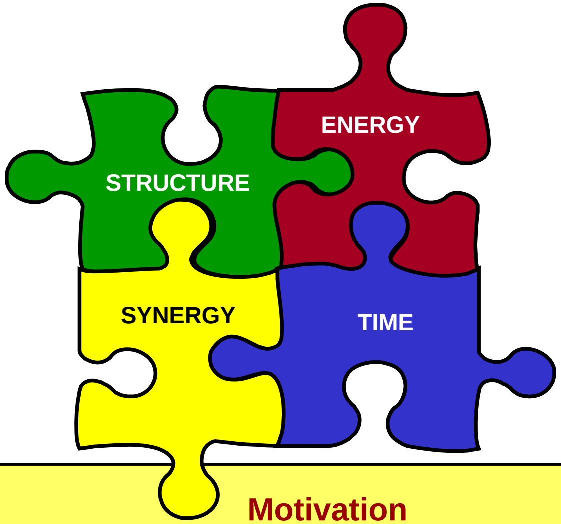
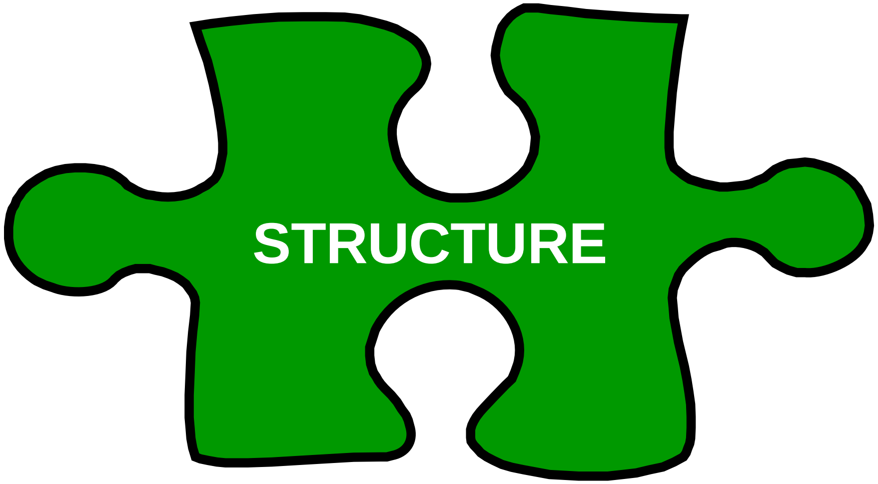
STRUCTURE

Process Intensification in Spatial Domain

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:

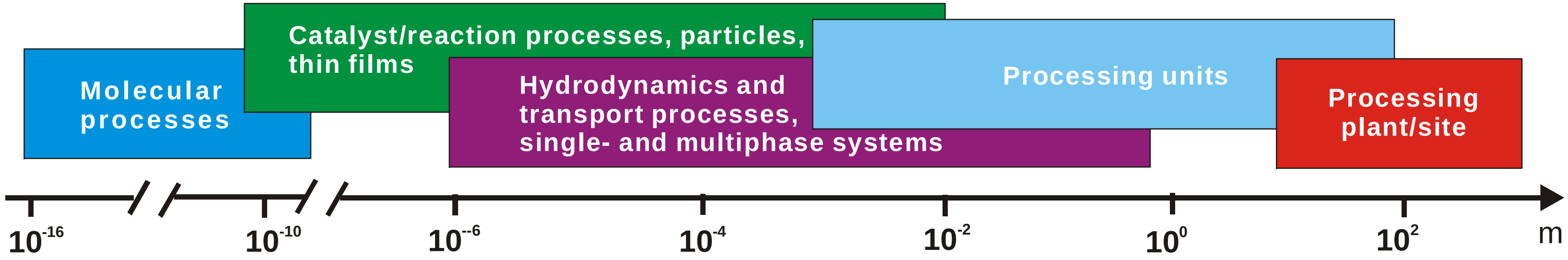


Domain	Main focus	Process Intensification concepts applied	Motivation
Spatial	Structured environment	Milli- and microchannels; structured (catalyst) surfaces	• well-defined geometry • creating maximum specific surface area at minimum energy expenses • creating high mass and heat transfer rates • precise 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

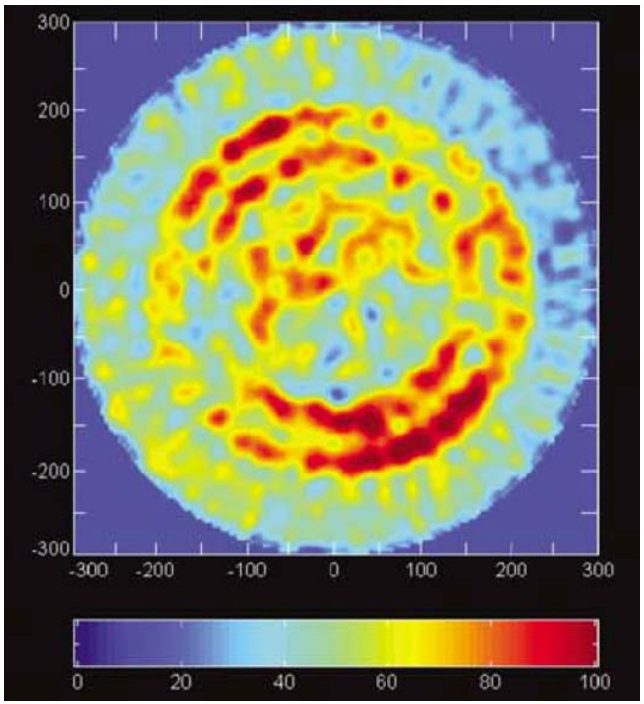


- Why structure?
- Structure on molecular scale
- Structured internals for reactors and separators
- Fractal structures in chemical processing
- Equipment: structured heat exchangers
- Equipment: structured mixers
- Equipment: structured microprocessing systems
- Movie: static mixers

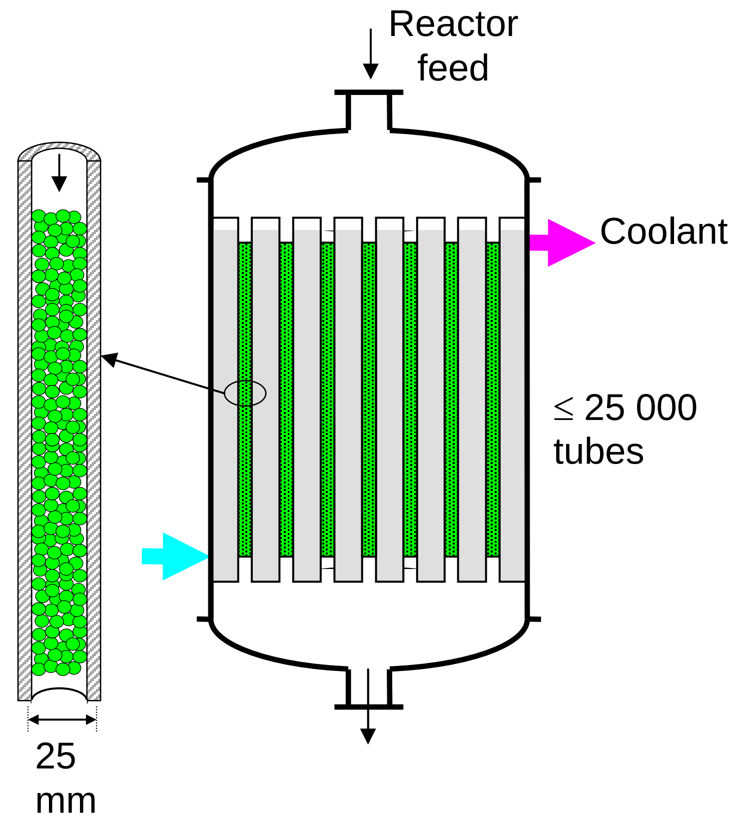
At all scales, from nano to macro



Randomness in spatial domain - catalyst beds in multitubular and trickle-bed reactors



Liquid maldistribution in a random trickle bed
(Boyer en Fanget 2001)



Why: structure?

- **Acting upon selected molecules**
- **Creating maximum specific surface area at minimum energy expenses**
- **Smaller equipment**
- **Ease of operation**
- **Higher productivity**
- **Lower costs**
- **Reduced material handling**
- **Ease of process scale-up**
- **Full predictability & control**
- **Better understanding**
- **Simplicity and exactness of mathematical descriptions (models)**
- **Reduction of human/computer time and effort**

MOLECULAR SCALE

Control of spatial orientation of molecules and geometry of collisions

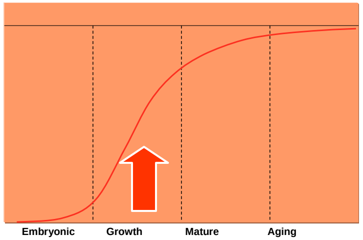
Methods for controlling molecular alignment and orientation

- **Orientation control via nano-structural confinement**
  - Shape-selective catalysts
  - Imprinted catalysts
  - Molecular reactors (cyclodextrins)
  - Liquid crystals
- **Alignment and orientation control via external fields**
  - Molecular beam
  - Stark's effect methods (electric field)
  - *Brute force* methods
    - Magnetic
    - Electric
  - Non-resonant laser
    - Adiabatic
    - Femtosecond

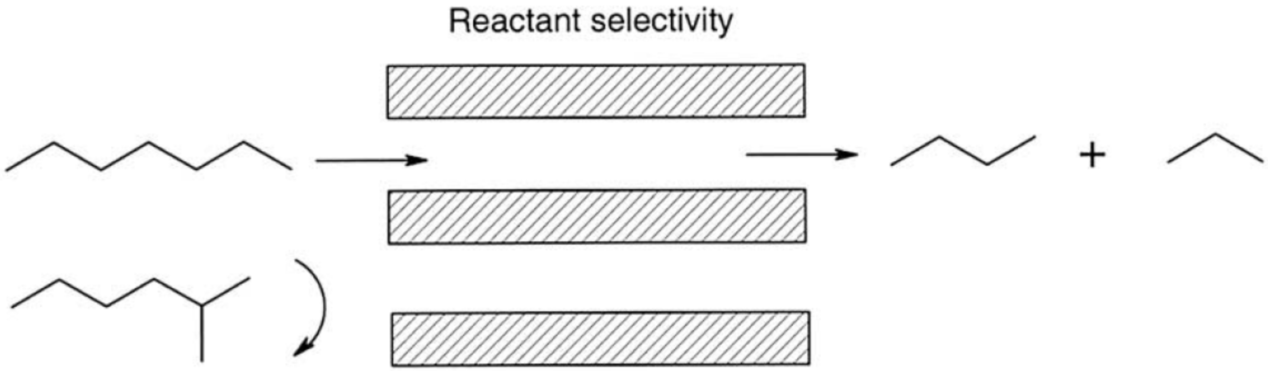
- Molecules get immobilized
- Structures confining the access
- "Take it or leave it"

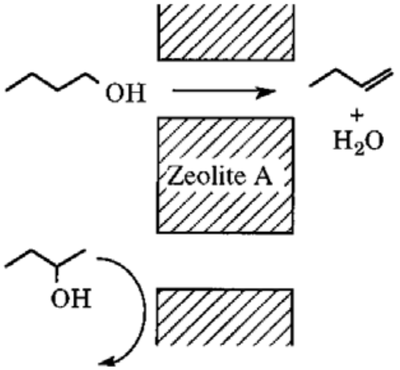
- Molecules move

Shape selective catalysis



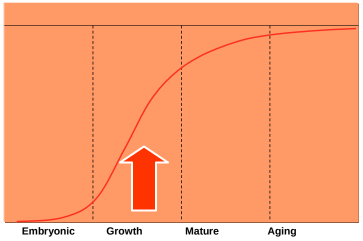
1. Reactant selectivity



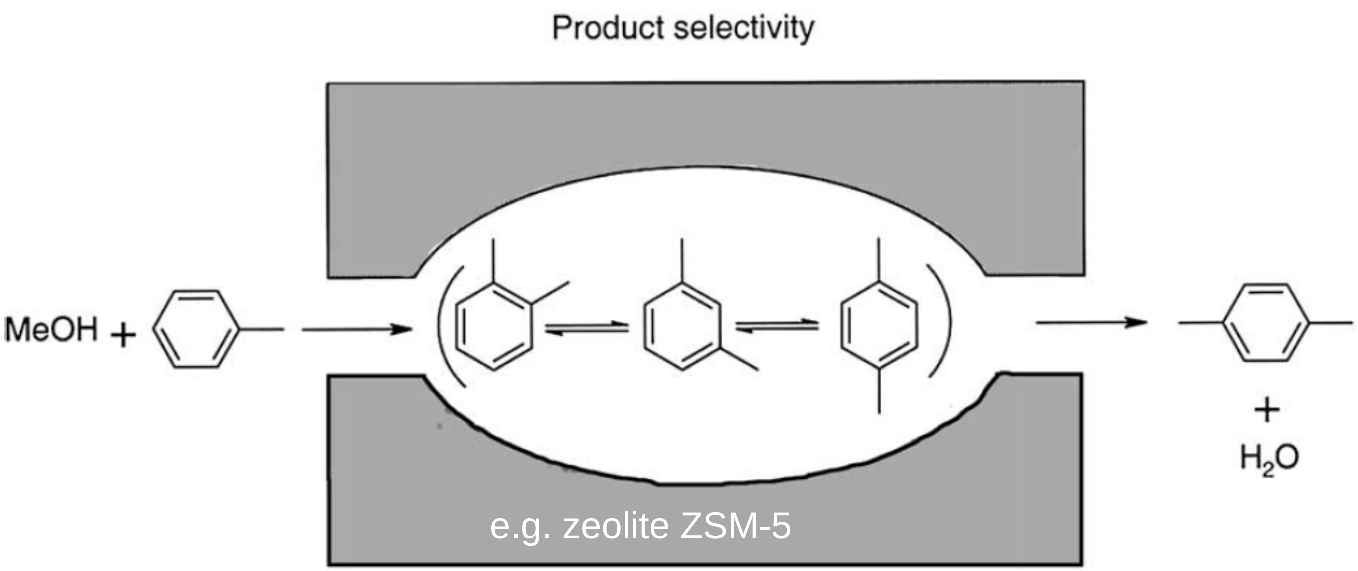


Davis, 1996; Stocker, 2005

Shape selective catalysis

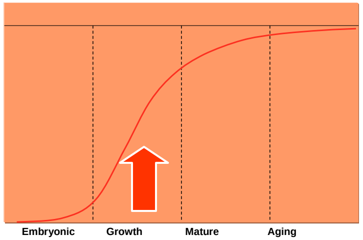


2. Product selectivity

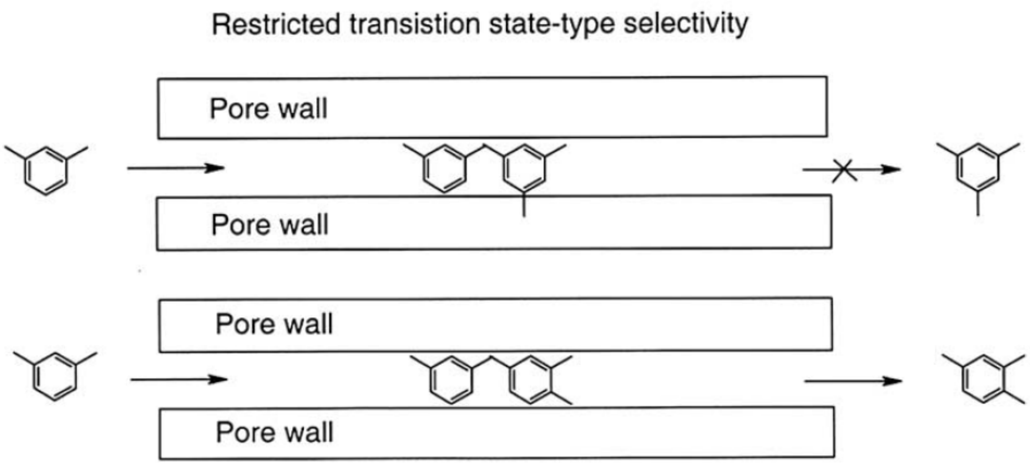


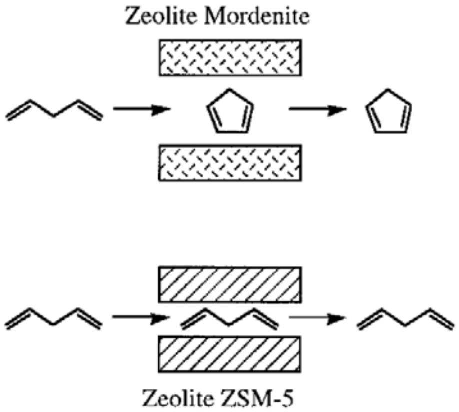
Stocker, 2005

Shape selective catalysis



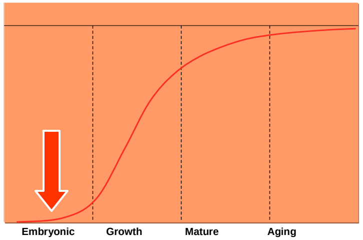
3. Restricted transition state-type selectivity

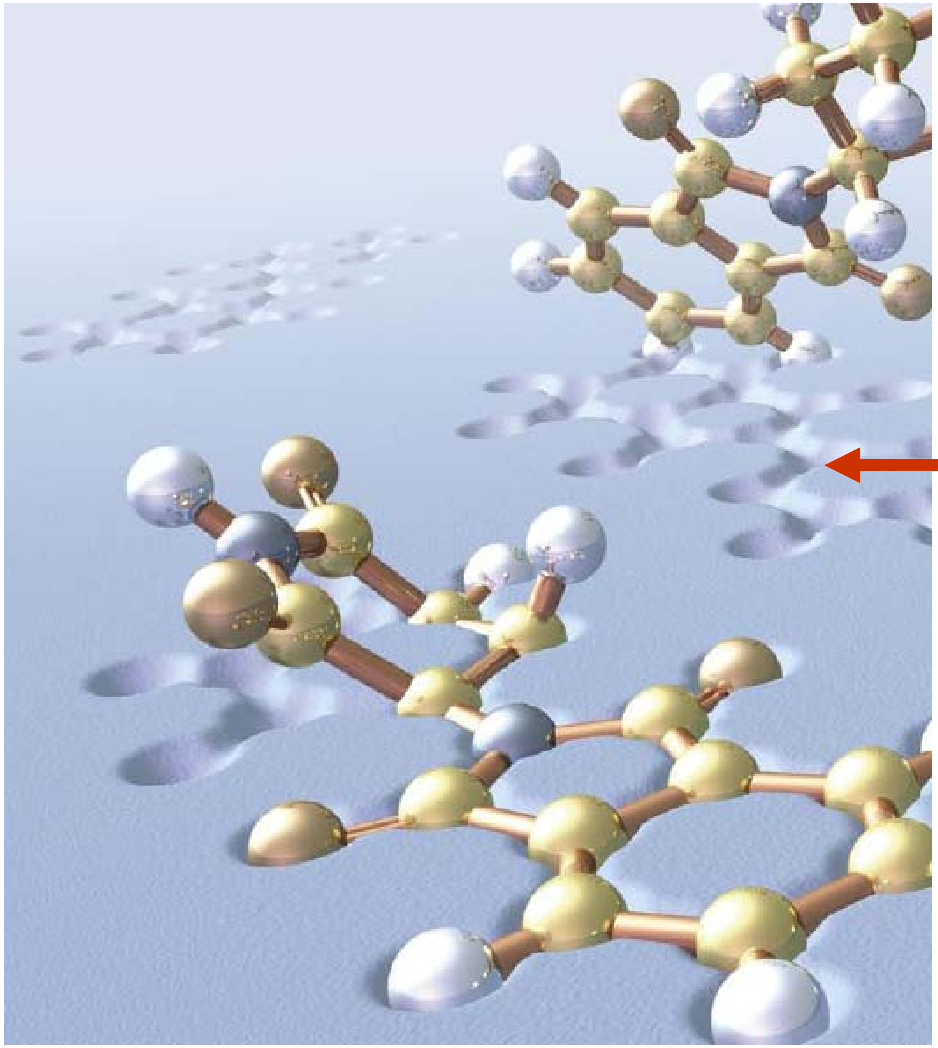




Davis, 1996; Stocker, 2005

Molecular imprinting

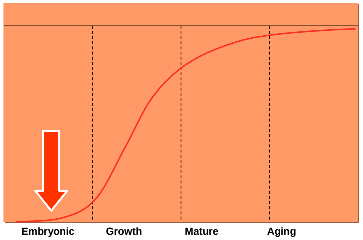


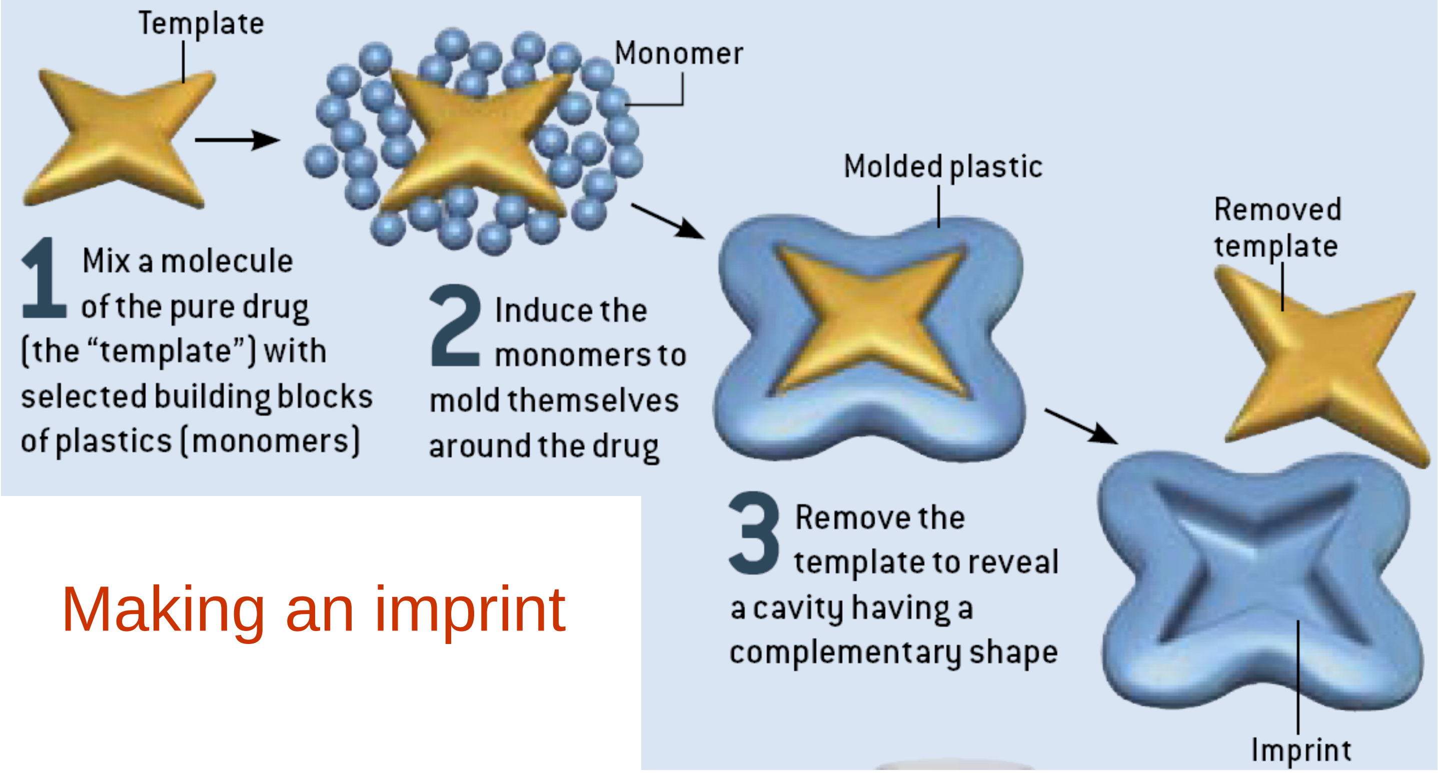


Molecularly imprinted polymers are essentially plastic casts of the selected molecules

Mosbach, Scientific American, 2006

Molecular imprinting

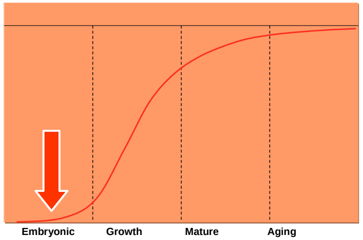


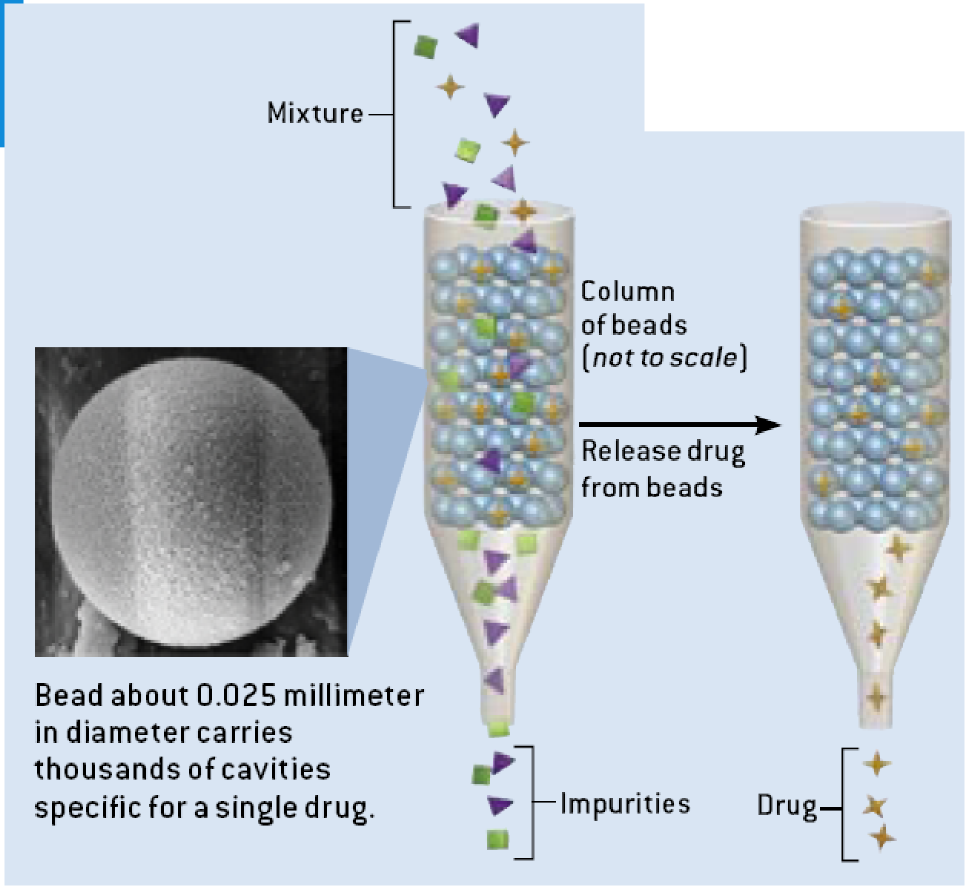


Making an imprint

Mosbach, 2006

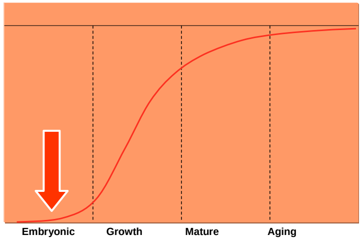
Molecular imprinting



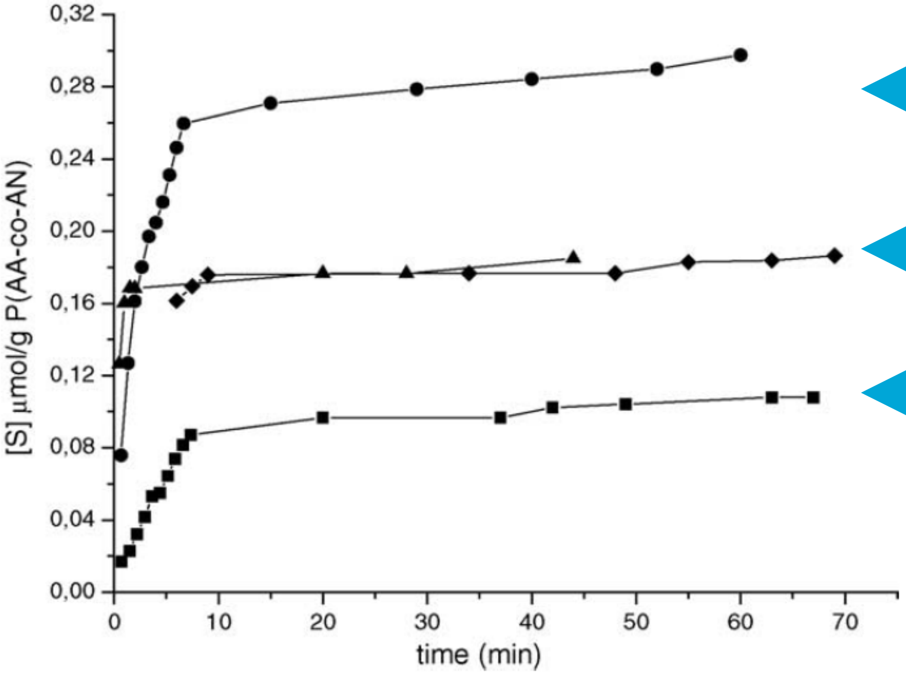


If an unpurified batch of drug were poured over a bed of imprinted beads, the cavities in the beads would capture the drug but ignore all other substances, which would flow away. Then the purified drug could be washed out.

Molecular imprinted membrane



Shape-selective membrane separation



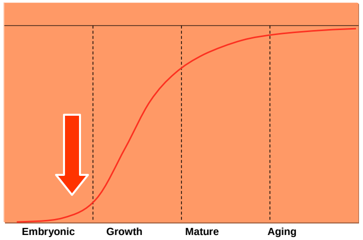
tetracycline hydrochloride through imprinted membrane

chloramphenicol through non-imprinted and imprinted membrane

tetracycline hydrochloride through non-imprinted membrane

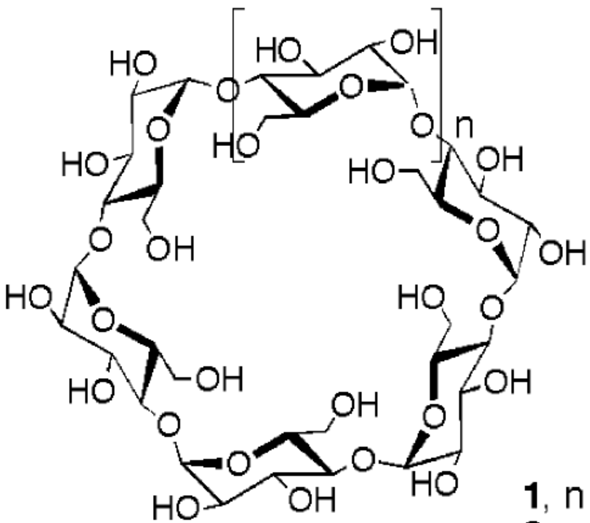
Trotta et al., 2005

Molecules as structured reactors

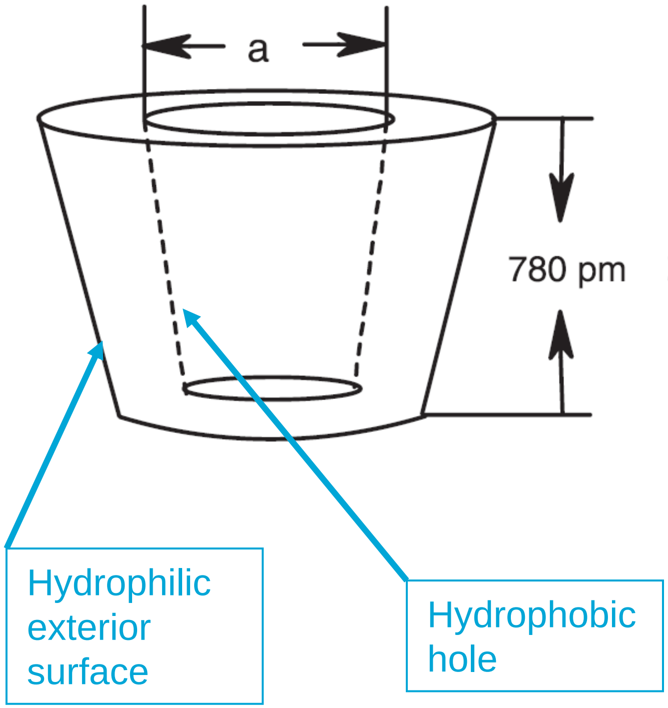


Typical example:
cyclodextrins

(cyclic oligosaccharides used in pharmaceutical industry, household and personal care products, as food additives)

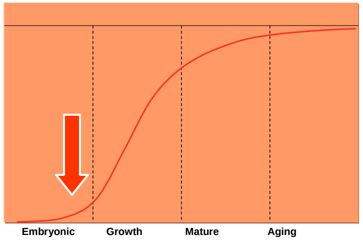


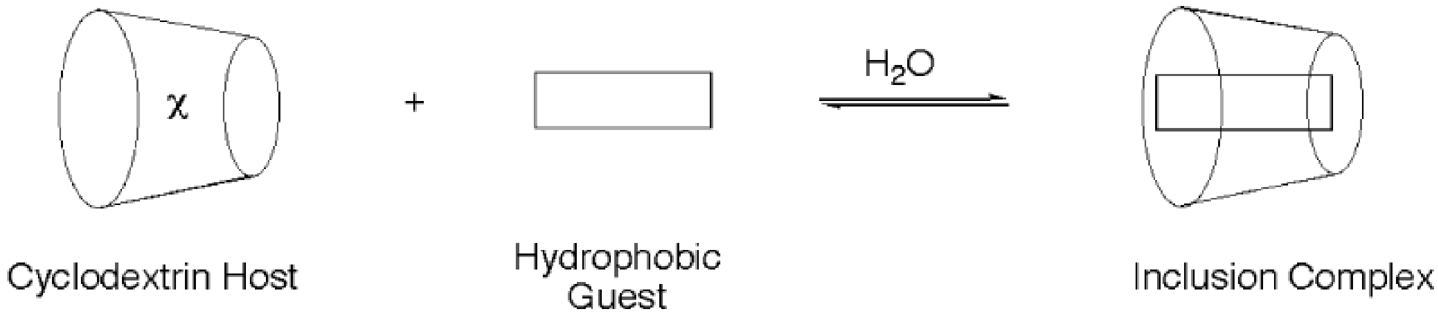
1, n = 1
2, n = 2
3, n = 3



1 a = ca. 500 pm
2 a = ca. 620 pm
3 a = ca. 800 pm

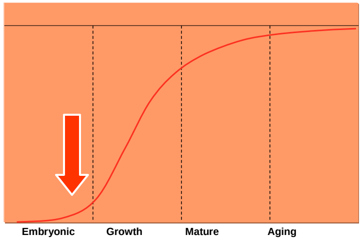
Cyclodextrins



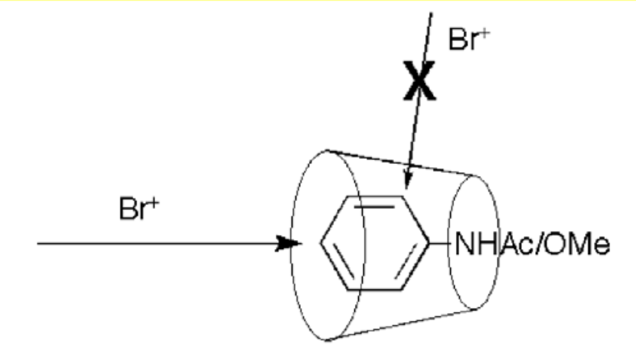


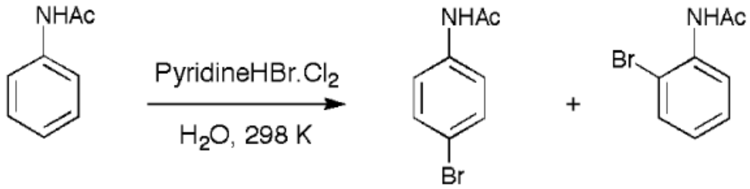
‘Structural’ behaviour of CD’s

Molecular reactors – selectivity



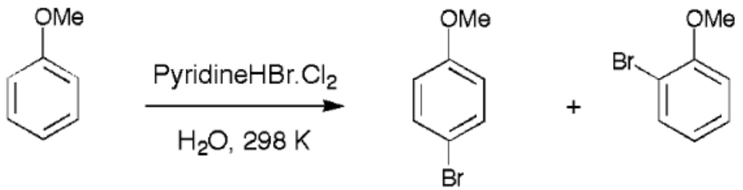
CD's block access of brominating agent to the *ortho* positions of the reagents, whereas *para*-brominated products are synthesized





4 5 6

	5	6	Selectivity ratio 5/6
no cyclodextrin	56	44	1.3
β-cyclodextrin	79	21	3.8
α-cyclodextrin	> 98	< 2	>49



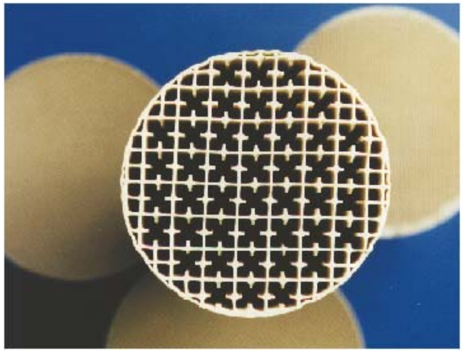
7 8 9

	8	9	Selectivity ratio 8/9
no cyclodextrin	86	14	6
β–cyclodextrin	93	7	13
α-cyclodextrin	97	3	32

Easton, 2005

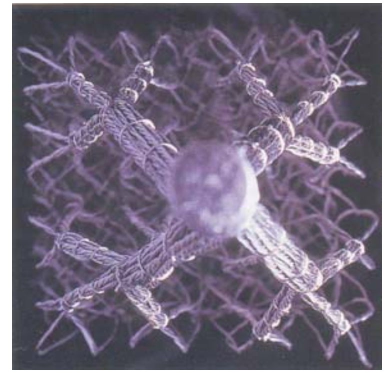
MESO SCALE

Structured packings and catalysts – a wealth of options



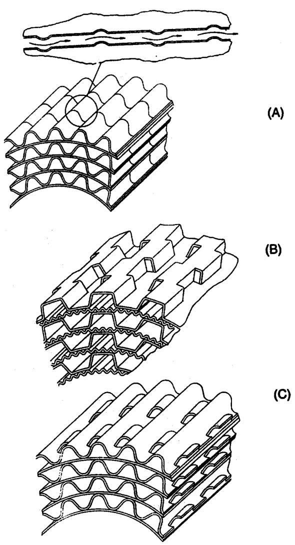
Internally finned monolith
TUD/Corning

KATAPAK-S
Sulzer



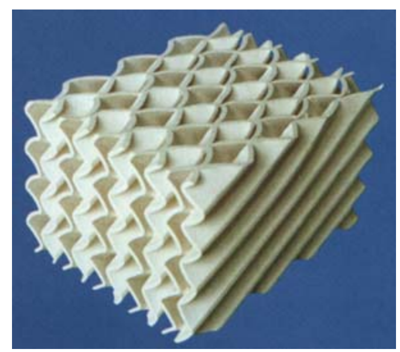
Reduction size and
pressure drop in
distillation
No separate L-distribution
needed

Up to 120.000
drip points/m^2
Nagaoka Corp



“Metal Monoliths”

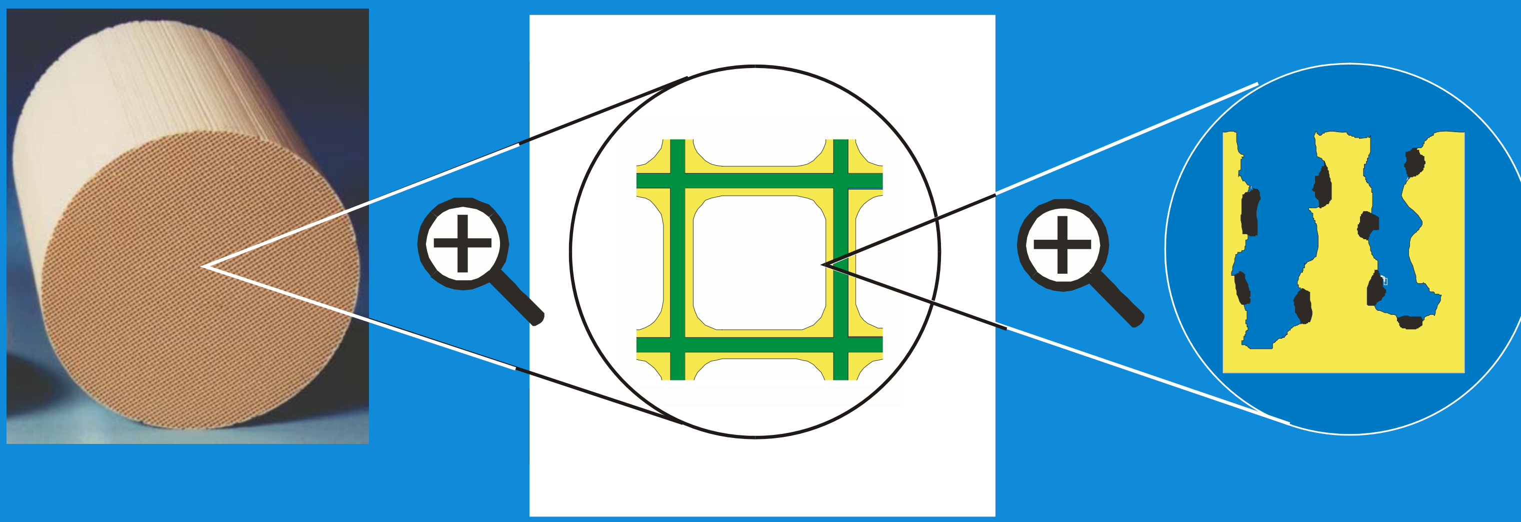
Gauzes



KATAPAK-M
Sulzer

Foams

Monolithic reactors



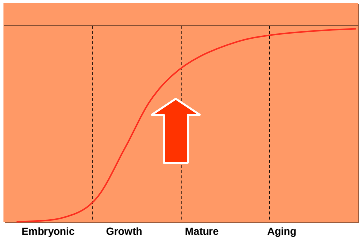
Monolithic catalyst

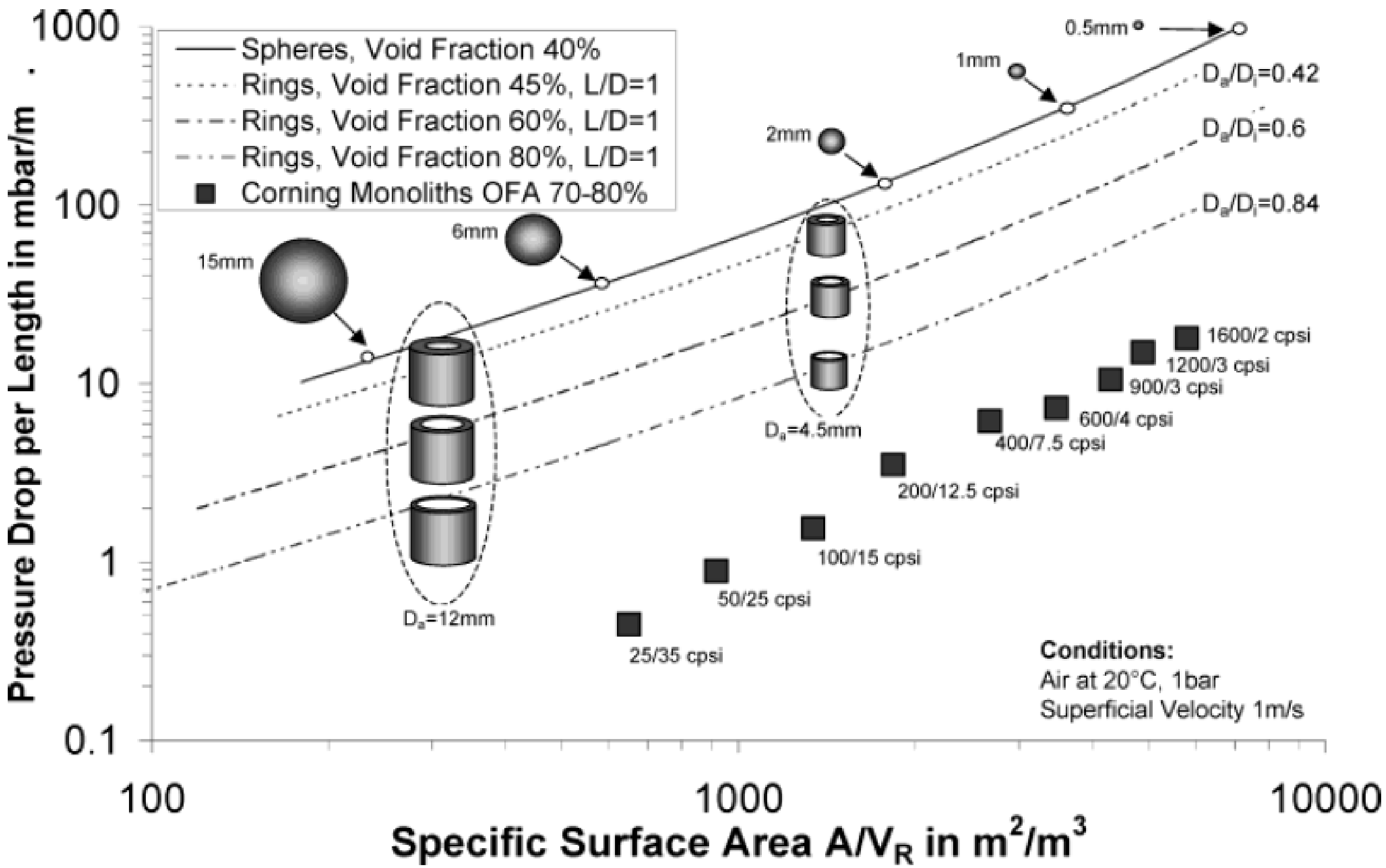
SUPPORT

WASHCOAT

CATALYTIC MATERIAL

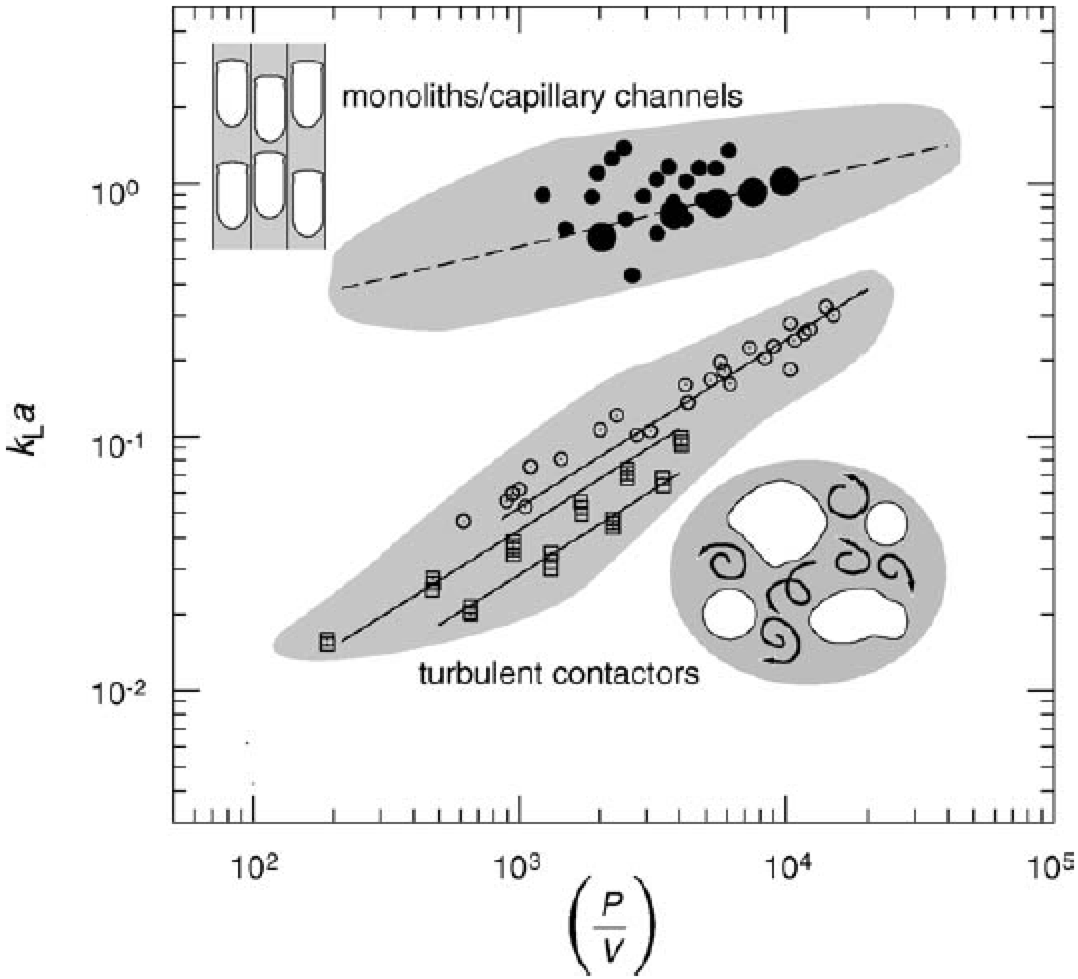
Monoliths – pressure drop

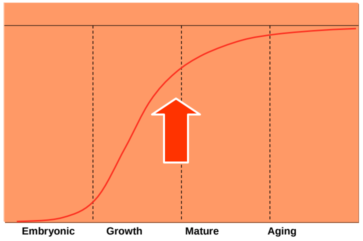




Boger et al., 2004

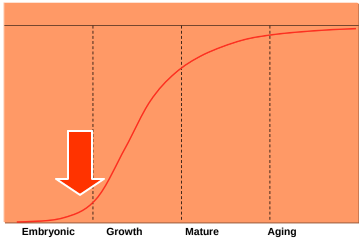
Monoliths – mass transfer



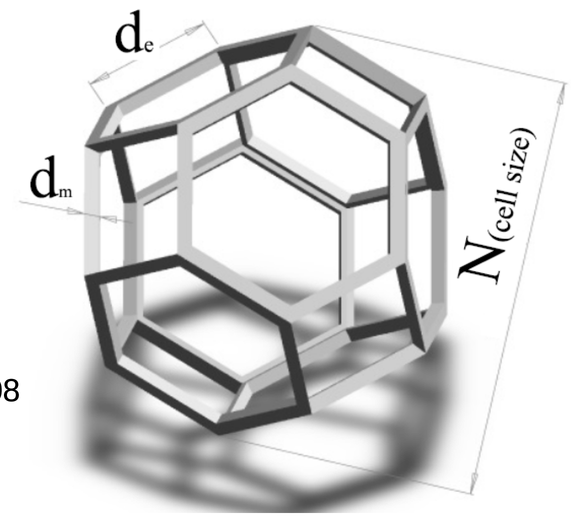


Kreutzer et al., 2006

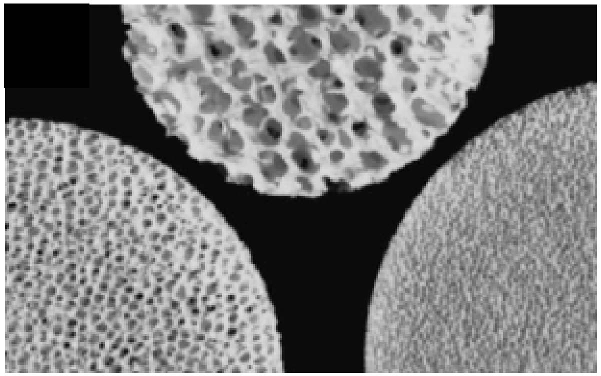
Foams – random structures?



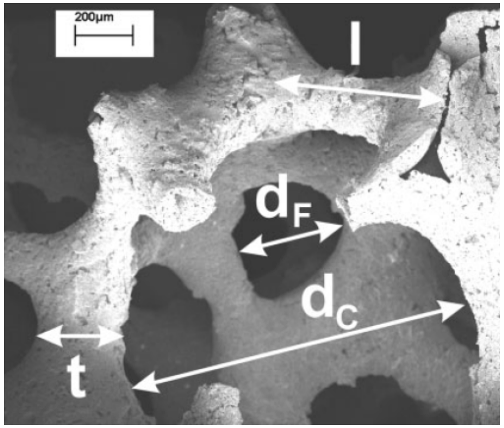
model…



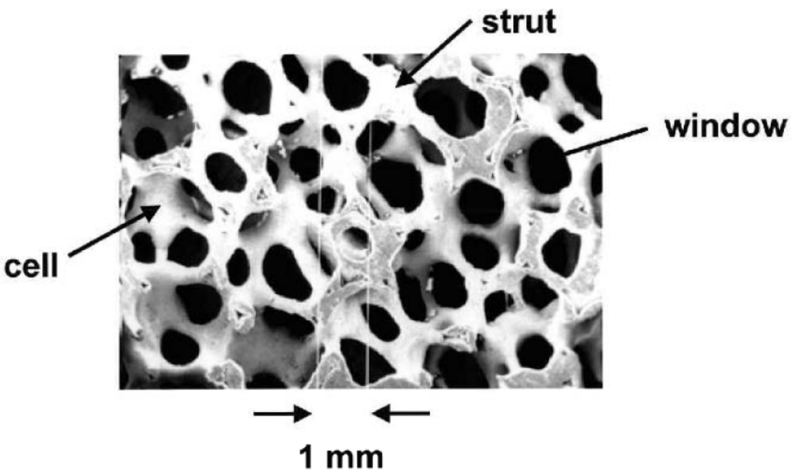
Stemmet, 2008



…and reality

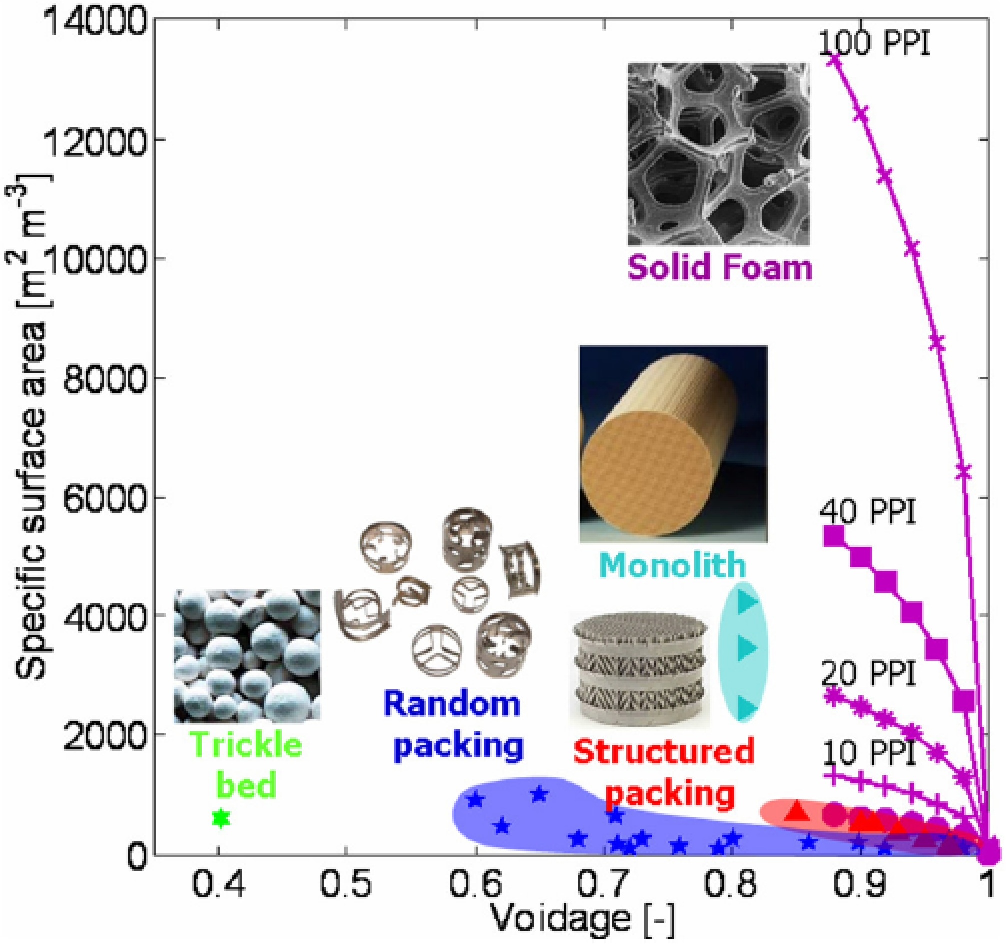


Reitzmann et al., 2006

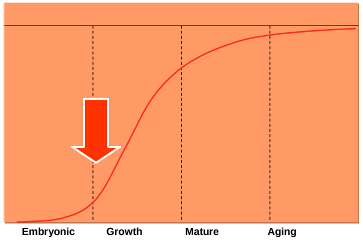


Twigg & Richardson, 2002

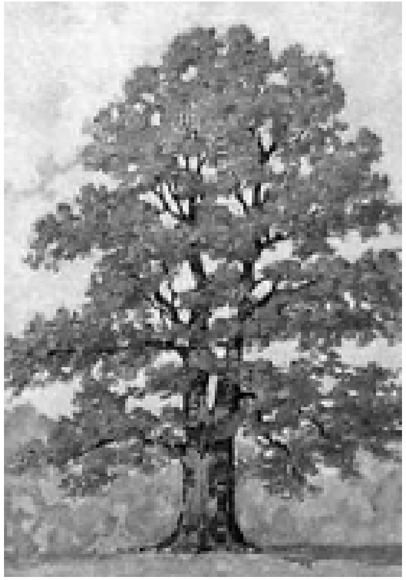
Comparison of structured packings

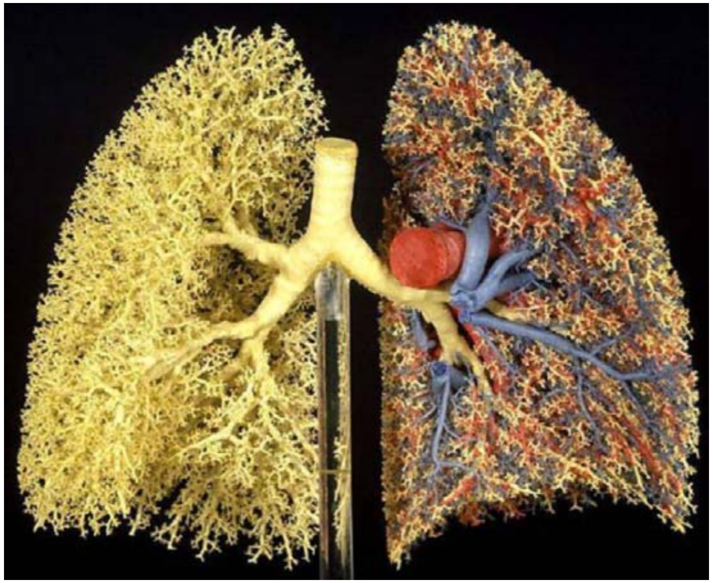


Fractal engineering

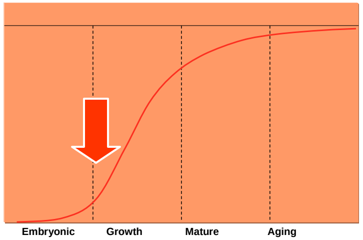


Mimicking natural phenomena

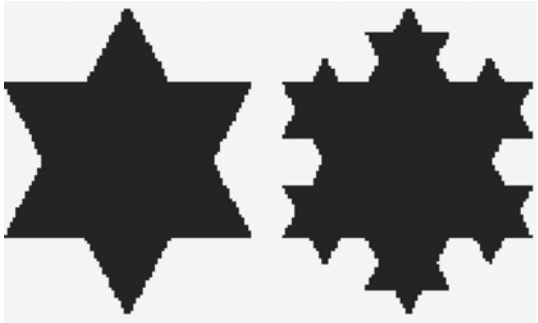


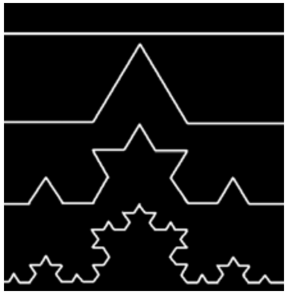


Fractals

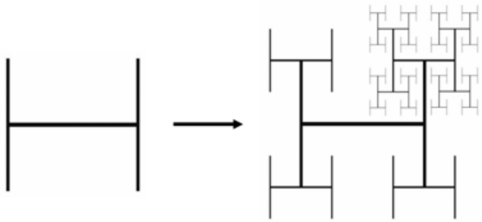


Progressively adding copies of a structure at smaller and smaller scales



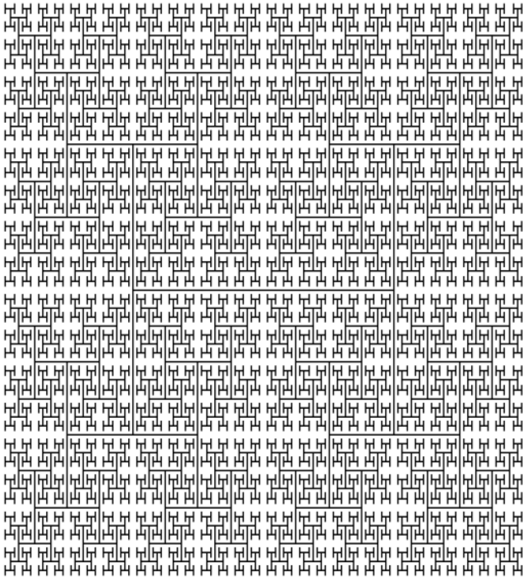


Koch curve

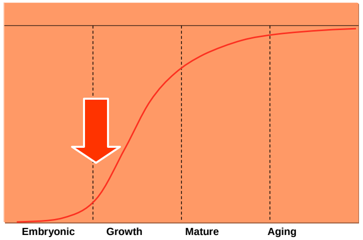


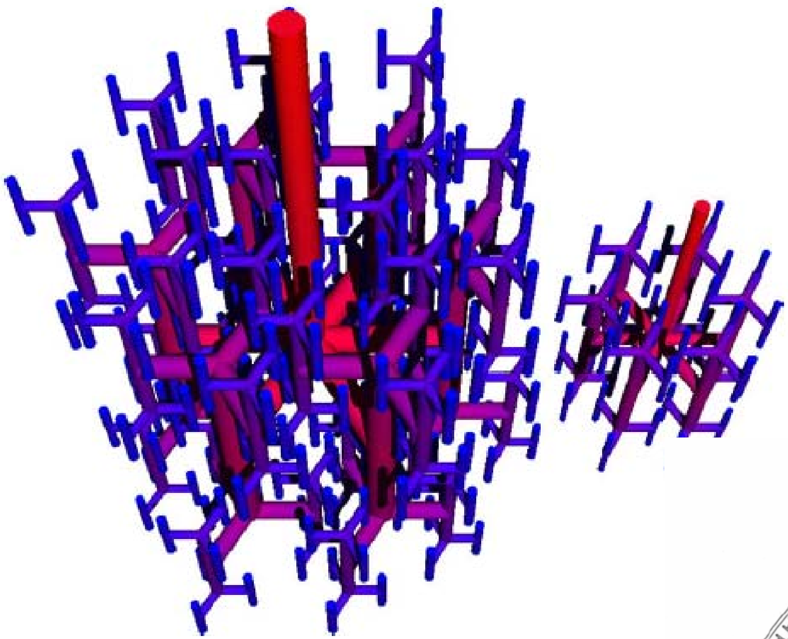
Fractal dimension - 2

After 5 iterations

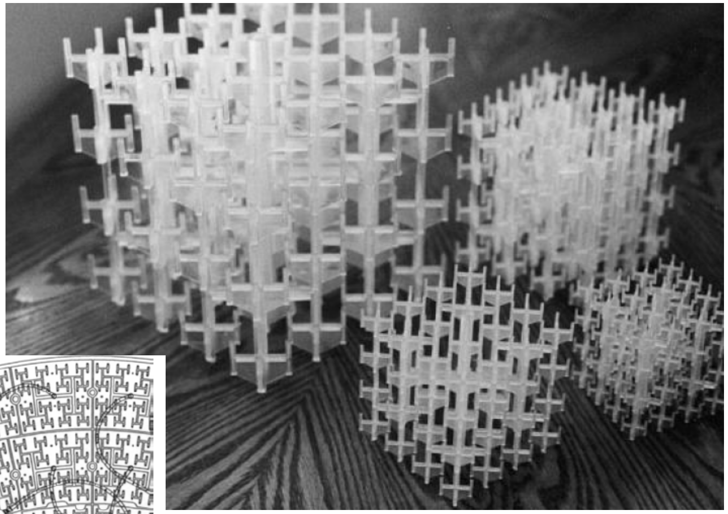


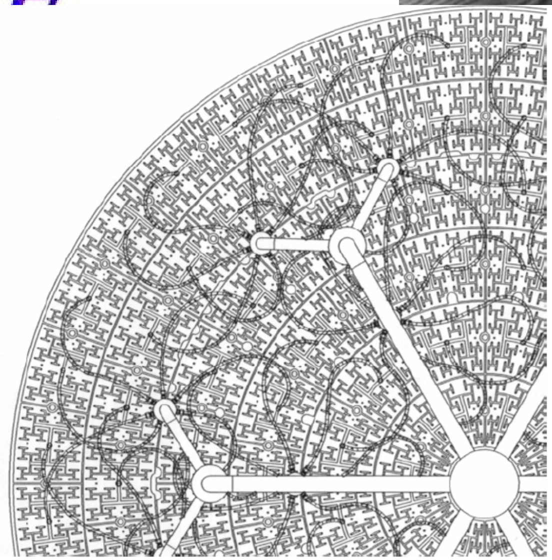
Fractal distributors/collectors

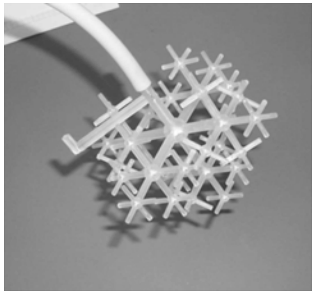




Coppens and Van Ommen., 2003

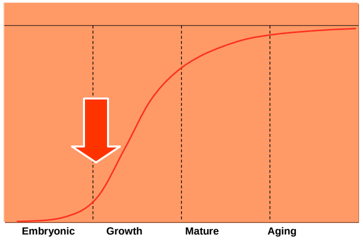


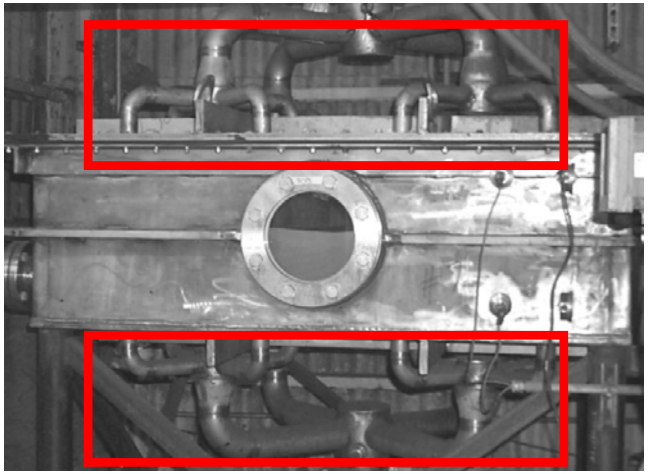




Kochergin and Kearney, 2006

Fluid separations - structure on macro scale





external and internal fractal distributors

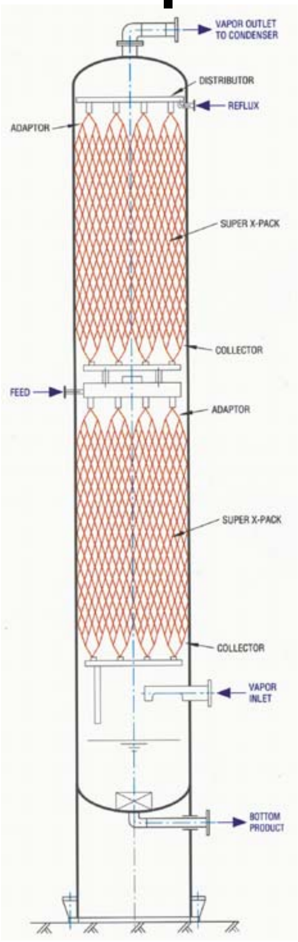
Weak cation softening of juice from sugar beets

Kochergin and Kearney, 2006

	Conventional ion exchange	Fractal ion exchange	Intensification factor
Resin bed depth (inches)	40	6	6.5
Exhaustion flow rate (bed volumes/hour)	50	500	10
Maximum resin bed pressure drop (bar)	3.5-5.6	0.1	>35
Regeneration flow rate (bed volumes/hour	30	150	5
Relative process size	10	1	10

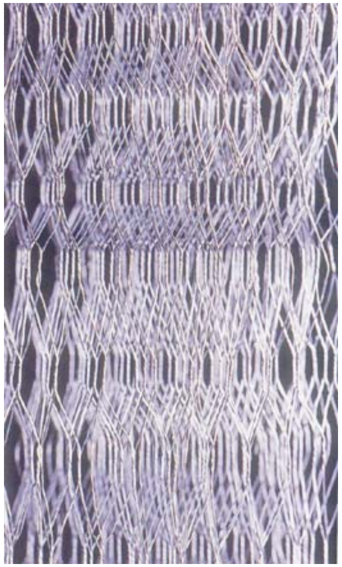
"Fractal" distillation packing

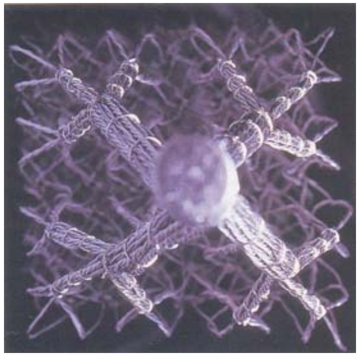
Improved internals for catalytic distillation



Super X-pack (Nagaoka Corp.)

up to 120,000 drip points per m^2





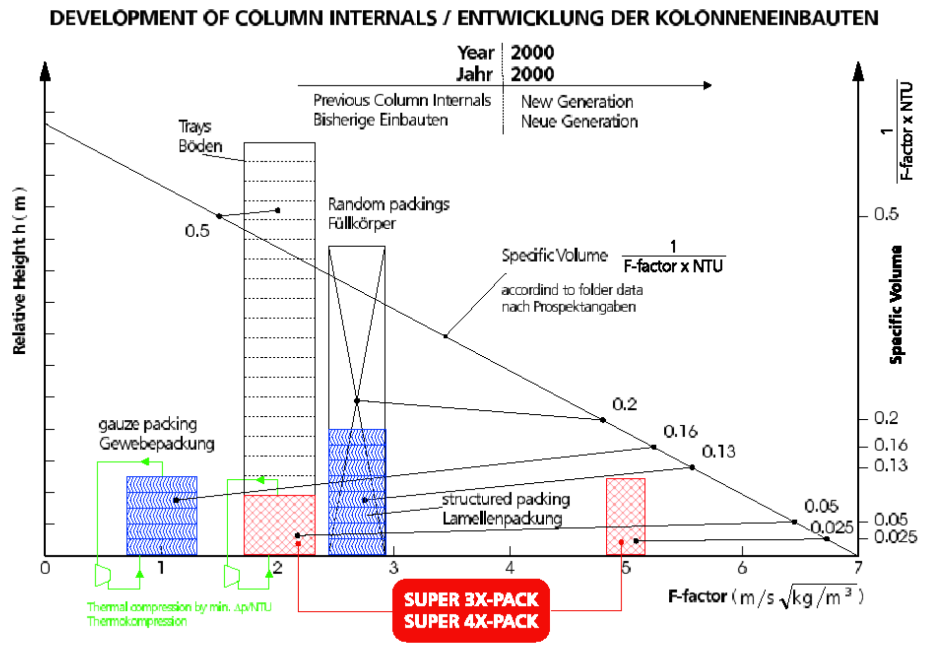
claimed to allow reduction of the size of a distillation column by a factor of 5, and pressure drop by a factor of 3

“Fractal” distillation packing

Improved internals for catalytic distillation

History & Comparison of Column Internals

	1	2	3	4
System				
Operation				
Type	Tray	Random Packing	Structured Packing	Regular Structured Packing
Year & Company	1850	1873	1966	1998 Manteufel NAGAOKA
Design	Various	Raschig Ring Pall Ring Intalox and others	Mellapak Flexipack Intalox and others	SUPER X-PACK
Max. F-Factor	1.5~2.5	1~2.5	2~3	4~7
NTU/h(1/m)	1~2	0.5~2	2~5	6~11
F×NTU	2~4	1~5	5~10	20~40
Spec.Vol 1/(F×NTU)	0.5~0.25	1~0.2	0.2~0.1	0.05~0.025
Ratio of Specific Vol.	1/1	1/2.5	1/3.8	Less than 1/20



MACROSCALE

Contents

- **Structure in heat exchangers**
  - **technologies of high-intensity heat exchangers and their applications**
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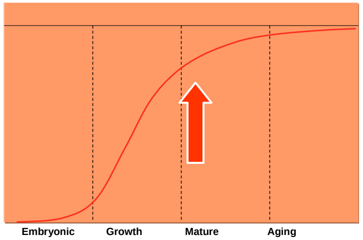
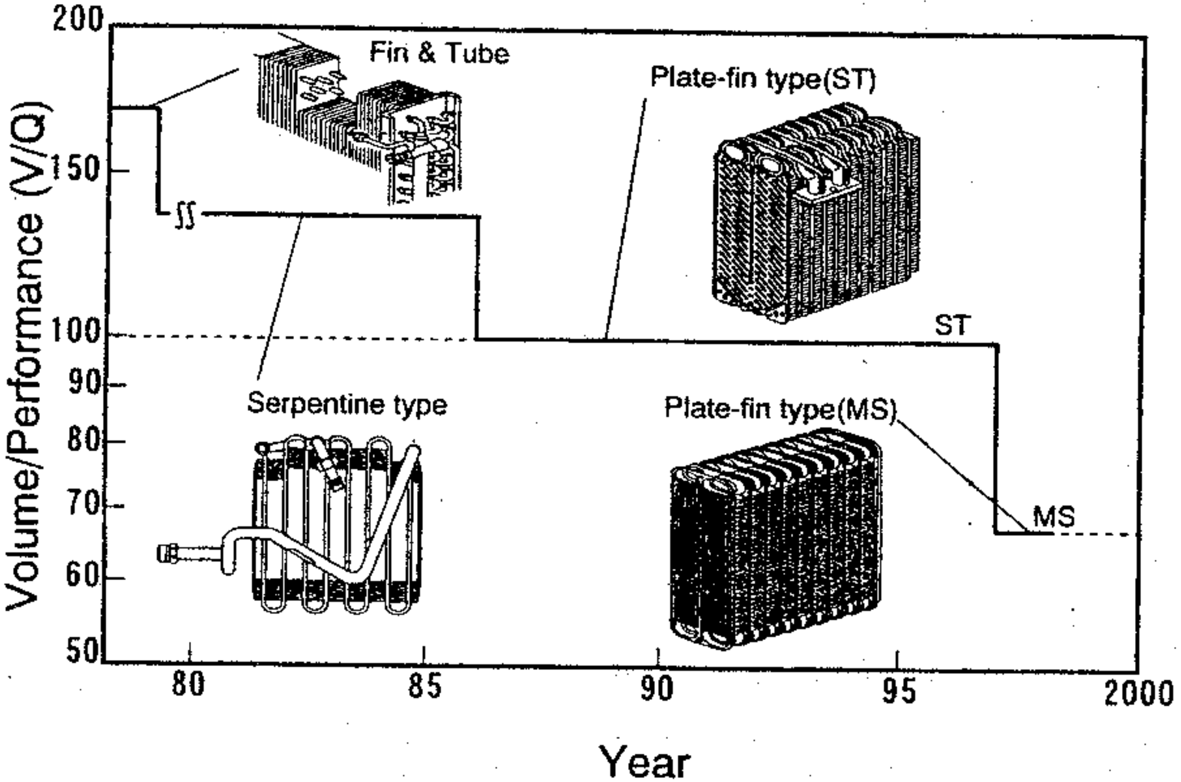
Progress in heat-exchange technology - evaporators

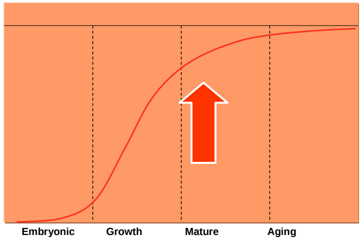


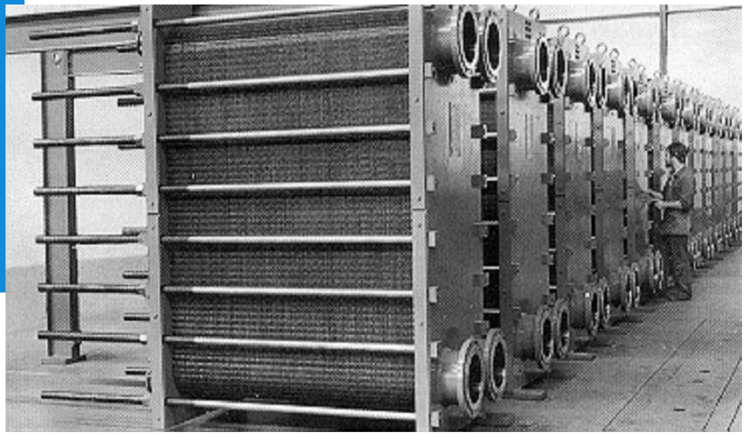


- between the 70's and nowadays the volume/heat capacity ratio has been divided by a factor two

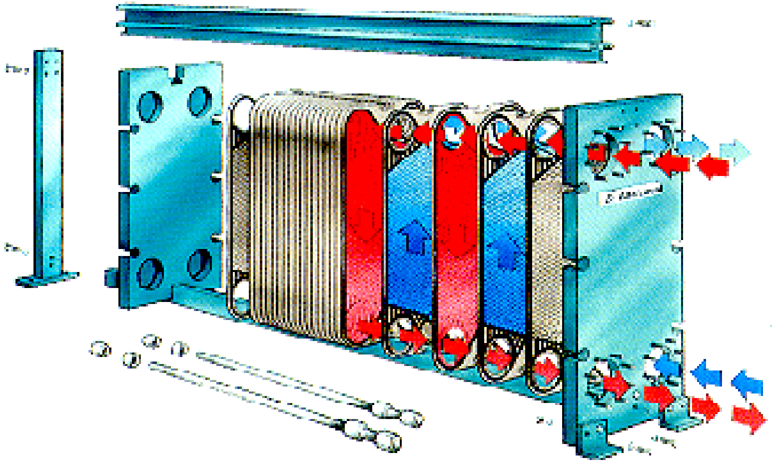
(source: B. Thonon and P. Tochon, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Plate Heat Exchangers (PHE's)

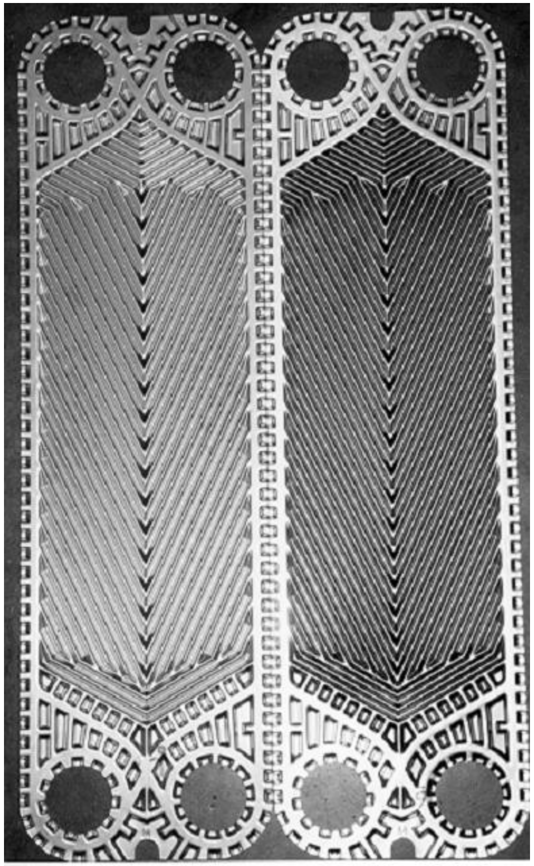




View of plate heat exchanger (courtesy of Alfa-Laval)

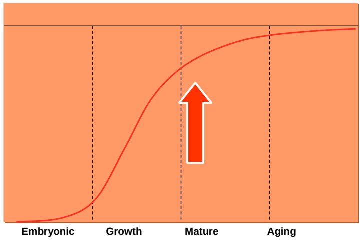


Flow pattern in a plate heat exchanger.



(source: B. Thonon and P. Tochon, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Plate Heat Exchangers (PHE's)

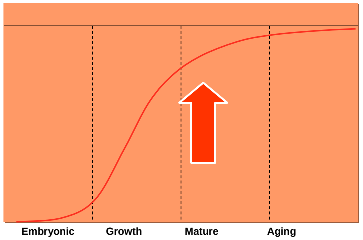


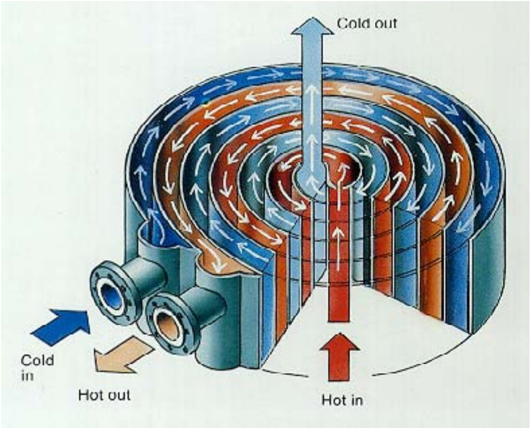
- gasketed PHE is the most common type
- gasket material is selected in function of the application (temperature, fluid nature ...)
- temperature up to 200°C and pressure up to 25 bars can be achieved by such heat exchangers.
- for applications where gaskets are undesirable (high pressure and temperature or very corrosive fluids), semi- welded or totally welded heat exchangers are available
- a welded heat exchanger cannot be opened, and fouling will limit the range of application

(courtesy of Alfa-Laval)

(Source: B. Thonon and P. Tochon, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Spiral Heat Exchangers

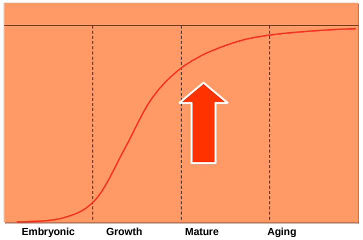




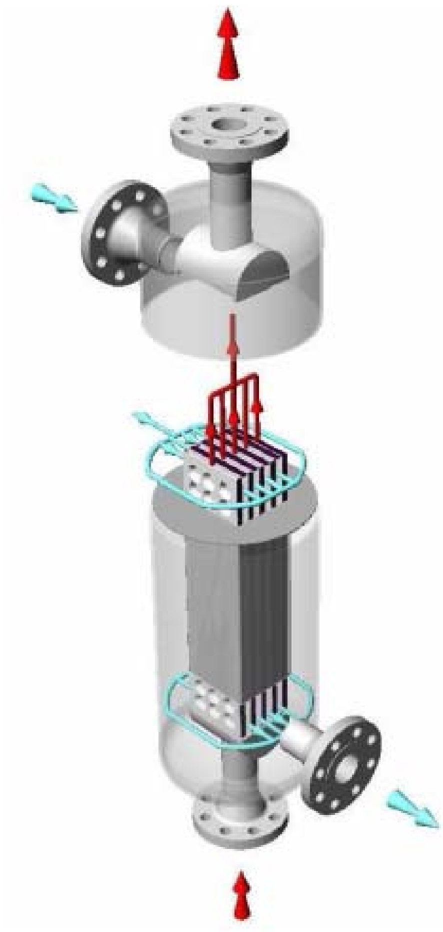
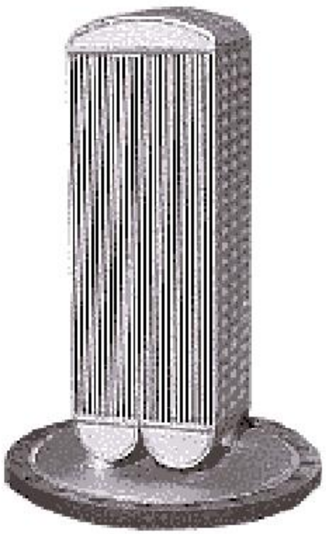
(courtesy of Alfa-Laval)

- two metal sheets that are welded together then rolled to obtain spiral passages
- passages can be either smooth or corrugated
- general flow configuration can be crossflow (single or multipass) or counterflow depending on the configuration of the inlet and outlet distribution boxes
- heat transfer surface ranges from 0.05 m^2 for refrigeration applications up to 500 m^2 for industrial processes

Plate-and-Shell Heat Exchangers



- bundle of plates inserted in a shell
- on the plate side, the fluid flows inside corrugated or embossed channels
- on the shell side, the flow is similar to shell and tube heat exchangers, and baffles can be inserted
- often used for revamping application, as the shell can be kept identical as for a bundle of tubes

Platular® heat exchanger
(Courtesy of Barriquand Technologies Termiques)

(source: B. Thonon and P. Tochon, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Selection of heat exchanger technology

Technology	Maximal pressure bars	Maximal temperature °C	Number of streams	Fouling
Aluminium plate fin heat exchanger	80-120	70-200	> 10	no
Stainless steel plate fin heat exchanger	80	650	> 2	no
Ceramic plate fin heat exchanger	4	1300	2	no
Diffusion bonded heat exchanger	500-1000	800-1000	> 2	no
Spiral heat exchangers	30	400	2	yes
Matrix heat exchangers	1000	800	> 2	no
Flat tube and Fin heat exchanger	200	200	2	no
Brazed plate heat exchanger	30	200	2	no
Welded plate heat exchanger	30-40	300-400	> 2	yes/no
Plate and shell heat exchangers	30-40	300-400	2	yes/no
Gasketed plate heat exchanger	20-25	160-200	> 2	yes
Graphite plate heat exchanger	7	180	2	yes
Plastic plate heat exchanger		200-250	> 2	yes/no

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- Microreactors

Why is mixing important

- **usually not a problem in a chemist’s beaker, where mixing can be very rapid**
- **if it scaled up into a batch stirred vessel, mixing inevitably becomes slower**
- **if mixing time is slower than the reaction time, the reaction will be artificially slowed down - it becomes mixing, rather than kinetic, limited**
- **in a typical process**

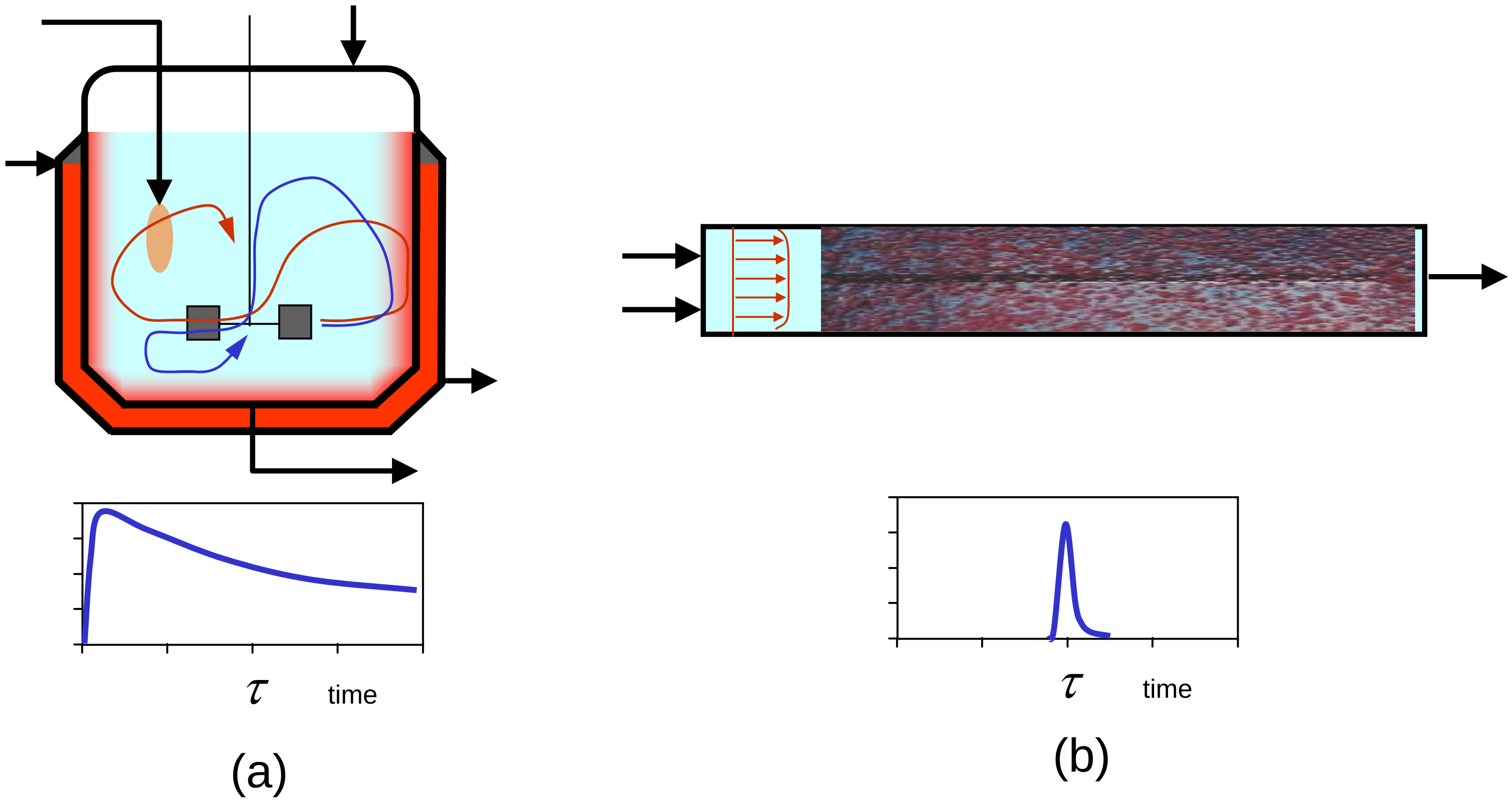
$$A + B \rightarrow R$$

$$R + B \rightarrow S$$

if the second reaction is much slower than the first, there should not be too much S formed; however if mixing is slow, the first reaction can be artificially slowed down, which will then tend to favour production of S – and yield of R will reduce

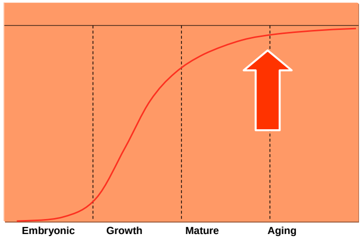
(source: A. Green, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

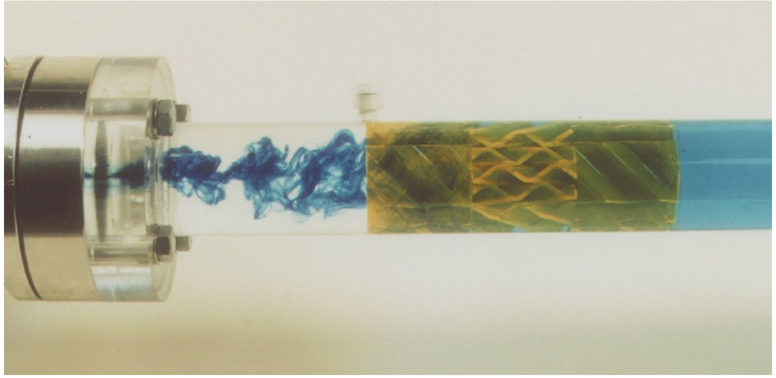
Why is mixing important



Giving each molecule the same processing history

Motionless or static mixers - advantages

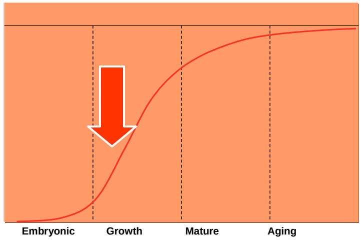


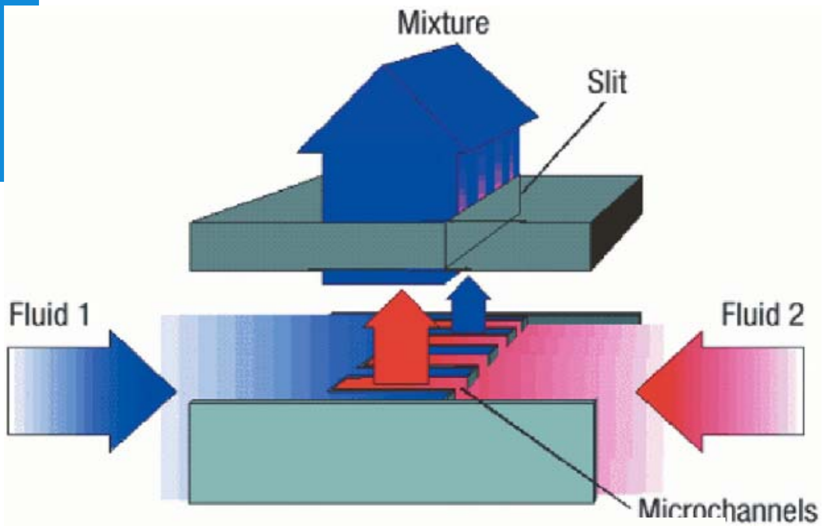


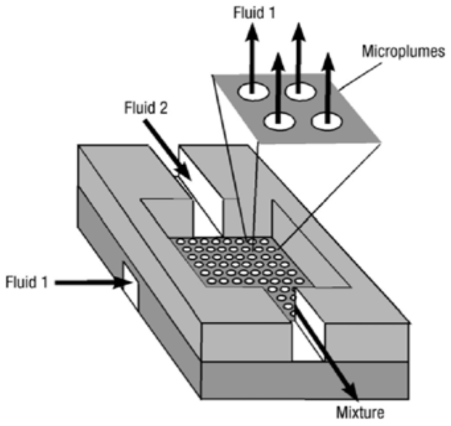
- motionless mixers are compact, thus requiring a small site and a lower capital expenditure (CAPEX)
- inherent safety is improved due to a smaller reacting inventory
- since there are no moving parts, sealing problems are reduced and maintenance is minimized
- resistance to interphase mass transfer is considerably smaller than in conventional equipment, mass transfer coefficient (kLa) can be 10 to 100 times higher than in a stirred tank
- flow pattern in a motionless mixer is approximately plug flow, i.e., different elements of fluid spend similar time periods in the mixer

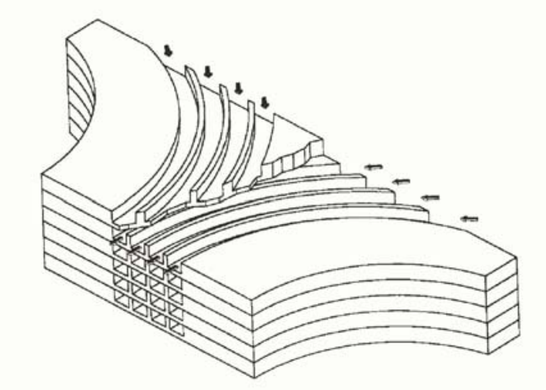
(source: A. Green, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

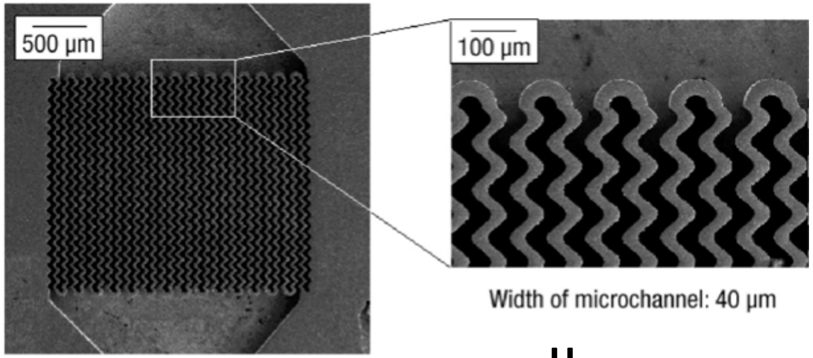
Structured microprocessing systems - micromixers











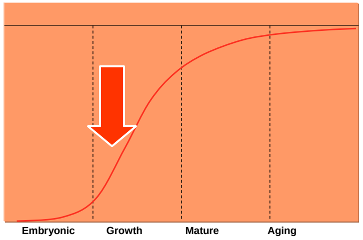
Mixing element with 2 x 15 microchannels

Width of microchannel: 40 µm

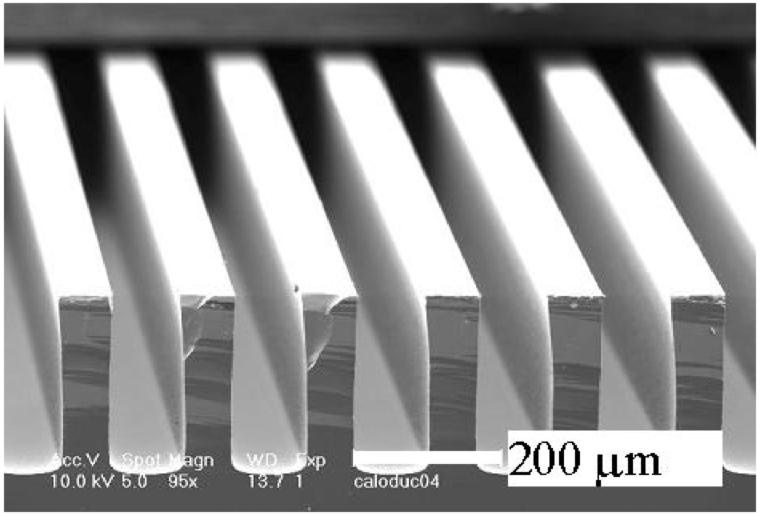
µ

(Ehrfeld, et al., Ullmann's Encyclopedia of Industrial Chemistry,1999)

Microchannel Heat Exchangers



- **MICRO HEAT EXCHANGERS: used for cooling of electronic devices or micro-reactors**
- **channel size usually below 200 µm**
- **single-phase or boiling**

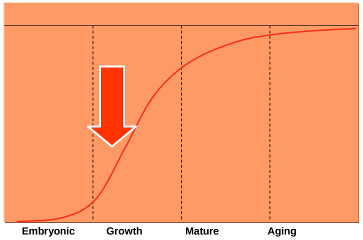


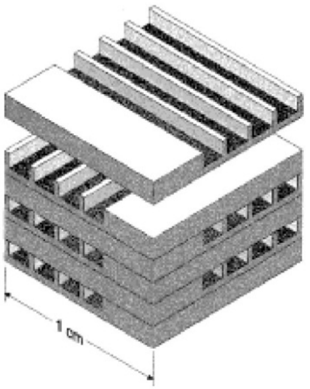
Silicium deep etching micro-channels (CEA)

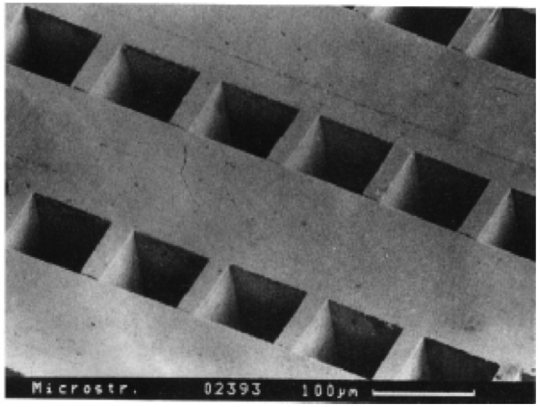
Micro heat exchangers (FZK)

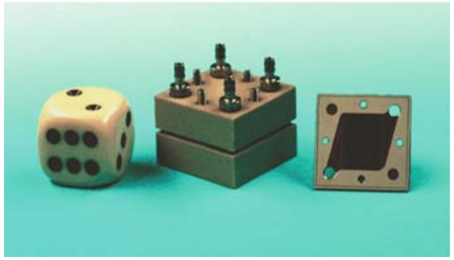
(source: B. Thonon and P. Tochon, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

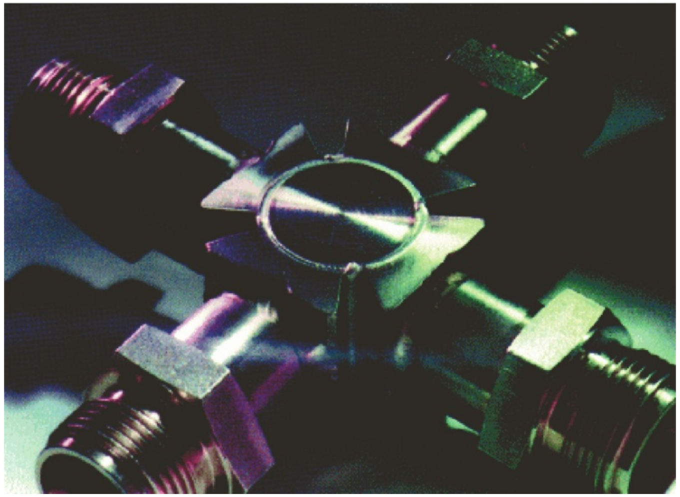
Microchannel Heat Exchangers

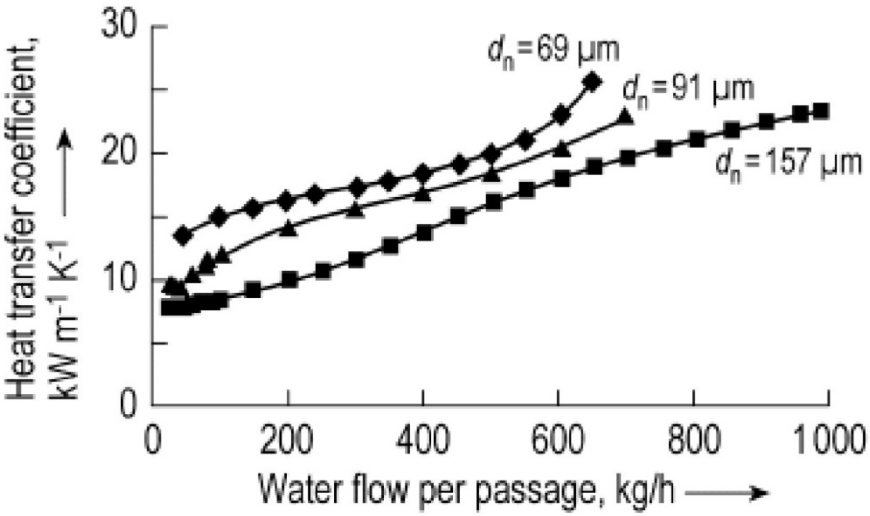








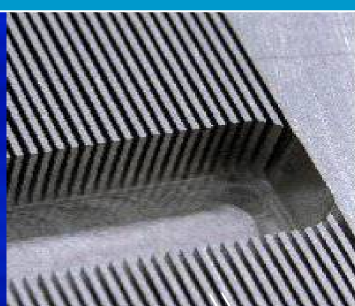




(Ehrfeld, et al., Ullmann's Encyclopedia of Industrial Chemistry,1999)

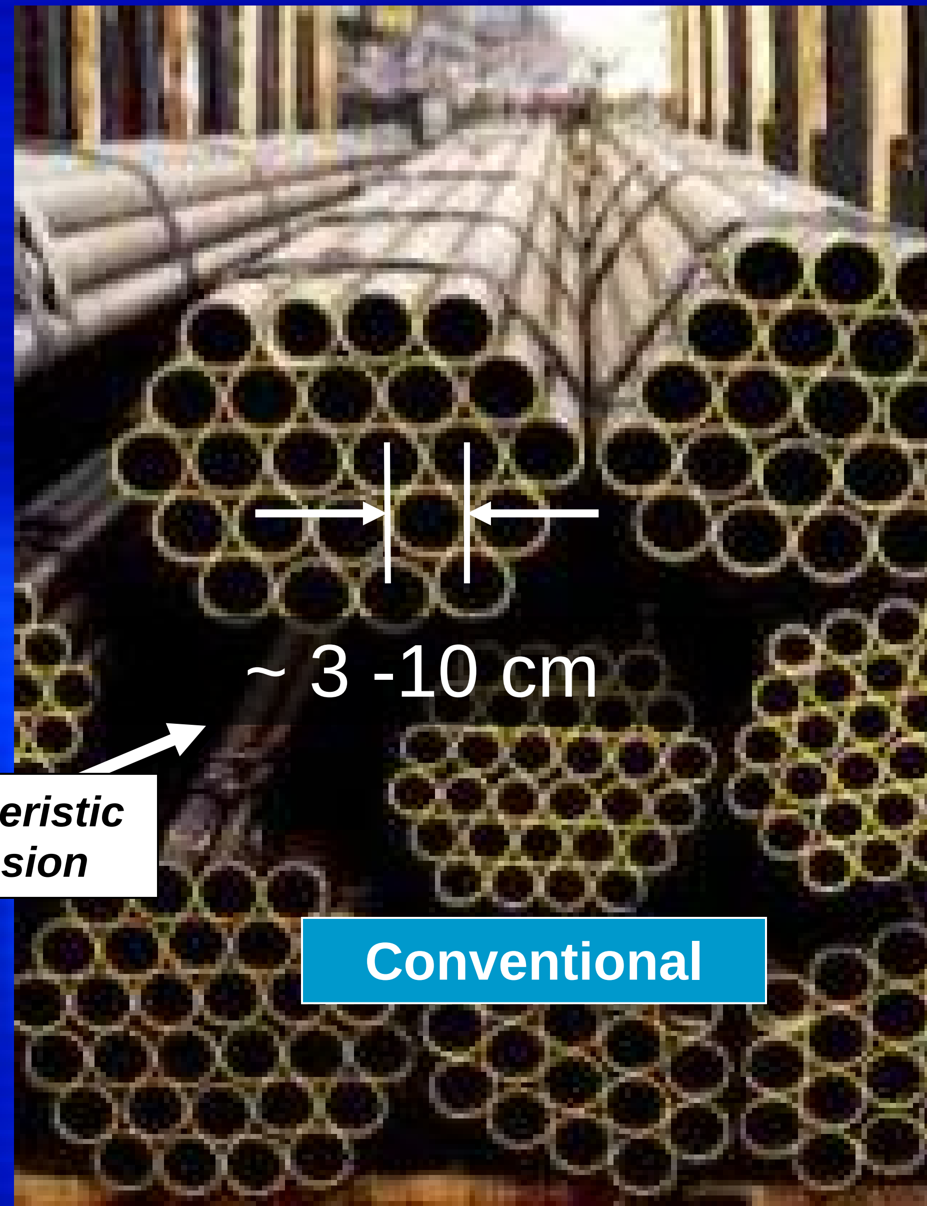
Microchannel Reactors

Velocys



~ 0.1-0.3 mm

Characteristic dimension



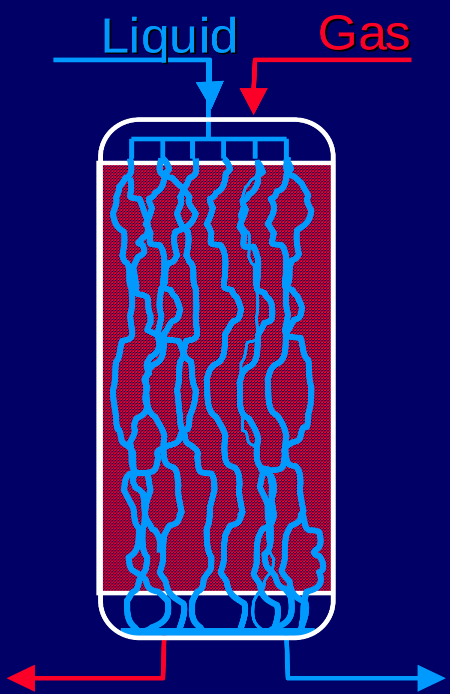
Velocys® Technology Microchannel Reactors

- Microchannel Steam Methane Reformer
- Same capacity
- 90% volume reduction
- ~25% reduction in overall plant costs

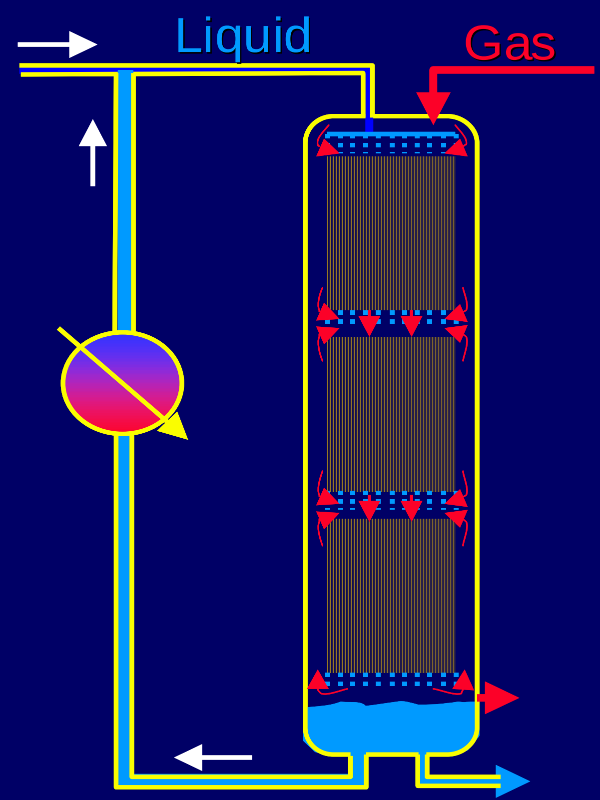
Structure versus randomness: an industrial example

Structure versus randomness:
Monolithic reactor versus trickle-bed reactor

Trickle Bed



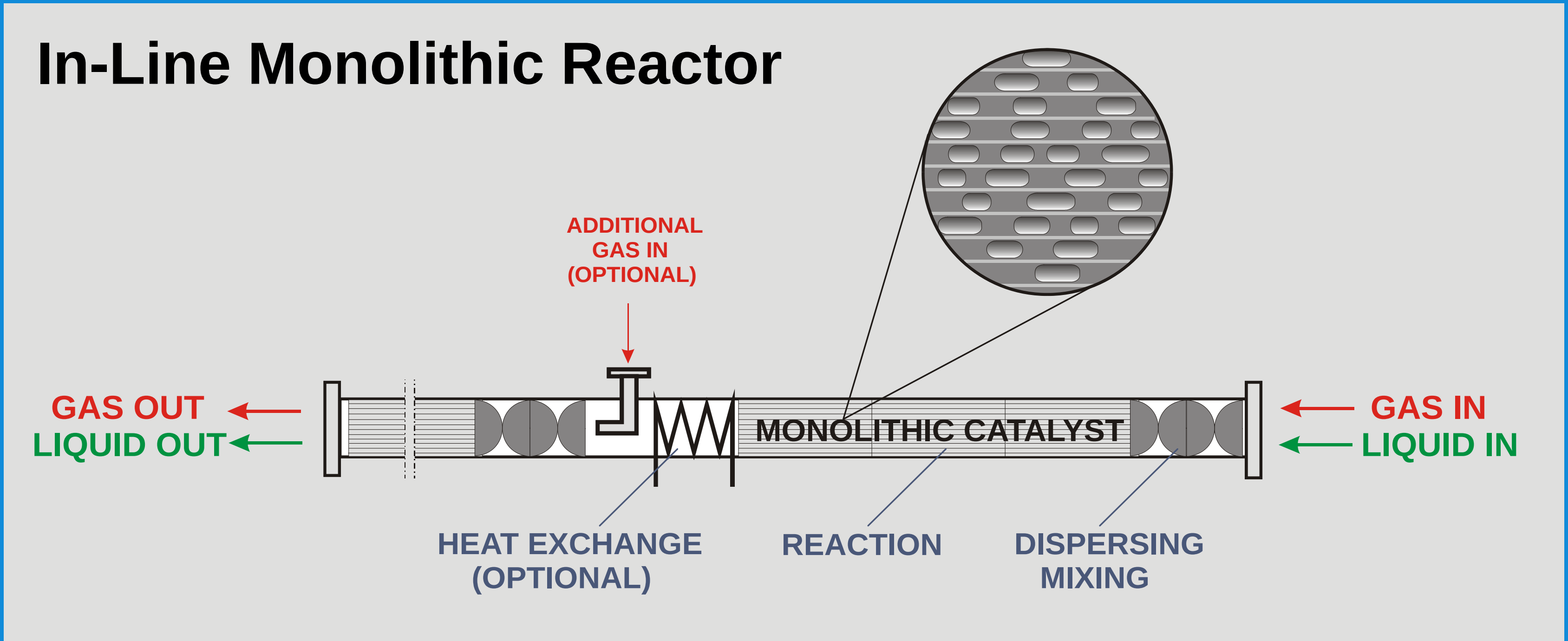
Monolithic Reactor



- ☹ low utilization of catalyst volume
- ☹ secondary flow low distribution – hot-spots/runaways
- ☹ considerable pressure drop
- ☹ uneasy scale-up

- ☺ very short diffusion path in the washcoat
- ☺ high specific surface areas
- ☺ very low pressure drop
- ☺ straightforward scale-up

PI in In-Line Monolithic Reactor (ILMR)



HAS ALL ADVANTAGES OF "CONVENTIONAL" MONOLITHIC REACTORS

+

- ☺ ENABLES STABLE OPERATION OVER A BROADER RANGE OF FLOW VELOCITIES
- ☺ CAN BE MUCH LONGER THAN VERTICAL UNITS (HIGHER CONVERSIONS PER PASS, SMALLER RECYCLES)
- ☺ ENABLES DISTRIBUTED GAS-FEED (TO INCREASE YIELD/SELECTIVITY)

+

Vision: safer processing in functional pipeline

Case study: industrial hydrogenation process

$A + H_2 \rightarrow C$

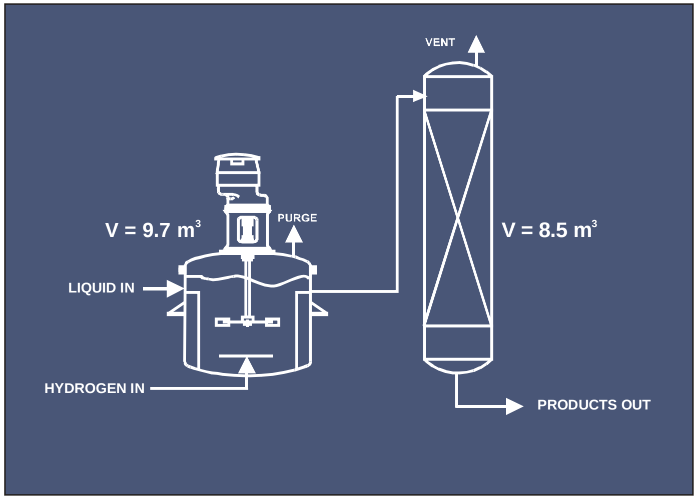
$B + H_2 \rightarrow D$

Kinetic experiments: slurry reactor

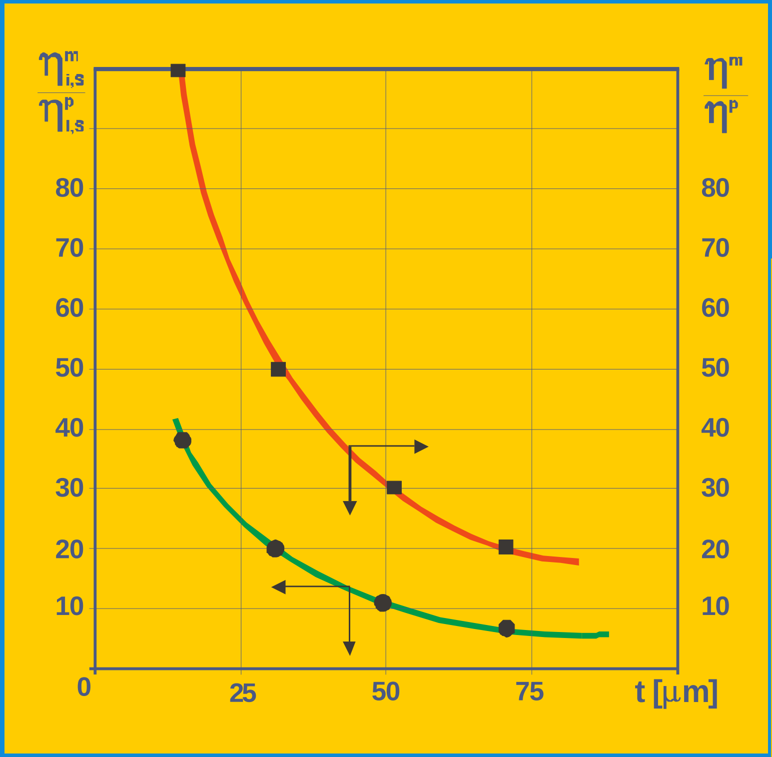
particle size: 20-50 µm

k_1 = 3.94E-03 $m_{liq}^3 s^{-1} kg_{cat}^{-1}$; E_{A1} = 56.8 kJ/mol;
k_2 = 5.13E-03 $m_{liq}^3 s^{-1} kg_{cat}^{-1}$; E_{A2} = 57.3 kJ/mol;

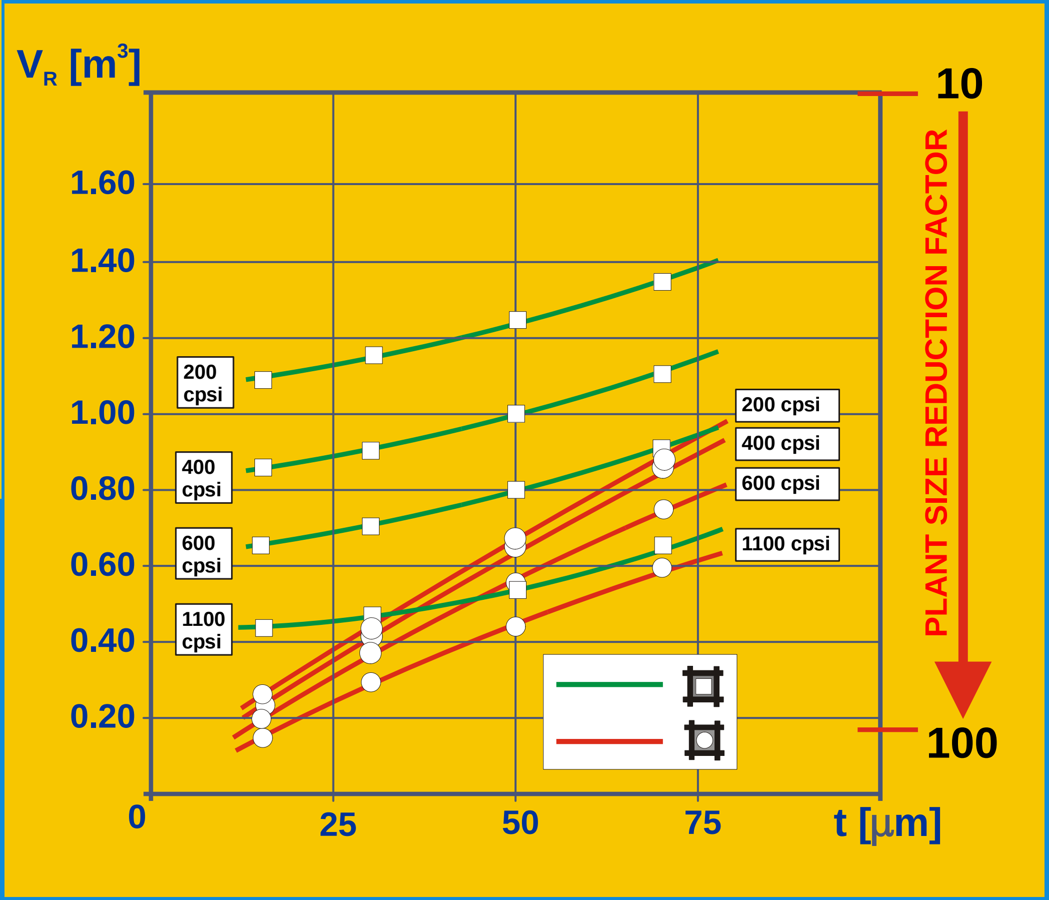
- **liquid-phase process**
- **Pd/C catalyst, ca. 3.5 mm**
- **concentration of A and B: low**
- **liquid viscosity: high**
- **residence time: long**
- **rate limited by diffusion of hydrogenated compounds;**



PI in In-Line Monolithic Reactor (ILMR)



Results



PI in In-Line Monolithic Reactor (ILMR)

30-100x reduction of equipment volume