EUROKIN – 20 years of Catalyst Performance Testing

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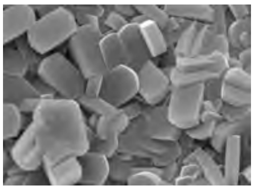
20th Anniversary Symposium Eurokin

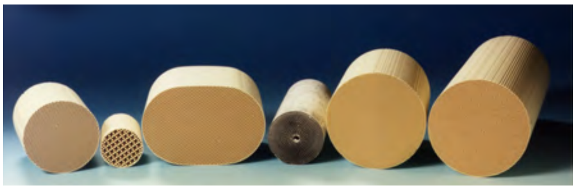
16 October 2018

Vaalsbroek, The Netherlands

What you can expect......

- Eurokin objectives
  - TUDelft philosophy and input
  - Selection of contributions
- Structuring catalysts, reactors and testing
- Some reflections on further opportunities





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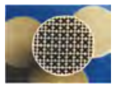
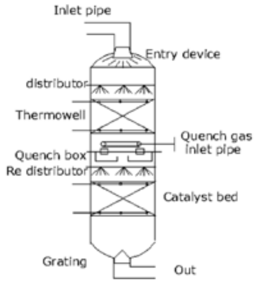
Catalysis Engineering – ChemE 2

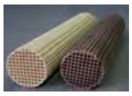
Catalytic processes - essentials

Design data? → Hydrodynamics
Transport phenomena
Catalytic kinetics

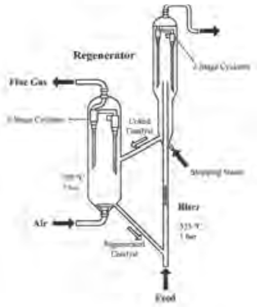


Trickle bed reactor





Riser reactor



Laboratory reactor ?

Fine chemicals synthesis
Exploratory catalyst research

- Catalysis Engineering, at three levels
  - Micro-level, Meso-level, Macro-level

Catalyst performance testing; a prime example of scaling down

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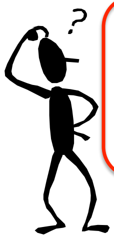
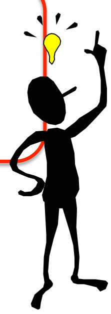
What did/does Eurokin want?

Among other things

- Simple, easy to use methods
  - Experimental, theoretical, computational
    - Hardware, software
    - Rules of thumb operation
    - Testing criteria
  - Catalyst performance – how?
    - Intrinsic kinetics, activity, selectivity, stability
    - Real catalyst particles

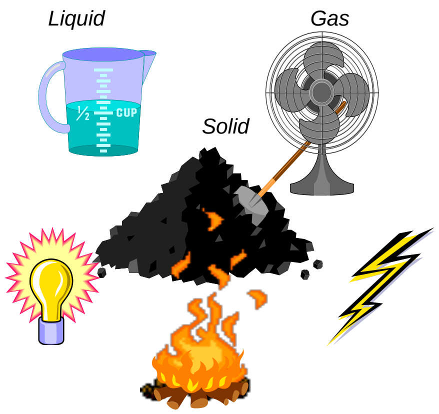




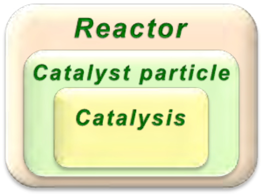
Berger, R. J.; Stitt, E. H.; Chewter, L.; Verstraete, J.; Marin, G. B.; Hoorn, J., *The Eurokin consortium: origin, topics and aims*. *Green Processing and Synthesis* **2013,** *2* (1), 67-69.

Catalysts – Multiphase operation

How to operate efficiently?



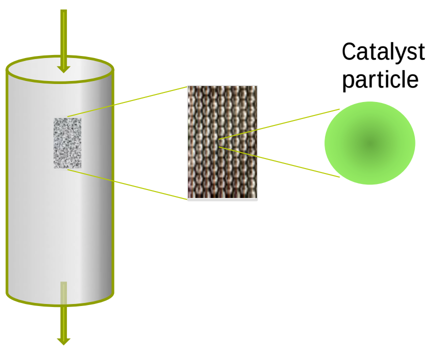
Distribution G-L
Contacting G-L-S
Convection
Diffusion
Reaction



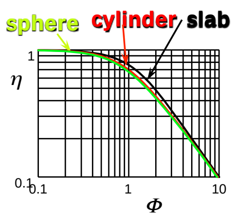
Catalysis in multiphase systems

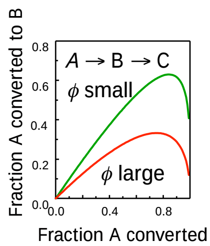
Microlevel & Mesolevel - packed bed reactor

Packed bed reactor



Diffusion-reaction interference





→ $\phi = L\sqrt{\dfrac{k_v}{D_{eff}}}$ small

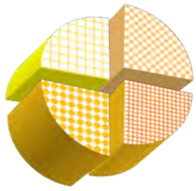
$\Delta p \sim (L_{particle})^{-2}$ → **Maximize *L***

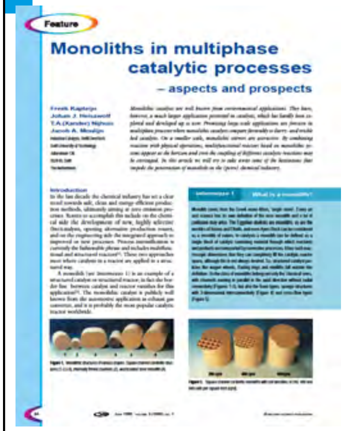
→ **Minimize *L***

Well-known trade-off

Structure in reactor-catalyst

Regular arrangement/packing





***Cattech 3 (1999) 24-41**-Kapteijn*
Adv. Catalysis 54 (2011)249-327-Moulijn
Catal.Sci.Technol. 5 (2015) 807–817-Gascon

Decouples:

- *chemistry*
- *(molecular) transport processes*
- *hydrodynamics*

Marrying scale-dependent and -independent processes

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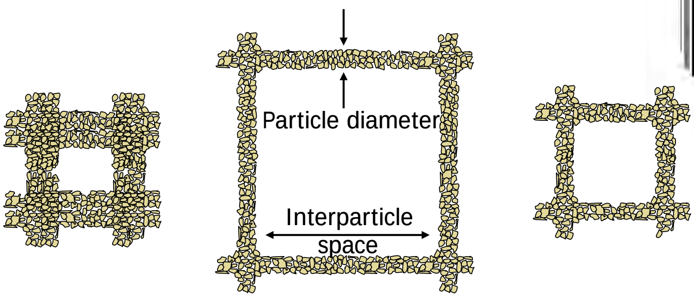
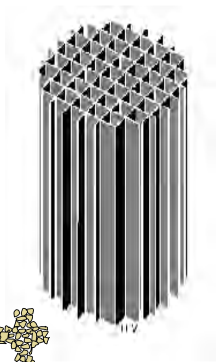
Solution: structure

Example: monoliths





Structure provides additional degree of freedom

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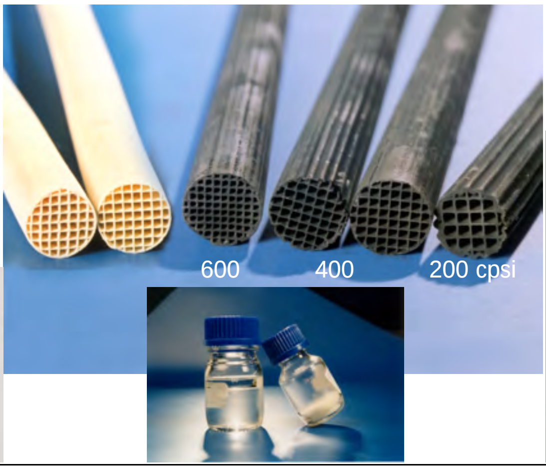
Fischer-Tropsch synthesis

Cordierite
1 cm ∅



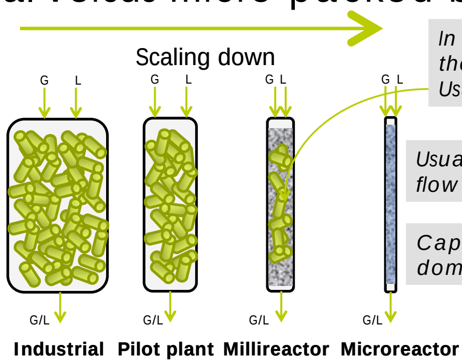
CoRe/Al_2O_3
cordierite

Downscaling
Industrial versus micro-packed beds (G/L)

In the oil refinery the standard Usually diluted bed

Usually trickle flow regime

Gravity dominates



Usually segregated flow regime

Capillary forces dominate

	Industrial	Pilot plant	Millireactor	Microreactor
$L_{reactor}$	20 m	8 m	40 mm	170 mm
$d_{reactor}$	> 1 m	40 mm	10 mm	2 mm
$d_{particle}$	3 mm	3 mm	0.1 (3) mm	0.1 mm
v_{liquid}	1 cm/s	0.4 cm/s	60 µm/s	200 µm/s

Van Herk et al, Catal. Today ***2005****, 106(1-4) 227-232*
Alsolami et al., Ind. Eng. Chem. Res. ***2013****, 52, 9069-9085*
Sie, Rev. l'Inst. Fran. du Pétr. ***1985****, 46(4) 501-515*

Downscaling
Industrial versus micro-packed beds (G/L)

Scaling down

G L G L G L G L

In the oil refinery the standard
Usually diluted bed

Usually flow re...

Grav... dom...

...ted

Downscaling:
- *Time and length scales change*
- *Other forces start dominating*

	Industrial	Pilot plant	Millireactor	Microreactor
$L_{reactor}$	20 m	8 m	40 mm	170 mm
$d_{reactor}$	> 1 m	40 mm	10 mm	2 mm
$d_{particle}$	3 mm	3 mm	0.1 (3) mm	0.1 mm
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Van Herk et al, Catal. Today ***2005****, 106(1-4) 227-232*
Alsolami et al., Ind. Eng. Chem. Res. ***2013****, 52, 9069-9085*
Sie, Rev. l'Inst. Fran. du Pétr. ***1985****, 46(4) 501-515*

Time-scales for heat transport - CFS

Conduction ⟷ Convection

$$t_{cond,L} = \frac{r^2}{a_L \varepsilon_L} \approx 8000 \text{ s} \quad >> \quad t_{conv} = \frac{r}{u_r \varepsilon_L} \approx 1 \text{ s}$$

$$t_{cond,steel} = \frac{r^2}{a_{steel} \varepsilon_{steel}} \approx 150 \text{ s}$$

Heat transport by convection is much more efficient than conduction in CFS

Symbols:
- r = tube radius
- a = thermal diffusivity
- ε = hold-up
- u_r = radial velocity

- *Vervloet et al. Chemical Engineering Journal 233 (**2013**) 265–273*
  → one-parameter model
- *Kaskes et al. Ind. Eng. Chem. Res. 53 (**2014**) 16579−16585*
  → bundled-channel model

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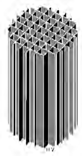
Micro- and mesolevel
Kinetics, Catalyst performance testing

- Scale down as far as possible
  - Smaller concentration, temperature gradients
  - Lower capital, utility demands
  - Safer
  - Less labour

- For catalyst selection, testing
  - Do not automatically mimic industrial reactor
    - Output industrial reactors: $$$ or €€€€
    - Catalyst testing: information
  - Mimicking industrial plant can be a logical choice
    - Structured reactors in theory identical at low and large scale

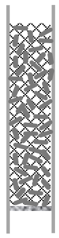


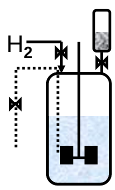
Use the instrument that yields what you want

Kapteijn & Moulijn, *Laboratory testing of solid Catalysts* in G. Ertl, H. Knözinger, F. Schüth and J. Weitkamp, (eds.) Handbook of Heterogeneous Catalysis, 2nd ed., Wiley-VCH, Weinheim, Ch.9, **2008**, pp. 2019-2045.

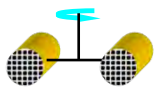
Micro- and mesolevel
Kinetics, Catalyst performance testing

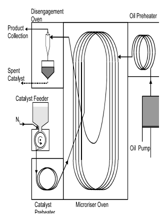
- Work horses
  - Fixed bed reactors
    - Convenient, usually continuous
  - Slurry reactors
    - Flexible, usually batch





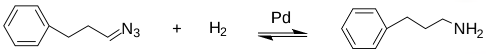
- How do we put the catalyst in the reactor?
  - Fixed-bed reactors
    - Catalytic coating on wall
    - Micropacked bed
  - Catalyst particles moving
    - Fluidized beds
    - Entrained flow reactors, microriser
    - Micro-slurry reactor





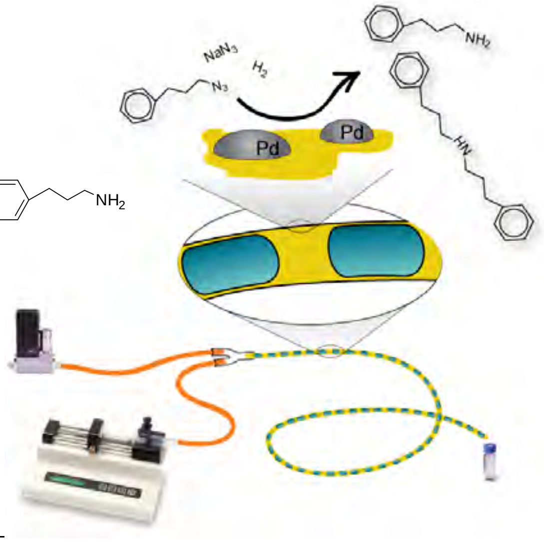
Gas-Liquid segmented flow – kinetic machine

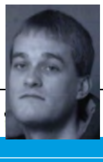
Kinetic tool, ideal for hazardous chemistry



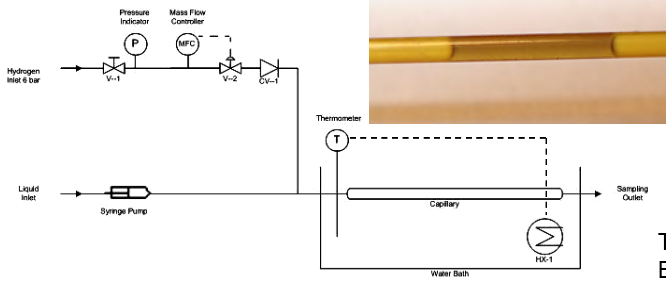
Azide hydrogenation to amines

Temperature low enough to maintain stereo-specificity

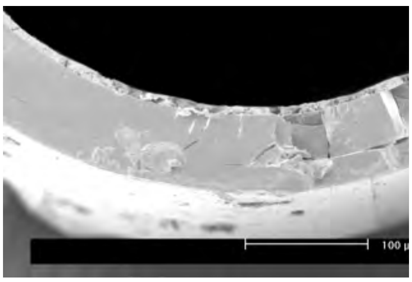




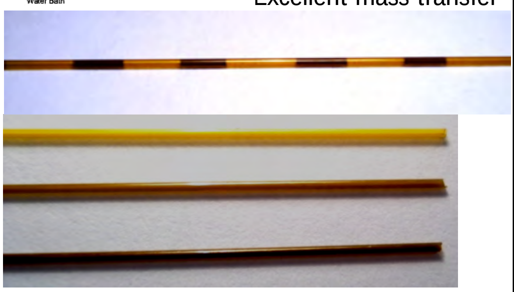
Jasper W.W. Bakker *et al.* ChemCatChem 3(2011) 1155 – 1157



Taylor flow
Excellent mass transfer

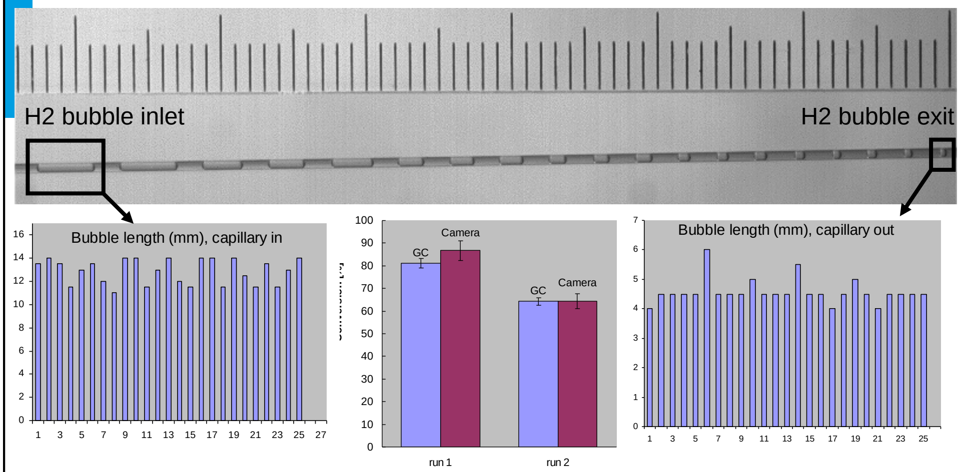


Pd/Al_2O_3 coating



Pd loading variation

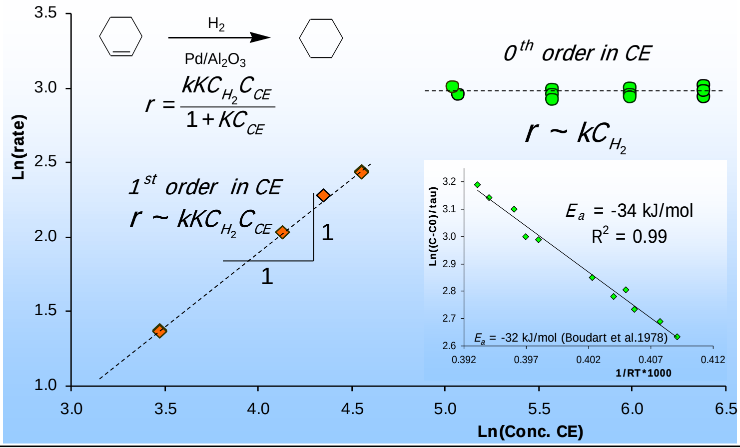
Conversion from GC analysis and from hydrogen consumption

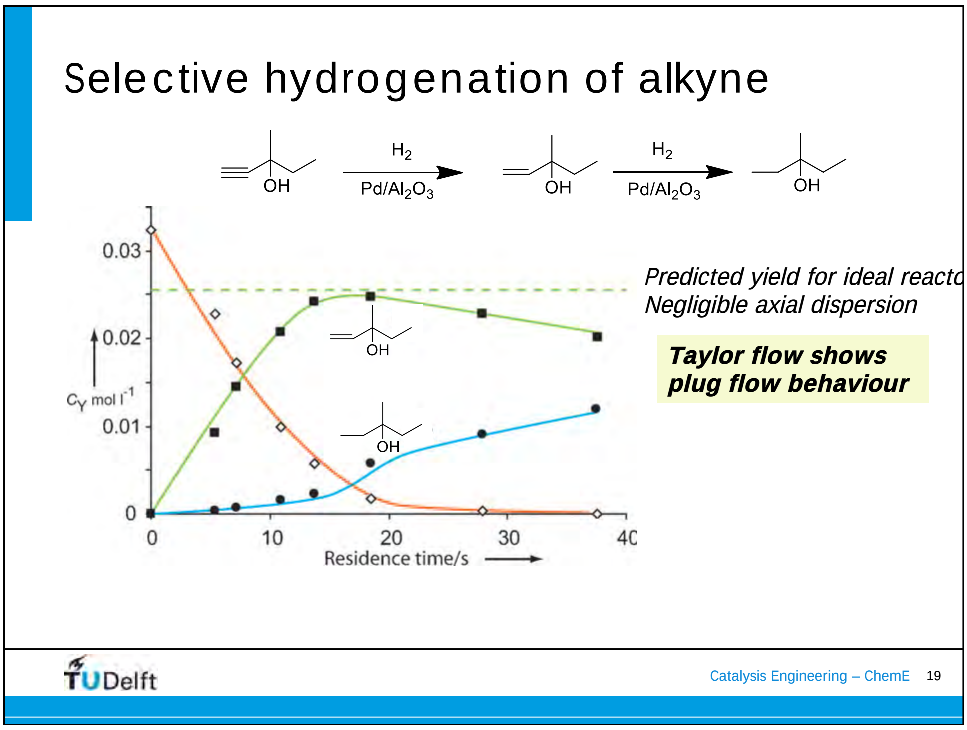


1.1 wt% Pd on alumina, CY = 295 mol/m³, ratio uG/uL = 860/100 and 1000/200.

Fast kinetics determination – 1 day only

no concern about non-ideal reactor behavior or transport issues




Selective hydrogenation of alkyne
H2
Pd/Al2O3
OH
H2
Pd/Al2O3
OH
OH
Predicted yield for ideal reacto
Negligible axial dispersion
Taylor flow shows
plug flow behaviour
0.03
0.02
CY mol l-1
0.01
0
0
10
20
30
40
Residence time/s
OH
OH
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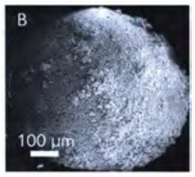
Monolithic Stirrer Reactor
I. Hoek et al.,
Chem Eng Sci 59 (2004) 4975-4981
Senior Moulton medal
IChemE 2007
TUDelft
K.M.de Lathouder et al. Chem.Eng.Research and Design 84 (2006) 390-398

Structuring – matching time scales

TAP reactor modeling - zeolites

Determination adsorption-diffusion parameters in zeolites

Response peak width/shape:
- Diffusion through bed
- Adsorption-diffusion in zeolite



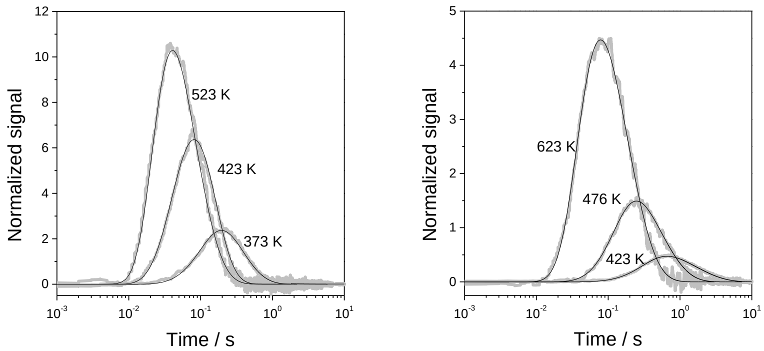
Strong adsorption – reduce amount
Slow diffusion – reduce particle size

$$D_{K_B} = \frac{2}{3}\left(\frac{2\varepsilon r_p}{3(1-\varepsilon)}\right)\sqrt{\frac{8RT}{\pi M}}$$

Solution:
- Thin bed small particles sandwiched between larger particles (?)
- Structured beds: coating thin layer on larger bed particles

Decouple bed diffusion and zeolite diffusion times

Results *n*-butane



J.A. Delgado *et al.*, *Chemical Engineering Science* **2004,** *59* (12), 2477-2487.

Criteria

Good modeling – parameter estimation depends on characteristic times

$$\alpha = \frac{\tau_{bed}}{\tau_{particle}}$$

$$\tau_{bed} = \frac{L_{bed}^2}{\left(\frac{D_{Kbed}\varepsilon}{\tau}\right)}\left[\varepsilon + (1-\varepsilon)(1-c^3)K_{dH}\right]$$

$$\tau_{particle} = \frac{\ell^2}{D_{pore}}$$

Shorter sample bed:
- difference with inert too small

$$0.05\ \text{s} < \tau_{bed} < 4\ \text{s}$$

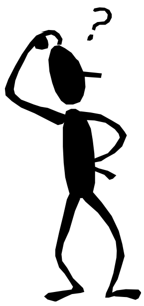
$$0.01 < \alpha < \frac{200\tau_{bed}}{1+\tau_{bed}}$$

Longer sample bed:
- too long tailing
- low signal

R.J. Berger *et al.*, Dynamic methods for catalytic kinetics. *Applied Catalysis A: General* **2008,** *342* (1-2) 3-28.

Intrinsic catalytic information

- Particle level
  - Absence transport limitations
- Reactor level
  - Ideal behaviour
    - Plug flow – axial dispersion
    - Isothermal
    - Packed bed wall porosity



Particle level 5% criteria – 'Observables'

'Ten commandments of catalyst testing' - Dautzenberg

- External (film) gradients
  - Concentration $$Ca = \frac{r_{v,obs}}{a'k_f c_b} < \frac{0.05}{n}$$
  - Temperature $$|\gamma_b \cdot \beta_e \cdot Ca| = \left|\left(\frac{E_a}{R \cdot T_b}\right) \cdot \left(\frac{(-\Delta H_r) \cdot k_f \cdot c_b}{h \cdot T_b}\right) \cdot \left(\frac{r_{v,obs}}{k_f \cdot a' \cdot c_b}\right)\right| < 0.05$$
- Internal (particle) gradients
  - Concentration (*Weisz-Prater*) $$\eta_i \phi^2 = \frac{r_{v,obs} \cdot L^2}{D_{eff} \cdot c_s} \cdot \left(\frac{n+1}{2}\right) < 0.15$$
  - Temperature $$|\gamma_s \cdot \beta_i \cdot \eta_i \phi^2| = \left|\left(\frac{E_a}{R \cdot T_s}\right) \cdot \left(\frac{(-\Delta H_r) \cdot D_{eff} \cdot c_s}{\lambda_{p,eff} \cdot T_s}\right) \cdot \left(\frac{r_{v,obs} \cdot L^2}{D_{eff} \cdot c_s}\right)\right| < 0.1$$

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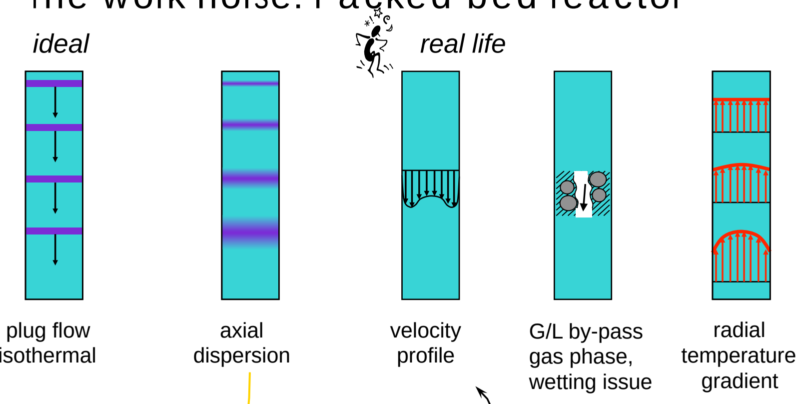
The work horse: Packed bed reactor



equal t_{res}, T

t_{res} varies

T varies

$$Pe_L = \frac{uL_b}{D_{ax}} \geq 8n \cdot \ln\left(\frac{1}{1-X}\right)$$

$$\left(\frac{d_{Tube}}{d_p}\right) > 35 \cdot X$$

Is my reactor a PFR? Isothermal?

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Temperature gradient in catalyst bed

Mears

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

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

> 100 > 1 ~ 1

temperature gradient in bed always develops first !

Catalyst bed properties important

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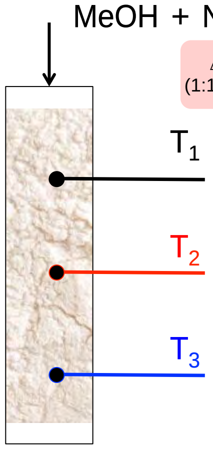
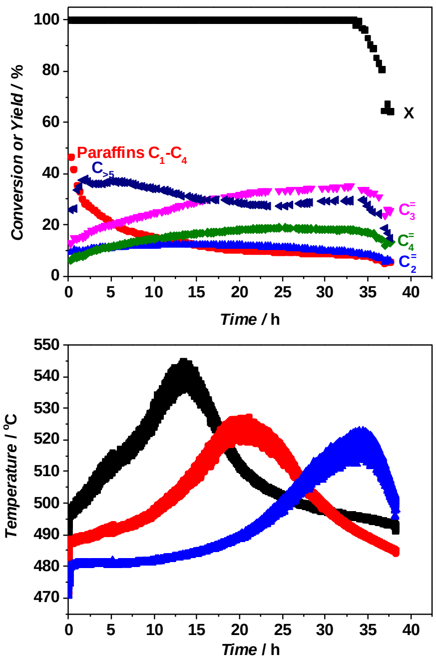
Temperature profiles inside catalytic bed: MTO – ZSM-5

MeOH + N_2 (1:1)

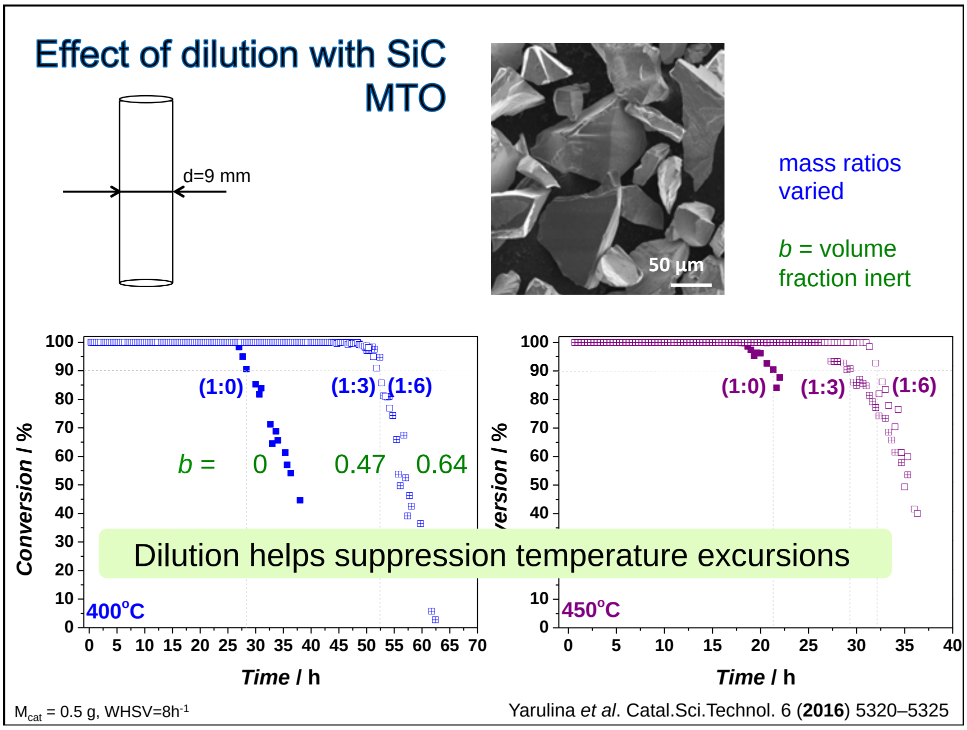
ΔT_{ad} ~ 135 K (1:1 mix MeOH/N_2)

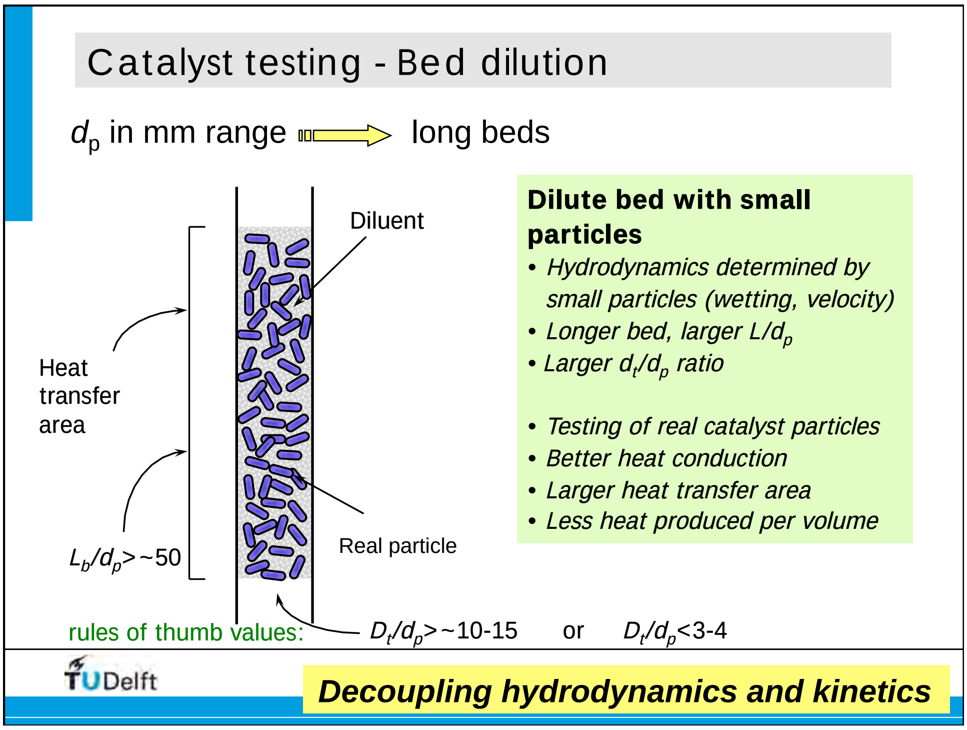


D = 9 mm ID
M_{cat} = 1.75 g
WHSV=4 h^{-1}



Yarulina et al. *Catal.Sci.Technol.* 6 (**2016**) 5320–5325


Effect of dilution with SiC
MTO
d=9 mm
50 µm
mass ratios varied
b = volume fraction inert
Conversion / %
(1:0) (1:3) (1:6)
b = 0 0.47 0.64
Dilution helps suppression temperature excursions
400°C
450°C
Time / h
Mcat = 0.5 g, WHSV=8h-1
Yarulina et al. Catal.Sci.Technol. 6 (2016) 5320–5325


Catalyst testing - Bed dilution
dp in mm range → long beds
Diluent
Heat transfer area
Lb/dp>~50
Real particle
Dilute bed with small particles
• Hydrodynamics determined by small particles (wetting, velocity)
• Longer bed, larger L/dp
• Larger dt/dp ratio
• Testing of real catalyst particles
• Better heat conduction
• Larger heat transfer area
• Less heat produced per volume
rules of thumb values: Dt/dp>~10-15 or Dt/dp<3-4
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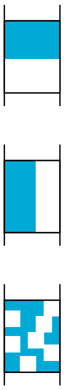
Decoupling hydrodynamics and kinetics

Bed dilution - bypassing ?

Inhomogeneous distribution
Catalyst by-passing

Berger, Perez et al.
*App.Catal.*227(2002)321
Chem.Eng.Sci. 57(2002)4921
Chem.Eng.J. 90(2002)173



Do not:
- dilute too much
- use too high conversion

b = volume fraction inert diluent

Criterion:

$$\Delta = \left(\frac{b}{1-b}\right)\frac{x_{obs}}{2}\left(\frac{d_p}{L_{bed}}\right) < 0.05$$

(= deviation rate constant less than 5%)

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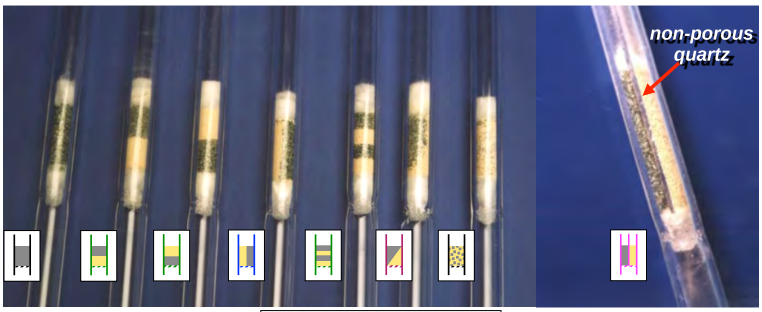
Bed dilution, how to do it? Inhomogeneous distribution detrimental??

Catalyst by-passing?
Inhomogeneous distribution?

Practical example
Effect of Catalyst/Diluent distribution in decomposition of N_2O

Catalyst-diluent distributions



Catalyst   Diluent

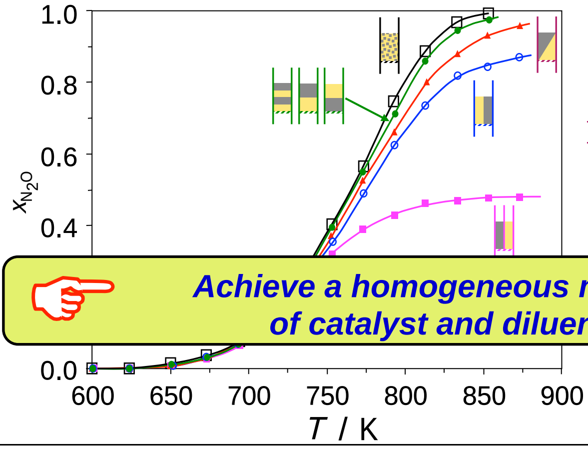
TUDelft

Berger et al. AppCatA227(2002)321-333
ChemEngJ 90(2002)173-183

Berger et al. AppCatA227(2002)321-333
ChemEngJ 90(2002)173-183

Bed dilution: experimental

Decomposition of N_2O



Catalyst

ex-FeZSM-5

Particle size range

125 - 200 µm

Conditions

P_{tot} = 1.0 bar

…mbar,

…nce He

$W_{cat}/F_{N_2O,0}$ = $8.65 \cdot 10^5$ g s mol^{-1}

Single-pellet-string reactors, feasible in catalyst testing?

Criterion (rule of thumb): $\frac{d_{reactor}}{d_{particle}} >> 10$ Size laboratory reactor microreactor would be large

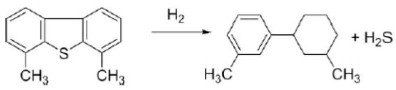
Clue: Radial transport high for $\frac{d_{reactor}}{d_{particle}} < 3$

Extrudates fit in tubes

$\frac{d_{reactor}}{d_{particle}} \approx 1$

Inner diameter 0.5 - 2.6 mm
Length: 40 - 500 mm

Comparison single-pellet-string reactor and established industrial bench-scale reactor



Major reaction in Hydrodesulfurization

Trickle bed reactor applied

Industrial feedstock 1.6 wt% S → <10—20 ppm S *Very high conversion*

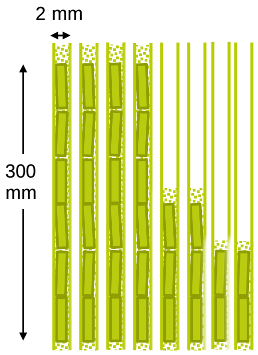
NiMo

Quadrulobe extrudates

1.3 mm diameter
3-5 mm length

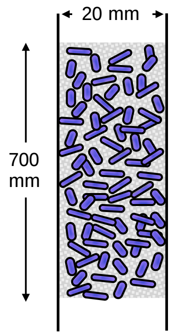
Comparison single-pellet-string reactor and established industrial bench-scale reactor

Single-pellet string reactors



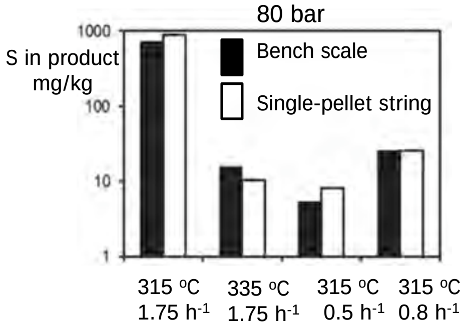
Bench-scale reactor

Diluted bed



Up-flow

Catalyst performance



Excellent agreement

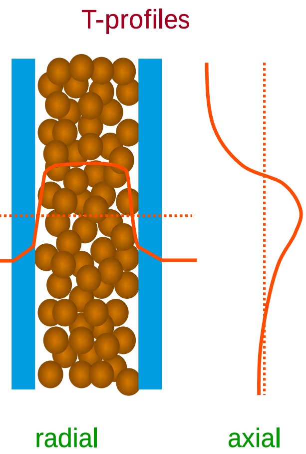
Heat effects in packed-bed reactor

Poor heat transfer
- in bed
- to wall $h \approx 50 \frac{W}{m^2K}$

Improvements:
- foams (ceramic, metal)
- catalytic coatings

$h \approx 10^4 \frac{W}{m^2K}$

- forced flow

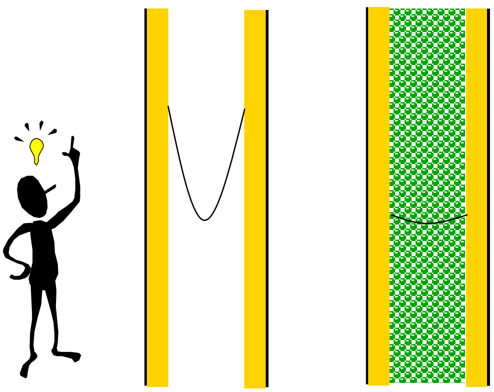


Heat production/ consumption

Cooling-heating:
- Reaction coupling
- Heat exchange
  - through wall
  - no wall
- Evaporation

G.Kolios et al. Chem.Eng.Sci. 57(2002)1505

Coated wall reactor



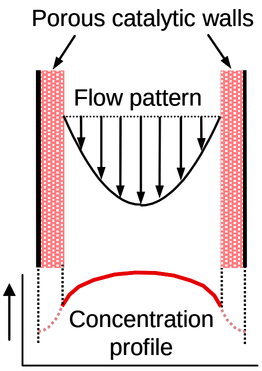
Better heat removal

Exothermal reactions
oxidation
hydrogenation

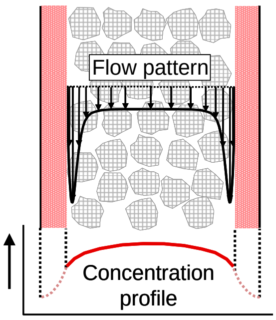
But:
Velocity profile?
Concentration gradients?

Monoliths, microreactors, kinetic studies

Coated wall – flow patterns



$$Pe' = \frac{u_0 L}{D_{A,rad}} \left(\frac{R}{L}\right)^2$$

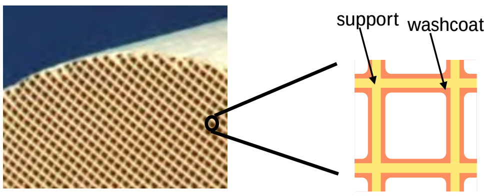


Criteria $X_{CWR} < \frac{0.16}{0.23 + nPe'}$ $X_{CWR} < \frac{1.48}{1.04 + nPe'}$

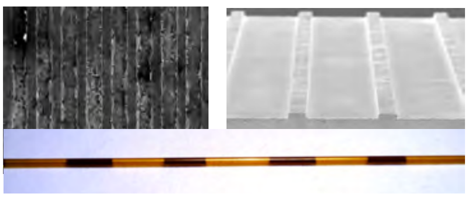
R.J. Berger & F. Kapteijn Ind. Eng. Chem. Res. 46 (2007) 3863
Ind. Eng. Chem. Res. 46 (2007) 3871

Coated wall reactors

- Monoliths
  mm size



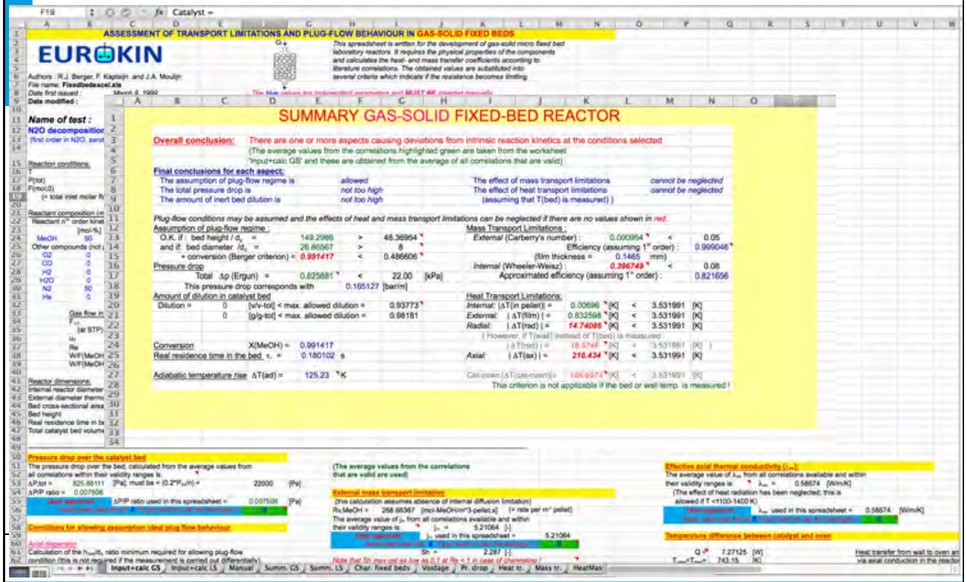
- Microreactors
  0.05-0.2 mm



- Kinetic studies
  5-15 mm

Redlingshöfer *et al.*
*Ind.Eng.Chem.Res.*41(2002)1445-1453

The Eurokin spreadsheet – Criteria check

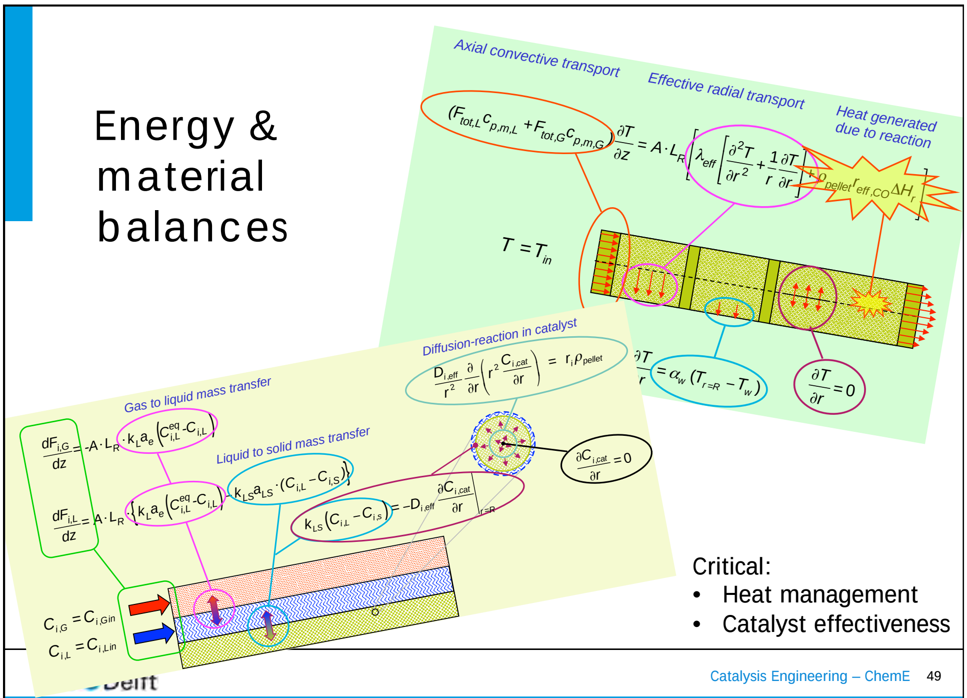


Some Eurokin challenges

- Conductive structure lab reactor
  - Exothermal reactions
- Resistances in reactor – what is desired?
- Adsorption-separation processes – PSA
  - Hydrodynamics, mass and heat transfer,
  - Competitive diffusion, -adsorption
  - Gas and liquid phase
- Multi-dimensional optimization
  - Efficient computational tools?
  - Similar as in PSA cycles

Transient operation

Energy & material balances



Critical:

- Heat management
- Catalyst effectiveness

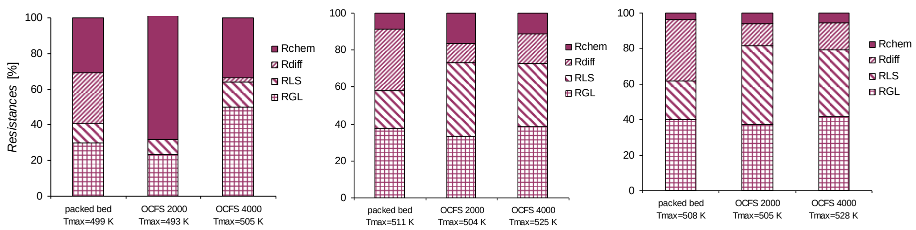
Resistances – FTS example

$R_{total} = R_{GL} + R_{LS} + R_{chem} + R_{diff}$

If:

Gas-Liquid
Liquid-Solid
Diffusion
Reaction

% Contributions of each resistance



T_{in}=490 K, YS=1 T_{in}=490 K, YS=5 T_{in}=490 K, YS=10

How to interpret the distribution of resistances?
What is desired?

Kalyani Pangarkar, PhD Thesis TUDelft, Ch.7, 2010

Model comparison RPB and PCCFS

Multidimensional optimization

> 200 000 reactor configurations

8 Parameters varied

- Catalyst activity factor *F*
  - Reference: 3 YS
  - Future: 10 YS
- Inlet syngas ratio H_2/CO
- Catalyst diameter (mm)
- Inlet temperature (K)
- Wall temperature (K)
- Tube length (m)
- Tube diameter (cm)
- Inlet sup. gas velocity (m/s)

Performance indicators

- *Space Time Yield*
  (kg C_{5+} / m^3 tube / h)
- *Productivity per catalyst mass*
  (kg C_{5+} / kg catalyst / h)

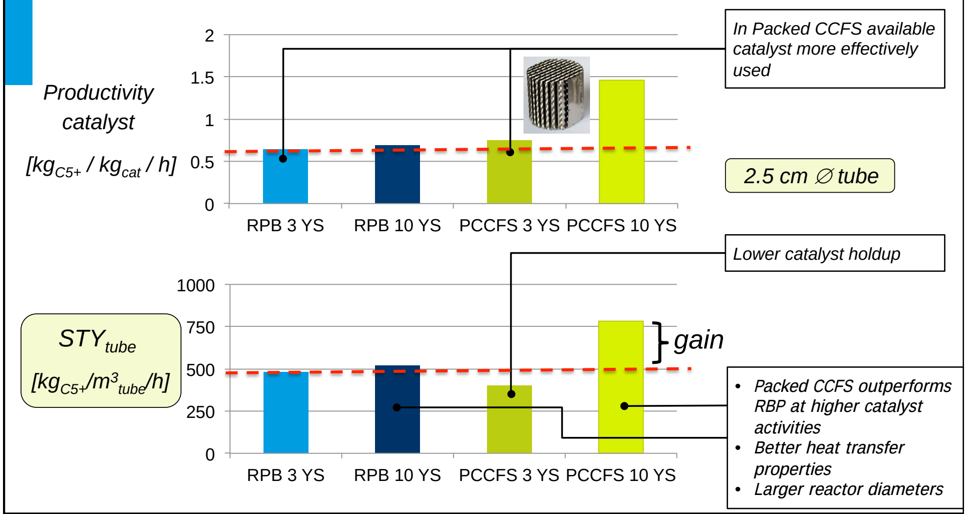
Constraints

- *CO Conversion > 0.25*
- *Chain growth (alpha) ≥ 0.90*
- *Pressure drop < 1 bar/m*
- *Water vapor pressure < 6 bar*
- *Temperature < 530 K*

TUDelft *Kaskes et al. Chem. Eng. Journal 283 (**2016**) 1465–1483* Catalysis Engineering – ChemE 52

STY comparison of selected optima

RPB vs Packed CCFS at different catalyst activities



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Looking back – 20 years Eurokin

- Unique consortium
  - Platform cross-fertilization industry-university
  - Establish fruitful contacts -
- Productive scientific meetings
  - Inspiring brainstorming sessions
    - Creation challenging subjects
    - Revisiting-reviving old topics
  - Build-up dynamic documentation library
    - Scientific and practical
    - Eurokin summer school
- Scientific productions

Berger, R. J.; Stitt, E. H.; Chewter, L.; Verstraete, J.; Marin, G. B.; Hoorn, J., *The Eurokin consortium: origin, topics and aims.* *Green Processing and Synthesis* **2013,** *2* (1), 67-69.

TU Delft – ChemE 54


EUROKIN – 20 years of
Catalyst Performance
Thank you for your attention
Eurokin
16 October 2018
Vaalsbroek, The Netherlands
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