SYNERGY – PART II
Contents

• Incentives
• Reactive separations and their applications
• Hybrid separations and their applications
• Degrees of freedom and feasible operation windows in multifunctional equipment/operations
Reactive separations – why?

- to improve yield/selectivity (e.g. via equilibrium shift)
- to lower investment costs (compact, integral design)
- to improve heat management/energy utilization
- to facilitate separation (e.g. azeotrope problems)
- for other reasons (e.g. extension of catalyst lifetime, etc.)
Reactive separations – what?

- Reactive distillation
- Reactive absorption
- Reactive extraction
- Reactive crystallization
- Reactive chromatography
- Membrane reactors
- Reactive adsorption
- Reactive crystallization
Reactive distillation

(a) Conventional process

(b) Reactive Distillation

Processing schemes for reaction $A + B \leftrightarrow C + D$

Reactive distillation
Reactive distillation

Processing schemes for reaction $A + B \rightleftharpoons C + D$

(a) MTBE
(b) cumene
(c) ethylene glycol

MeOH
n-butene
i-butene

propene

benzene

water

n-butene
i-butene

n-butene
i-butene

n-butene
i-butene

(2000), 5183-5229)
**Reactive distillation**

**APPLICATIONS OF REACTIVE DISTILLATION**

**MTBE SYNTHESIS**

- conventional
- via reactive distillation

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Reactive distillation

Process synthesis via reactive distillation: methyl acetate process by Eastman Chemical

acetate-water azeotrope (outside immiscible region, cannot use decanter)
acetate-MeOH azeotrope (boils lower than acetate-water azeotrope)

Conventional plant:
Ethyl acetate used as solvent/entrainer (totally recycled).
Ethylene glycol used as high-boiling solvent for extractive distillation (to break acetate-water azeotrope)
Reactive distillation

Process synthesis via reactive distillation: methyl acetate process by Eastman Chemical

Evolutionary Modification:

- two flash column combined (similar feeds, overheads to the same decanter, both underflows to wastewater treatment);
- acetic acid color column skipped;
- one solvent eliminated (ethylene glycol replaced by acetic acid).

Reactive distillation

Process synthesis via reactive distillation: methyl acetate process by Eastman Chemical

Task identification:

Reactive distillation

Reactive distillation as a powerful separation method

FORWARD REACTION

reactive and inert components

intermediate product

reactive entrainer

FORWARD REACTION

inert component

reactive component

BACKWARD REACTION

intermediate product

reactive entrainer

BACKWARD REACTION

inert component

reactive component
Reactive distillation as a powerful separation method

- How to separate isobutene from non-reactive n-butene?

(ideal case)

E. Stein et al., Chem. Eng., 107 (13), 68 (2000)
Reactive distillation

Reactive distillation as a powerful separation method

- How to separate isobutene from non-reactive n-butene?
  
  (real case: diisobutene (DIB) formed)

\[ 2 \text{iB} = \text{DIB} \]

E. Stein et al., Chem. Eng., 107 (13), 68 (2000)
Reactive distillation

Reactive distillation as powerful separation method

How to separate isobutene from non-reactive n-butene?

(real case: diisobutene (DIB) formed)

2 iB = DIB

Solution No. 2: MTBE vapor-side draw saves one column

E. Stein et al., Chem. Eng., 107 (13), 68 (2000)
Reactive distillation

- **Reaction rate**
  - **Fast**
  - **Slow**

- **Relative volatility**
  - **Low**
  - **High**

- **Focus on**
  - **Residence time**
  - **Separation efficiency**
  - **Little separation efficiency**

- **Embryonic**
- **Growth**
- **Mature**
- **Aging**

(H. Schoenmakers, ARS-1, Dortmund 2000)
Reactive distillation

reaction and distillation (examples)

homogeneous catalysis

- rectification column
- column with larger volume in the bottom
- stirred vessel with rectifying column
- stirred vessel with full column
- vessel cascade with column
- stirred vessel with evaporator
- evaporator
- ........

(H. Schoenmakers, ARS-1, Dortmund 2000)
Reactive distillation

**heterogeneous catalysis**

- rectification column with catalytic packings
- rectification column with catalytic internals in the downcomers
- rectification column with side stream reactors
- column and reactor with pumparound
- evaporator and reactor with pumparound
- ......

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(H. Schoenmakers, ARS-1, Dortmund 2000)
Reactive distillation

Commercial applications:
- ether technologies (MTBE, TAME, ETBE);
- methyl acetate from methanol and acetic acid;
- selective hydrogenations of dienes (butadiene, pentadiene, hexadiene)
- ethylbenzene via alkylation of benzene;
- cumene via propene alkylation with benzene;

Application potential goes far beyond that!

Other possibilities:
- ethers-to-olefins decomposition;
- selective dimerization of olefins;
- alkylation of isobutane with n-butens (gasoline blending);
- hydrogenation of olefinic and di-olefinic impurities;
- hydroisomerisation (e.g. butenes);
- hydrolysis (e.g. isobutylene to tert-butyl alcohol);
- dehydration of alcohols to ethers;
- oxidative dehydrogenations (e.g. isobutane to isobutylene);
- carbynylation reactions (e.g. propene + syngas to n-butanol).
Membrane reactors

Membrane functions in a reactor

Membrane functions define configuration

Catalytic membranes

1. Catalytic
2. Interphase contactor
   - Short contact time
   - No solvent needed

- Catalytic
- Selective product removal
- Selective reactant supply
  - Increased conversion
  - Increased selectivity

McLeary et al., 2006
Membrane functions define configuration

Inert membranes

- selective product removal
- selective reactant supply
  - increased conversion
  - increased selectivity

- reactant distributor
  (no synergy)
  - increased selectivity
  - better controllability

- catalyst poisoning protection
- selective product removal
- selective reactant supply
  - increased selectivity
  - prolonged cat. lifetime

Embryonic           Growth               Mature                 Aging

McLeary et al., 2006
Membrane reactors - industrial example

Production of S-ibuprofen

S-ibuprofen: non-steroidal anti inflammatory drug

enzyme selectivity is very high
product causes enzyme-deactivation
enzyme-free product is required: laborious downstream processing
Membrane reactors - industrial example

Even better: on-line UF or membrane reactor

water → ibuprofen-ester → enzyme → S-ibuprofen → substrate → product
Membrane reactors - industrial example

- UF replaces 6 unit operations
- costs UF: < $1,-/kg S-ibuprofen
Membrane reactors - industrial example

- 13.62 wt%, high flux
- 13.59 wt%, low flux
- 14.43 wt%, without UF

Embryonic Growth Mature Aging
Reactive adsorption

(after M. Morbidelli)
Reactive adsorption

(after M. Morbidelli)
Reactive adsorption

**TRUE COUNTERCURRENT MOVING BED CHROMATOGRAPHIC REACTOR**

- Moving solid adsorbent + catalyst
- Feed point
- Fluid phase

**SIMULATED COUNTERCURRENT MOVING BED CHROMATOGRAPHIC REACTOR**

(feed and product ports move in the same direction as carrier)

- Carrier
- Product
- Feed

Reactants (more strongly adsorbed species)

- Catalyst + adsorbent (fixed bed)
Simulated Moving Bed (SMB) Chromatographic Reactor

4-section design
Simulated Moving Bed (SMB) Chromatographic Reactor

5-section design

Reactants meet in the reaction section

> reactants are fed at two different nodes
> different direction of propagation of the reactants

(from: J. Fricke, H. Schmidt-Traub)
Simulated Moving Bed (SMB) Chromatographic Reactor

4-section vs. 5-section design: production of n-Butyl methacrylate

<table>
<thead>
<tr>
<th>Section</th>
<th>Segmentation</th>
<th>Conversion</th>
<th>Acetate purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-section</td>
<td>2-2-3-1</td>
<td>65.79%</td>
<td>60.76%</td>
</tr>
<tr>
<td>5-section</td>
<td>2-2-2-1-1</td>
<td>70.25%</td>
<td>89.55%</td>
</tr>
</tbody>
</table>

(from: J. Fricke, H. Schmidt-Traub)
Reactive adsorption

**ROTATING CYLINDRICAL ANNULUS CHROMATOGRAPHIC REACTOR**

![Diagram of rotating cylindrical annulus chromatographic reactor]

Examples of processes investigated:
- hydrolysis of aqueous methyl formate;
- dehydrogenation of cyclohexane to cyclohexene;

(Carr, 1993)
Reactive adsorption

**GAS-SOLID-SOLID TRICKLE FLOW REACTOR**
(Kuczynski and Westerterp, 1987)

- catalyst pellets stationary in packed bed
- adsorbent powder trickles downwards
- reacting gas flows in counter-current upwards

Concept checked experimentally on methanol synthesis: in principle 100% conversion can be achieved.

Economical evaluation versus Lurgi process (1000 tpd):
- cooling water consumption reduced by 50%
- recirculation energy reduced by 70%
- catalyst amount reduced by 70%
- high pressure export steam 0.25 t/t methanol
- raw materials consumption reduced by 12%

Reactive adsorption

Moving bed reactor – solids flow
(co- and counter-current)
Reactive extraction

Combination of reaction and liquid-liquid separation

Immiscibility:

• natural

• introduced deliberately by addition of solvent

Application areas:

• improvement of yields/selectivities in multi-reaction systems

• separation of “hard-to-separate” waste by-products

• selective separation of amino acids
Reactive extraction

Agitated extractors (left to right: RDC, Karr, Oldshue–Rushton, Scheibel, Kühni extraction columns)

Reactive extraction

Non-agitated extractors (left to right: spray, packed, sieve tray (light), sieve tray (heavy) column)

Reactive crystallization (precipitation)

Processes of industrial relevance:

• liquid-phase oxidation of para-xylene to terephthhalic acid
• acidic hydrolysis of sodium salicylate to salicylic acid
• absorption of ammonia in aqueous sulfuric acid to form ammonium sulfate
• production of uniform nano-size particles of calcium carbonate (in high-gravity field)
Reactive crystallization (precipitation)

In pharmaceutical industry:

Diastereomeric crystallization for resolution of enantiomers

\[(DL)-A + (L)-B \rightleftharpoons (D)-A\cdot(L)-B + (L)-A\cdot(L)-B\]

- racemate
- resolving agent
- n-salt
- p-salt

Production of:
- ampicillin,
- ethambutol,
- chloramphenicol,
- diltiazem,
- fosfomycin,
- naproxen

Easy separable by crystallization
Reactive absorption

Most widely applied type of reactive separation

Application areas:

• nitric acid process
• sulfuric acid process
• carbon dioxide removal
• hydrogen sulfide removal
• olefin/paraffin separation (research stage)
Absorption plant consisting of 4 units (8 columns)

- Each unit is separated by a metal plate into two sections
- Diameter of each column is 2.2 m, its height is 7 m
- Packing height is 3.2 m
- Packing consists of 35 mm INTALOX ceramic saddles
- Liquid feeds entering columns 7 and 8 are low concentrated nitric acids

Hybrid separations

Integrate two or more different separation methods in a single operation, making use of synergy between them.
Hybrid separations

- Absorption, Stripping
- Adsorption
- Membrane
- Distillation, Condensation
- Extraction
- Crystallization
Contents

• Extractive distillation
• Adsorptive distillation
• Membrane distillation
• Membrane absorption/stripping
• Adsorptive membranes (membrane chromatography)
Extractive distillation

• The oldest and most widely applied hybrid separation.
• Particularly useful in close-boiling-point problems.
• A third component (solvent) added
• Solvent does not form azeotropes with feed components.
• Solvent alters the relative volatility of original feed components, allowing to distill overhead.
• Solvent leaves the column with the bottom products and is separated in a binary column.
Extractive distillation

Example of extractive distillation: BTX process of GTC Technology Corp.

- alternative to liquid-liquid extraction-based process;
- 25% lower capital cost;
- 15% lower energy consumption
Extractive distillation

Solvent selection – always a trade-off between the selectivity and solvency

Think of environmental effect!
Adsorptive distillation

- Three-phase mass transfer operation.
- Adsorbent: fine powder (usually ca. 10 μm), fluidized and circulated by an inert carrier.
- Process carried in two columns:
  - adsorptive distillation column for increasing separation ability, and
  - distillative desorption column for enhancing the regeneration of the adsorbent.
Adsorptive distillation

Separation of azeotrope-forming components A and B via adsorptive distillation
Adsorptive distillation

Application fields:

- close-boiling components;
- azeotropes;
- trace impurity removal in fine chemicals.

Systems investigated:

- ethanol - water
- ethyl acetate – water – n-butanol
- p-xylene – m-xylene
Membrane distillation

**Conditions:**

- aqueous solutions
- porous, hydrophobic membrane
- no capillary condensation in membrane pores
- only vapor transported through the membrane
- at least one side of membrane in contact with the liquid
- driving force: partial pressure gradient in vapor phase
Membrane distillation

Direct Contact Membrane Distillation

Air Gap Membrane Distillation

Sweep Gas Membrane Distillation

Vacuum Membrane Distillation

(E. Drioli)
Membrane distillation

**Benefits of MD:**

- lower operating temperatures than conventional distillation;
- lower operating pressures than conventional pressure-driven membrane separation;
- reduced chemical interaction between membrane and process solutions;
- less demanding membrane mechanical property requirements;
- reduced vapor spaces compared to conventional distillation.

Membrane distillation

Application areas investigated:

• water desalination;
• water decontamination (removal of e.g. halogenated VOCs, benzene etc.)
• recovery of alcohols (e.g. ethanol, 2,3-butanediol) from fermentation broths
• concentration of oil-water emulsions
• removal of water from azeotropic mixtures
Membrane distillation

Solar desalination plant by WRPC, Takenaka Corp. and Organo Corp.

09 December 2011
Membrane distillation

Another type of MD:

Pervaporation unit combined with conventional distillation
Membrane distillation

for olefin/paraffin splitting…

(Source: USA Department of Energy)
Membrane distillation

Another type of MD:

Pervaporation unit combined with reactive distillation

Membrane-assisted reactive distillation for synthesis of fatty acid esters
Membrane absorption/stripping

Membrane absorption – invented by Mother Nature:

- lungs
- darms
Membrane absorption/stripping

Most important application areas:

• CO₂ removal from anesthetic gases
• CO₂ separation from turbine exhaust gases
• Carbon dioxide capture and management (general)
• VOC’s removal from air/nitrogen streams
• H₂S removal from natural gas
Membrane absorption/stripping

Kvaerner process for CO₂ separation/capture from turbine exhaust gases: 65% saved on inventory and weight

(source: H. Herzog, O. Falk-Pedersen)
Membrane absorption/stripping

Membrane absorption modules by Nagayananagi Co. Ltd.

Hollow fibre modules

Artificial lung
Adsorptive membranes (membrane chromatography)

- hybrid combination of liquid chromatography and membrane filtration
- based on microporous or macroporous membranes that contain functional ligands attached to their inner pore structure, which act as adsorbents
- higher throughput than in traditional systems
- easy scale-up
Adsorptive membranes (membrane chromatography)

- Convective flow between particles
  - film diffusion
  - pore diffusion

- Convective flow through pores

- Micropore
- Macropore

1. - film diffusion
2. - pore diffusion
Adsorptive membranes
(membrane chromatography)

Courtesy: Sartorius
Adsorptive membranes (membrane chromatography)

**Used almost exclusively in biopharmaceutical manufacturing**

- protein separation, purification and concentration
- DNA removal
- virus purification
Synergy – multiple functions

More integration means less degree of freedom

(Tlatlik and Schembecker, ARS-1, Dortmund 2000)

(Tlatlik and Schembecker, ARS-1, Dortmund 2000)
Synergy – multiple functions

Important issue: size of the feasible operation window

- Function 1
- Function 2
- Apparatus design

(after Tlatlik and Schembecker, ARS-1, Dortmund 2000)
Synergy – multiple functions

Main issue: size of the feasible operation window

Example for reactive separations

Synergy – multiple functions

How to enlarge small feasibility window?

- By speeding-up partial processes, to allow for different equipment type, size and materials.
- By changing phase equilibrium (e.g. extra compound, local superheating, etc.) or switching to non-equilibrium.
- By changing type of catalyst or conditions on catalysts.

Synergy – multiple functions

Example: How to enlarge small feasibility window in catalytic distillation?

- Catalyst temperature determined by VLE conditions
- Catalyst temperature “uncoupled” from VLE, reaction accelerated