Distillation and absorption
in the era of bio, info and process intensification
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!
“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. Traveling through time in a modified DeLorean car, Marty encounters young versions of his parents (Crispin Glover, Lea Thompson), and must make sure that they fall in love or he'll cease to exist. Even more dauntingly, Marty has to return to his own time and save the life of Doc Brown.”

“In 1987, it was recognized that more frequent meetings were needed, so the following conferences were in 1992 in Birmingham (UK), 1997 in Maastricht (Netherlands), 2002 in Baden-Baden (Germany), 2006 in London (UK), 2010 in Eindhoven (Netherlands), and the last in 2014 in Friedrichshafen (Germany)“.

Elisabetta Brunazzi  Chair
Eva Sorensen  Scientific Chair

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

<table>
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<tr>
<th>2018</th>
<th>2014</th>
<th>2010</th>
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<td>Basic data</td>
<td>Basic data</td>
<td>Basic data</td>
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<td>Absorption</td>
<td>Carbon capture</td>
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<td>Conceptual process design and LCA</td>
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<td>Trays, packings</td>
<td>Trays, packings</td>
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Hot(?) topics in the last 30 years of D&A conferences
Hot(?) topics in the last 30 years of D&A conferences

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

- Equipment
  - Trays
  - Packing
  - Measurement
  - Operation
  - Troubleshooting

- Processes
  - Reactive
  - Hybrid
  - Novel
  - Energy
Revisit old ideas for new fluid separations

Process intensification
- Bioreactive Separations
- Enzymatic processes

Modeling and simulation
- Rate-based approach
Modeling and Simulation

Equilibrium stage model

no gradients in the gas or liquid
flows leaving the stage are in equilibrium

Sorel (1893)

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

$\mu_i^{G,l} = \mu_i^{L,l}$
Modeling and simulation

Rate-based approach

Few subjects are critically important both theoretically and practically. For years complications and even paradoxes have been the order of the day. This paper claims to clear up the confusion and contribute to the clarification of the subject of absorption. The work is based on the theory of the two-film gas absorption process, which is the subject of this paper.

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

W. Whitman (1923)
Modeling and simulation

Non-Equilibrium stage model = Rate-based approach

thin ‘film’ resistances for mass and heat transfer;

1980s

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


multicpomonent mixtures
Modeling and simulation

Non-Equilibrium stage model = Rate-based approach


thin ‘film’ resistances for mass and heat transfer;

multicomponent mixtures
Simulation of an SO₂ 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

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

Absorption of Carbon Dioxide Using Enzyme Activated Amine Solution in Columns with Random Packings

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

Rate-based Modeling of CO₂ Absorption with Sandwich Packings

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

Кениг Е.Я., Баклачан Р.А., Холланов 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
Rate-based approach, reactive separations

Chemical reaction

phase equilibrium at the interface

thin ‘film’ resistances for mass and heat transfer;
mass and heat fluxes cause gradients
Rate-based approach, biochemical reactive separations

Biochemical reaction

phase equilibrium at the interface

thin ‘film’ resistances for mass and heat transfer;
mass and heat fluxes cause gradients
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)

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
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 columns **but** rotational equipment

Trayed HiGee: distillation applications in China

- Anhydrous ethanol extractive dist.
- THF-water extractive dist.
- n-butanol-water azeotropic dist.
- Dichloromethane-methanol-water azeotropic dist.

230+ companies
700+ HIGEEs

Courtesy: Prof. Guangquan Wang
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 $\frac{\text{di}}{\text{da}}$
  - Axial height
  - Droplet flow
  - Casing behavior

- Liquid distribution
  - Nozzle type
  - Nozzle position
  - Flow conditions

- Type of packing
  - Mesh / Foams
  - Stability
  - Hold-up

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

- Higher rotational speed enhances maldistribution

300 RPM

600 RPM

1200 RPM

Liquid load: 82 m³m⁻²h⁻¹
F-Factor: 3-4 Pa⁰.⁵

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

Intensified separations

PRINCIPLES (GOALS)
maximizing the effectiveness of intra- and intermolecular events

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

maximizing the effectiveness of intra- and intermolecular events

maximizing the effectiveness of intra- and intermolecular events

giving each molecule the same processing experience

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 the driving forces and maximizing the specific surface areas to which these forces apply

maximizing synergistic effects from partial processes

maximizing synergistic effects from partial processes

maximizing synergistic effects from partial processes

maximizing synergistic effects from partial processes

Enzymatic Reactive Distillation
Enzymatic Reactive Absorption
Enzymatic reactive distillation

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

Enantioselective transesterification

\[
\begin{align*}
\text{(R,S)-PE} & \quad \overset{\text{CalB}}{\longrightarrow} \quad \text{ISOPR} \\
\text{SPE} & \quad + \quad \text{R-PEA} \\
& \quad + \quad \text{ACE}
\end{align*}
\]

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

Transesterification (test system)

\[
\begin{align*}
\text{ethyl butyrate (EtBu)} & \quad + \quad \text{n-butanol (BuOH)} \\
\text{butyl butyrate (BuBu)} & \quad + \quad \text{ethanol (EtOH)}
\end{align*}
\]


Structured catalytic packings

Well known: Immobilised chemical catalyst

KATAPAK® -SP
Structured catalytic packings

New: Enzymes immobilised on beads

KATAPAK® -SP
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?

Structured catalytic packings

Production of biocatalytic coatings for structured packings

Patent DE 102010 028788 A1
Technical University of Hamburg
Institute of Thermal Separation Processes
Rate-based approach, enzymatic reactive distillation

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

\[
\text{ethyl butyrate (EtBu)} \quad \text{n-butanol (BuOH)} \quad \text{butyl butyrate (BuBu)} \quad \text{ethanol (EtOH)}
\]

**Simplified Ping Pong Bi Bi mechanism** \(^{[1]}\)

\[
\frac{d[\text{BuBu}]}{dt} = \frac{m_{\text{cat}} V_f V_r}{\frac{1}{K_{\text{eq}}} [\text{BuBu}] [\text{EtOH}]} \left( [\text{EtBu}] [\text{BuOH}] - \frac{1}{K_{\text{eq}}} [\text{BuBu}] [\text{EtOH}] \right)
\]

\[
= \frac{V_f}{K_{\text{eq}}} \left( K_{m,BuBu} [\text{EtOH}] + [\text{BuBu}] [\text{EtOH}] \right) + V_r [\text{EtBu}] [\text{BuOH}]
\]

---

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


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%


Andrzej Górak, Distillation and Absorption, Firenze, 2018
Enzymatic reactive absorption

- **Greenhouse**:
  - Main contributor: CO₂-emission
  - 40% of emissions by fossil-fueled power plants
- **Most investigated concept for PCC**
  - Solvent-based absorption of CO₂ in columns, especially with alkanolamines
    - Monoethanolamine (MEA)

**Desired properties:** Tertiary amines

<table>
<thead>
<tr>
<th>Amines</th>
<th>Enthalpy of Reaction</th>
<th>Enthalpy of Evaporation</th>
<th>Reaction Rate</th>
<th>Corrosivity</th>
<th>Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
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<tr>
<td>Secondary</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Tertiary</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

Bottlenecks:
- High temperatures and high energy costs
- Desorption: 80% of energy costs

References:
- Mondal et al., Energy, 46 (1), 2012

Andrzej Górk, Distillation and Absorption, Firenze, 2018
Enzymatic reactive absorption

- Drawback of tertiary amines: Slow reaction rates
  - Compensation for slow reaction:
    - Activator: Piperazine $\rightarrow$ amine blends
      $\rightarrow$ Compromised thermodynamic properties
  - Catalyst: **Enzyme Carbonic Anhydrase (CA)**
    $\rightarrow$ Fastest catalyst for CO$_2$ hydration
    $\rightarrow$ Advantages: non-volatile, sustainable, bio-degradable, highly selective
Enzymatic reactive absorption

Different strategies for Carbon Anhydrase application

Leimbrink, M.; Sandkämper, S.; Wardhaugh, L.; Maher, D.; Green, P.; Puxty, G.; Conway, W.; Bennett, R.; Botma, H.; Feron, P.; Górak, A.; Skiborowski, M.

Scalability

- Scale up factor 15: TUDO DN110 0.11 m → 0.42 m
- Scale up factor 30: ENVIMAC DN420/600 0.60 m

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


Andrzej Górak, Distillation and Absorption, Firenze, 2018
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**

Intensified equipment – HiGee

Rotating Packed Bed

Setup and operation:
- tailored RPB setup
- rotational speed 600 rpm – 1200 rpm
- rotor dimensions $d_0 = 600$ 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"
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"
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.
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

Modules?

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,

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

Development of a unique modular distillation column using 3D printing, S. Mardani, L.S. Ojala, P. Uusi-Kyyn, V. Alopaeus,
Hot topics for D&A 2025

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

Bio instead chem
Hot topics for D&A 2025

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

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

Batch distillation: determination of residue curves using benchtop NMR spectroscopy

Friebel et al.: Fluid Phase Equilib. 438 (2017) 44-52
Hot topics for D&A 2025

Chemistry 4.0

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

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

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

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

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

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

Chemistry 1.0:
- First chemical companies

Mass Transfer: Yesterday, Today and Tomorrow

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

Hot topics for D&A 2025

- Business as usual

- Separations 4.0

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

Multiscale modelling using the same model family

Exploitation of data cementary

Molecular processes
- Catalysis
- Reaction processes

Hydrodynamics and transport processes
- Single- and multiphase systems

Processing units
- Equipment
- Trays
- Packing
- Measurement
- Operation
- Troubleshooting

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

Processes
- Reactive
- Hybrid
- Novel
- Energy

Electronic laboratory journal incorporated into the equipment design

Source BASF – Steamcracker Antwerpen

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

https://lancecoolidgepetnews.wordpress.com/

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

BASF – Steamcracker Antwerpen

50 Jahre bci 2019