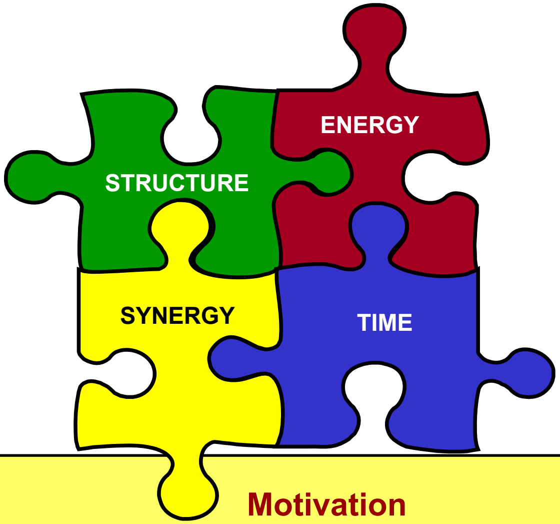
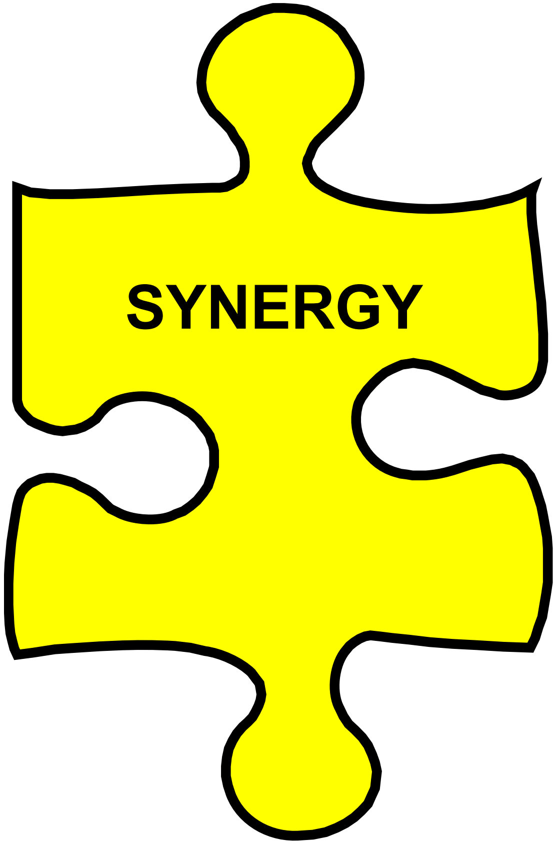
SYNERGY – PART I

Reminder…

Fundamental principles and approaches of Process Intensification are applicable to any chemical process or operation. Intensification needs simultaneous addressing the four domains, as given below:



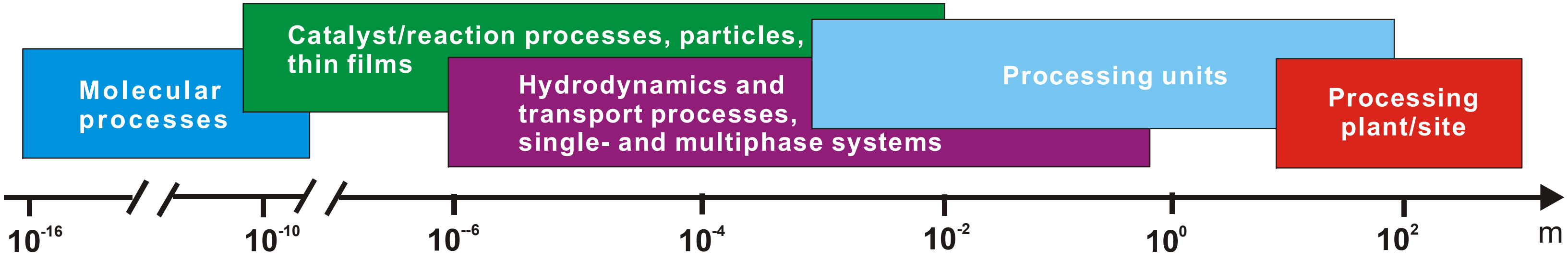
Domain	Main focus	Process Intensification concepts applied	Motivation
Spatial	Structured environment	Milli- and microchannels; structured (catalyst) surfaces	• well-defined geometry • creating maximum specific surface area at minimum energy expenses • creating high mass and heat transfer rates • precise mathematical description • easy understanding, simple scale-up
Thermodynamic	Alternative forms and transfer mechanisms of energy	Electric and electromagnetic fields	• manipulation of molecular orientation • excitation of targeted molecules • selective, gradientless and local energy supply
Functional	Integration of functions/steps	Combination of alternative energy forms (e.g. electric and laser fields), combination of catalyst and energy source or energy-absorbing material.	• synergistic effects • better heat management • increase of overall efficiency • more compact equipment
Temporal	Timing of the events, introducing dynamics	Dynamic (pulsed) energy supply, millisecond contacting	• controlled energy input • utilizing resonance • increased energy efficiency • side reactions minimized



- small-scale synergy in catalysis
- combining energy forms
- synergy in processing units – multifunctional equipment and combined operations
  - integrated reaction and mixing
  - integrated reaction and heat exchange

(to be continued in part II)

At all scales, from nano to macro


Molecular processes

Catalyst/reaction processes, particles, thin films

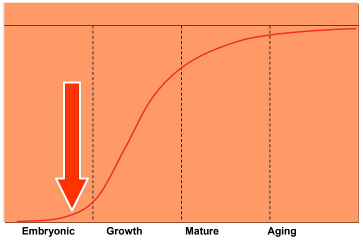
Hydrodynamics and transport processes, single- and multiphase systems

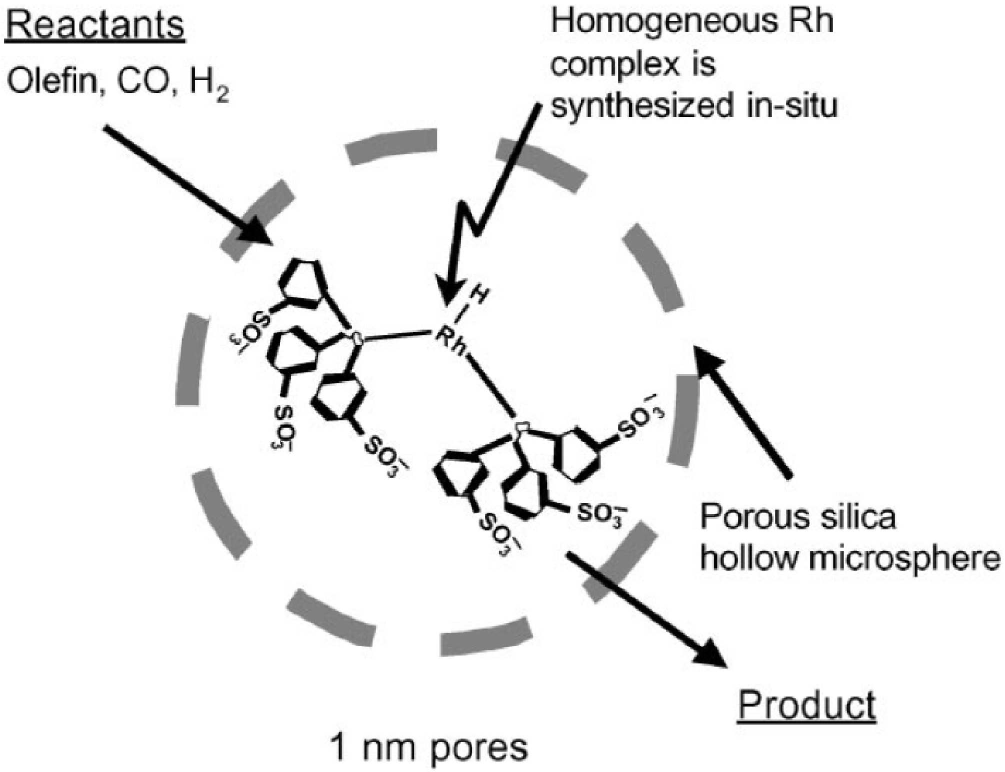
Processing units

Processing plant/site

Small-scale synergy in catalysis

Catalytic function + mass transport control function





Reactants

Olefin, CO, H_2

Homogeneous Rh complex is synthesized in-situ

Porous silica hollow microsphere

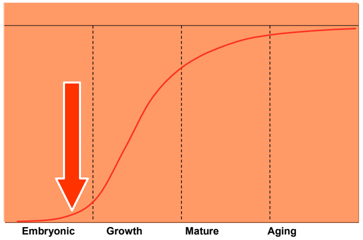
Product

1 nm pores

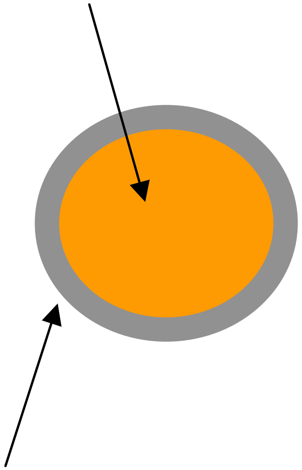
Homogeneous Rh catalyst encapsulated by a porous and hollow silica microsphere causing deliberate diffusion-limited input of reactants leading to enhanced product selectivity.

Dautzenberg & Mukherjee, 2001

Catalytic function + separation function

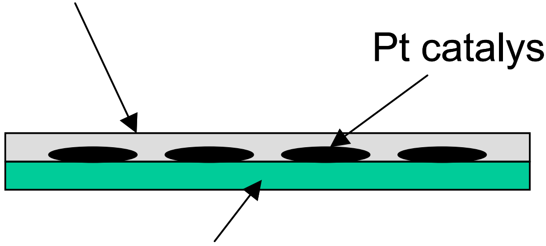


Membrane coated catalyst



ordinary Si-Al catalyst

Carbon molecular sieve layer (~ 0.5 nm pores)



Silicalite-1 coating

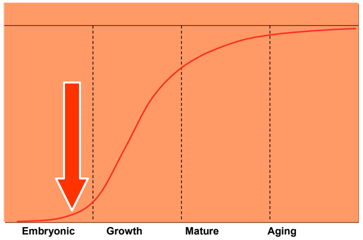
Pt catalyst

TiO_2 support

Controlled feed to active sites
Selective feed to active sites
Selective product removal

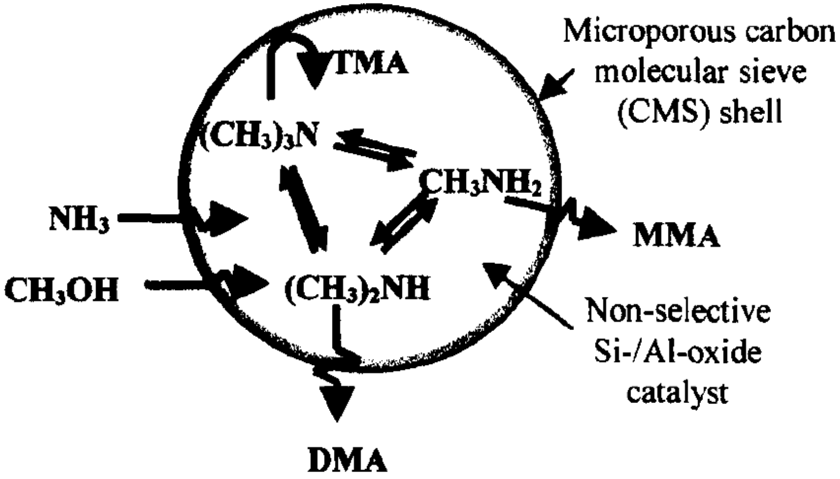
(F. Kapteijn – personal communication)

Catalytic function + separation function



methanol + ammonium ⟶ monomethylamine + dimethylamine + trimethylamine

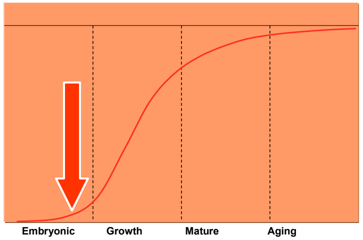
(MMA) (DMA) (TMA)

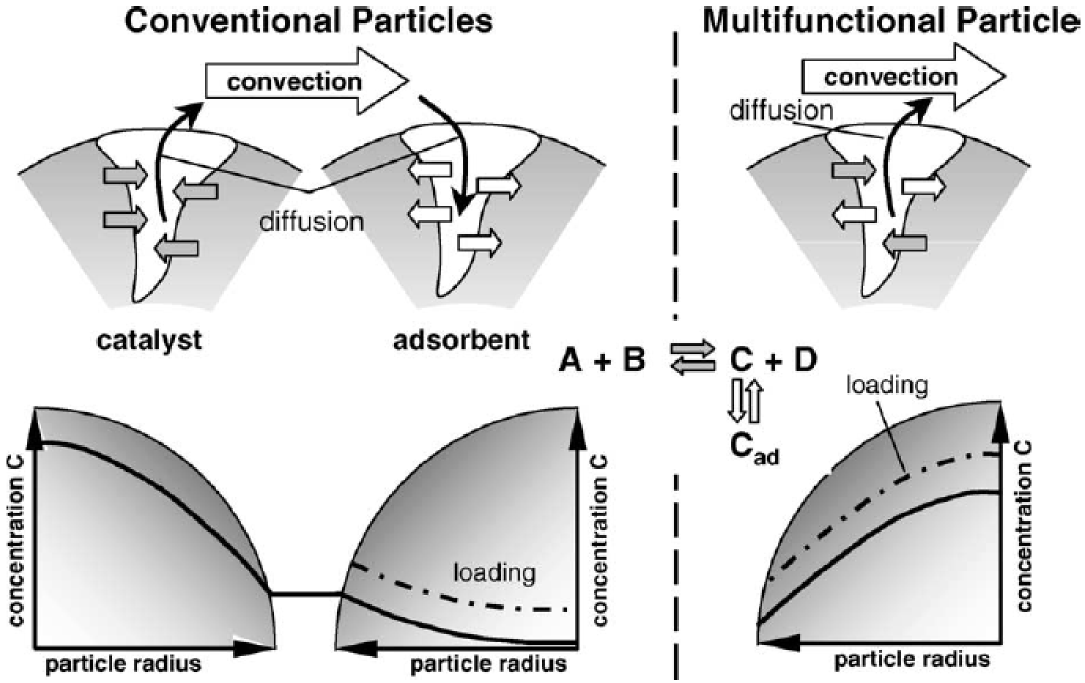


	Selectivity (MMA+DMA) / TMA
catalyst	2
catalyst + membrane	5

Agar, 1999

Catalytic function + separation function: example of reactive adsorption



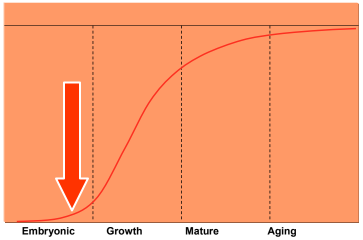


Reaction and adsorption in a multifunctional catalyst:

- better removal of C due to higher concentrations
- higher rate due to lower surface concentration of C
- better adsorbent utilization (loading)

Dietrich et al., 2005

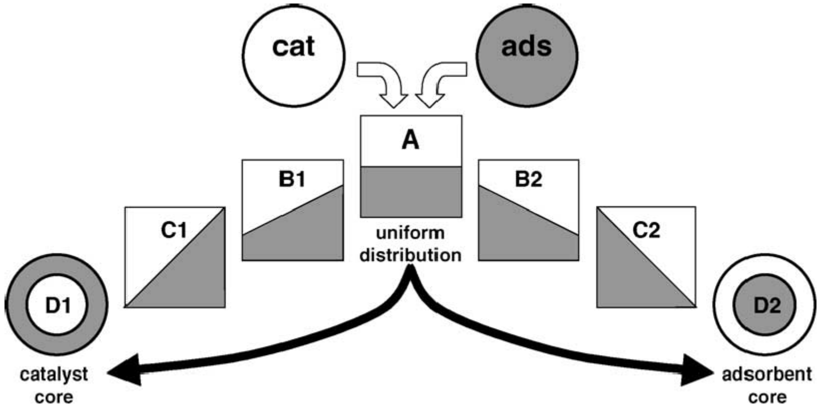
Catalytic function + separation function: example of reactive adsorption

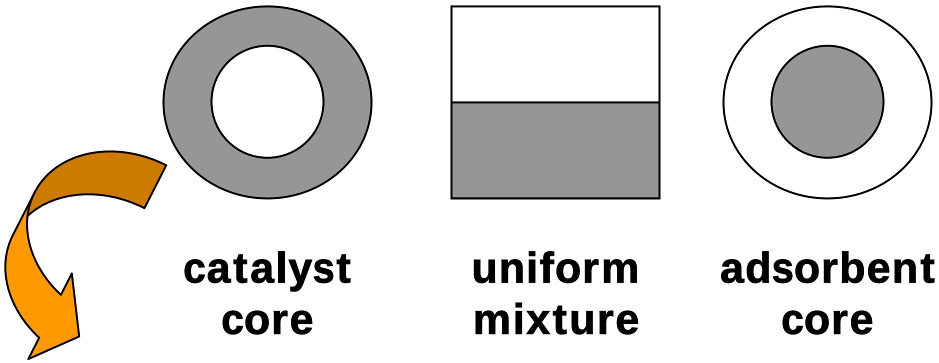


$$CH_4 + H_2O \Leftrightarrow CO + 3H_2, \quad \Delta H_{R,I,298} = 206.2 KJ/mol$$

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2, \quad \Delta H_{R,II,298} = 164.9 KJ/mol$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2, \quad \Delta H_{R,III,298} = -41.1 KJ/mol$$



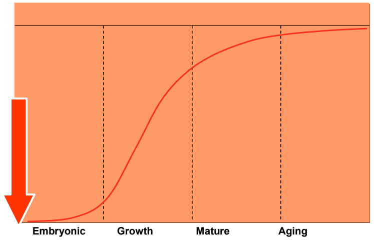


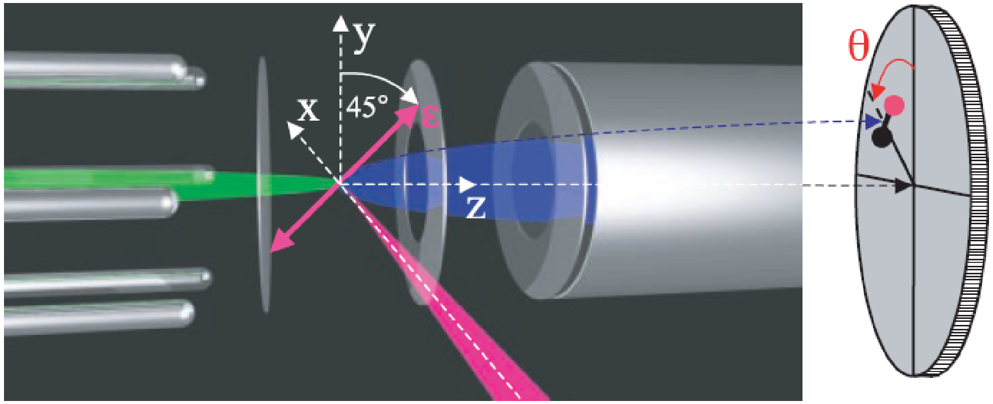
	catalyst core	uniform mixture	adsorbent core
Simulated hydrogen yield	8.732	150.76	401.46

Dietrich et al., 2005; Kapil et al., 2008

Combining energy forms

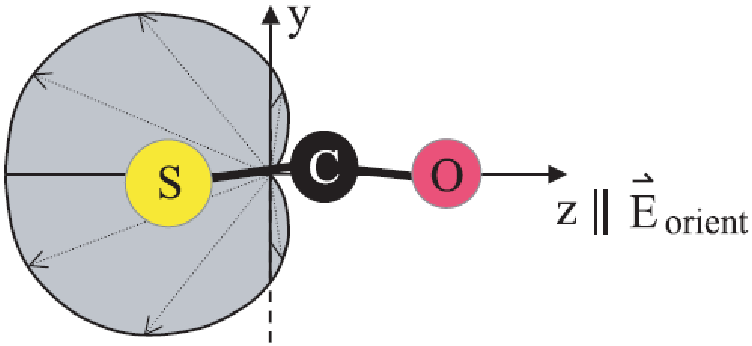
Combining energy forms: electric field + laser beam





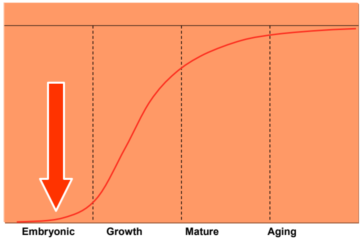
(A)

(B)



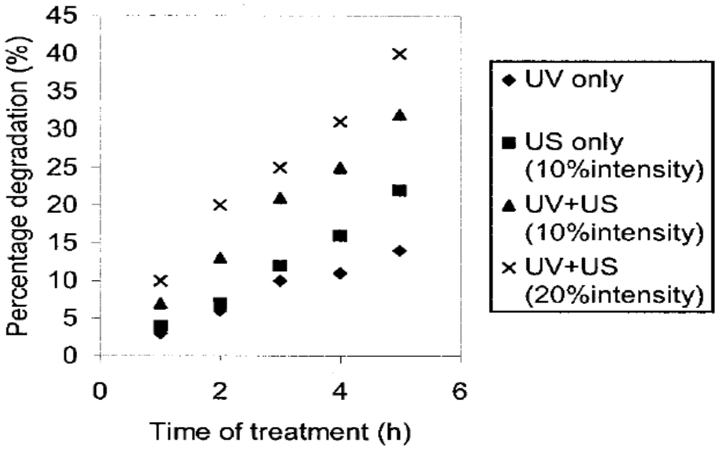
(A)- Orientation of a molecular beam of carbonyl sulphide molecules moving along the z-axis by a hexapole electric field (left) followed by their dissociation by a laser beam acting along the x-axis (from Rakitzis, et al, 2004); (B) - Probability plot of the molecular orientation of the OCS molecule; dotted arrows are proportional to the orientation probability of the OCS dipole moment along each direction.

Combining energy forms: ultrasound + light



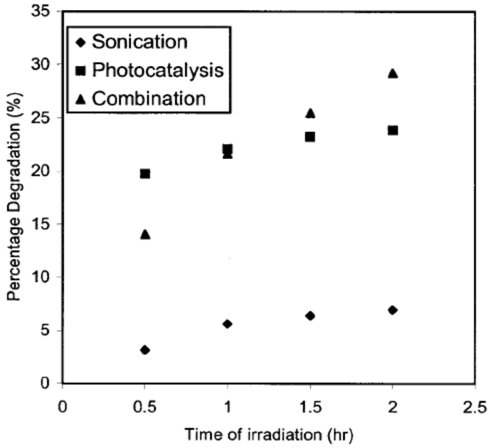
Additional benefits of US in photocatalytic reactions:

- increased local T and P
- cleaning and sweeping of photocatalyst (e.g., TiO2)
- improved mass transport towards the catalyst
- new solid surfaces available (due to fragmentation/deagglomeration of catalyst)
- cavitation-induced radical formation



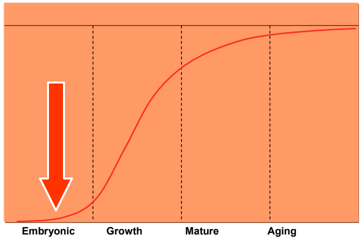
Degradation of trichlorophenol

Degradation of formic acid

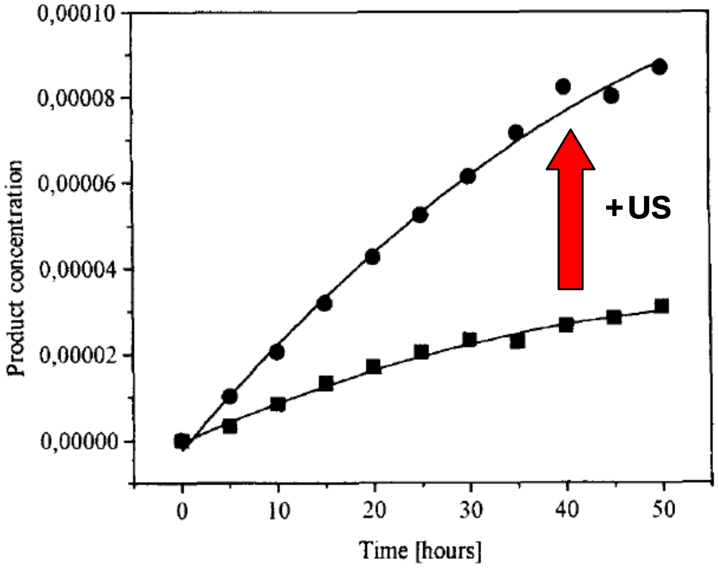


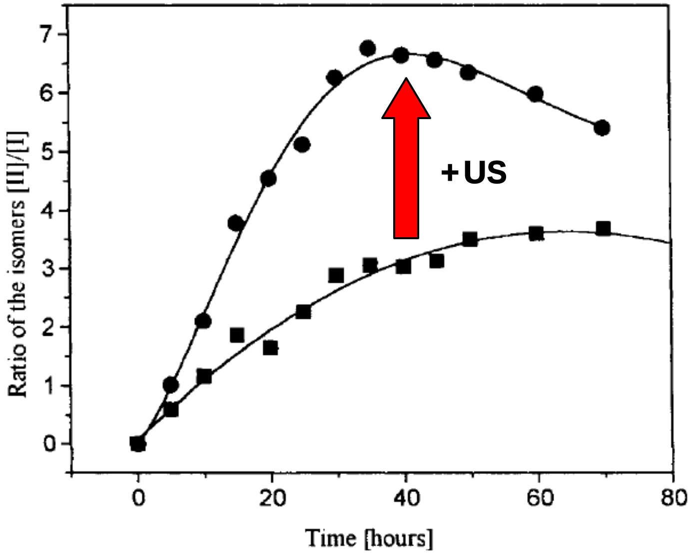
Gogate and Pandit, 2004

Combining energy forms: ultrasound + light



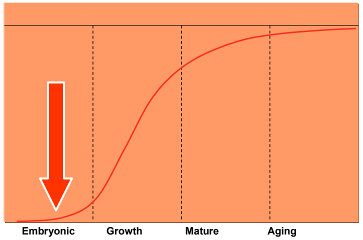
Ultrasound improves photochemical synthesis reactions and alters isomer ratios

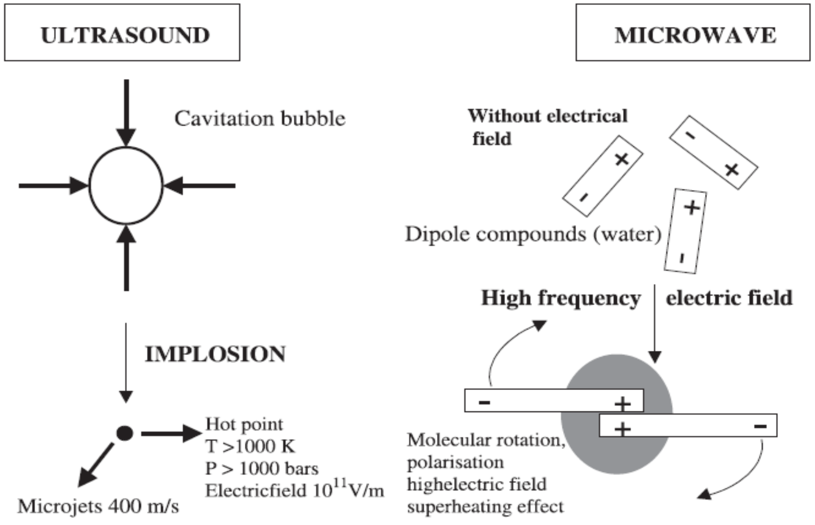




Gaplovsky et al., 1997

Combining energy forms: ultrasound + microwaves

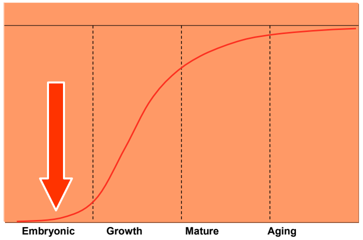




	digestion of sunflower oil (yield>90%)	digestion of sesame oil (yield>90%)
classical	50 min	70 min
microwave	40 min	50 min
microwave + ultrasound	25 min	35 min
time intensification (MW+US/class.)	**2**	**2**

Chemat, 2004

Combining energy forms: ultrasound + microwaves



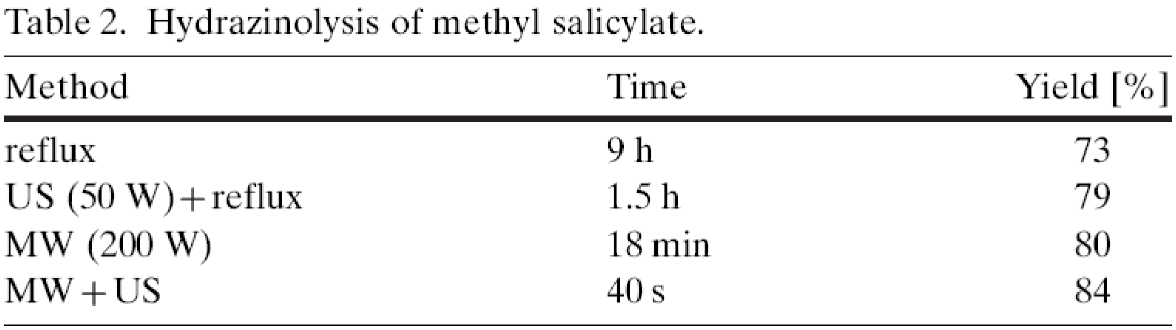


Table 2. Hydrazinolysis of methyl salicylate.

Method	Time	Yield [%]
reflux	9 h	73
US (50 W)+reflux	1.5 h	79
MW (200 W)	18 min	80
MW+US	40 s	84

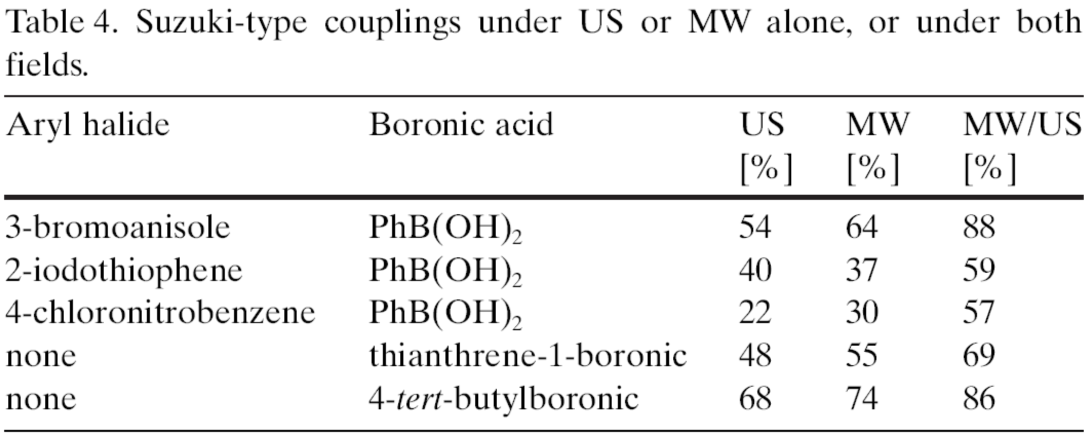


Table 4. Suzuki-type couplings under US or MW alone, or under both fields.

Aryl halide	Boronic acid	US [%]	MW [%]	MW/US [%]
3-bromoanisole	$\mathrm{PhB(OH)_2}$	54	64	88
2-iodothiophene	$\mathrm{PhB(OH)_2}$	40	37	59
4-chloronitrobenzene	$\mathrm{PhB(OH)_2}$	22	30	57
none	thianthrene-1-boronic	48	55	69
none	4-*tert*-butylboronic	68	74	86

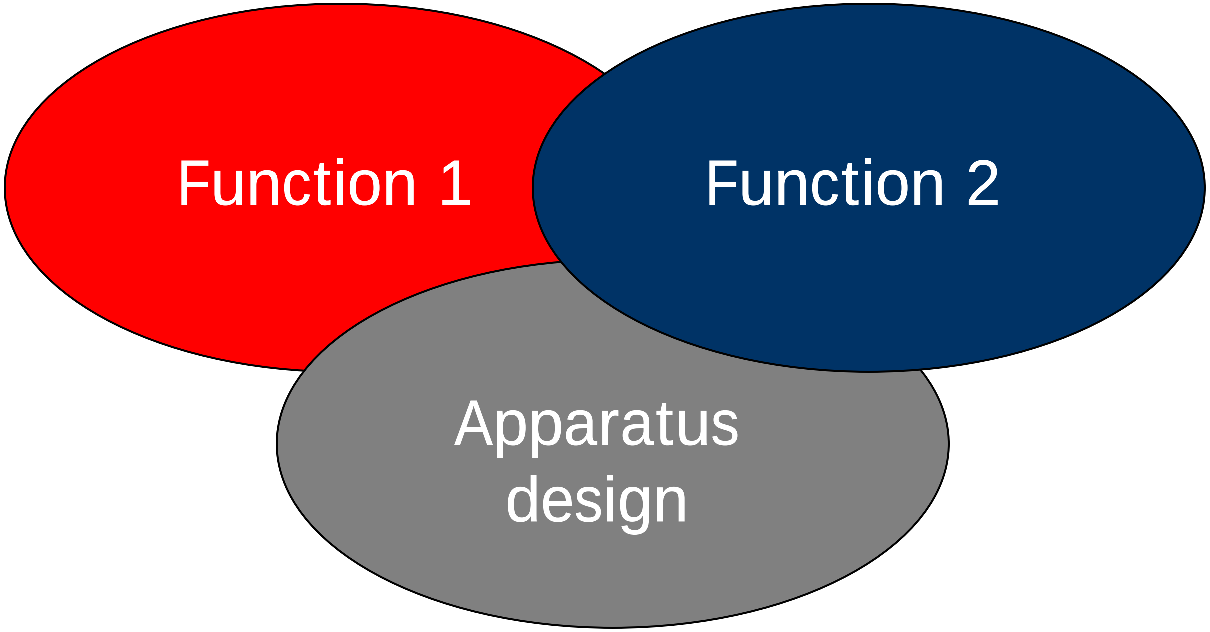
Cravotto, 2007

Synergy in processing units

- Multifunctional reactors
- Hybrid separations

Synergy – multiple functions

Design criteria on processing unit level difficult to combine



(after Tlatlik and Schembecker, ARS-1, Dortmund 2000)

Multifunctional reactors - definition

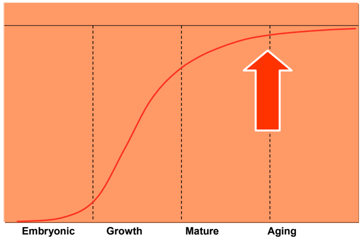
Reactors, which alongside chemical conversion (and for the sake of it) integrate at least one more function (usually unit operation) that conventionally would have to be performed in a separate piece of equipment.

Examples:

- **integrated reaction and mixing**
- **integrated reaction and heat exchange**
- **integrated reaction and separation (reactive separation)**
- **integrated reaction and power generation (fuel cells)**
- **integrated reaction and phase transition (reactive extrusion)**
- **integrated reaction and comminution**

Integrated reaction and mixing

Integration of (exothermic) reaction and mixing

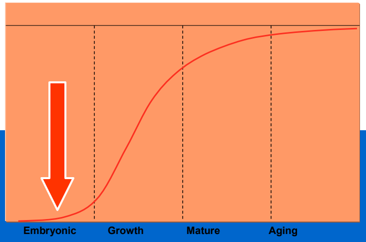


- can be used as chemical reactors for carrying highly exothermic single- or multiphase reactions
- mixer elements are made from cooling tubes
- another option: shell-and-tube heat exchanger with static mixers inside the tubes

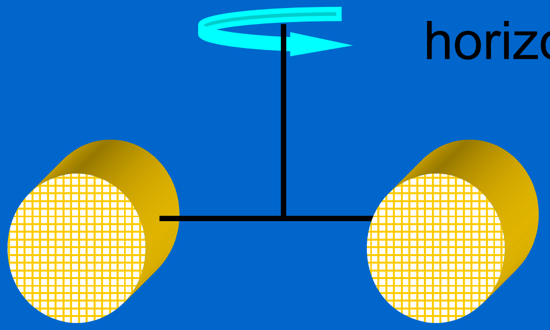



(source: A. Green, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Integration of catalytic reaction and mixing



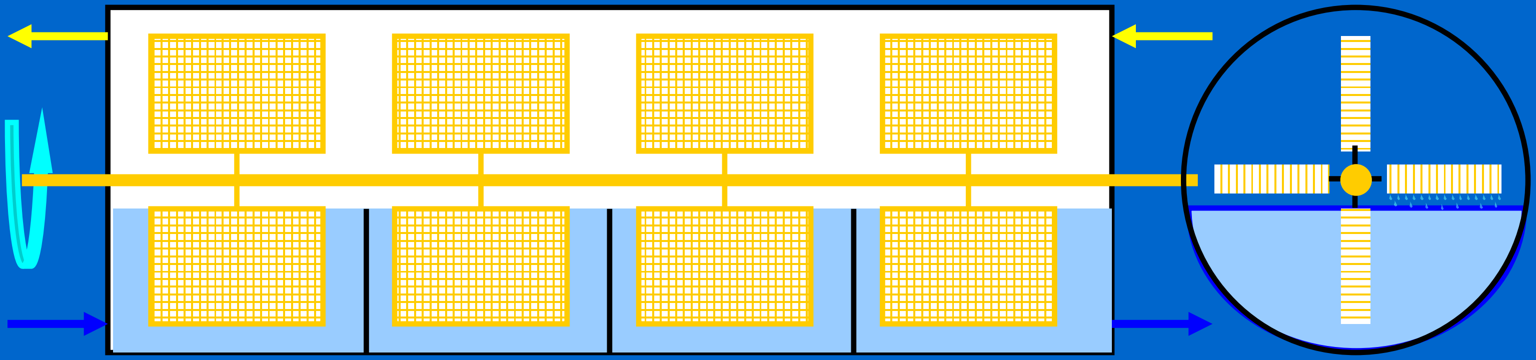
Monolithic stirrer reactor



horizontal mode

Liquid phase reactions
Hydroformylation
Food processing

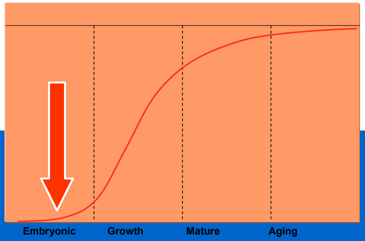
vertical mode



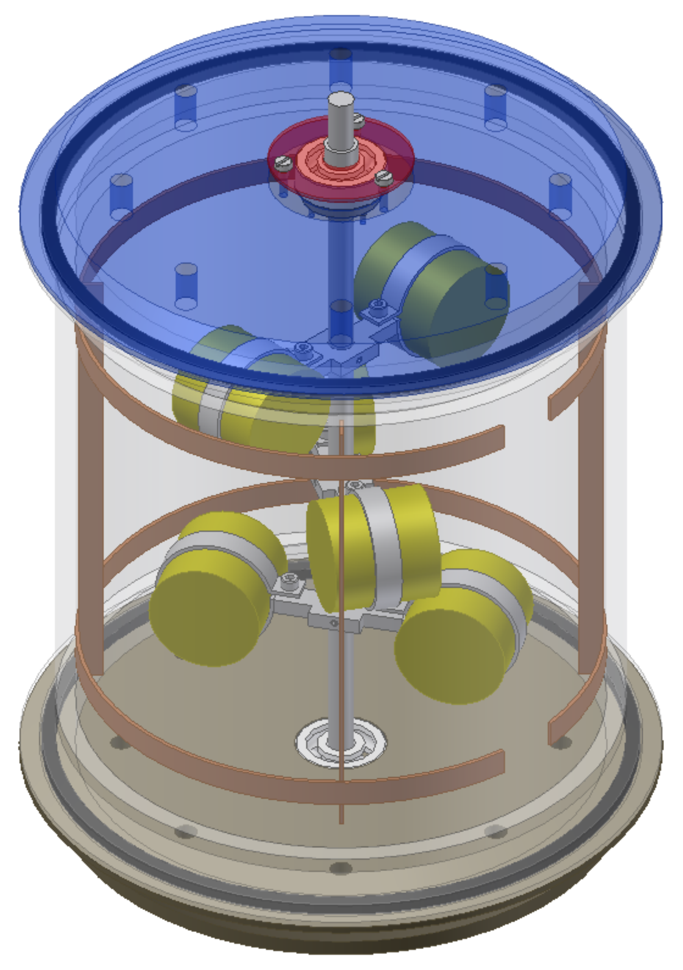
Staging possible
Cross-, co- and countercurrent

F.Kapteijn et al., CATTECH 3(1999)24

Integration of catalytic reaction and mixing



Monolithic Stirrer Reactor



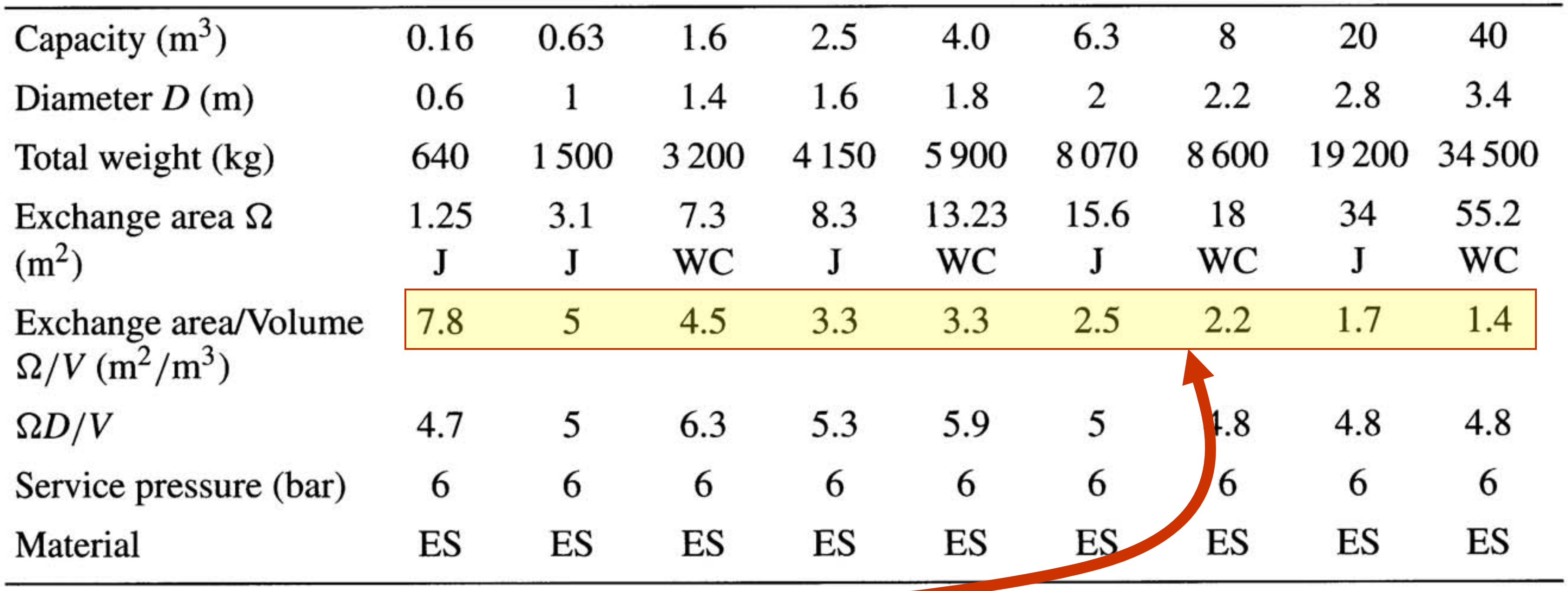
- Very suitable for biocatalysis
- Retrofitting
- Easy catalyst separation
- Safety

I.Hoek et al. *Chem.Engng.Sci.* 59 (2004) 4975-4981
R.K.Edvinsson-Albers et al. *AIChE J.* 44 (1998) 2459-2464

Integrated reaction and heat exchange

Heat transfer area – thermal problem in stirred-tank reactors

Standard parameters of commercial stirred tanks



Capacity (m^3)	0.16	0.63	1.6	2.5	4.0	6.3	8	20	40
Diameter D (m)	0.6	1	1.4	1.6	1.8	2	2.2	2.8	3.4
Total weight (kg)	640	1 500	3 200	4 150	5 900	8 070	8 600	19 200	34 500
Exchange area Ω (m^2)	1.25 J	3.1 J	7.3 WC	8.3 J	13.23 WC	15.6 J	18 WC	34 J	55.2 WC
Exchange area/Volume Ω/V (m^2/m^3)	7.8	5	4.5	3.3	3.3	2.5	2.2	1.7	1.4
$\Omega D/V$	4.7	5	6.3	5.3	5.9	5	4.8	4.8	4.8
Service pressure (bar)	6	6	6	6	6	6	6	6	6
Material	ES	ES	ES	ES	ES	ES	ES	ES	ES

The bigger, the worse

Heat transfer area – thermal problem in stirred-tank reactors

A typical exothermal reaction test: sodium thiosulfate oxidation

$$2\,Na_2S_2O_3 + 4H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O$$

$$\Delta H_r = -586.2\ \text{kJ.mol}^{-1}\ Na_2S_2O_3$$

- Heat that could be removed in a batch reactor, with an optimistic overall heat transfer coefficient U= 500 W.m^{-2}.K^{-1}

Volume (m^3)	1.10^{-3}	1.10^{-2}	0,1	1
Diameter (m)	0,08	0,2	0,4	0,9
Height (m)	0,2	0,3	0,8	1,4
A (m^2)	0,055	0,22	1,13	4,6
Q_{max}/V (kW.m-^{3})	1200	500	250	100
t_c (s)	230	560	1120	2800

$$\dot{N}_{thio}^{\max} = \frac{Q_{\max}}{\Delta H_r} \qquad \text{with} \qquad t_c = \frac{m_{thio}}{M_{thio} \cdot \dot{N}_{thio}^{\max}}$$

C. Gourdon, Rhodia Sustainability Conference, 2008

Integration of reaction and heat exchange

Why integrate?

- Better energy management (less losses)
- Higher yields/selectivities
- Less investment (compacter equipment)
- Longer catalyst lifetime (less severe conditions)
- Safety reasons
  - better controlability of reaction
  - smaller volume
- …

Factors influencing reactor performance

- **Inputs**
- **Contacting pattern**
- **Cumulative kinetics**

(+ thermodynamics)

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Factors influencing reactor performance

Reaction kinetics depend on local:

- **Temperatures**
- **Concentrations**
- **Catalytic activities**

i.e. $r_i\,(A_c, \mathbf{C}, T)$

Reactor performance can be regulated *via*:

- **Temperature profile**
- **Concentration profiles**
- **Activity distribution**

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Strategies for manipulating temperature profiles

- **Convective heat transfer**
- **Recuperative heat transfer**
- **Regenerative heat transfer**
- **Reactive heat transfer**

PI possibilities

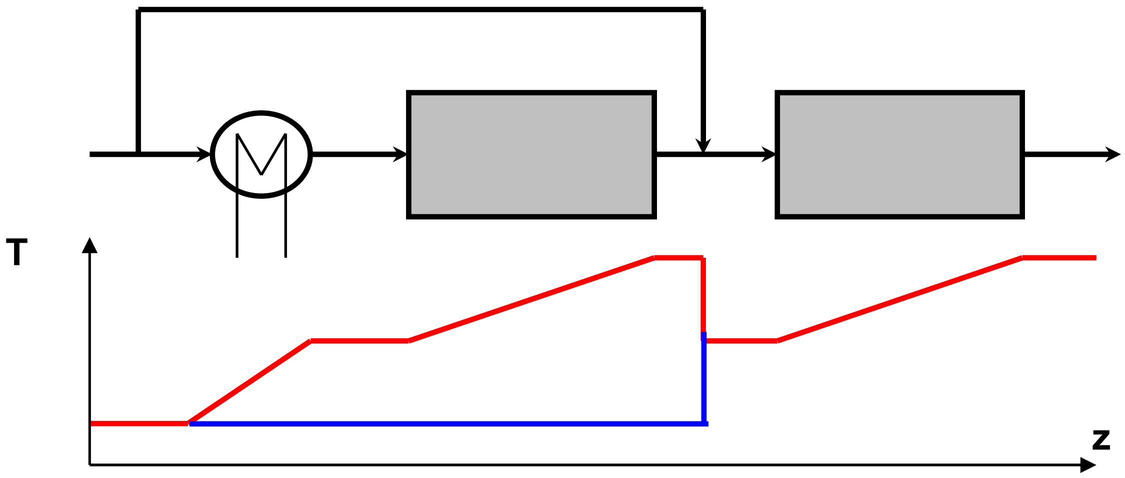
(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Strategies for manipulation of temperature profiles in the reactor

A. Convection

addition or withdrawal of sidestreams

e.g. cold-shot reactor

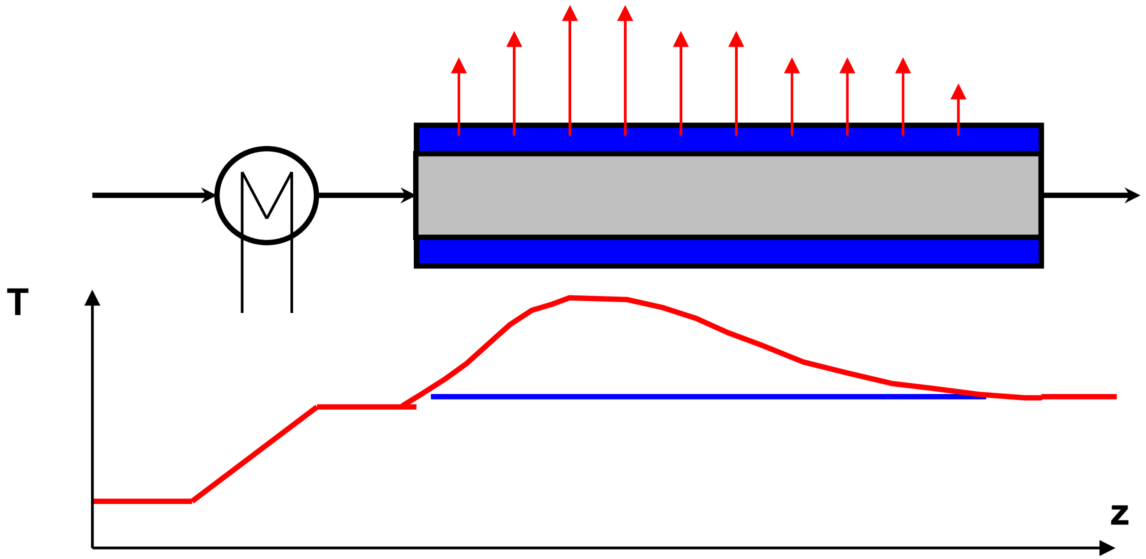


(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Strategies for manipulation of temperature profiles in the reactor

B. Recuperation

spatial segregation between reaction medium & material/heat-sink/source
e.g. multitubular reactor



PI focus: heat transfer coefficients, heat exchange specific surface areas

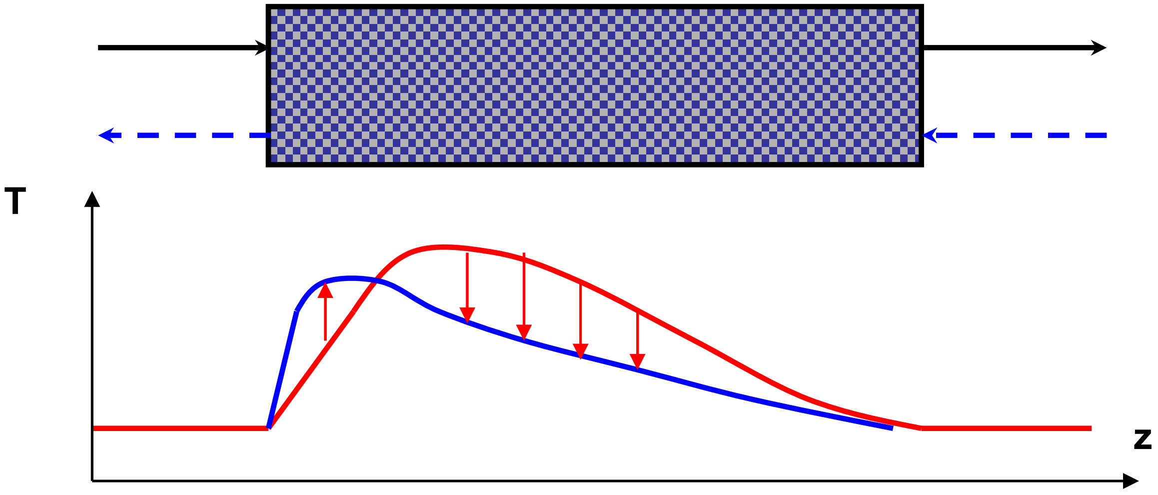
(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Strategies for manipulation of temperature profiles in the reactor

C. Regeneration

chronological segregation between reaction medium & material/heat - sink/source

e.g. reverse flow reactor



PI focus: feasibility windows, system dynamics and control

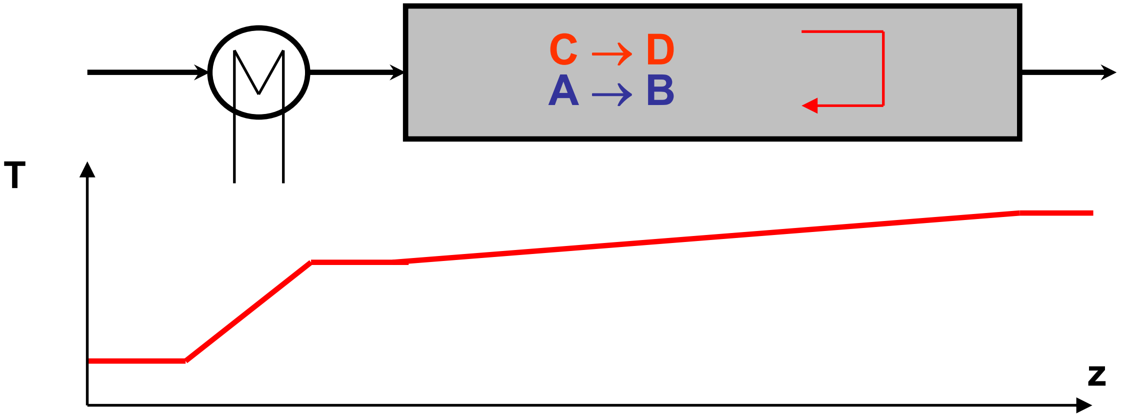
(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Strategies for manipulation of temperature profiles in the reactor

D. Reaction

direct coupling of main reaction with thermally/materially compatible supplementary reaction

e.g. oxydehydrogenation



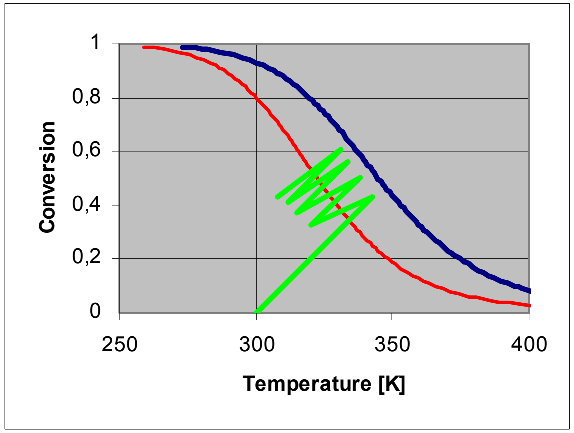
PI focus: feasibility windows, system dynamics and control

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Convective heat transfer

Simple exothermic reversible reaction, A⇔B $\Delta_r H<0$ (e.g. ammonia synthesis)

A. Cold-shot feed sidestream

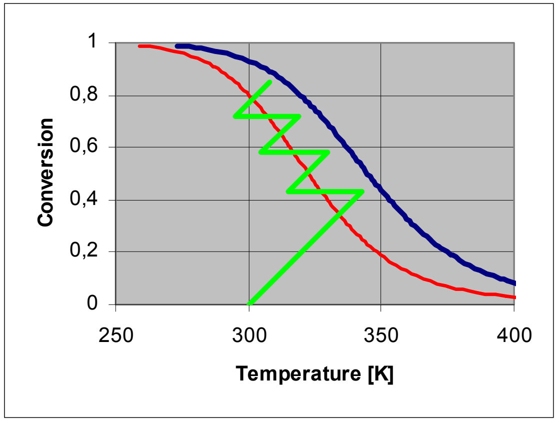


equilibrium

max. rate

reactor operation

B. Cold-shot inert sidestream



Cons:
- Each shot decreases conversion
- Limited cooling capacity

Cons:
- Product dilution – complicated DSP

PI: injection of liquid inert – exploit heat of evaporation, much less quantities coolant needed

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Hot-spots – thermal problem in catalytic reactors

Unwanted temperature maxima arising in tubular reactors with exothermic reactions due to heat transfer limitations

Heat exchange area (A)

~ 100 m²/m³

Heat transfer coefficient (h)

~ 100 W/m²K

Hot-spot adversely effects:

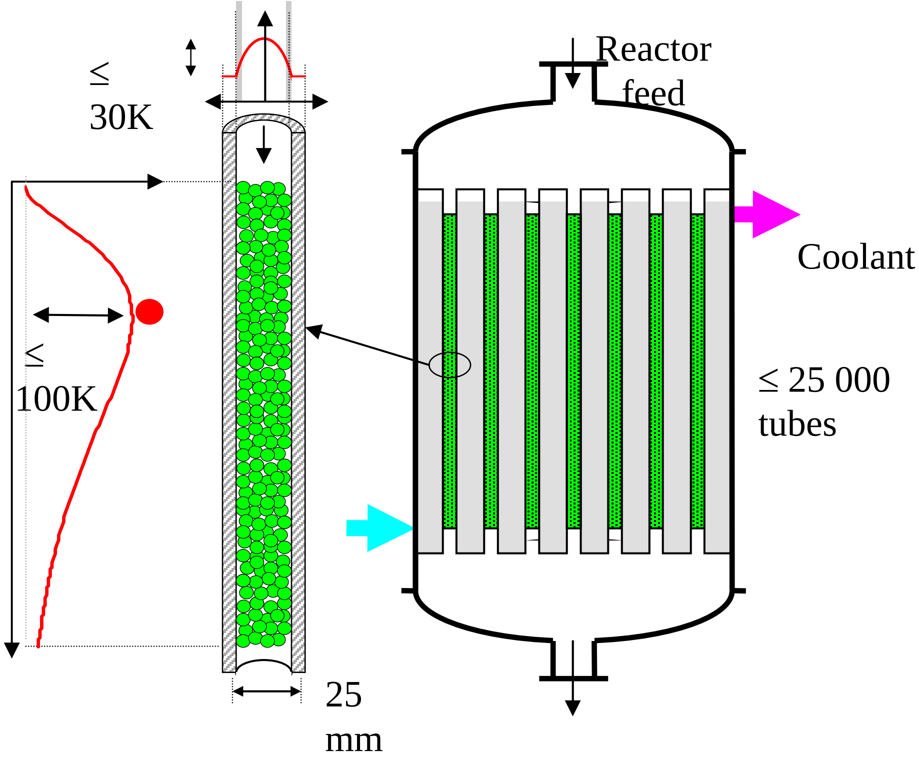
- conversion

- selectivity

- safety

- catalyst lifetime

- choice of reactor materials



(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Eliminating heat exchange problems in reactors

Improved co-ordination between the rates of heat generation & heat removal in reactor

- diminish reaction rate and/or catalyst activity (defensive)
- *e.g. slow-down reactants dosing, dilute the system/catalyst*

- enlarge heat exchange surface (partial solution)
- e.g. Linde-reactor

- raise heat transfer coefficient (partial solution)
- e.g. Fluidised bed

- increase both A & h (PI solution)
- Microreactor
- **Millireactor**

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Hot-spots - eliminating

Improved co-ordination of reaction & cooling using Catalyst dilution with inert

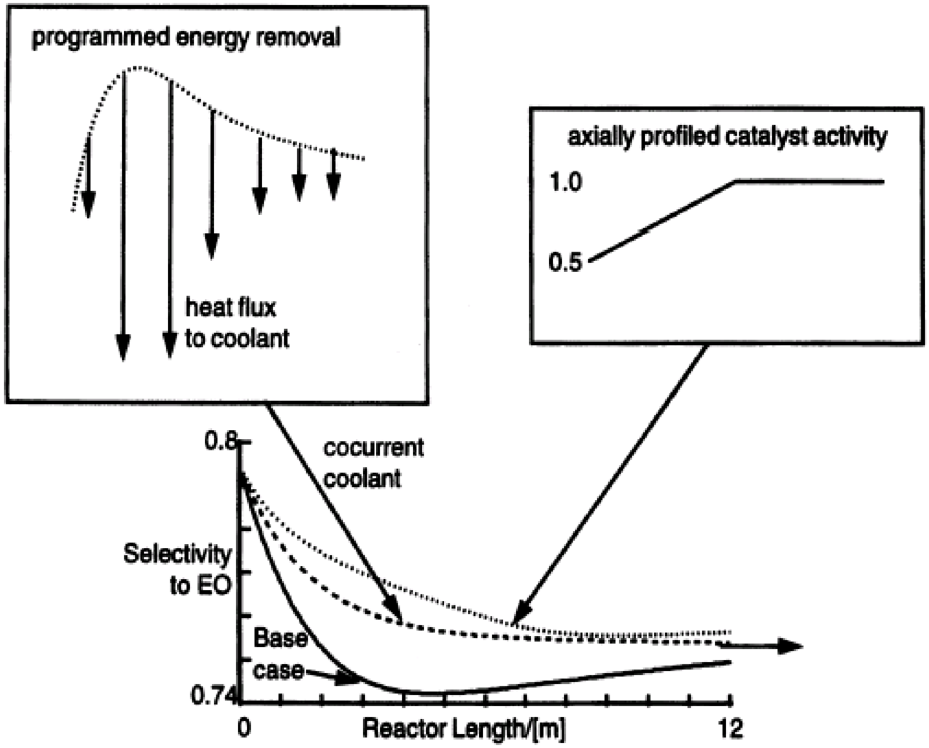
Reaction is distributed more evenly over the cooling surface

+ **simple procedure**

+ **exact activity profile not critical**

+ **significant selectivity improvement of ~1%**

– **much larger reactor & ΔP necessary**



(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Hot-spots - eliminating

Improved co-ordination of reaction & cooling using a Linde™ reactor

Increased specific heat exchange surface of convoluted coolant tube coil in catalyst bed

+ good isothermal behaviour (±20K)

+ slightly higher heat transfer coefficients (h~150 W/m²K)

– complex reactor construction

– temperature limited to <550K by boiling water coolant

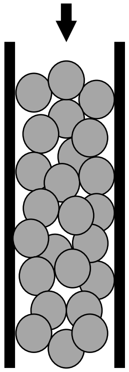
– catalyst removal?

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

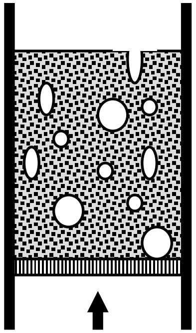
Hot-spots - eliminating

Improved co-ordination of reaction & cooling using a Fluidised bed reactor

Increased heat transfer coefficients due to efficient convective-regenerative particle transport mechanism



- \+ excellent isothermal behaviour (h~600 W/m²K)
- \+ higher degree of catalyst utilisation
- \+ facile catalyst regeneration
- – very mechanically resilient catalyst needed
- – limited hydrodynamic loading range
- – undesirable backmixing
- – scale-up?

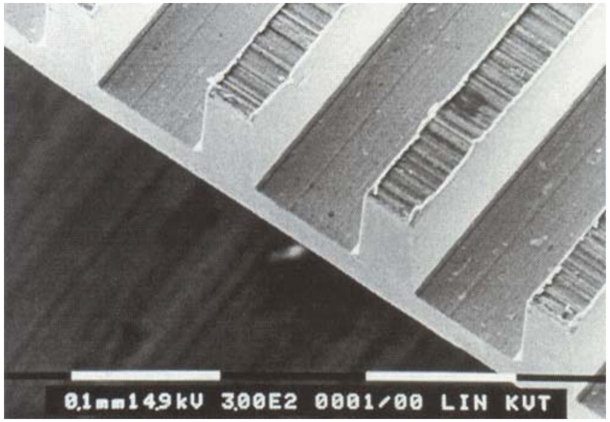


(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Hot-spots - eliminating

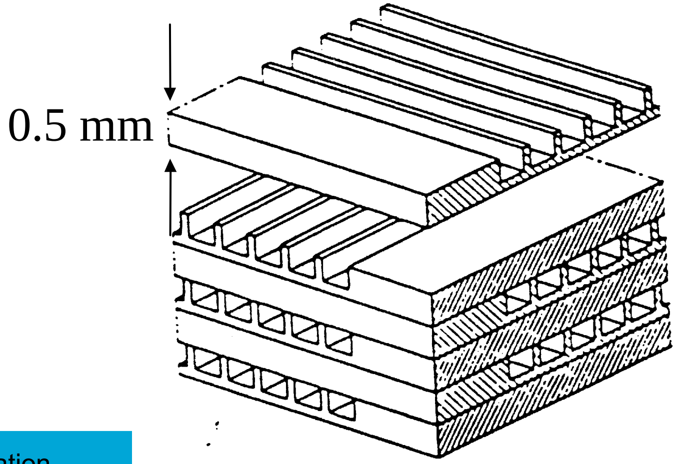
Improved co-ordination of reaction & cooling using a Microreactor

Vast specific heat exchange surface in direct contact with reactants/catalyst



+ specific heat exchange surface up to 30,000 m²/m³!
+ heat transfer coefficient up to 20000 W/m²K
+ good transverse mixing by diffusion
+ simple numbering-up feasible
+ flexible modular format

– complex, if robust, reactor construction
– relatively low amount of accessible catalyst
– restricted to metal and metal-composite catalysts
– gas distribution/collection, external connections
– susceptibility to blockage

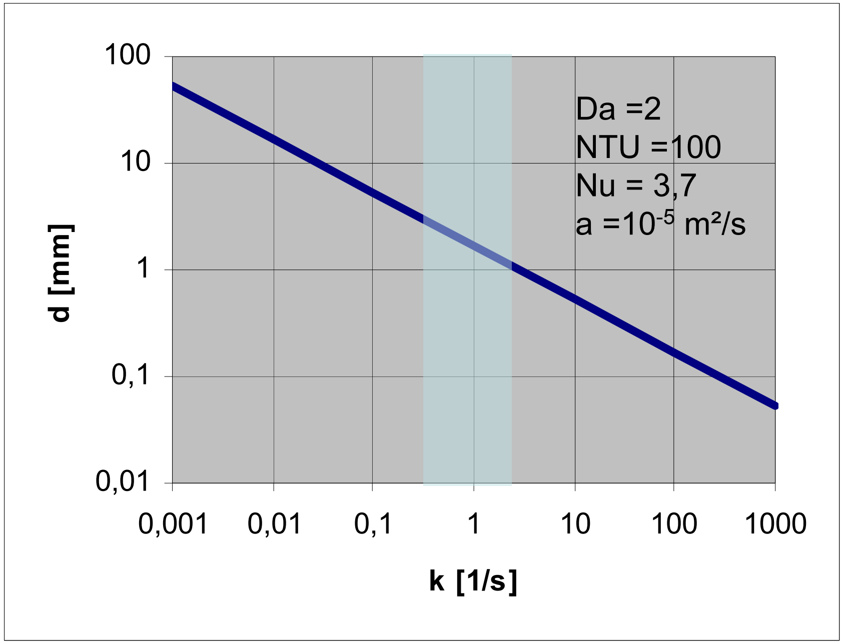


(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Limitations of catalytic activity

- the chemical processes occurring at the active sites impose an upper limit on reaction rate (~1µmol/g_{cat}s*) and heat generation (~500kW/m³)

- for chemically limited kinetics, acceptable temperature gradients of ca. 2K and thermal conductivity of typically 1 W/mK, a specific heat exchange surface of ~1,000 m²/m³ is usually adequate to ensure rapid heat removal.



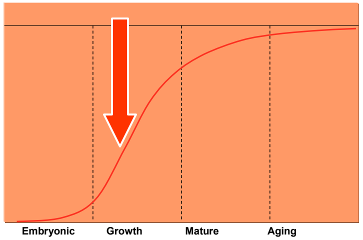
⇒**Microreactors offer unnecessarily excessive heat exchange surface**

⇒ **reactor dimensions of 1-5mm, i.e. 'Millireactors' (or HEX reactors)**

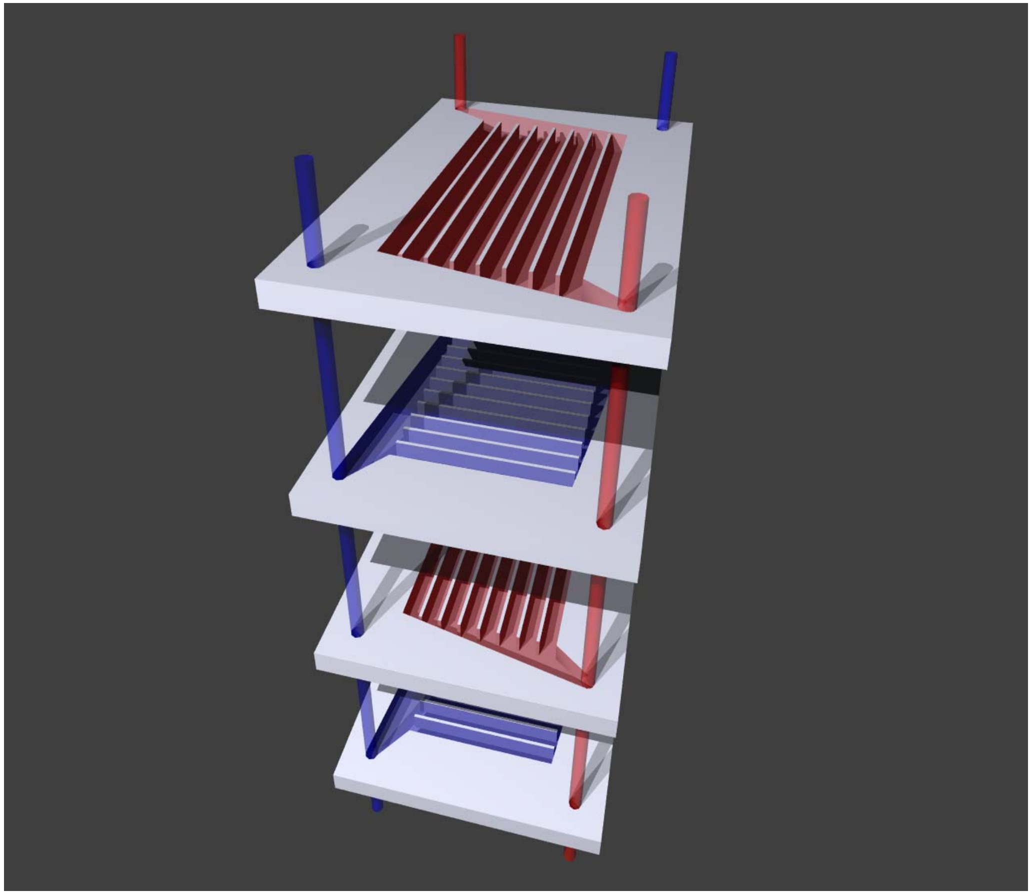
* for typical industrial synthesis reactions

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Catalytic plate millireactors (HEX reactors)

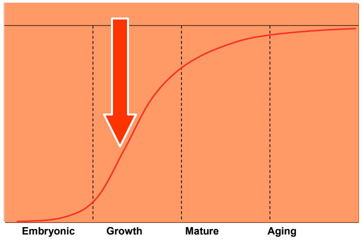


- structure & scale similar to plate heat exchanger
- porous catalyst plates 1-2 mm thick
- alternating plain & laser -engraved profile plates
- plates stacked and ‘cemented’
- cocurrent, countercurrent & X-flow cooling possible
- combination of modules for complex T-profiles

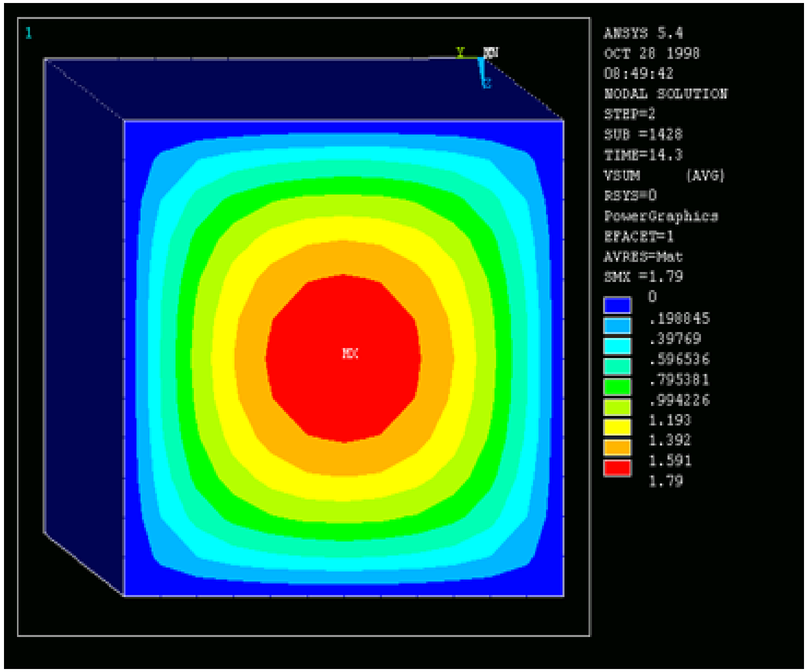


(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Catalytic plate millireactors (HEX reactors)



- well-defined laminar flow conditions
- amenable to Computational fluid dynamic modelling
- deliberate local turbulence to yield plug flow behaviour
- channel structure for uniform gas & coolant distribution



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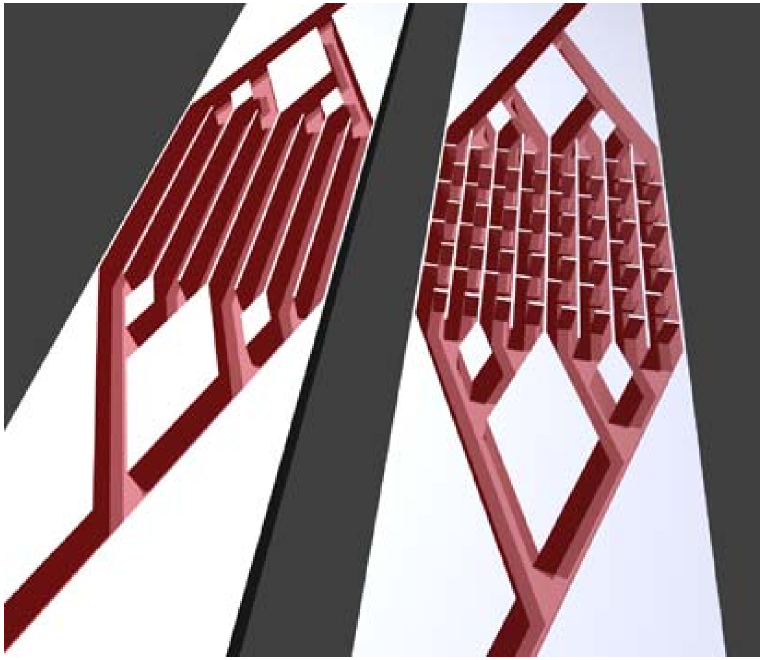
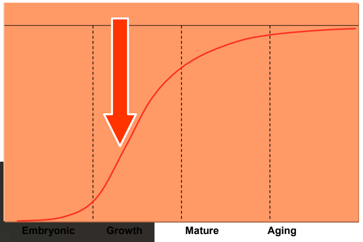


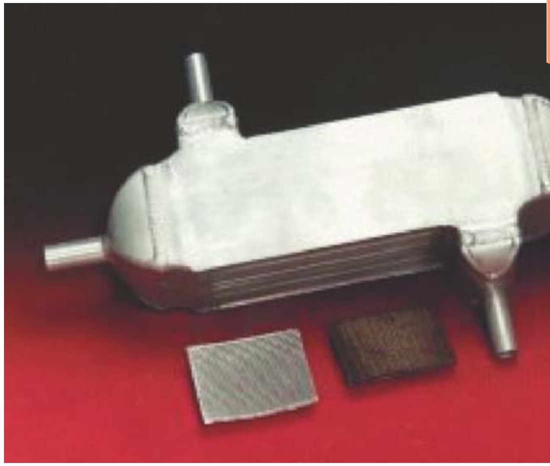
(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Heat exchanger (milli-) reactors



BENEFITS:

- higher yields
- improved product purity
- very good reaction control
- no thermal runaways
- continuous production
- low running costs
- low capital costs - small plant
- high pressure capability



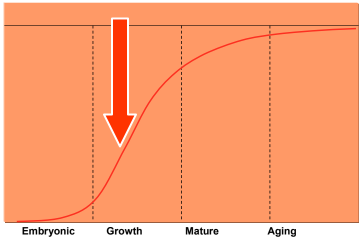
ECN reactor with washcoated catalyst

Marbond reactor (Chart Heat Exchangers) - with heat transfer area up to 1000 m^2/m^3

APPLICATIONS (examples):

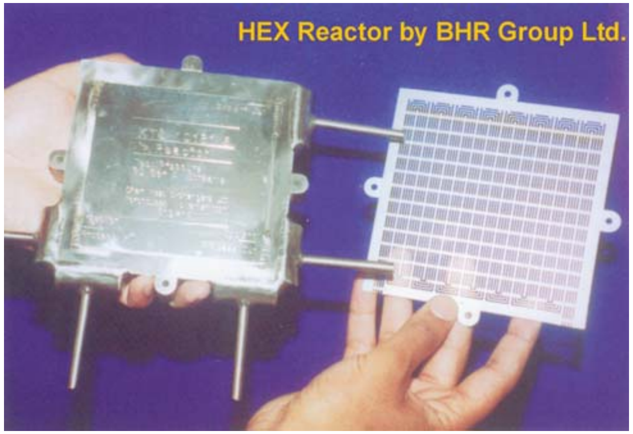
- nitration
- azo coupling
- halogenation
- hydrogenation
- oxidation
- sulfonation

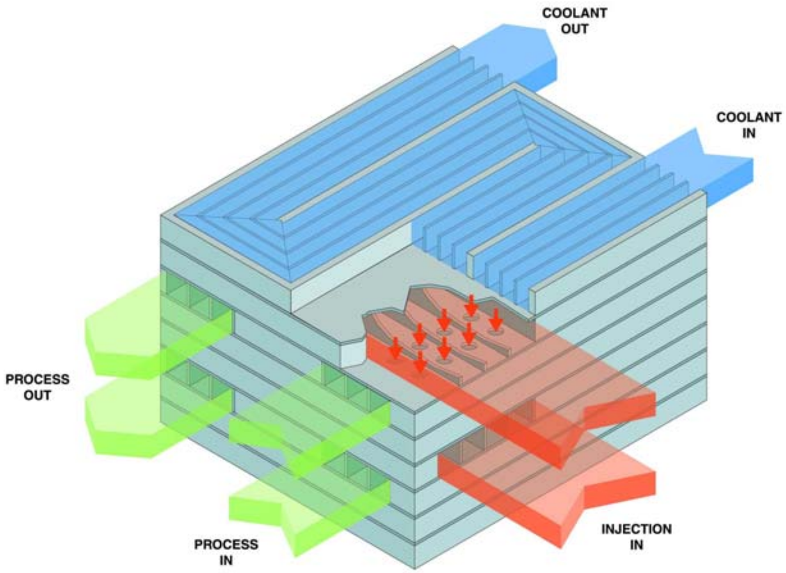
Heat exchanger (milli-) reactors



Hickson & Welch process (two-stage catalyzed oxidation of a thioether to a sulfone):

- reaction time reduced from 18 hrs to 15 mins

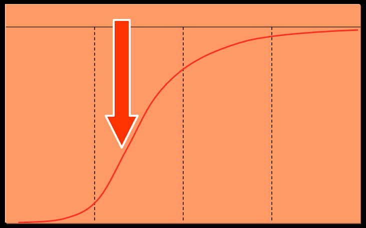


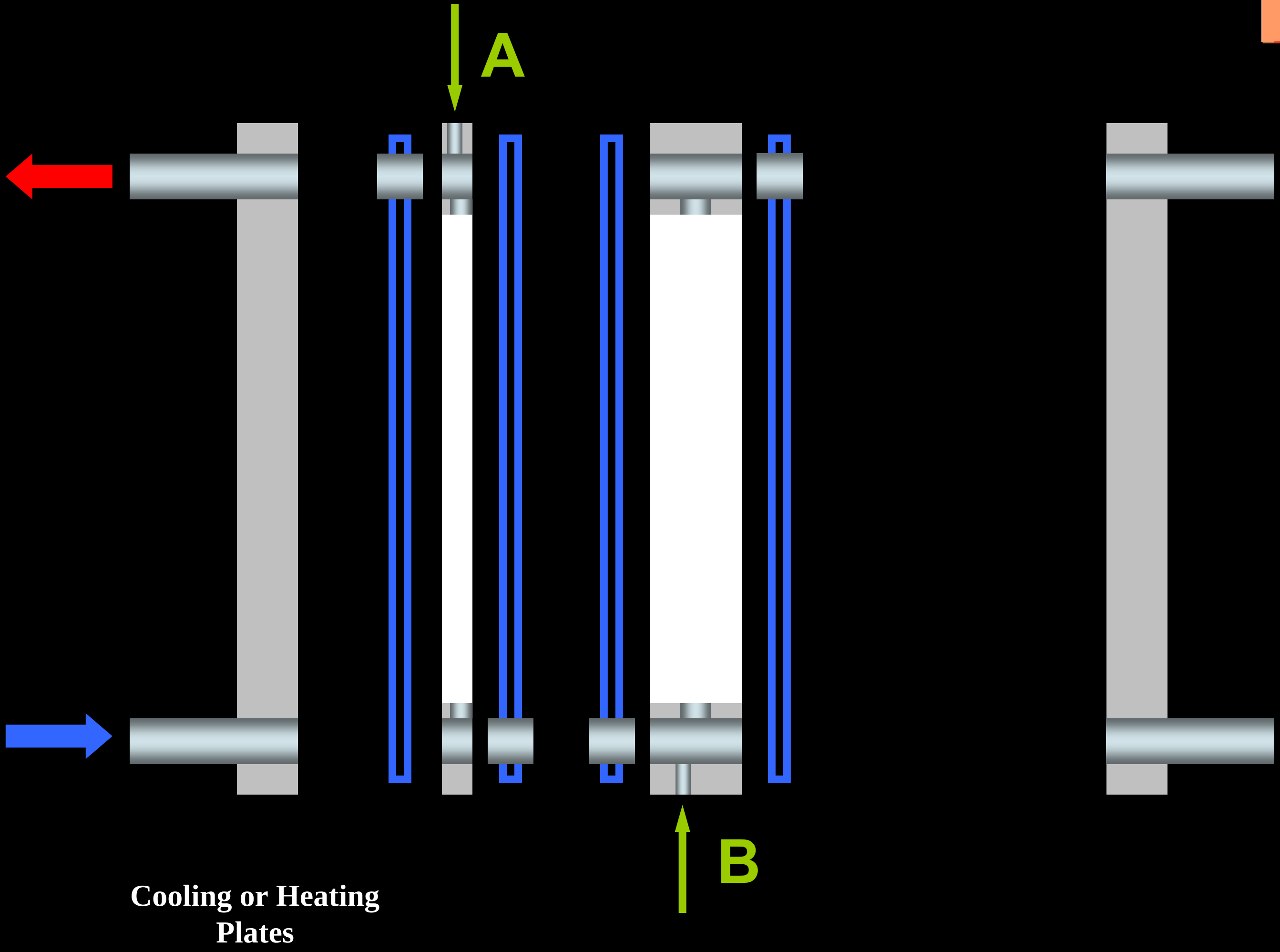


ICI Acrylics process:

- by-product formation decreased from 2% to 0.5% (simulation)

Alfa Laval - the Plate Reactor Concept



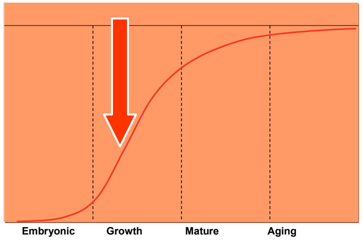


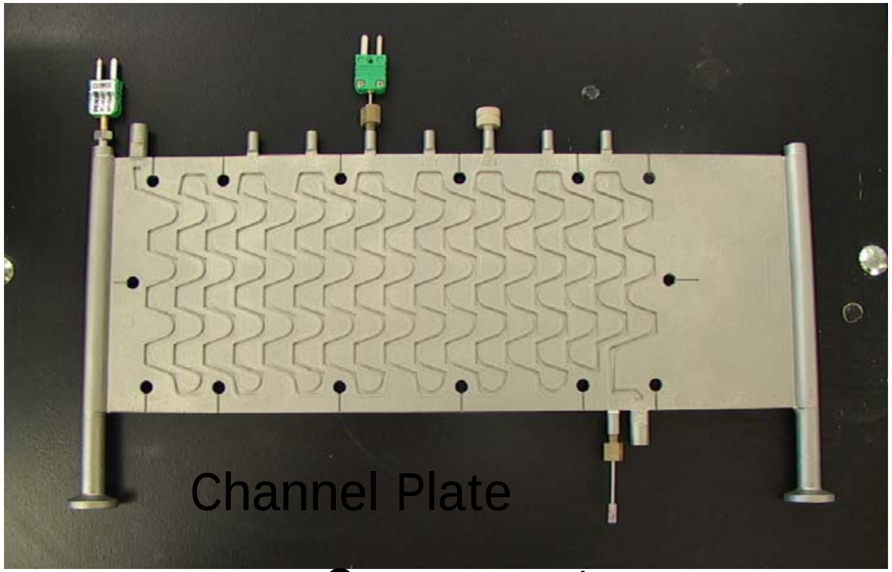
Cooling or Heating Plates

Courtesy: Alfa Laval

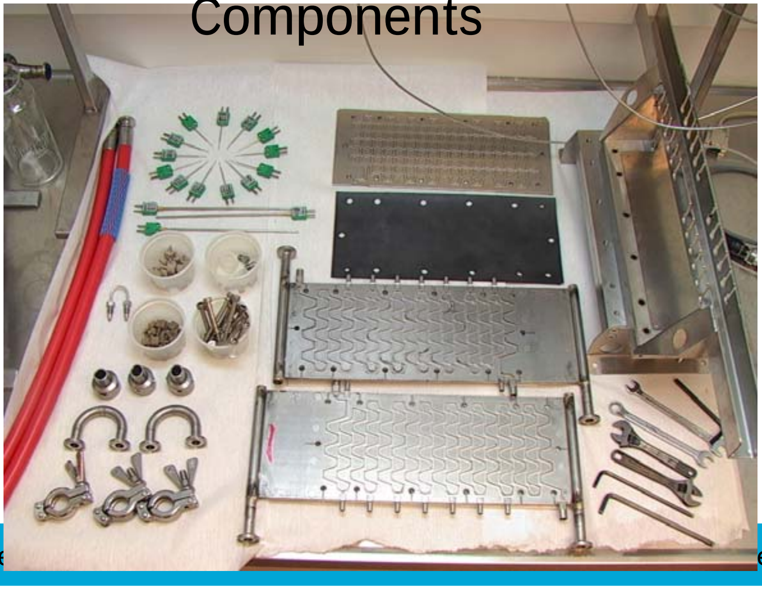
Alfa Laval - the Plate Reactor Concept

Based on Plates





Channel Plate



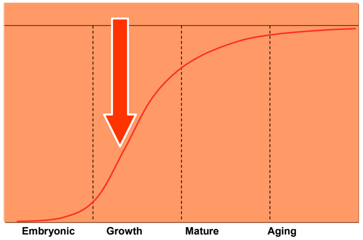
Components

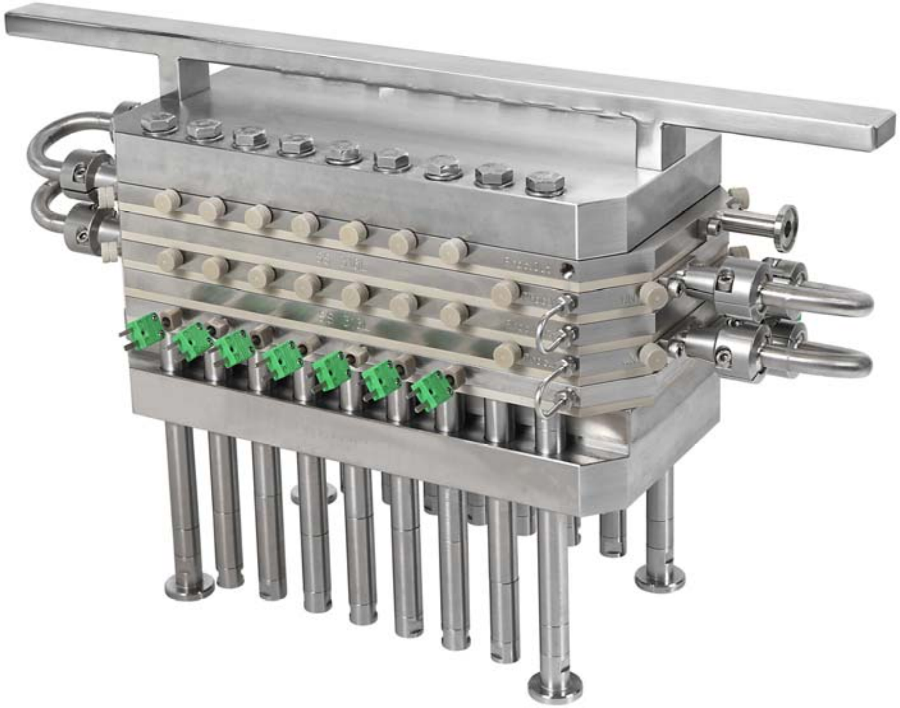
Full Reactor

Lab Scale

1 – 10 l/hr

Alfa Laval - the Plate Reactor Concept





Pilot Scale

3 Plates → Volume ≈ 1.4 litres

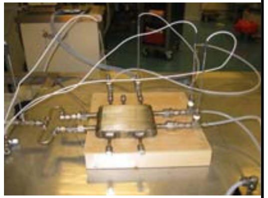
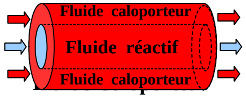
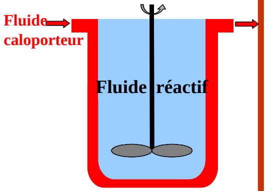
90 sec residence time at 50 l/hr

Production Scale

Initial Target : 1 – 2 m^3/hr

Heat exchange in chemical reactors

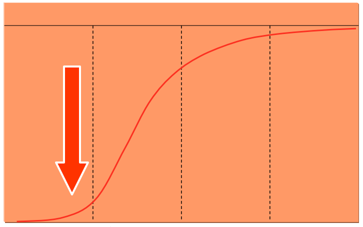
Equipment characterization

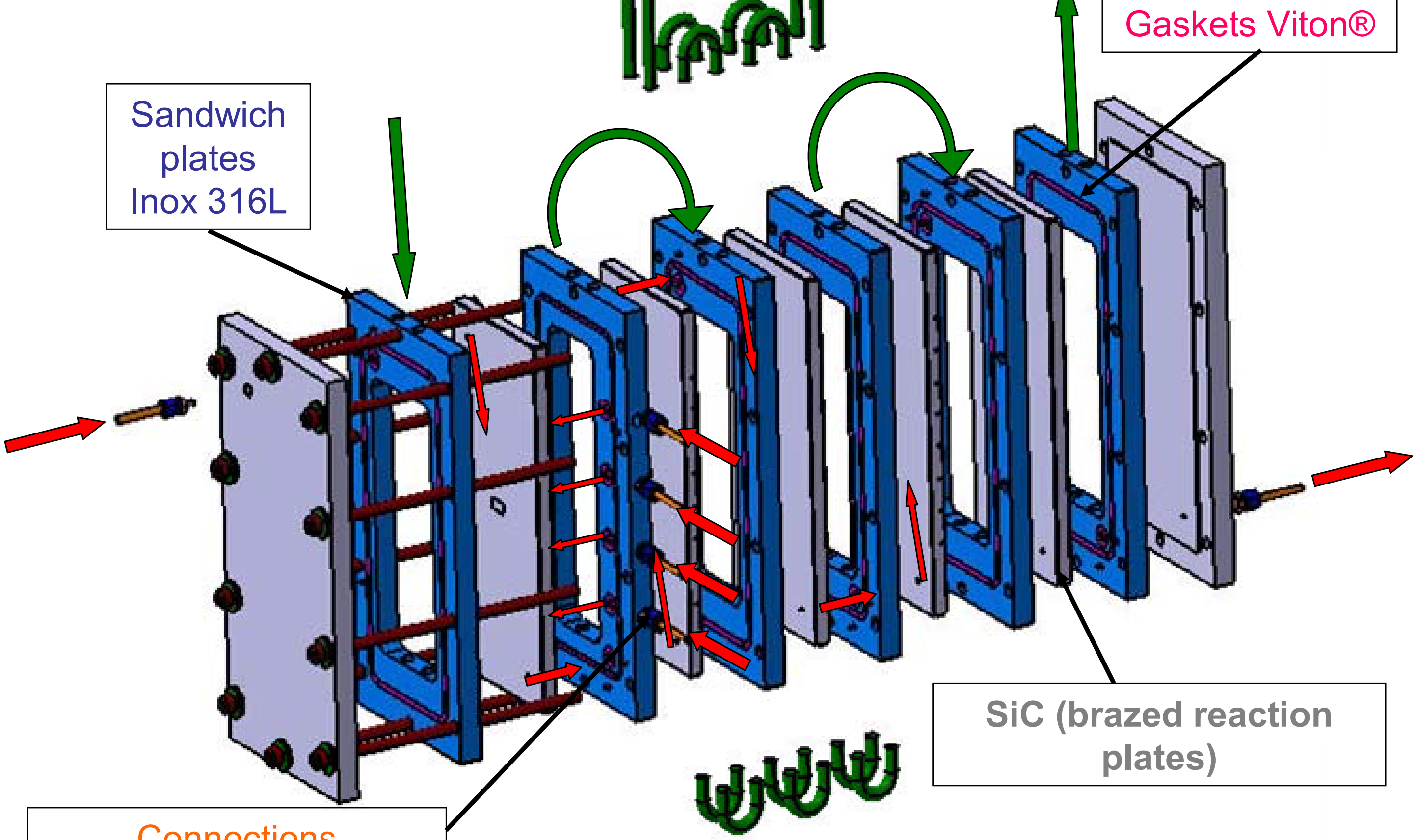
Devices	FZK microreactor	HEX reactor Shimtec (Chart)	HEX reactor Glass (Corning)	HEX reactor Stainless steel (Alfa Laval)	Tubular reactor	Batch reactor
Picture						
Overall heat coefficient U (W/m^2.K)	2000	3000	660	2500	500	400
Maximal residence time	A few seconds	A few seconds	A few seconds – minutes	A few minutes	A few minutes	A few hours
Compactness S/V (m^2/m^3)	9000	2000	2500	400	400	2.5
Intensification factor US/V *(kW/m^3.K)*	18 000	6000	1650	1000	200	1

C. Gourdon, Rhodia Sustainability Conference, 2008

Heat exchanger (milli-) reactors

Importance of the material and of the design





Gaskets Viton®

Sandwich plates Inox 316L

SiC (brazed reaction plates)

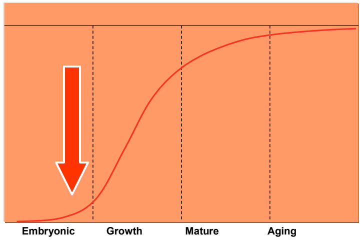
Connections

Swagelok (316L)

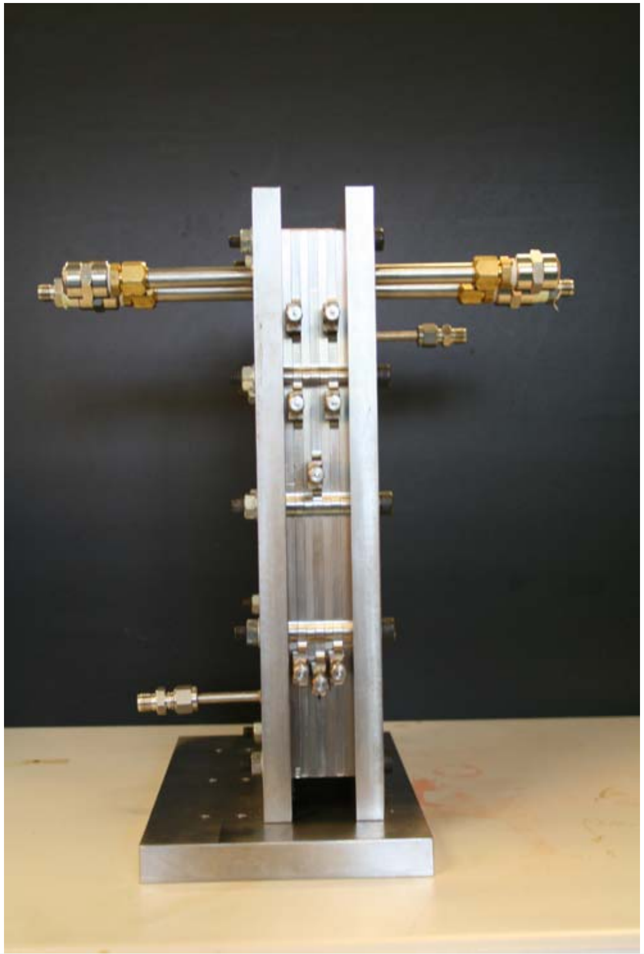
Prototype

C. Gourdon, Rhodia Sustainability Conference, 2008

Heat exchanger (milli-) reactors



Importance of the material and of the design



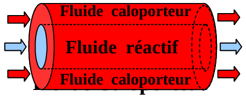
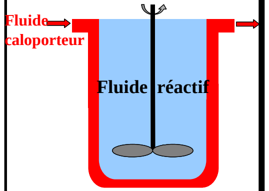
	SiC	Steel	Glass
λ (20°C) W.m-1.K-1	**180**	**16**	**1**
Cp (20°C) J.kg-1.K-1	680	500	800
ρ (kg.m-3)	3210	7900	2600
Effusivity b $b = (\lambda.\ Cp.\ \rho)^{1/2}$	20000	8000	1500

Larger b = Surface Temperature imposed by the material and higher dynamics

C. Gourdon, Rhodia Sustainability Conference, 2008

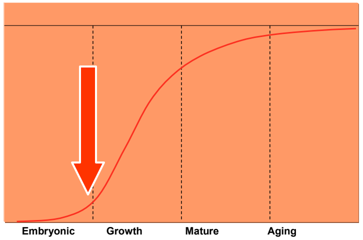
Heat exchanger (milli-) reactors

Importance of the material and of the design

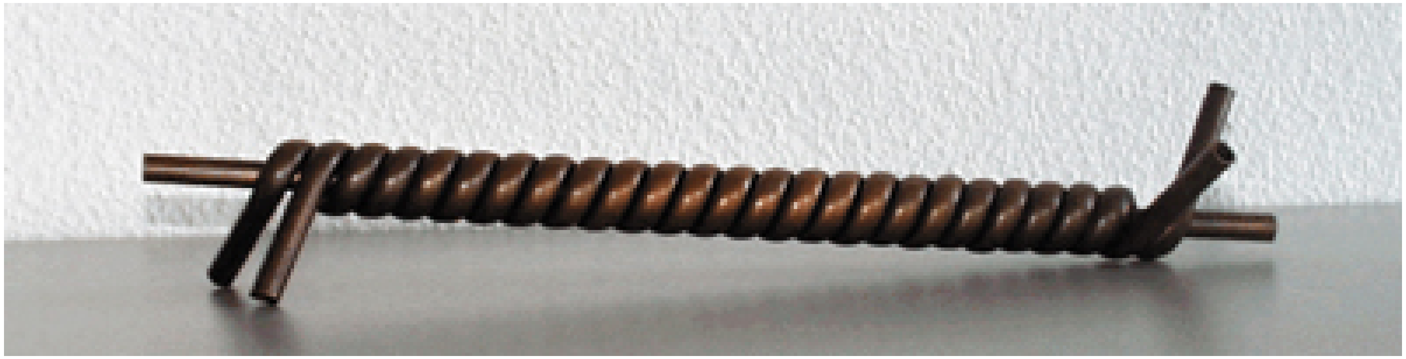
Devices	HEX reactor SiC (Boostec/LGC)	HEX reactor Glass (Corning)	HEX reactor Stainless steel (Alfa Laval)	Tubular reactor	Batch reactor
Picture					
Overall heat coefficient U (W/m².K)	7000	660	2500	500	400
Maximal residence time	A few minutes	A few seconds - minutes	A few minutes	A few minutes	A few hours
Compactness S/V (m^2/m^3)	2000	2500	400	400	2.5
Intensification factor US/V (*$kW/m^3.K$*)	14 000	1650	1000	200	1

C. Gourdon, Rhodia Sustainability Conference, 2008

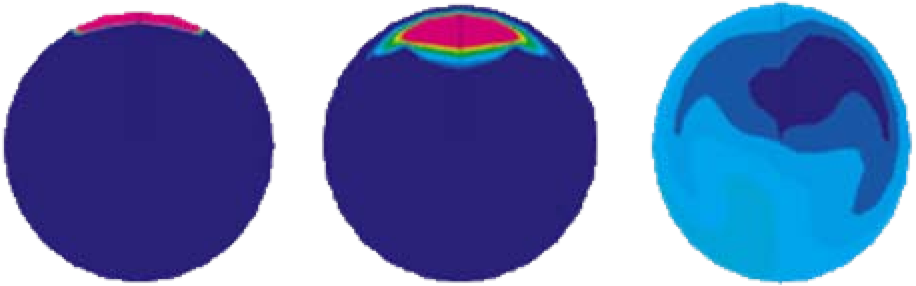
Heat exchanger (milli-) reactors – other concepts



Helix reactor (TNO Institute)

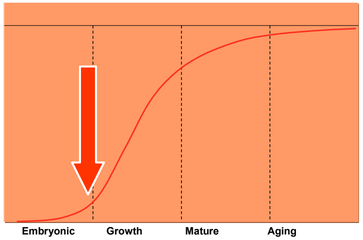


- intensive heat transfer
- plug-flow characteristics
- good radial mixing

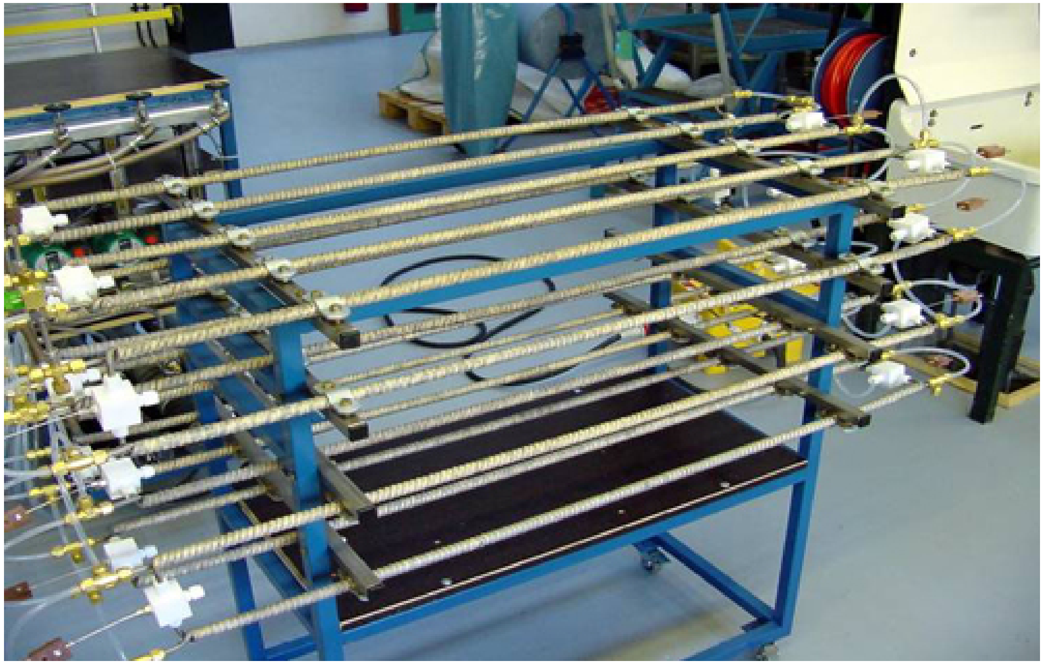


Straight pipe (inlet) | Straight pipe (outlet) | Helix reactor (outlet)

Heat exchanger (milli-) reactors – other concepts



Helix reactor (TNO Institute)



Pilot-scale tests with an industrial highly exothermic process:

- 4x increase of production capacity at 3x less volume
- 75% less energy
- 30% less waste
- variable costs 3x lower
- full pay-back 1 year less

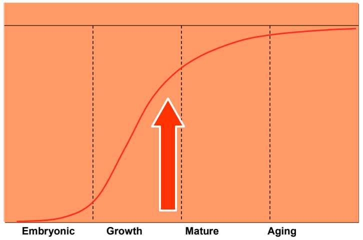
Heat exchanger (milli-) reactors

Evaluation:

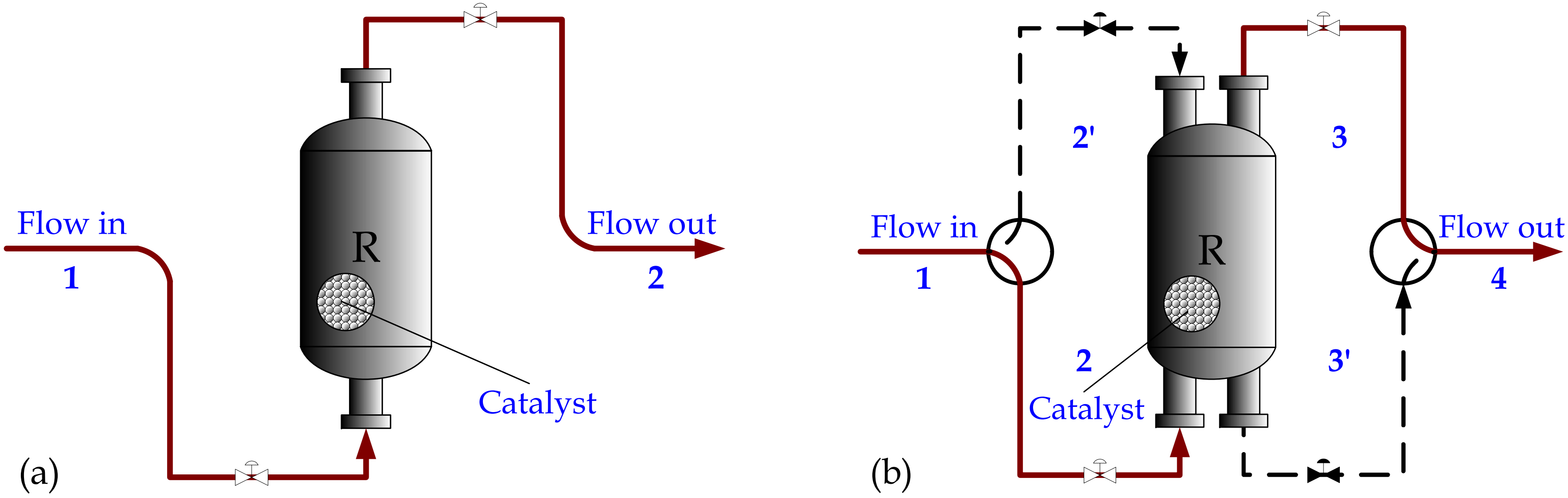
- **cost-effective alternative to both conventional & microreactor technology for industrial applications**
- **based on proven catalyst materials and state-of-the-art fabrication techniques**
- **non-specific, generally applicable concept**
- **low development costs, short time-to-market**
- **straightforward modelling, reliable scale-up**
- **flexible and operationally robust reactor configuration**
- **compatible with catalyst regeneration, recycling or disposal**

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

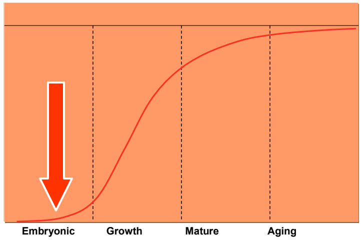
Regenerative heat transfer

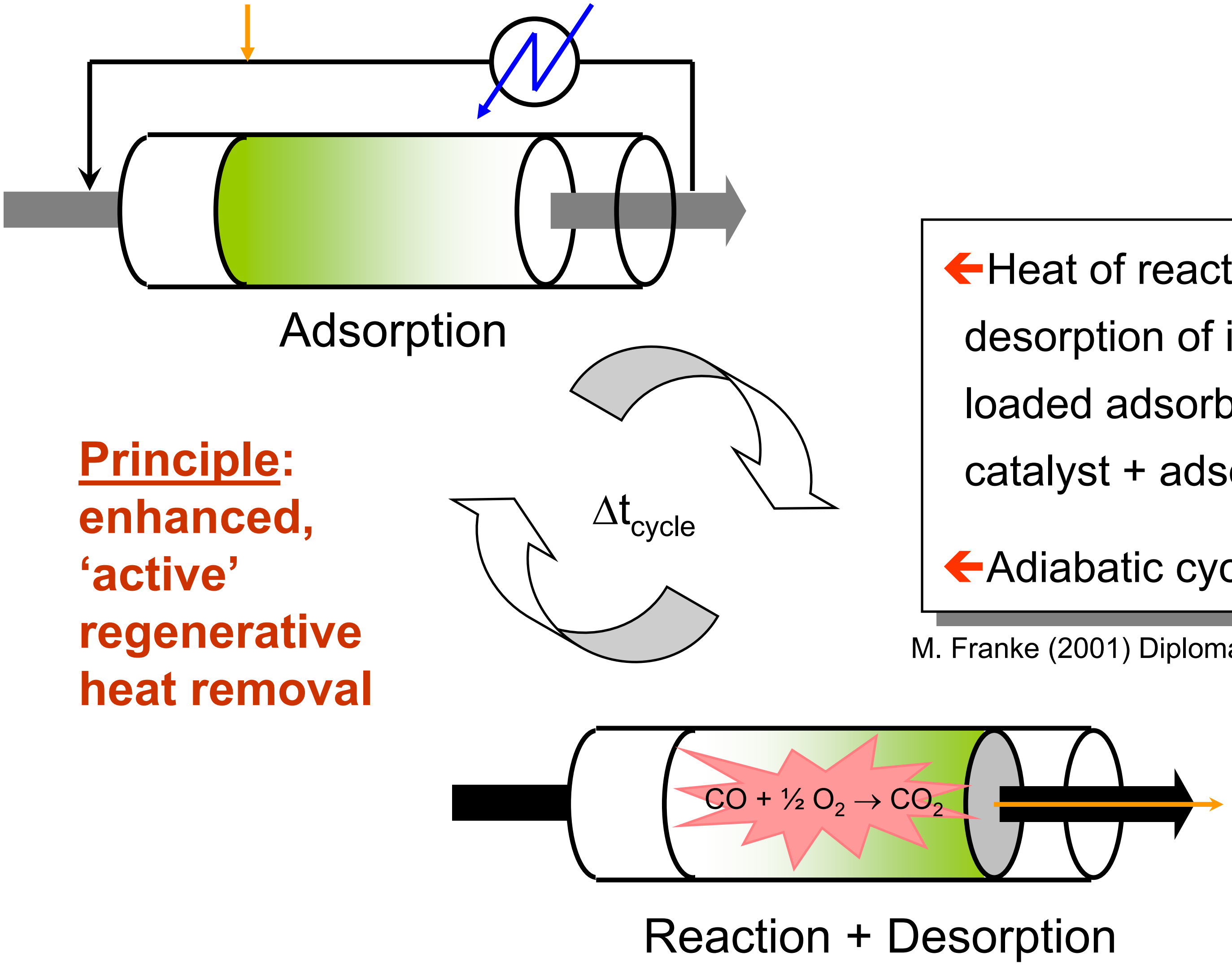


Reverse-flow reactors – will be discussed in TIME lecture



Desorptive cooling





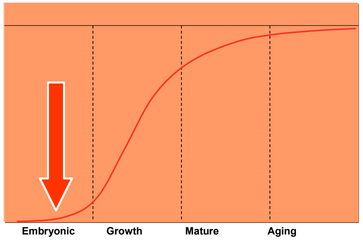
Principle:
enhanced,
'active'
regenerative
heat removal

- Heat of reaction consumed by desorption of inert (●) from loaded adsorbent in mixed catalyst + adsorbent fixed-bed
- Adiabatic cyclic reactor operation

M. Franke (2001) Diploma thesis, University of Dortmund

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Desorptive cooling



Pros and Cons:

+ high intensity cooling system

+ no heat exchange surface in reactor

+ self-regulating heat uptake process

+ customised heat removal *via* adsorbent distribution

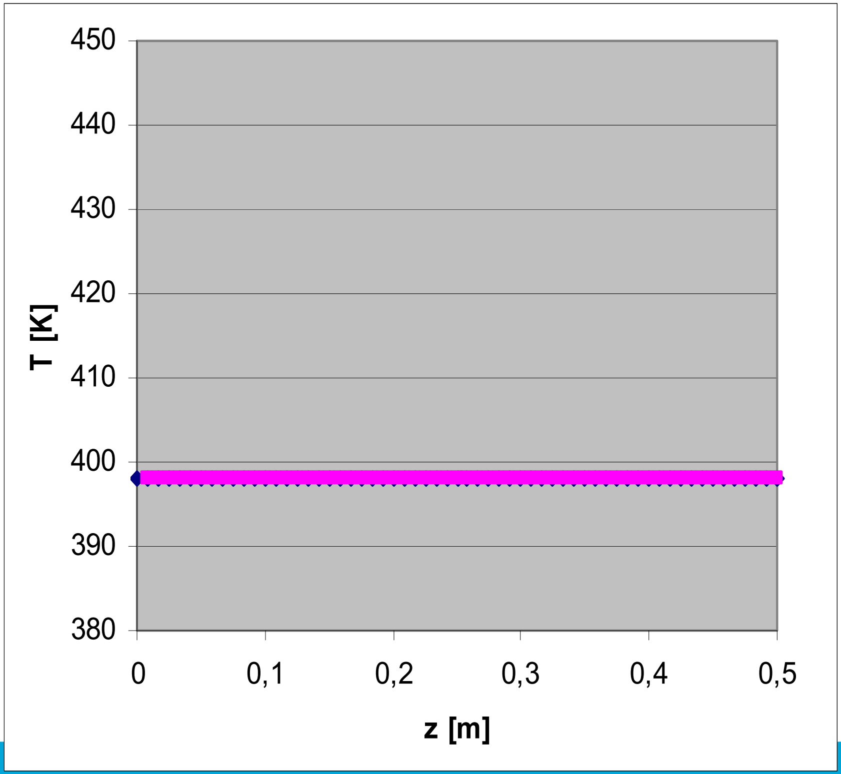
– unsteady-state operation

– lower space time yields

– compatibility of adsorption & reaction systems

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

- Simulation of desorptive cooling (t = 0 s)

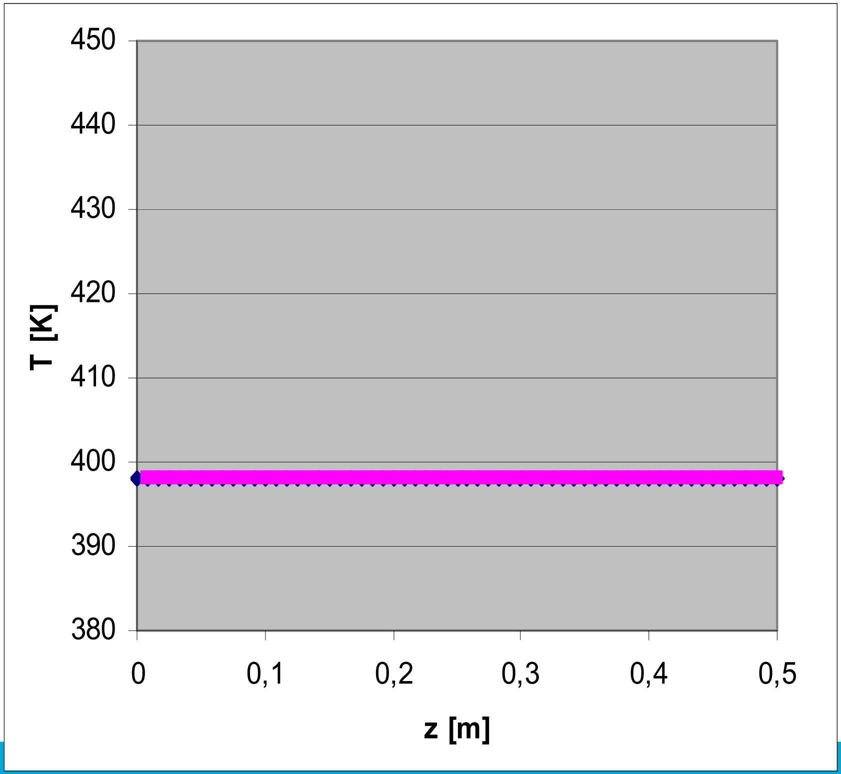


Operating parameters:
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:
- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 0 s)



Operating parameters:

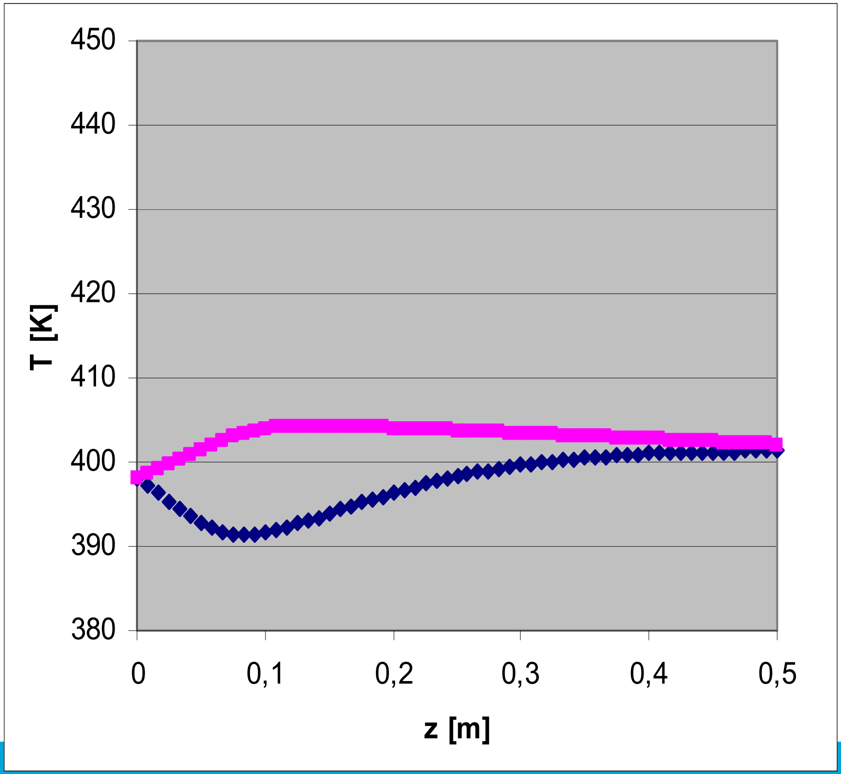
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 50 s)



Operating parameters:

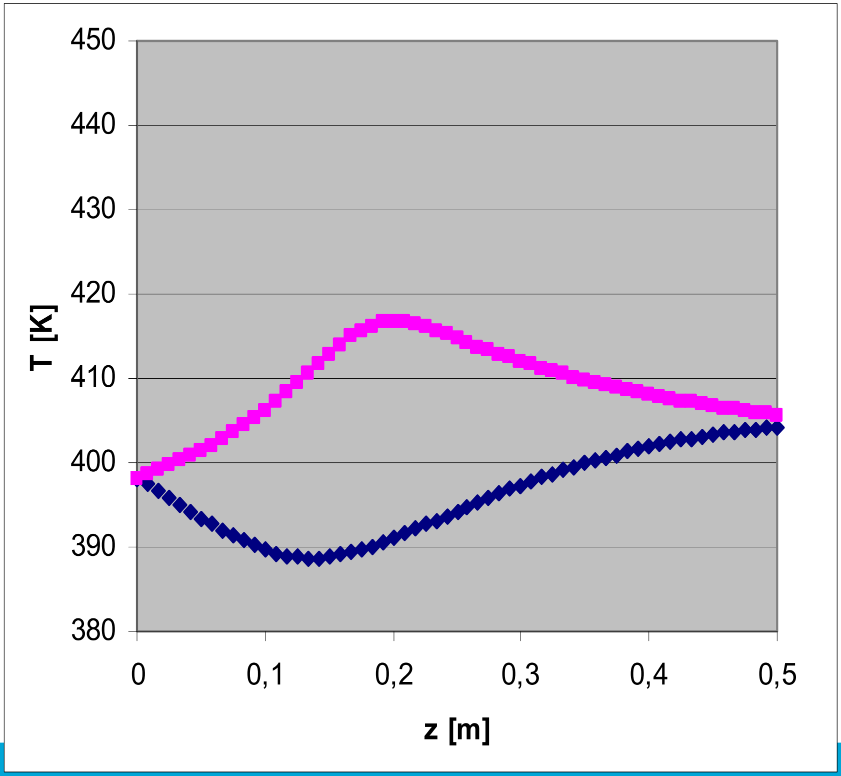
- $\dot{V}_{ein}$ = 6000 l/h
- $v = 0.5$

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 100 s)



Operating parameters:

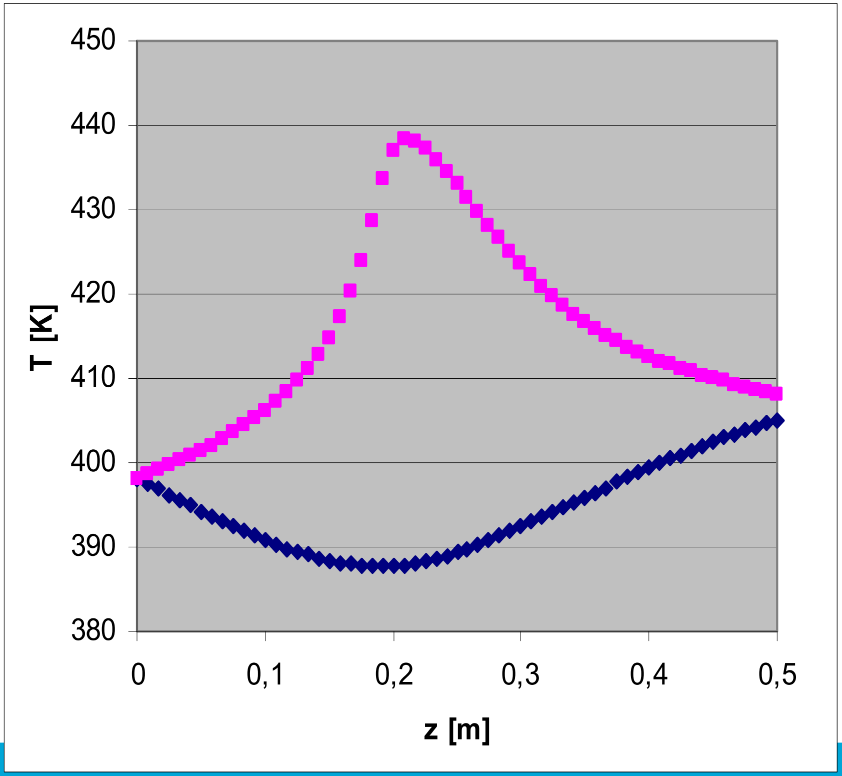
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 150 s)



Operating parameters:

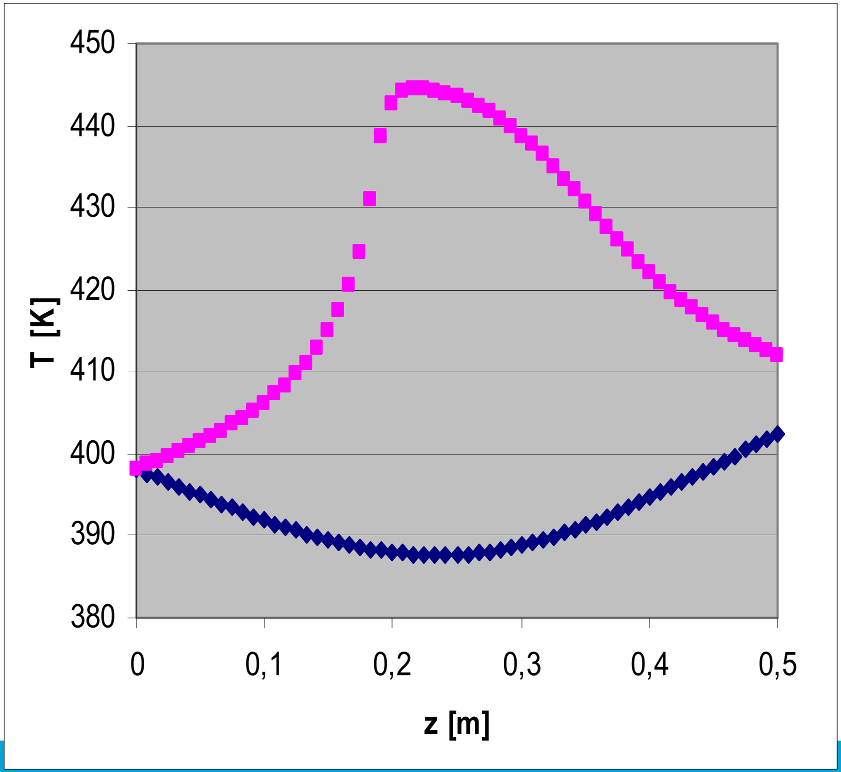
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 200 s)



Operating parameters:

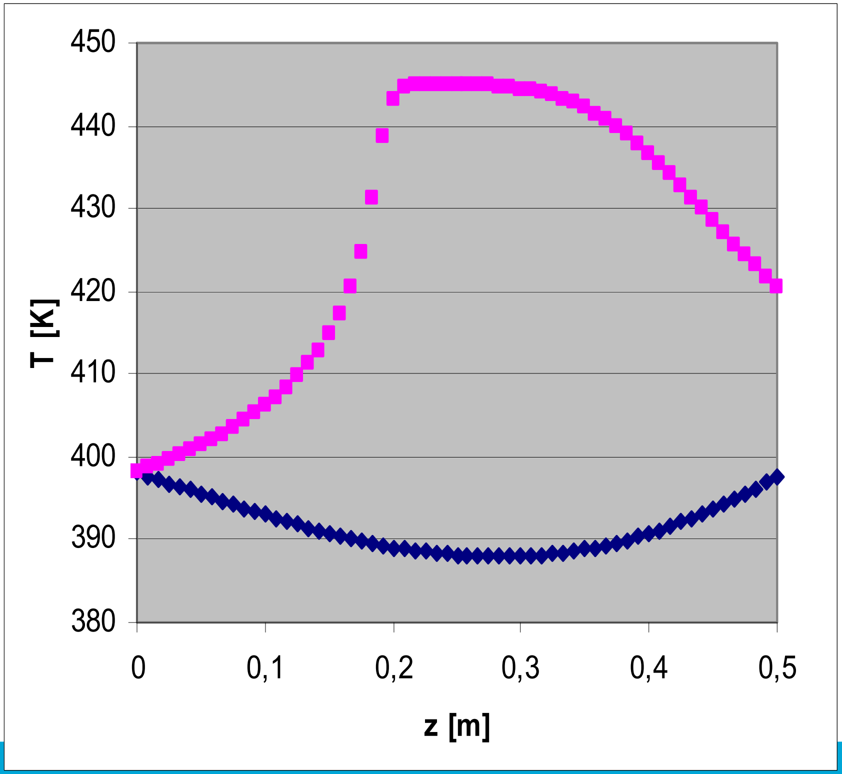
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 250 s)



Operating parameters:

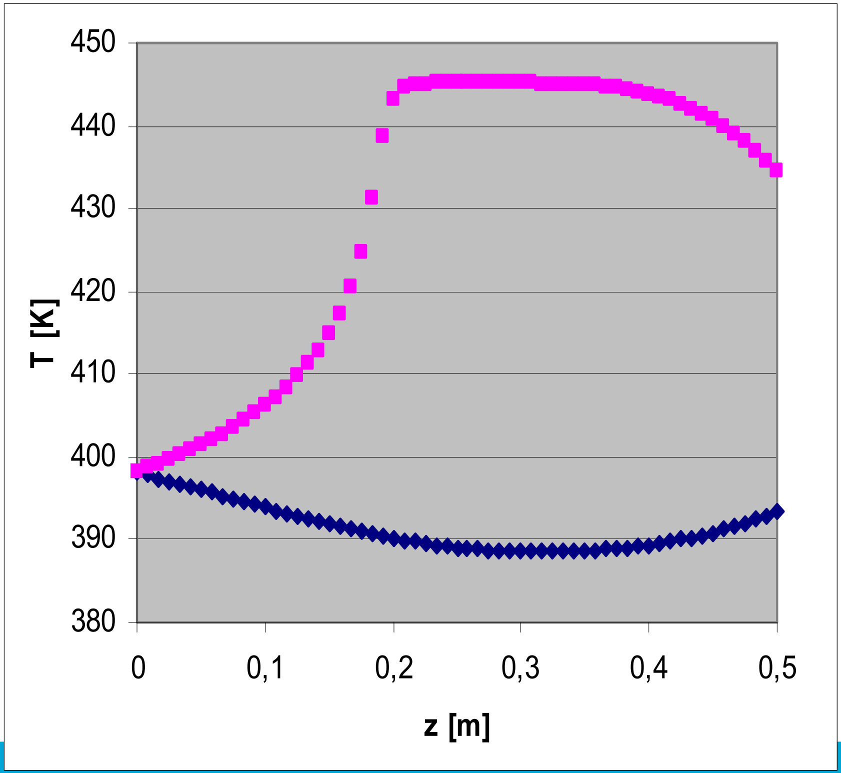
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 300 s)

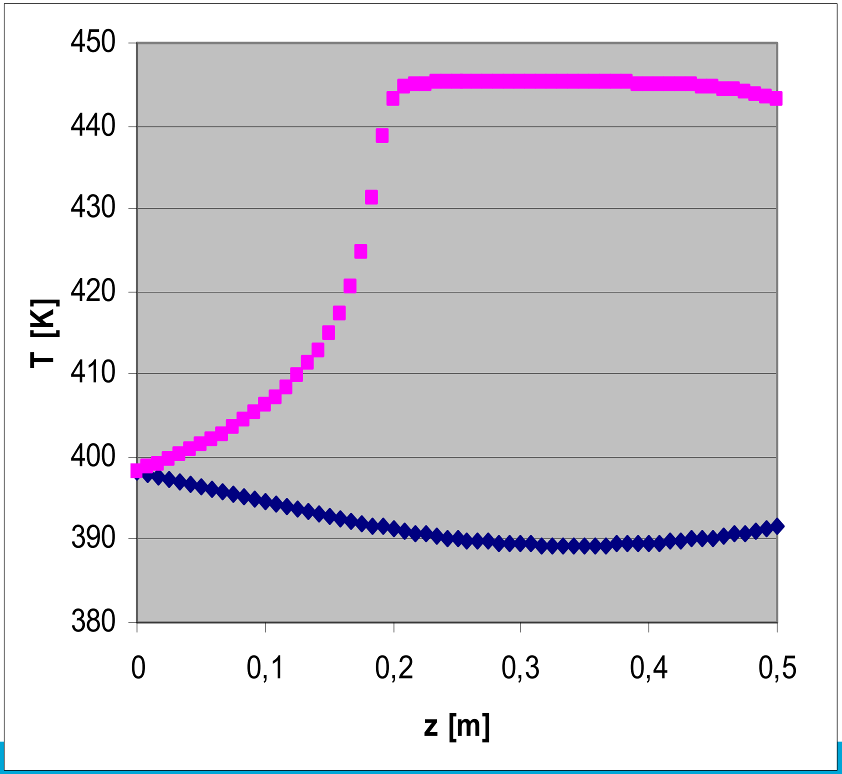


Operating parameters:
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:
- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 350 s)



Operating parameters:

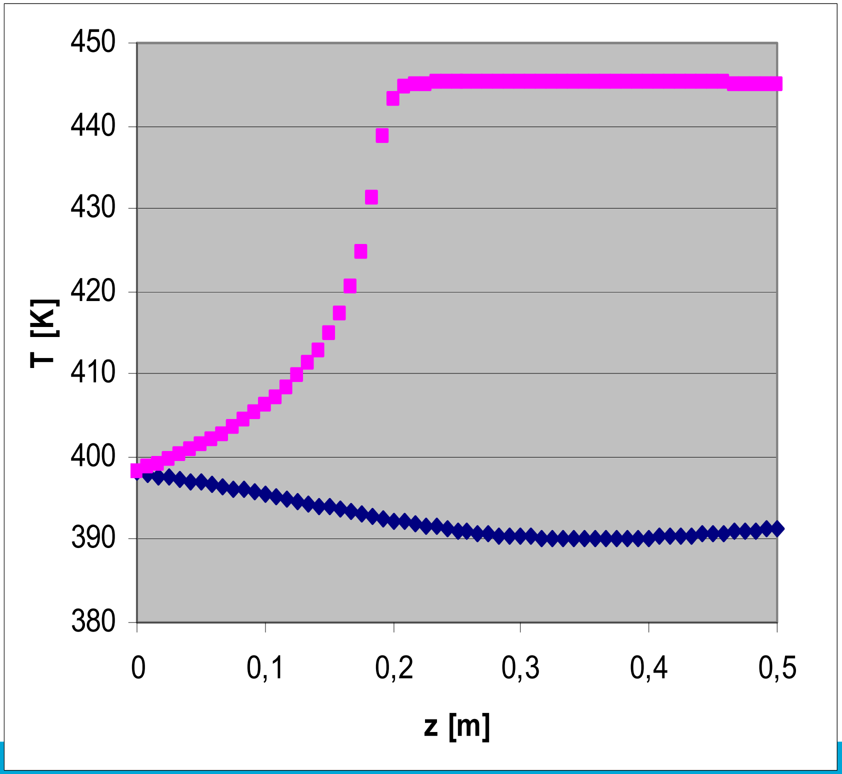
- $\dot{V}_{ein}$ = 6000 l/h
- $v = 0.5$

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 400 s)

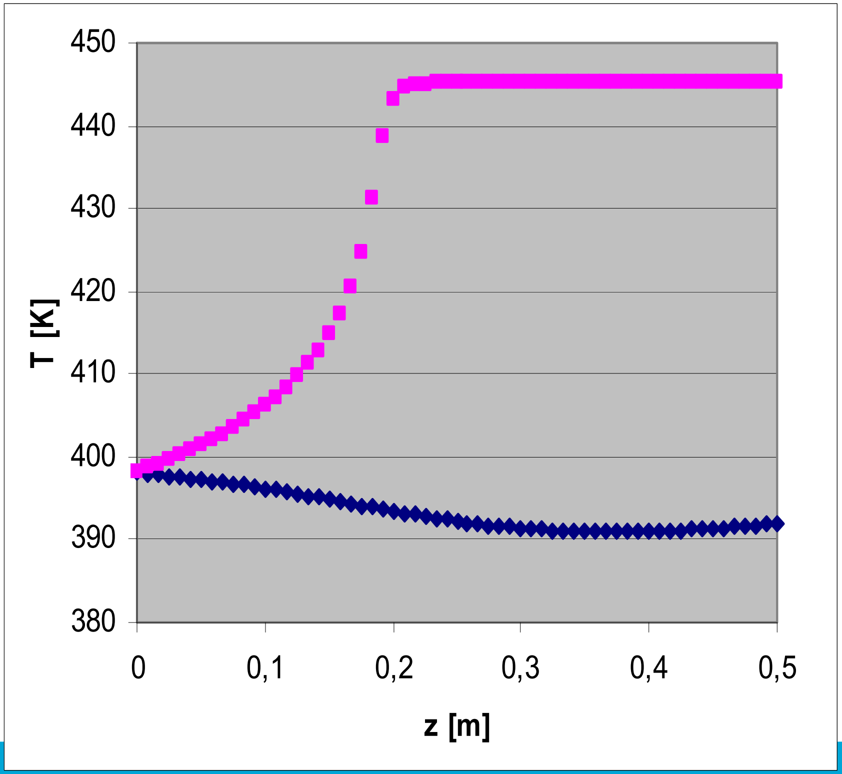


Operating parameters:
- $\dot{V}_{ein}$ = 6000 l/h
- $\nu = 0.5$

Feed stream:
- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 450 s)



Operating parameters:

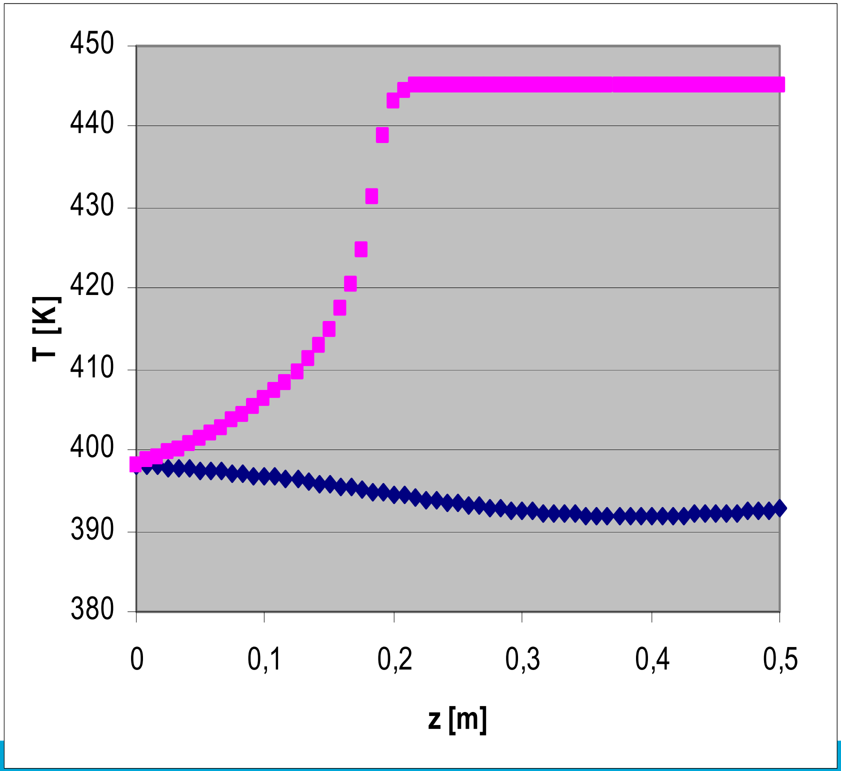
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 500 s)



Operating parameters:

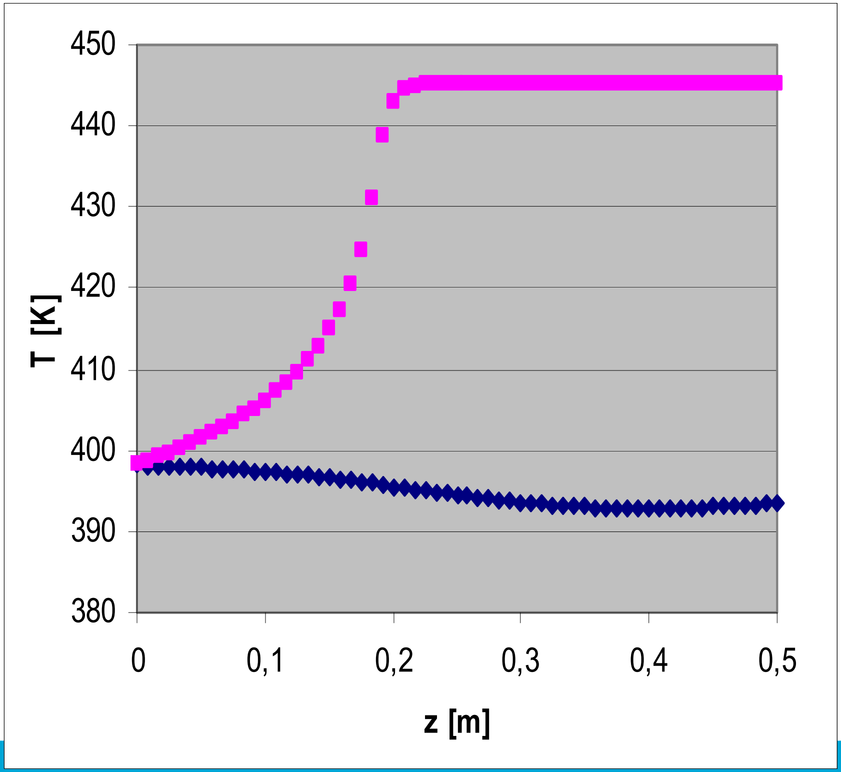
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 550 s)



Operating parameters:

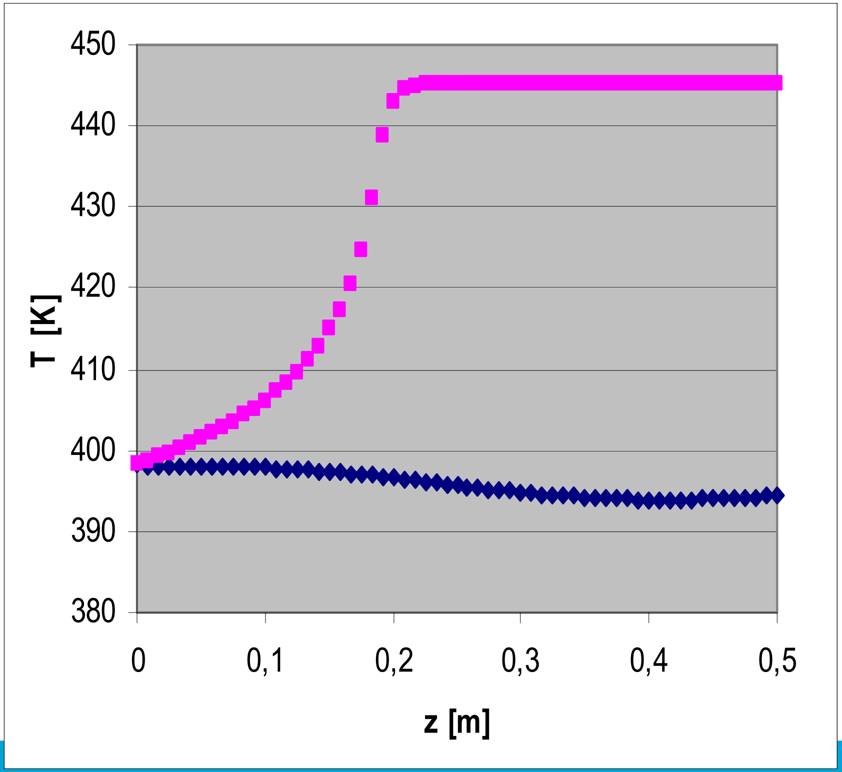
- $\dot{V}_{ein}$ = 6000 l/h
- $v = 0.5$

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 600 s)

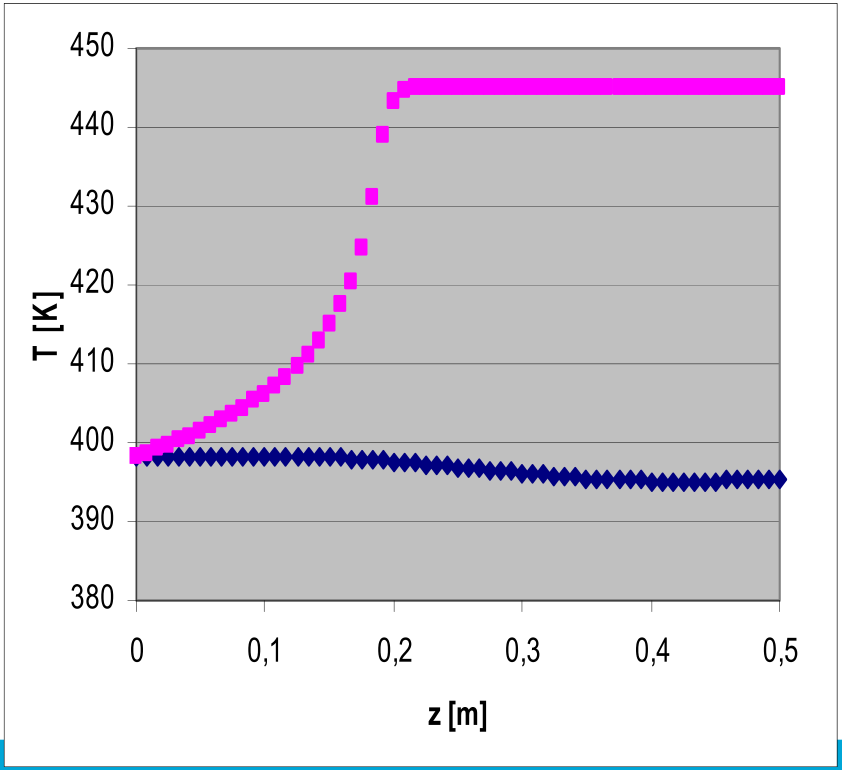


Operating parameters:
- $\dot{V}_{ein}$ = 6000 l/h
- $v = 0.5$

Feed stream:
- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 650 s)

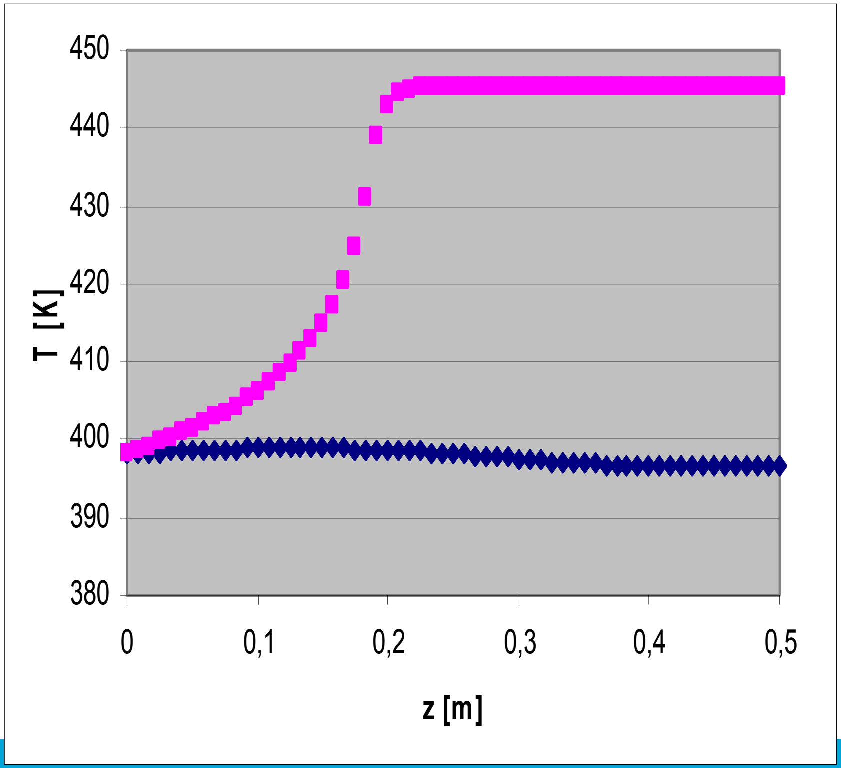


Operating parameters:
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:
- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 700 s)



Operating parameters:

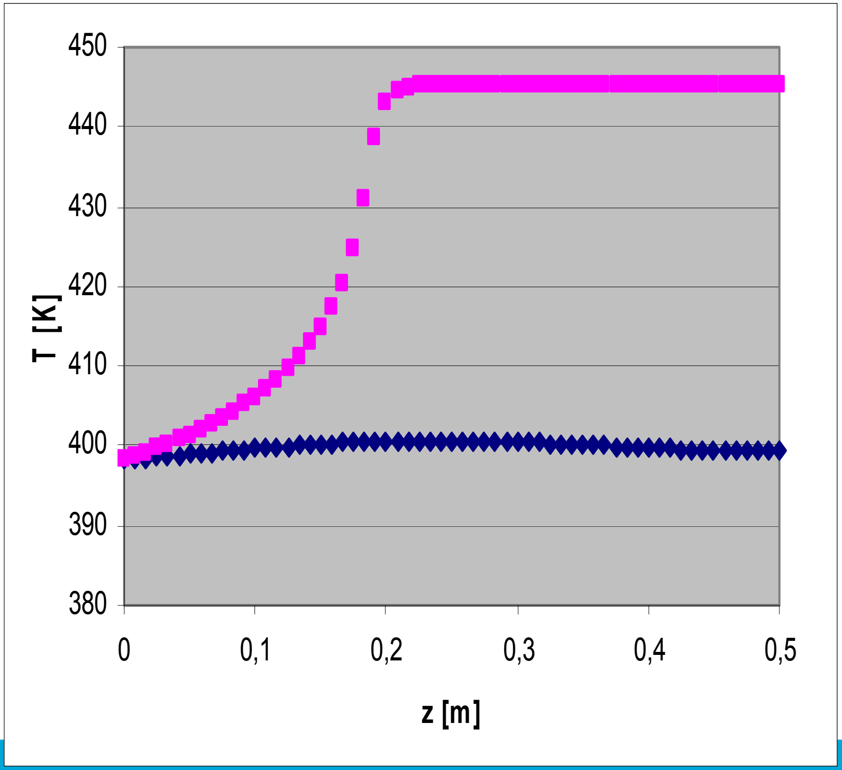
- $\dot{V}_{ein}$ = 6000 l/h
- $v = 0.5$

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 750 s)

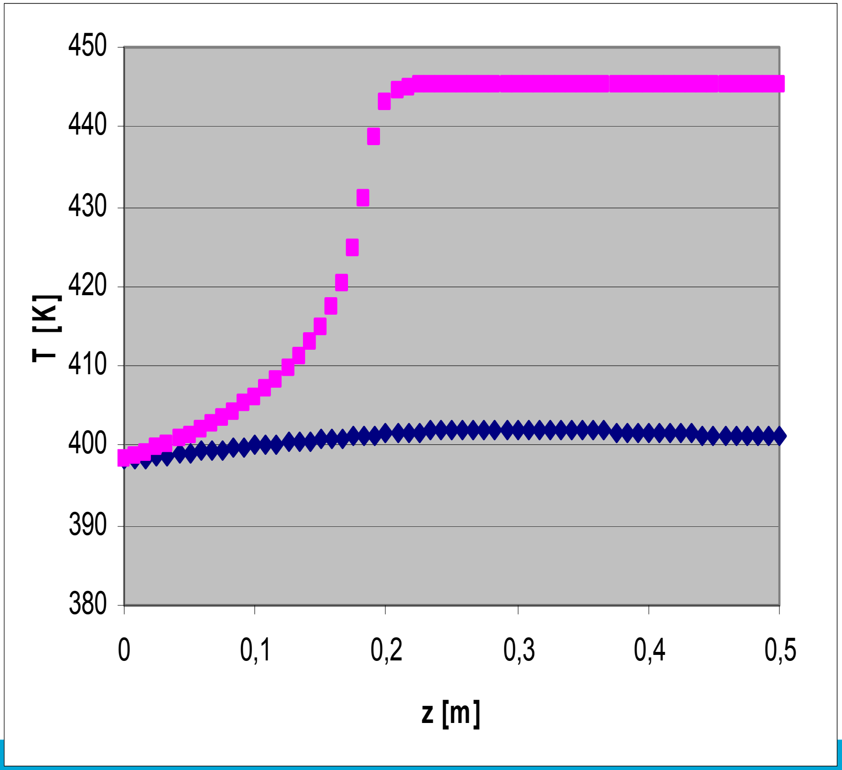


Operating parameters:
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:
- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 800 s)



Operating parameters:

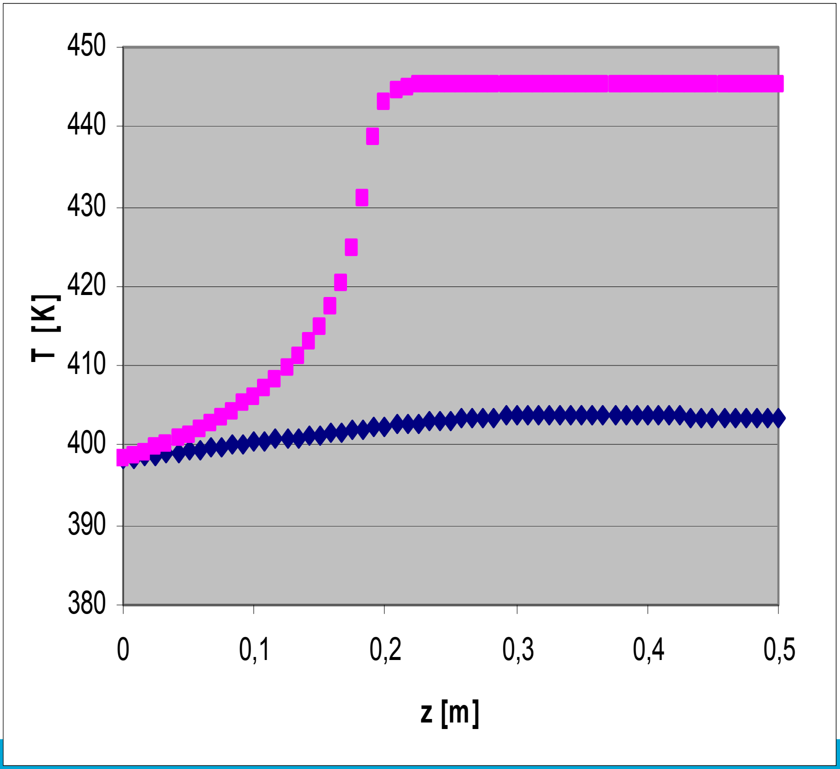
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 850 s)



Operating parameters:

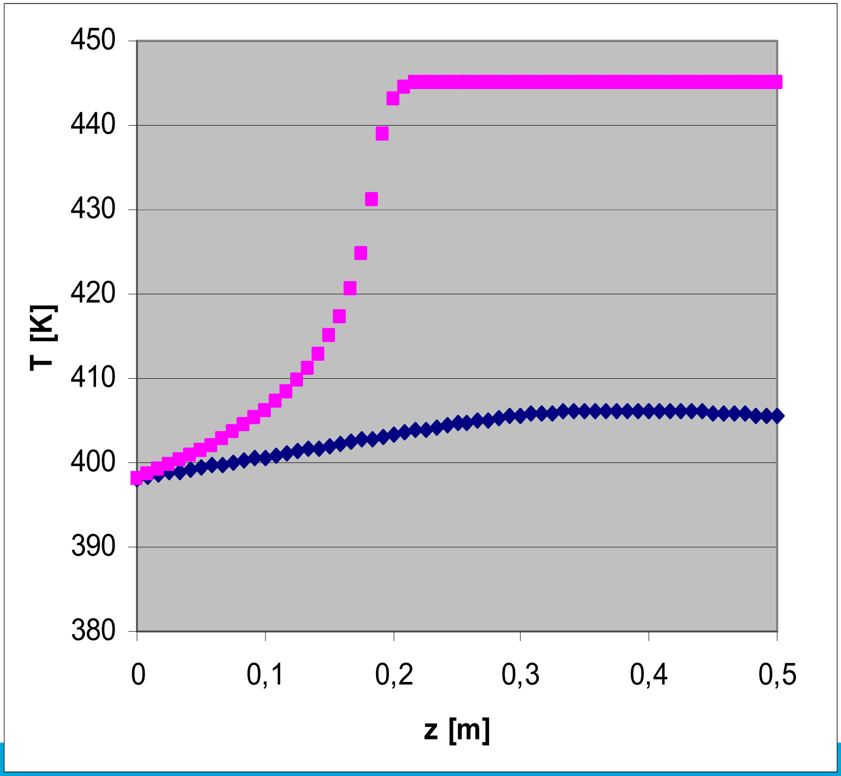
- $\dot{V}_{ein}$ = 6000 l/h
- $v = 0.5$

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 900 s)



Operating parameters:

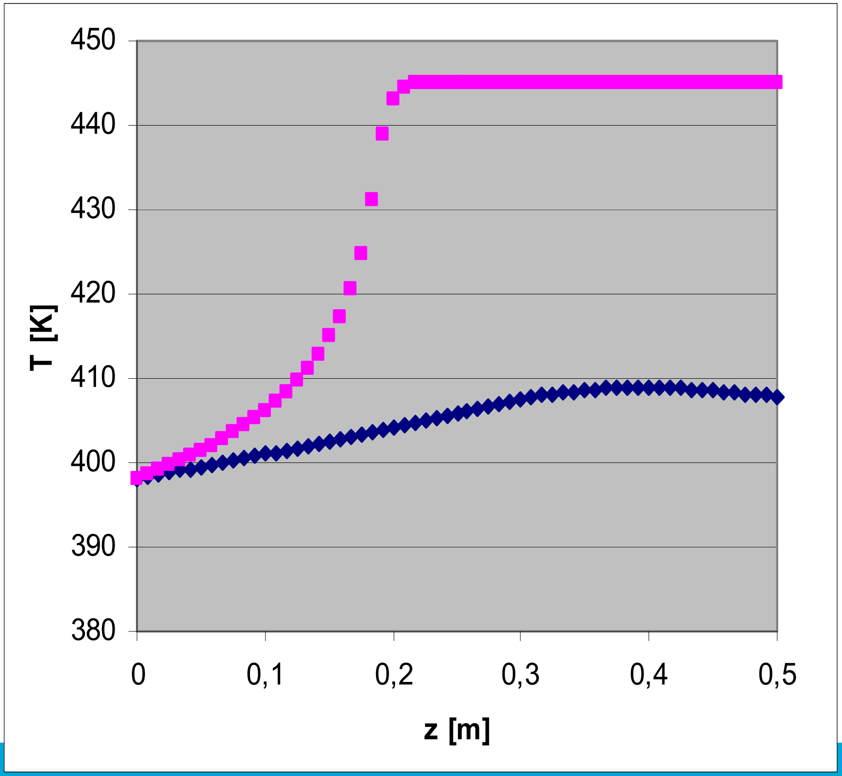
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

- Simulation of desorptive cooling (t = 950 s)



Operating parameters:

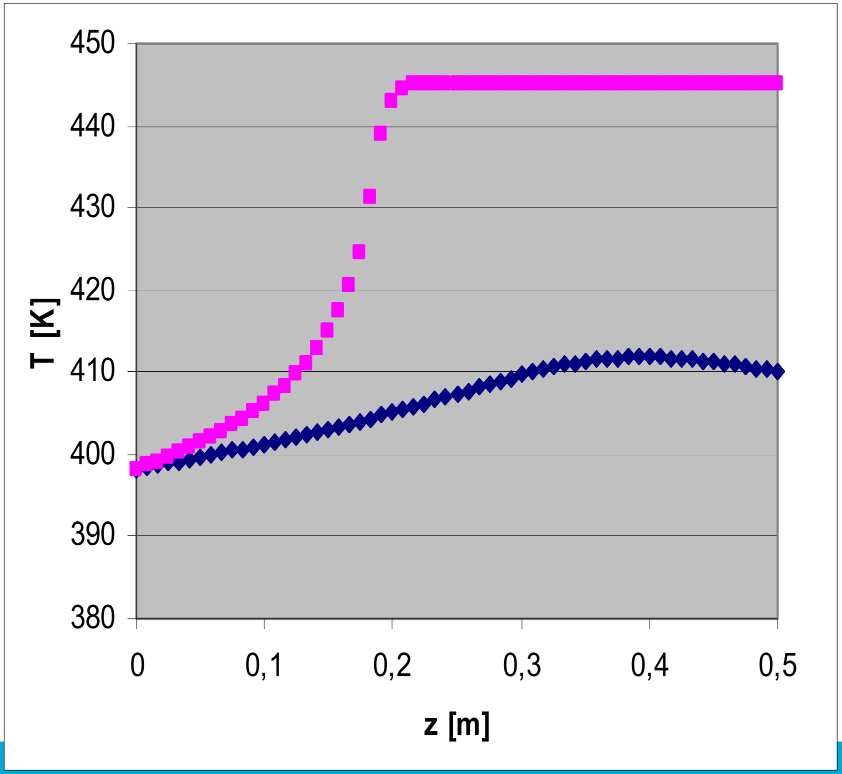
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1000 s)



Operating parameters:

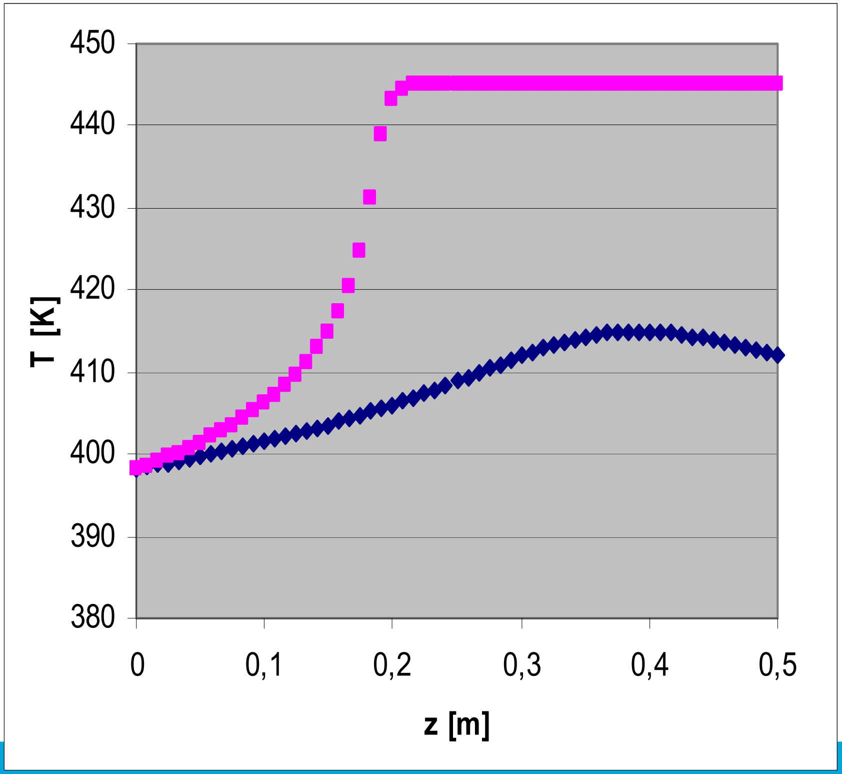
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1050 s)



Operating parameters:

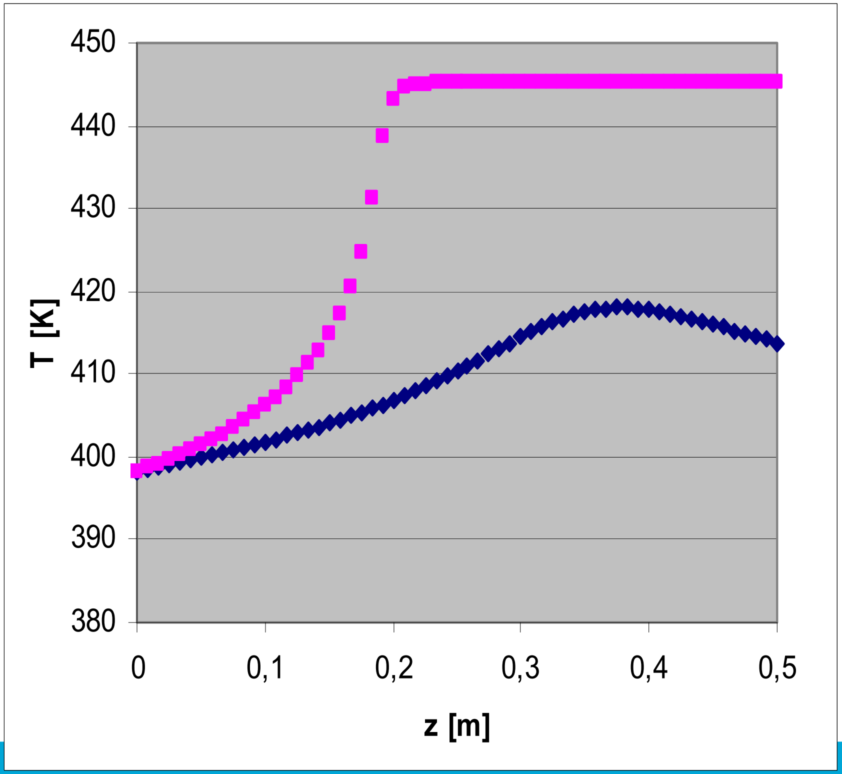
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1100 s)



Operating parameters:

- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

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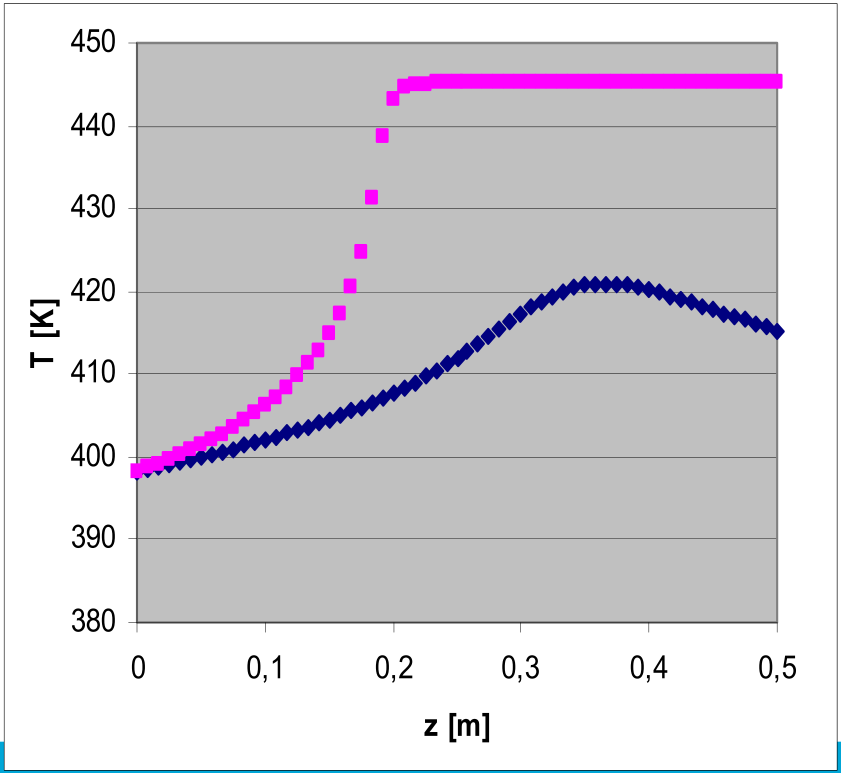
•Simulation of desorptive cooling (t = 1150 s)



Operating parameters:

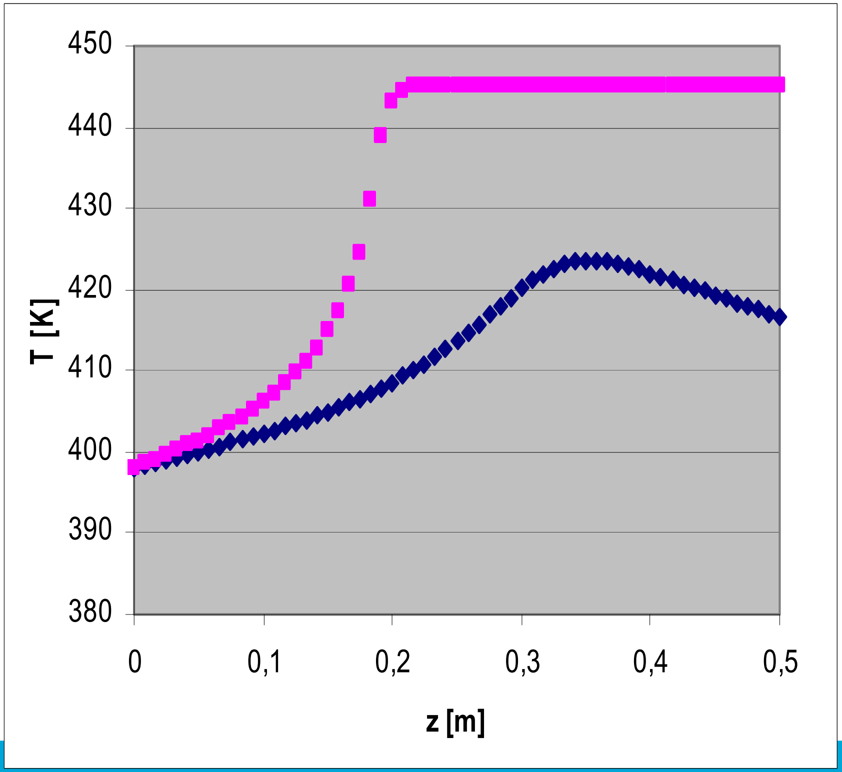
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1200 s)



Operating parameters:

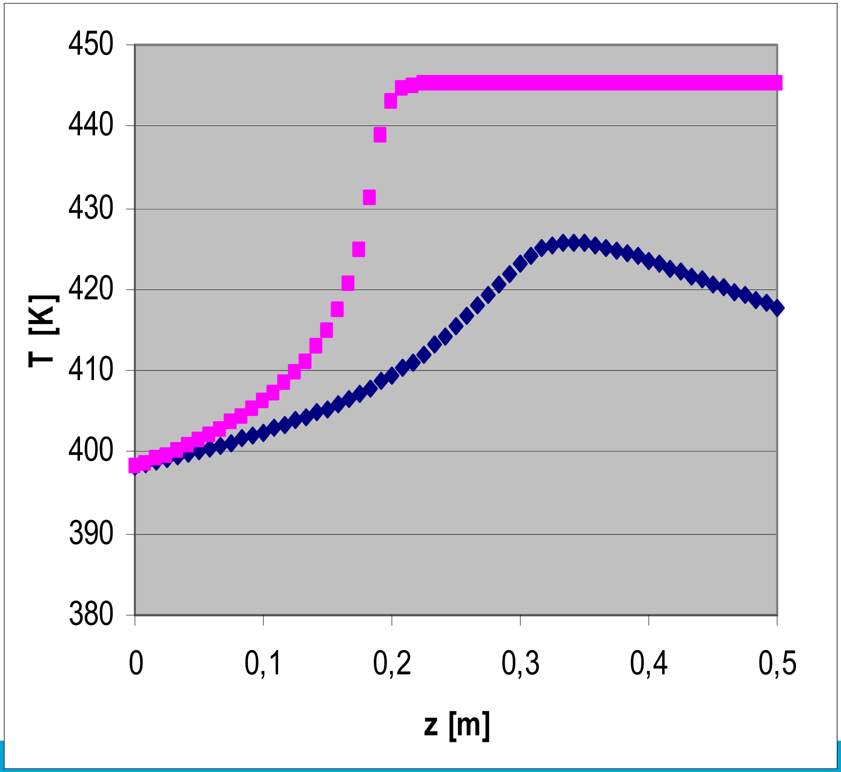
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1250 s)



Operating parameters:

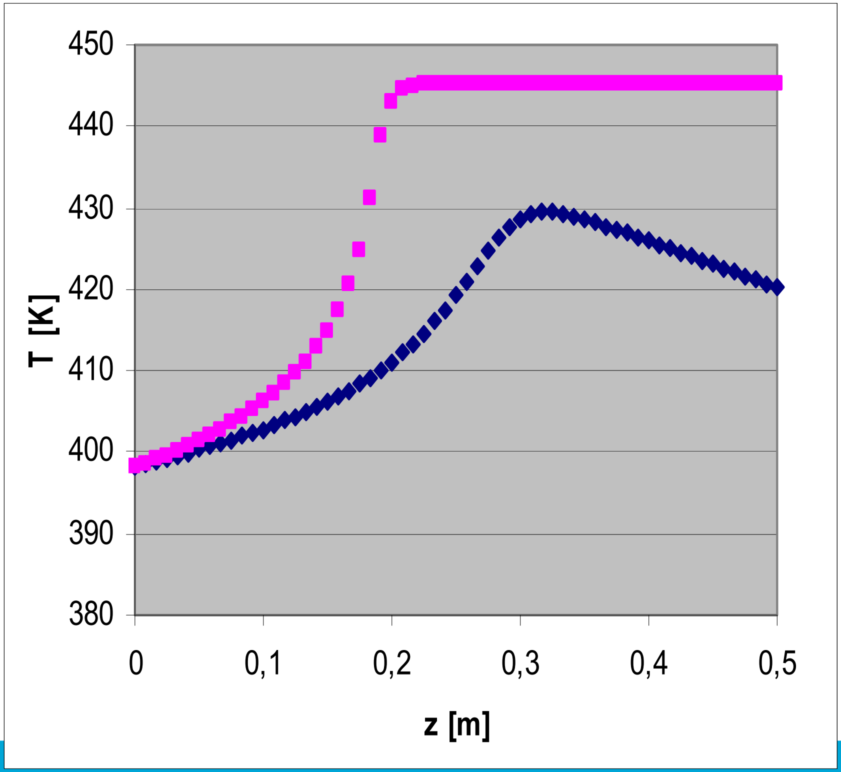
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1350 s)



Operating parameters:

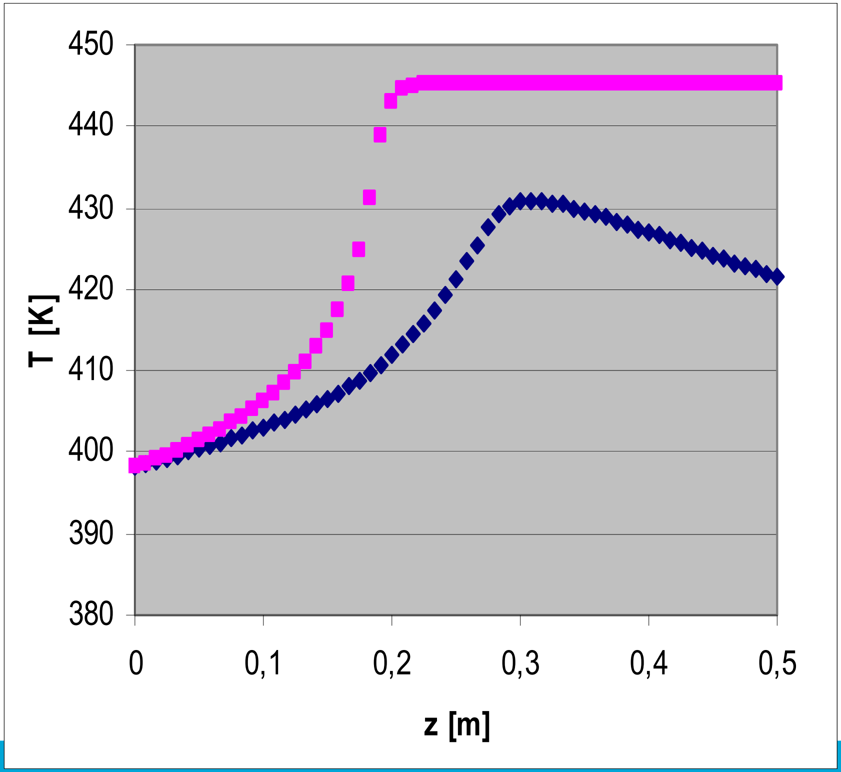
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1400 s)



Operating parameters:

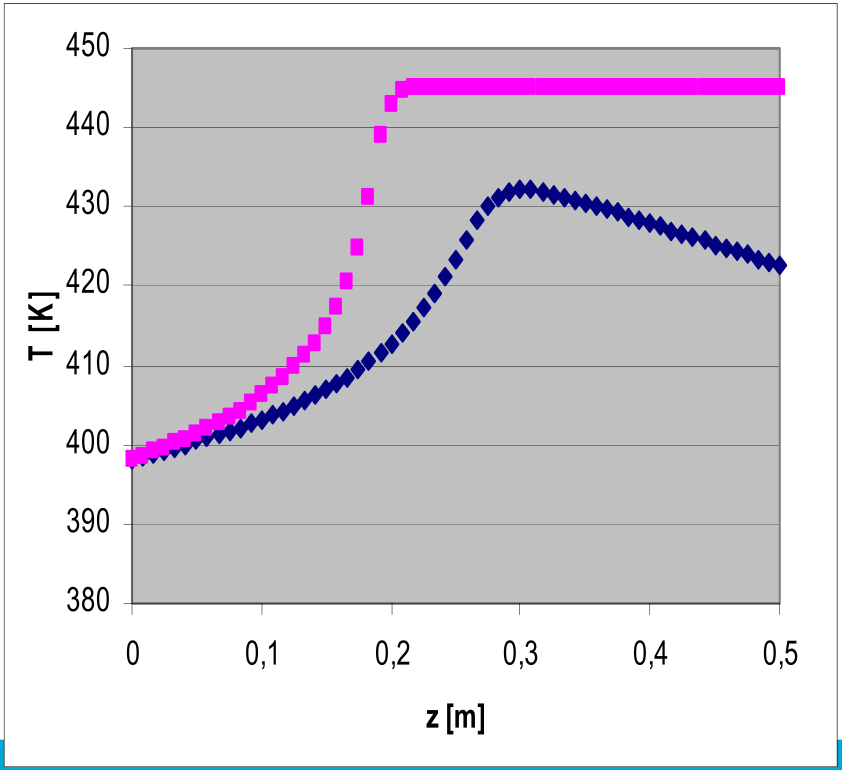
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1450 s)



Operating parameters:

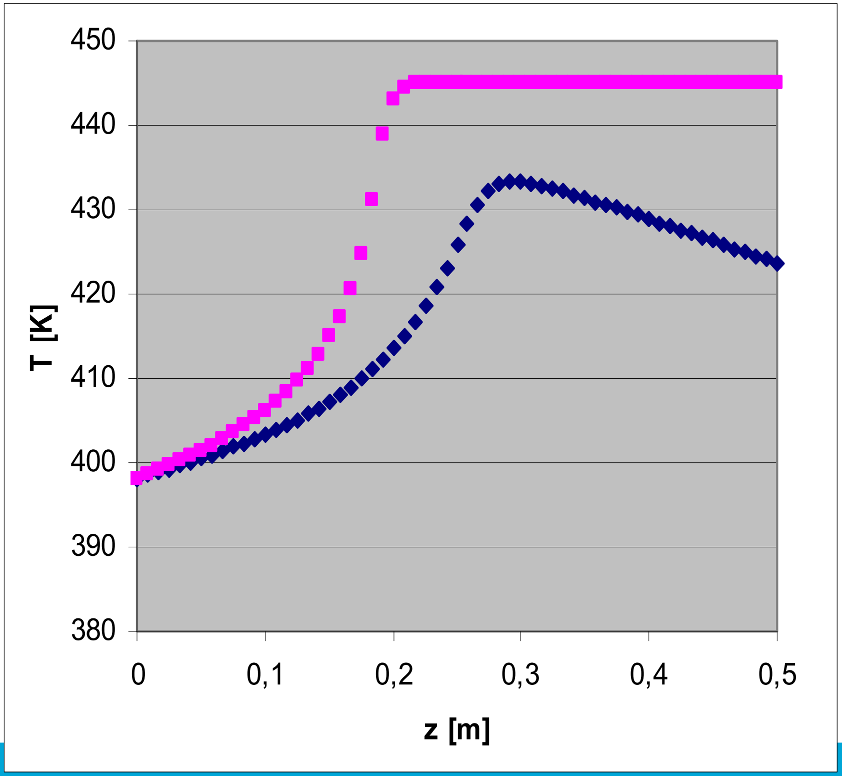
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1500 s)



Operating parameters:

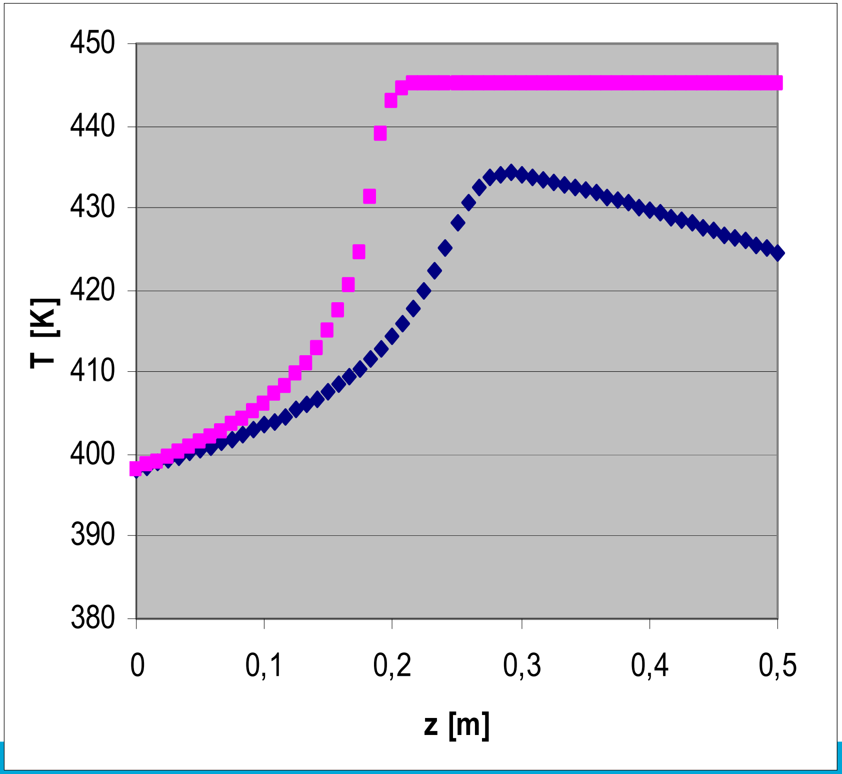
- $\dot{V}_{ein}$ = 6000 l/h
- ν = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desortive cooling (t = 1550 s)



Operating parameters:

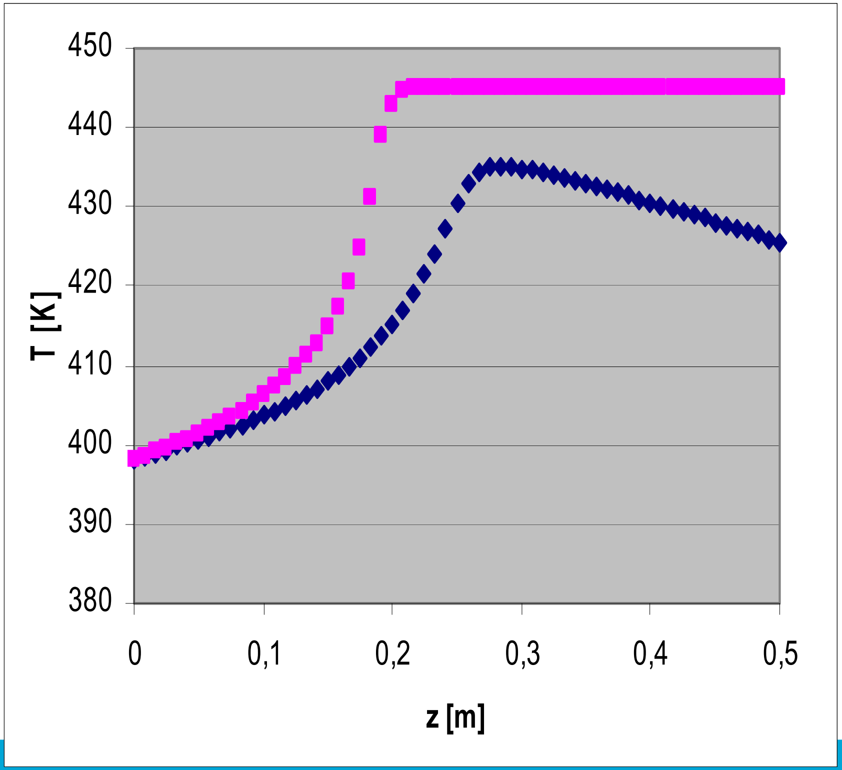
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1600 s)



Operating parameters:

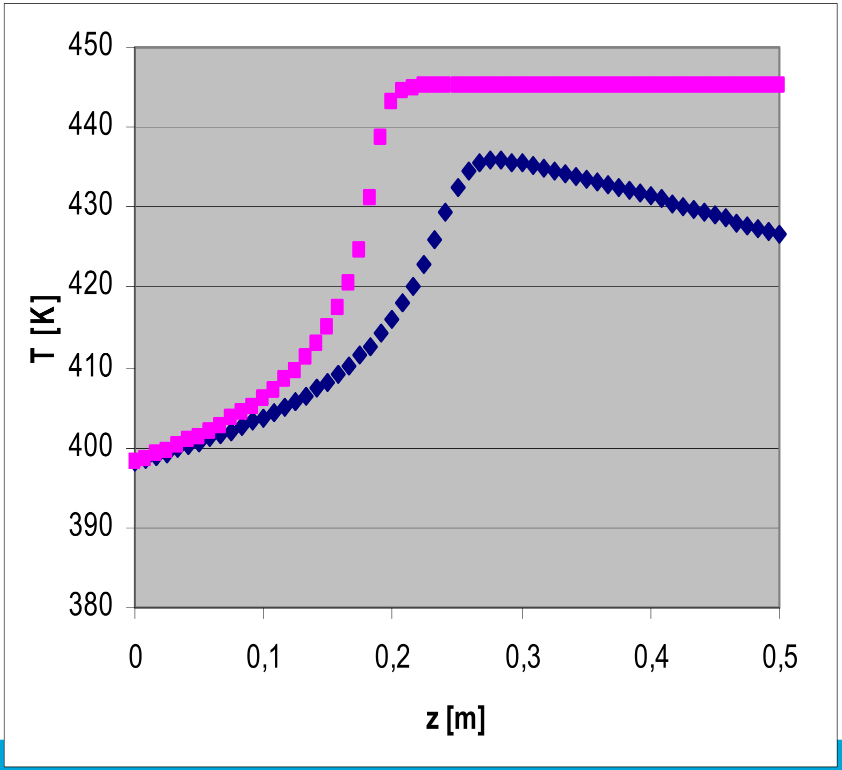
- $\dot{V}_{ein}$ = 6000 l/h
- $v = 0.5$

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1650 s)



Operating parameters:

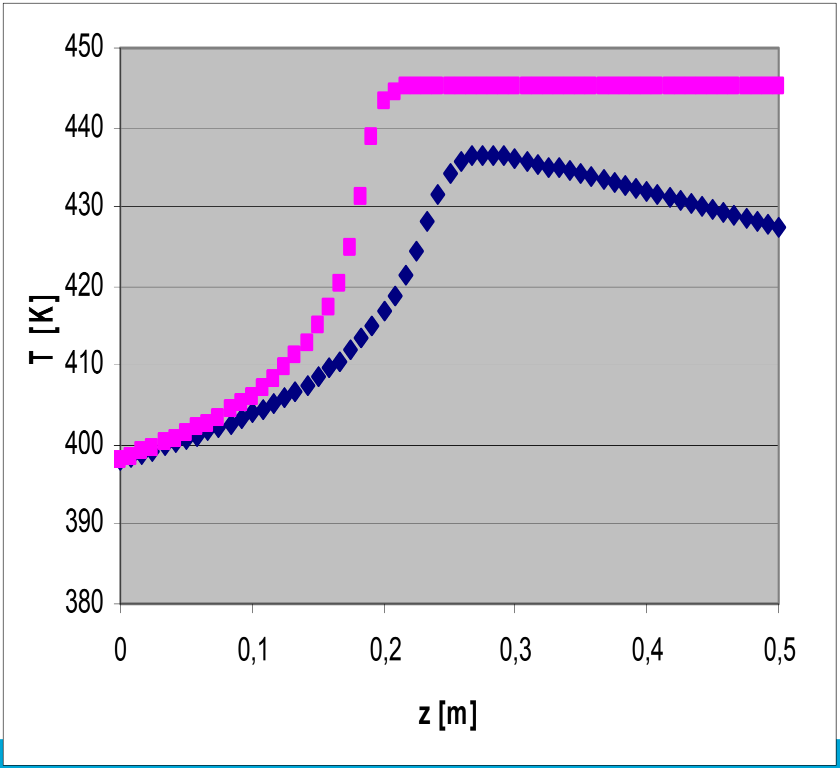
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1700 s)



Operating parameters:

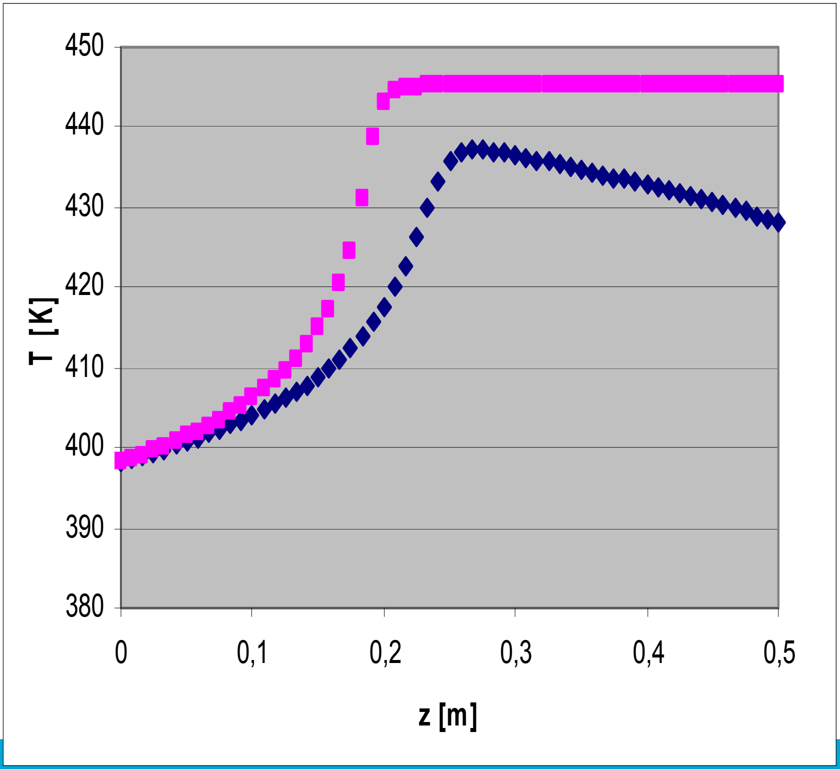
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1750 s)



Operating parameters:

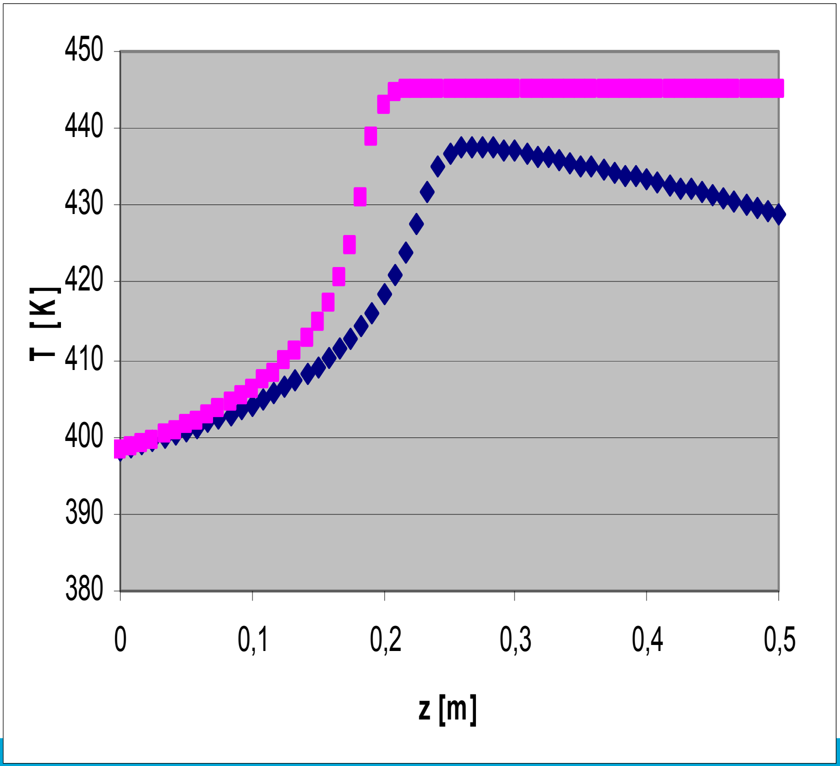
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1800 s)



Operating parameters:

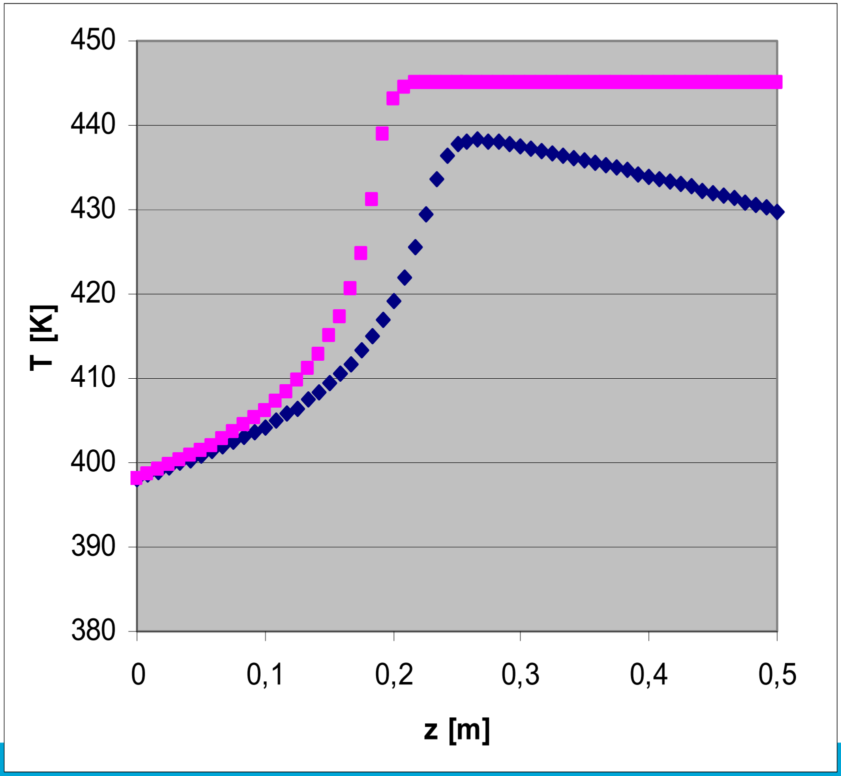
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1850 s)



Operating parameters:

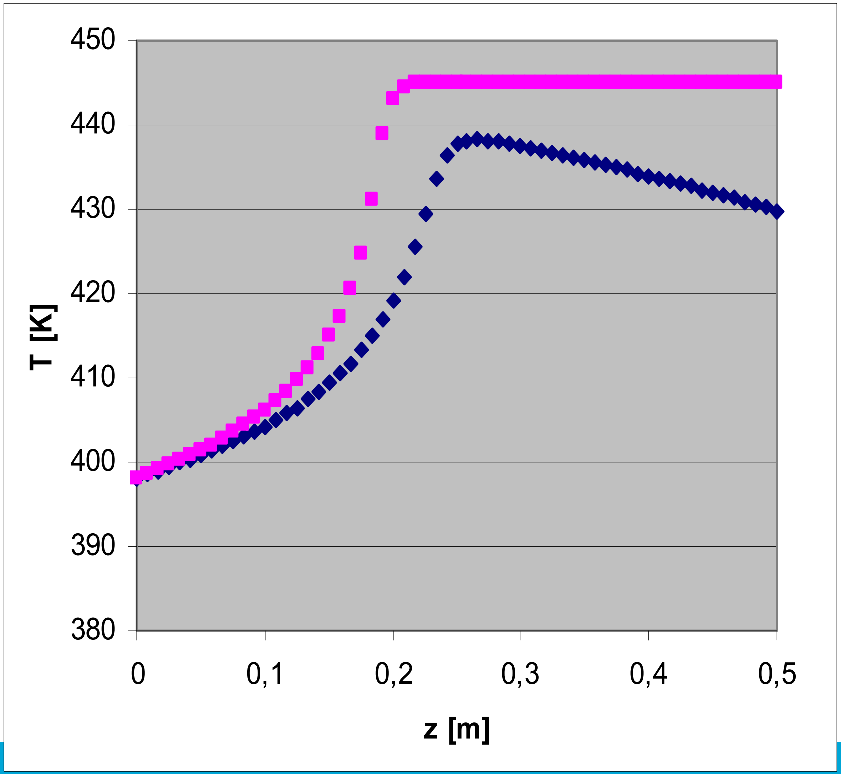
- $\dot{V}_{ein}$ = 6000 l/h
- $v = 0.5$

Feed stream:

- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

•Simulation of desorptive cooling (t = 1850 s)



Operating parameters:

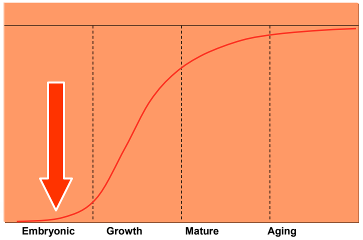
- $\dot{V}_{ein}$ = 6000 l/h
- v = 0.5

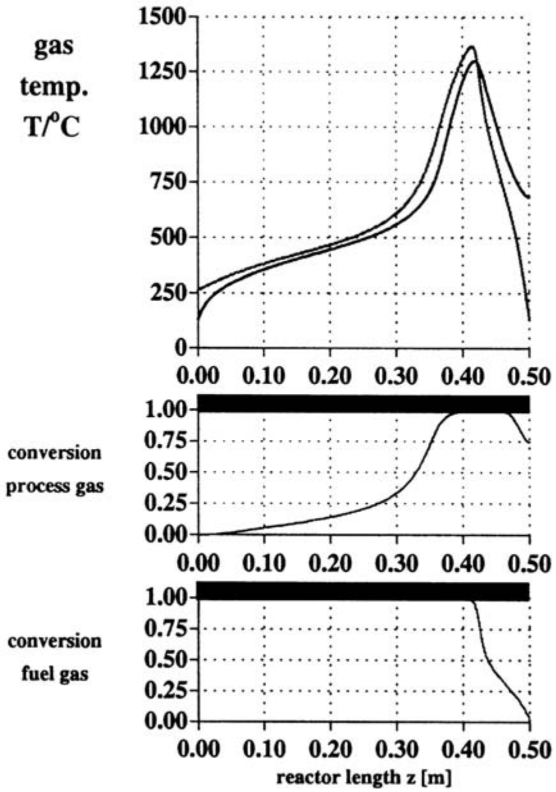
Feed stream:

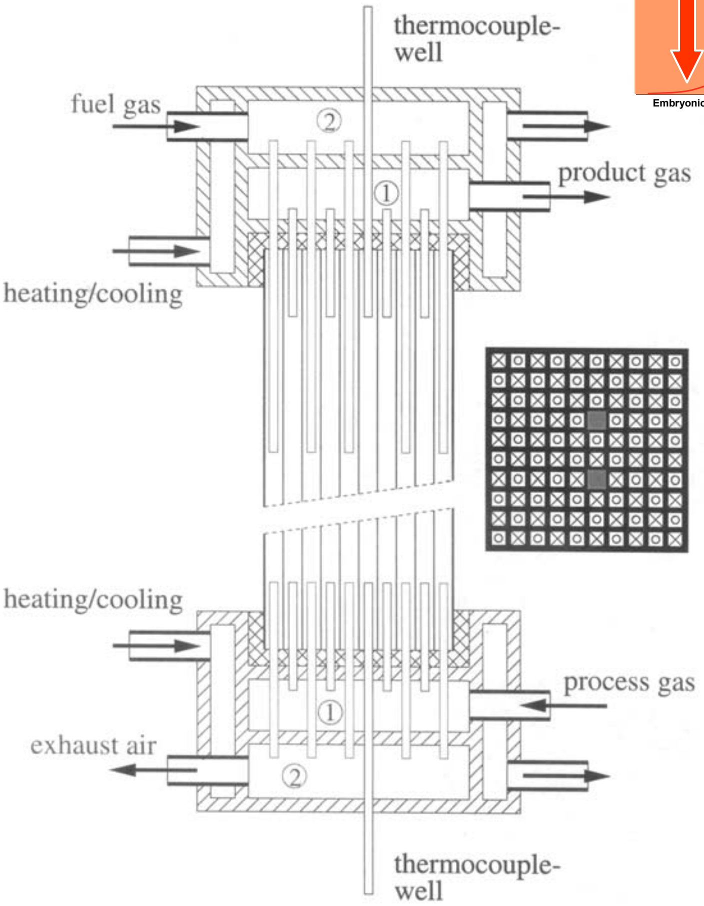
- T_{in} = 125 °C
- c_{in} = 0.2 mol/l

(source: D. Agar)

Reactive-recuperative heat transfer



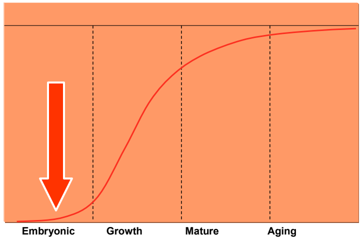


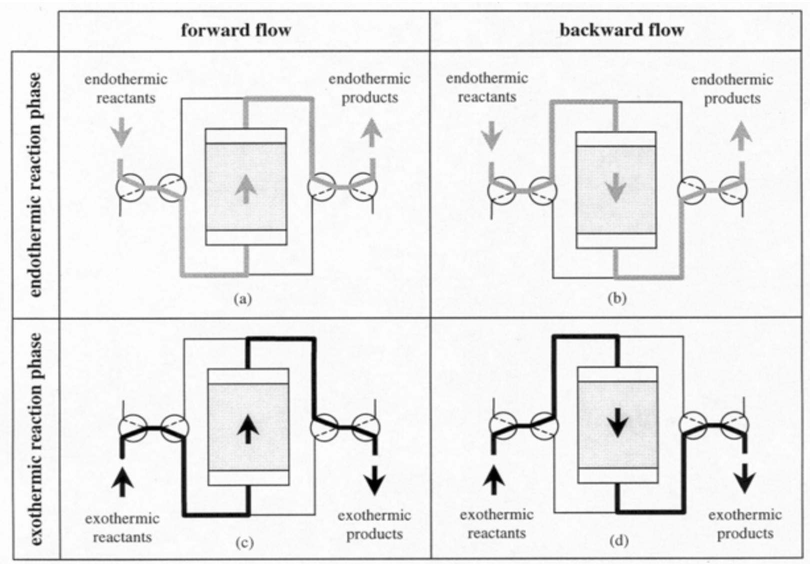


Problems with temperature control & reaction localisation!

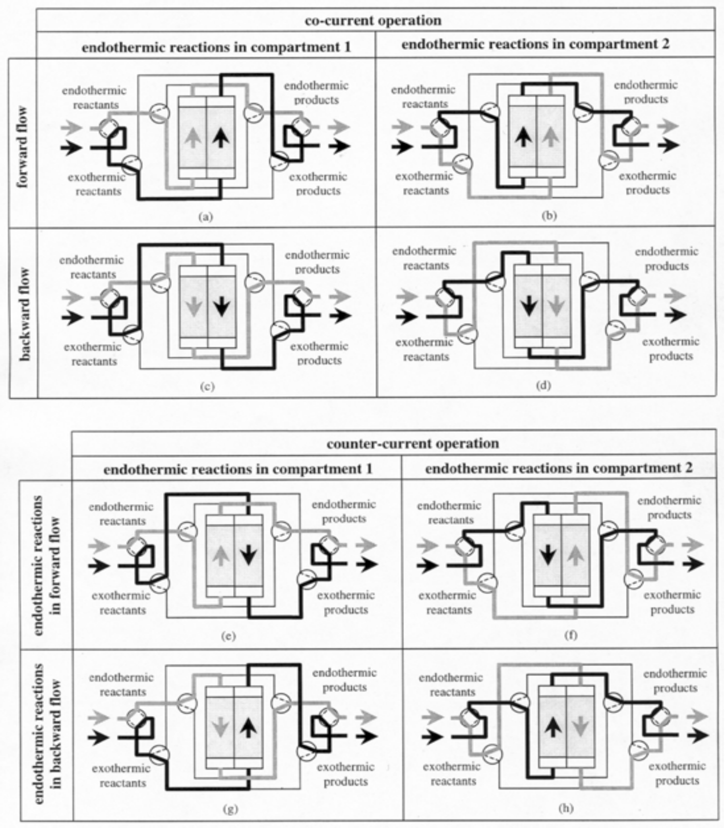
[G.Kolios et al. (2000) Chem.Engng. Sci. 55:5945-5967]

Reactive-regenerative heat transfer





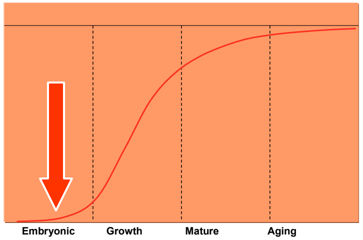
Sequential configurations



Simultaneous configurations

(M. van Sint Annaland, 2000)

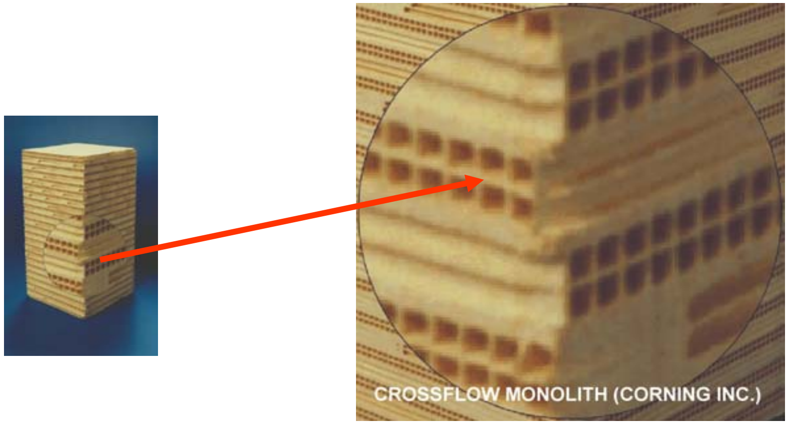
Millireactors for reactive heat transfer

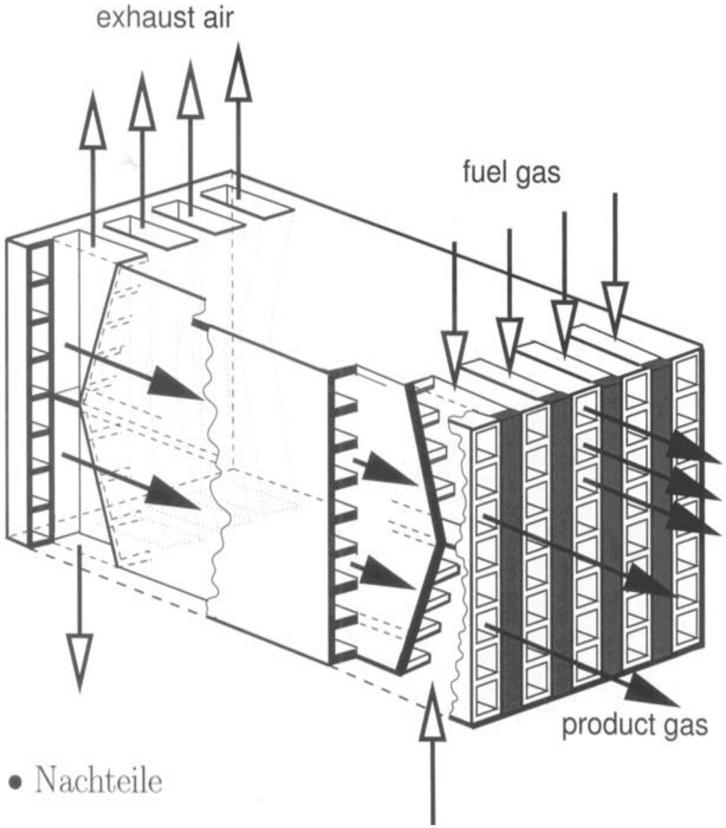


Monolithic bulk catalyst structures

Numerous complications:

- **complex fabrication of ceramic millistructures**
- **sealing**
- **even media distribution**





(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Heat exchange integration in industrial reactions

T-Profiling technique	***Ethylbenzene Dehydrogenation*** $C_8H_{10} \leftrightarrow C_8H_8 + H_2$ 600°C	***Steam Reforming*** $CH_4 + H_2O \leftrightarrow CO + 3H_2$ 900°C	***Hydrogen Cyanide Manufacture*** $CH_4 + NH_3 \leftrightarrow HCN + 3H_2$ 1200°C
Convection	Badger/Mobil 'adiabatic' process		
Recuperation	BASF 'isothermal' process	conventional primary steam reforming	Degussa BMA process
Regeneration			?
Reaction		autothermal reforming (fuel cell applications)	Andrussow ammonoxidation process

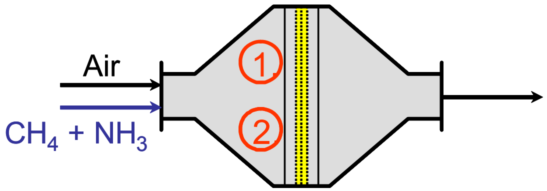
(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

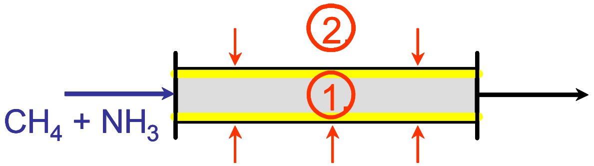
Heat exchange integration in industrial reactions

HCN synthesis

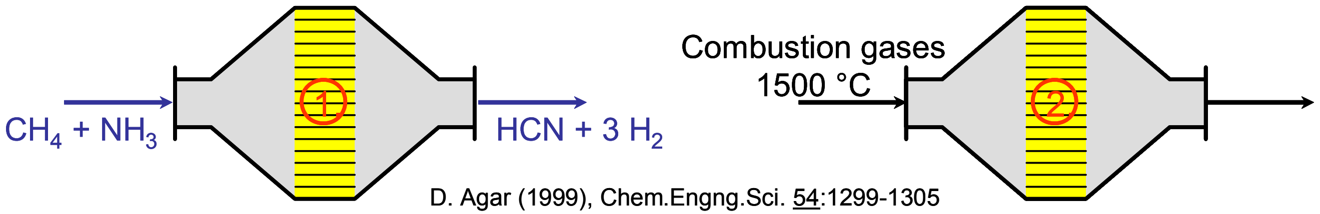
① Synthesis reaction: $CH_4 + NH_3 \xrightarrow{1200\ °C} HCN + 3\ H_2$; $\Delta_r H = +\ 256$ kJ/mol

② Heat generation: $3\ H_2 + 1{,}5\ O_2 \longrightarrow 3\ H_2O$; $\Delta_r H = -\ 726$ kJ/mol


1. Andrussow-Process


2. BMA-Process

3. Regenerator-Reactor
(regenerative heat exchange)

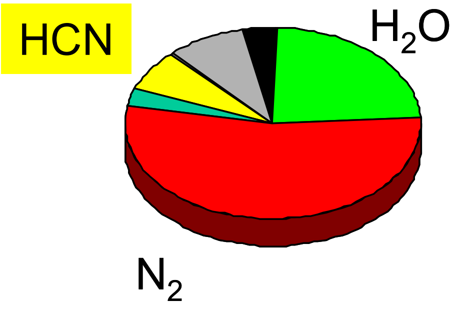


D. Agar (1999), Chem.Engng.Sci. 54:1299-1305

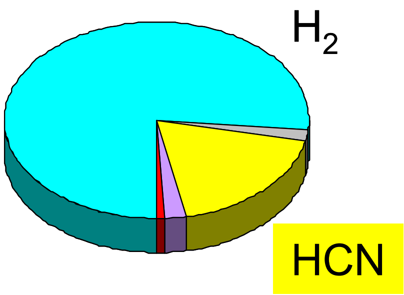
(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Heat exchange integration in industrial reactions

Andrussow



BMA



Comparison of reactor concepts

Process	Andrussow	BMA	Regenerator-Reactor
Catalyst	Pt/Rh-gauze	Pt-layer on tube wall	Supported Pt-cat. Fixed bed
Temp. [°C]	1100	1250	1200
C-Yield	60 %	91 %	91 %
N-Yield	65 %	82 %	82 %
HCN-Concn.	6 %	23 %	23 %
Energy demand [MJ/kg HCN]	~ 60	~ 60	< 50
$\eta_{thermal}$ of reactor	> 90 %	> 50 %	> 90 %
Reactor construction	simple, robust	ceramic, fragile	simple, robust

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)