technische universität dortmund

fvt laboratory of fluid separations

Distillation and absorption

in the era of bio, info and process intensification

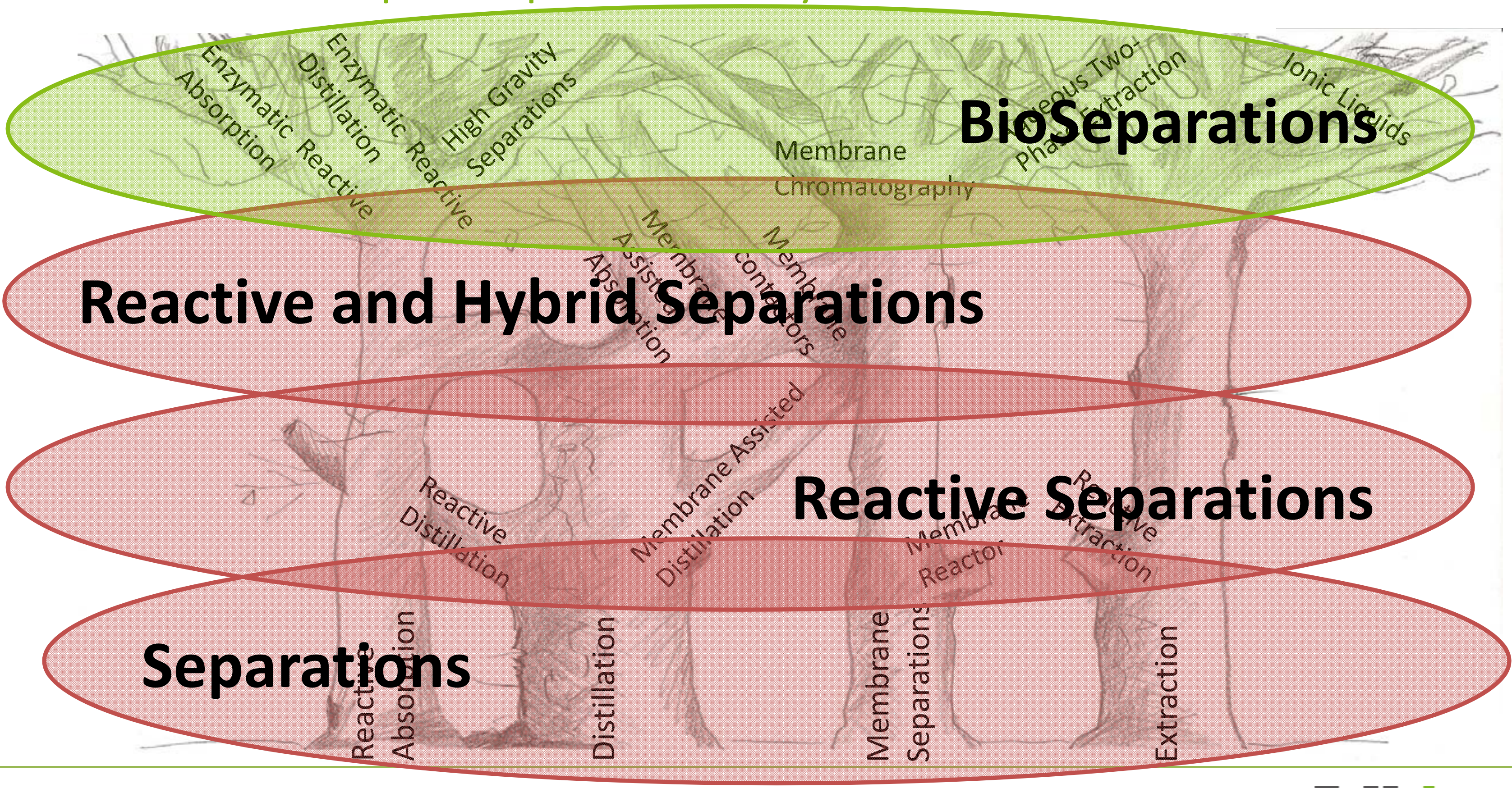
BACK TO THE FUTURE

Politechnika Łódzka

TU Dortmund University
Department of Biochemical
and Chemical Engineering
Laboratory of Fluid Separations
andrzej.gorak@tu-dortmund.de
www.fvt.bci.tu-dortmund.de

50 Jahre bci 2019

Separations become complex: a personal story

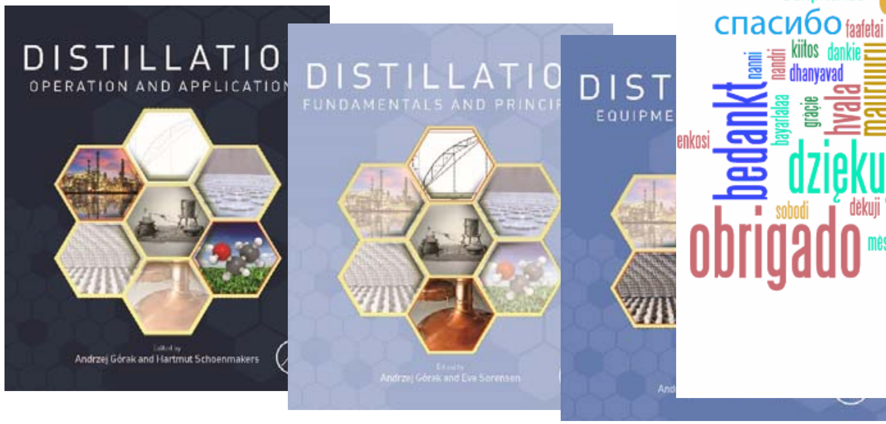


Separations become complex: a personal story

… therefore I worked on them last 25 years **together** with:

- 50 PhD students
- 40 industrial partners
- 40 academic partners
- 40 research projects including 8 European projects

Example: 5 edited books



Thanks to partner institutions and persons for their trust and patience!

technische universität dortmund

laboratory of fluid separations

Script

“In this 1980s sci-fi classic, small-town California teen Marty McFly (Michael J. Fox) is thrown back into the '50s when an experiment by his eccentric scientist friend Doc Brown (Christopher Lloyd) goes awry. ... ions of his paren ... 'll cease to exist. ... oc Brown.”

„Hardly anyone works in conventional distillation these days. I know of two retired staff in the UK with a residual interest -- Professor Richard Darton of Oxford University and Dr. Geof Priestman of the University of Sheffield.” *(August 2018)*

“In ... eeded, so the ... 7 in Maa ... 6 in London (UK), 2010 in Eindhoven (Netherlands), and the last in 2014 in Friedrichshafen (Germany)“.

Elisabetta Brunazzi — *Chair*
Eva Sorensen — *Scientific Chair*

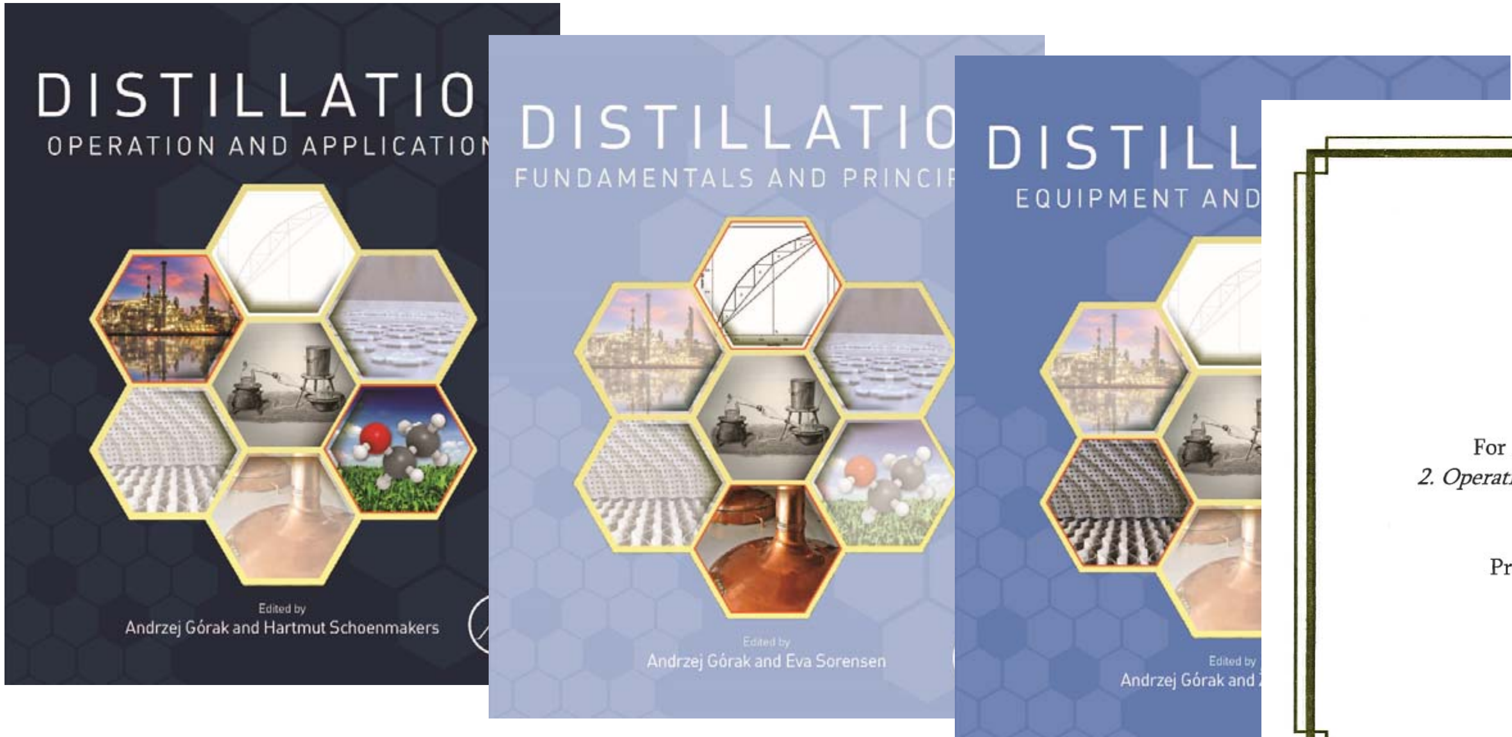
11th International Conference on Distillation & Absorption 2018

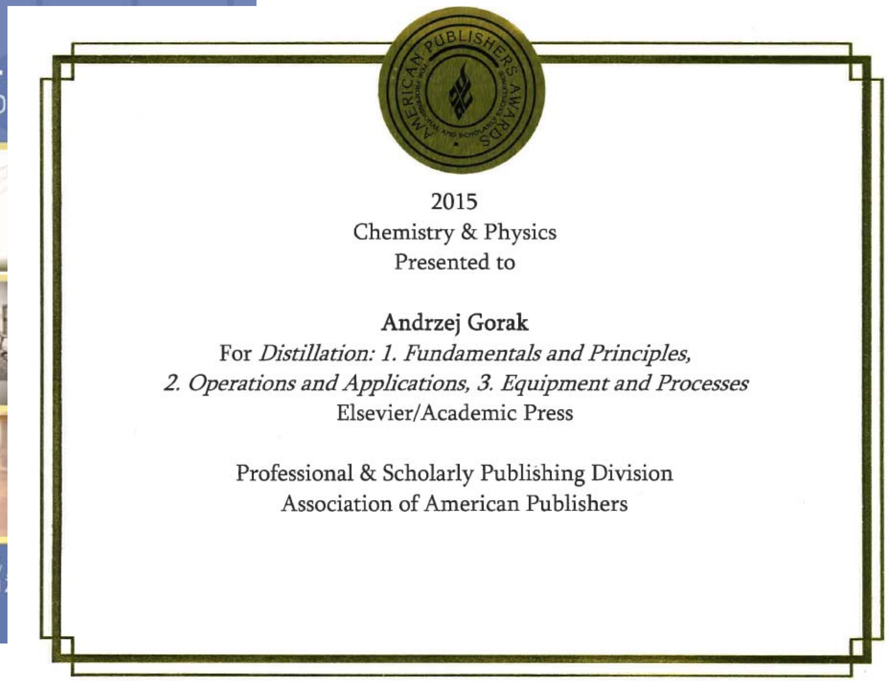
16-19 September 2018, Florence – Italy

Hot(?) topics in the last 30 years of D&A conferences

2018	2014	2010
Basic data	Basic data	Basic data
Carbon capture and absorption	Absorption	Carbon capture
Conceptual process design and LCA		
Modelling and simulation	Modelling and simulation	Modelling and simulation
Control, operation, troubleshooting and manufacturing excellence	Operation and control, Troubleshooting	Operation and control, Troubleshooting
Reactive and hybrid separations, Emerging separations	Integrated processes	Novel processes
Energy efficiency and technology	Energy efficiency	
Equipment design	Equipment design Trays, packings	Equipment design Trays, packings

Hot(?) topics in the last 30 years of D&A conferences



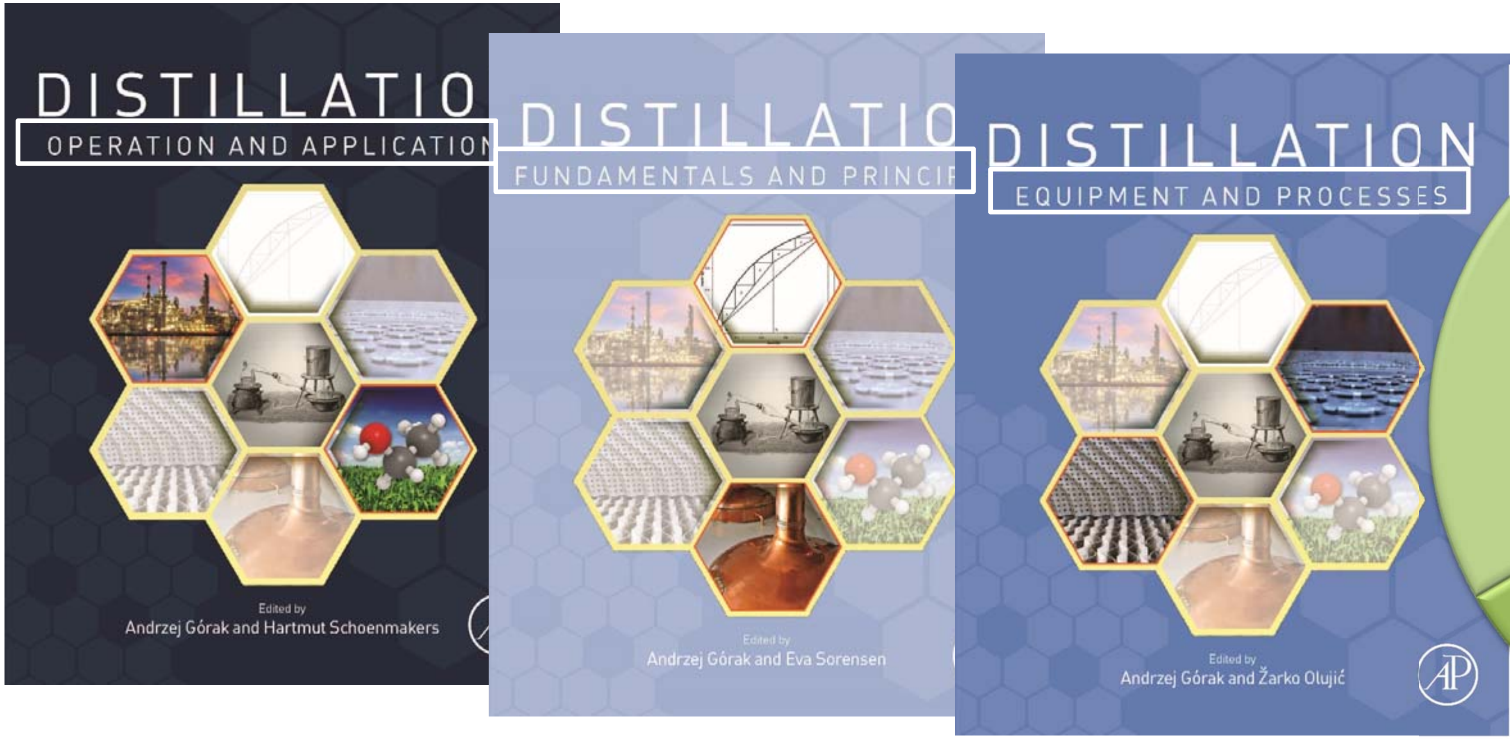

AMERICAN PUBLISHERS AWARDS

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

Hot(?) topics in the last 30 years of D&A conferences



Processes
- Reactive
- Hybrid
- Novel
- Energy

Methods
- Basic data
- Modelling and simulation
- Conceptual process design

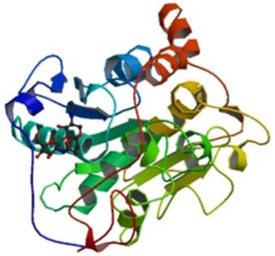
Equipment
- Trays
- Packing
- Measurement
- Operation
- Troubleshooting

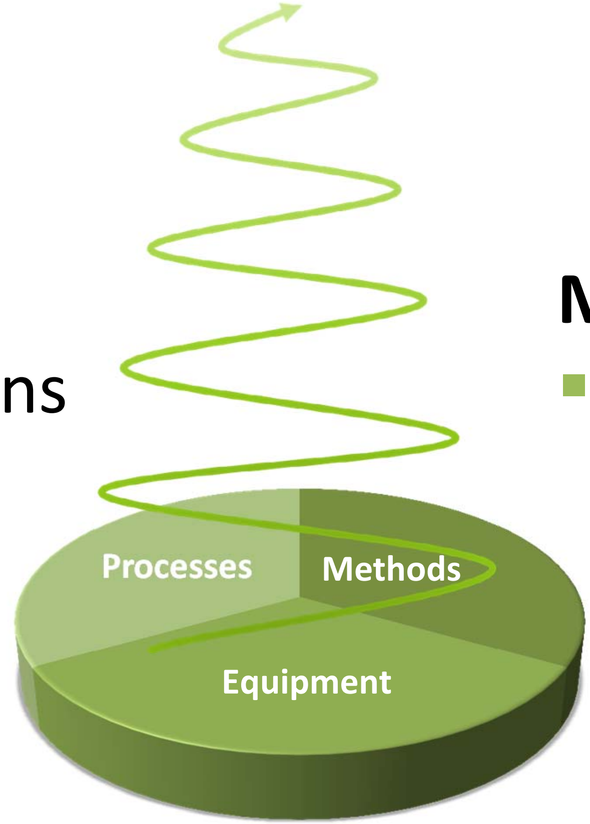
Revisit old ideas for new fluid separations

Model meets Reality:
Distillation Simulation at BASF

Process intensification

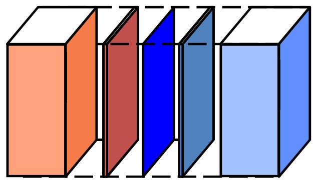
- Bioreactive Separations
- Enzymatic processes





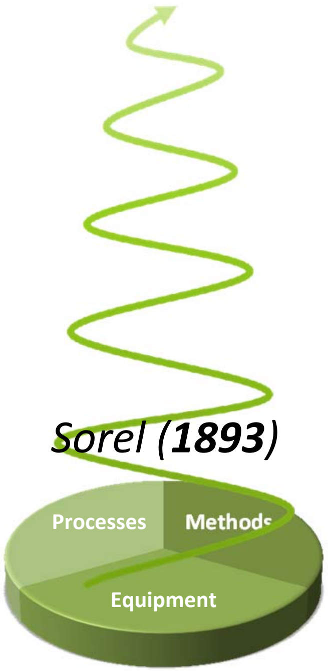
Modeling and simulation

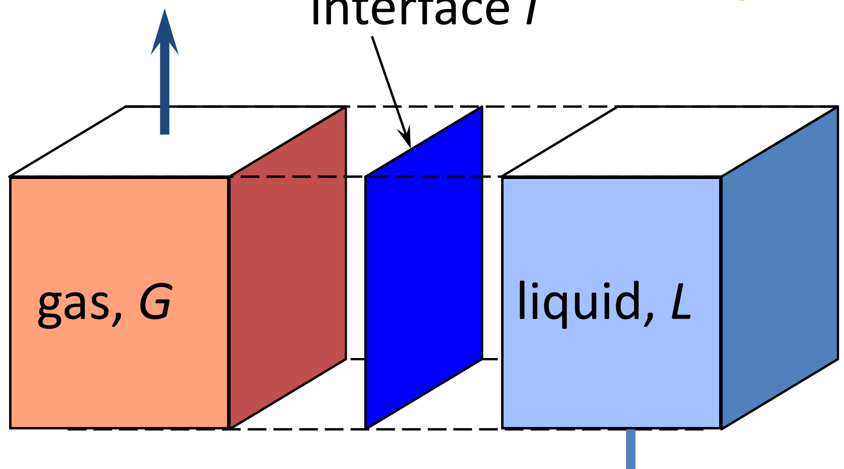
- Rate-based approach



Modeling and Simulation

Equilibrium stage model



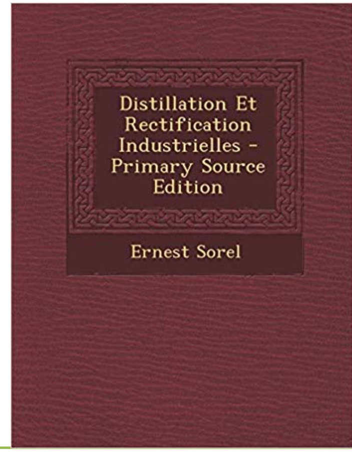


$$T^{G,I} = T^{L,I}$$

$$\mu_i^{G,I} = \mu_i^{L,I}$$

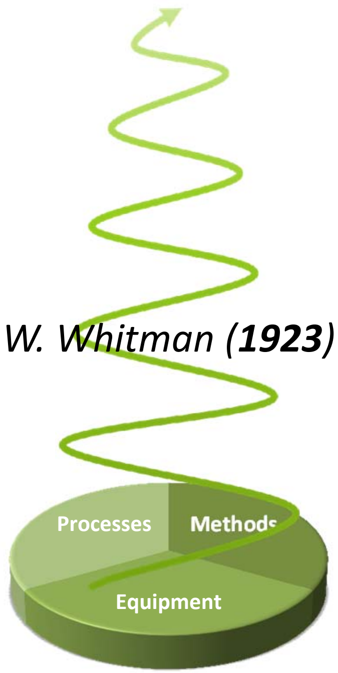
no gradients in the gas or liquid

flows leaving the stage are in equilibrium



Modeling and simulation

Rate-based approach



146 CHEMICAL AND METALLURGICAL ENGINEERING *Vol. 29, No. 4*

A Preliminary Experimental Confirmation of

The Two-Film Theory of Gas Absorption

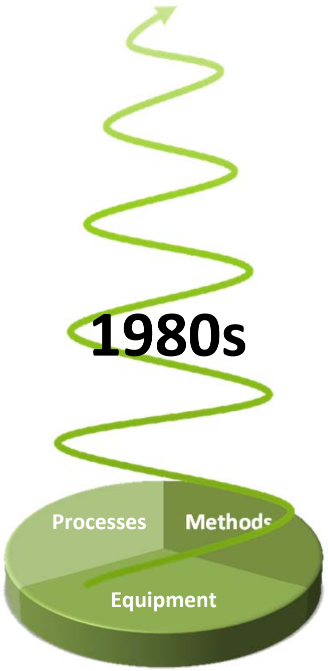
It Seems to Explain Satisfactorily the Well-Recognized Differences of Absorption Rate for Varying Concentrations

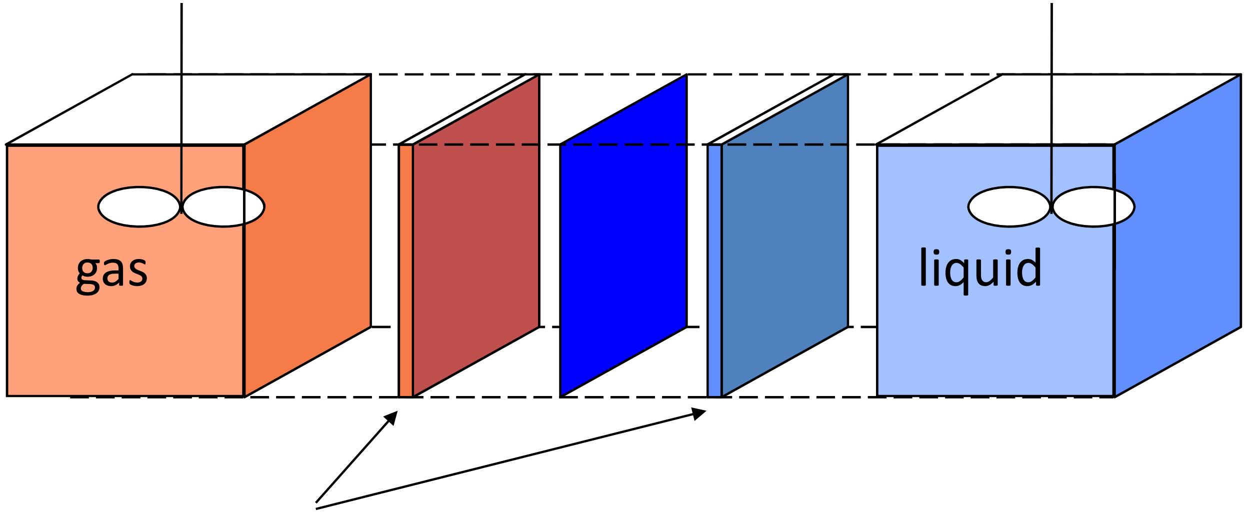
BY WALTER G. WHITMAN
Assistant Professor of Chemical Engineering, Massachusetts Institute of Technology

Few subjects are cr… theoretically and pr… tion. For years ent… plications and even… there have been de… that seem to shed s… ism. This paper cl… around the potenti… tribute in helping to put this unit process on a substantial basis. One of the slogans should perhaps be, "No more monstrosities as absorption towers!" No more of the old formula, "Let's make it a foot bigger in diameter and 5 ft. higher just for good luck."

Modeling and simulation

Non-Equilibrium stage model = Rate-based approach





multicpomonent mixtures

thin ‘film’ resistances for mass and heat transfer;

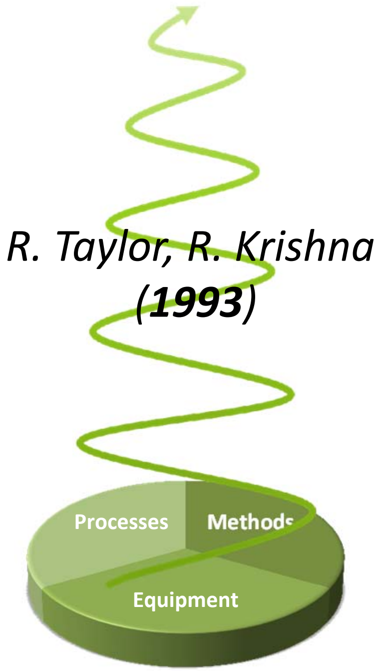
A. Górak: „Neu Methode zur Berechnung von Konzentrationsprofilen in Mehrstoffrektifikation“, *Verfahrenstechnik vt, Mainz*; 17 (**1983**) 539-,545

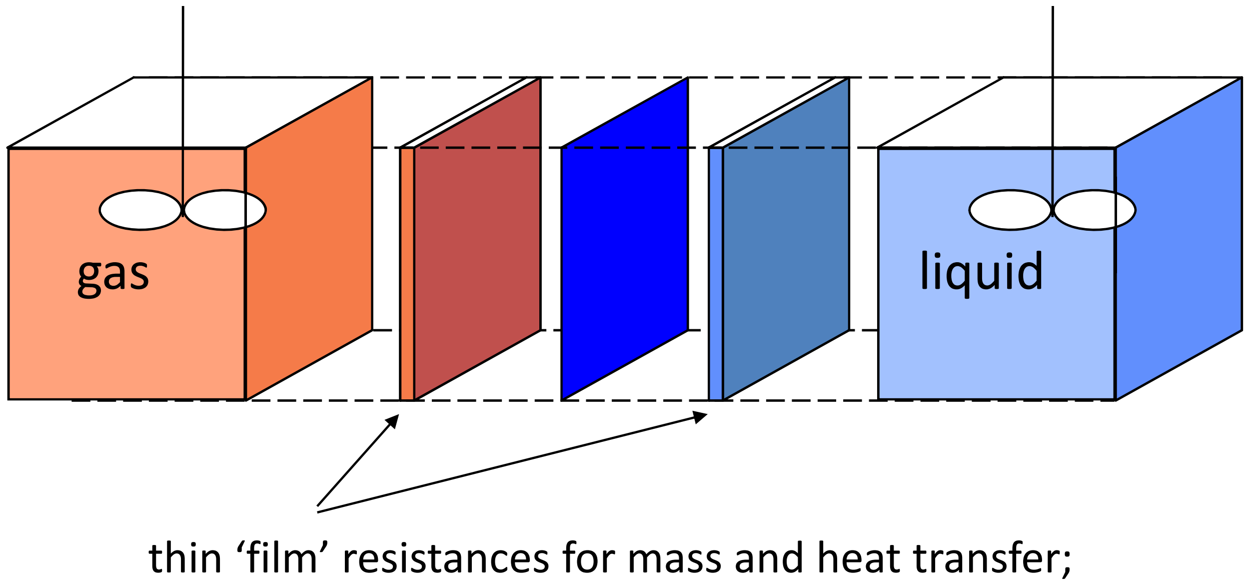
Кениг Е.Я., Баклачян Р.А., Холпанов Л.П., Лотхов В.А., Малюсов В.А. Методика расчета тепломассопереноса при пленочной ректификации многокомпонентных смесей. Теоретические основы химической технологии, (**1981**), том 15, №4, стр. 483

R. Krishnamurthy, **R. Taylor**, "A nonequilibrium stage model of multicomponent separation processes. Part I: model description and method of solution", *AIChE J.*, Vol. 31 (**1985**), pp. 449-456.

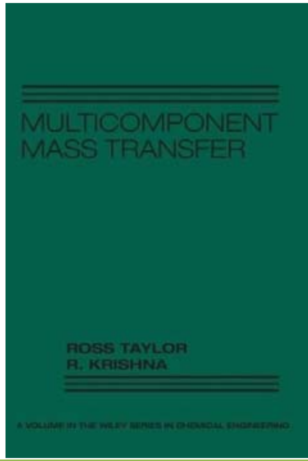
Modeling and simulation

Non-Equilibrium stage model = Rate-based approach



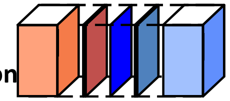


multicpomonent mixtures

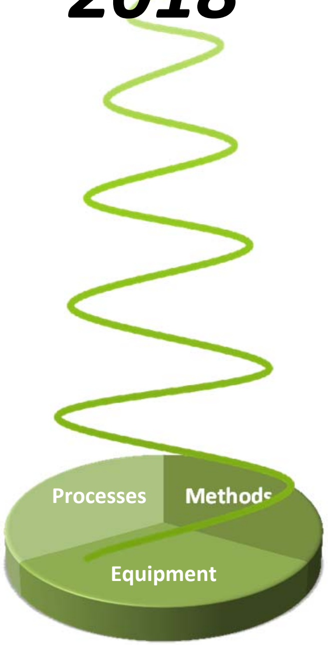


Modeling and simulation

Simulation of an SO_2 Tolerant Amine Based Post Combustion CO2 Capture Process
A. Cousins, G. Puxty, P. Pearson, R. Weiland, B. Garg, V. Verheyen, P. Feron
Pilot Tests and Rate-based Modeling of CO2 Capture in Cement Plants Using an Aqueous Ammonia Solution
Jose-Francisco Perez-Calvo, D. Sutter, F. Milella, M. Gazzani, M. Mazzotti



2018



Choosing the Right Model for Distillation Processes in Packed Columns: Theory and Experiments
*T. Waltermann, R. Benfer, S. Schlueter, A. Reinhardt, C. Knoesche, **A. Górak**, M.Skiborowski*

Absorption of Carbon Dioxide Using Enzyme Activated Amine Solution in Columns with Random Packings
*J.F. Mackowiak, K. Syring, A. Thomas, M. Leimbrink, M. Skiborowski, **A. Gorak**, J. Mackowiak*

Rate-based Modeling of CO2 Absorption with Sandwich Packings
*S.Flechsig, J.Sohr, M. Schubert, U. Hampel**, E. Kenig***

A Rate-based Equation-oriented Parallel Column Model: Application to Dividing Wall Columns
*Ji. Zhou, H. Kooijman, **R. Taylor***

11th International Conference on Distillation & Absorption 2018

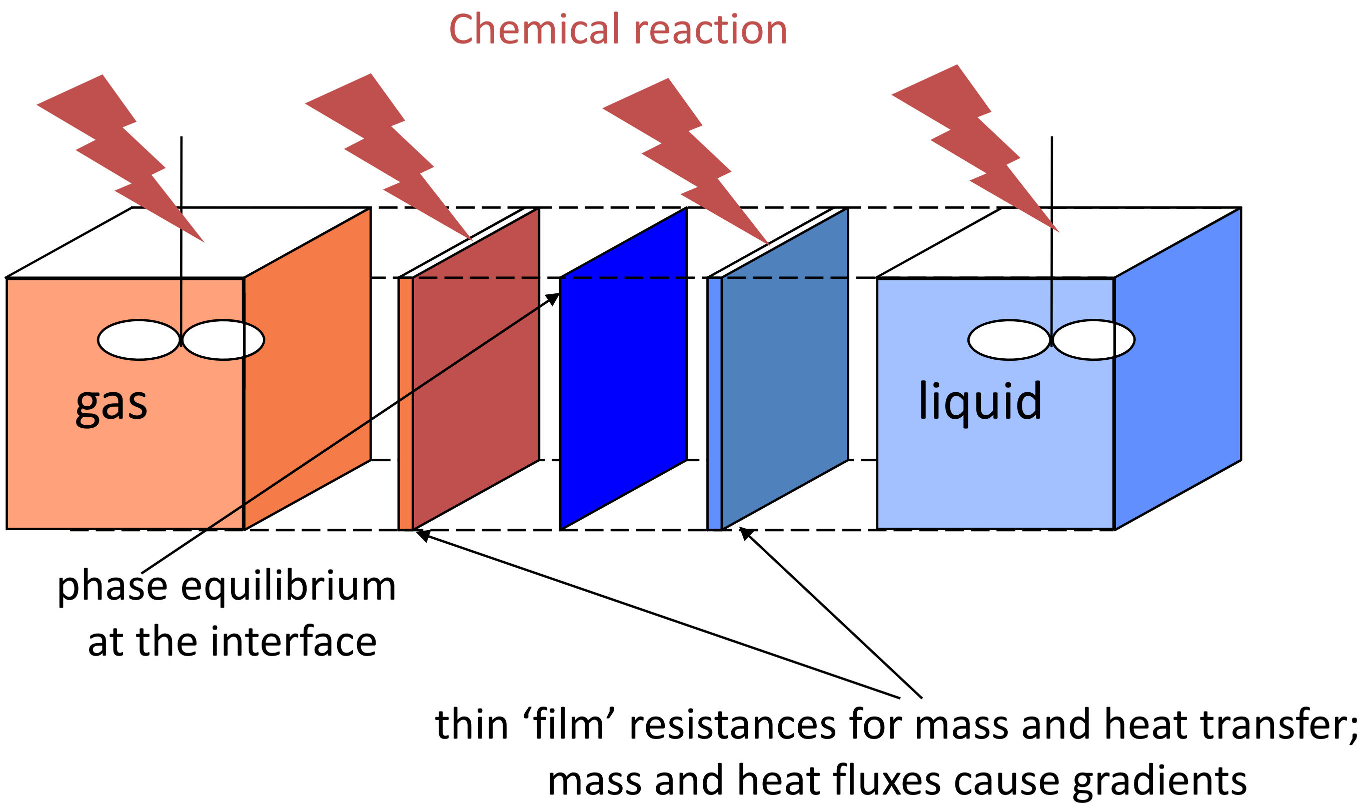
16-19 September 2018, Florence – Italy

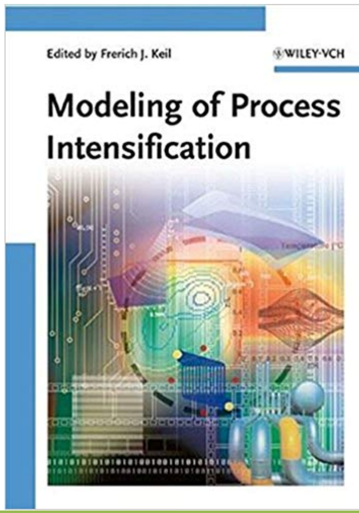
A. Górak: „Neu Methode zur Berechnung von Konzentrationsprofilen in Mehrstoffrektifikation“, *Verfahrenstechnik vt, Mainz*; 17 (**1983**) 539-,545

Кениг Е.Я., Баклачян Р.А., Холпанов Л.П., Лотхов В.А., Малюсов В.А. Методика расчета тепломассопереноса при пленочной ректификации многокомпонентных смесей. Теоретические основы химической технологии, (**1981**), том 15, №4, стр. 483

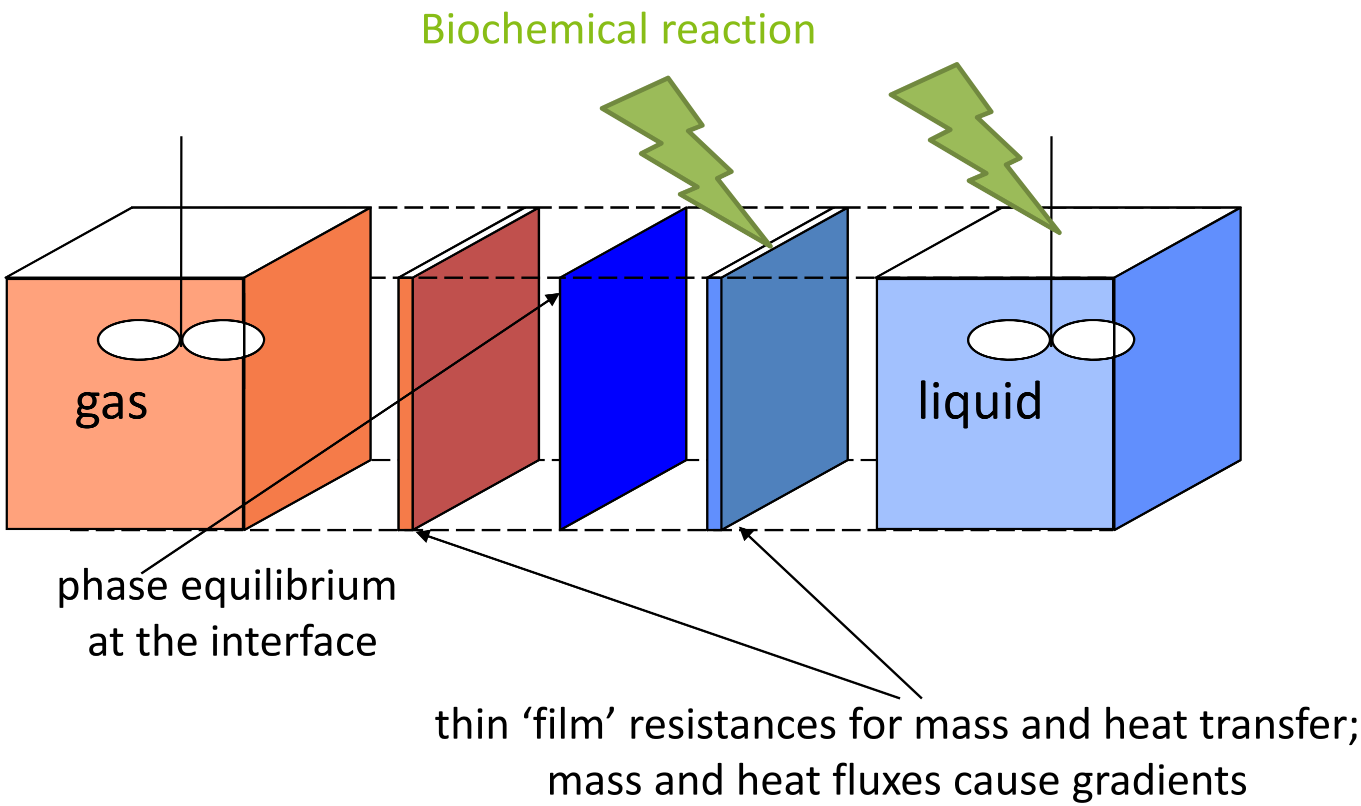
R. Krishnamurthy, **R. Taylor**, "A nonequilibrium stage model of multicomponent separation processes. Part I: model description and method of solution", *AIChE J.*, Vol. 31 (**1985**), pp. 449-456.

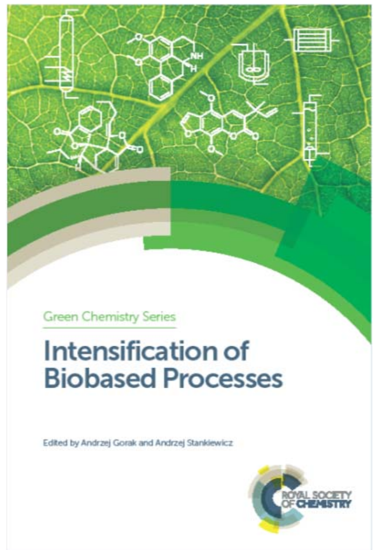
Rate-based approach, reactive separations





Rate-based approach, biochemical reactive separations

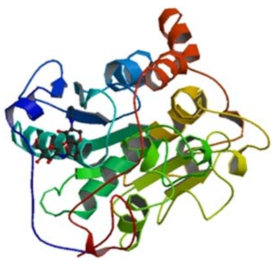


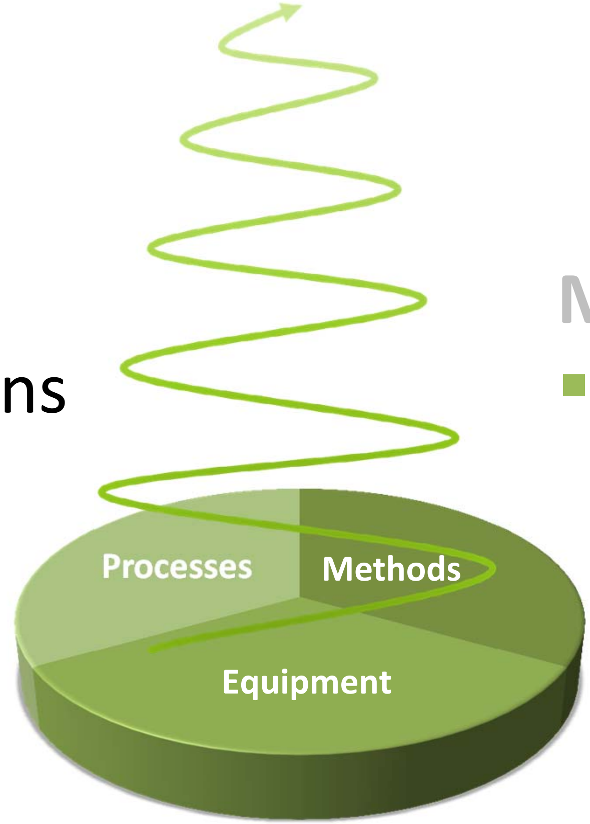


Revisit old ideas for new fluid separations

Process intensification

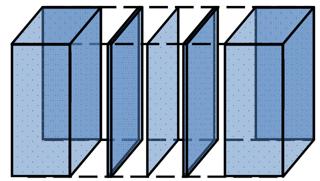
- Bioreactive Separations
- Enzymatic processes





Modeling and simulation

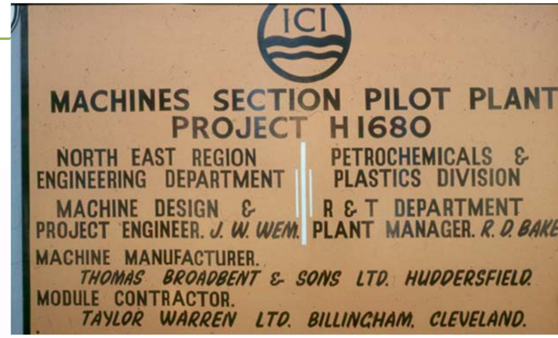
- Rate-based approach



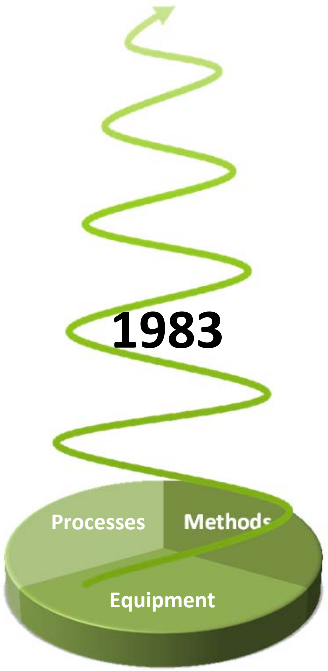
Fundamentals of Process Intensification

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)

Intensified equipment – HiGee technology



Idea



- Superimposing the gravitational acceleration with **centrifugal acceleration**

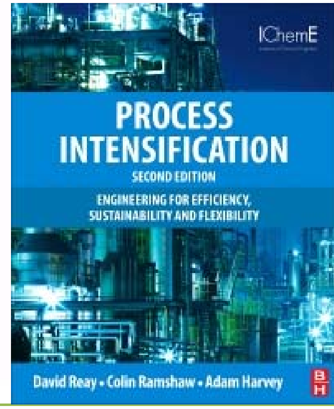
Pros and cons

- Higher liquid and gas loads

  but lower liquid holdup
- Intensification of heat and mass transfer

  but complex hydrodynamics
- More compact device than traditional colums

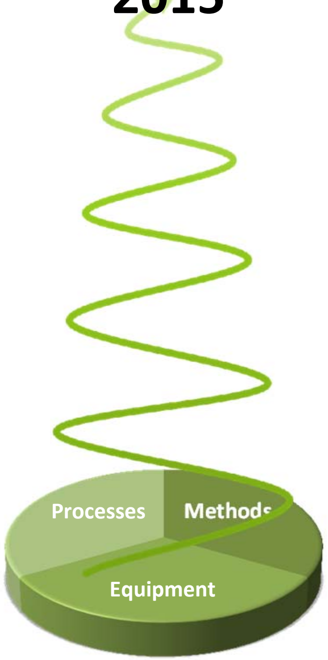
  but rotational equipment



*C. Ramshaw: HIGEE—An Example of process intensification Chem. Engr., Feb (**1983**), p. 13R*

Trayed HiGee: distillation applications in China

2015



Anhydrous ethanol Extractive dist.

THF-water extractive dist.

230+ companies
700+HIGEEs

dichloromethane-methanol-water azeotropic dist.

***n*-butanol-water azeotropic dist.**

Courtesy: Prof. Guangquan Wang

浙江工业大学 ZHEJIANG UNIVERSITY OF TECHNOLOGY

Intensified equipment – HiGee technology

No reported applications for distillation in Europe

Because it is too complex?

Fundamental research necessary

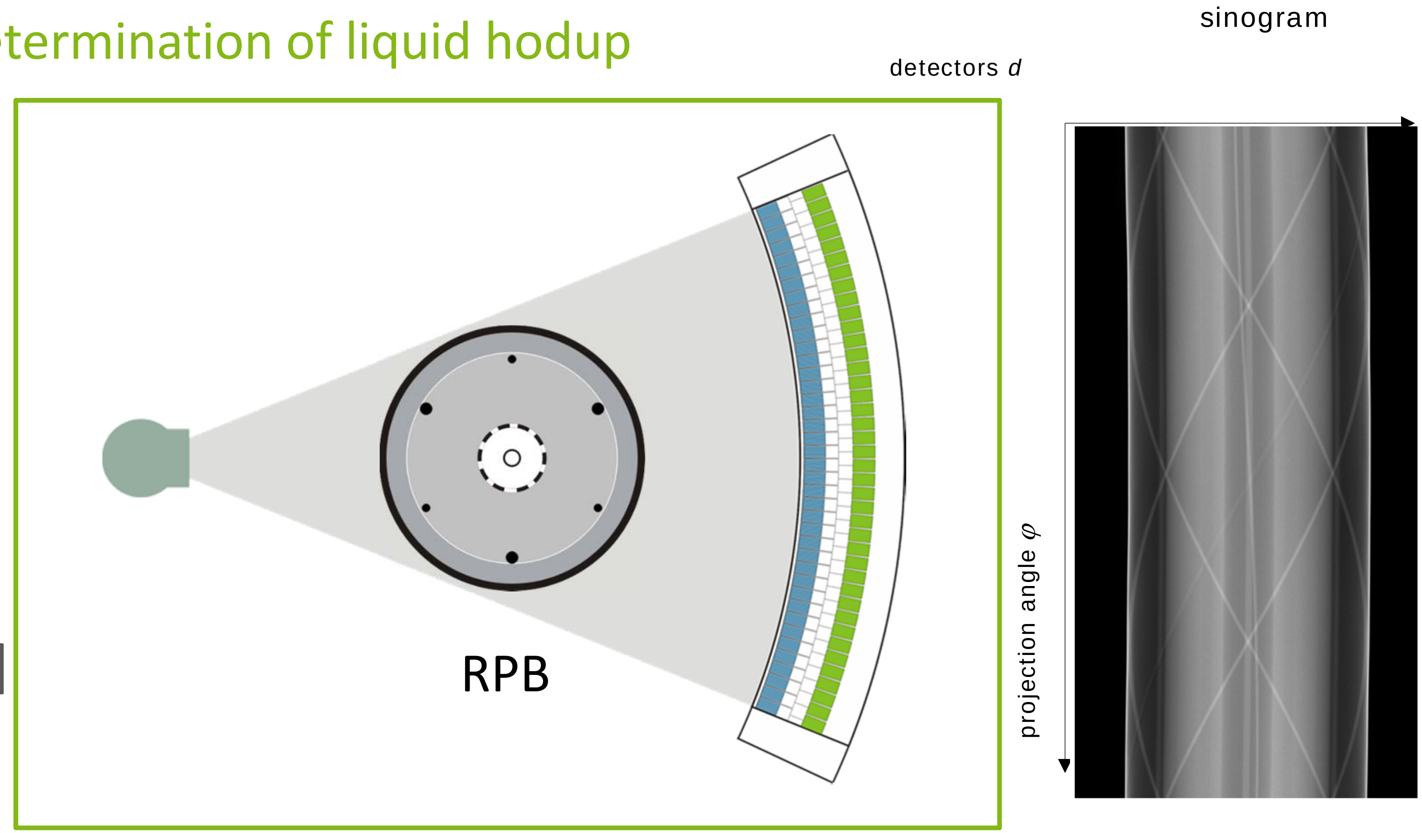
- Main parameters
  - Pressure drop
  - Operating Range
  - Mass transfer
  - Rotational speed
- Rotor design
  - Relation $\frac{di}{da}$
  - Axial height
  - Droplet flow
  - Casing behavior

- Liquid distribution
  - Nozzle type
  - Nozzle position
  - Flow conditions
- Type of packing
  - Mesh / Foams
  - Stability
  - Hold-up

G. Garcia, J. van der Schaaf, A. A Kiss, A review on process intensification in HiGee distillation, J. Chem.Techn.Biotech. 92(2017) 1136-1156
Neumann, K.; Gladyszewski, K.; Groß, K.; Qammar, H.; Wenzel, D.; Górak, A.; Skiborowski, M., A guide on the industrial application of rotating packed beds, ChemEngResDes 134 (2018), pp. 443

Non-invasive determination of liquid hodup

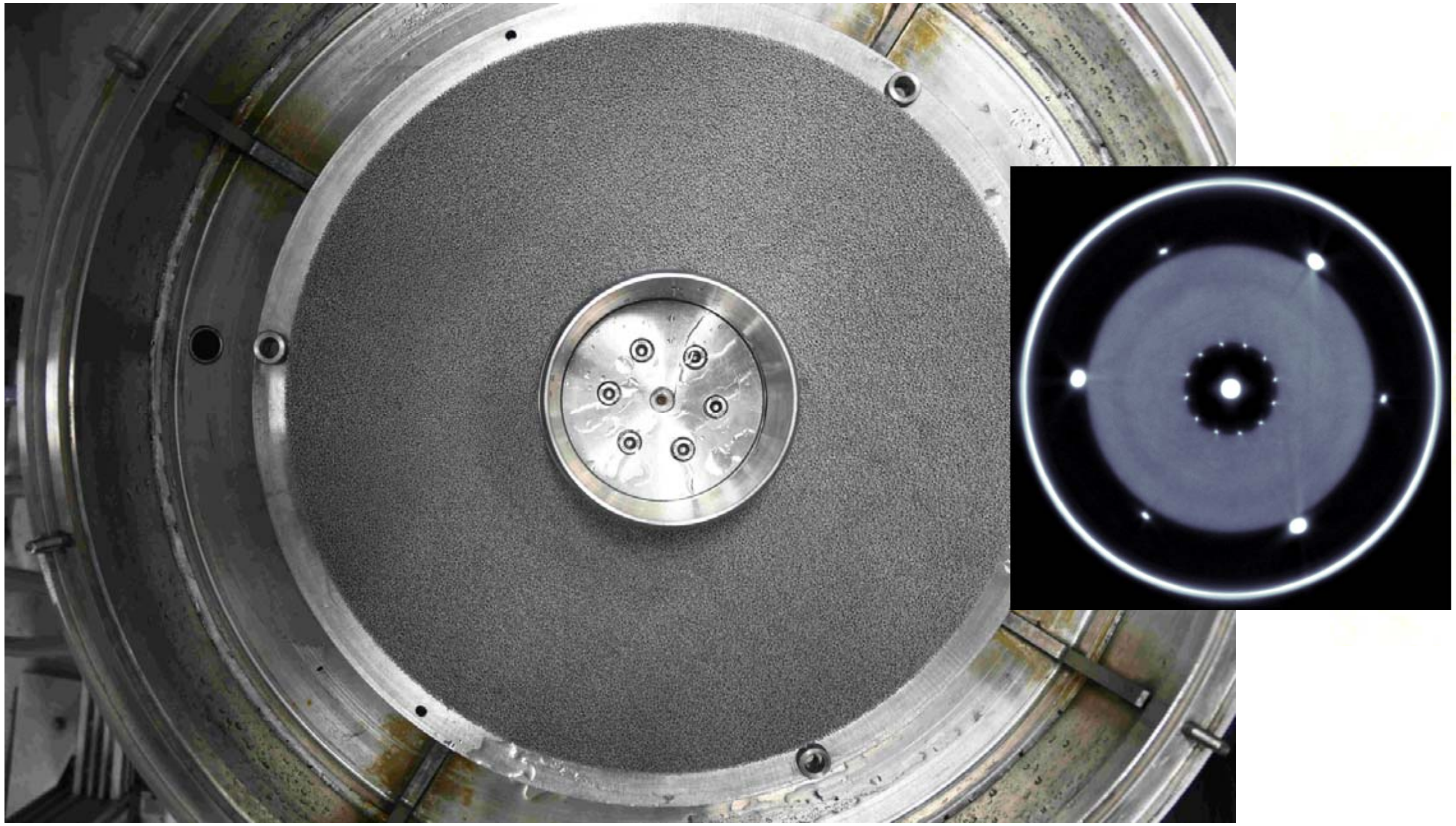
Gamma-ray tomography

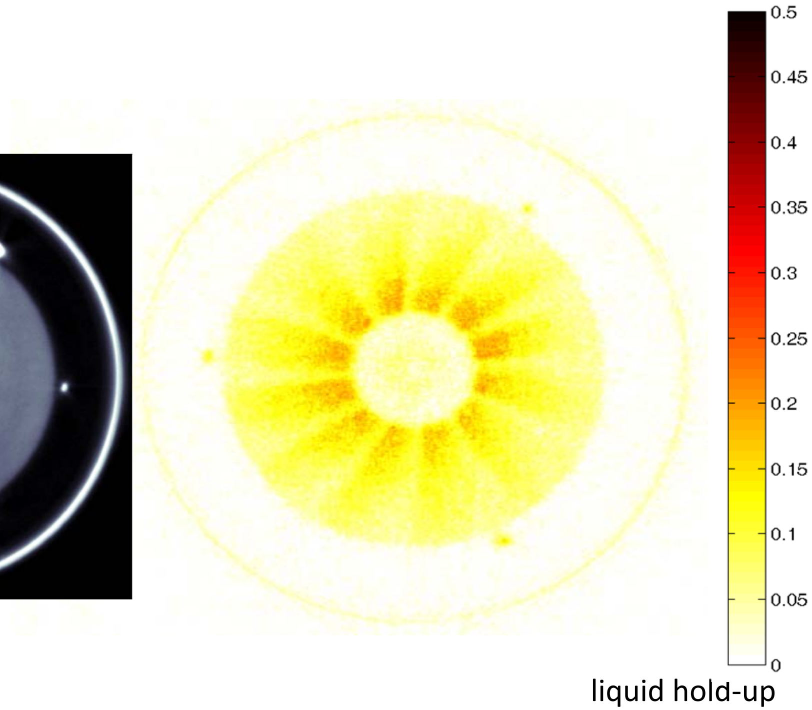


Fundamental research

A. Bieberle et al. Data acquisition system for angle synchronized gamma-ray tomography of rapidly rotating objects Measurement Science and Technology, 18(2007)3384

Reality/Reconstruction

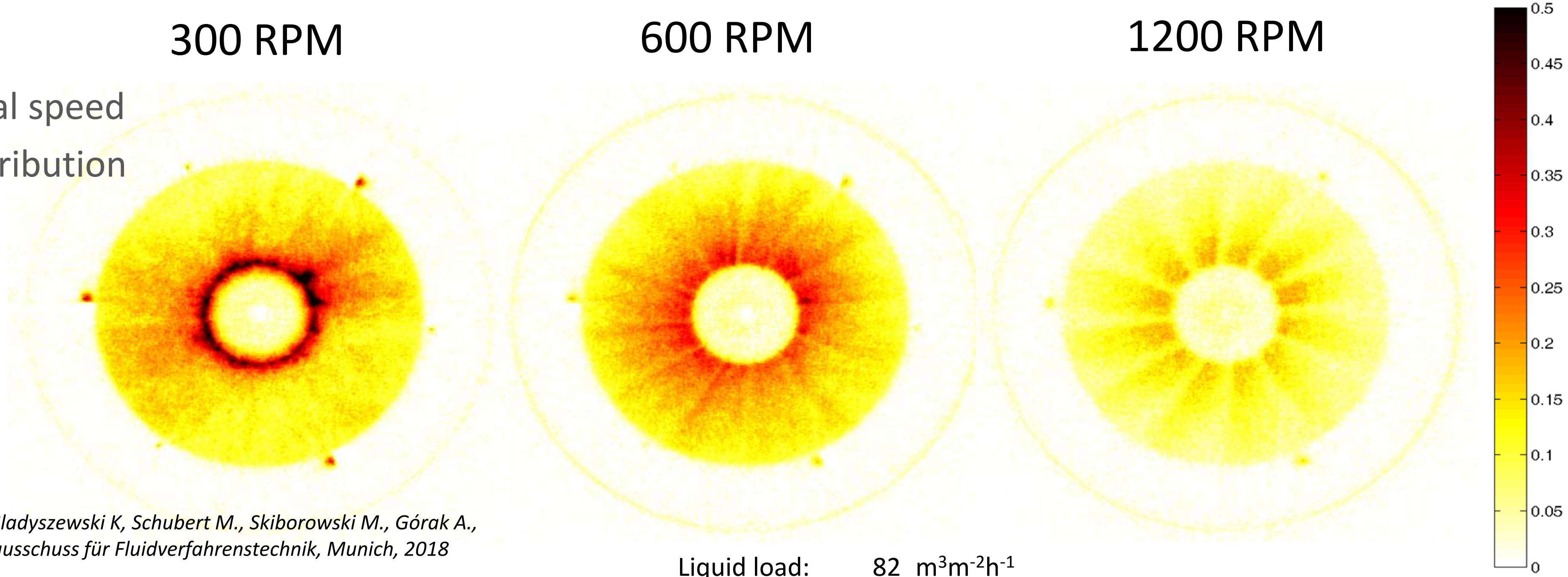




Maldistribution of liquid in rotor

Analyzing the Operating Limits in High Gravity Equipment
K. Gross, K. Neumann, M. Skiborowski, A. Gorak

- Higher rotational speed enhances maldistribution



Groß K., Bieberle A., Gladyszewski K, Schubert M., Skiborowski M., Górak A., Presentation on Fachausschuss für Fluidverfahrenstechnik, Munich, 2018

Liquid load: 82 $m^3m^{-2}h^{-1}$

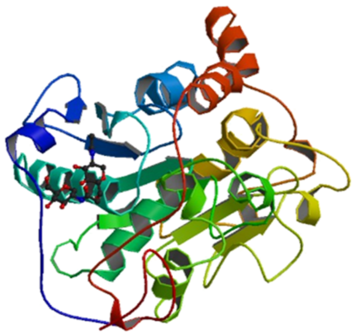
F-Factor: 3-4 $Pa^{0.5}$

Yucheng Yang et al., Chem. Eng. Sci., 138, (2015) 244

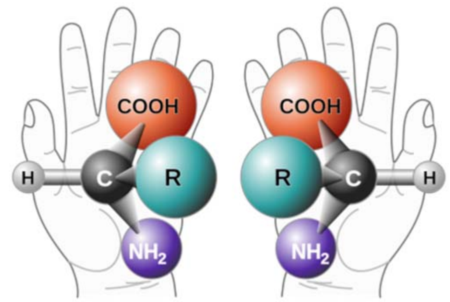
Intensified separations

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)

Enzymatic Reactive Distillation
Enzymatic Reactive Absorption



Enzymatic reactive distillation

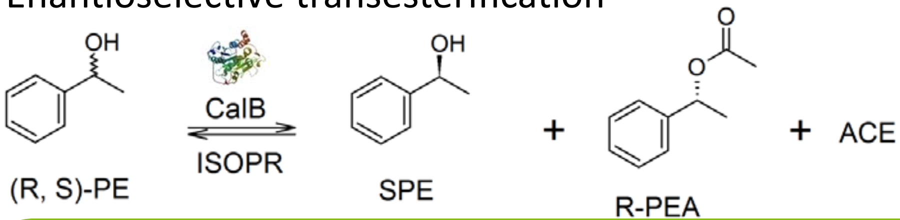


Wikipedia.org

Chiral molecules

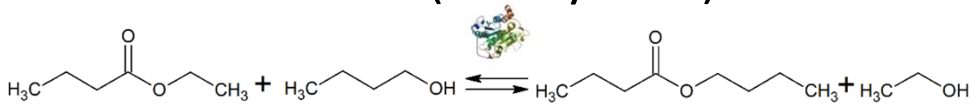
- Optically active intermediates in pharmaceuticals
- New products/new efficient production routes
- Separation of chiral molecules in one distillation column

Enantioselective transesterification

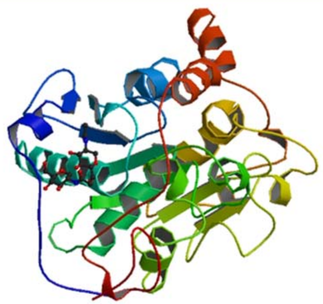


(R,S)-PE:	(R,S)-phenyethanol
ISOPR:	isopropenyl acetate
SPE:	(S)-phenylethanol
R-PEA:	(R)-phenyl ethyl acetate
ACE:	acetone

Transesterification (test system)



ethyl butyrate (EtBu) | *n*-butanol (BuOH) | butyl butyrate (BuBu) | ethanol (EtOH)

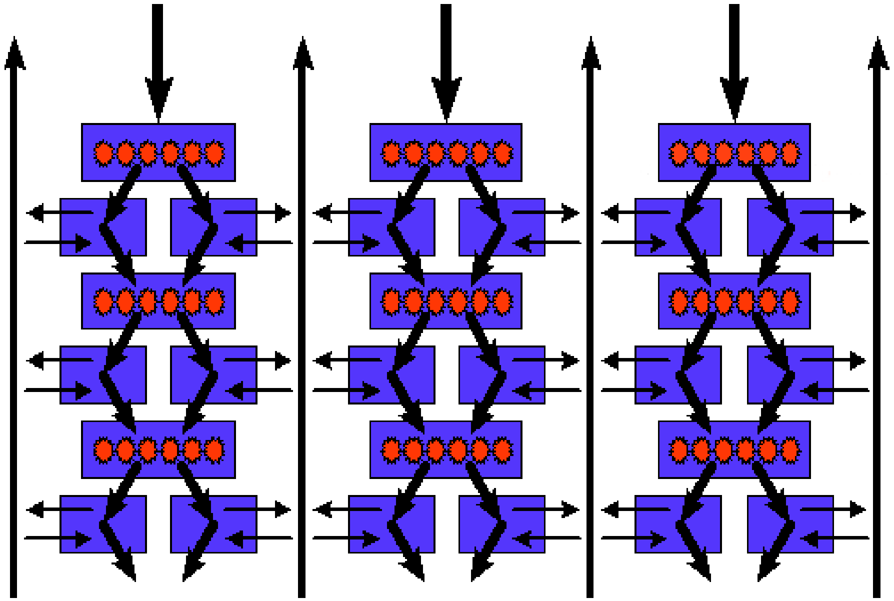


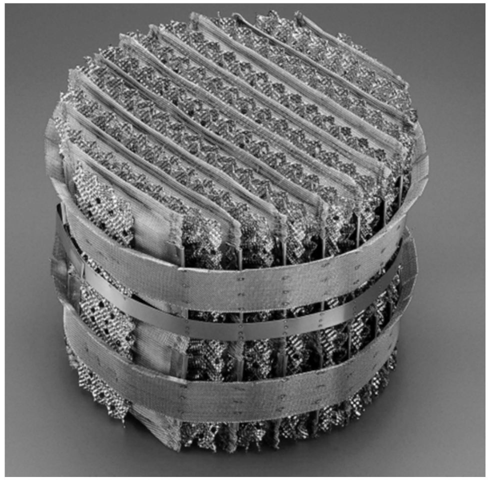
Enzymatic Reactive Distillation: Kinetic Resolution of rac-2-Pentanol with Biocatalytic Coatings on Structured Packings, R. Heils, J. Jensen, S. Wichert, N. Behrens, M. Fabuel-Ortega, A. Liese, I. Smirnova, Indu.Eng.Chem.Res.54 (2015) (38), 945

Horizontal reactive distillation for multicomponent chiral resolution, P. Au-Yeung, S. Resnick, P. Witt, T. Frank, F. Donate, AIChEJ 59 (2013) 2603

Structured catalytic packings

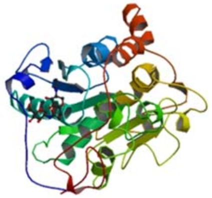
Well known: Immobilised chemical catalyst



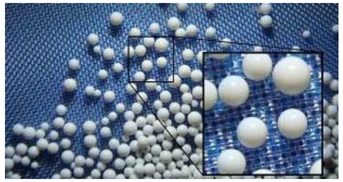


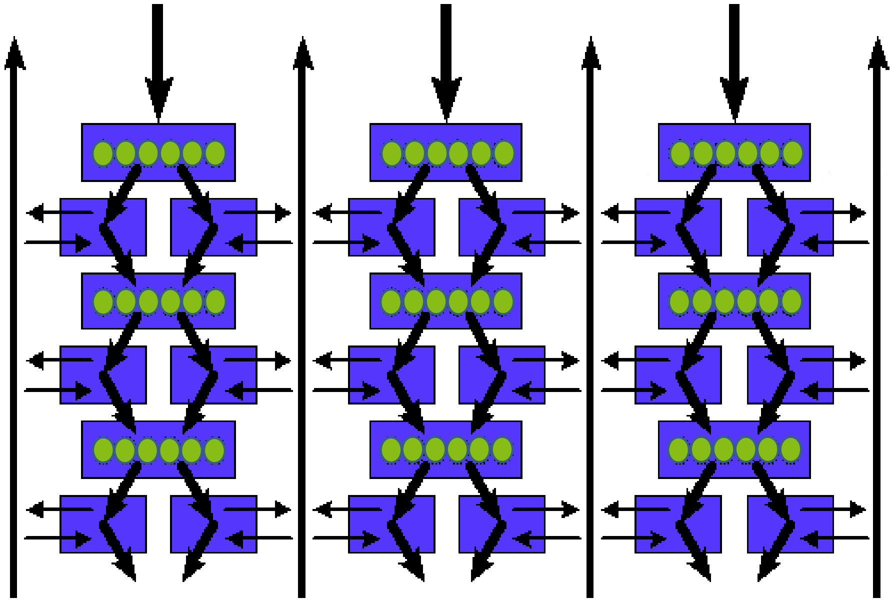
KATAPAK® -SP

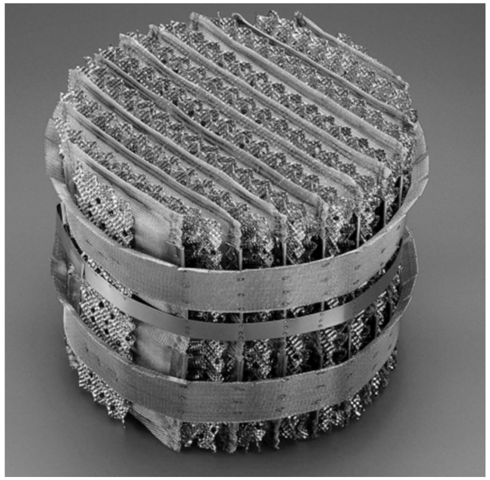
Structured catalytic packings



New: Enzymes immobilised on beads





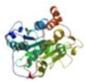


KATAPAK® -SP

technische universität dortmund

laboratory of fluid separations

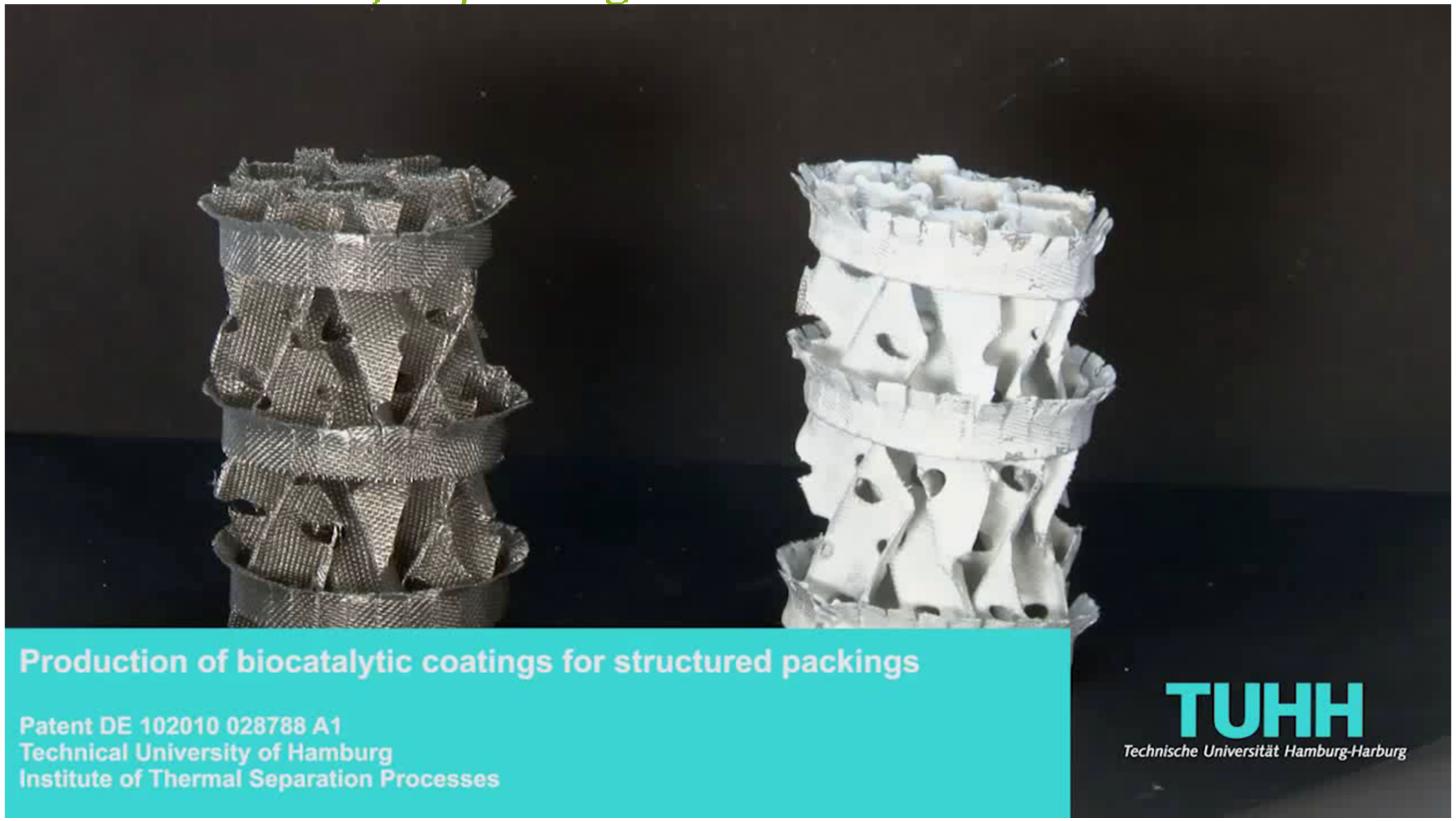
Structured catalytic packings

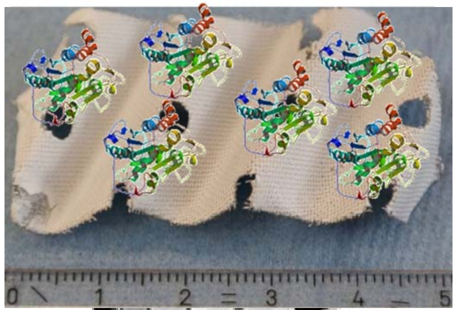


- Another immobilisation approach
  - Coating of wire gauze packing
    - Sulzer BX
    - Sol-gel method to entrap enzymes
    - Stability sufficient for several batches
- Long-term stability and kinetics?

Wierschem, M.; Schlimper, S.; Heils, R.; Smirnova, I.; Kiss, A.; Skiborowski, M.; Lutze, P.: Chemical Engineering Journal 312 (2017), pp. 106–117

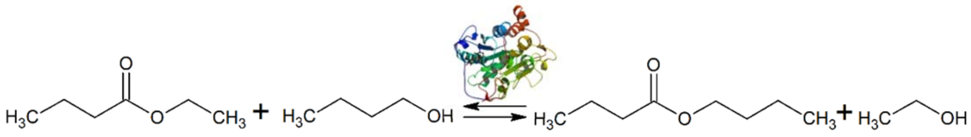
Structured catalytic packings



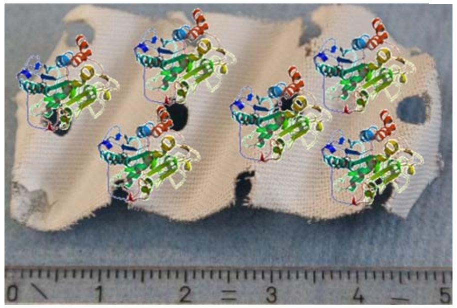


Rate-based approach, enzymatic reactive distillation

- Chemical system (model system)
  - Transesterification of ethyl butyrate
  - Catalyzed by *Candida antarctica* lipase B (CalB)



ethyl butyrate (EtBu) | *n*-butanol (BuOH) | butyl butyrate (BuBu) | ethanol (EtOH)



Coated packing element

Schott glass with coated packing element

Simplified Ping Pong Bi Bi mechanism [1]

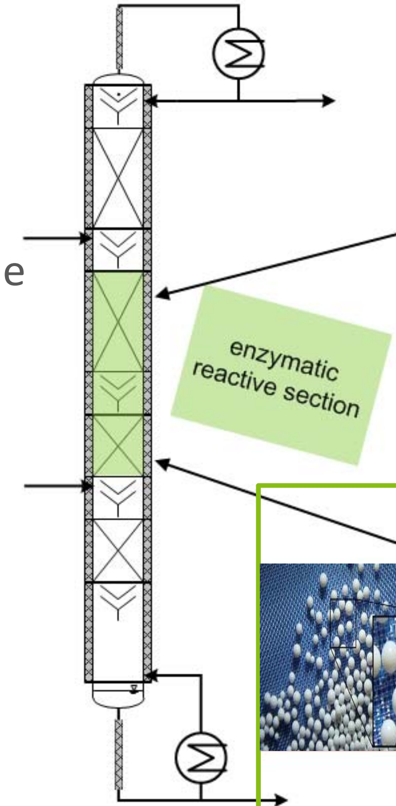
$$\frac{d[BuBu]}{dt} = \frac{m_{cat}\, v_f\, v_r \left([EtBu][BuOH] - \frac{1}{K_{eq}} [BuBu][EtOH] \right)}{\frac{v_f}{K_{eq}} \left(K_{m,BuBu} [EtOH] + [BuBu][EtOH] \right) + v_r [EtBu][BuOH]}$$

R.Heils, A.Niesbach, M.Wierschem, (…),P.Lutze, I.Smirnova: Ind.Eng.Chem.Research 53 (2014),19612

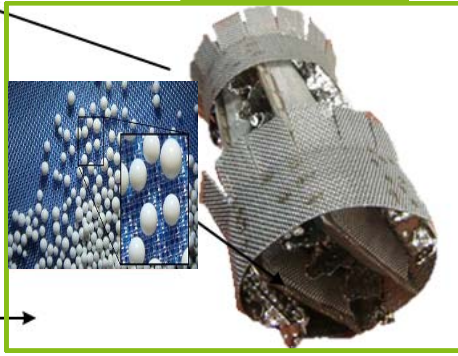
[1] Paiva, A. L. et al., Biotechnol. Prog., 19 (3), p. 750–754 (2003)

Rate-based approach, enzymatic reactive distillation

- Enzymatic reactive distillation integrates biochemical reaction and separation
- Reaction equilibrium shifted to the side of reaction product
- Immobilized enzyme



enzymes in coating of wire gauze packing



structured packing filled with immobilized enzymes

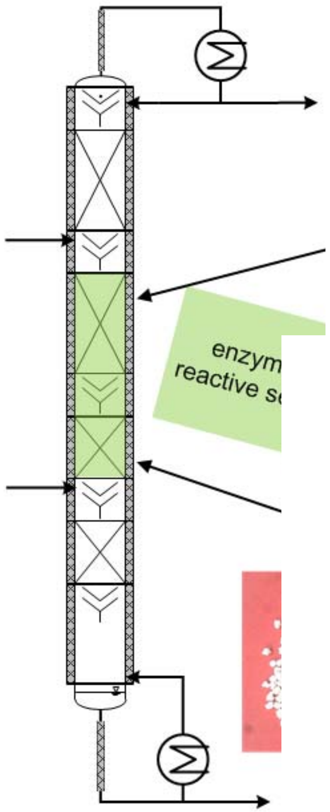
R.Heils, A.Sont, P.Bubenheim, A.Liese, and I.Smirnova. Integration of Enzymatic Catalysts in a Reactive Distillation Column with Structured Packings; Industrial & Engineering Chemistry Research 2012 51 (35), 11482

J. Xu, C. Liu, M. Wang, L. Shao, L., K. Nie, F. Wang, Rotating packed bed reactor for enzymatic synthesis of biodiesel, Bioresource Technology, 224(2017)292

Rate-based approach, enzymatic reactive distillation

- Simulation vs. experiment (coated packing)
- Kinetics implemented in model

Good agreement between experiment & simulation using rate-based approach

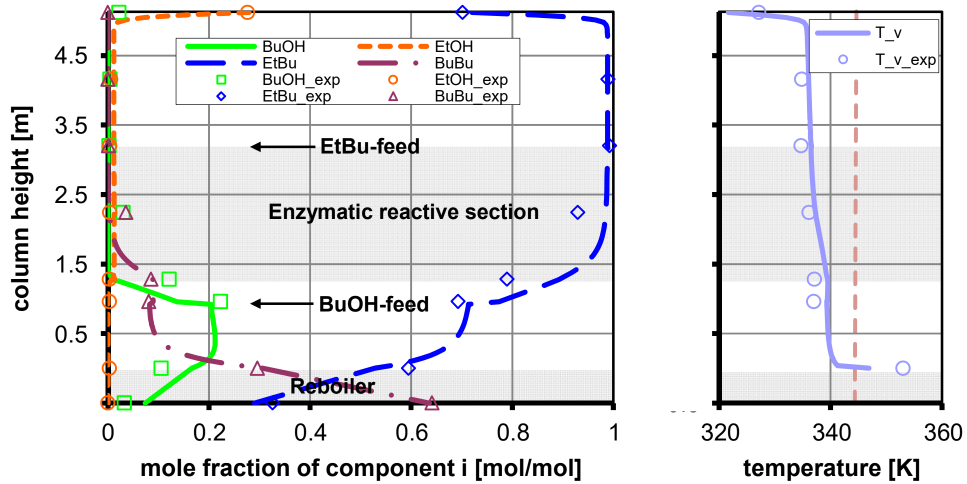


Experimental conditions

EtBu-feed:	1.70 kg/h
BuOH-feed:	0.30 kg/h
Distillate stream:	1.26 kg/h
Bottom stream:	0.74 kg/h
Pressure: 146 mbar	

Conversion

BuOH:	89 %
EtBu:	25 %



Wierschem, M.; Schlimper, S.; Heils, R.; Smirnova, I.; Kiss, A.; Skiborowski, M.; Lutze, P.: Chemical Engineering Journal 312 (2017), 06

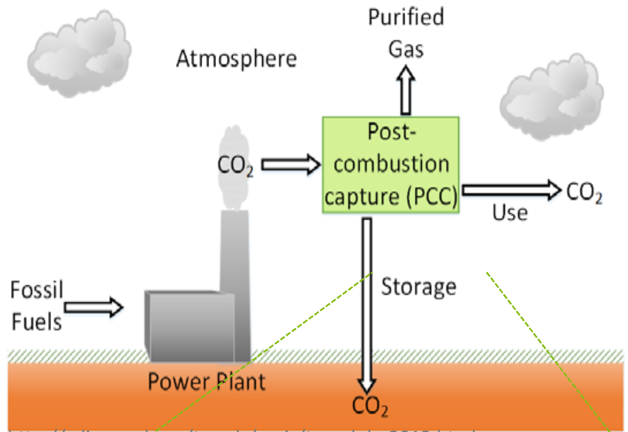
Enzymatic reactive absorption

- **Greenh**
  - Maj
  - 40%
- **Most in**
  - Solv
  - Espe
  - → Mo

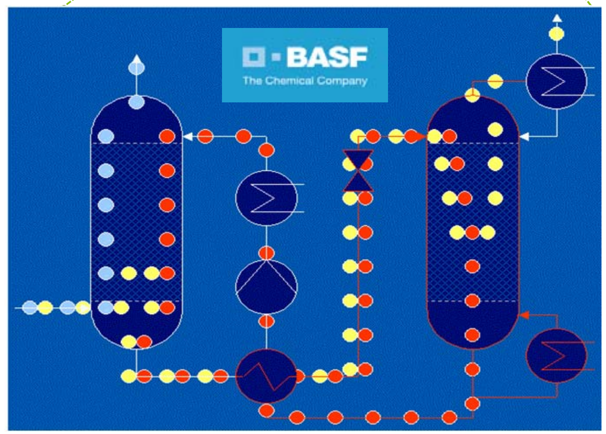
Amines		
Primary MEA	Secondary DEA	Tertiary TEA, MDEA
High	← enthalpy of reaction	Low
High	← enthalpy of evaporation	Low
High	← reaction rate	Low
High	← corrosivity	Low
Low	loading →	High

Bottlenec
- High t
- Desor

Desired properties: **Tertiary amines**



http://cdiac.ornl.gov/trends/emis/tre_glob_2013.html



Ö. Yildirim et al., Chem. Eng. J., 213, 2012

Mondal et al., Energy, 46 (1), 2012

technische universität dortmund

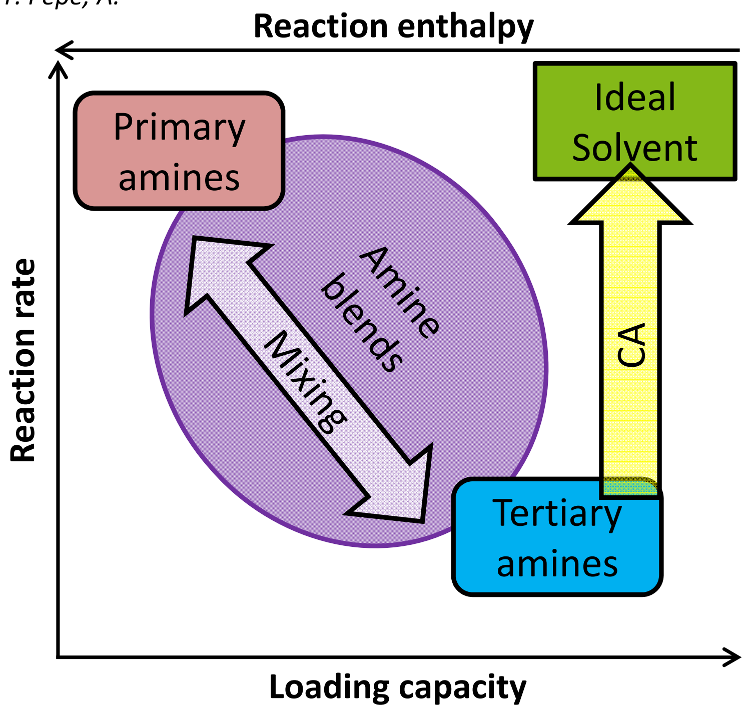
Absorption of Carbon Dioxide Using Enzyme Activated Amine Solution in Columns with Random Packings
J.F. Mackowiak, K. Syring, A.Thomas, M. Leimbrink, M. Skiborowski, A. Gorak, J. Mackowiak

laboratory of fluid separations

Enzymatic reactive absorption

Modelling of Enzymatic Reactive CO2 Absorption
M.E. Russoa, P. Bareschino, F. Pepe, A. Marzocchella, P. Salatino

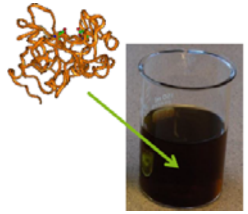
- Drawback of tertiary amines: Slow reaction rates
- Compensation for slow reaction:
  - Activator: Piperazine → amine blends
    → Compromised thermodynamic properties
- Catalyst: **Enzyme Carbonic Anhydrase (CA)** novozymes Rethink Tomorrow
  → Fastest catalyst for CO_2 hydration
  → Advantages: non-volatile, sustainable, bio-degradable, highly selective



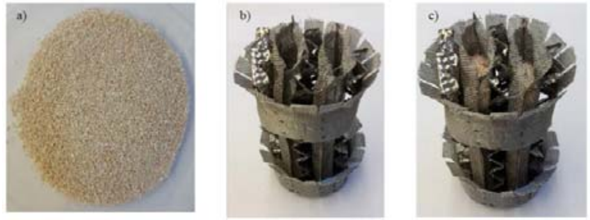
Enzymatic reactive absorption

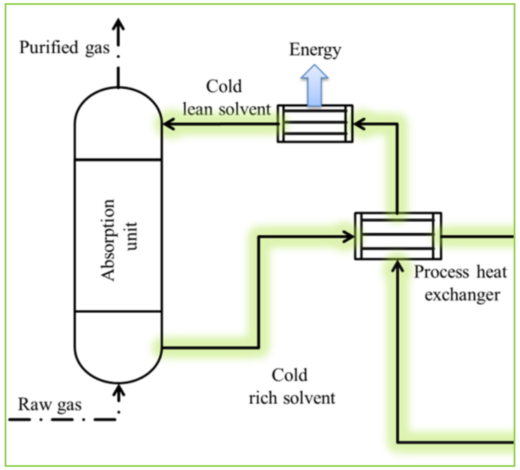
- Different strategies for Carbon Anhydrase application

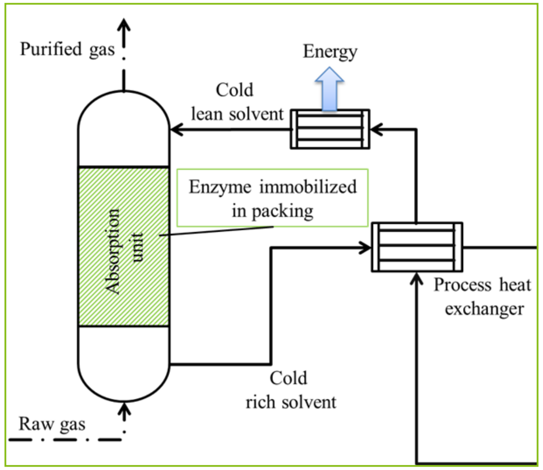
dissolved enzyme



immobilized enzyme







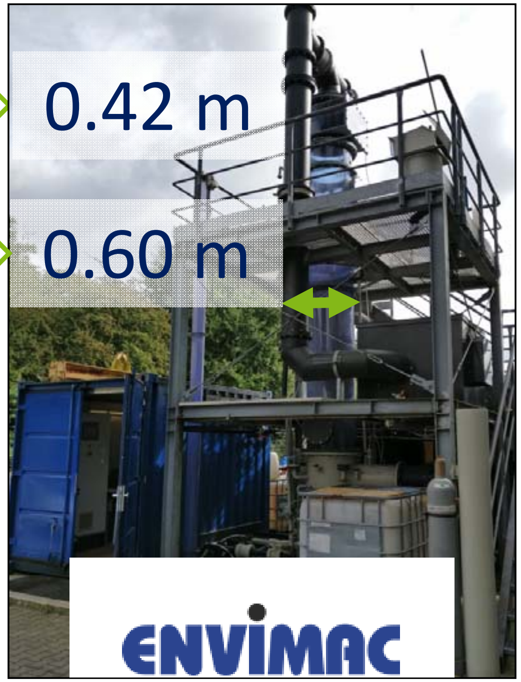
Leimbrink, M.; Sandkämper, S.; Wardhaugh, L.; Maher, D.; Green, P.; Puxty, G.; Conway, W.; Bennett, R.; Botma, H.; Feron, P.; Górak, A.; Skiborowski, M. "Energy-efficient solvent regeneration in enzymatic reactive absorption for carbon dioxide capture„, Applied Energy 208 (2017), pp. 263–276

Scalability

TUDO DN110

Scale up factor 15

Scale up factor 30



ENVIMAC DN420/600

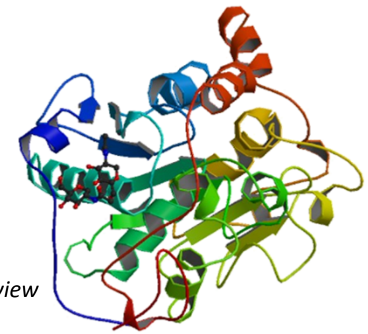
- Scalability successfully proven
- Results from small scale are transferable to larger scales

Leimbrink, M.; Limberg, T.-L.; Kunze, A.-K.; Skiborowski, M. Energy Procedia 114C (2017), pp. 781–794

Intensified separations

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)

Enzymatic Reactive Absorption



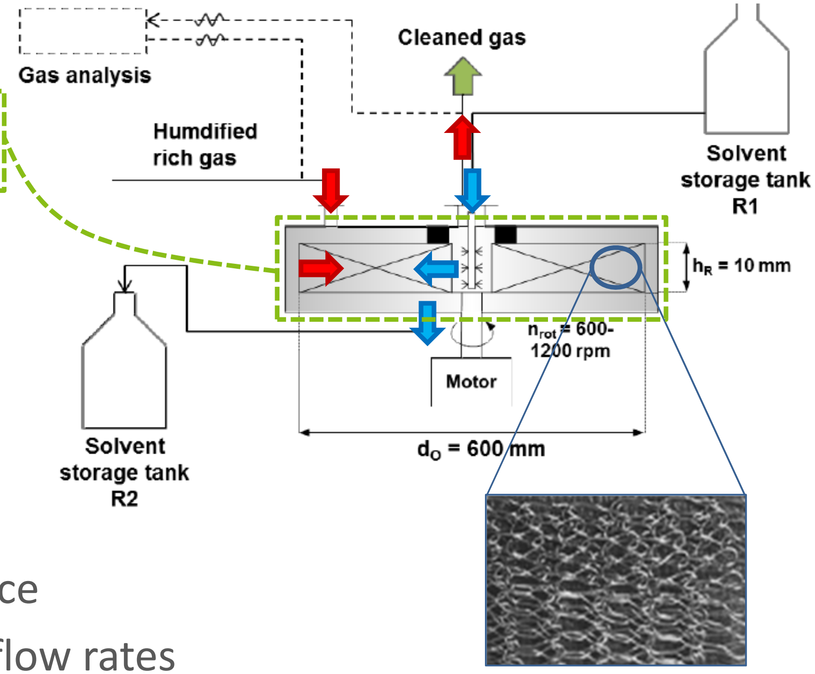
B. Zhao, W. Tao, et al, Process, performance and modeling of CO2 capture by chemical absorption using high gravity: A review Renewable and Sustainable Energy Reviews, 65 (2016), 44

Intensified equipment – HiGee

Rotating Packed Bed

Setup and operation:

- tailored RPB setup
- rotational speed   600 rpm – 1200 rpm
- rotor dimesnions d_O = 600 mm, h_R = 10 mm
- counter current flow
- wired mesh packing



- Expected advantages:
  - **intensification of mass transfer** through improved turbulence
  - **higher capacities accessible** - flooding occurs at higher gas flow rates

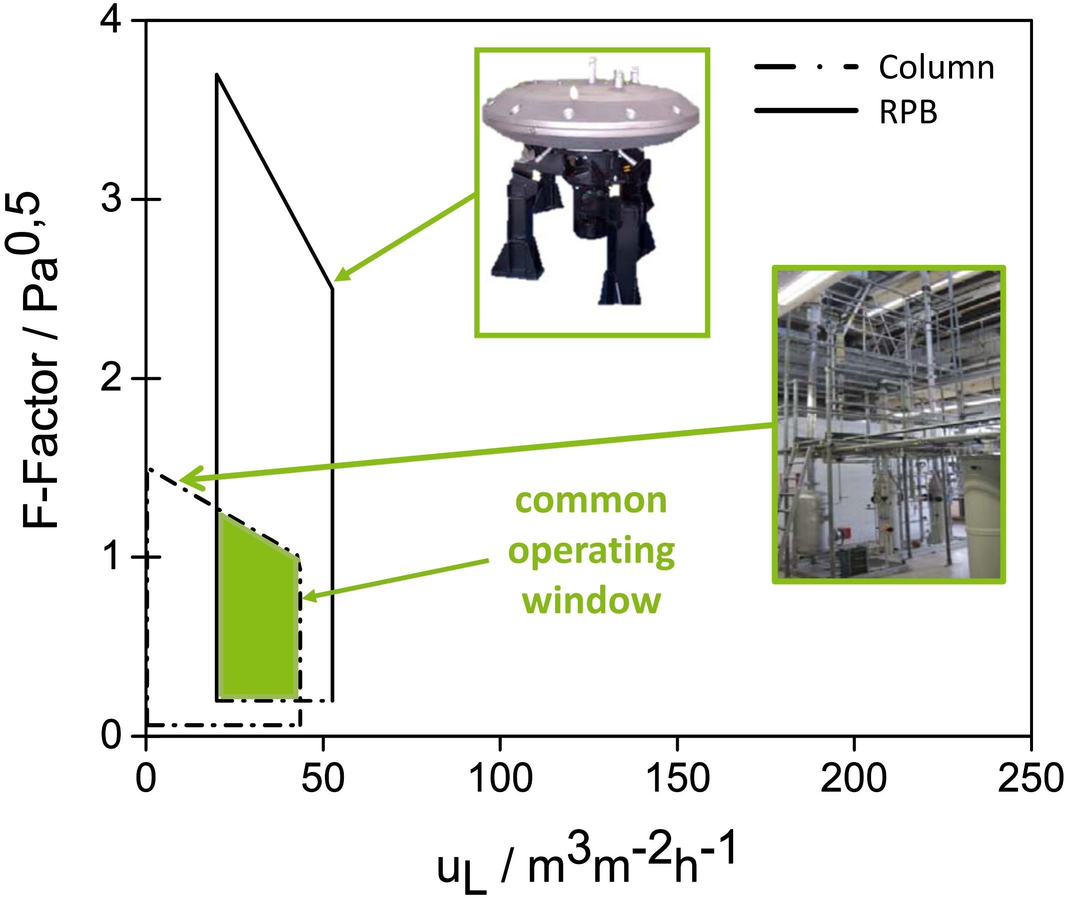
Comparison of operating windows

Column:

- Low gas and liquid flow rates

RPB:

- High gas flow rates



Leimbrink, M.; Neumann, K.; Kupitz, K.; Górak, A.; Skiborowski, M.
"Enzyme accelerated carbon capture in different contacting equipment - a comparative study"
Energy Procedia 114C (2017), pp. 795–812

Performance evaluation of intensified equipment

Normalization of results to interfacial area

With enzyme(CA):

- RPB shows slightly improved normalized absorption rate, compared to the packed column

→ RPB utilizes available interfacial area most efficiently

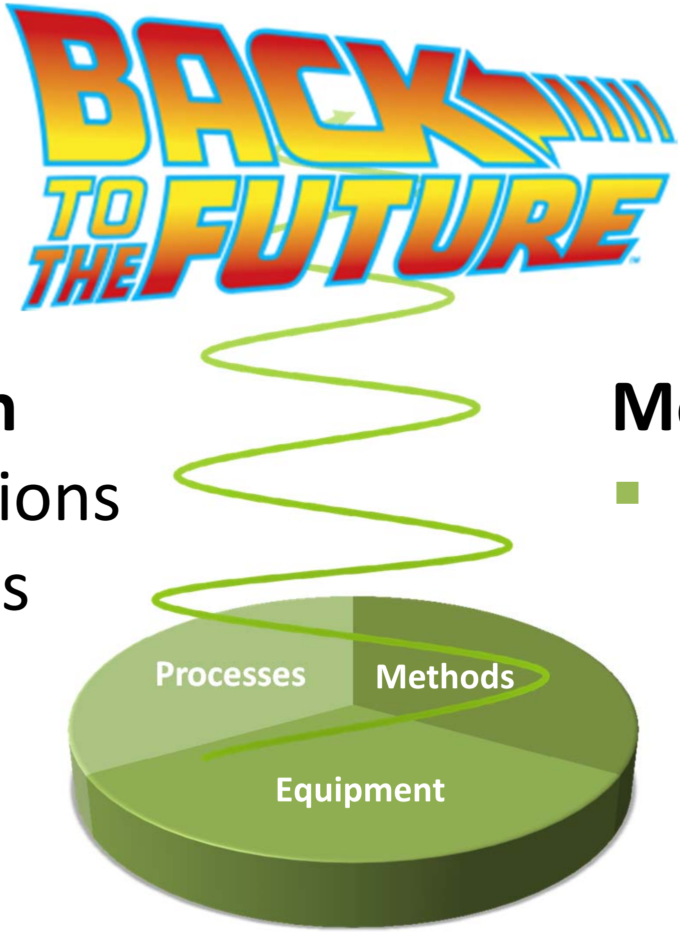
Normalization of results to equipment volume

With enzyme(CA):

- Improved volume-specific absorption rate in RPB

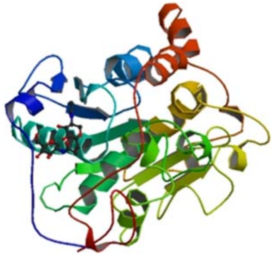
→ RPB allows for reducing equipment size by half

Leimbrink, M.; Neumann, K.; Kupitz, K.; Górak, A.; Skiborowski, M.
"Enzyme accelerated carbon capture in different contacting equipment - a comparative study"
Energy Procedia 114C (2017), pp. 795–812



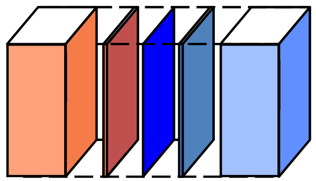
Process intensification

- Bioreactive Separations
- Enzymatic processes



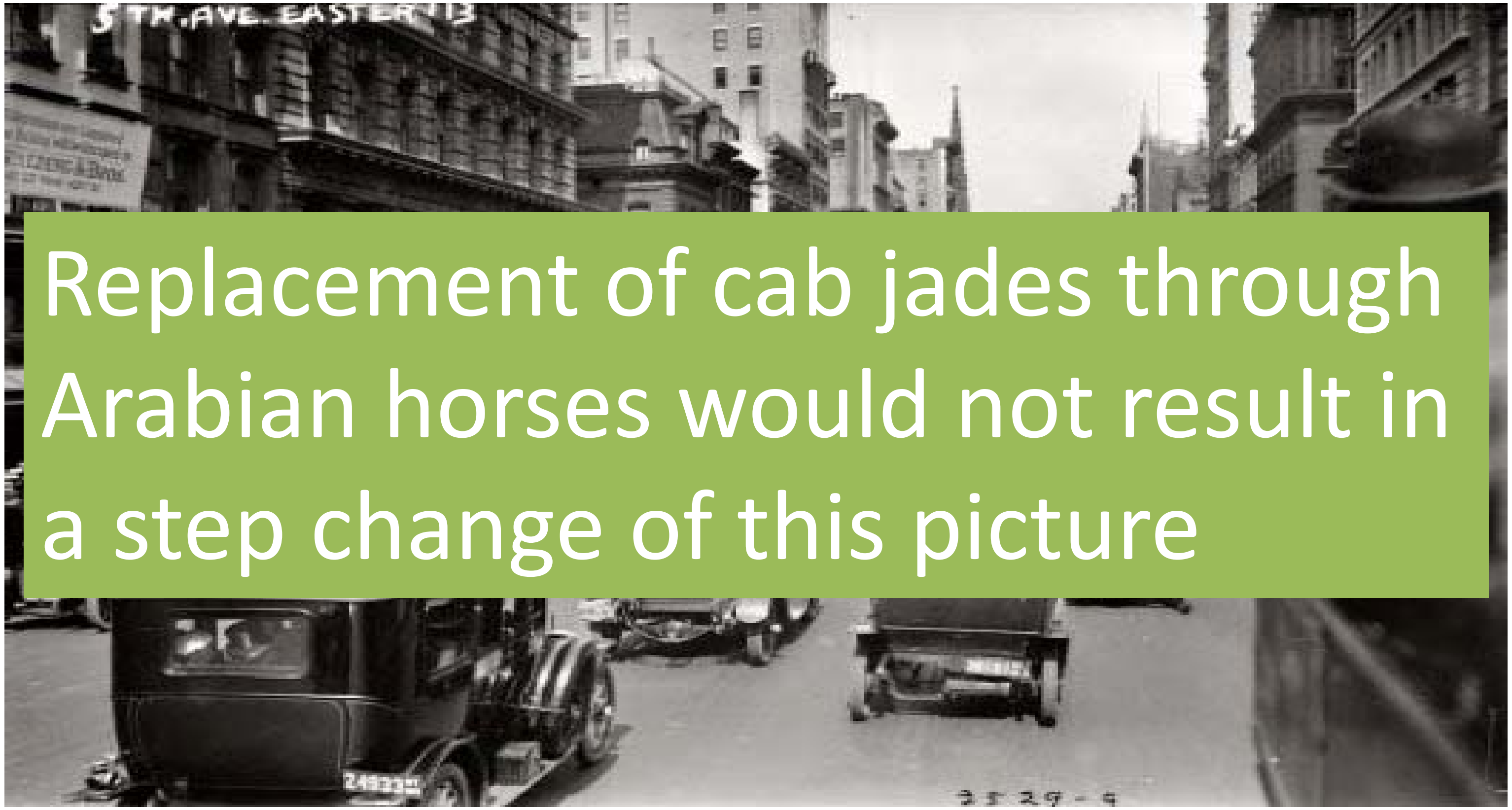
Modeling and simulation

- Rate-based approach



New York 5th Avenue – 1900

Dream of
step change innovation

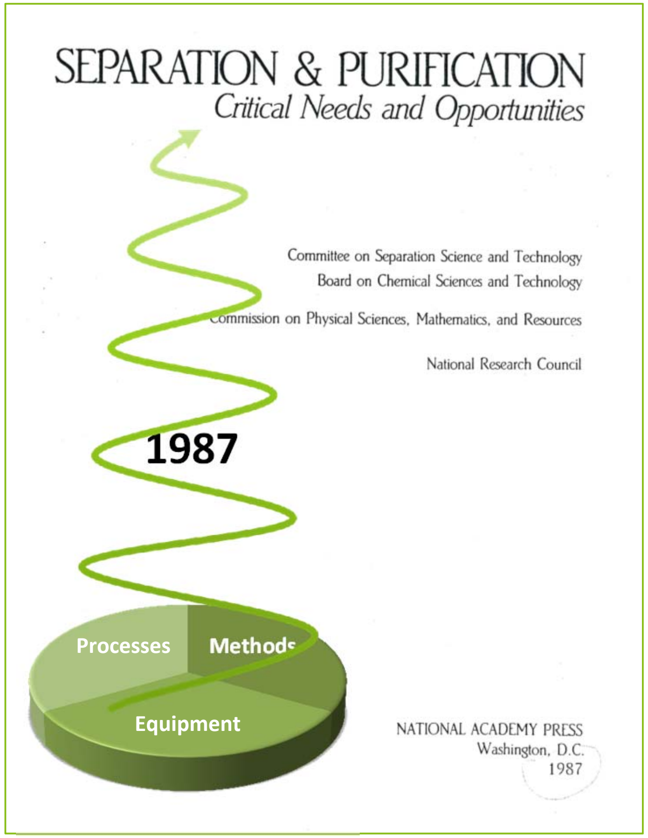


Replacement of cab jades through Arabian horses would not result in a step change of this picture

New York 5th Avenue – 1913

Dream of
step change innovation

Back to the roots; back to the future

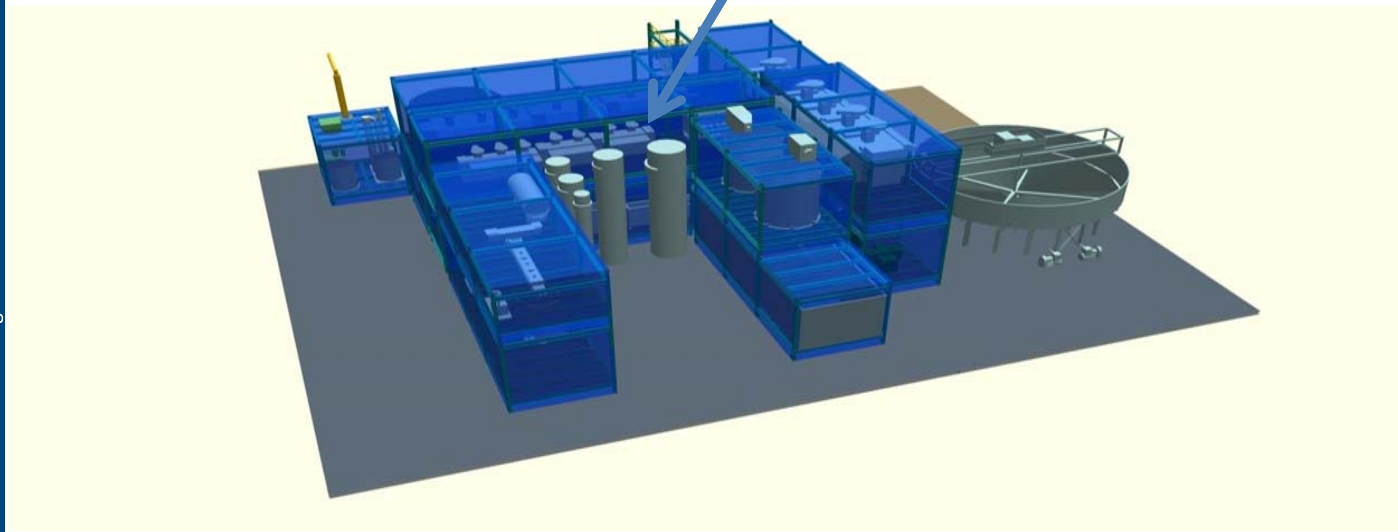


- **Important areas**
  - Biotechnology
  - Critical and strategic metals
  - Environment
  - Ultrapurification
  - Energy and natural feedstock
- **Research directions**
  - Improved selectivity in separations
  - Diluted solutions purification
  - Control of interfacial phenomena
  - Increasing rate of separations
  - Improving separation configurations
  - Improving energy efficiency

Hot topics for D&A 2025

Experience from Plant Design with Modular

Modules?



FLUOR

Modularisation

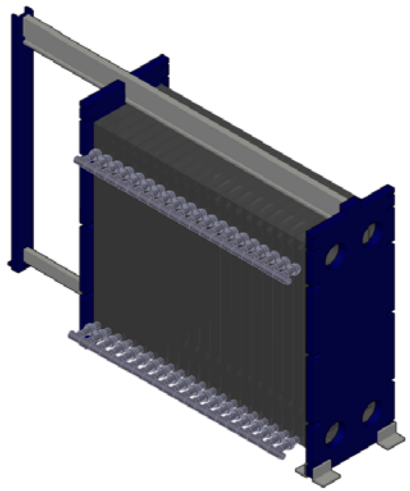
Hot topics for D&A 2025

Separation modules?

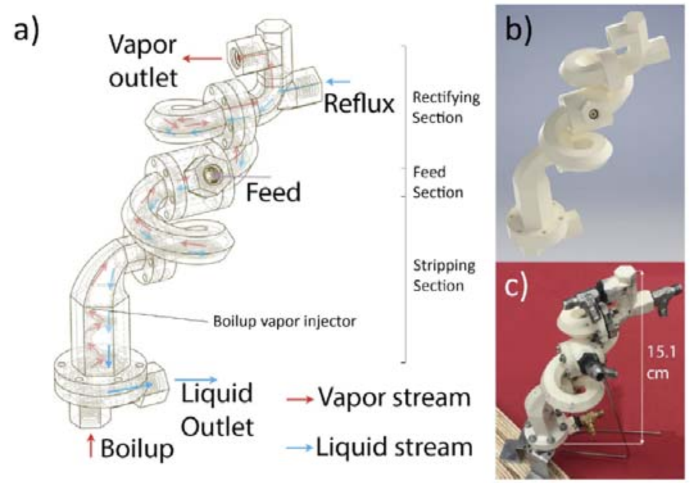
Modularisation

Hot topics for D&A 2025

- **Modularisation**
- **Additive Manufacturing**



Modular Process Engineering: Development of Apparatuses for Transformable Production Systems
S. Lier, S. Paul, D. Ferdinand, M Grünewald, Chem.Bio.Eng. Rev 1(2017)60



Development of a unique modular distillation column using 3D printing, S. Mardani, L.S. Ojala, P. Uusi-Kyyny, V. Alopaeus, Chem.Eng.Proc.: Process Intensification 109, 2016)136

Polymeric replica of metal foam with comparable performance @ 1% of cost

Full control over all structural parameters for tailoring!

Additive manufacturing of packings for rotating packed beds
Gładyszewski, K.; Skiborowski, M.
Chemical Engineering and Processing - Process Intensification 127 (2018), pp. 1–9

Hot topics for D&A 2025

- Charactarize complex mixtures with many undefined components
- Enlarge narrow windows of operation
- Deal with hiqh viscosity
- Combine „cold“ and „warm“ separations
- Use „One way“ equipment
- **Water, water, water….**

Bio instead chem

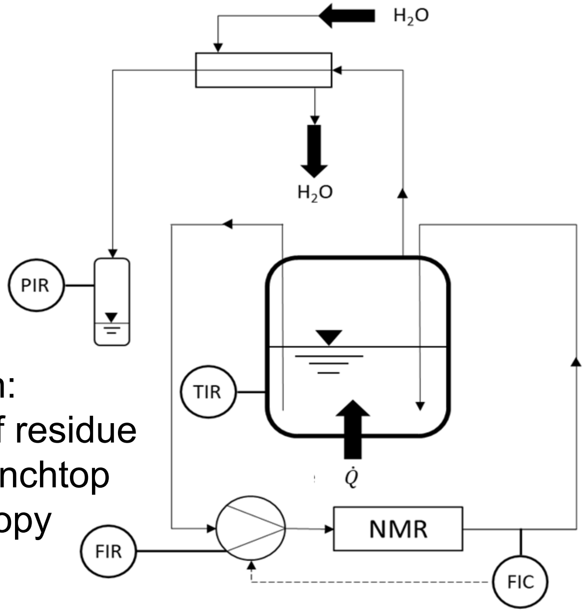
Hot topics for D&A 2025

Intra and interdisciplinarity

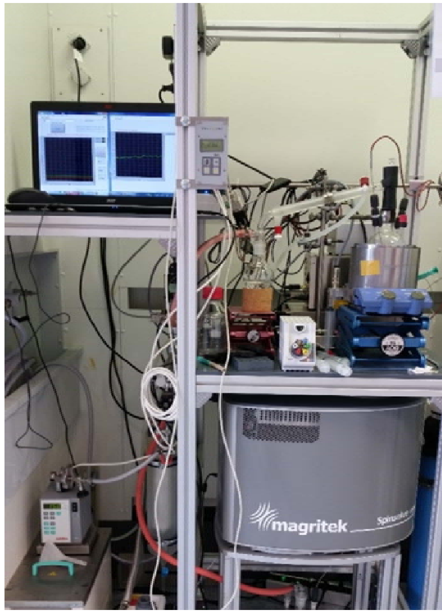
Absorb achievements of other disciplines and distill the best of them out!

- Material sciences (membranes, advanced liquids like ionic liquids)
- Process system engineering (process syntehsis, automation and robotics, energy efficiency, process control, supply chain)
- Biotechnology (stable enzymes, natural raw materials)
- Sensoring (tomography, NIR, NMR)

Batch distillation: determination of residue curves using benchtop NMR spectroscopy



TECHNISCHE UNIVERSITÄT KAISERSLAUTERN



Friebel et al.: Fluid Phase Equilib. 438 (2017) 44-52

Hot topics for D&A 2025

Chemistry 4.0

Separations 1.0:
- Batch distillation
- Separations for process
- make-up

Separations 2.0:
- Continous distillation
- Big scale
- CAPE
- Absorption as end-of-pipe

Separations 3.0:
- Conceptual process design
- Energy efficiency
- Hybrid and reactive separations
- Process control
- Better equipment

Separations 4.0:
- Data driven operation
- Additive manufactuting
- Modularisation
- Automated design and operation
- ??????

Chemistry 1.0:
- First chemical companies

Chemistry 2.0:
- Industrial chemicals from a few primary chemicals
- Construction of large-scale plants

Chemistry 3.0:
- Natural gas and renewable raw materials
- Biotechnology
- Internationalization of production facilities

Chemistry 4.0:
- Digitisation and sustainability
- Horizontal networking of value chains
- „Predictive Maintenance“
- Radio tags (RFID chips)

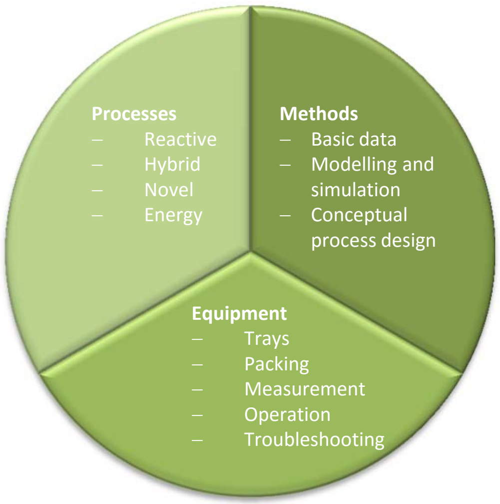
https://www2.deloitte.com/global/en/pages/consumer-industrial-products/articles/cip-chemistry.html

1865 | 1950 | 1980 | 2010

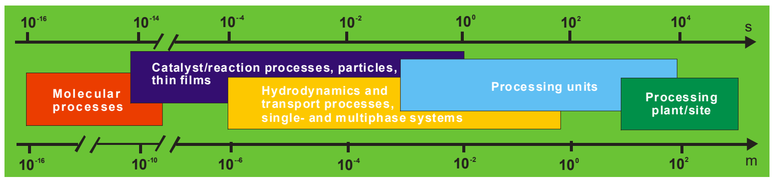
Mass Transfer: Yesterday, Today and Tomorrow

Hot topics for D&A 2025

- Bussiness as usual



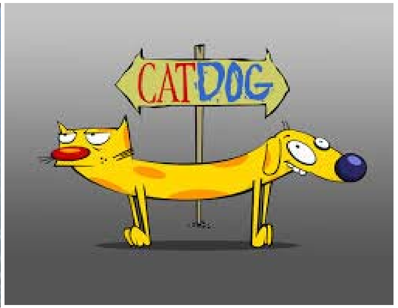
Multiscale modelling using the same model family



- **Separations 4.0**

Hybrid models (data driven + causal mechanistic)
for hybrid processes (synergy of different unit operations)

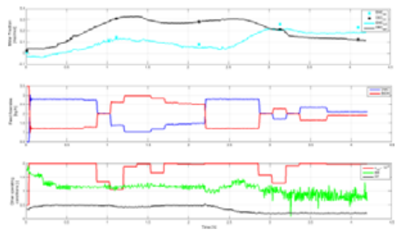
http://www.petliferadio.com/magicalcreatures.html

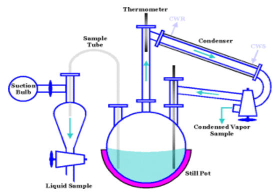


https://lancecoolidgepetnews.wordpress.com/

Electronic laboratory journal incorporatated into the equipment design

Explotiation of data cementary





https://kochmodular.com/pilot-testing/equilibrium-studies/

Source BASF – Steamcracker Antwerpen