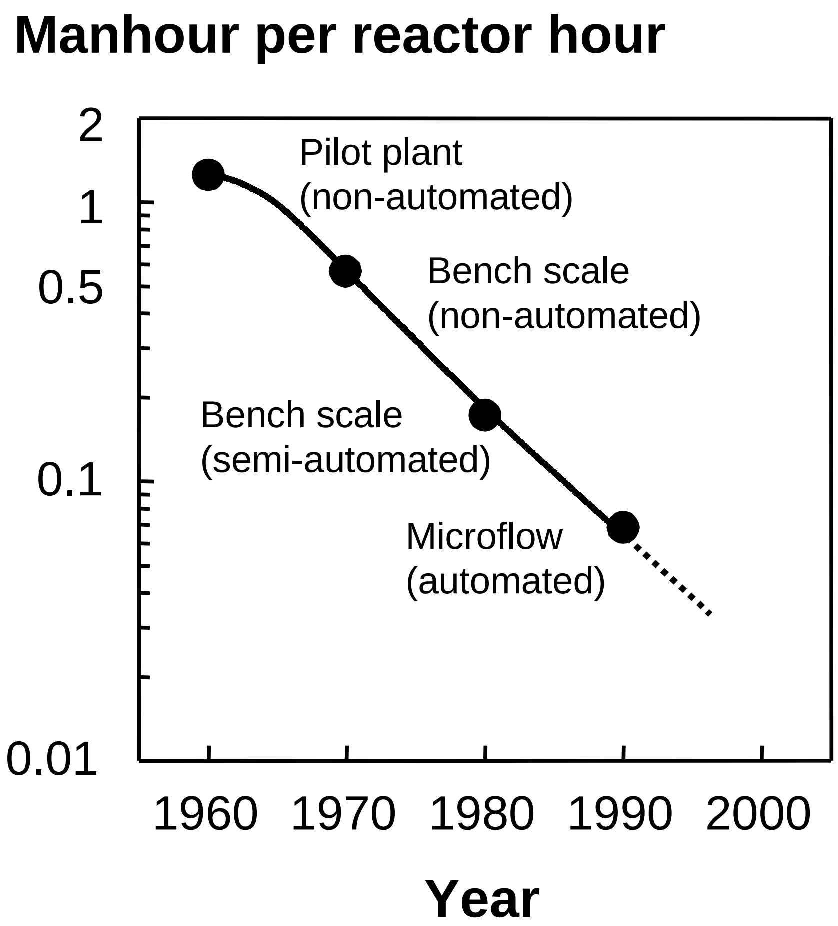
decoupling hydrodynamics and kinetics



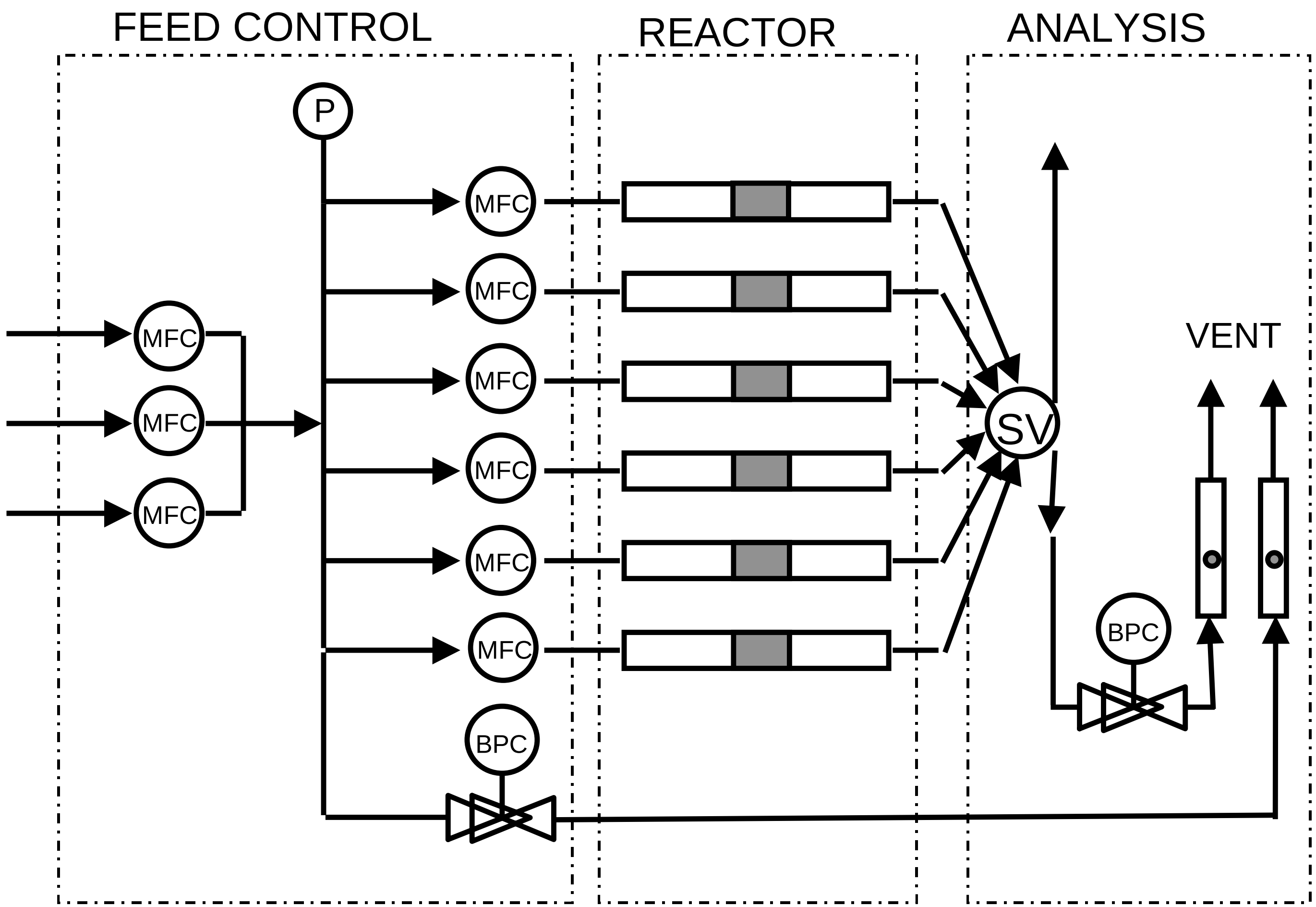
Bed dilution (e.g. SiC)

- *Hydrodynamics determined by small particles (wetting, velocity)*
- *Longer bed, larger L/d_p*
- *Testing of real catalyst particles*
- *Better heat conduction*
- *Larger heat transfer area*
- *Less heat produced per volume*

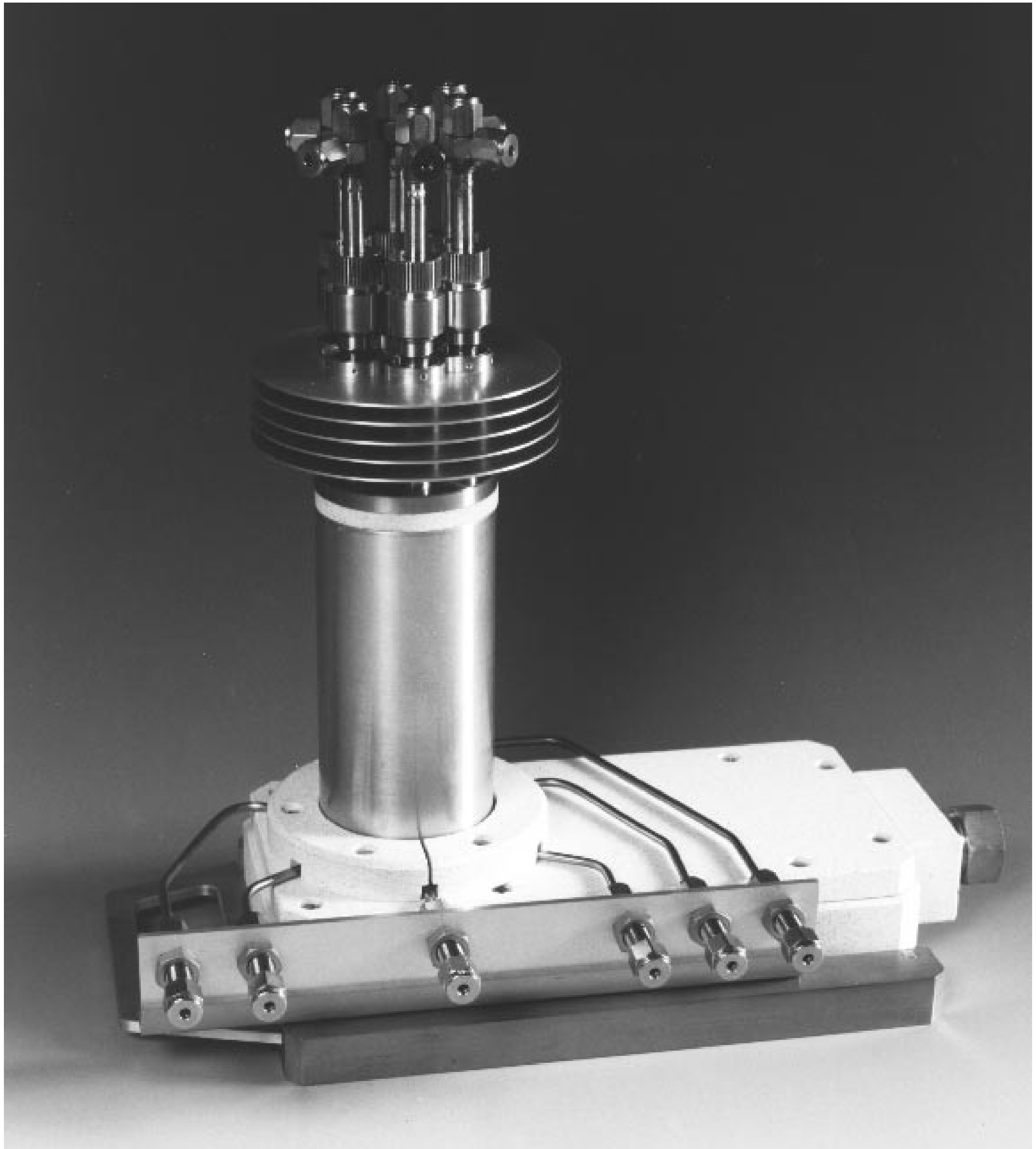
Sie, AIChE-J. 1996

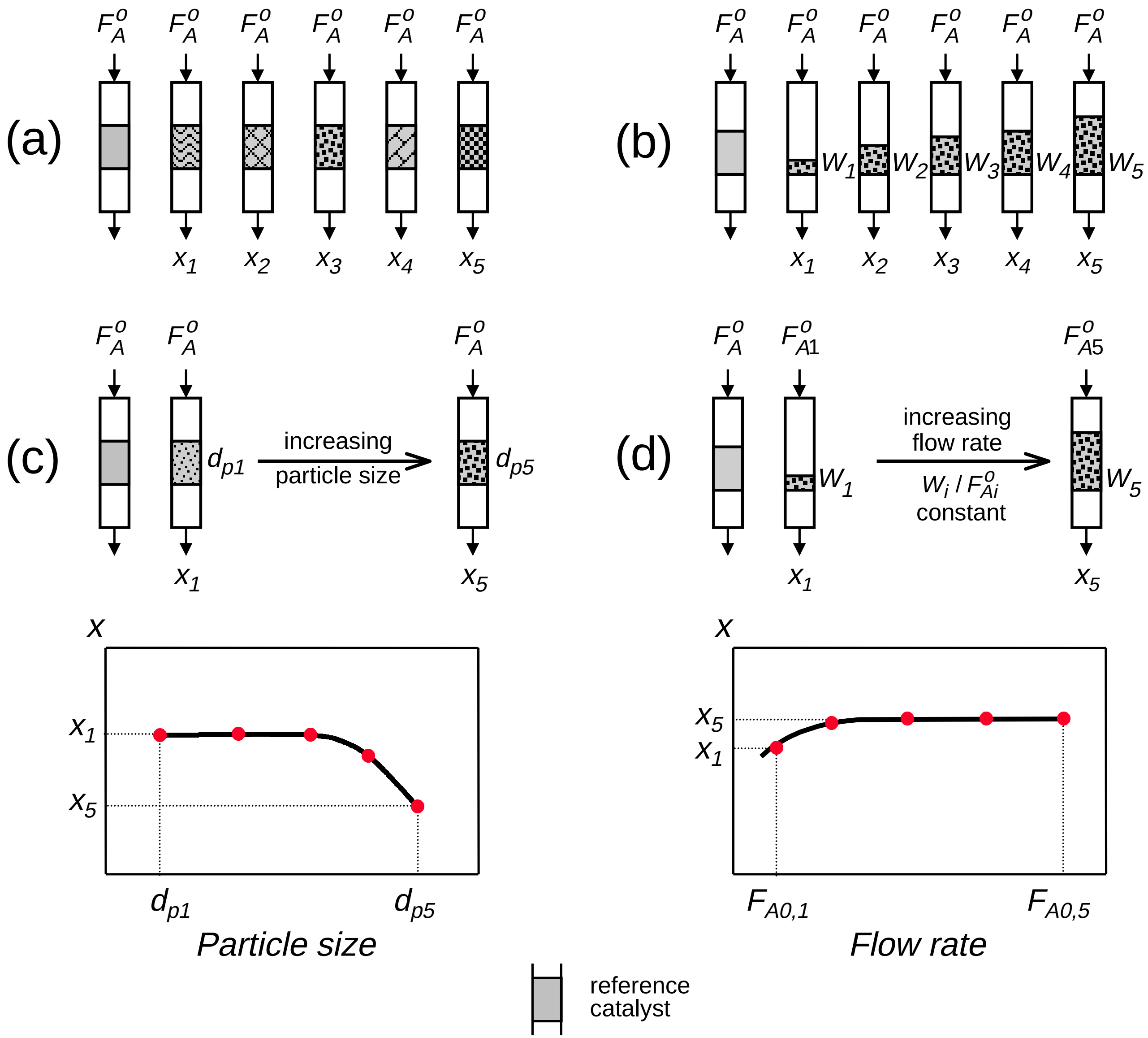


Parallelization catalyst testing



Six-flow reactor





(a)
(b)
(c)
(d)
F_A^o
x_1
x_2
x_3
x_4
x_5
W_1
W_2
W_3
W_4
W_5
d_{p1}
increasing
particle size
d_{p5}
F_{A1}^o
increasing
flow rate
W_i / F_{Ai}^o
constant
F_{A5}^o
x
Particle size
Flow rate
$F_{A0,1}$
$F_{A0,5}$
reference
catalyst

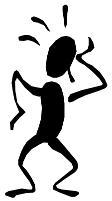
Kinetics

Procuring rate data laborious task

conversion vs. *space time W/F*
temperature
partial pressures / concentrations

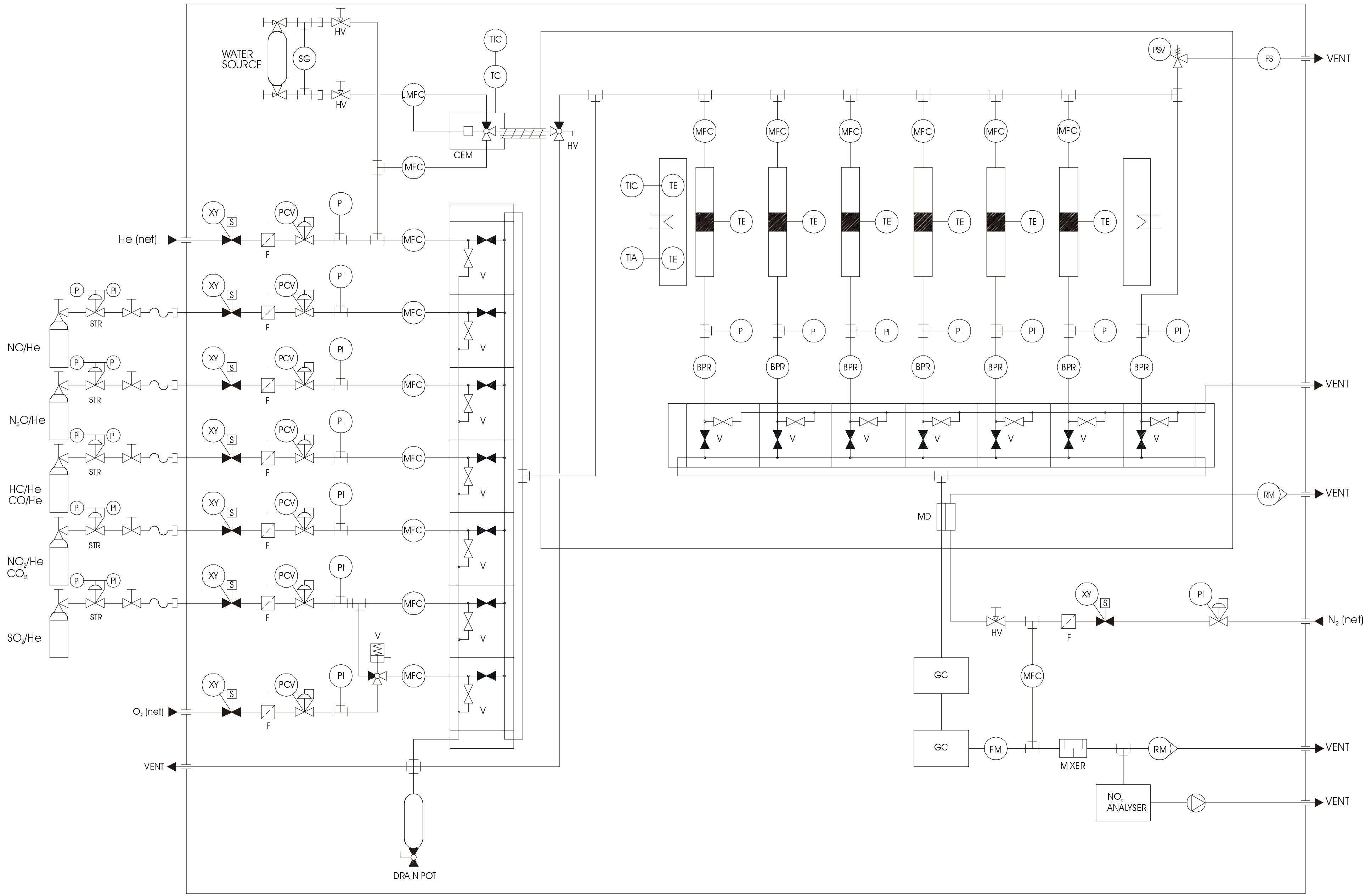
Improve speed:

- *PC controlled equipment*
- *Six-flow set-up (parallel reactors)*
- *Temperature scanning*
- *Sequential experimental design*



Don’t forget: *stable catalyst, blank runs, duplicates*
check criteria

Set-up Six-flow reactor



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