technische universität dortmund

Department of Biochemical and Chemical Engineering

Distillation goes
bio, micro, hybrid, cylic, high gravity:
hype or high potential?

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Politechnika Łódzka

fvt laboratory of fluid separations

Energy consumption

Total energy consumption in Germany (2010): 2517 TWh

Source: umweltbundesamt.de

Transport sector 28.3 %

Business, trade and service sector 15.2 %

Private households 28.5 %

Industry 28.0 %

Figures: Source Fotolia, dena, ICHEM
Courtesy: Peter Kreis, EVONIK

Energy consumption

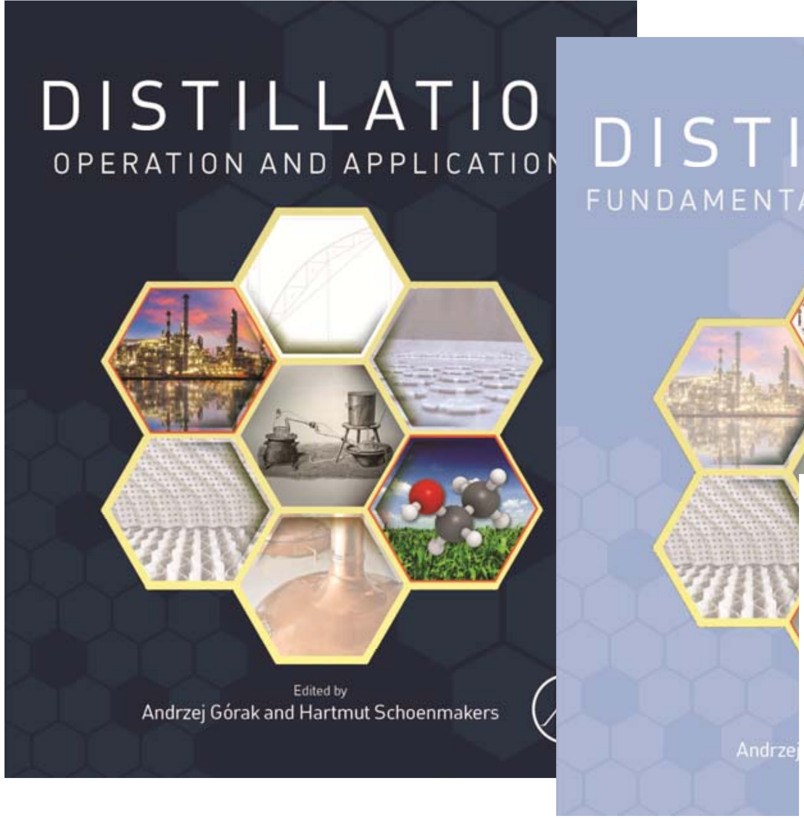
Facts:

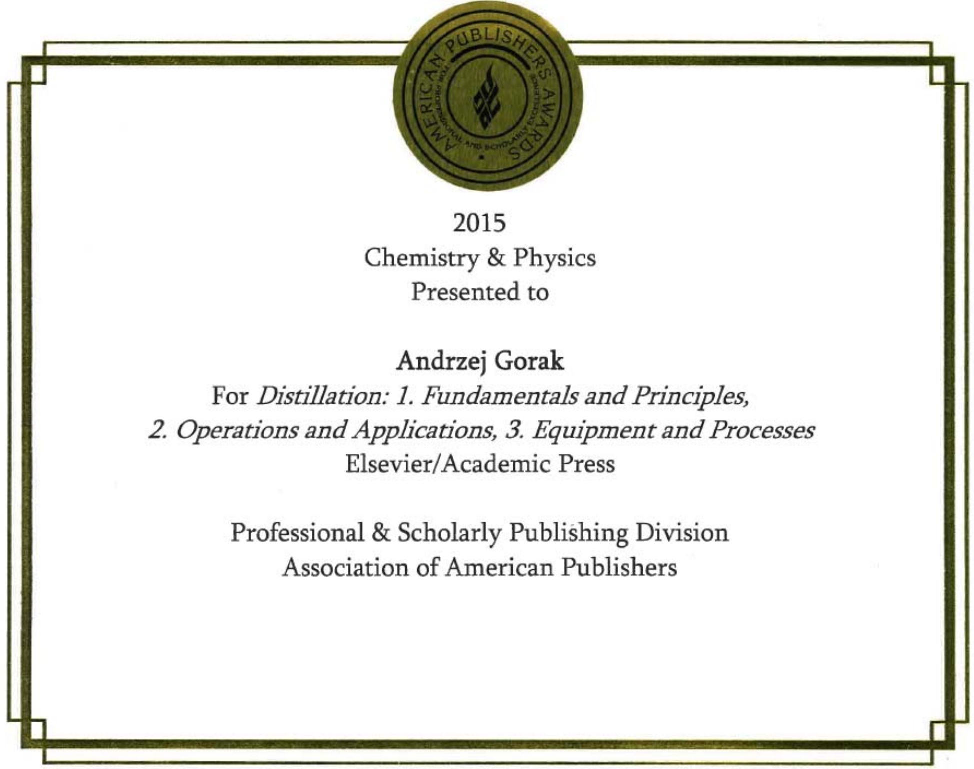
- In 2009, the chemical industry consumes 19% of the total energy in Europe – European Commission, 2011
- 40-60% of the total energy used in the chemical industry is for fluid separations – *Harvey, 2010; Sattler, 1995*
- Around 95% of thermal energy necessary for separation is used by distillation - *Industrial Technologies Programme, 2005*
- Caloric value of an organic compound is 20 GJ/t; for the production 70 GJ/t of total fossil input introduced - *Sanders et al., 2012*
- 6 per cent of total US energy consumption goes for distillation

Additional challenges:

- Worldwide need for energy will increase
- Further increase in energy prices
- Large amount of energy is currently losted in waste streams
- Change in raw materials (bio-based) may lead to more diluted systems

All about distillation!





2015
Chemistry & Physics
Presented to

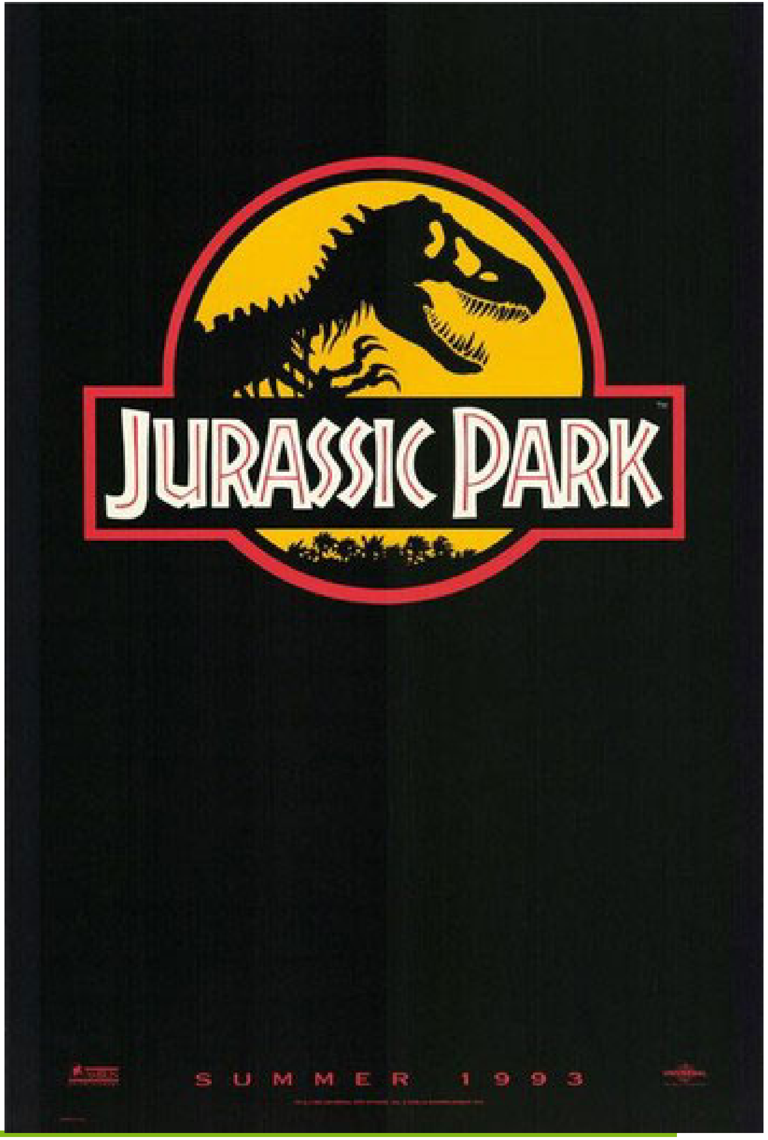
Andrzej Gorak
For *Distillation: 1. Fundamentals and Principles,*
2. Operations and Applications, 3. Equipment and Processes
Elsevier/Academic Press

Professional & Scholarly Publishing Division
Association of American Publishers

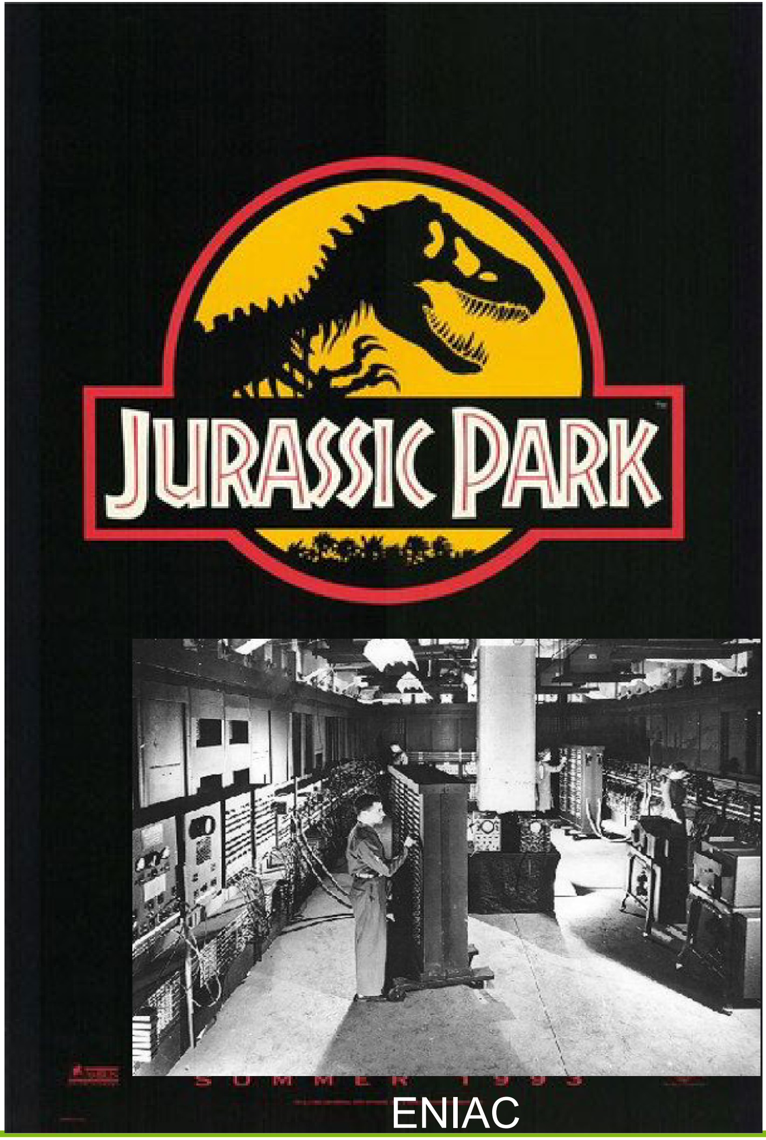
Dinosaurs of chemical industry

https://www.flickr.com/photos/yumiko_sato/13270111055

Dinosaurs of chemical industry



Process Intensification



ENIAC

What is Process Intensification (PI)?

A strategy for making dramatic reductions in the size of a chemical plant so as to reach a given production objective – Ramshaw 1995

Any chemical engineering development that leads to a substantially smaller, cleaner, and more efficient technology is process intensification – Stankiewicz 2000

smartphone

Process Intensification

FUNDAMENTALS OF
PROCESS INTENSIFICATION

Ind. Eng. Chem. Res. **2009**, *48*, 2465–2474 **2465**

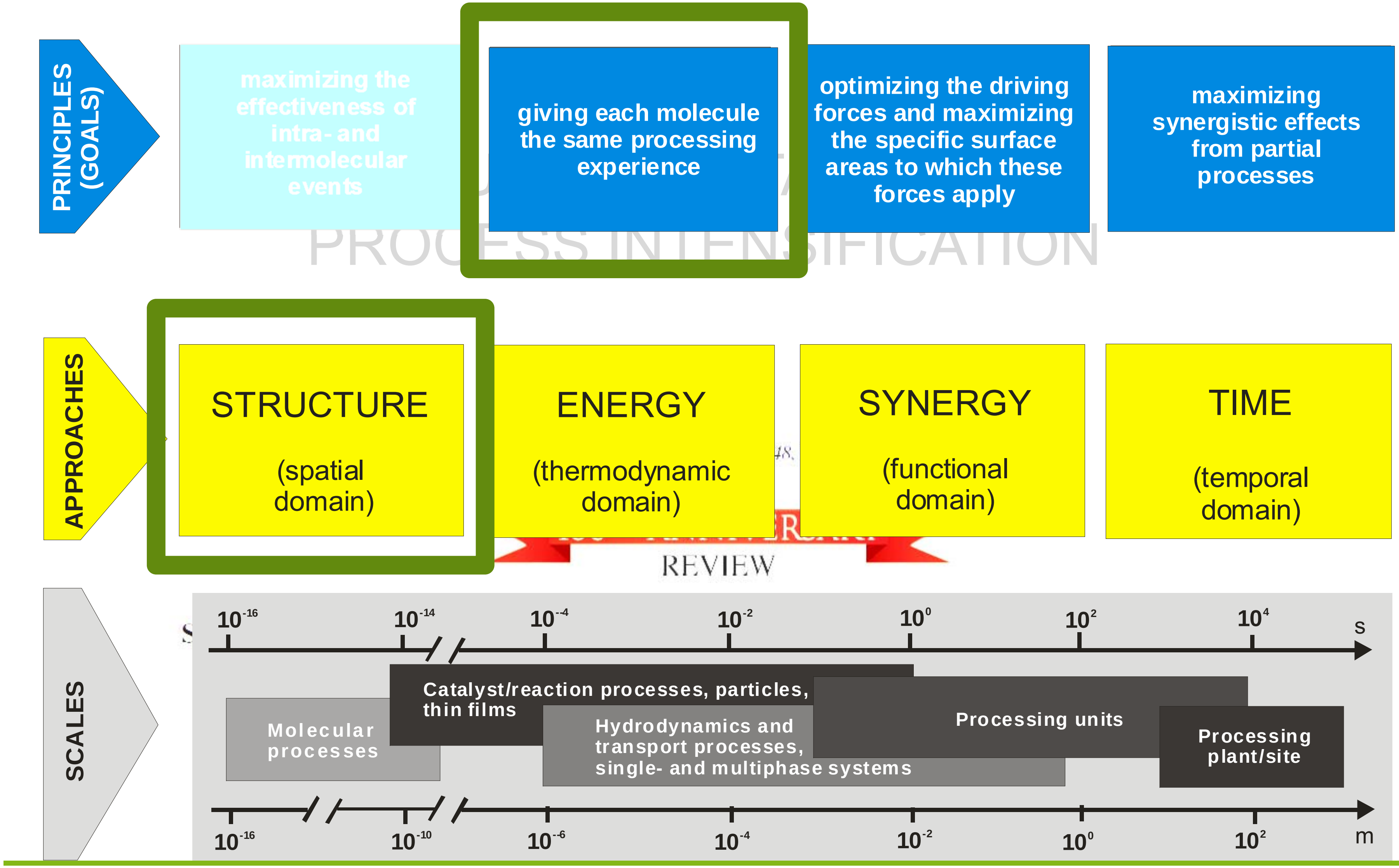
100TH ANNIVERSARY
REVIEW

Structure, Energy, Synergy, Time—The Fundamentals of Process Intensification

Tom Van Gerven[†] **and Andrzej Stankiewicz***

Process & Energy Department, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

Process Intensification: **Intensifying distillation**



PRINCIPLES (GOALS)

- maximizing the effectiveness of intra- and intermolecular events
- giving each molecule the same processing experience
- optimizing the driving forces and maximizing the specific surface areas to which these forces apply
- maximizing synergistic effects from partial processes

APPROACHES

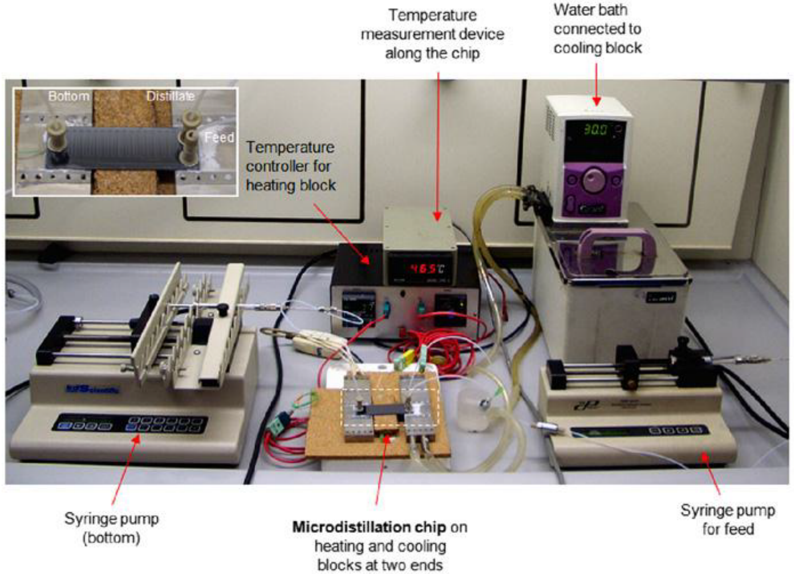
- STRUCTURE (spatial domain)
- ENERGY (thermodynamic domain)
- SYNERGY (functional domain)
- TIME (temporal domain)

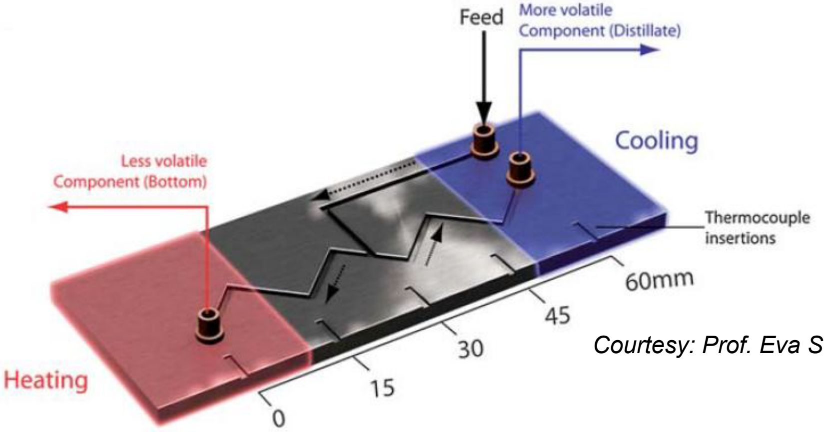
SCALES

Distillation goes micro: microdistillation

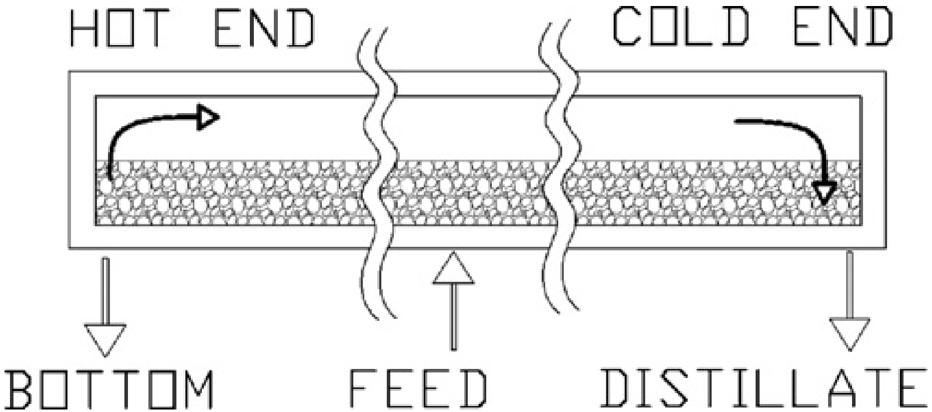
Distillation on the chip

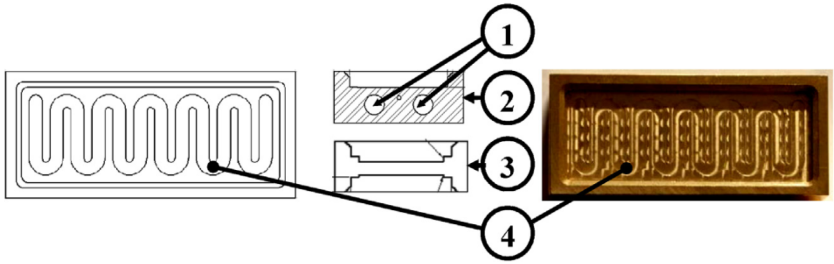
K.F. Lam, E. Cao, E. Sorensen, A. Gavriilidis, Development of multistage distillation in a microfluidic chip, Lab Chip 11 (2011) 1311-1317.





Courtesy: Prof. Eva Sorensen, UCL

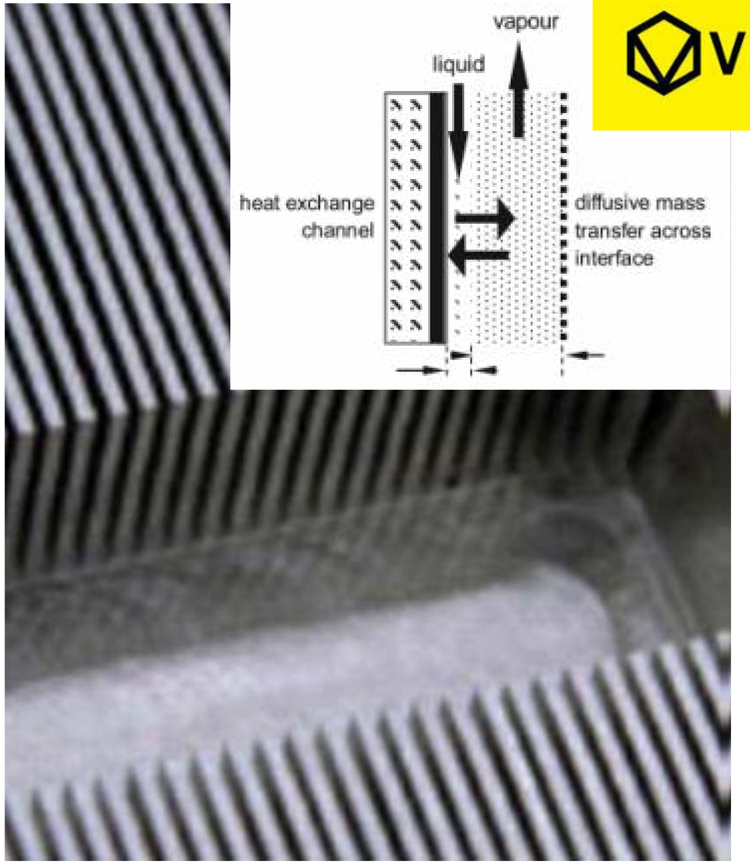




heating cartridges (1); reboiler and preheater design (2); heat exchanger design (3); process fluid channel (4).

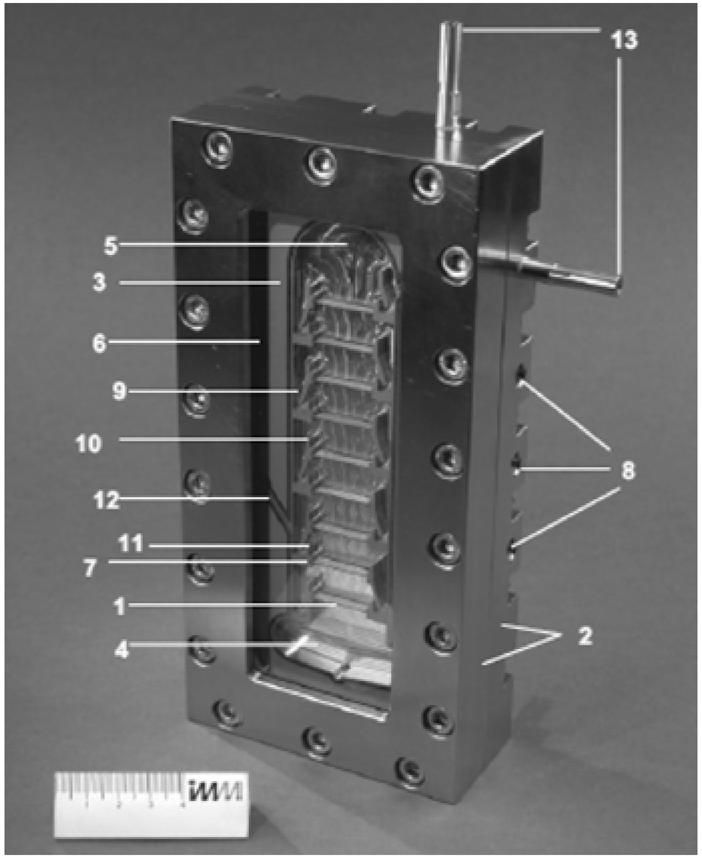
A. Sundberg et.al, Control of reflux and reboil flowrates for milli and micro distillation, Chem.Eng.Res.Des. 91 (2013)753

Micro: for regulated substances (pharma applications)



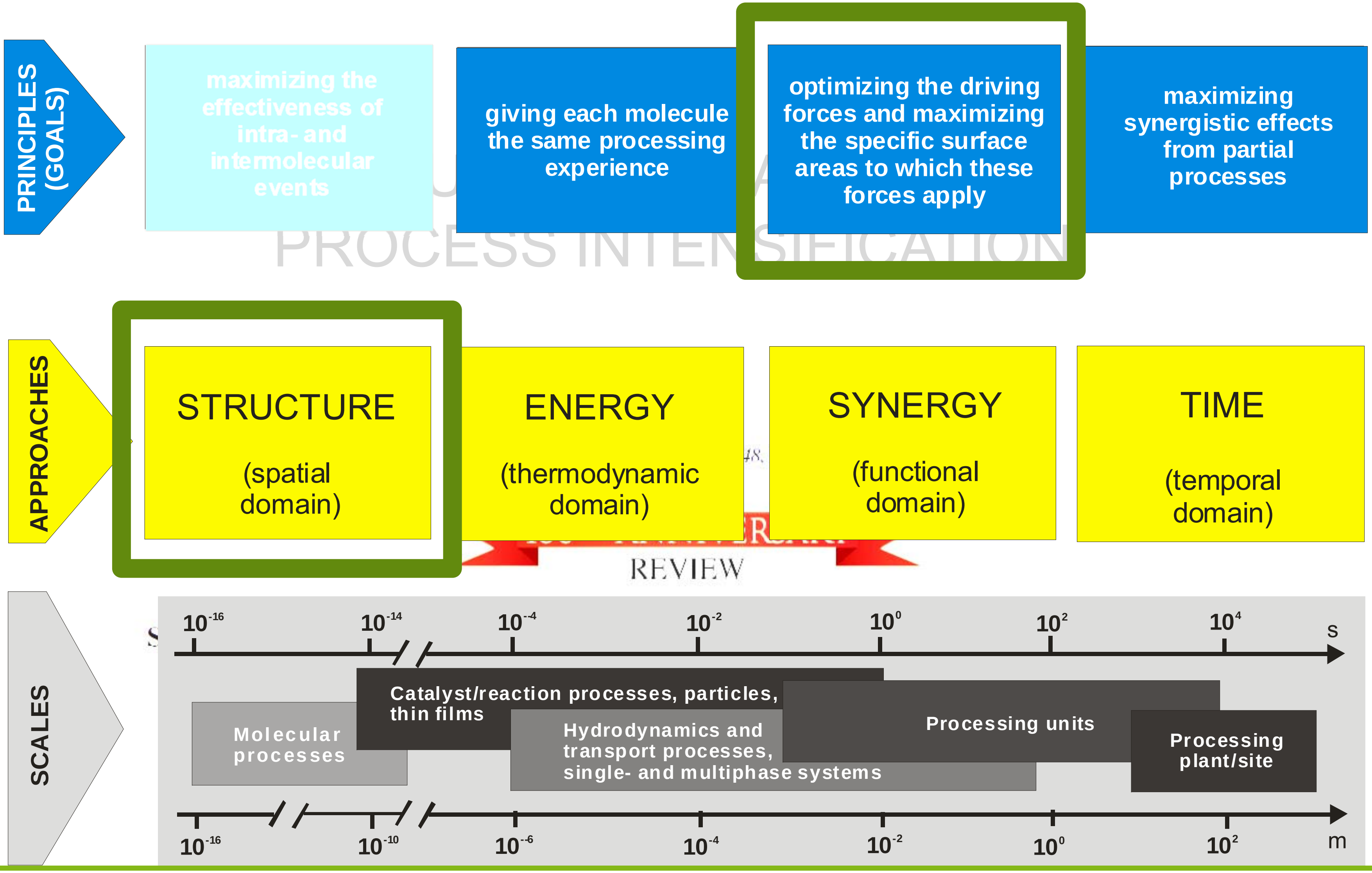
VELOCYS

Microchannel Technology Enables Advanced Distillation Processes



E. Kenig, Y. Sua, A. Lautenschleger, P. Chasanis, M. Grünewald:Technology Micro-separation of fluid systems: A state-of-the-art review, Sep. Purif., 120(2013)245
T. Wellsandt, B. Stanisch, J. Strube: Characterization Method for Separation Devices Based on Micro Technology, Chemie Ingenieur Technik 87(2015)150

Process Intensification: **Intensifying distillation**



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APPROACHES

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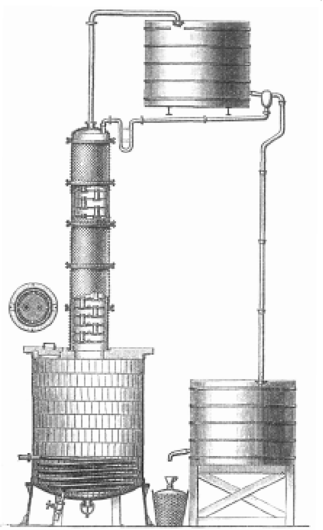
- SYNERGY (functional domain)
- TIME (temporal domain)

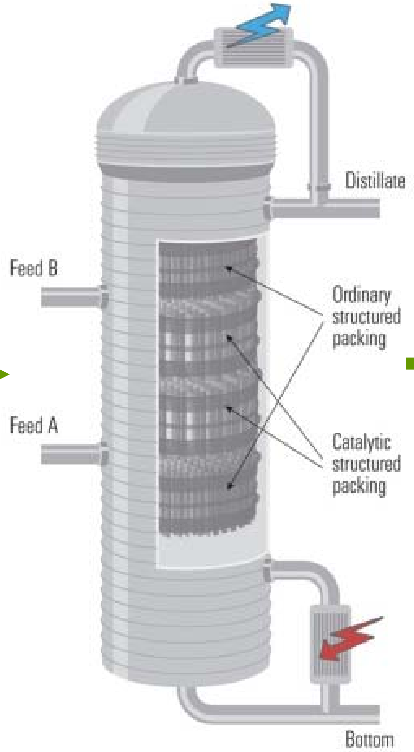
SCALES

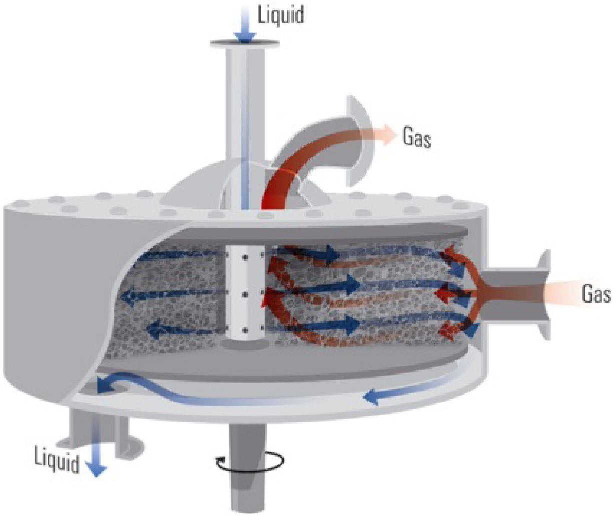
- Molecular processes
- Catalyst/reaction processes, particles, thin films
- Hydrodynamics and transport processes, single- and multiphase systems
- Processing units
- Processing plant/site

Distillation goes high gravity: HiGee distillation



www.zeno.org





Ramshaw, C.: 'HIGEE' Distillation - An Example of Process Intensification. Chem. Eng.(London) (1983) 389, 13

Distillation goes high gravity: HiGee distillation

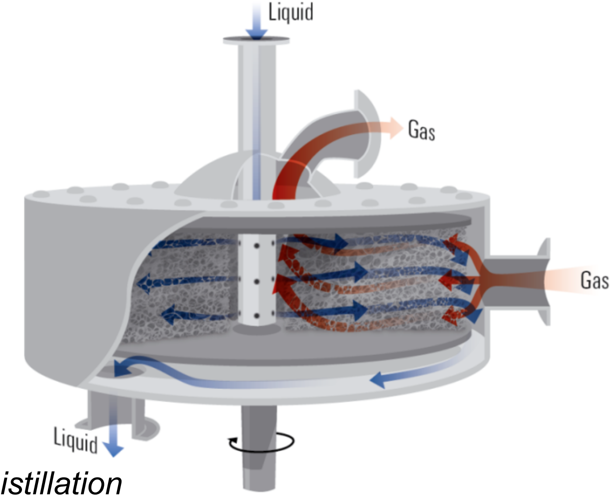
Rotating (reactive) Packed Bed vs. Packed Column

Advantages of RPB

- high centrifugal forces:
  - higher capacity (less flooding)
  - higher specific surface area
  - enhanced mass transfer (liquid/gas)
  - → less space requirements
  - → individually designed packings
  - → short residence time
- additional degree of freedom:
  - rotational frequency
- high shear forces

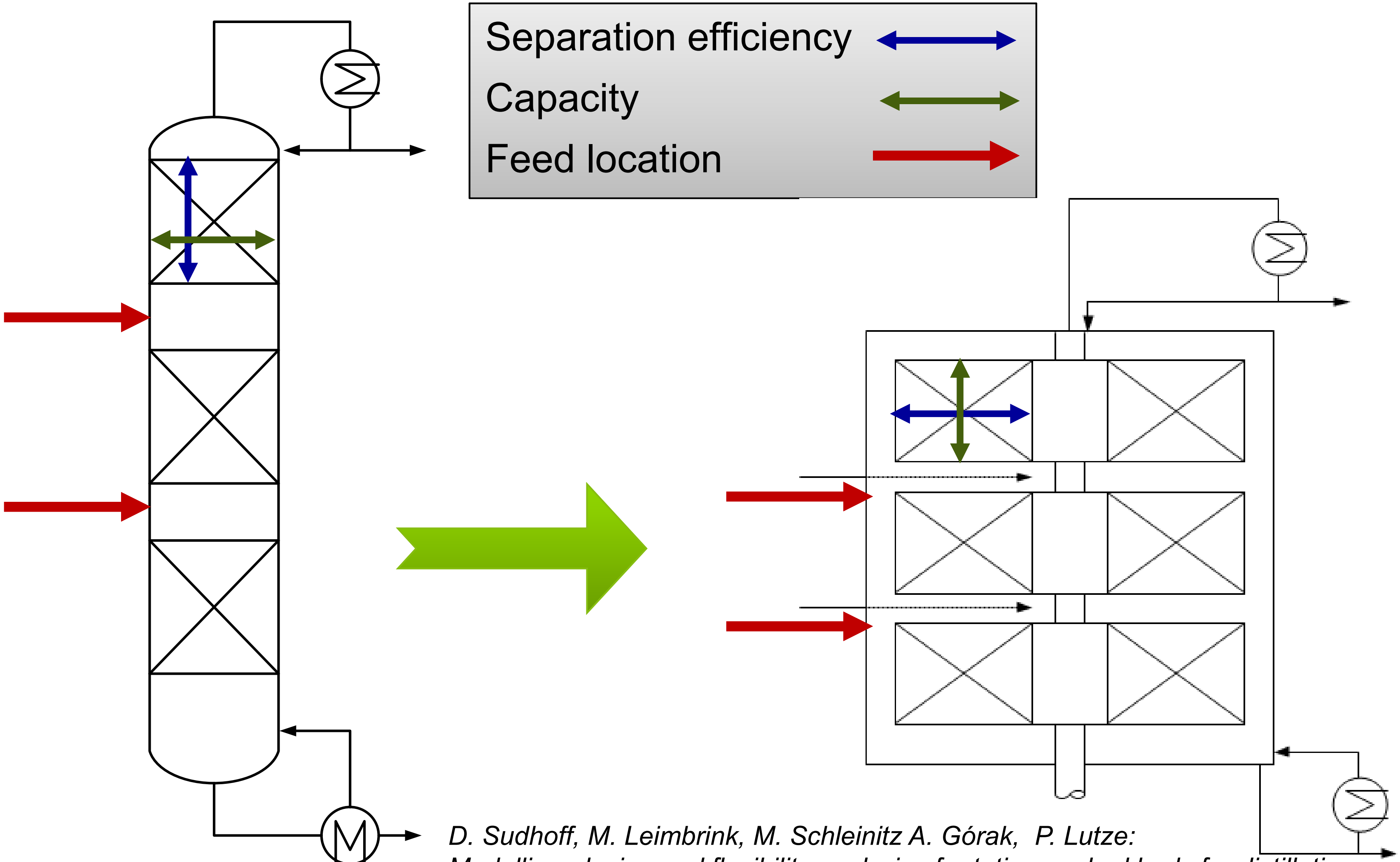
Challenges of RPB

- inhomogeneous fluid dynamics
- hardly predictable behaviour
  - → stochastically investigated
- moving parts (seals, vibration etc.)
- not yet established



E. Sørensen, K.F Lam, D. Sudhoff: Special Distillation Applications in „Distillation: Operations ans Application“, Elsevier (2015)

Distillation goes high gravity: HiGee distillation



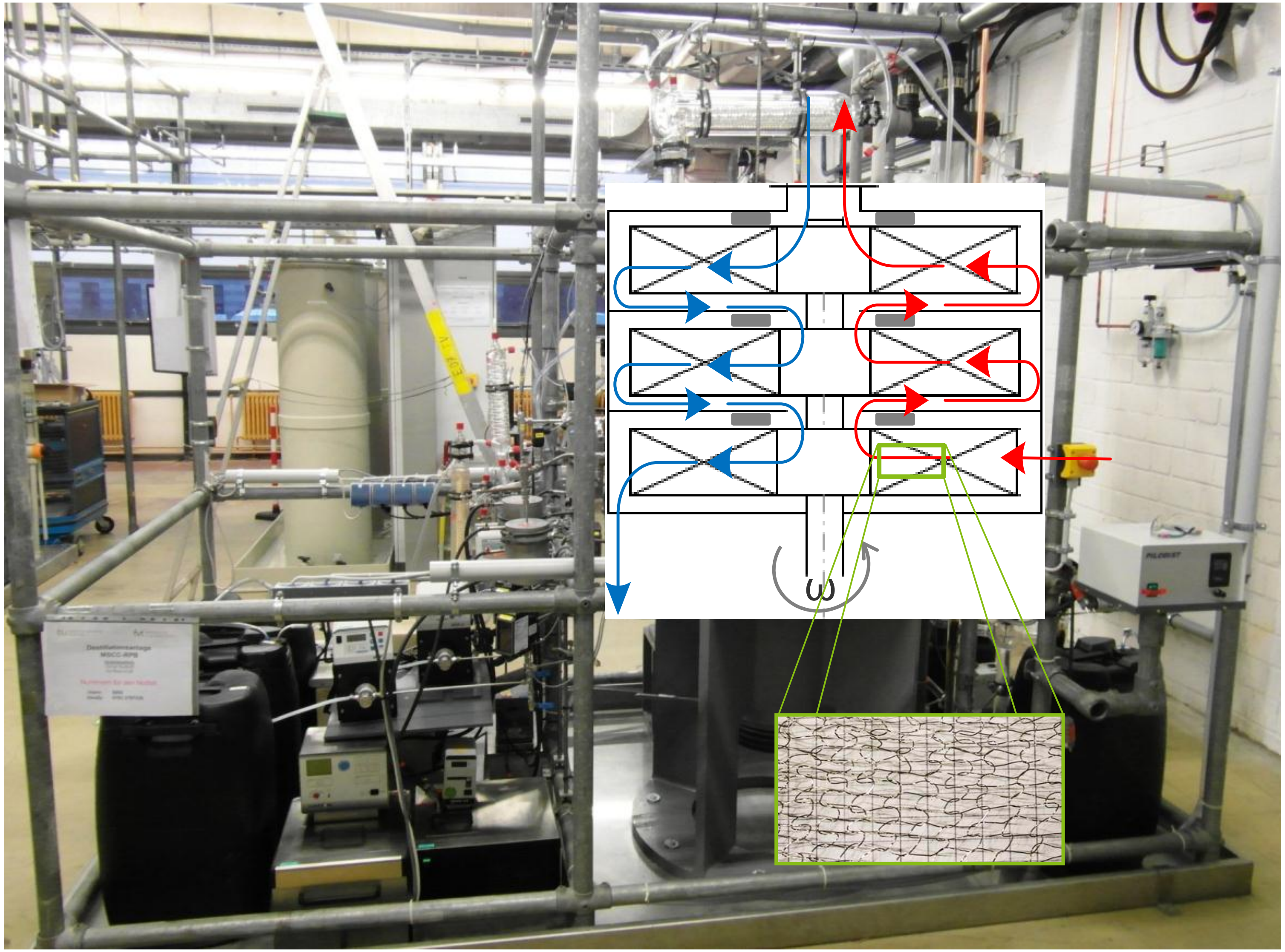
Separation efficiency ⟷

Capacity ⟷

Feed location →

D. Sudhoff, M. Leimbrink, M. Schleinitz A. Górak, P. Lutze:
Modelling, design and flexibility analysis of rotating packed beds for distillation
Chem.Eng.Res.Design 94 (2015), 72

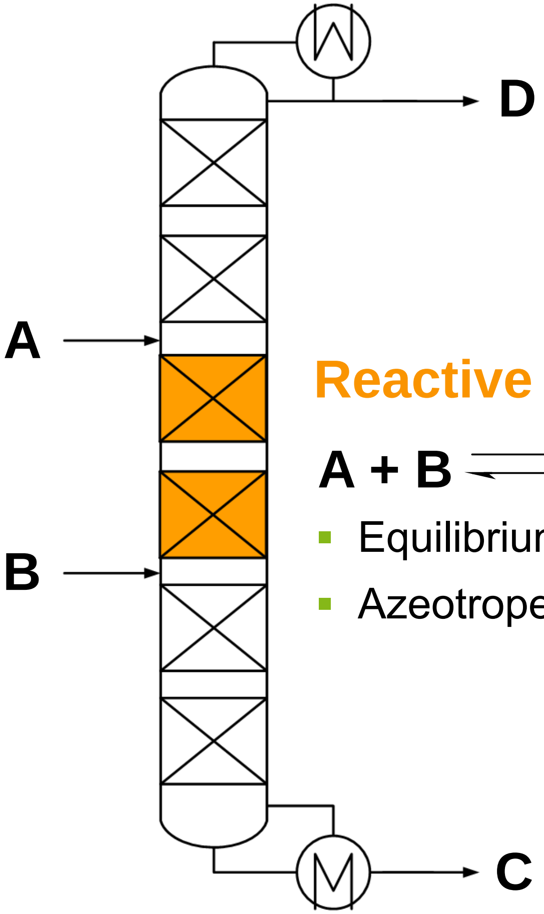
Distillation goes high gravity: HiGee distillation



HiGee distillation: flexible, modular equipment for special applications

Distillation goes reactive and bio: reactive distillation for bioproducts

Process intensification using reactive distillation



Reactive section

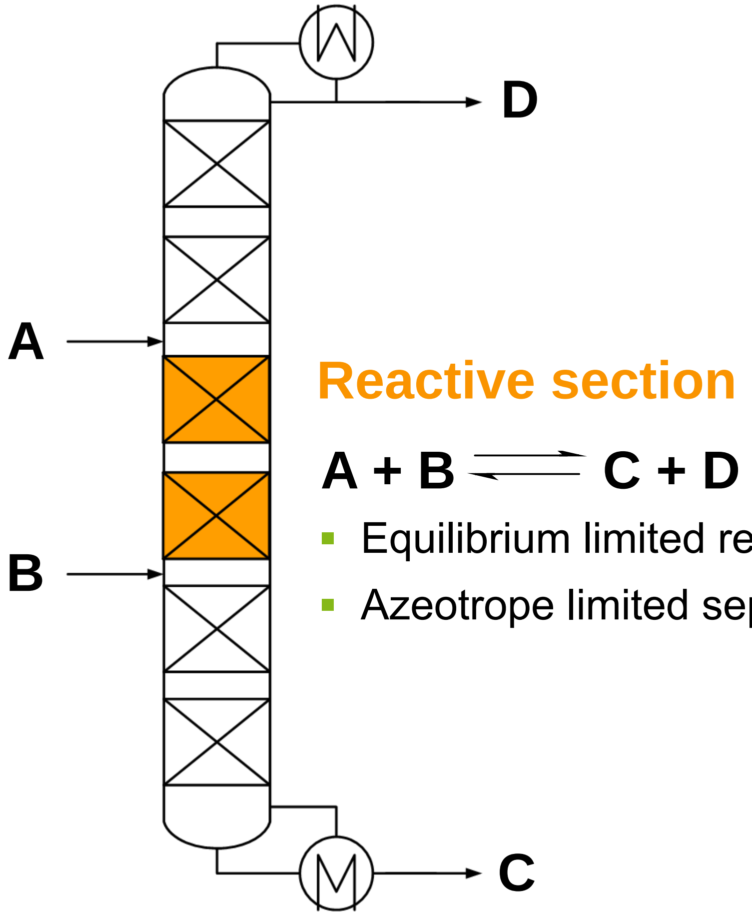
$$A + B \rightleftharpoons C + D$$

- Equilibrium limited reactions
- Azeotrope limited separations

- Chemical equilibrium shift
  - → Increased conversion
- Product separation from reaction zone
  - → Increased selectivity
- Direct heat integration
  - → Decrease in heat demand
- Avoidance of hot-spots
- Circumventing of azeotropes
- Reduced investment costs
- Reduced operation costs

Distillation goes reactive and bio: reactive distillation for bioproducts

Process intensification using reactive distillation



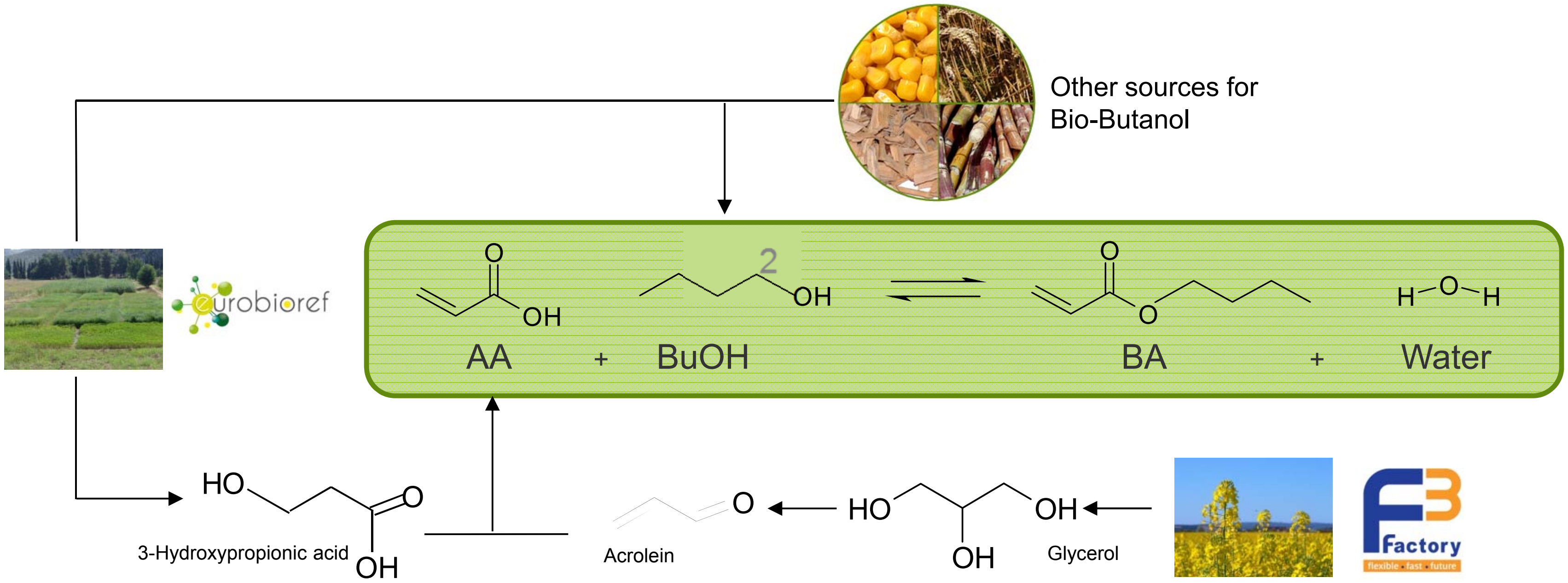
$$A + B \rightleftharpoons C + D$$

- Equilibrium limited reactions
- Azeotrope limited separations

- Heterogeneous catalysis
  - ⊕ High product purity
  - ⊕ Variable but well-defined reactive section
  - ⊕ No Corrodibility
  - ⊖ Catalyst poisoning
  - ⊖ Temperature limit
  - ⊖ Complicated catalyst exchange
- Homogeneous catalysis
  - ⊕ Low costs
  - ⊕ Fast reactions
  - ⊖ Corrodibility
  - ⊖ Product impurity
  - ⊖ Non-defined reaction zone

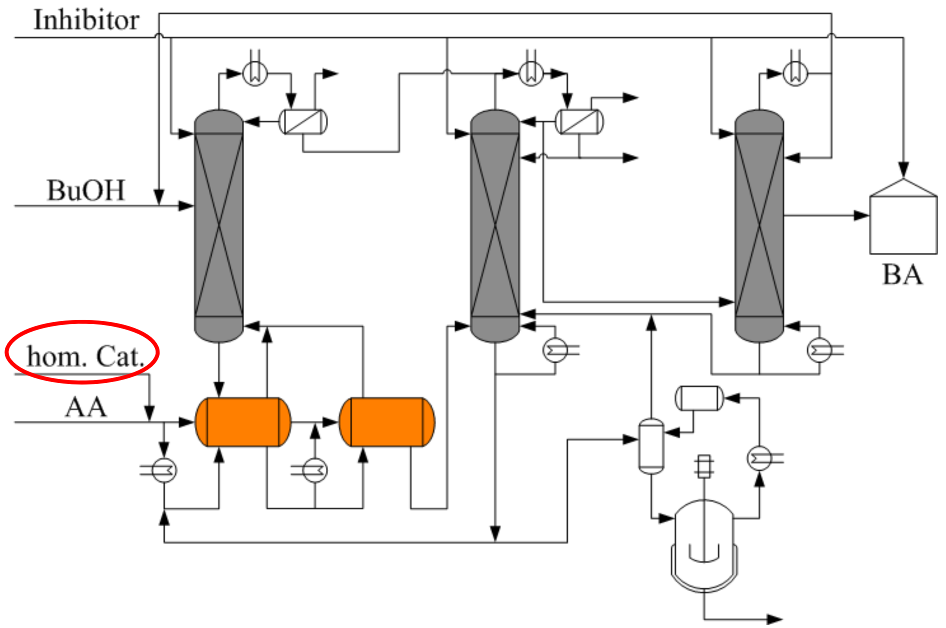
Distillation goes reactive and bio: reactive distillation for bioproducts

- Synthesis of *n*-butyl acrylate from acrylic acid and *n*-butanol
- Utilisation of biobased feedstocks

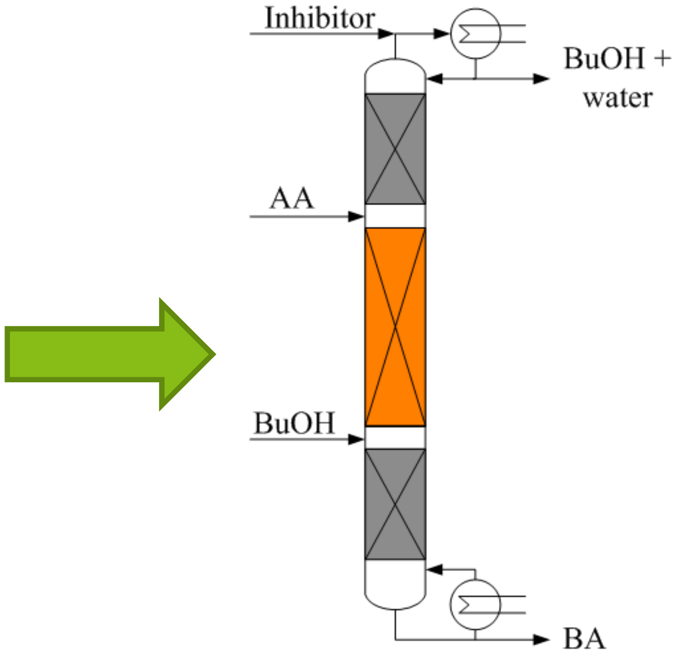


Distillation goes reactive and bio: reactive distillation for bioproducts

- Conventional process:



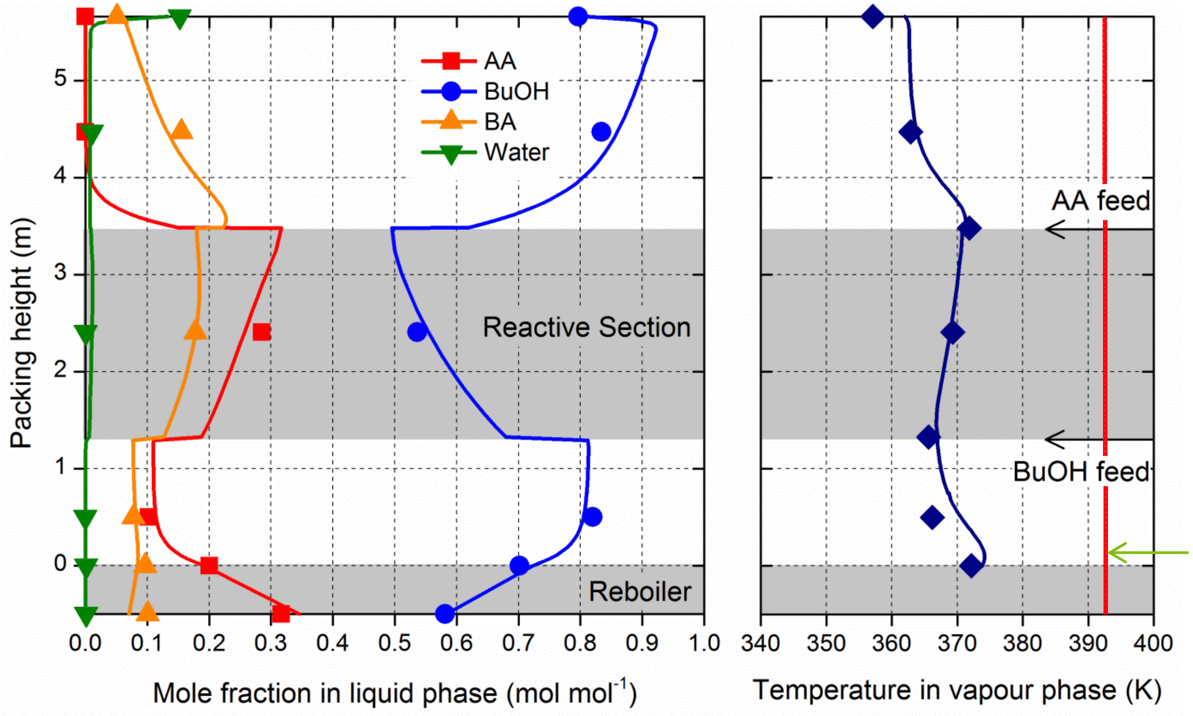
- Potential RD-process:



- Complex and cost-intensive process
- Homogeneous catalyst

- 1 RD column
- Heterogeneous catalyst

Distillation goes reactive and bio: reactive distillation for bioproducts



ARKEMA INNOVATIVE CHEMISTRY

Maximum operating temperature of Amberlyst 46

Pilot-plant DN50

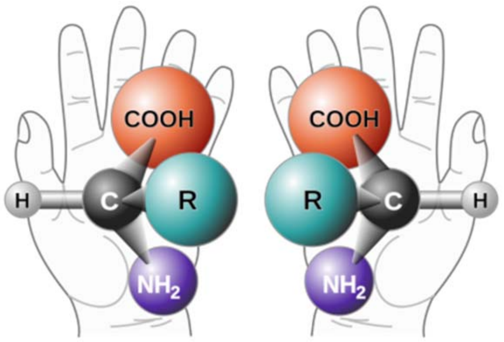
- Successful synthesis of BA in pilot-scale RD column
  - Nonequilibrium-stage modelling approach

→ **Excellent agreement between experiments and simulations**

A.Niesbach, H.Kuhlmann,T. Keller, P.Lutze, A.Górak:
"Optimisation of industrial-scale n-butyl acrylate production using reactive distillation"
Chemical Engineering Science 100 (100), (2013), 36

Distillation goes reactive and bio: enzymatic reactive distillation

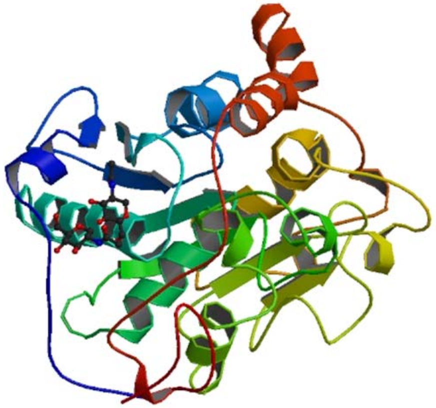
Efficient production of chiral molecules through
Enzymatic Reactive Distillation

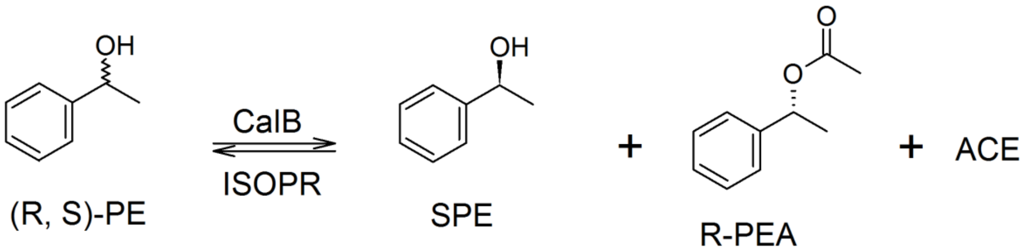


Wikipedia.org

Chiral molecules

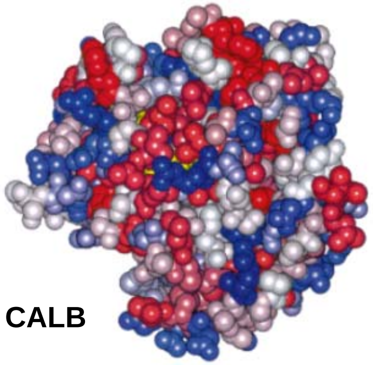
- Optically active intermediates in pharmaceuticals
- Single enantiomers reaching $ 6.63 billion in 2001 (Stinson,2001)
- New products/new efficient production routes
- Separation of chiral molecules





(R,S)-PE:	(R,S)-phenyethanol
ISOPR:	isopropenyl acetate
SPE:	(S)-phenylethanol
R-PEA:	(R)-phenyl ethyl acetate
ACE:	acetone

Distillation goes reactive and bio: enzymatic reactive distillation

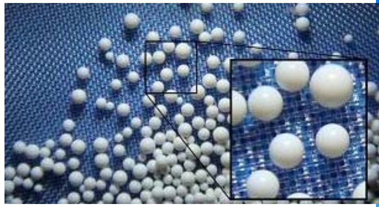


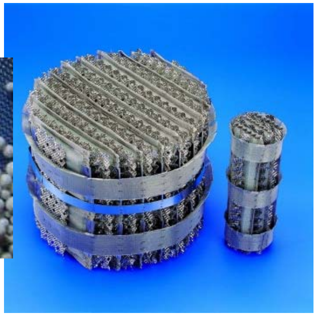
Lipase CALB

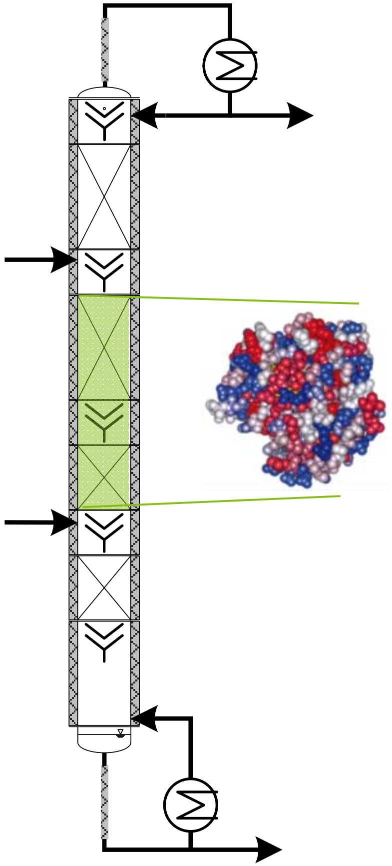
Enzyme immobilisation

Andreas Liese,
Irina Smirnova

TUHH
Thermische
Verfahrenstechnik







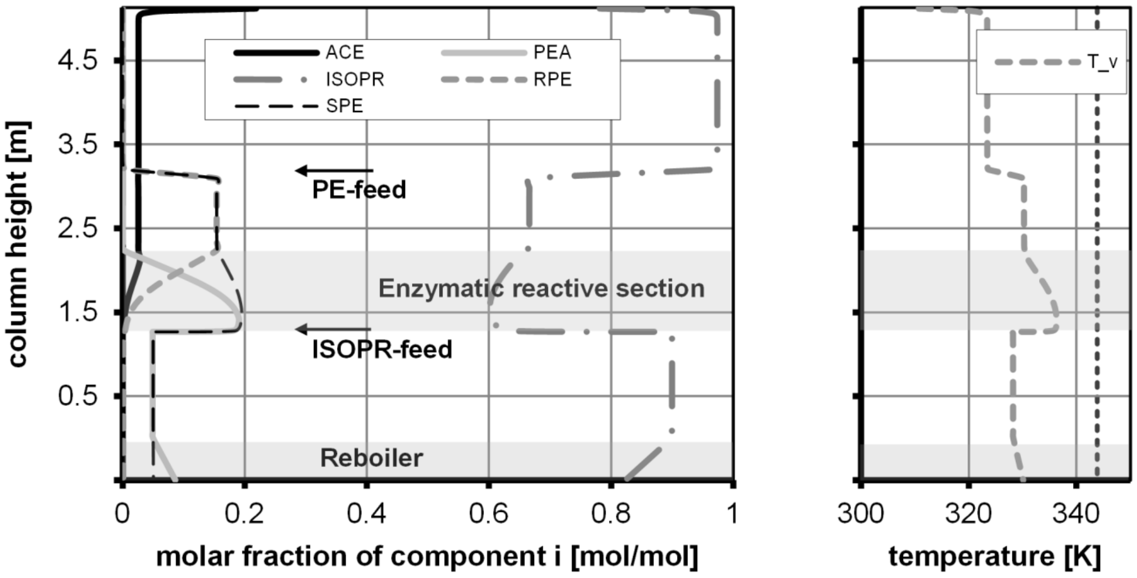
R.Heils, A.Sont, P.Bubenheim, A. Liese. I. Smirnova: Integration of enzymatic catalysts in a reactive distillation column with structured packings, Ind.Eng.Chem.Res. 51 (2012) 11482
R.Heils, A.Niesbach, M.Wierschem, (…),P.Lutze, I.Smirnova: Integration of Enzymatic Catalysts in a Continuous Reactive Distillation Column: Reaction Kinetics and Process Simulation. Ind.Eng.Chem.Research 53 (2014),19612

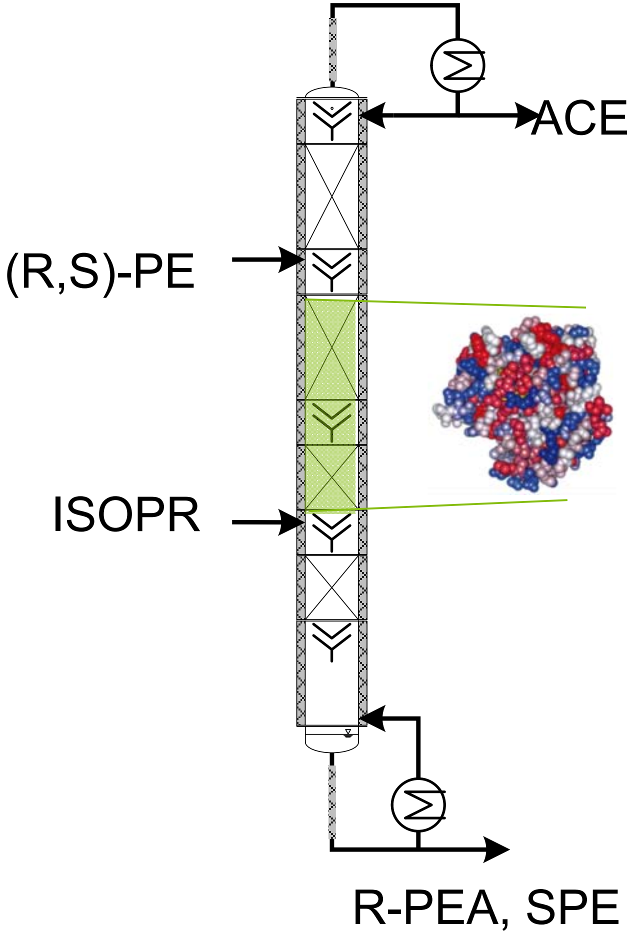
Reactive distillation: important niche apllication, also for bio-products

Efficient production of chiral molecules through

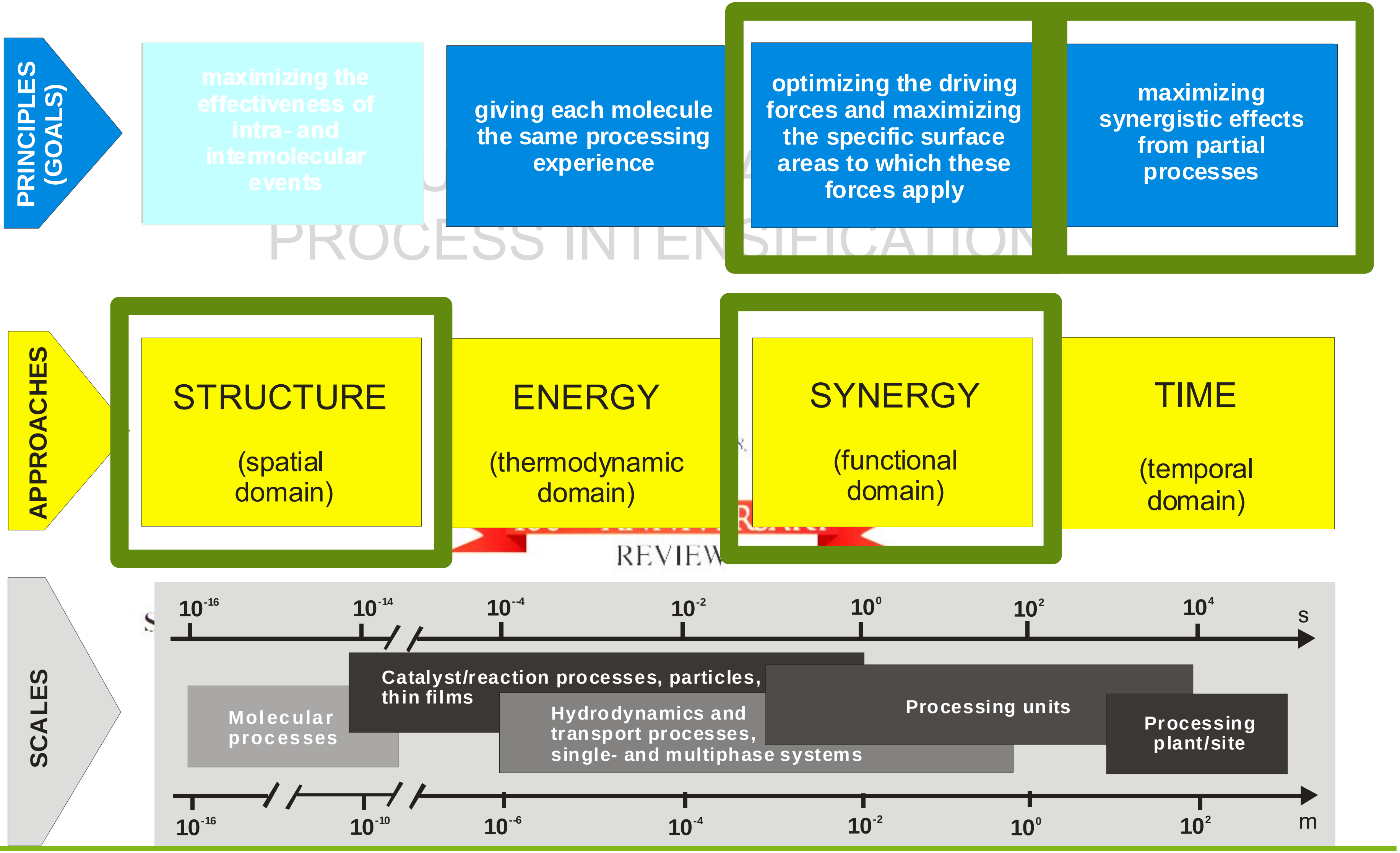
Enzymatic Reactive Distillation

- High conversion
- Separation of products
- SPE unconverted





Process Intensification: **Intensifying distillation**



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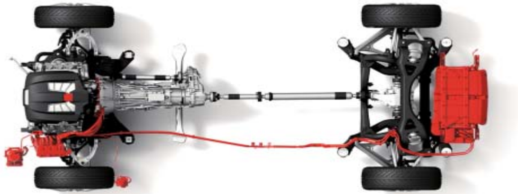
- Processing units
- Processing plant/site

Distillation goes hybrid


http://www.petliferadio.com/magicalcreatures.html

What is Hybrid?

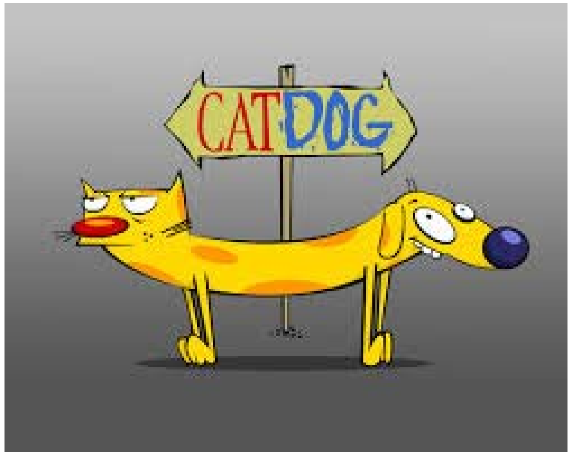
a creature combining body parts
of two or more species


http://www.evwaudi.com/blog/wp-content/uploads/2010/10/cayenne-s-hybrid-5.jpg

a vehicle using both
internal combustion
and electric power sources

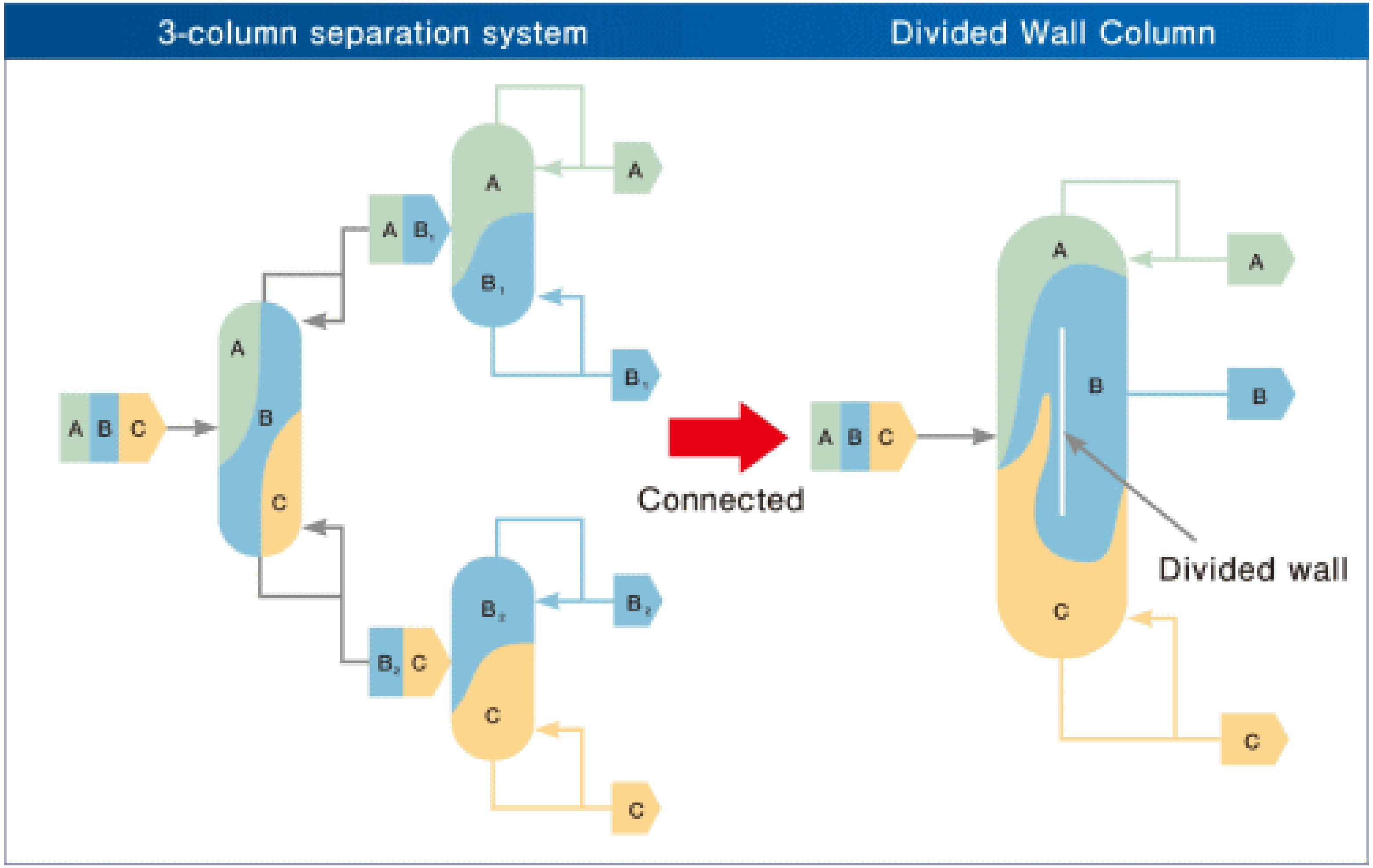
In **hybrid separations** at least two unit operations are combined to solve a defined separation task. By using each unit operation in its optimal range synergy effects arise and offer more sustainable and intensified processes

M.Franke, N.Nowotny, E.Ndocko, A.Górak, J.Strube: Design and Optimization of a Hybrid Distillation / Melt Crystallization Process AIChEJ. 54(2008)292



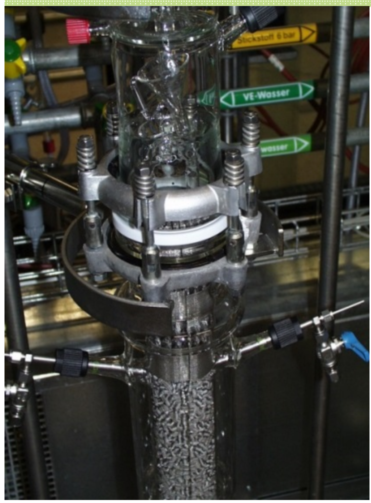
https://lancecoolidgepetnews.wordpress.com/

Distillation goes hybrid: divided wall column

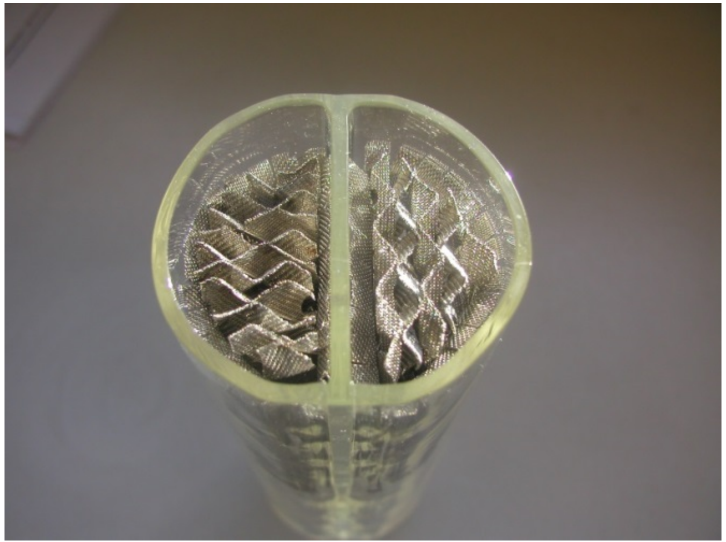


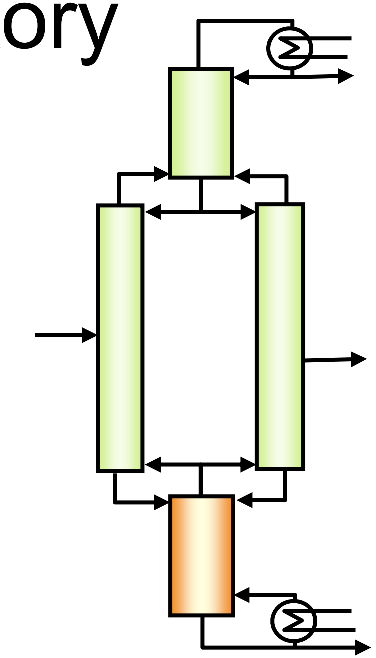
http://imagestack.co/46435477-dividing-wall-column-distillation.html

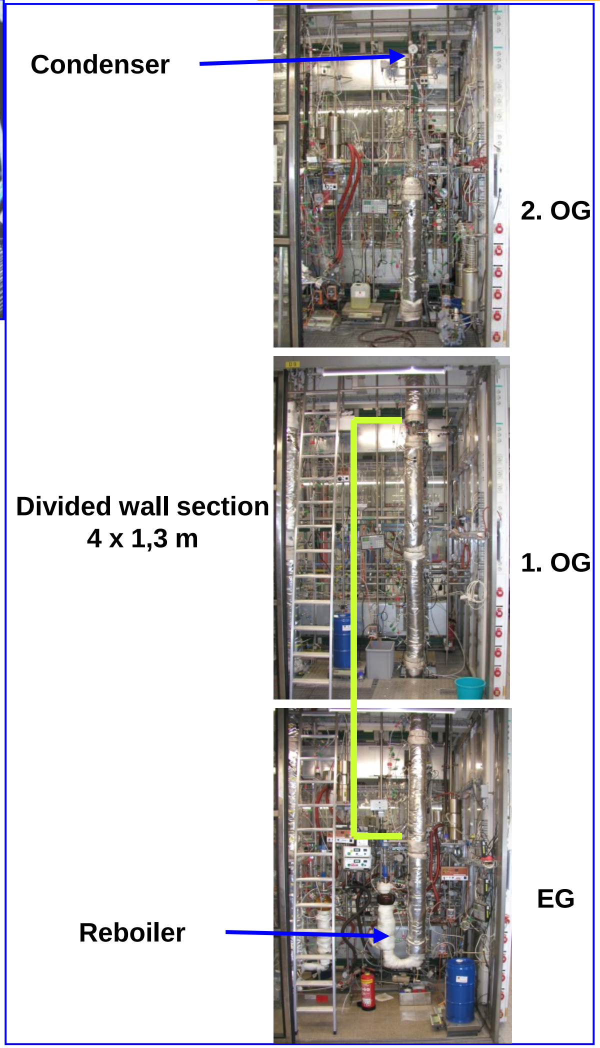
Distillation goes hybrid: divided wall column



From laboratory to pilot scale





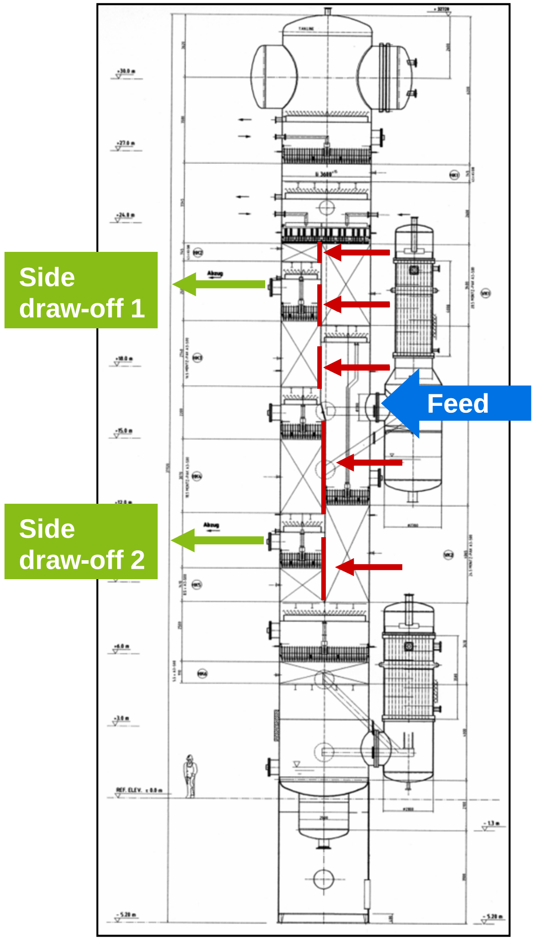


Courtesy: Dr. Regina Benfer, BASF

Distillation goes hybrid: divided wall column

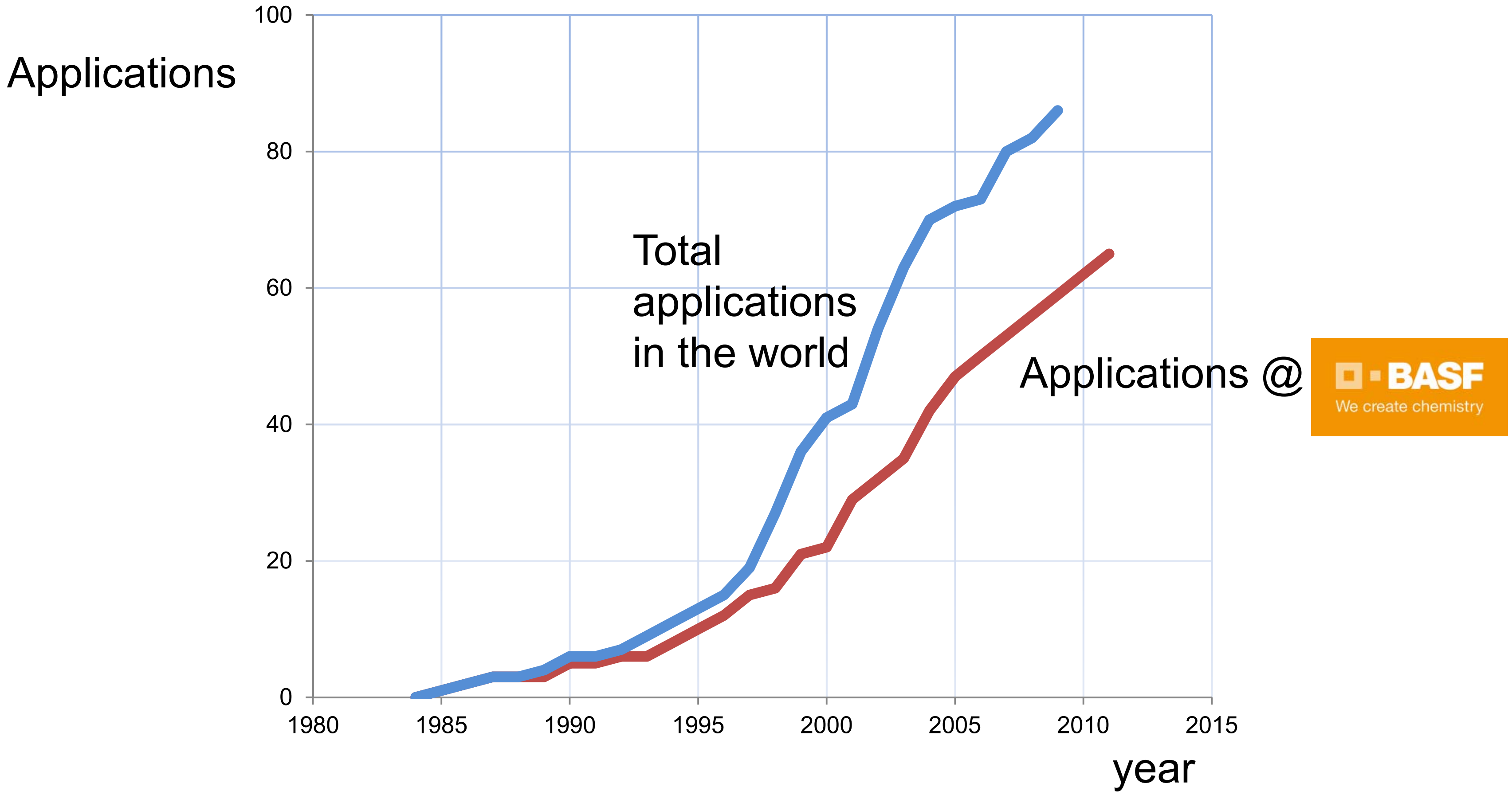
Just do it!

- Several products in one shell
- Different configurations of column interior through flexible internal modules
- Mainly structured packings used
- Trays become more important



Courtesy: Dr. Regina Benfer, BASF

Distillation goes hybrid: divided wall column

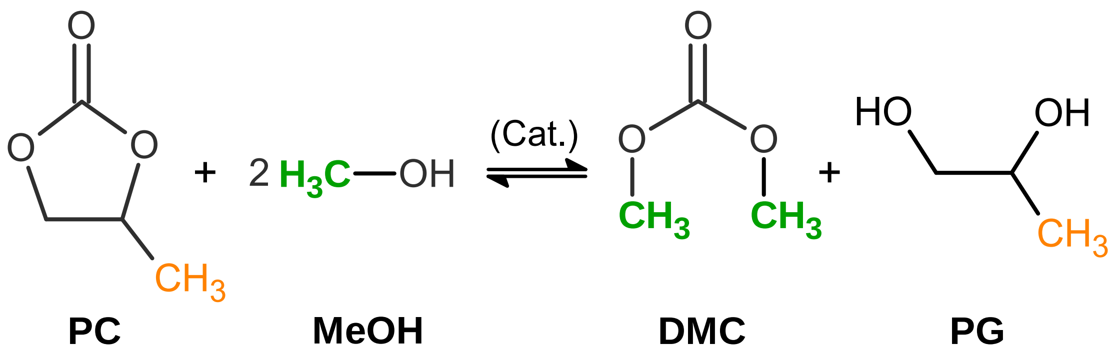


Courtesy: Dr. Regina Benfer, BASF

World's Largest DWC, 107 m tall and 5 m diameter Constructed by Linde AG for Sasol

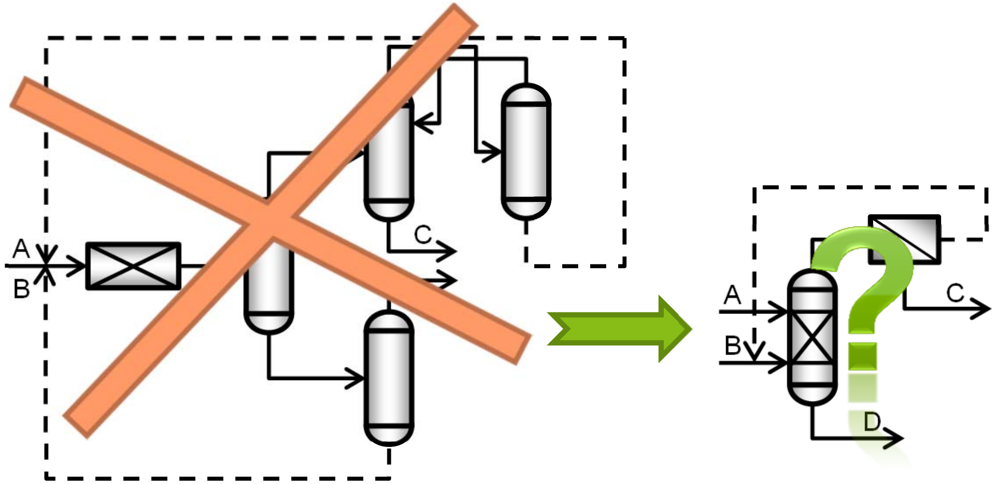
Distillation goes hybrid: membrane assisted reactive distillation

- Transesterification of propylene carbonate (PC) with methanol (MeOH):



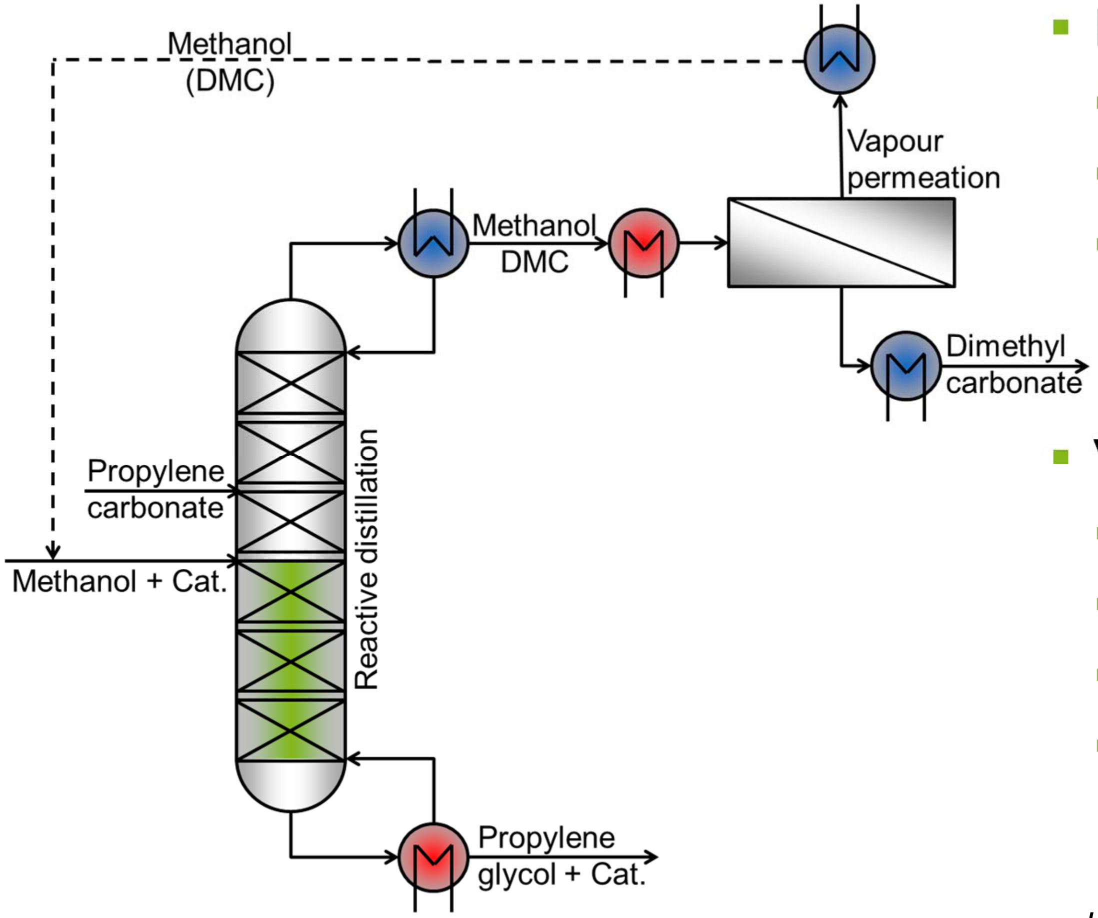
<u>Boiling points at 1.013 bar:</u>

MeOH-DMC	🟦	336 K
MeOH	🟩	338 K
DMC	🟨	363 K
PDO	🟧	461 K
PC	🟥	515 K



Use of the homogeneous catalyst sodium methoxide

Distillation goes hybrid: membrane assisted reactive distillation



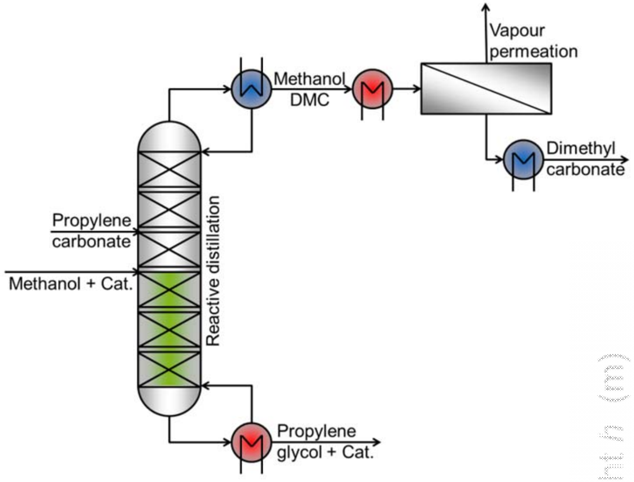
Membrane-assisted Reactive Distillation

- Reactive distillation
  - Integration of reaction and distillation
  - Increased conversion and selectivity
  - Azeotropic mixture consisting of DMC and MeOH as top product
- Vapour permeation
  - Separation independent on VLE
  - High selectivity
  - Purification of DMC
  - Recovery of unreacted MeOH

J. Holtbruegge, S.Heile, P.Lutze, A.Górak: Synthesis of dimethyl carbonate and propylene glycol in a pilot-scale reactive distillation column: Experimental investigation, modeling and process analysis" Chem.Eng.J. 234 (2013) 448

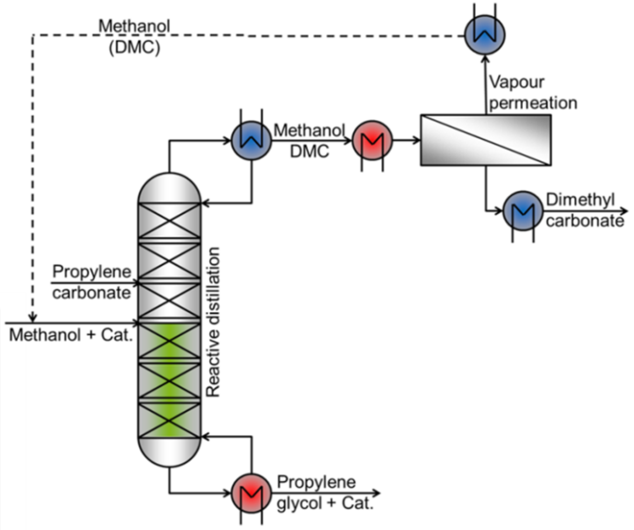
Hybrid distillations: divided wall columns become standard, membrane assisted distillation needs better membranes

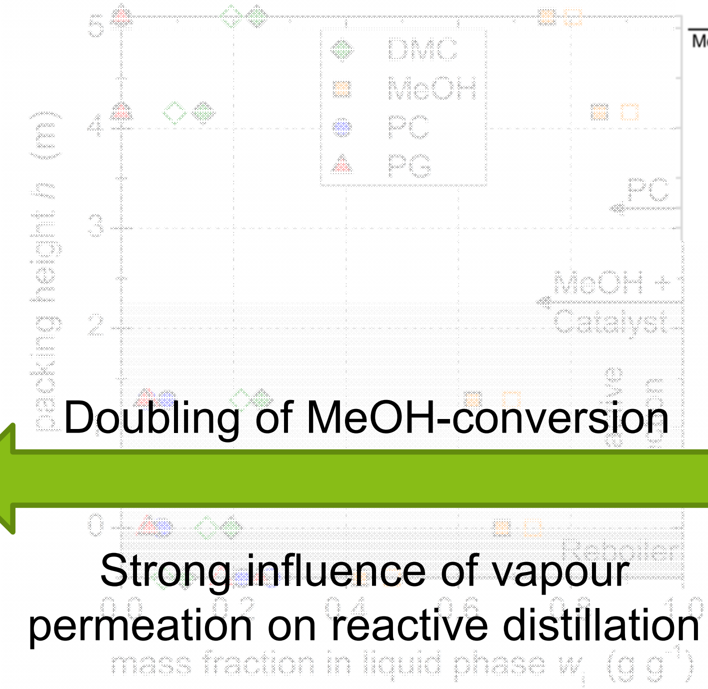
Open recycle operation



DF (kg kg^{-1})	0.55
RR (-)	1.80
X_{Col} (mol mol^{-1})	10.0
w_{cat} (g g^{-1})	$6 \cdot 10^{-3}$

Closed recycle operation





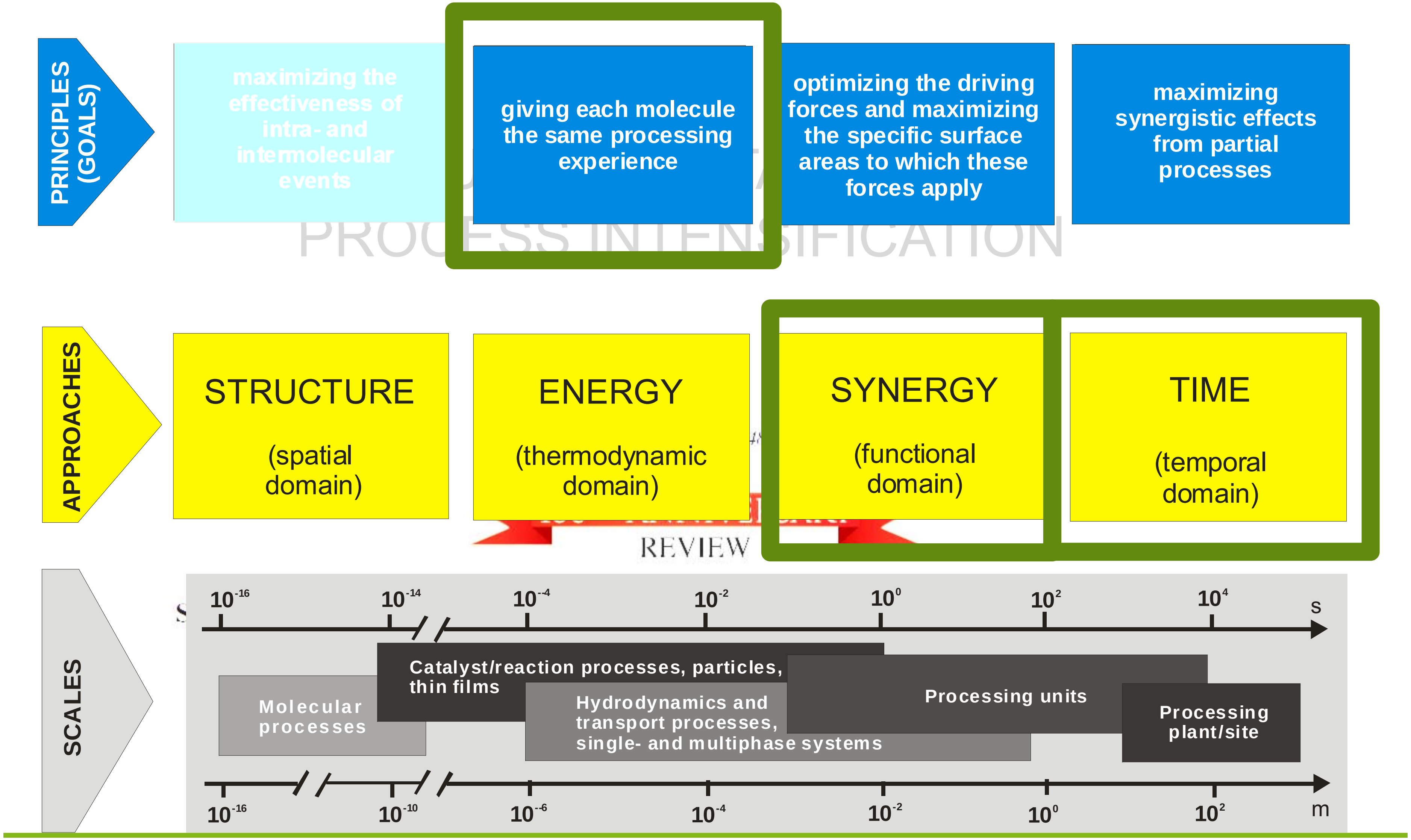
X_{MeOH} (%)	13.3
X_{PC} (%)	66.1

Doubling of MeOH-conversion

Strong influence of vapour permeation on reactive distillation

X_{MeOH} (%)	25.1
X_{PC} (%)	60.6

Process Intensification: **Intensifying distillation**



PRINCIPLES (GOALS)

- maximizing the effectiveness of intra- and intermolecular events
- giving each molecule the same processing experience
- optimizing the driving forces and maximizing the specific surface areas to which these forces apply
- maximizing synergistic effects from partial processes

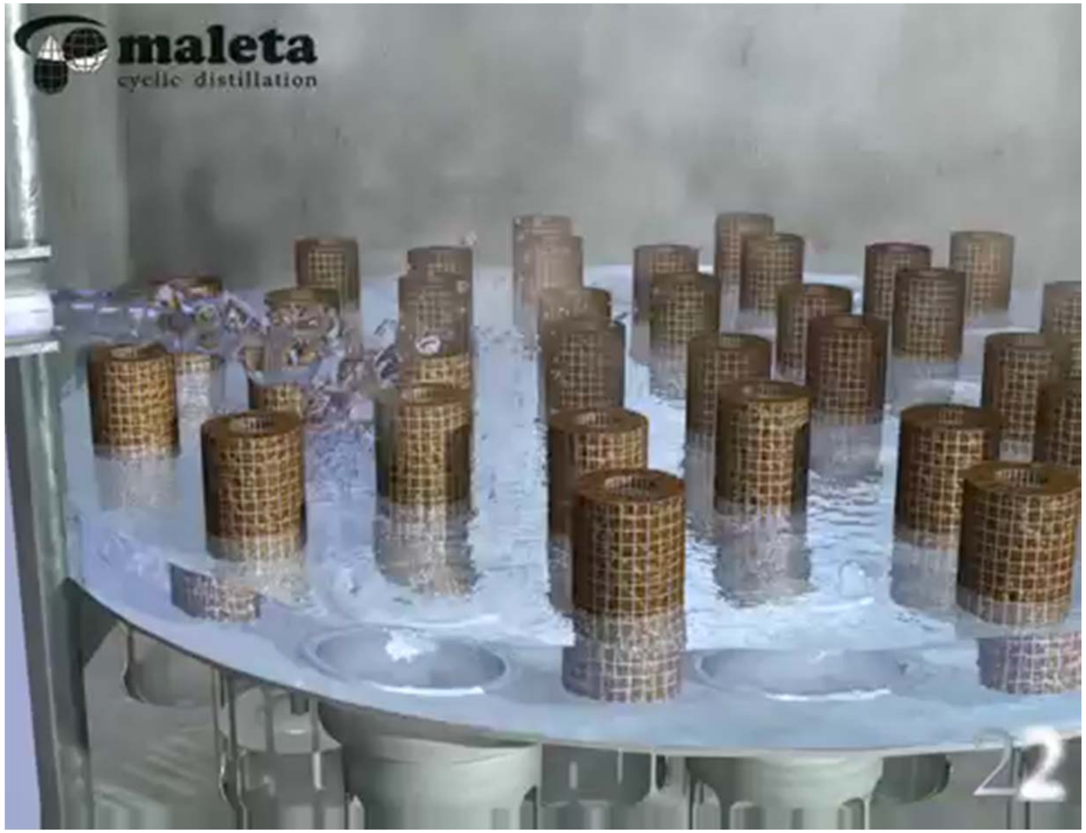
APPROACHES

- STRUCTURE (spatial domain)
- ENERGY (thermodynamic domain)
- SYNERGY (functional domain)
- TIME (temporal domain)

SCALES

- Molecular processes
- Catalyst/reaction processes, particles, thin films
- Hydrodynamics and transport processes, single- and multiphase systems
- Processing units
- Processing plant/site

Distillation goes cyclic: cyclic reactive distillation



V.N.Maleta, A.Kiss, A.Taran, B.V.Maleta: Understanding process intensification in cyclic distillation systems Chem. Eng.Proc: Process Intensification 50 (2011)655
C. Pătruţ, C. Bîldea, AA.Kiss,: Catalytic cyclic distillation - A novel process intensification approach in reactive separations Chem. Eng.Proc: Process Intensification 81(2014)1
S.Buetehorn, J.Paschold, T.Andres, A.Shilkin, C. Knoesche, Impact of the Duration of the Vapor Flow Period on the Performance of a Cyclic Distillation, Chem.Ing.Tech, 87(2015)1070

Outlook

More during this conference…

Rotating packed beds:

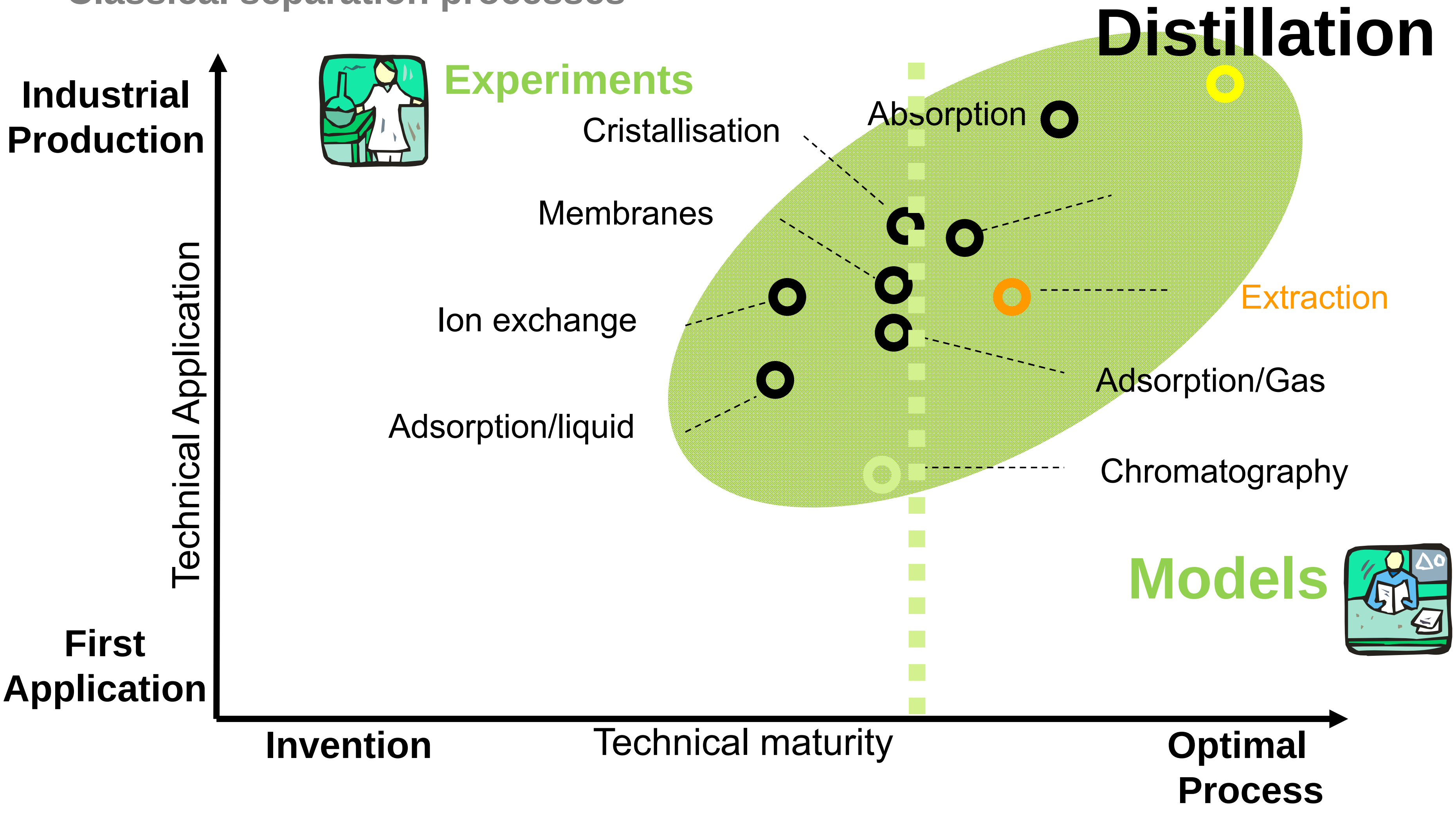
- MODELLING OF CO2 ABSORPTION IN ROTATING PACKED BEDS, **K. Neumann**, P. Lutze, M. Skiborowski, A. Górak
- PROCESS INTENSIFICATION WITH THE ROTATING LIQUID SHEET CONTACTOR, **L. T. Wardhaugh**, C. Solnordal, A. Allport

Reactive and hybrid distillation:

- CONTROL OF A REACTIVE DISTILLATION COLUMN WITH DOUBLE REACTIVE SECTIONS FOR TWO-STAGE CONSECUTIVE REACTIONS, **D. B. Kymak**, H. Unlu, T. Ofkeli
- INFLUENCE OF FEED STAGE LOCATION IN THE DESIGN OF REACTIVE DISTILLATION PROCESSES INVOLVING KINETICALLY CONTROLLED REACTIONS, J.-C. Cárdenas-Guerra, S. Hernández, F. O., Barroso-Muñoz, H. Hernández-Escoto
- EXPERIMENTAL AND MODEL-BASED INVESTIGATION OF CONTINUOUS ENZYMATIC REACTIVE DISTILLATION: KINETICS AND STABILITY OF COATED PACKING. **M. Wierschem**, M. Termuhlen, C. Schach, R. Heils, I. Smirnova, A. Gorak, P. Lutze
- REACTIVE DISTILLATION FOR EFFICIENT BIO-RENEWABLE PRODUCT FORMATION IN THE BIO-REFINERY, A. **Kolah**
- REACTIVE DISTILLATION FOR MULTIPLE REACTION SYSTEMS: COUPLING OF ESTERIFICATION AND TRANSESTERIFICATION FOR AN EFFICIENT BIODIESEL PROCESS, **K. Werth**, A. Hnida, M. Skiborowski
- INVESTIGATION OF COMMERCIAL MEMBRANES FOR THE DEHYDRATION OF ACETIC ACID BY A HYBRID DISTILLATION / PERVAPORATION PROCESS, C. Servel, **D. Roizard**, D. Horbez, E. Favre
- EXPERIMENTAL VALIDATION OF REACTIVE DIVIDED WALL COLUMN DESIGN METHOD, T. D. Nguyen, **D. Rouzineau**, M. Meyer, X. Meyer
- A CONTROL STRATEGY FOR EXTRACTIVE AND REACTIVE DIVIDED WALL COLUMNS, **M. Rodriguez**, I. Diaz, P.Z. Li

Outlook

Classical separation processes



Distillation

Experiments

Absorption

Cristallisation

Membranes

Extraction

Ion exchange

Adsorption/Gas

Adsorption/liquid

Chromatography

Models

Industrial Production

Technical Application

First Application

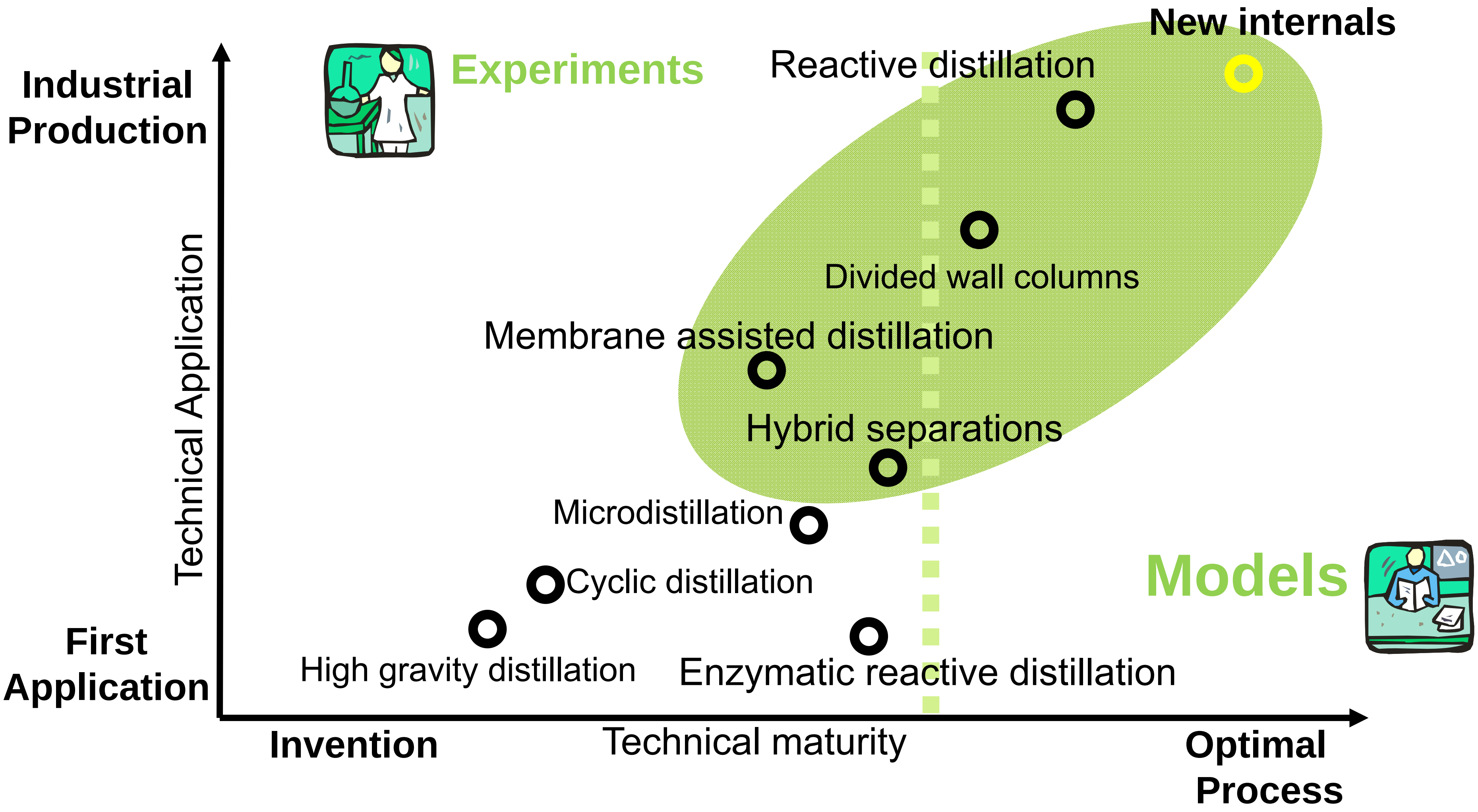
Invention

Technical maturity

Optimal Process

Outlook

Distillation



New internals

Experiments

Reactive distillation

Industrial Production

Technical Application

Divided wall columns

Membrane assisted distillation

Hybrid separations

Microdistillation

Cyclic distillation

Models

First Application

High gravity distillation

Enzymatic reactive distillation

Invention

Technical maturity

Optimal Process

Outlook

New/Old Challenges:

- Diluted systems/low and fluctuating product compositions
- Close boiling and wide boiling components
- High viscosities
- High energy prices
- High purity components

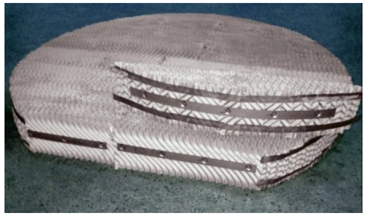
New intensified distillation technologies:

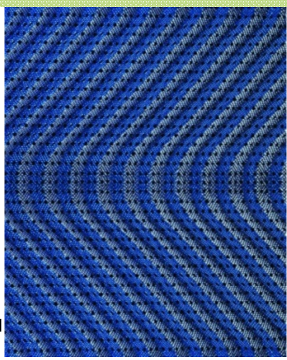
- **Micro**: for regulated substances (pharma applications)
- **Reactive** distillation: important niche apllication, also for bio-products
- **Hybrid** distillations: divided wall columns become standard, membrane assisted distillation needs better membranes
- **Cyclic** distillation: hardware (valves, trays) remains a challange
- **Higee** distillation: flexible, modular equipment for special applications

Intensification of traditional distillation technologies:

- New separation sequences and better process synthesis methods
- New internals

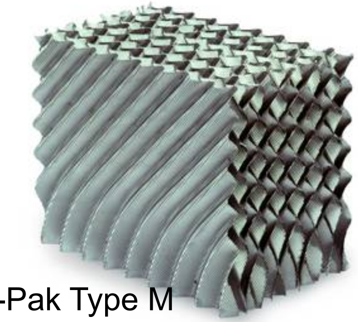
Variety of column internals

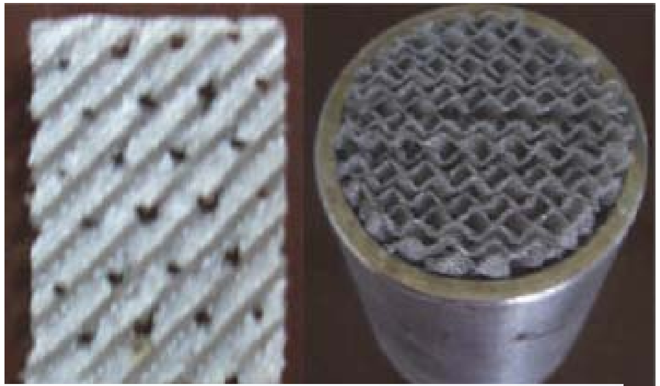

AYPlus™ DC


MellapakPlus™

Shell ConSep Tray

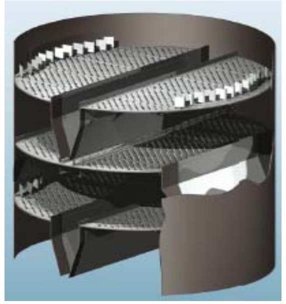

Sandwich packing

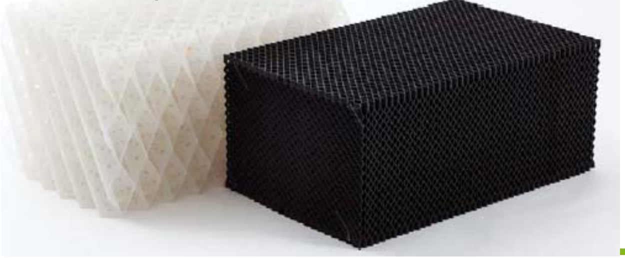


Montz-Pak Type M

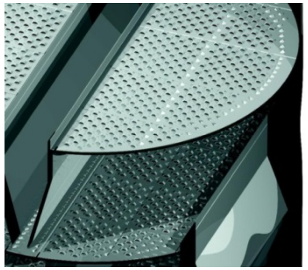
PACK-^{13}C


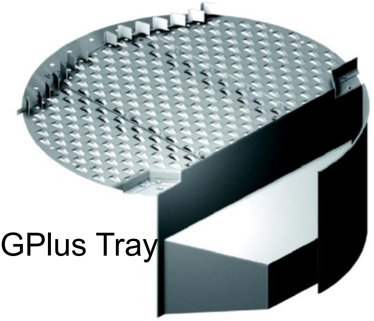

UFM™


ULTRA-FRAC®


2-pass VGPlus

Flexipac® HC



2-pass VG AF


1-pass VGPlus Tray


Optiflow