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

Andrzej Górak
TU Dortmund University
Department of Biochemical and Chemical Engineering
Laboratory of Fluid Separations
Emil-Figge-Straße 70
D-44227 Dortmund
Tel.: +49 231-755 23 23
Fax: +49 231-755 30 35
andrzej.gorak@tu-dortmund.de
www.fvt.bci.tu-dortmund.de

Politechnika Łódzka

fvt laboratory of fluid separations
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!
Dinosaurs of chemical industry

https://www.flickr.com/photos/yumiko_sato/13270111055
Dinosaurs of chemical industry

Andrzej Górak, EPIC, 2015
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
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**
- Molecular processes
- Catalyst/reaction processes, particles, thin films
- Hydrodynamics and transport processes, single- and multiphase systems
- Processing units
- Processing plant/site
Distillation goes micro: microdistillation

**Distillation on the chip**


Microchannel Technology Enables Advanced Distillation Processes

Micro: for regulated substances (pharma applications)


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

**Scales:**
- $10^{-16}$ to $10^{-4}$
- $10^{-4}$ to $10^{2}$
- $10^{2}$ to $10^{6}$
Distillation goes high gravity: HiGee distillation

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

Distillation goes high gravity: HiGee distillation

Distillation goes high gravity: HiGee distillation

Separation efficiency ↔
Capacity ↔
Feed location →

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

- 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

Reactive section

A + B ⇌ C + D
- Equilibrium limited reactions
- Azeotrope limited separations
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

- 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 bioproduts

- Conventional process:
  - Complex and cost-intensive process
  - Homogeneous catalyst

- Potential RD-process:
  - 1 RD column
  - Heterogeneous catalyst
Distillation goes reactive and bio: reactive distillation for bioproducts

- 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
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

Efficient production of chiral molecules through Enzymatic Reactive Distillation
Distillation goes reactive and bio: enzymatic reactive distillation

Lipase CALB

Enzyme immobilisation

Andreas Liese, Irina Smirnova

**Reactive distillation:**

important niche application, also for bio-products

Efficient production of chiral molecules through

**Enzymatic Reactive Distillation**

- High conversion
- Separation of products
- SPE unconverted

![Diagram of reactive distillation](chart)

- ACE
- ISOPR
- RPE
- SPE

![Enzymatic reactive section](enzyme)

- PE-feed
- ISOPR-feed
- Reboiler

![Temperature vs. column height](graph)

- molar fraction of component [mol/mol]
- temperature [K]

Andrzej Górak, EPIC, 2015
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

**10^-16, 10^-14, 10^-12, 10^-10, 10^-8, 10^-6, 10^-4, 10^-2, 10^0, 10^2, 10^4, 10^6, 10^8, 10^10, 10^12, 10^14, 10^16**

Andrzej Górak, EPIC, 2015
Distillation goes hybrid

What is Hybrid?

- a creature combining body parts of two or more species
- 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.

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

Applications in the world

Applications @

year


100
80
60
40
20
0

Total applications in the world

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):

\[
\text{PC} + 2 \text{MeOH} \rightarrow \text{DMC} + \text{PDO}
\]

Boiling points at 1.013 bar:
- 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

- 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

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

**Open recycle operation**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>DF (kg kg(^{-1}))</td>
<td>0.55</td>
</tr>
<tr>
<td>RR (-)</td>
<td>1.80</td>
</tr>
<tr>
<td>(X_{Col}) (mol mol(^{-1}))</td>
<td>10.0</td>
</tr>
<tr>
<td>(w_{cat}) (g g(^{-1}))</td>
<td>6 \cdot 10^{-3}</td>
</tr>
</tbody>
</table>

**Closed recycle operation**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>DF (kg kg(^{-1}))</td>
<td>0.55</td>
</tr>
<tr>
<td>RR (-)</td>
<td>1.80</td>
</tr>
<tr>
<td>(X_{Col}) (mol mol(^{-1}))</td>
<td>10.0</td>
</tr>
<tr>
<td>(w_{cat}) (g g(^{-1}))</td>
<td>6 \cdot 10^{-3}</td>
</tr>
</tbody>
</table>

Doubling of MeOH-conversion

Strong influence of vapour permeation on reactive distillation

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

\(X_{MeOH}\) (%) 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
- Hydrodynamics and transport processes, single- and multiphase systems
- Processing units
- Processing plant/site

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

Andrzej Górak, EPIC, 2015
Distillation goes cyclic: cyclic reactive distillation

V.N.Maleta, A.Kiss, A.Taran, B.V.Maleta: Understanding process intensification in cyclic distillation systems

C. Pătrulț, C. Bildea, AA.Kiss: Catalytic cyclic distillation - A novel process intensification approach in reactive separations

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
- 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 / PERVAPORIZATION PROCESS, C. Servel, D. Roizard, D. Horbez, E. Favre
- A CONTROL STRATEGY FOR EXTRACTIVE AND REACTIVE DIVIDED WALL COLUMNS, M. Rodriguez, I. Diaz, P.Z. Li
Outlook

Classical separation processes

- Membranes
- Adsorption/liquid
- Ion exchange
- Chromatography
- Extraction
- Adsorption/Gas
- Distillation

Experiments
- Cristallisation
- Absorption

Technical Application

- Invention
- Technical maturity
- Optimal Process

First Application

Industrial Production

Andrzej Górak, EPIC, 2015
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 application, also for bio-products
- **Hybrid** distillations: divided wall columns become standard, membrane assisted distillation needs better membranes
- **Cyclic** distillation: hardware (valves, trays) remains a challenge
- **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™
- PACK™
- Flexipac® HC
- Shell ConSep Tray
- Sandwich packing
- Montz-Pak Type M
- UFM™
- ULTRA-FRAC®
- 2-pass VGPlus
- 2-pass VG AF
- 1-pass VGPlus Tray
- Optiflow

Andrzej Górkak, EPIC, 2015