

# SYNERGY – PART II

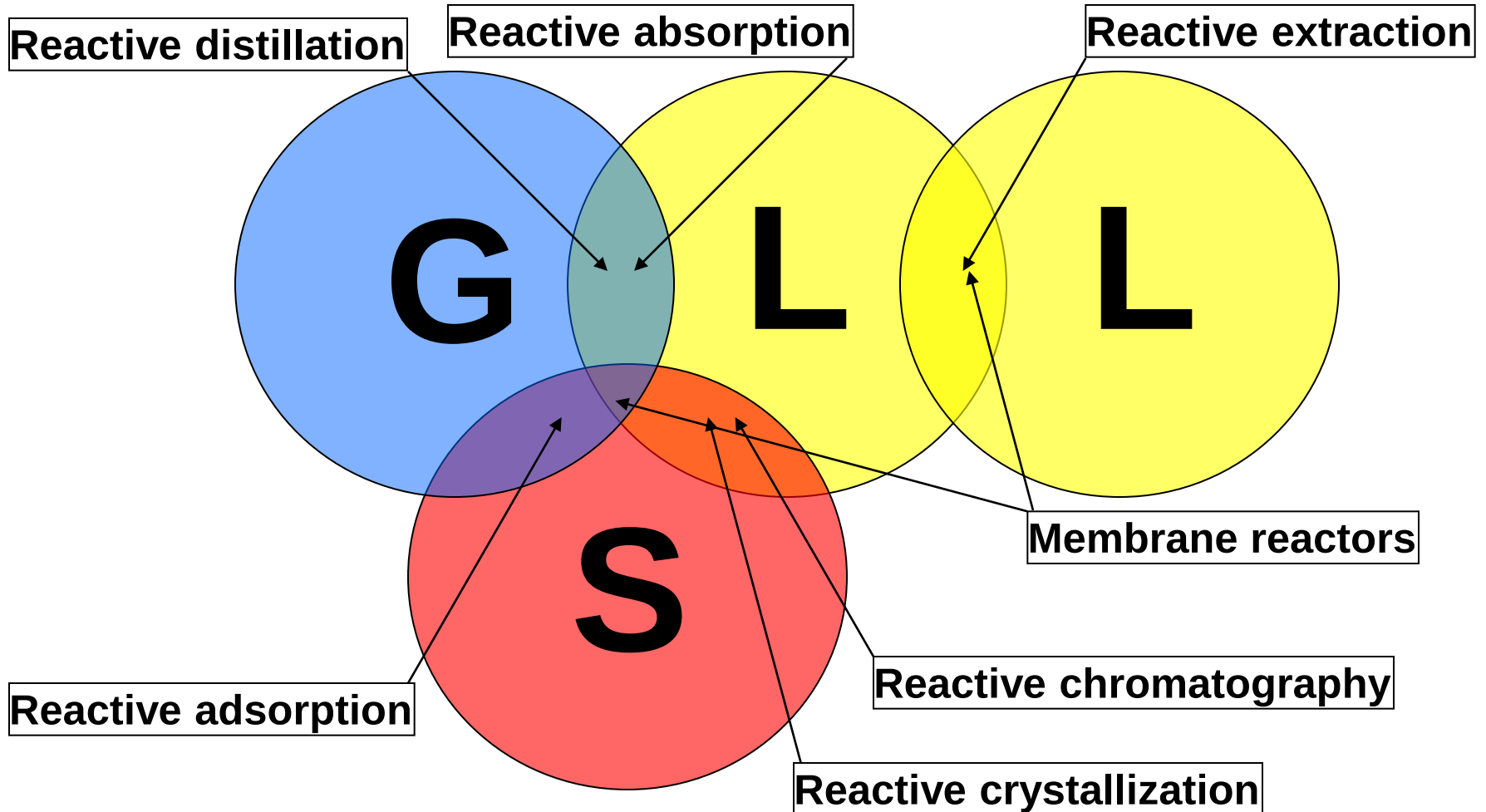
# Contents

- Incentives
- Reactive separations and their applications
- Hybrid separations and their applications
- Degrees of freedom and feasible operation windows in multifunctional equipment/operations

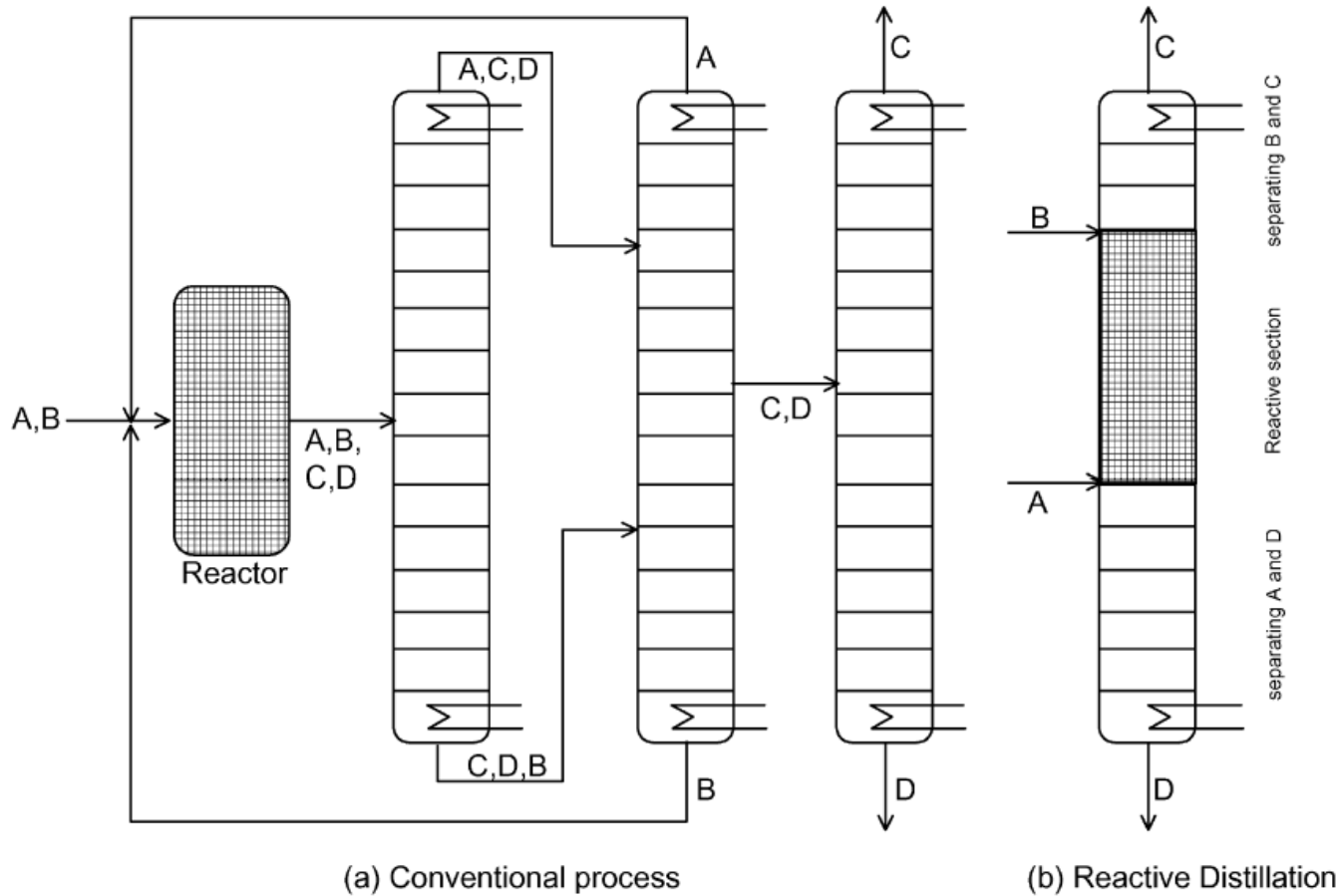
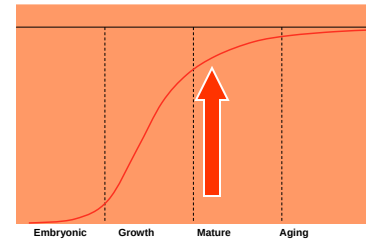
# Reactive separations – why?

- **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?

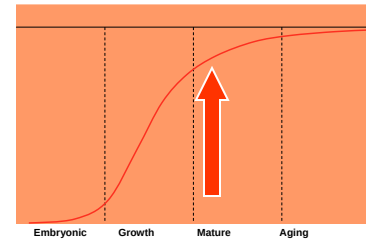
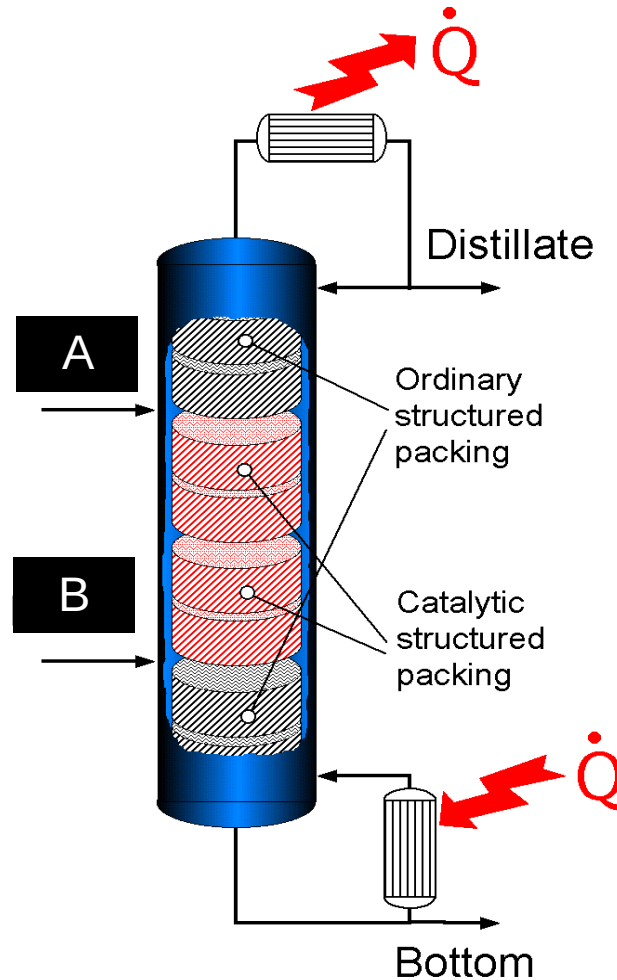


# Reactive distillation

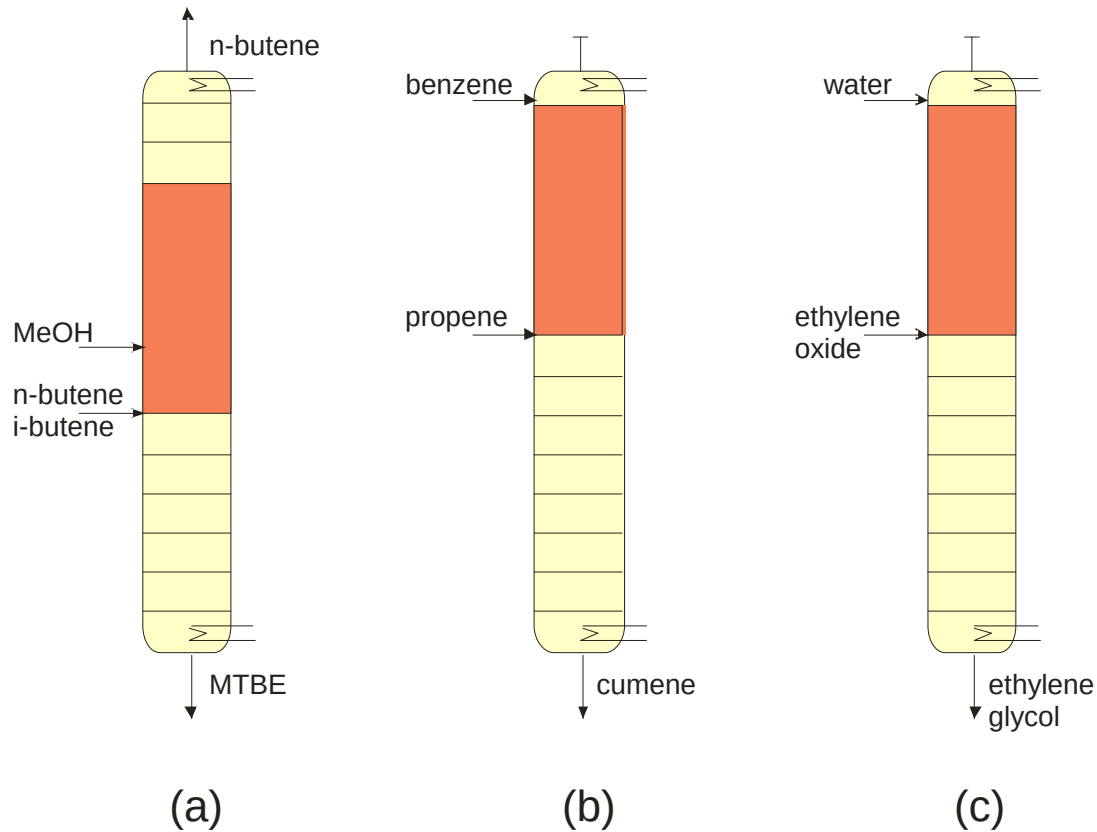
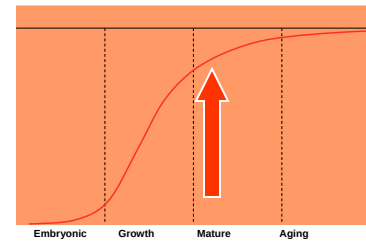


**Processing schemes for reaction  $A + B \rightleftharpoons C + D$**

# Reactive distillation

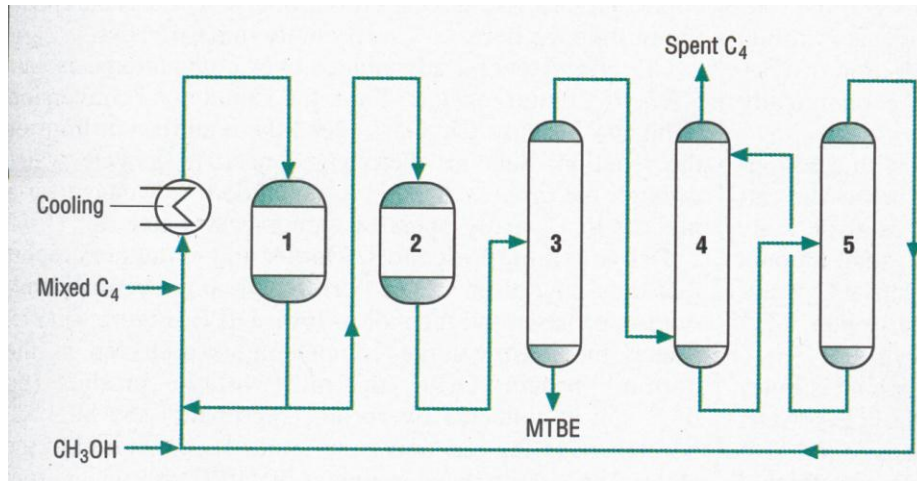
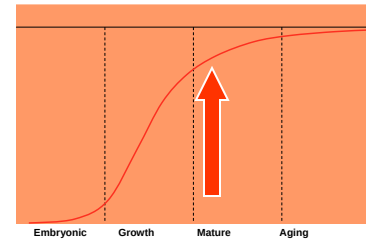


# Reactive distillation



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

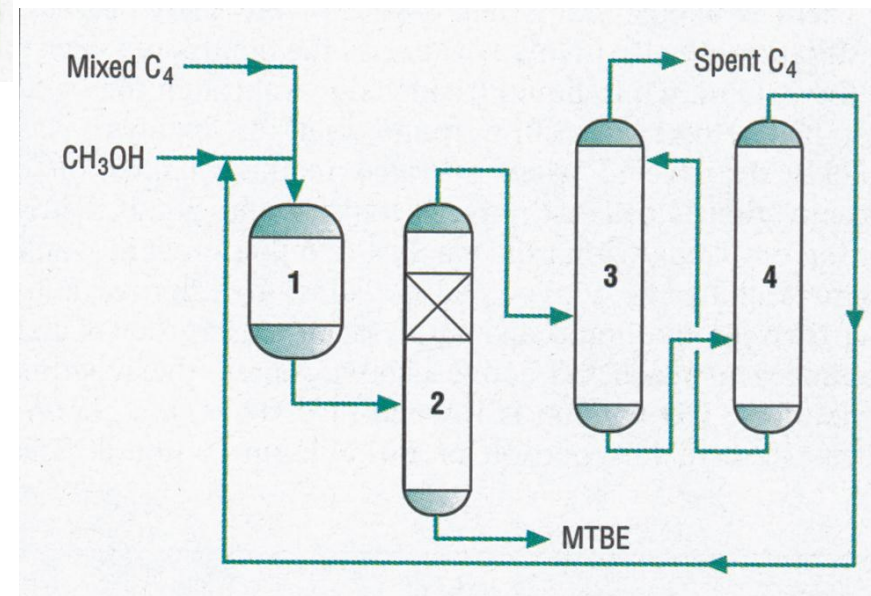
# Reactive distillation



**conventional**

## MTBE SYNTHESIS

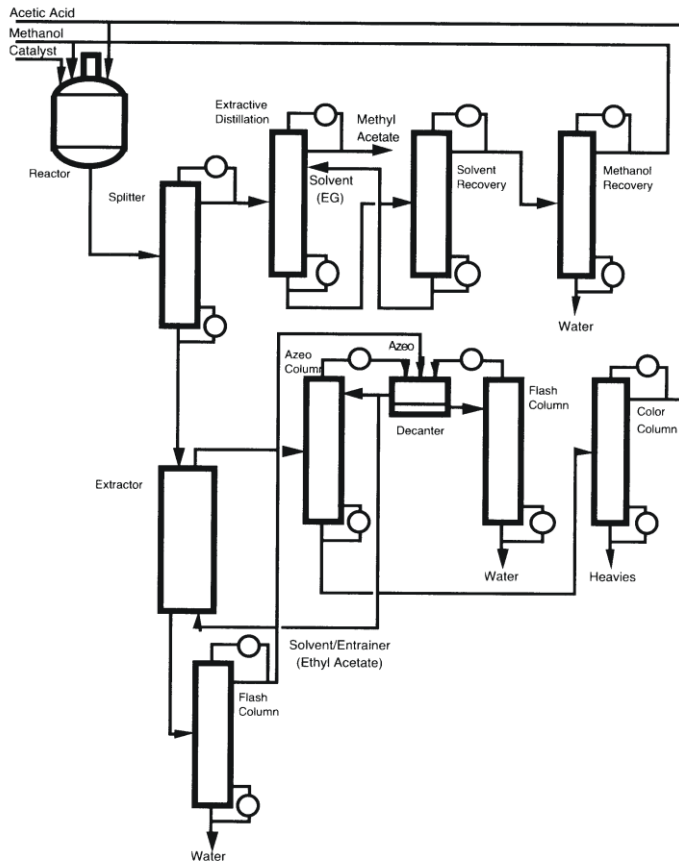
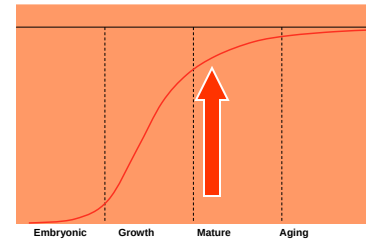
**via reactive  
distillation**



## APPLICATIONS OF REACTIVE DISTILLATION

# 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)**

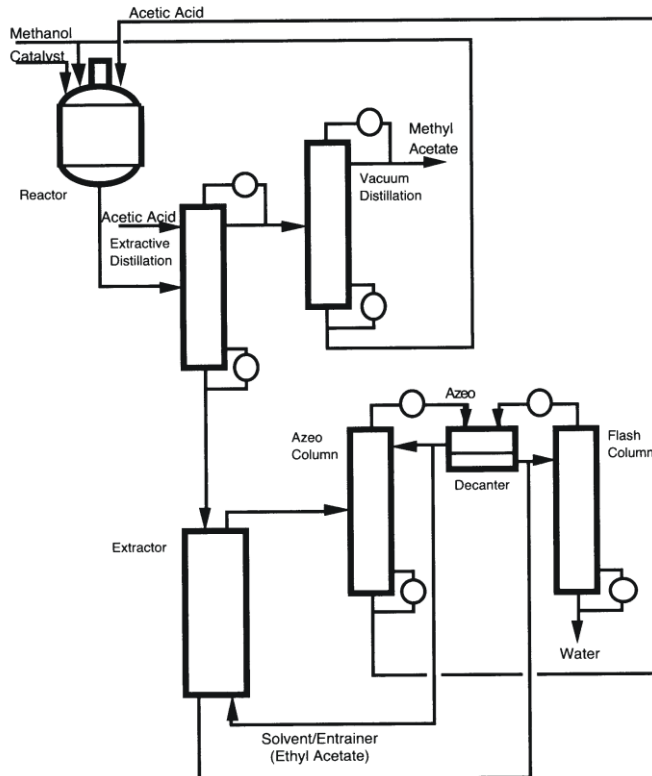
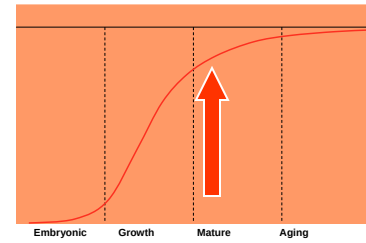
### Conventional plant:

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

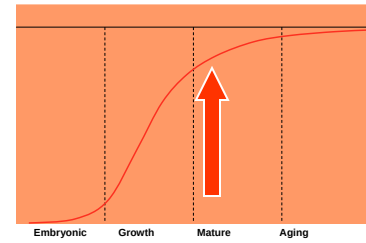


### Evolutionary Modification:

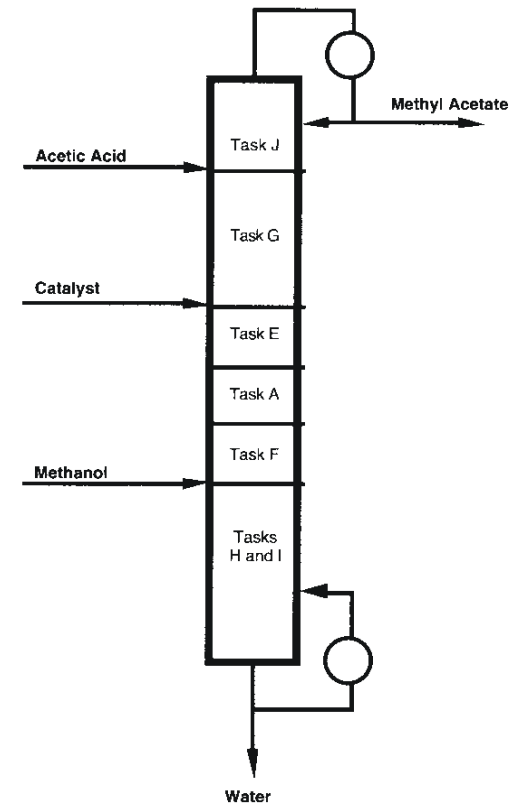
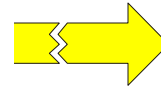
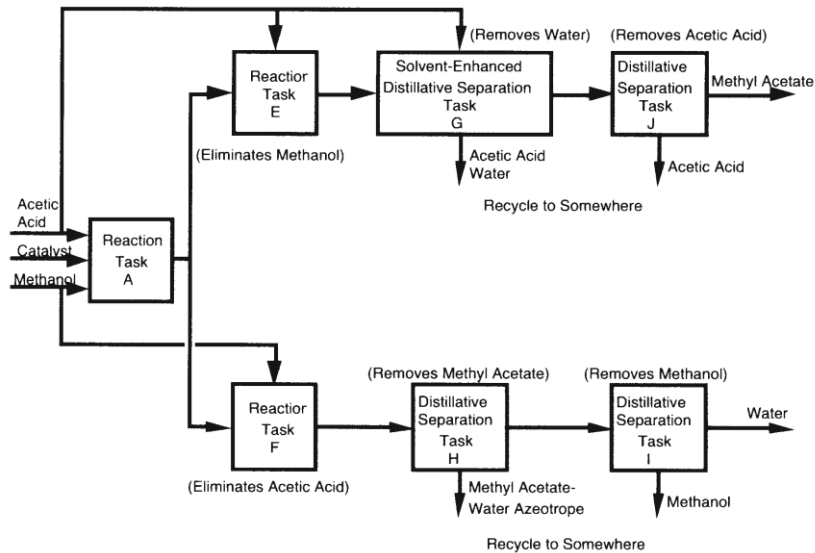
- two flash column combined (similar feeds, overheads to the same decanter, both underflows to wastewater treatment);
- acetic acid color column skipped;
- one solvent eliminated (ethylene glycol replaced by acetic acid).

# Reactive distillation

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

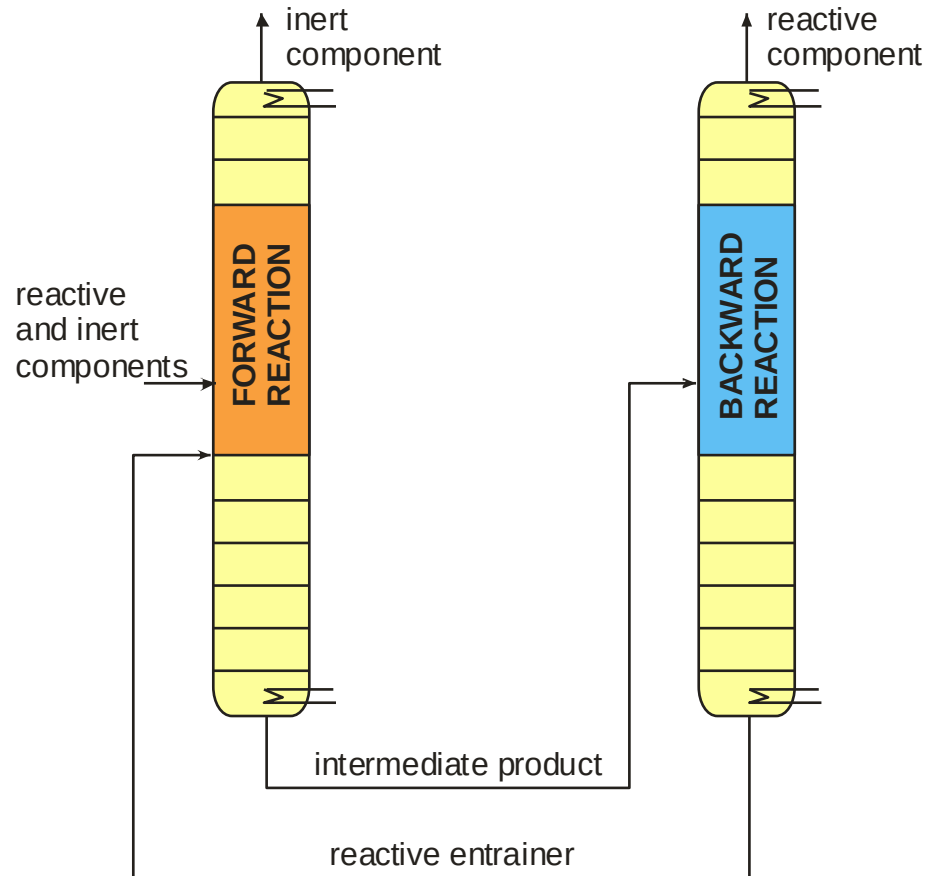
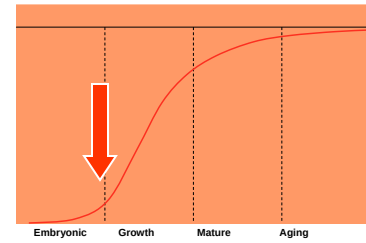


### Task identification:



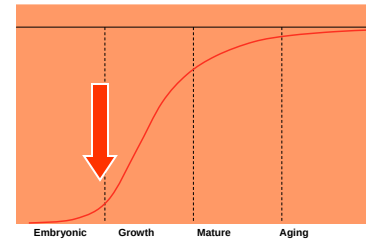
# Reactive distillation

## Reactive distillation as a powerful separation method



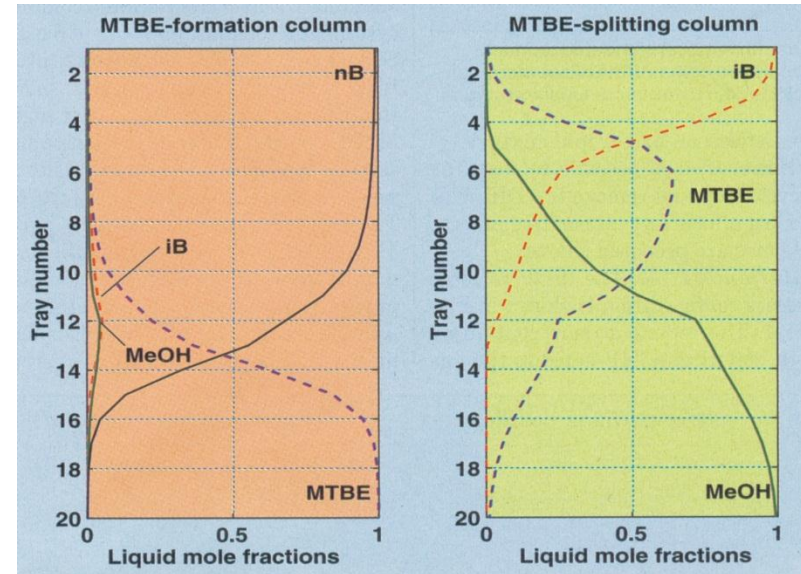
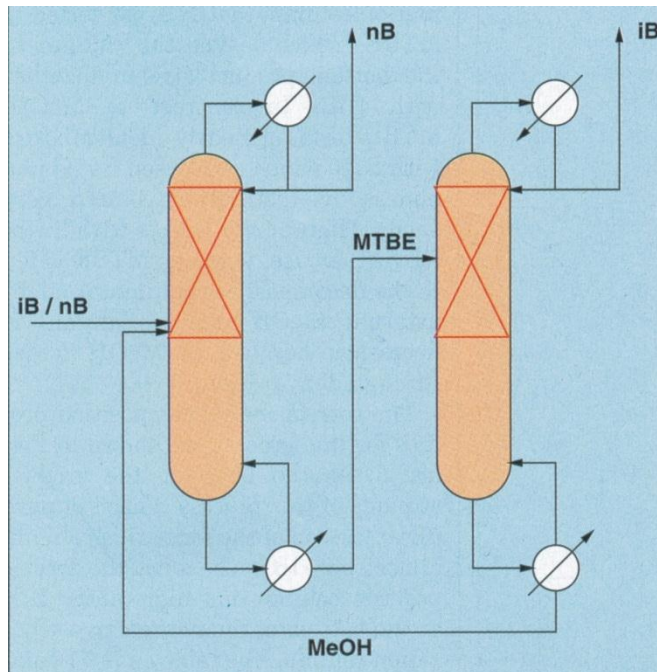
# Reactive distillation

## Reactive distillation as a powerful separation method



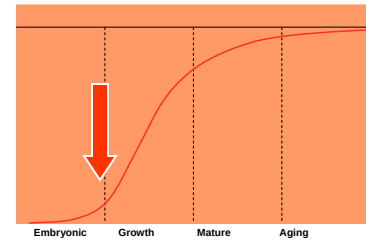
- How to separate isobutene from non-reactive n-butene?

(ideal case)

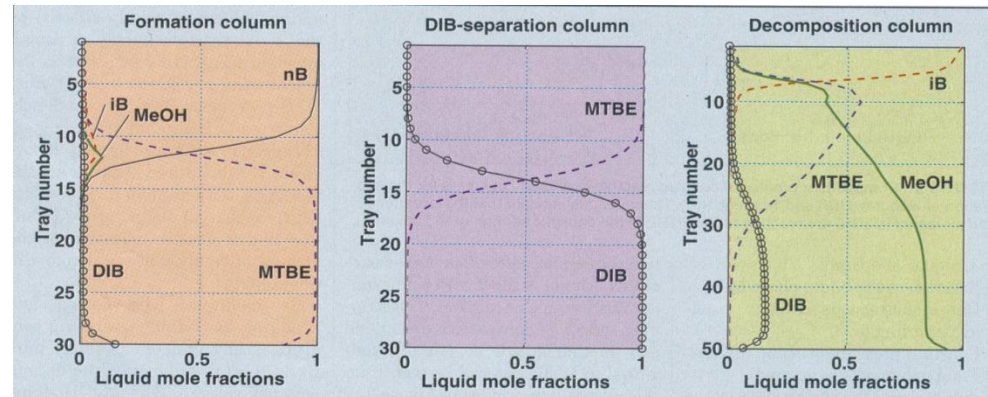
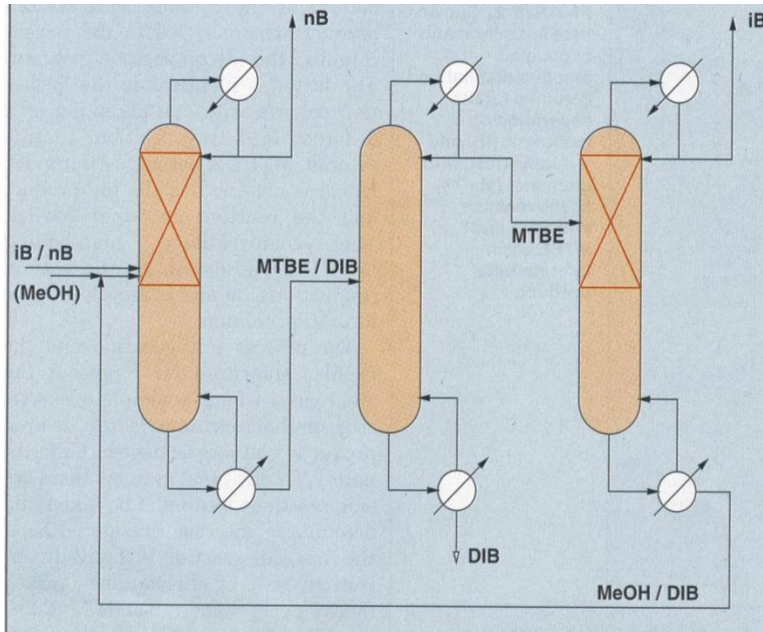
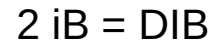


# Reactive distillation

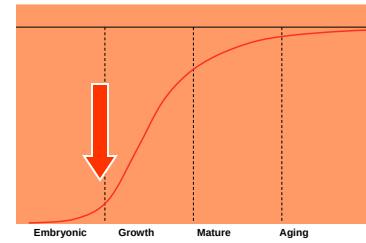
## Reactive distillation as a powerful separation method



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



# Reactive distillation

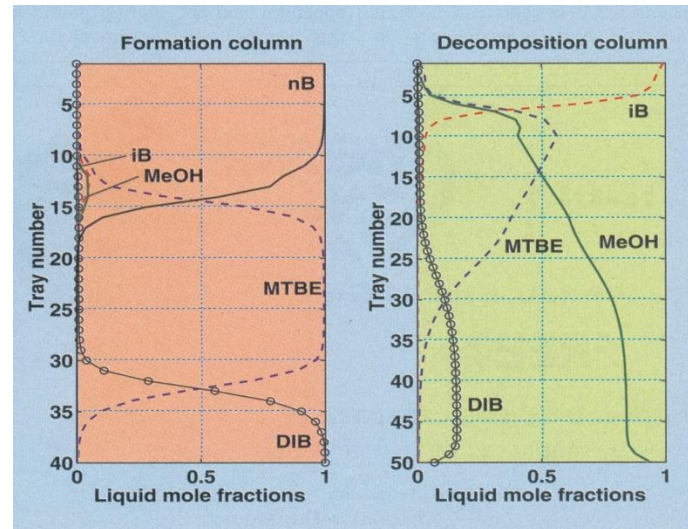
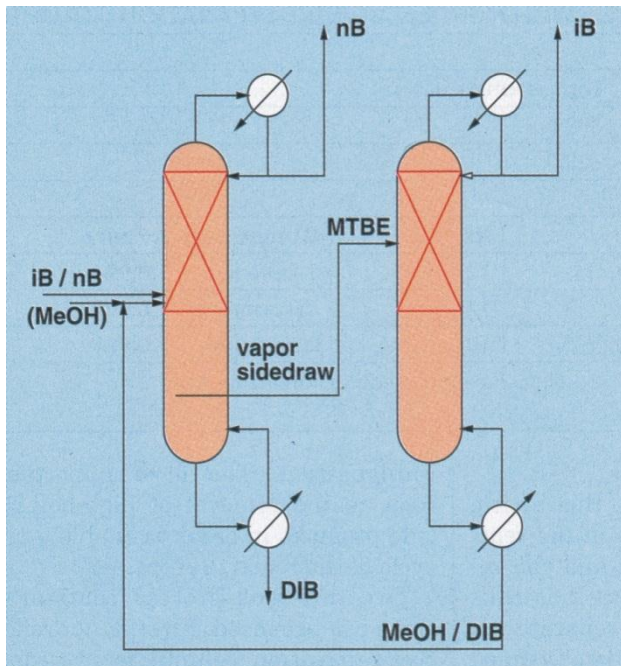


## Reactive distillation as powerful separation method

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

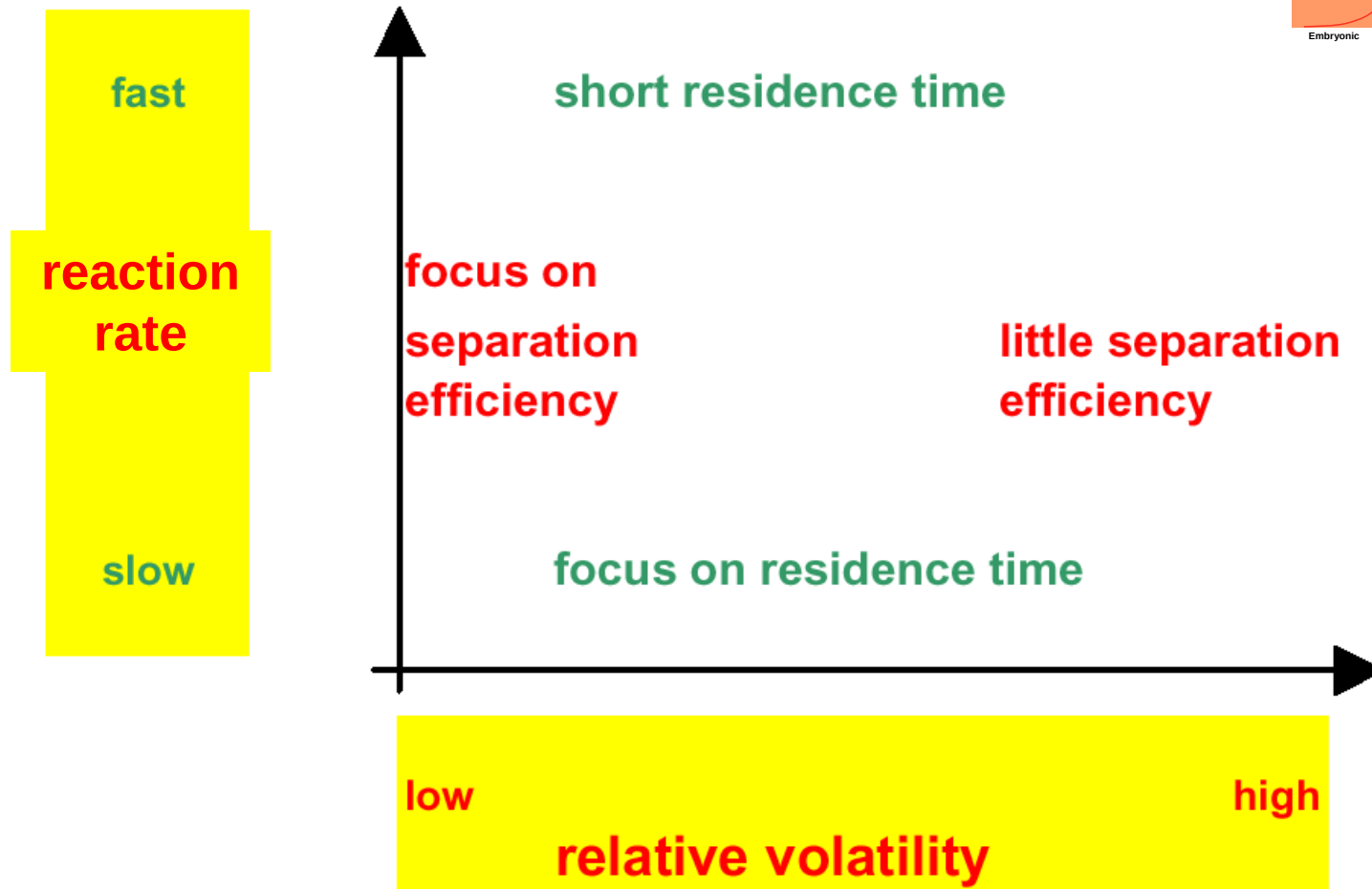
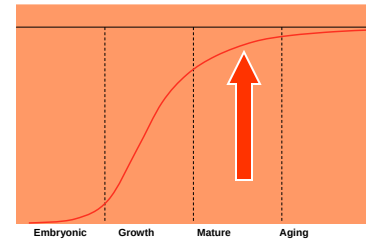
(real case: diisobutene (DIB) formed)

$2 \text{ iB} = \text{DIB}$

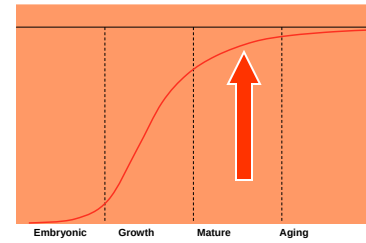


Solution No. 2: MTBE vapor-side draw saves one column

# Reactive distillation



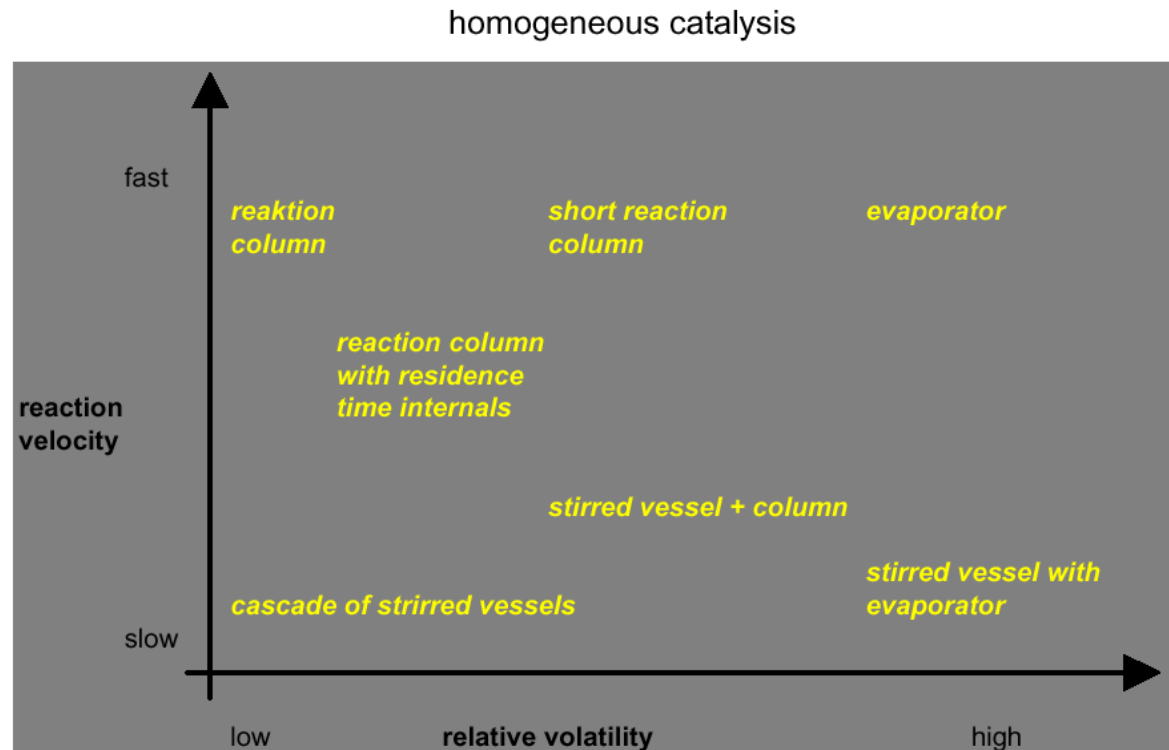
# Reactive distillation



## reaction and distillation (examples)

### homogeneous catalysis

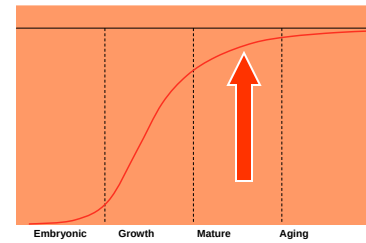
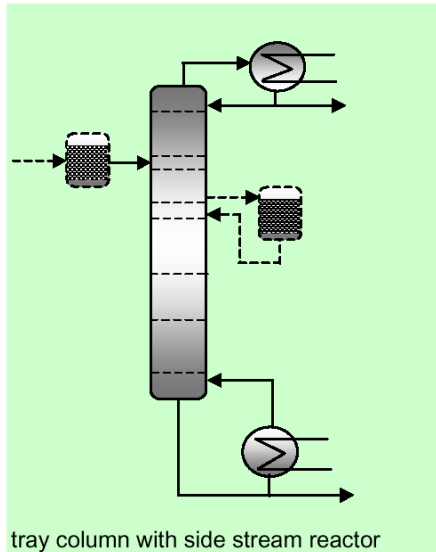
- rectification column
- column with larger volume in the bottom
- stirred vessel with rectifying column
- stirred vessel with full column
- vessel cascade with column
- stirred vessel with evaporator
- evaporator
- .....



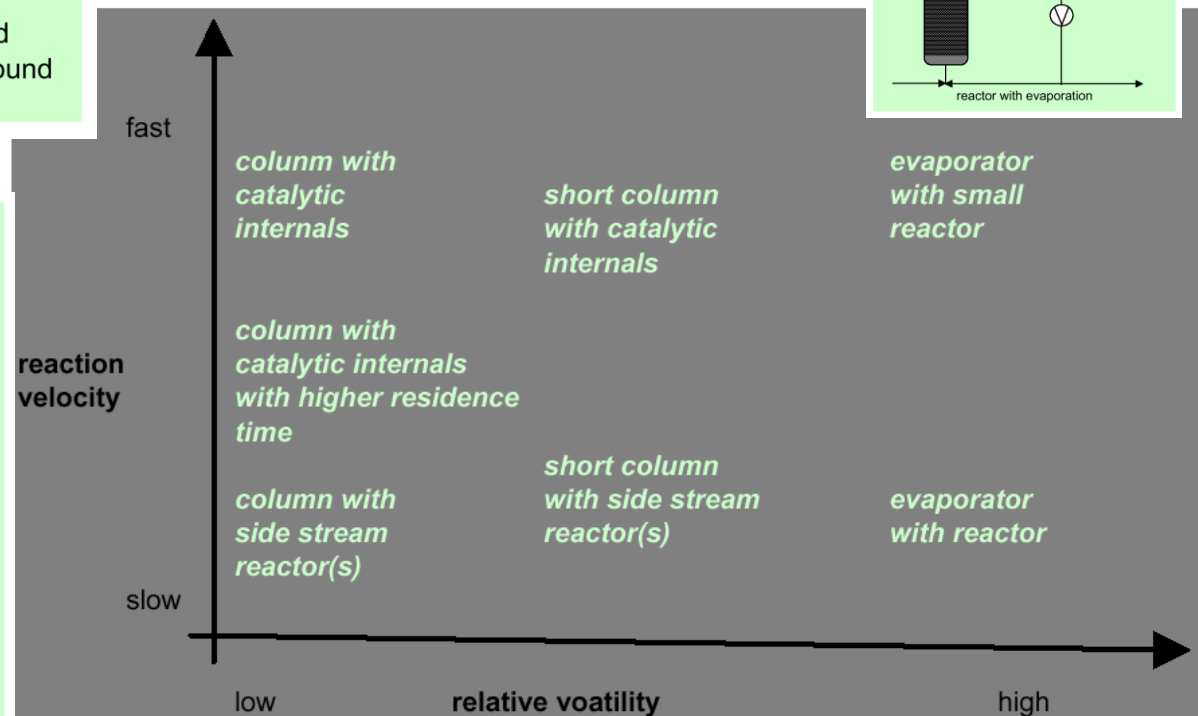
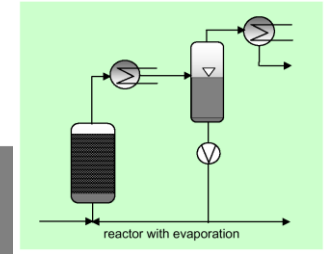
# Reactive distillation

## 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
- .....



## heterogeneous catalysis



# Reactive distillation

## Commercial applications:

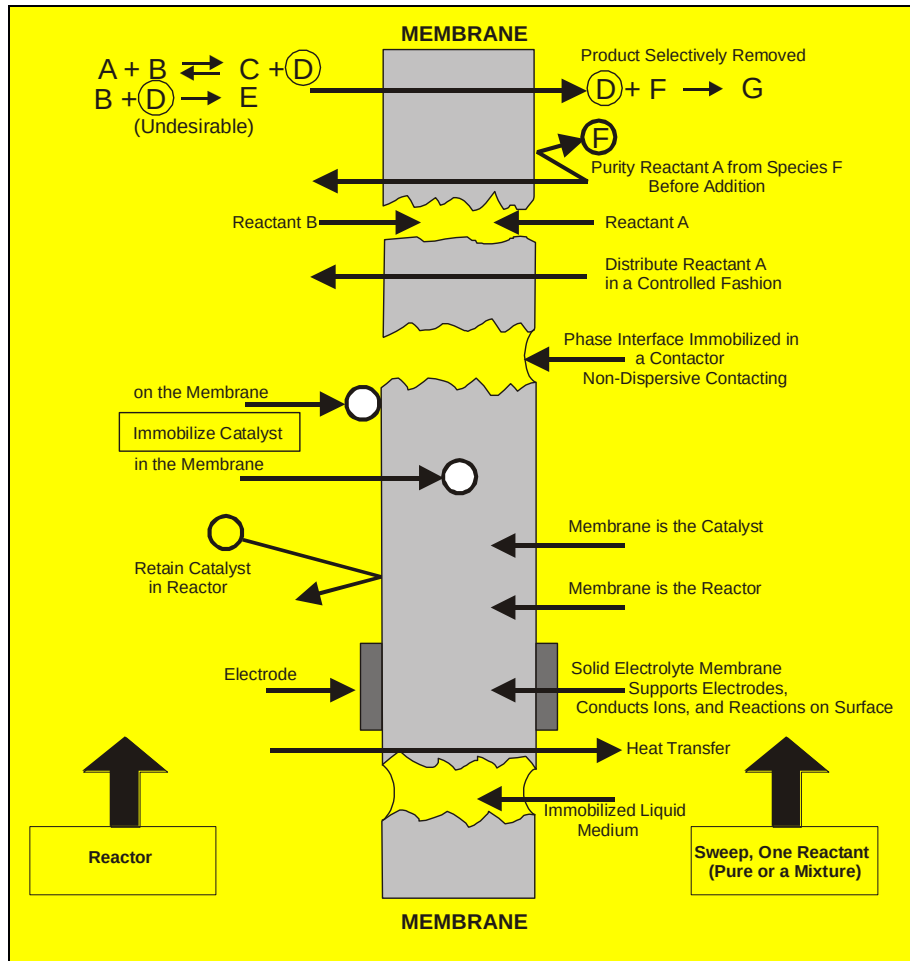
- ❏ ether technologies (MTBE, TAME, ETBE);
- ❏ methyl acetate from methanol and acetic acid;
- ❏ selective hydrogenations of dienes (butadiene, pentadiene, hexadiene)
- ❏ ethylbenzene via alkylation of benzene;
- ❏ cumene via propene alkylation with benzene;

**Application potential goes far beyond that!**

## Other possibilities:

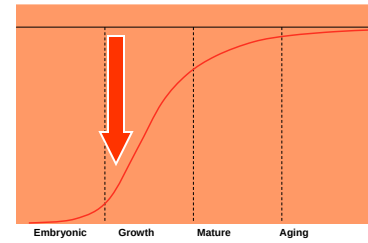
- ❏ ethers-to-olefins decomposition;
- ❏ selective dimerization of olefins;
- ❏ alkylation of isobutane with n-butenes (gasoline blending);
- ❏ hydrogenation of olefinic and di-olefinic impurities;
- ❏ hydroisomerisation (e.g. butenes);
- ❏ hydrolysis (e.g. isobutylene to *tert*-butyl alcohol);
- ❏ dehydration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

# Membrane reactors



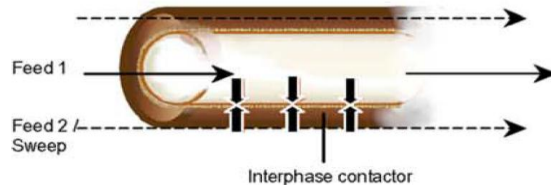
## Membrane functions in a reactor

# Membrane functions define configuration



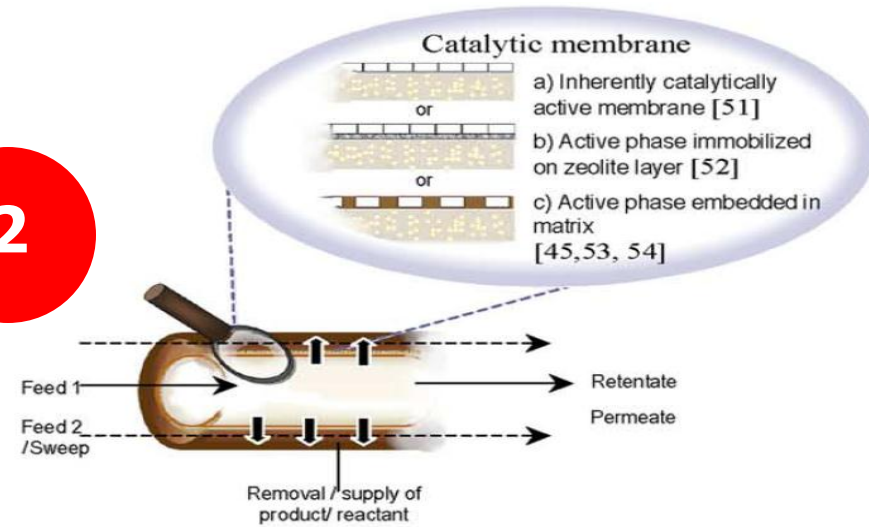
## Catalytic membranes

1



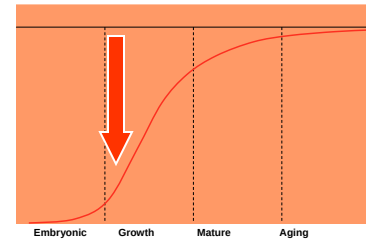
- catalytic
- interphase contactor
  - short contact time
  - no solvent needed

2



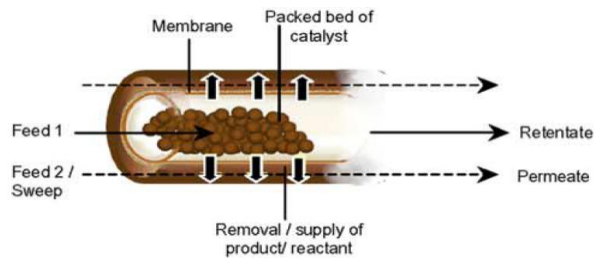
- catalytic
- selective product removal
- selective reactant supply
  - increased conversion
  - increased selectivity

# Membrane functions define configuration



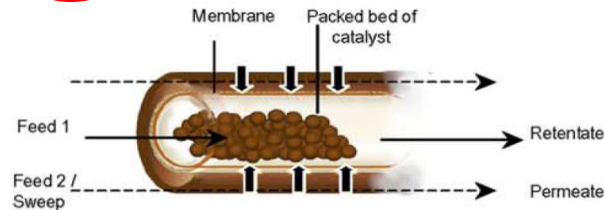
## Inert membranes

3



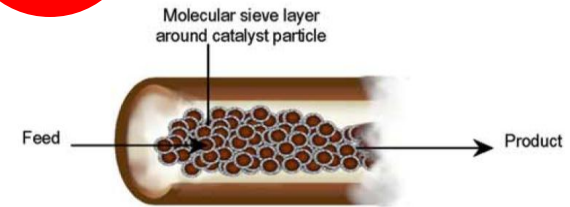
- selective product removal
- selective reactant supply
  - increased conversion
  - increased selectivity

4



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

5

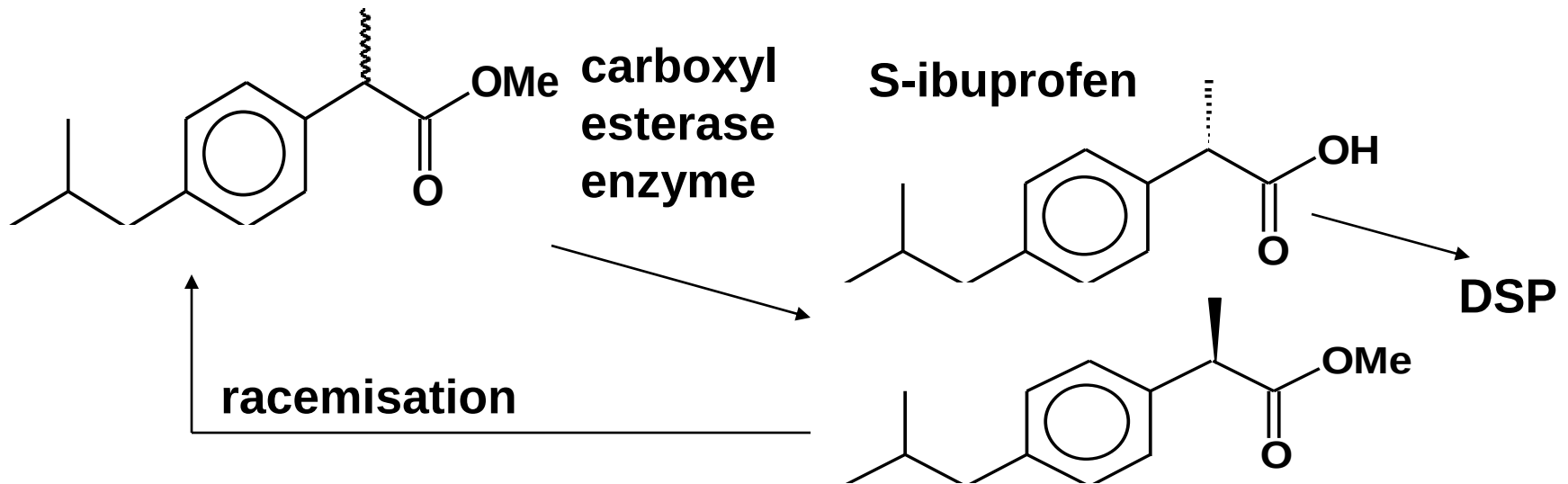


- catalyst poisoning protection
- selective product removal
- selective reactant supply
  - increased selectivity
  - prolonged cat. lifetime

# Membrane reactors - industrial example

## Production of S-ibuprofen

S-ibuprofen: non-steroidal anti inflammatory drug

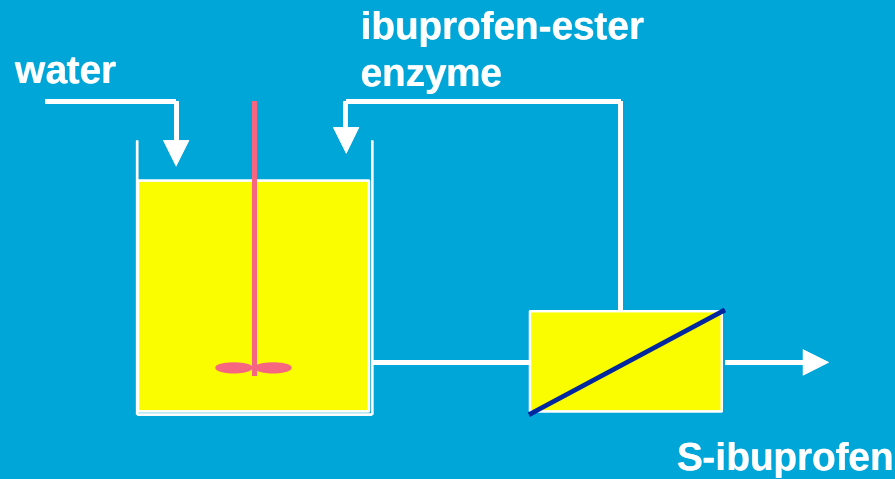
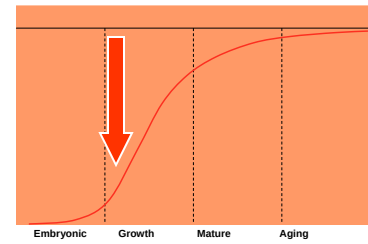


enzyme selectivity is very high

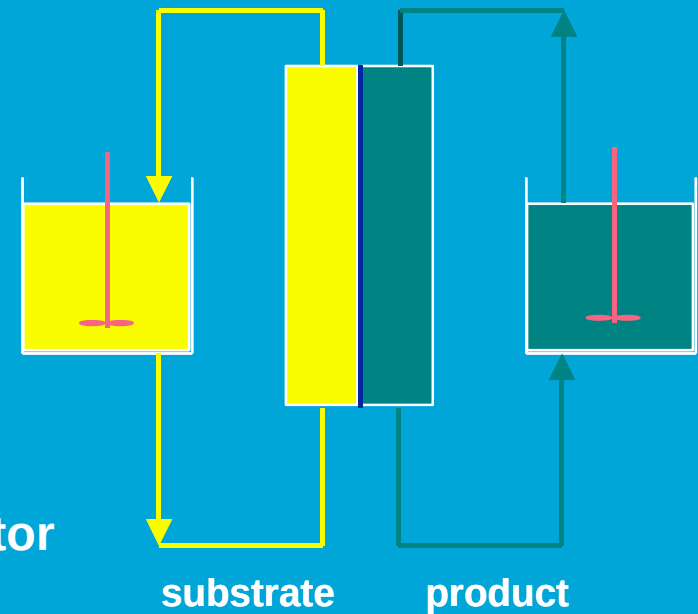
product causes enzyme-deactivation

enzyme-free product is required: laborious downstream processing

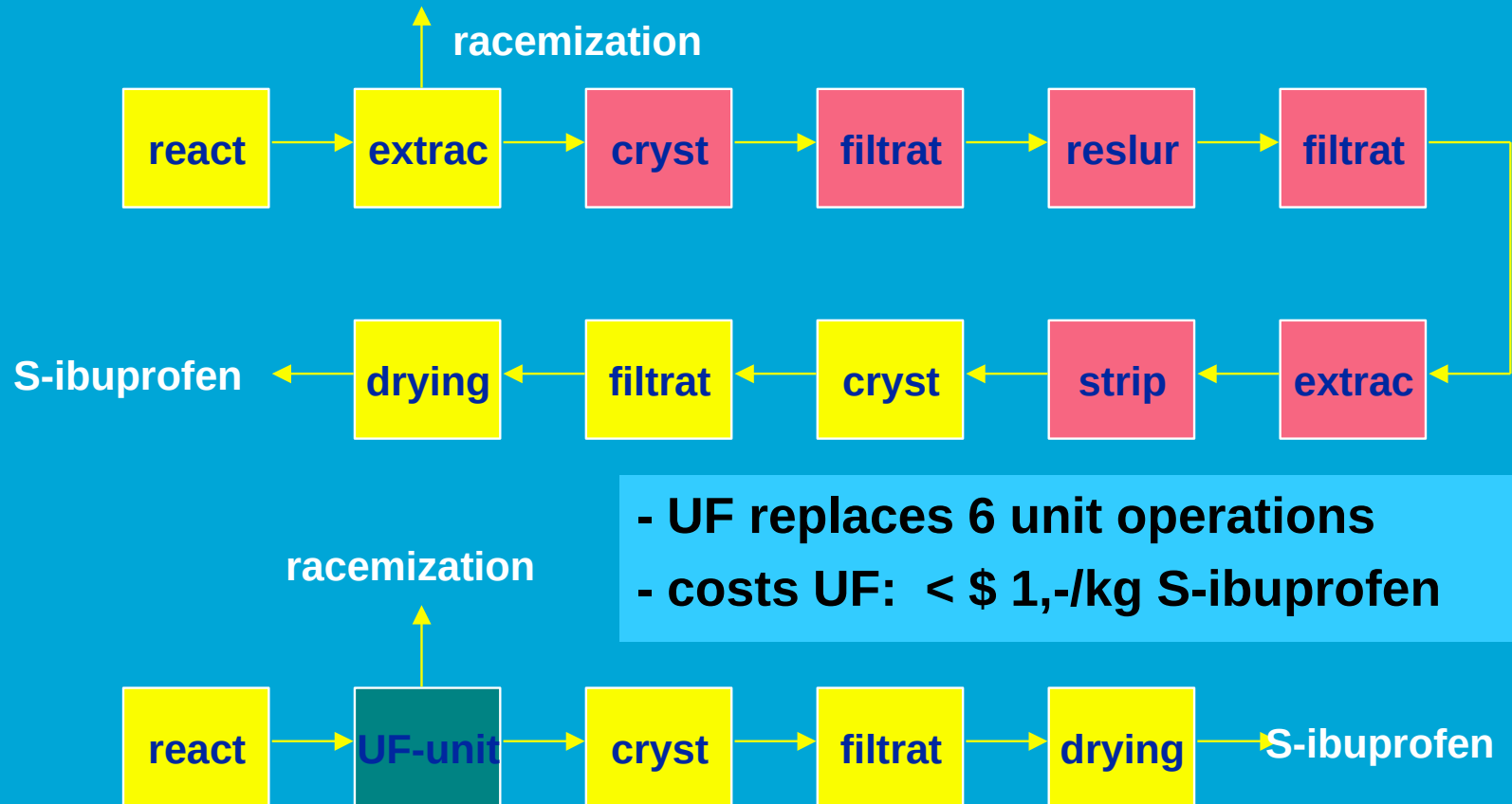
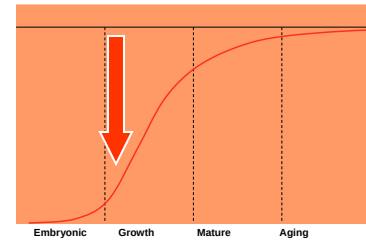
# Membrane reactors - industrial example



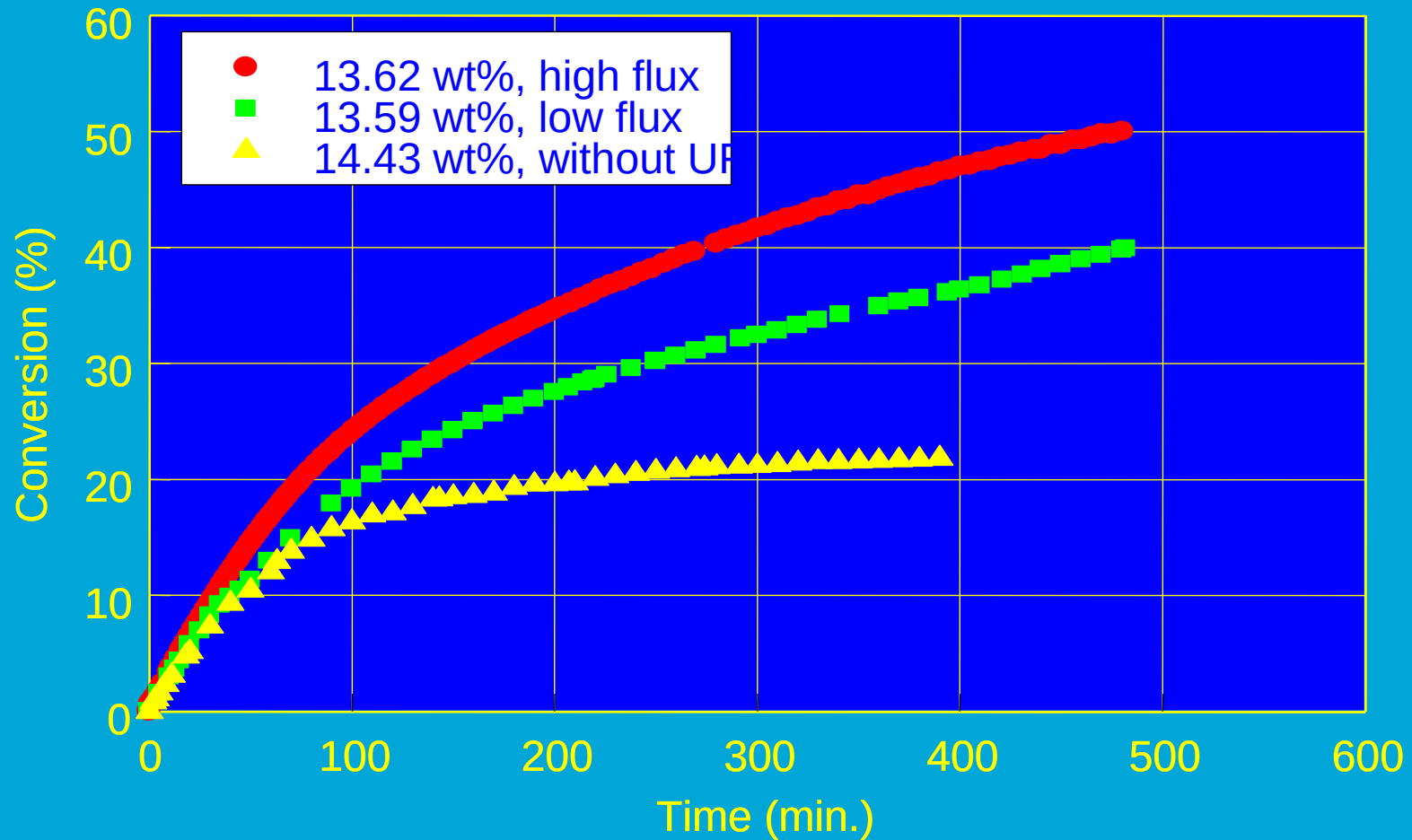
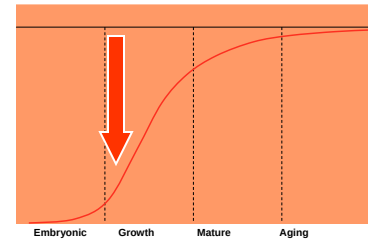
Even better:  
on-line UF or  
membrane reactor



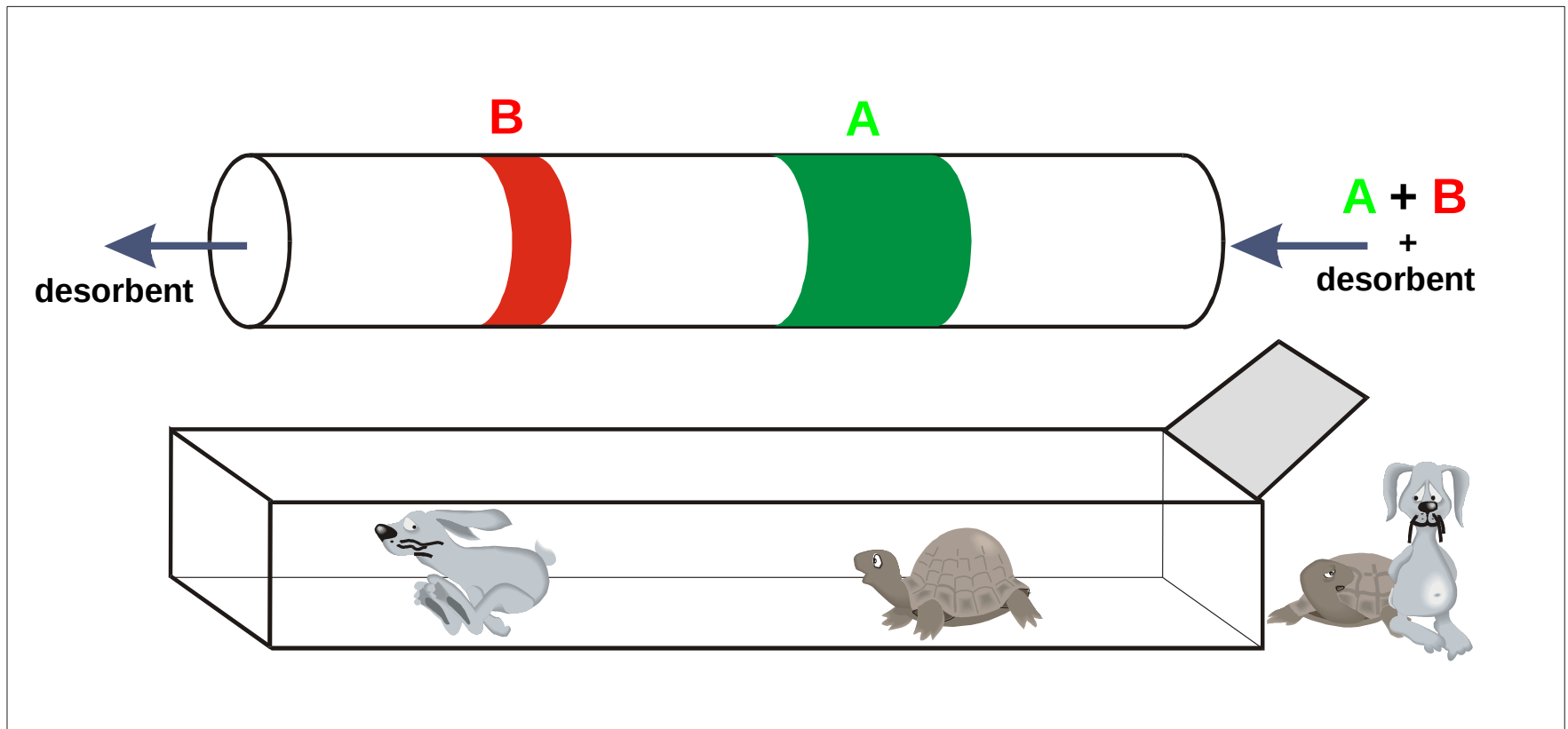
# Membrane reactors - industrial example



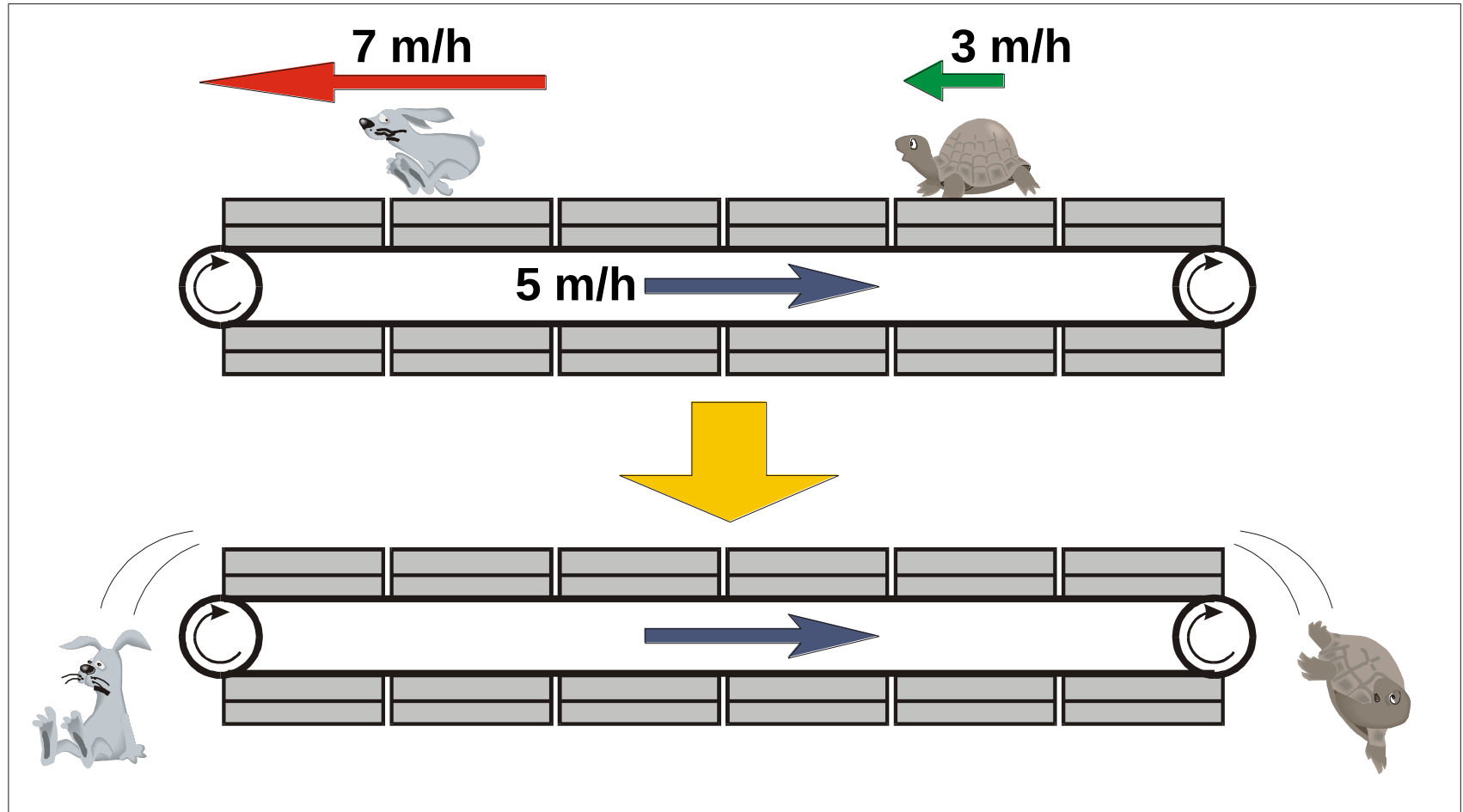
# Membrane reactors - industrial example



# Reactive adsorption

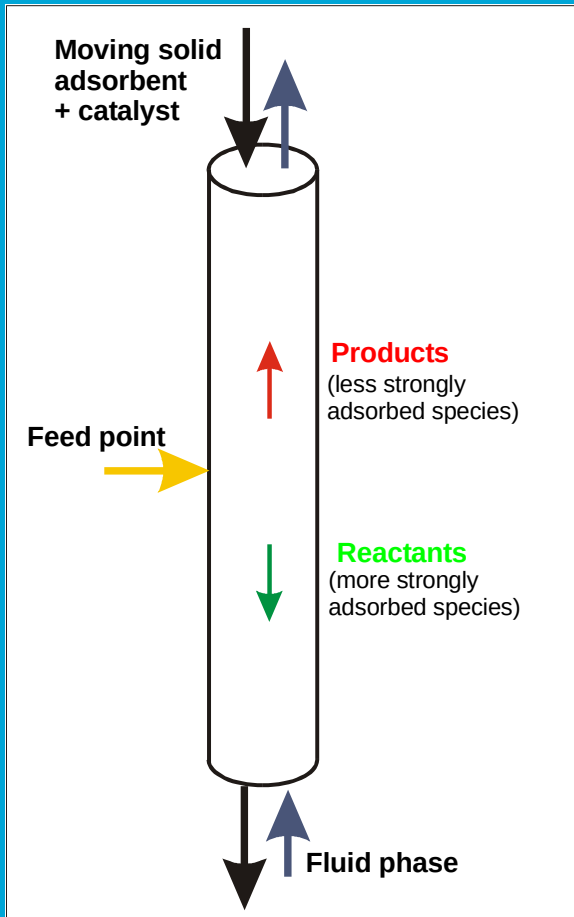


# Reactive adsorption



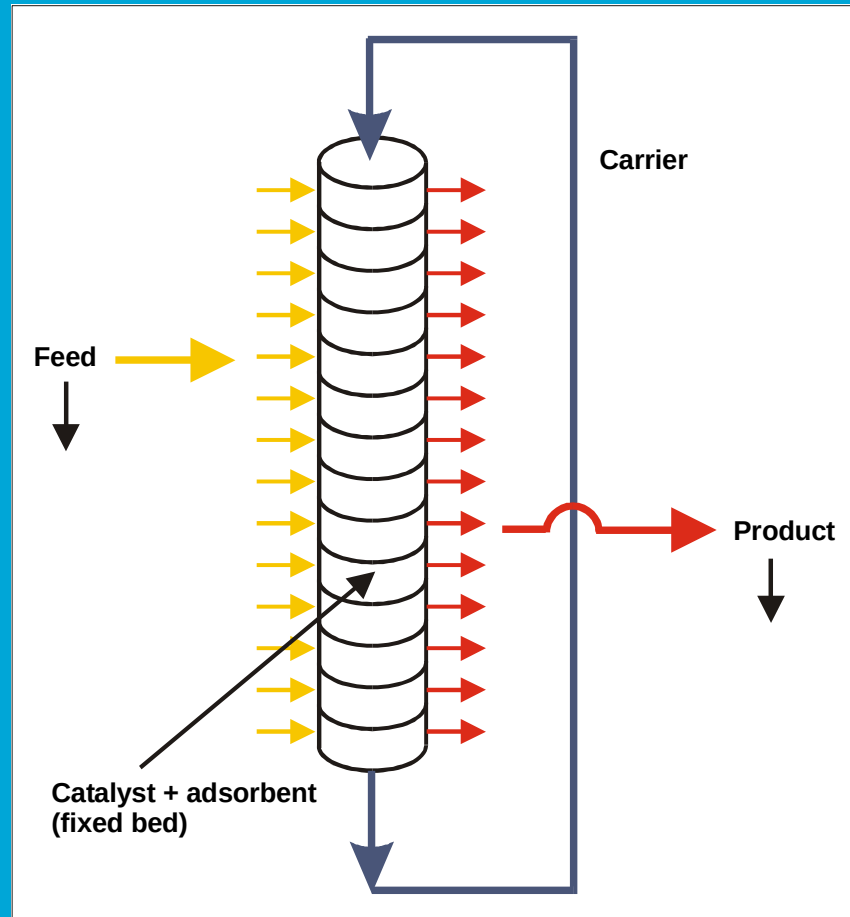
# Reactive adsorption

## TRUE COUNTERCURRENT MOVING BED CHROMATOGRAPHIC REACTOR

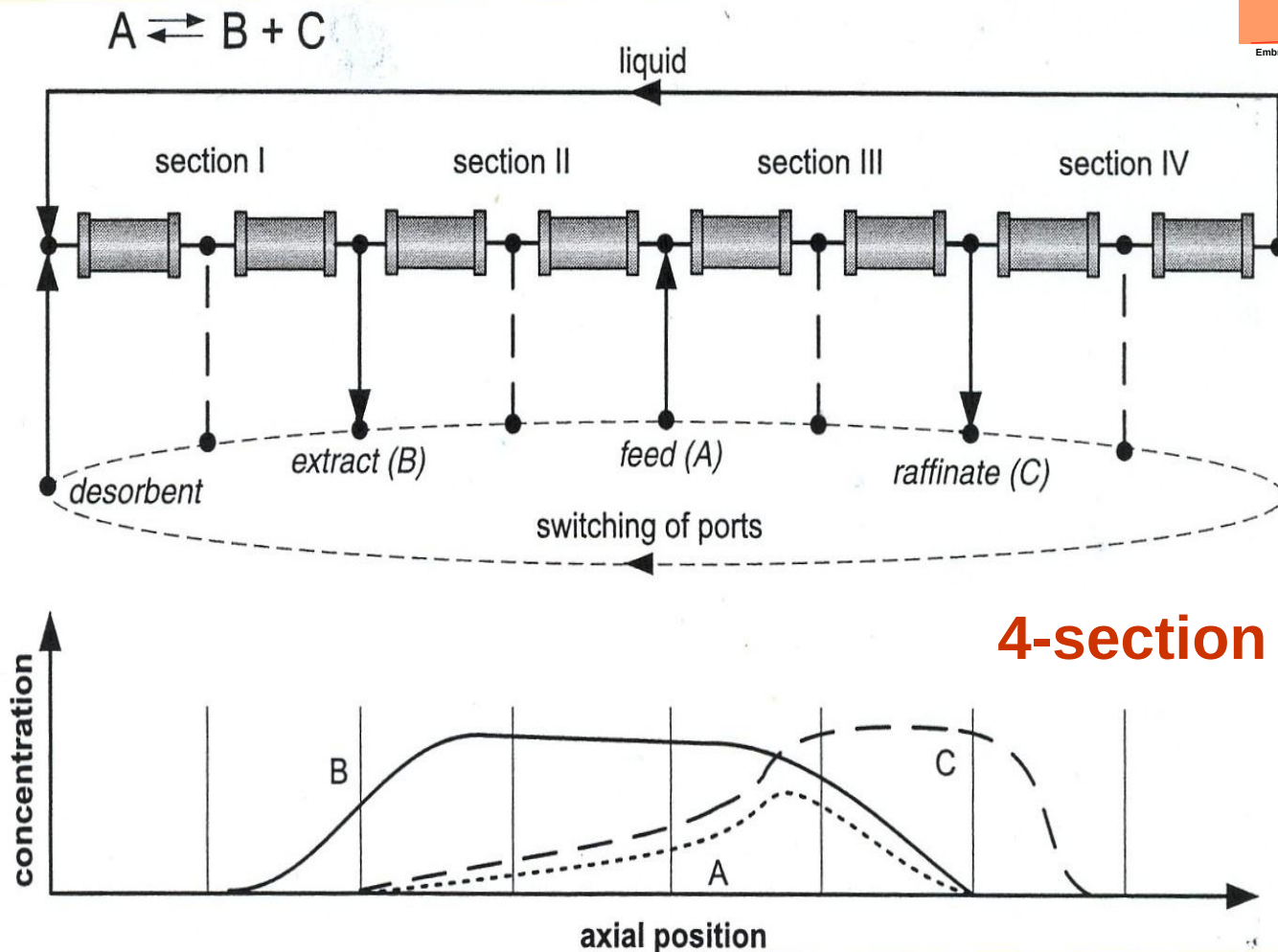
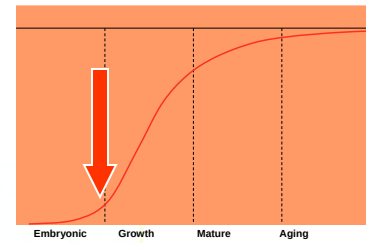


## SIMULATED COUNTERCURRENT MOVING BED CHROMATOGRAPHIC REACTOR

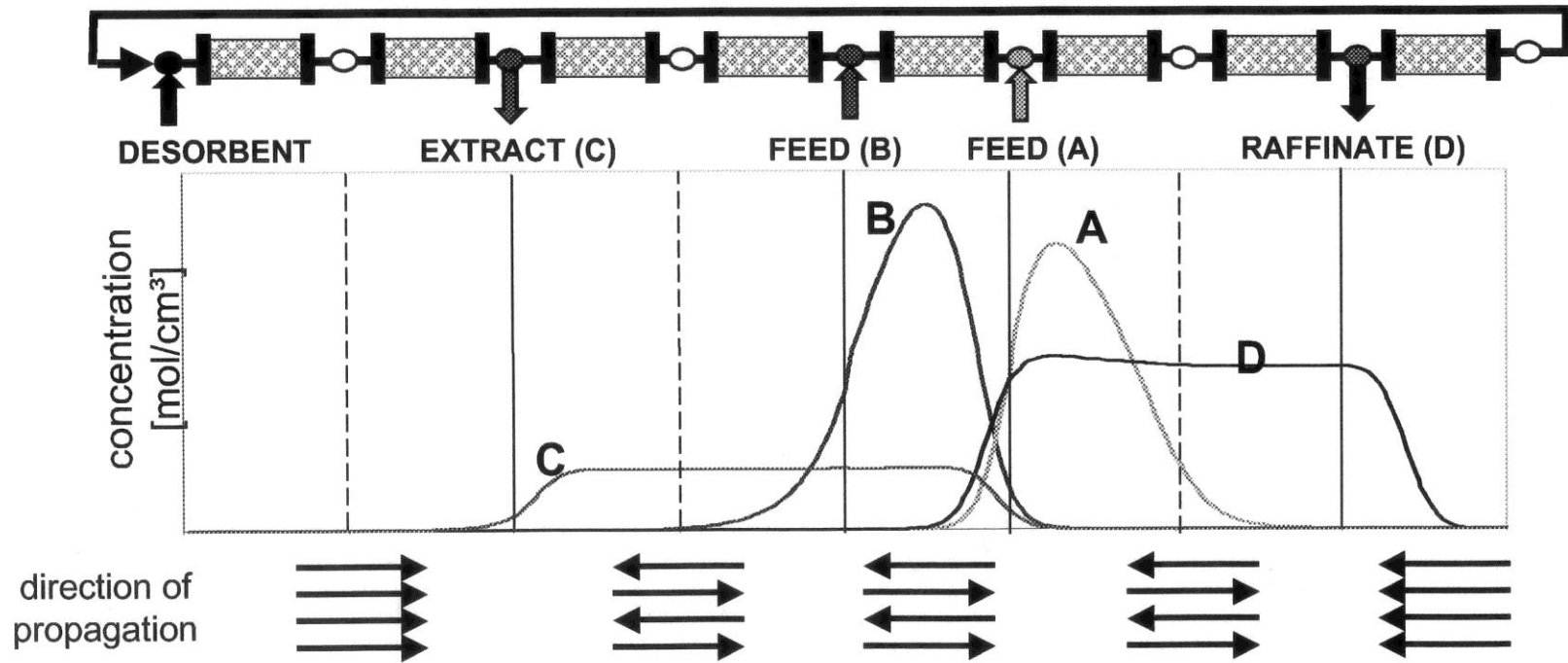
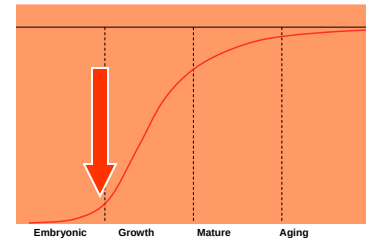
(feed and product ports move in the same direction as carrier)



# Simulated Moving Bed (SMB) Chromatographic Reactor



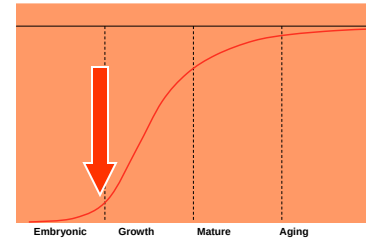
# Simulated Moving Bed (SMB) Chromatographic Reactor



- reactants are fed at two different nodes
- different direction of propagation of the reactants
- 👉 **Reactants meet in the reaction section**

**5-section design**

# Simulated Moving Bed (SMB) Chromatographic Reactor



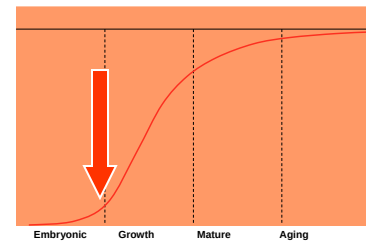
## 4-section vs. 5-section design: production of n-Butyl methacrylate

### 4-section SMBCR:

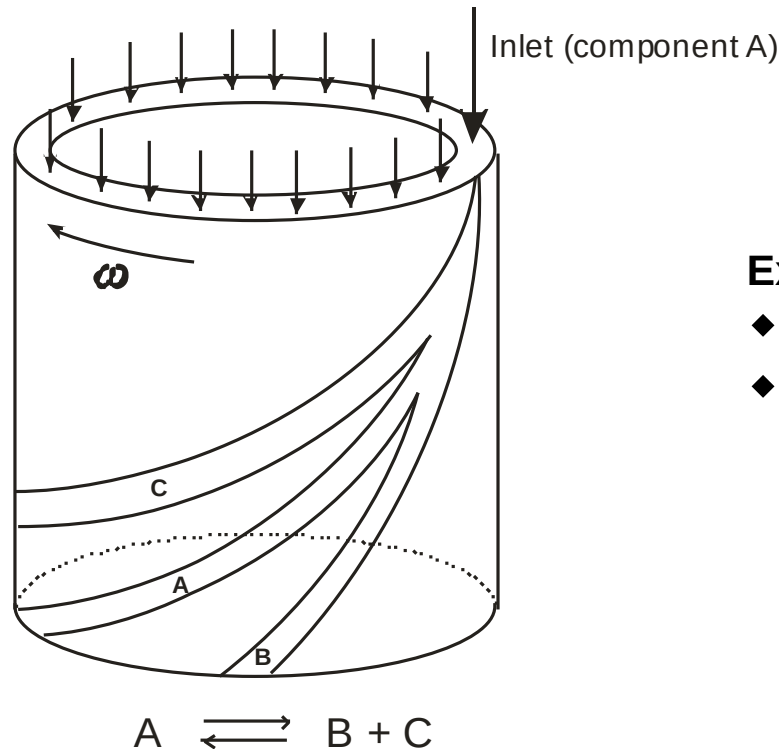
Segmentation: 2-2-3-1  
Conversion: 65.79%  
Acetate purity: 60.76%

### 5-section SMBCR:

Segmentation: 2-2-2-1-1  
Conversion: 70.25%  
Acetate purity: 89.55%



## 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)

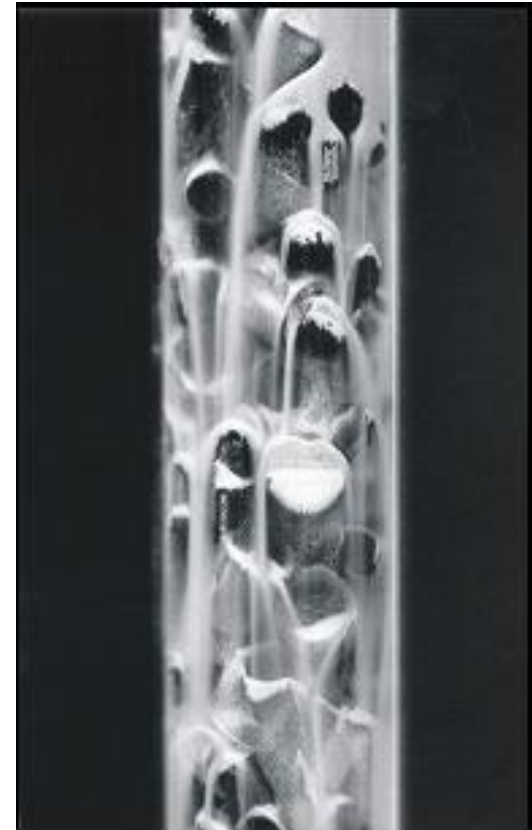
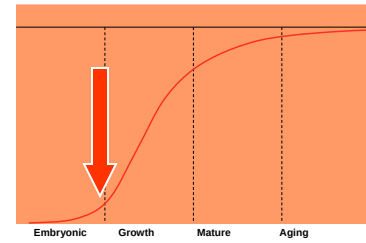
- ✓ catalyst pellets stationary in packed bed
- ✓ adsorbent powder trickles downwards
- ✓ reacting gas flows in counter -current upwards

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

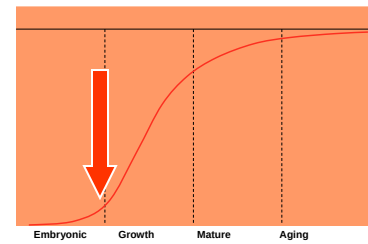
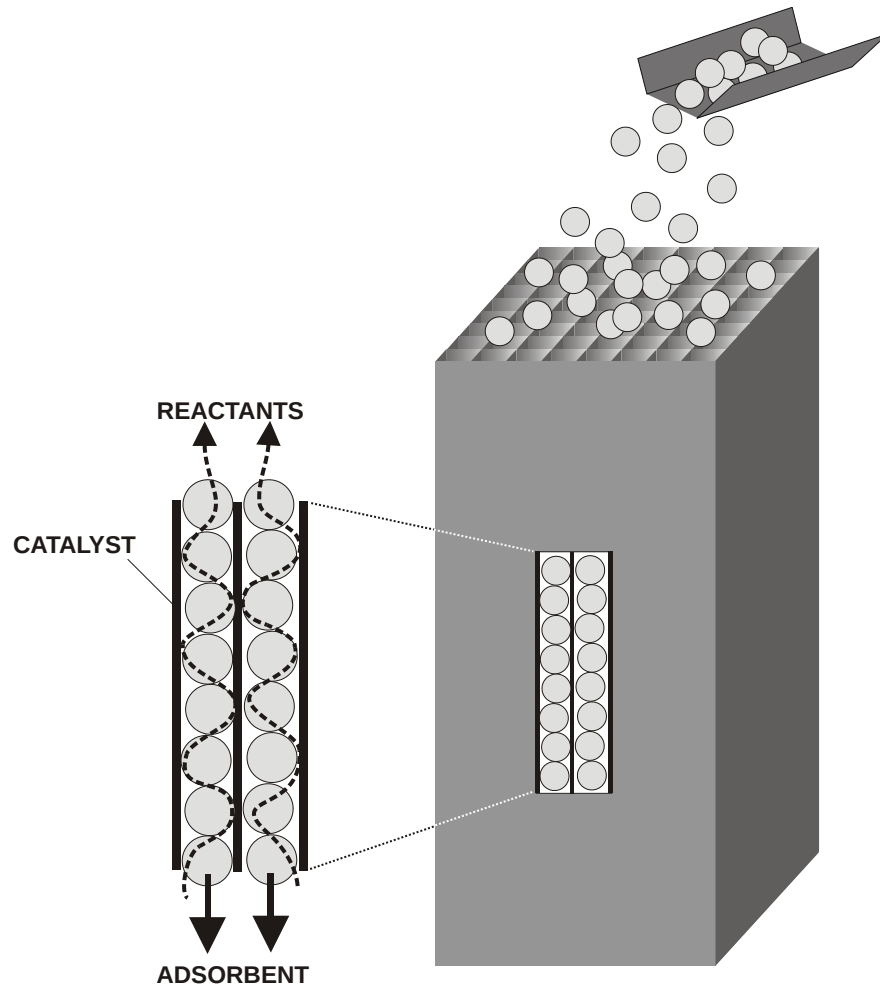
Economical evaluation versus Lurgi process (1000 tpd):

- ✓ 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%

(Knäbel K., et al., in: "Emerging Separation and Separative Reaction Technologies for Process Waste Reduction", AIChE, 1999)



# Reactive adsorption



**Moving bed reactor –  
solids flow**

**(co- and counter-  
current)**

# Reactive extraction

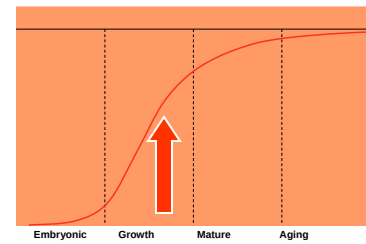
## Combination of reaction and liquid-liquid separation

### Immiscibility:

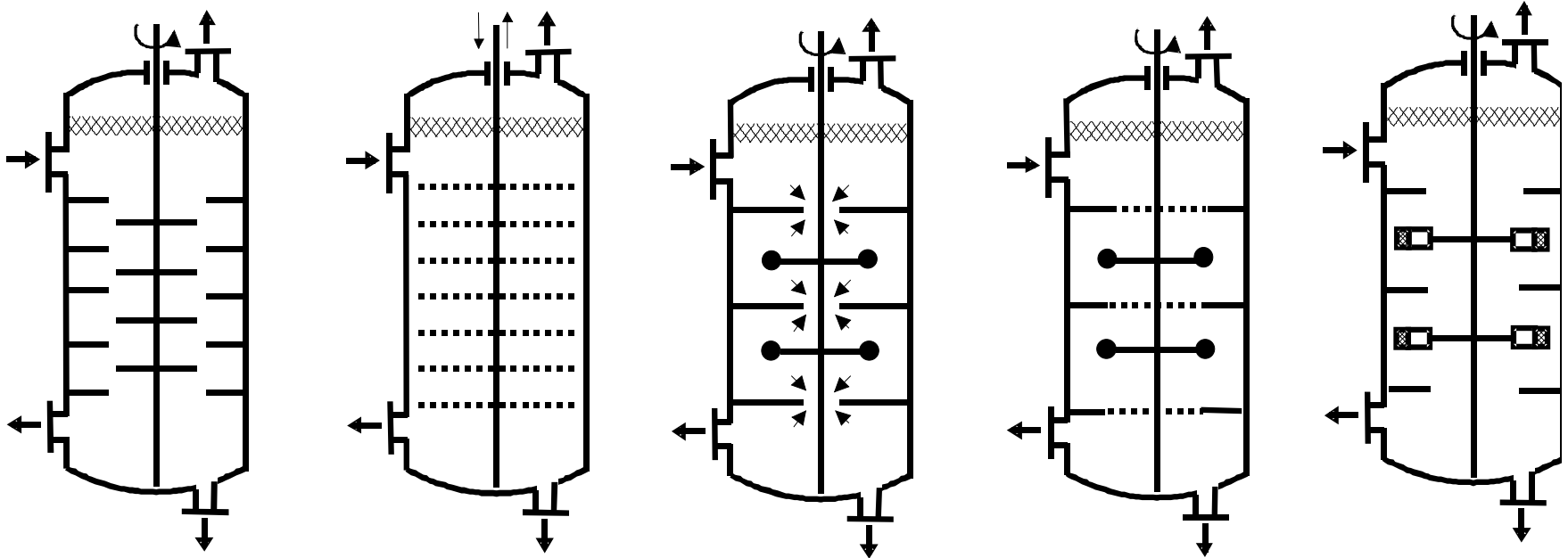
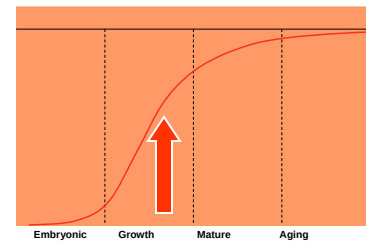
- natural
- introduced deliberately by addition of solvent

### Application areas:

- improvement of yields/selectivities in multi-reaction systems
- separation of “hard-to-separate” waste by-products
- selective separation of amino acids

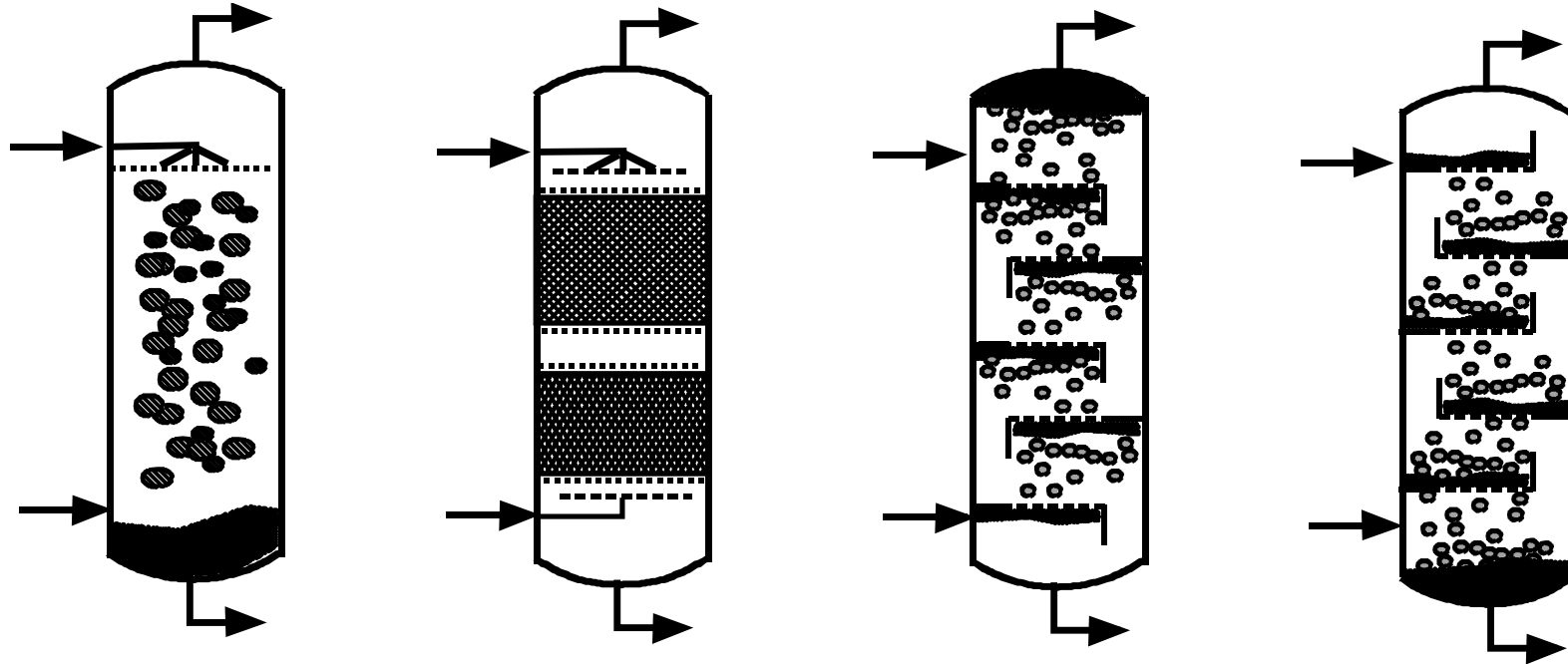
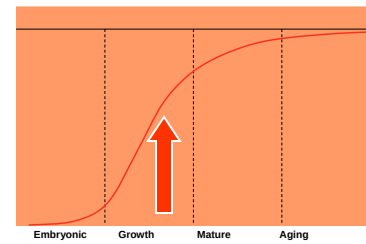


# Reactive extraction



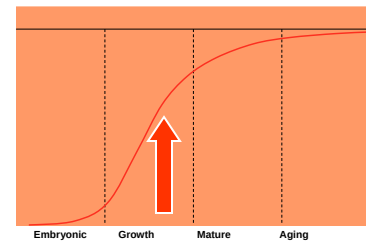
Agitated extractors (left to right: RDC, Karr, Oldshue–Rushton, Scheibel, Kühni extraction columns)

# Reactive extraction



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

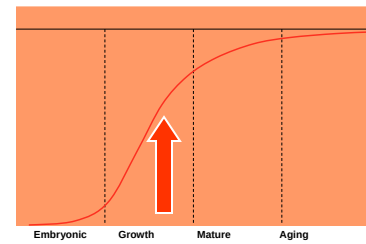
# Reactive crystallization (precipitation)



## Processes of industrial relevance:

- **liquid-phase oxidation of para-xylene to terephthalic 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



racemate   resolving agent

n-salt

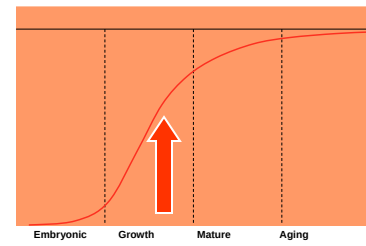
p-salt

Production of:

- ampicillin,
- ethambutol,
- chloramphenicol,
- diltiazem,
- fosfomycin,
- naproxen

Easy separable by crystallization

# Reactive absorption

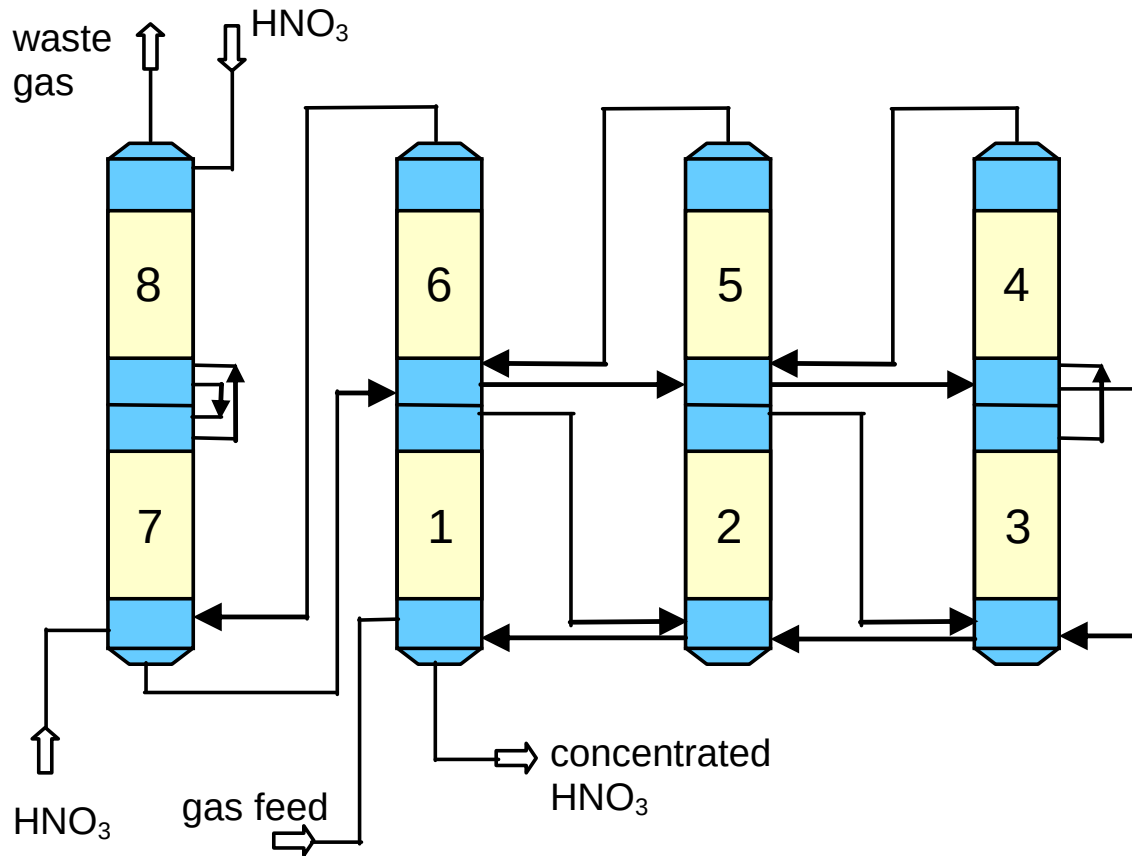
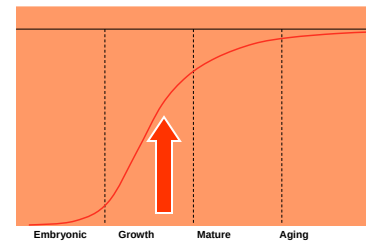


## Most widely applied type of reactive separation

Application areas:

- nitric acid process
- sulfuric acid process
- carbon dioxide removal
- hydrogen sulfide removal
- olefin/paraffin separation (research stage)

# NO<sub>x</sub> absorption in nitric acid process



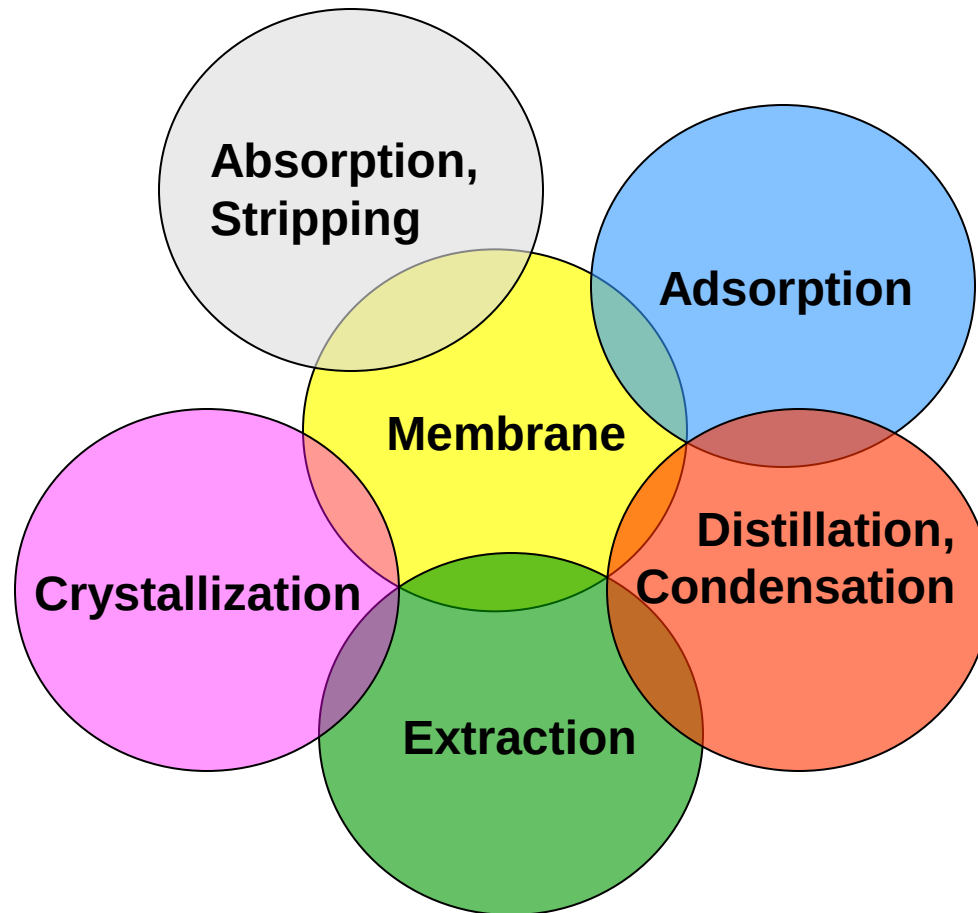
- Each unit is separated by a metal plate into two sections
- diameter of each column is 2.2 m, its height is 7 m
- packing height is 3.2 m
- packing consists of 35 mm INTALOX ceramic saddles
- liquid feeds entering columns 7 and 8 are low concentrated nitric acids

Absorption plant consisting of 4 units (8 columns)

# Hybrid separations

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

# Hybrid separations



# Contents

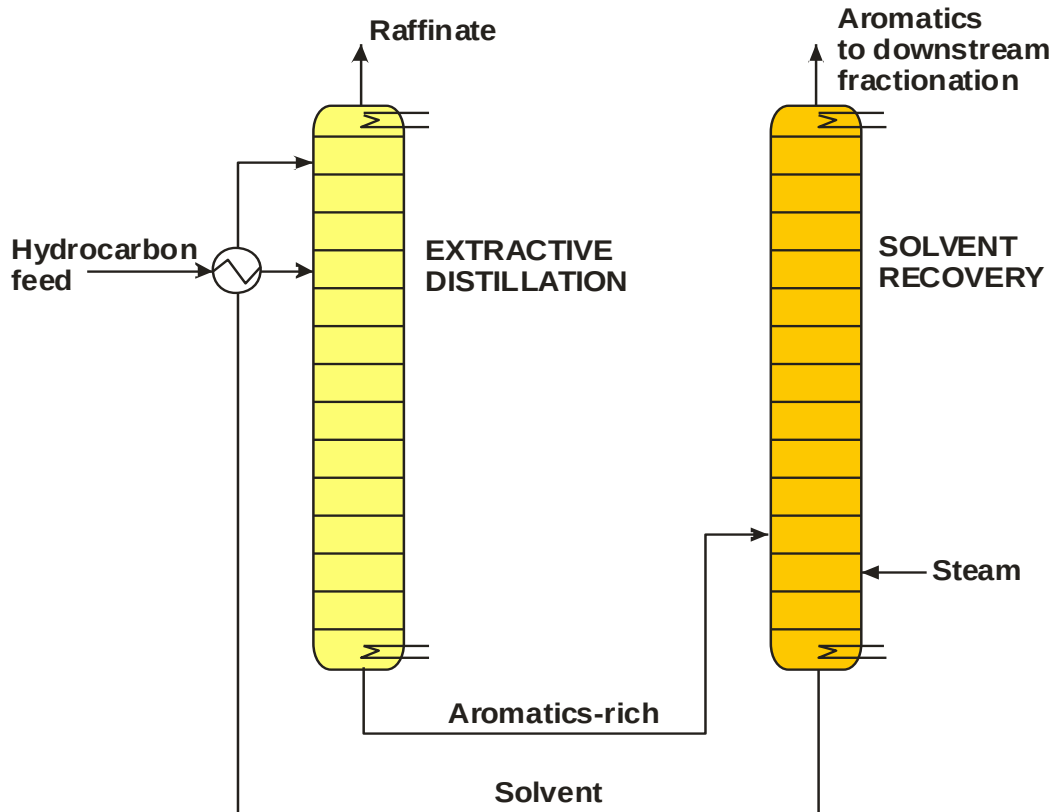
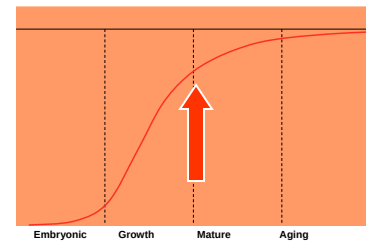
- **Extractive distillation**
- **Adsorptive distillation**
- **Membrane distillation**
- **Membrane absorption/stripping**
- **Adsorptive membranes (membrane chromatography)**

# 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.

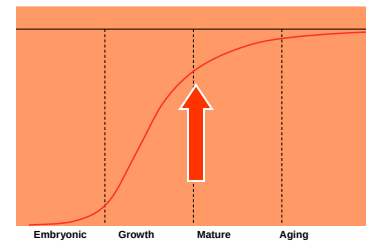
# Extractive distillation

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



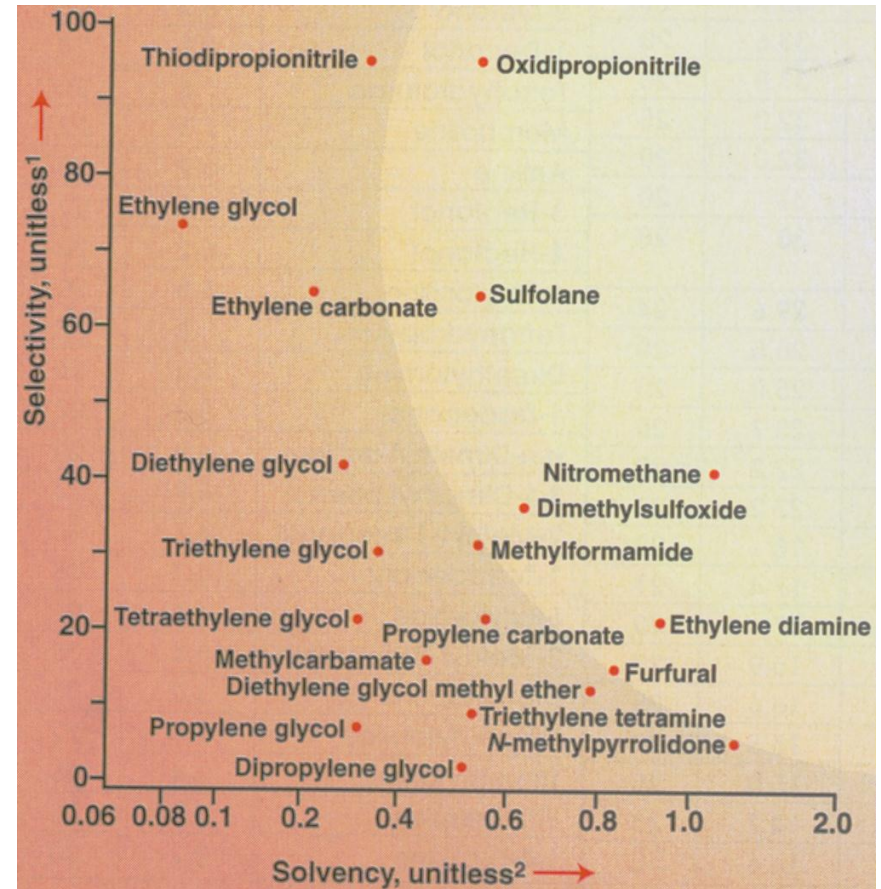
- **alternative to liquid-liquid extraction-based process;**
- **25% lower capital cost;**
- **15% lower energy consumption**

# Extractive distillation

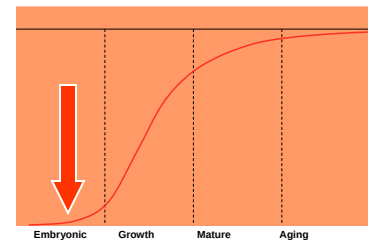


**Solvent selection –  
always a trade-off  
between the selectivity  
and solvency**

**Think of environmental  
effect!**

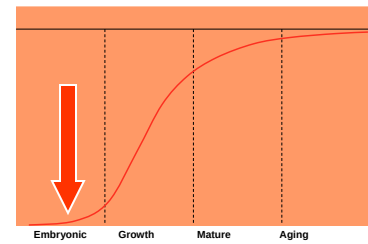
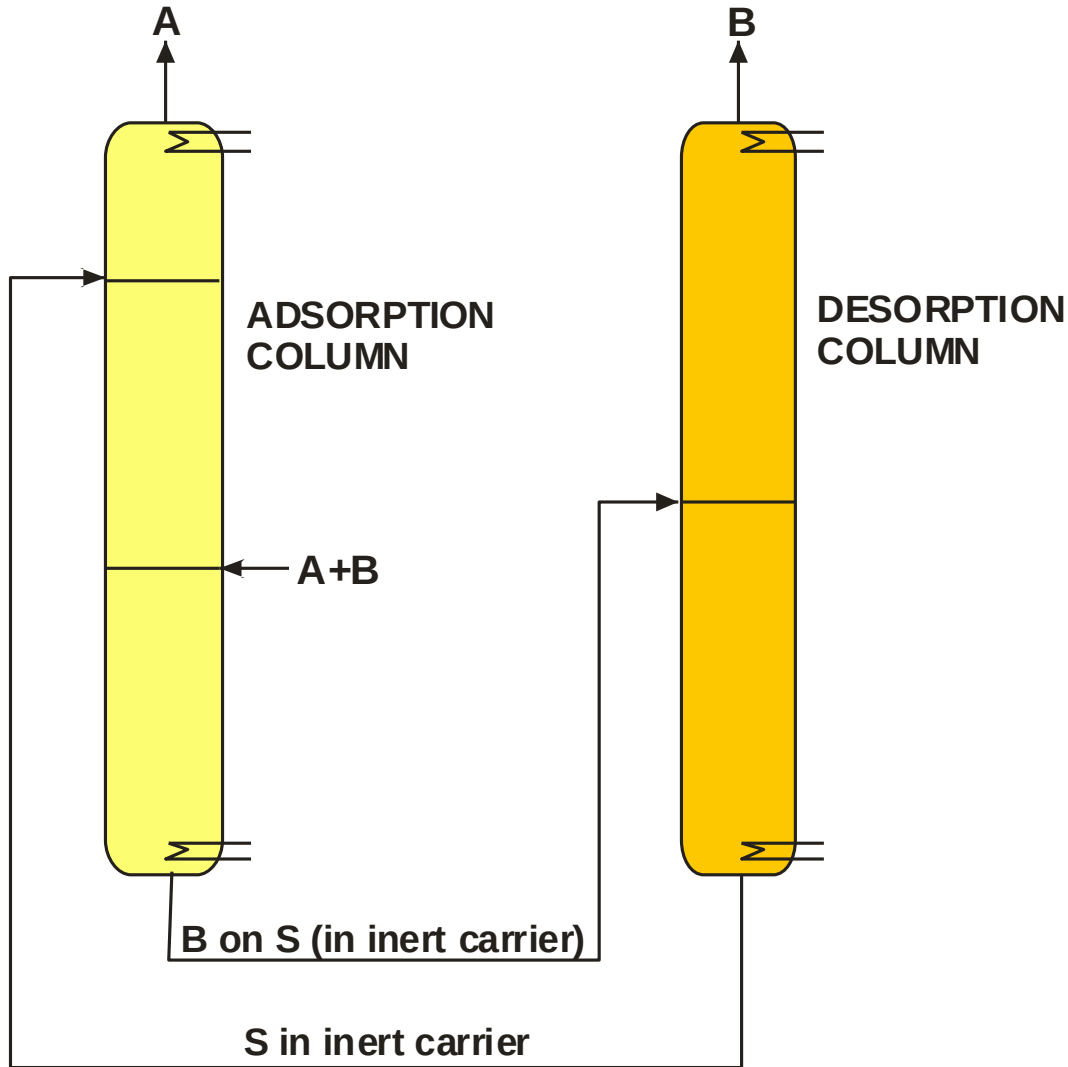


# Adsorptive distillation



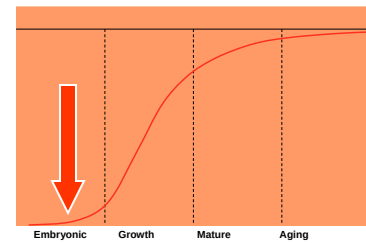
- Three-phase mass transfer operation.
- Adsorbent: fine powder (usually ca. 10  $\mu\text{m}$ ), fluidized and circulated by an inert carrier.
- Process carried in two columns:
  - adsorptive distillation column for increasing separation ability, and
  - distillative desorption column for enhancing 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.

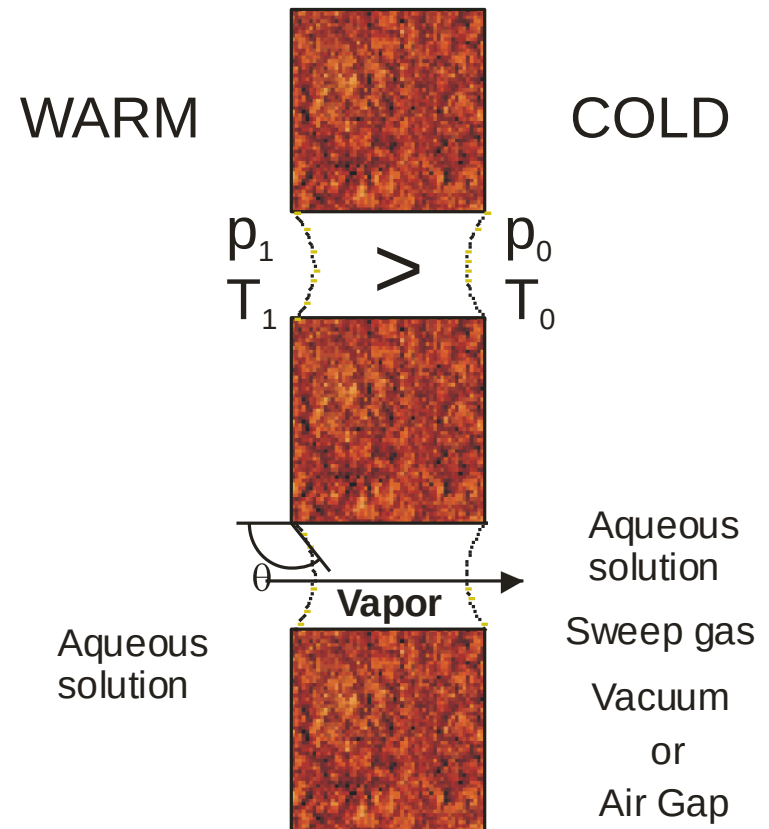
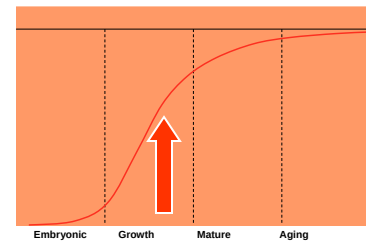
## Systems investigated:

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

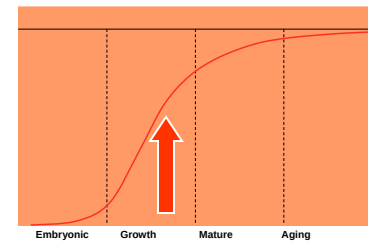
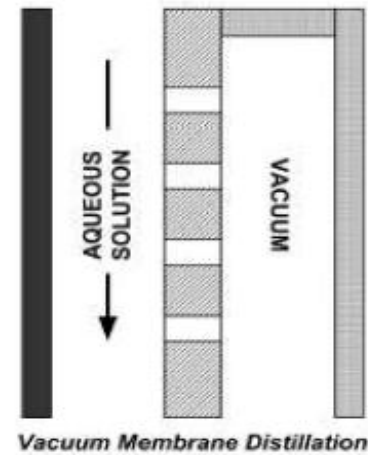
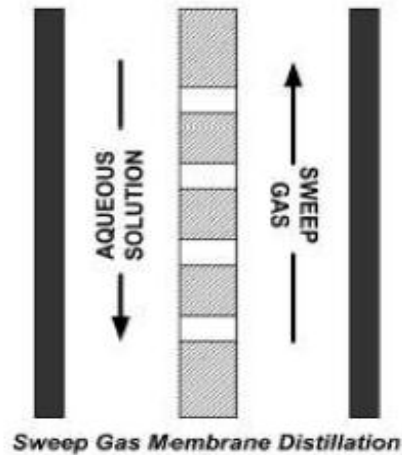
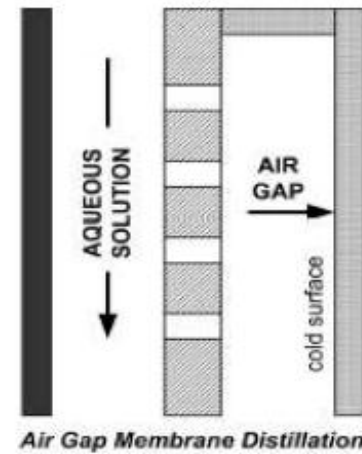
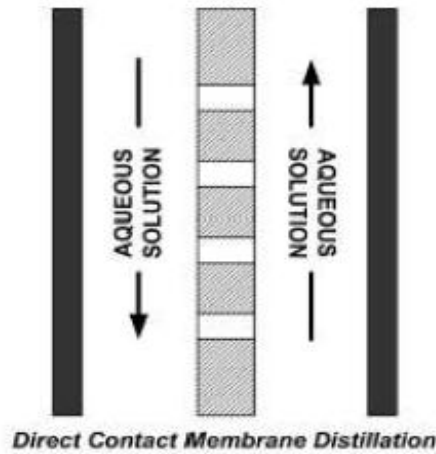
# Membrane distillation

## 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



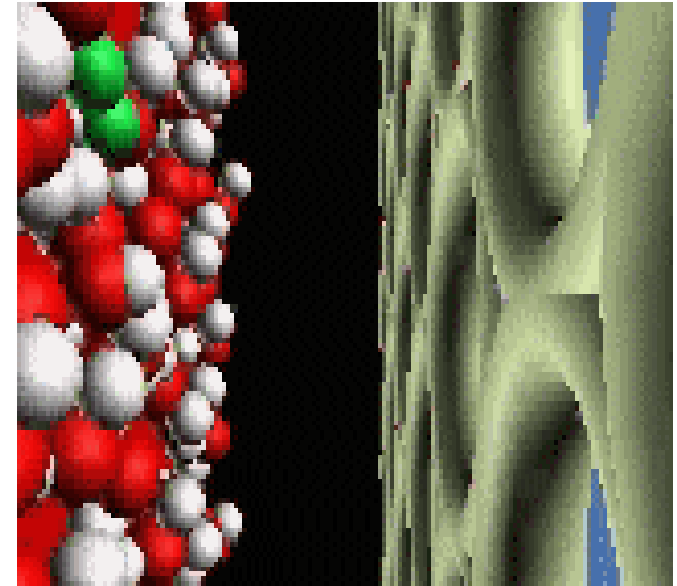
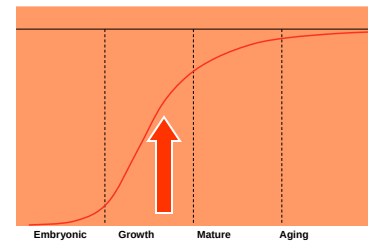
# Membrane distillation



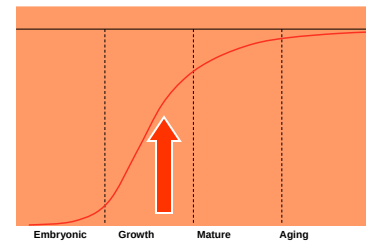
# Membrane distillation

## 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.



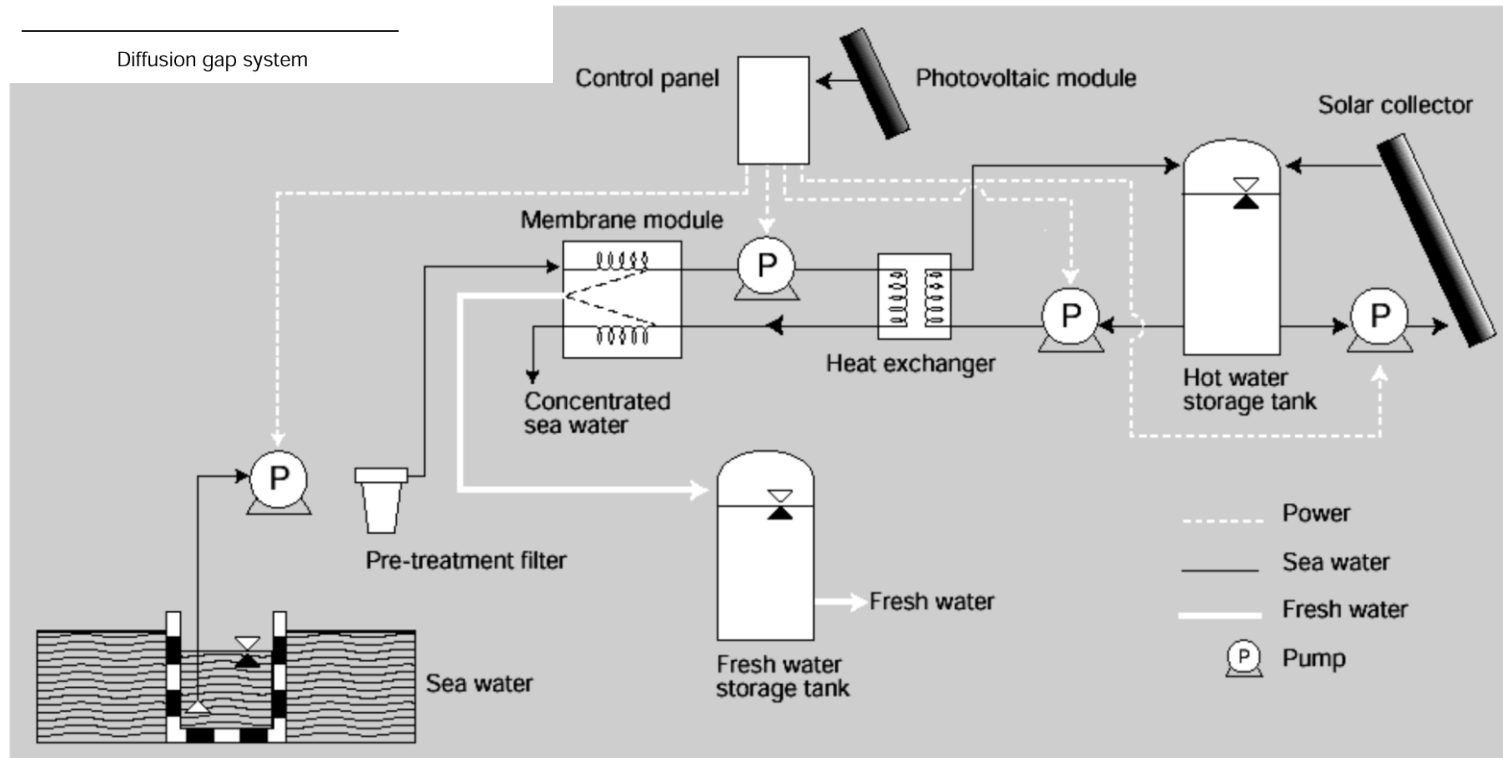
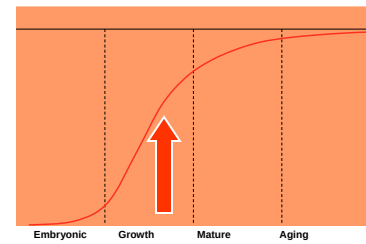
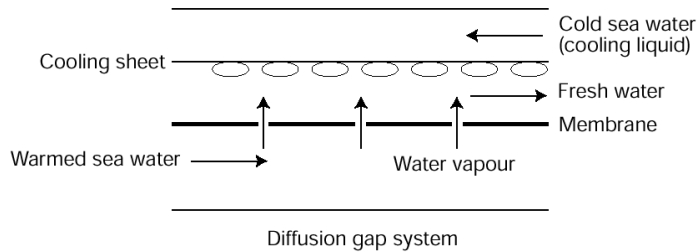
# Membrane distillation



## 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

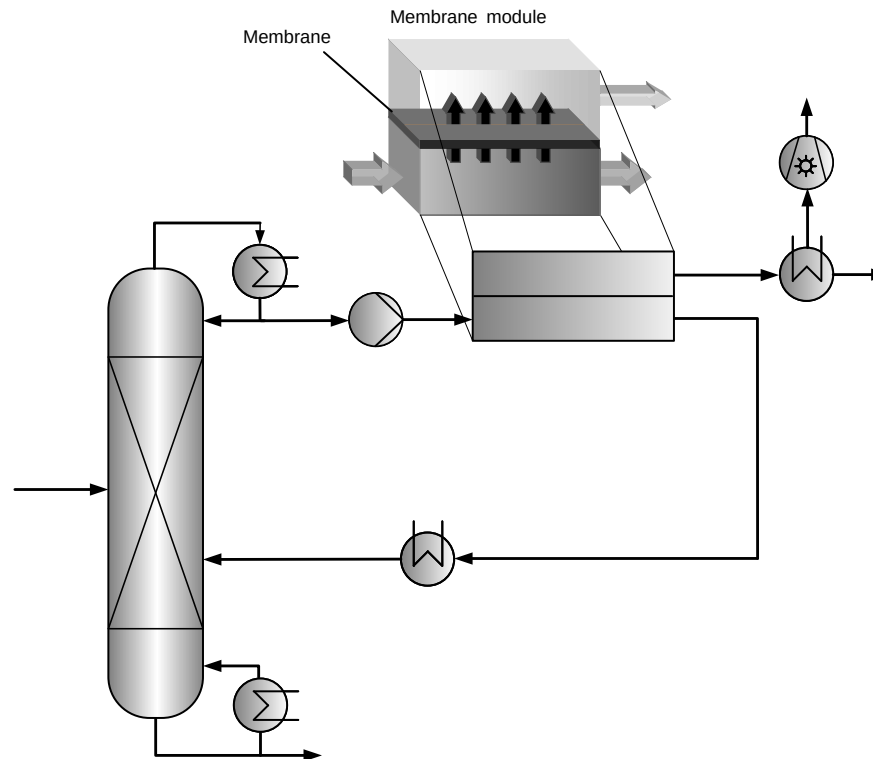
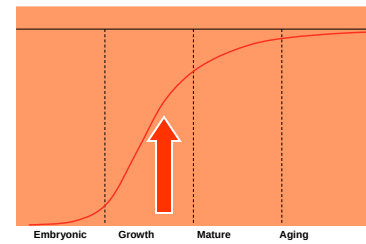


Solar desalination plant by WRPC, Takenaka Corp. and Organo Corp.

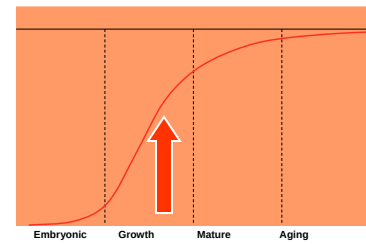
# Membrane distillation

## Another type of MD:

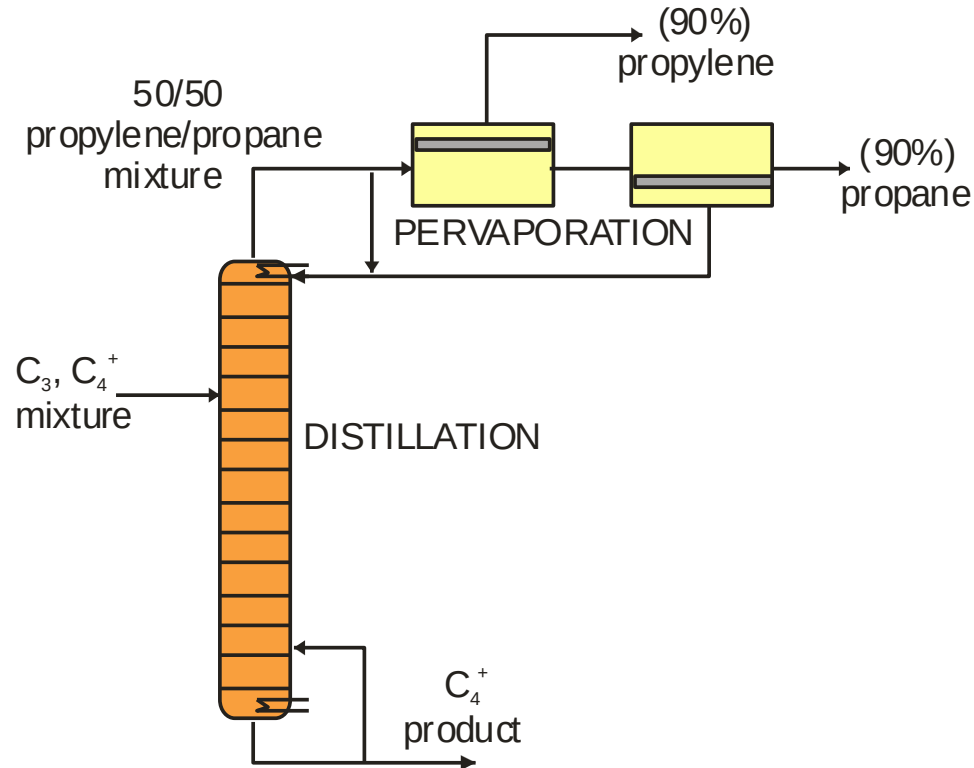
Pervaporation unit combined with conventional distillation



# Membrane distillation



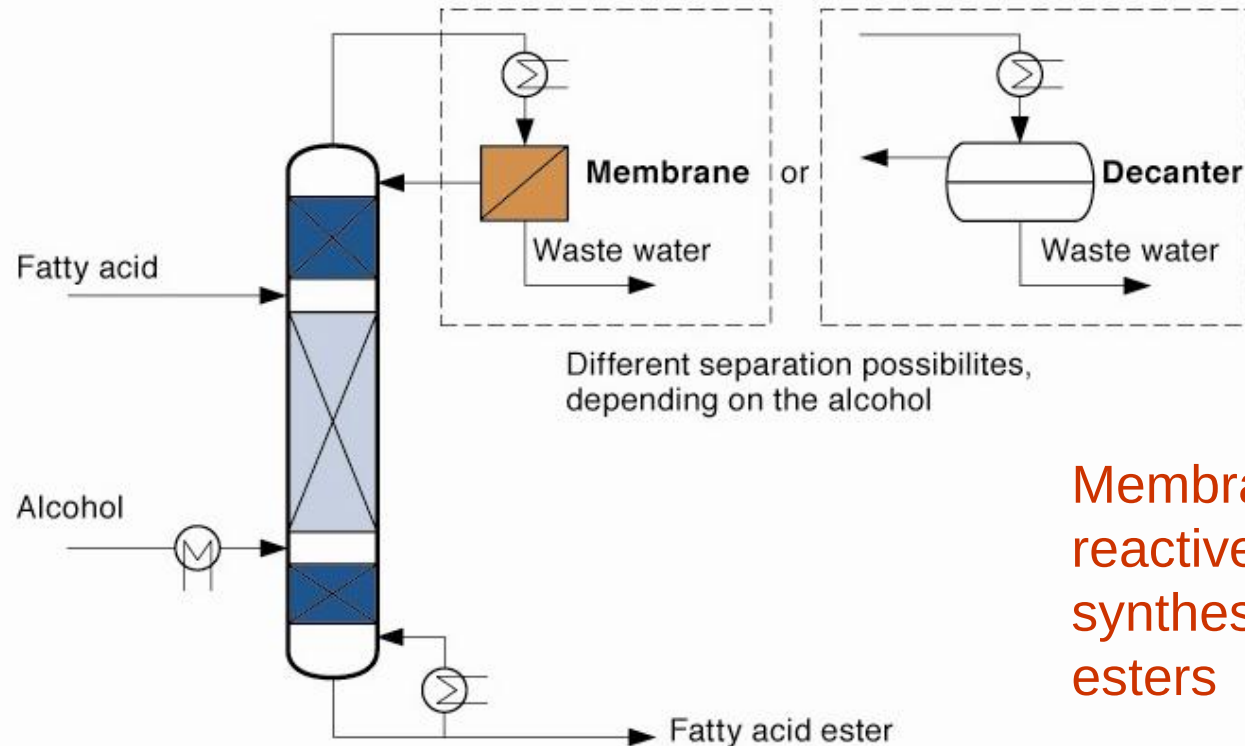
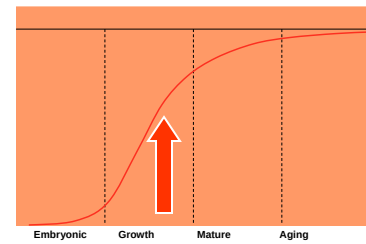
for  
olefin/paraffin  
splitting...



# Membrane distillation

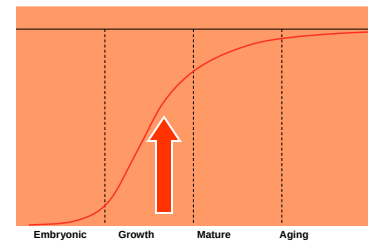
## Another type of MD:

Pervaporation unit combined with **reactive** distillation



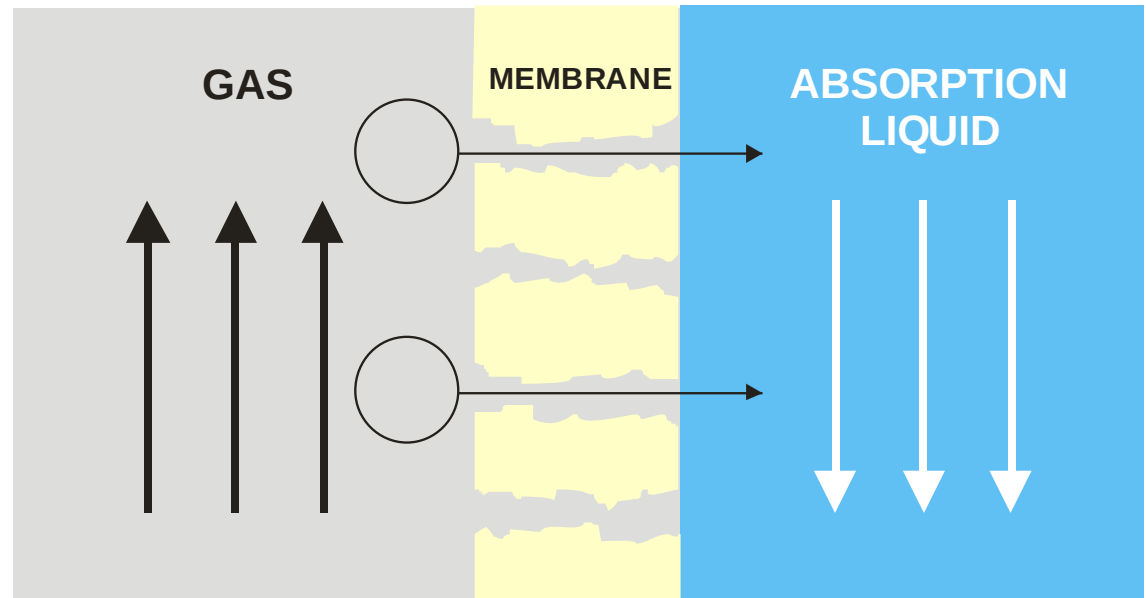
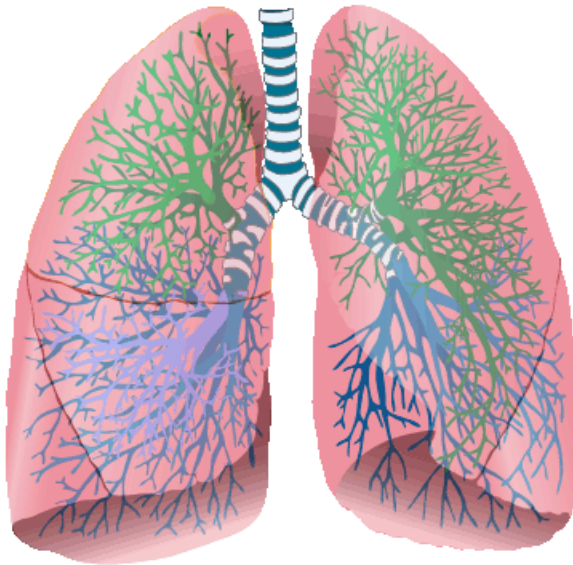
Membrane-assisted  
reactive distillation for  
synthesis of fatty acid  
esters

# Membrane absorption/stripping

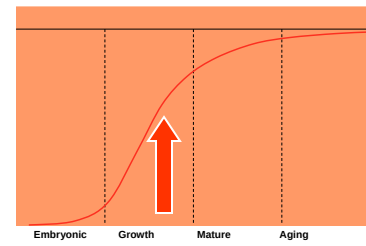


**Membrane absorption – invented by Mother Nature:**

- **lungs**
- **darms**



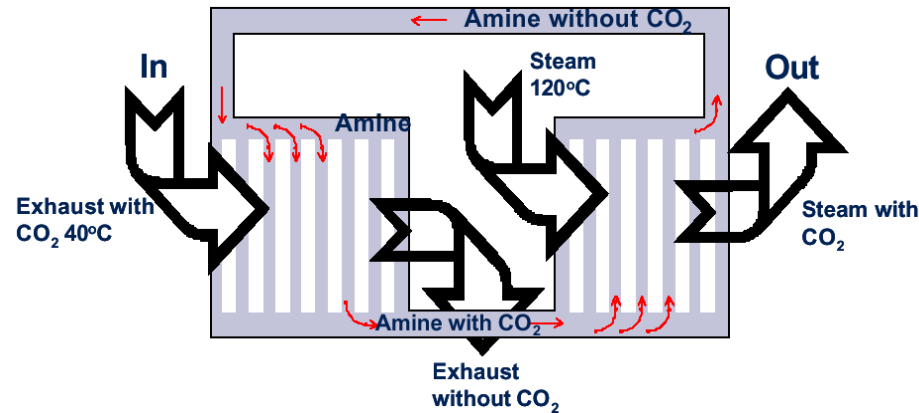
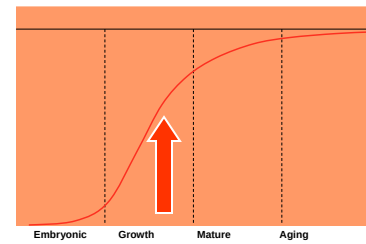
# Membrane absorption/stripping



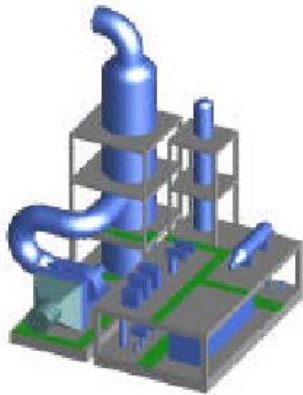
## Most important application areas:

- CO<sub>2</sub> removal from anesthetic gases
- CO<sub>2</sub> separation from turbine exhaust gases
- carbon dioxide capture and management (general)
- VOC's removal from air/nitrogen streams
- H<sub>2</sub>S removal from natural gas

# Membrane absorption/stripping



Conventional Process

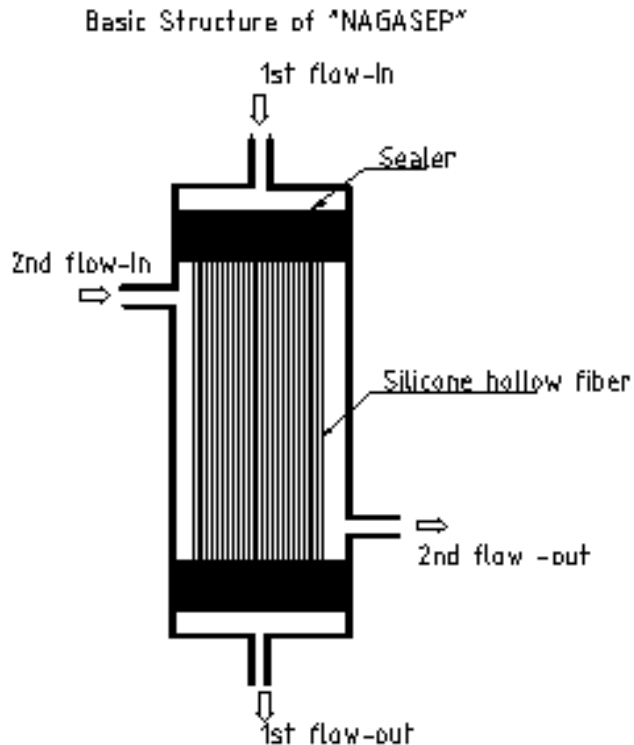
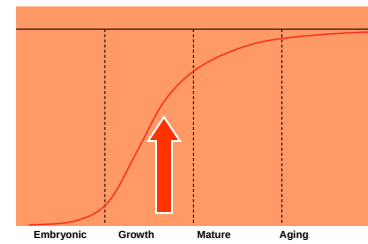


Membrane Process



Kvaerner process for CO<sub>2</sub> separation/capture from turbine exhaust gases: **65% saved on inventory and weight**

# Membrane absorption/stripping



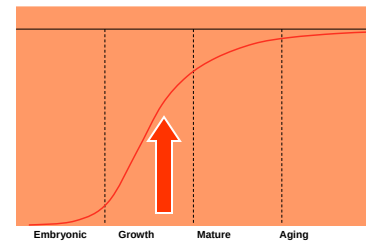
Hollow fibre modules



Artificial lung

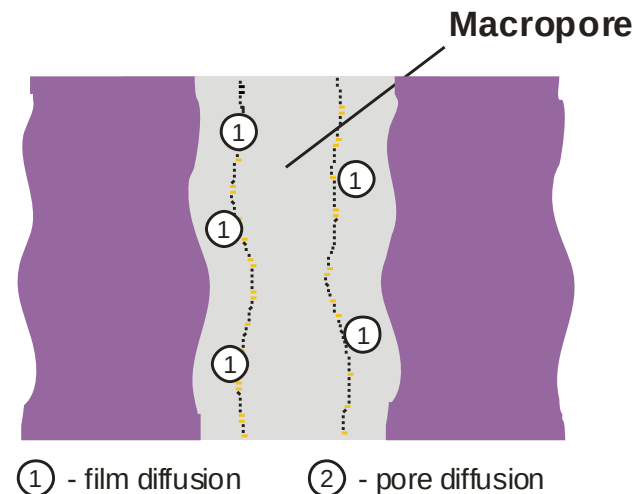
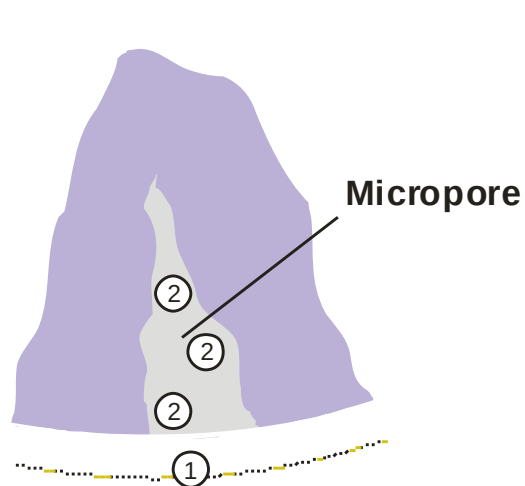
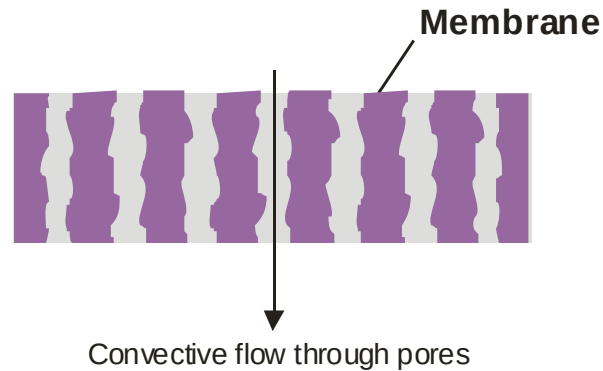
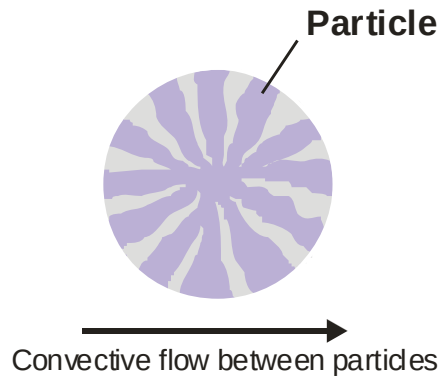
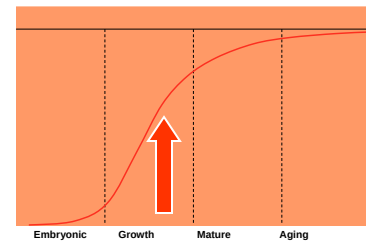
Membrane absorption modules by Nagayanagi Co. Ltd.

# Adsorptive membranes (membrane chromatography)

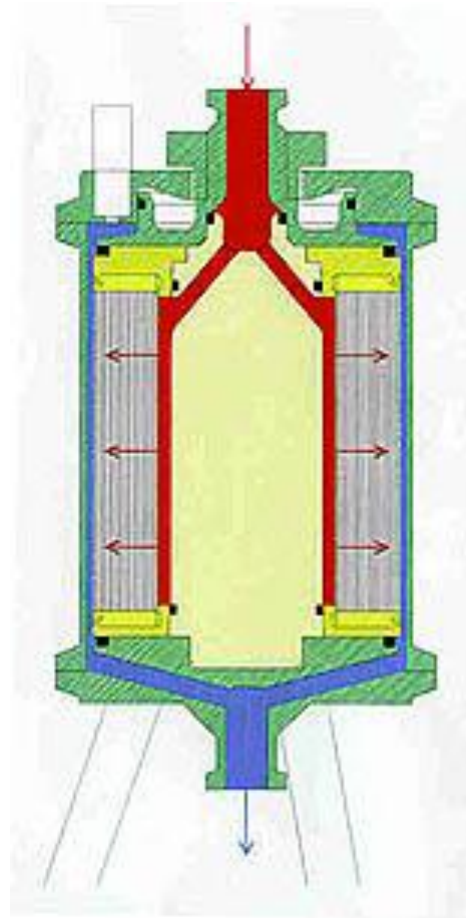
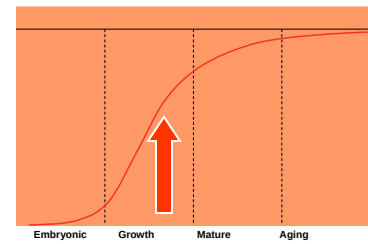


- hybrid combination of liquid chromatography and membrane filtration
- based on microporous or macroporous membranes that contain functional ligands attached to their inner pore structure, which act as adsorbents
- higher throughput than in traditional systems
- easy scale-up

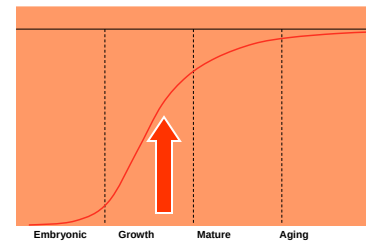
# Adsorptive membranes (membrane chromatography)



# Adsorptive membranes (membrane chromatography)



# Adsorptive membranes (membrane chromatography)

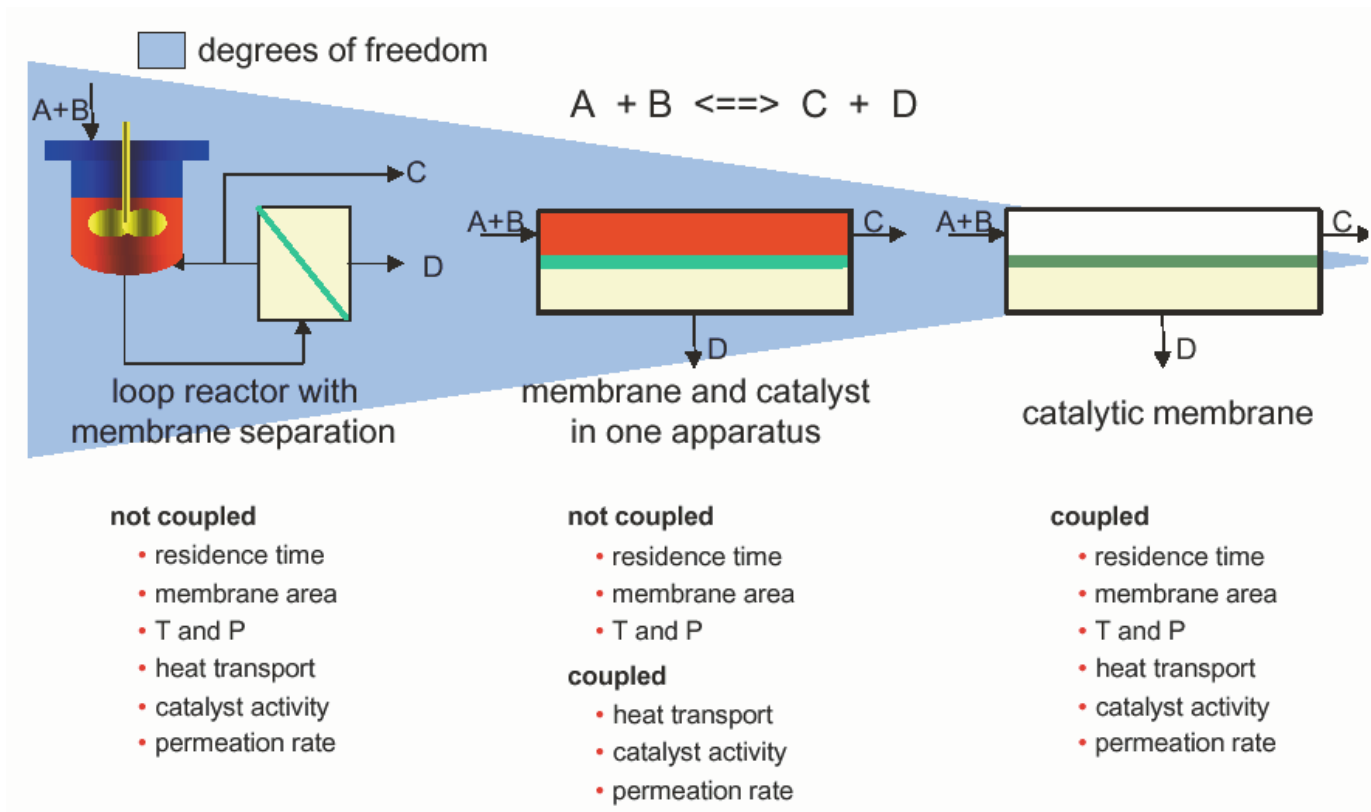


## Used almost exclusively in biopharmaceutical manufacturing

- protein separation, purification and concentration
- DNA removal
- virus purification

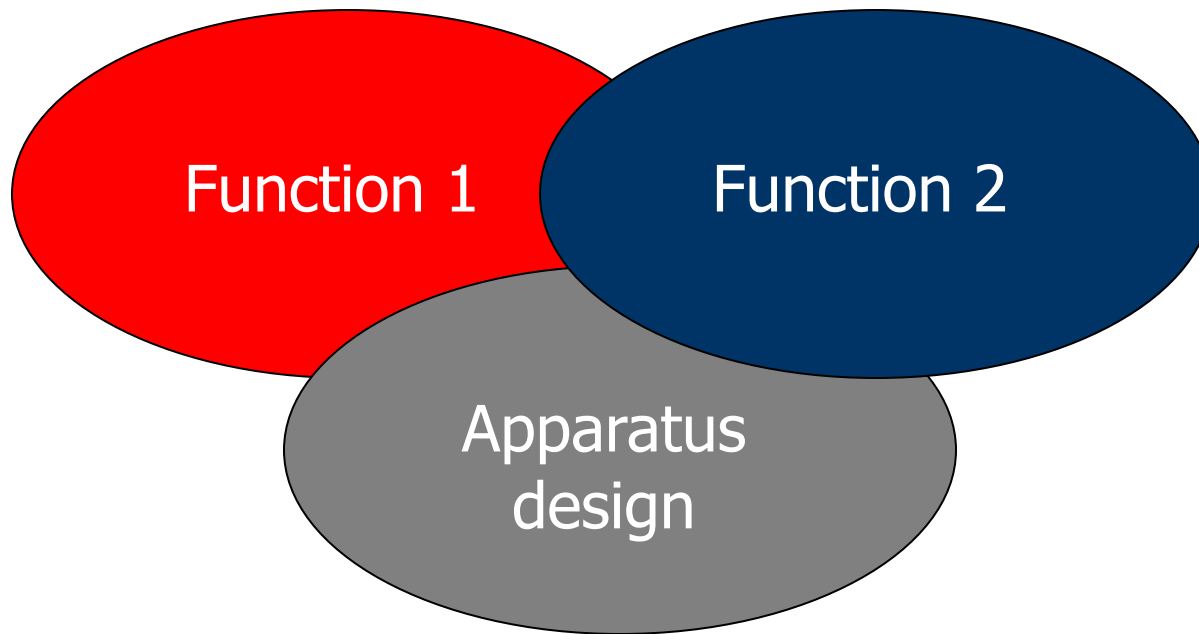
# Synergy – multiple functions

More integration means less degree of freedom



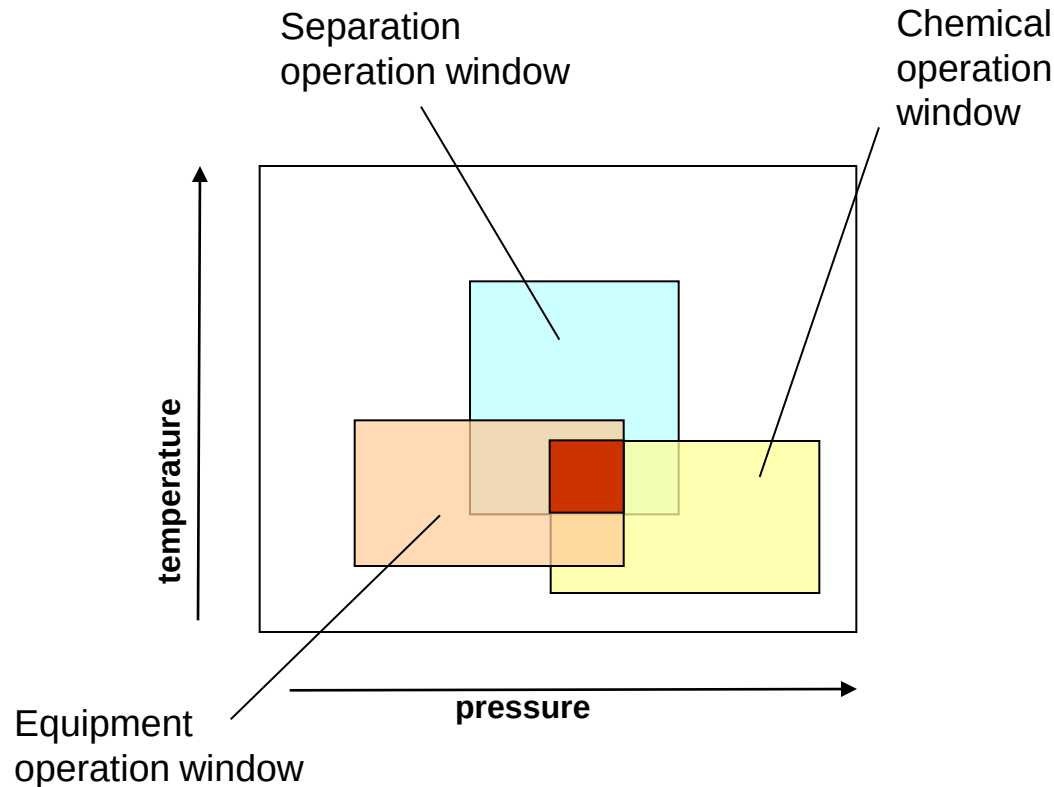
# Synergy – multiple functions

**Important issue: size of the feasible operation window**



# Synergy – multiple functions

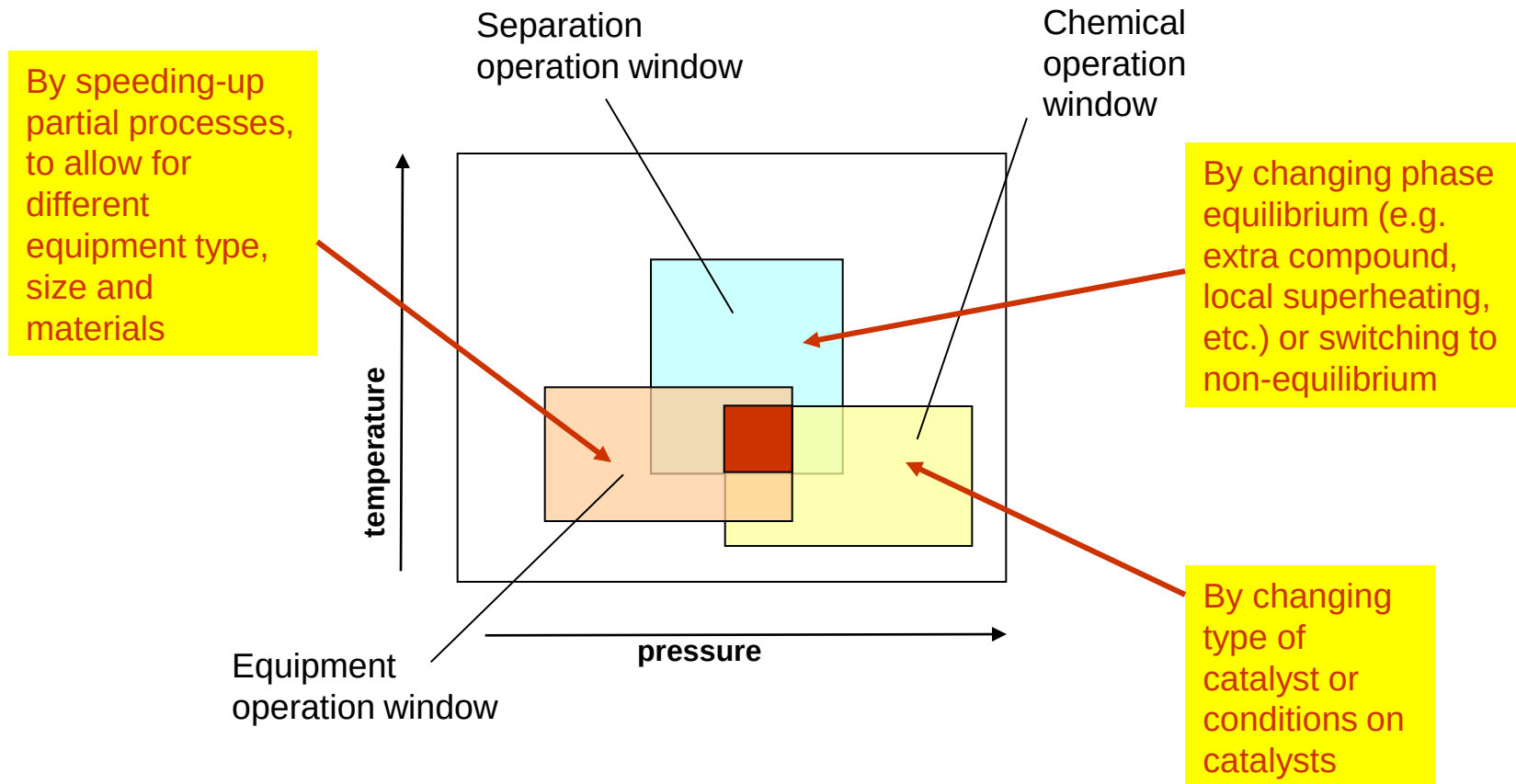
**Main issue: size of the feasible operation window**



**Example for  
reactive  
separations**

# Synergy – multiple functions

## How to enlarge small feasibility window?



# Synergy – multiple functions

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

