School of Industrial and Information Engineering
Course 096125 (095857)
Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Process Intensification.

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https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

Chemical Industry Priorities.

1) continuous processing,

2) bioprocesses,

3) separation and reaction technology,

4) solvent selection,

5) process intensification,

6) life-cycle analysis and risk assessment,

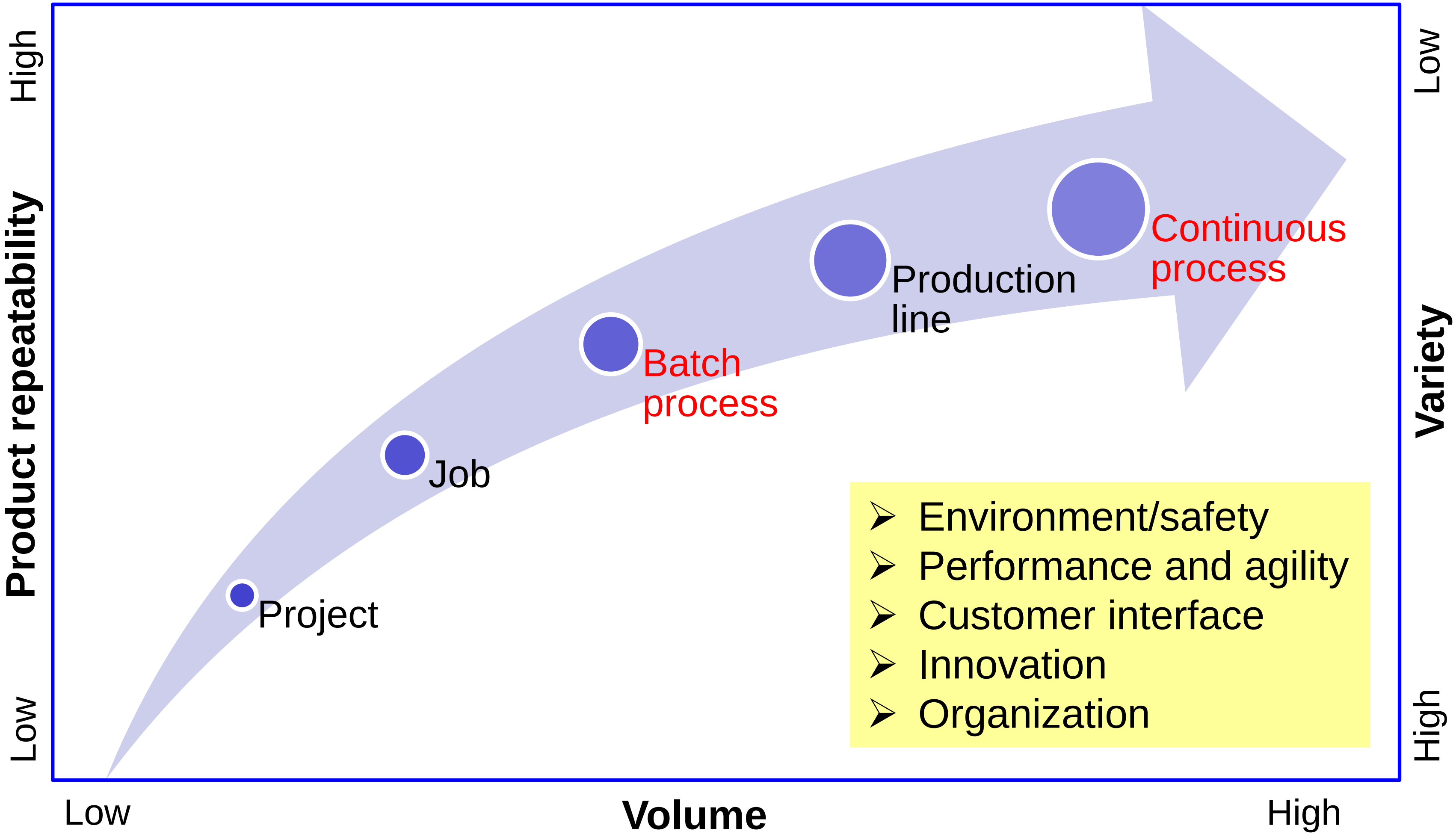
7) integration of chemistry and engineering,

8) scale-up,

9) process energy intensity, and

10) mass and energy integration.

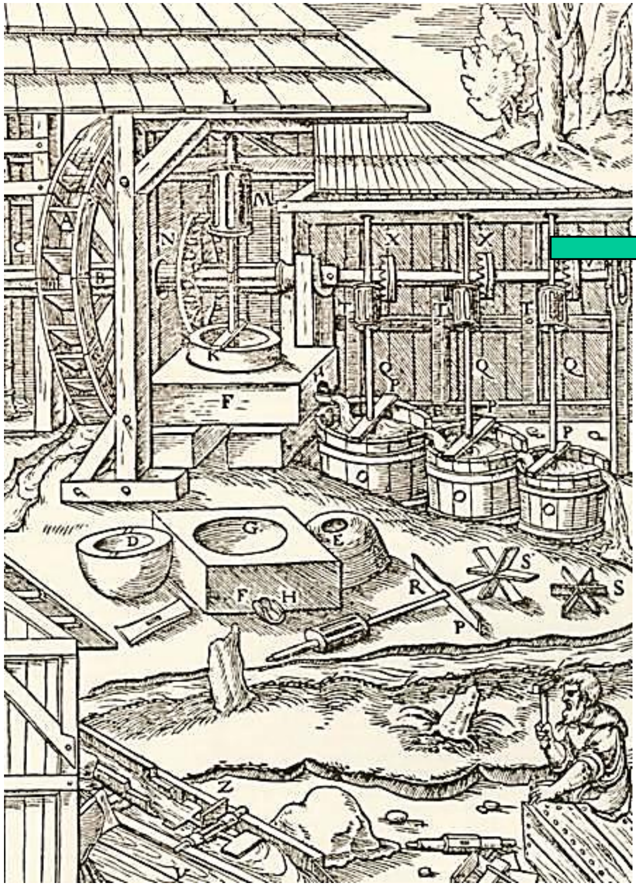
Process Dependence on Variety, Repeatability and Production Volume.



- Environment/safety
- Performance and agility
- Customer interface
- Innovation
- Organization

S. Afr. J. Ind. Eng. vol.24 no.3 Pretoria Nov. 2013

Chemical Engineering Mature Technology ????



room for innovation

AD 2002

Needed

- **Cleaner, intensified plants**
  - **Less waste**
  - **Higher activity, selectivity, efficiency**
  - **Milder conditions**

Process Intensification

Better Chemistry!
Better Chemical Engineering!
Better Biochemical Engineering!

Agricola *De Re Metallica* 1556

Source: TU DELFT

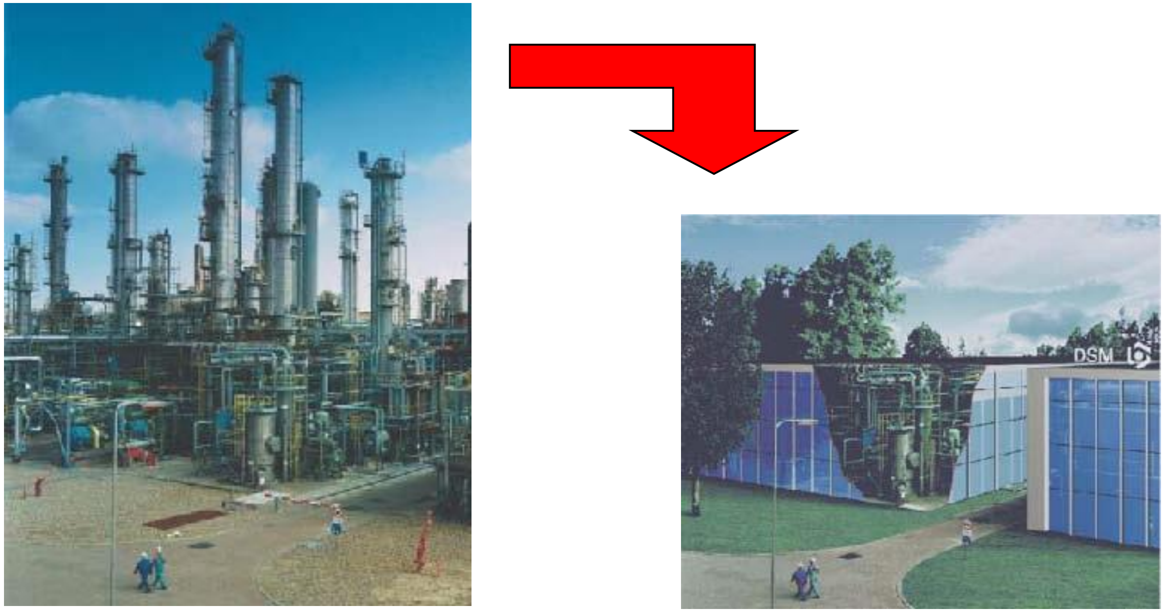
Difference in Characteristics of Bulk Chemicals vs. Fine Chemicals.

Characteristics	Bulk chemical	Fine chemical	Pharmaceutical
Volume (tons/y)	$10^4 – 10^6$	$10^2 – 10^4$	$10 – 10^3$
Price ($/kg)	< 10	> 10	> 100
Added value	Low	High	Very high
Processing	Continuous	Batch-wise	Batch-wise
Plants	Dedicated	Multi-purpose	Multi-purpose
Flexibility	Low	High	High
Safety and environmental efforts	Relatively low	High	Relatively high
Aspect	V. Technological	Technological	More Styled

Process Intensification (PI).

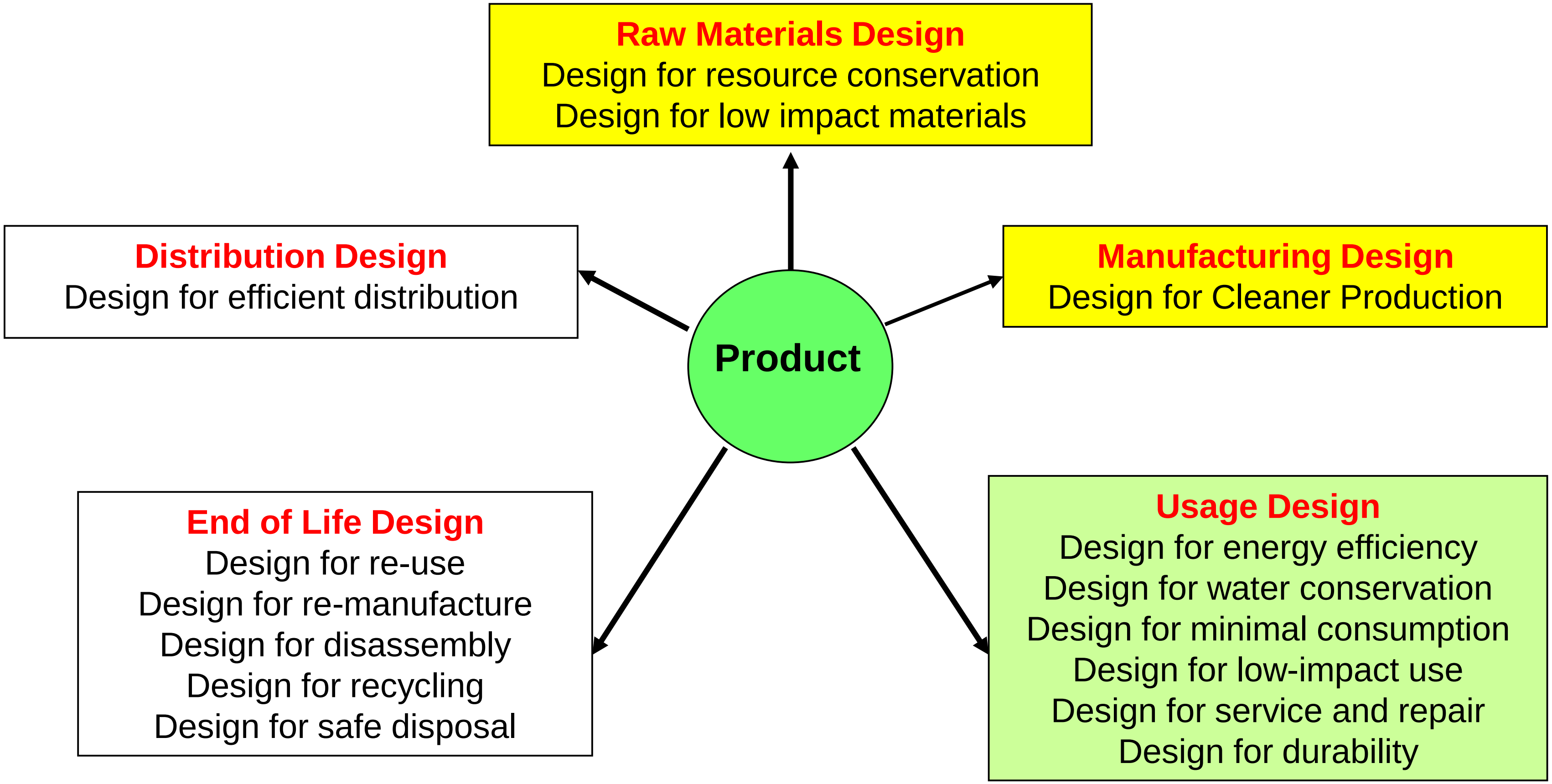
‘Any ***innovative*** *Chemical Engineering development leading to*
substantial improvements
in (bio)chemical manufacturing’

Stankiewicz& Moulijn , CEP 96 (2000)22, IECR 41(2002)1920
Re-engineering the Chemical Processing Plant, Marcel Dekker 2004



Source: DSM

Reduction of Impacts of Products over their Total Product Life Cycle.



Raw Materials Design
Design for resource conservation
Design for low impact materials

Distribution Design
Design for efficient distribution

Product

Manufacturing Design
Design for Cleaner Production

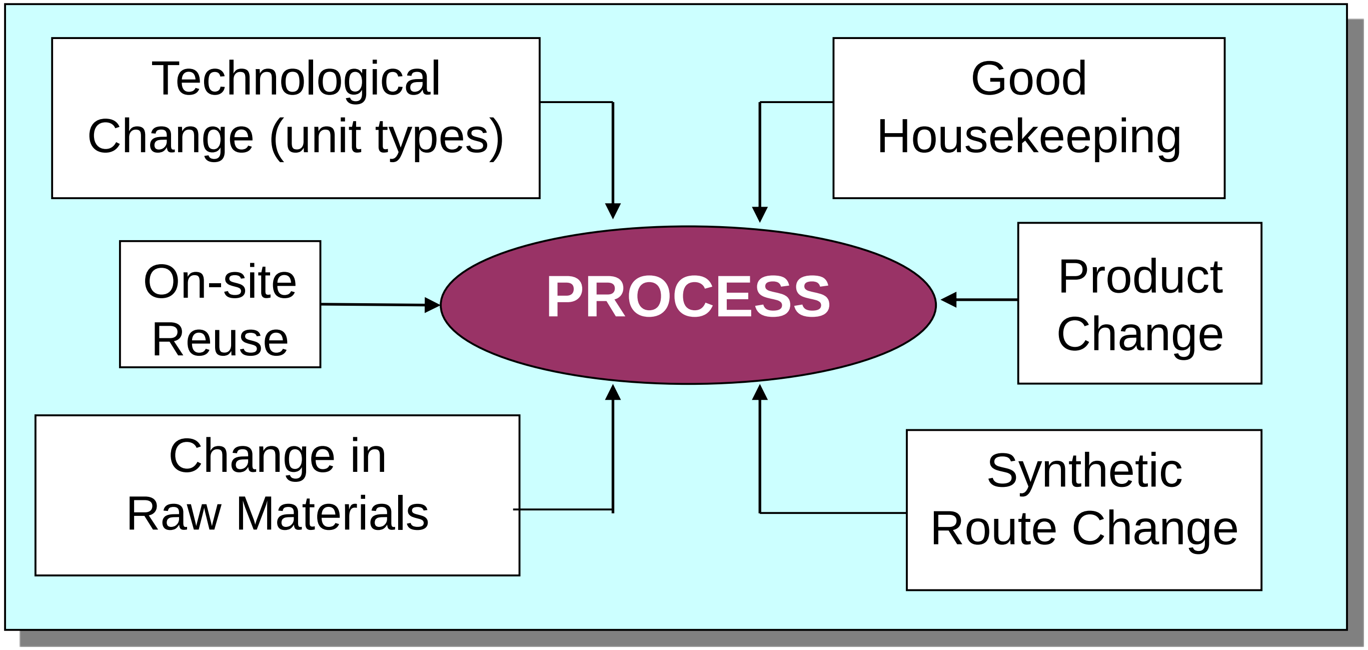
End of Life Design
Design for re-use
Design for re-manufacture
Design for disassembly
Design for recycling
Design for safe disposal

Usage Design
Design for energy efficiency
Design for water conservation
Design for minimal consumption
Design for low-impact use
Design for service and repair
Design for durability

Clean Production (CP) aims to reduce impacts of products over their entire *product life cycle.* Using much less to produce much more.

Process and Services Impact Reduction.

It can be suggested one or more combination of measures during the production process.


Technological Change (unit types)

Good Housekeeping

On-site Reuse

PROCESS

Product Change

Change in Raw Materials

Synthetic Route Change

- CP implies incorporating environmental concerns into designing and delivering services.
- Sustainable value-added utility function vs. Product-Service System (PSS) concept.

CP/EMIE Strategy.

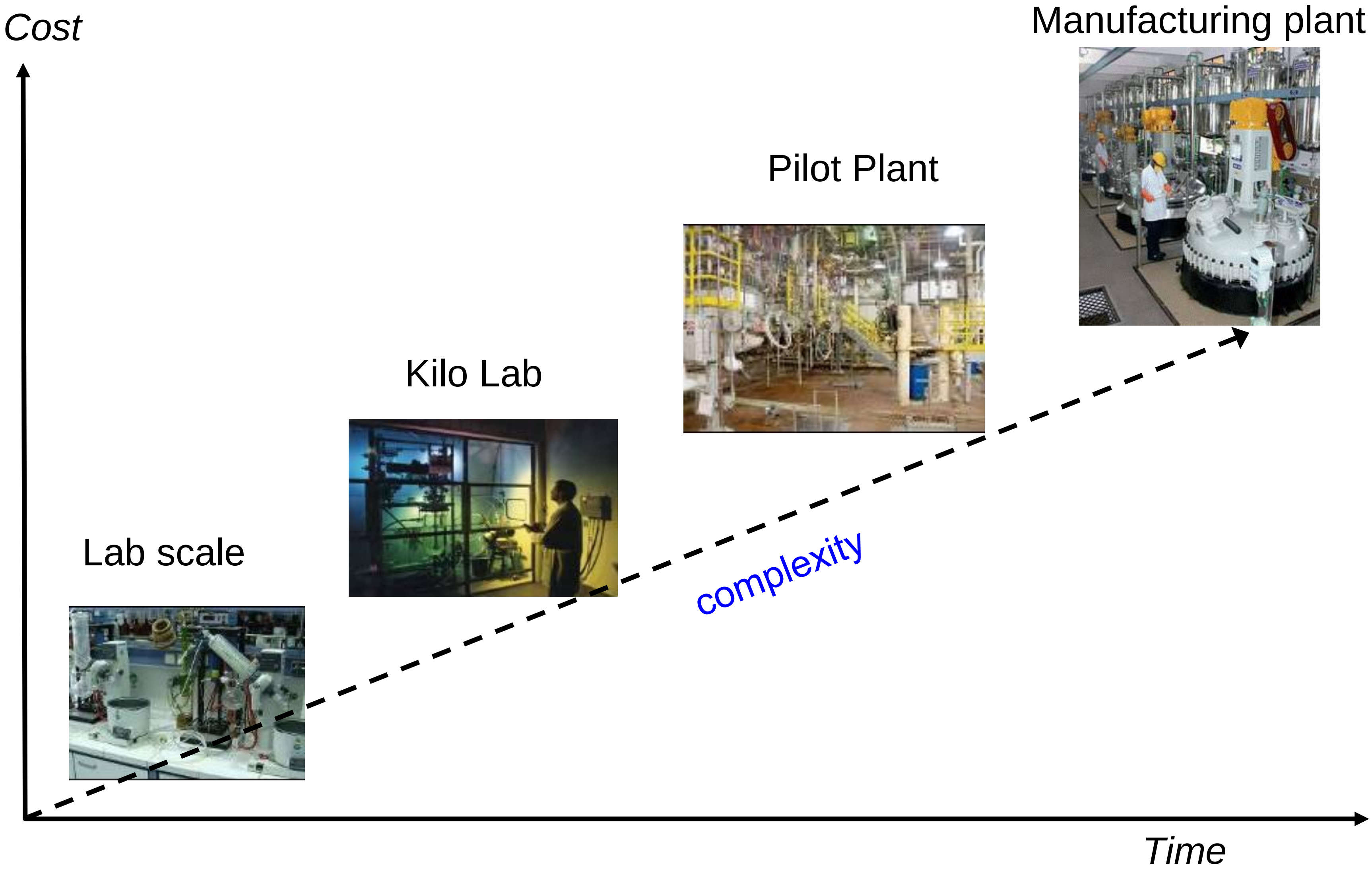
1. CP Strategy
    1. Strategy is composed of a pattern of “means” that connects to the “desired result”.
    2. External conditions should be considered for crafting the strategy.

2. EMIE Management System
    1. Internal management system provides a framework for the strategy to align its resources.
    2. Appropriate alignment of the resources leads to the desired result.

CP = strategy

EMIE = management system

Batch Process Scale up.



Cost

Manufacturing plant

Pilot Plant

Kilo Lab

Lab scale

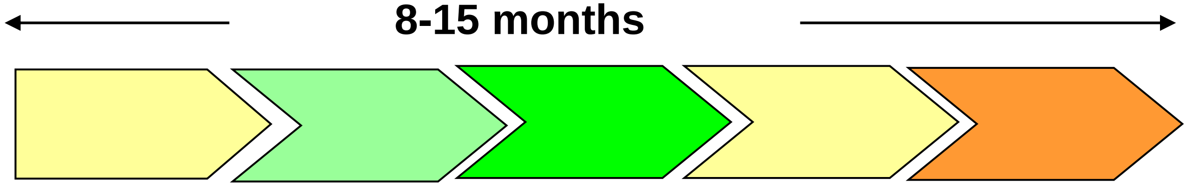
complexity

Time

Fine and Pharma Industries – Micro-reactor Technology.

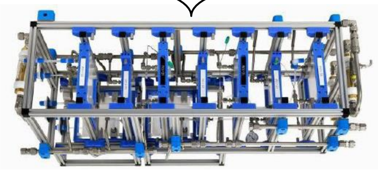
Advanced Flow
Reactor Technology

Production banks

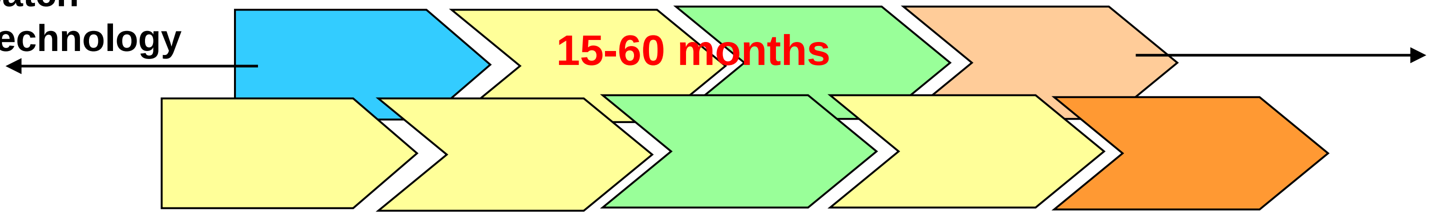


8-15 months

Laboratory **Pilot plant** **Scale-up** **Technology transfer** **Large scale production**



One tool engineered to fit all needs



Batch Technology

Discovery **Development** **Production** **Distribution**

15-60 months

Laboratory **Pilot plant** **Scale-up** **Technology transfer** **Large scale production**

from: Fine Chemicals
Peter Pollak,
Wiley 2007

Paradigm Change in Chemical Plants.

Dr. STEFAN-ROBERT DEIBEL, Pdt Corporate Engineering, BASF in *CHE Manager* 2, 2006

- **The classical world-scale plant is phase-out model**
- **Paradigm change in plant engineering**
- **'Too late with products' – time-to-market**
- **Modular plant technique; standard**
- **Micro process engineering will have a role**
  - **more on plant philosophy than on absolute size**

Same view in 2015

The chemicals industry is going through a tremendous period of change that will help define opportunities and challenges in both the short and the long term.

Roberge, Lonza

> «The question of whether microreactors are going to be used in the future, I think this is already answered «yes».
> Dominique Roberge

Nature 442, 7101 351-352, 2006.

$\text{Cost} \approx \text{size}^{0.6}$

Doch liegt die Zukunft neuer Anlagenprojekte nicht zwangsläufig weiterhin im Großen, wie die Achema 2006 aufzeigen wird. Dr. Stefan-Robert Deibel, President Corporate Engineering der BASF, ist jedenfalls sicher, dass die klassische World-Scale-Anlage eher zu den Auslaufmodellen zu zählen sei: „Da ist ein Paradigmenwechsel notwendig. Wir arbeiten bereits an neuen Konzepten. Denn das Dilemma der World-Scale-Anlage ist doch offensichtlich: Baue ich die Anlage erst dann, wenn der Markt ein Produkt bereits stark nachfragt, dann bin ich im Grunde zu spät am Markt. Oder wir bauen die Anlage womöglich parallel zum Wettbewerb, dann brechen die Preise wegen des Überangebots zusammen." Das bedeutet: Die Chemieindustrie benötigt Anlagenkonzepte, um Marktbedürfnisse zeitnah zu befriedigen. Da wird die Modultechnik eine gewisse Rolle spielen, auch eine strikte Standardisierung. Sicher werden dann auch Elemente der Mikroverfahrenstechnik eine Rolle spielen – weniger was die absolute Größe der Anlage betrifft, eher hinsichtlich der Philosophie.

“Doing More with Less”.

Process Intensification (IP) is a strategy to adapt the process to the chemical reaction

and not anymore the physico-chemical transformation

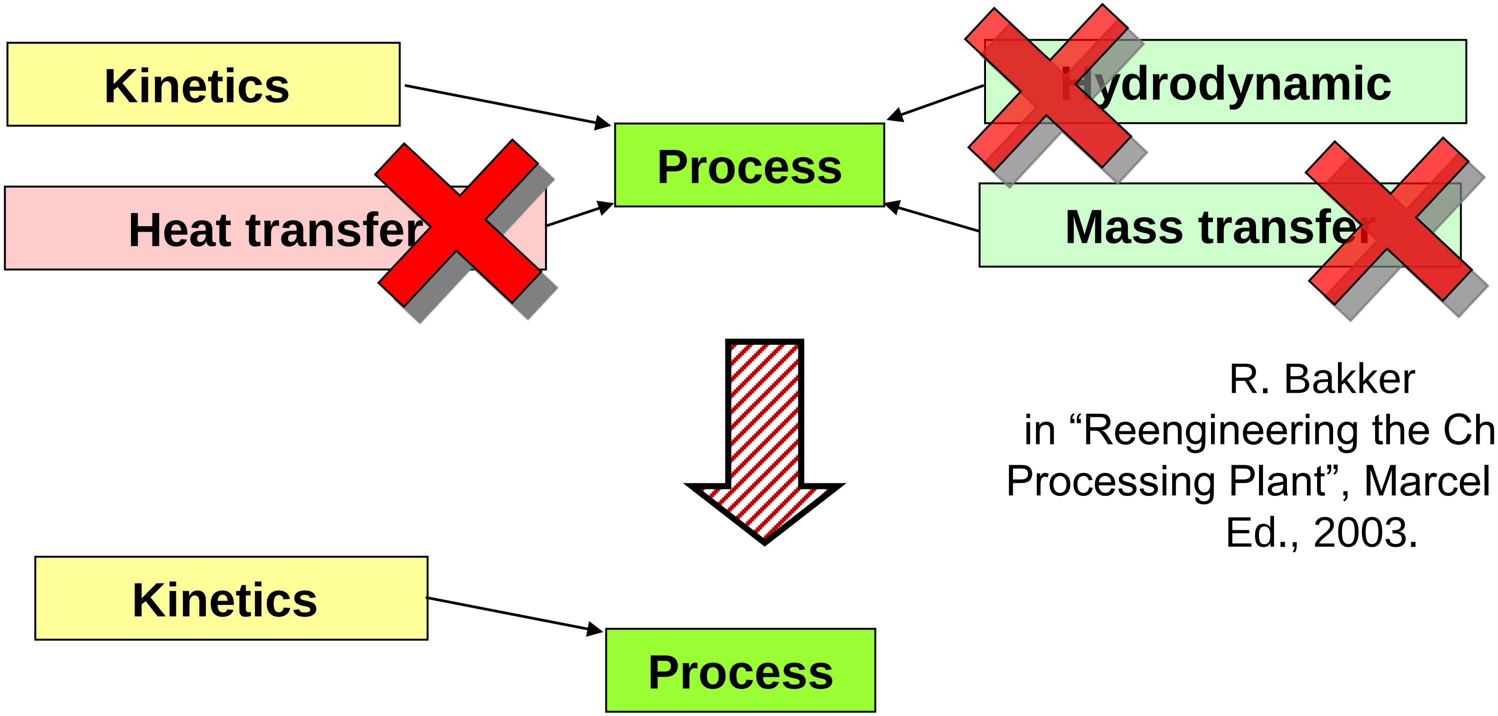
to existing, known, depreciated

but often unadapt equipment

i.e.:

- Adapting the size of equipment to the reaction
- Replacing large, expensive, inefficient equipments by smaller, more efficient and less costly
- Choosing the technology best suiting each step
- Sometimes combining multiple operations in fewer apparatuses.
- **LESS = raw materials, space, time, energy, investment, inventory, ...**
- **MUCH = factors, order of magnitude!!**

Process Intensification Strategy.



R. Bakker
in “Reengineering the Chemical Processing Plant”, Marcel Dekker Ed., 2003.

Reach the inherent kinetics of phenomena

Maximize the transfer rate

Fick Law : flow = coefficient × interface × gradient

Process Intensification Strategy (2).

Principle 1: **multifunctionality** (design methodology)

unit operations have to be “compatibilized”

Principle 2: **energetics**

create force fields at a mesoscopic level

Principle 3: **thermodynamics**

increase potential of reactants, by activity or diffusivity

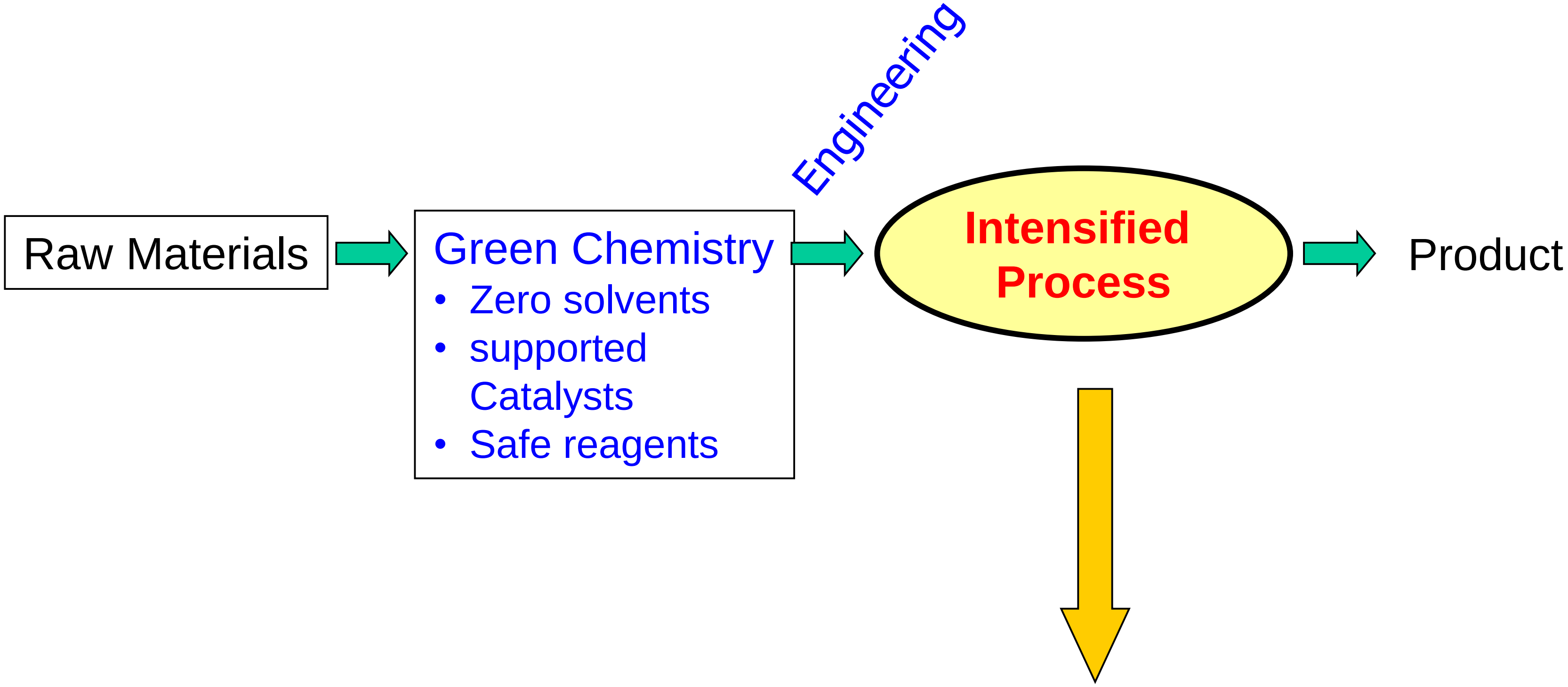
Principle 4: **miniaturization to increase force fields**

microreactors, micromixing, microseparators, …

microsensors, microvalves, …

MESO-Technologies

Process Characteristics of an Intensified Plant.



Raw Materials

Green Chemistry
- Zero solvents
- supported Catalysts
- Safe reagents

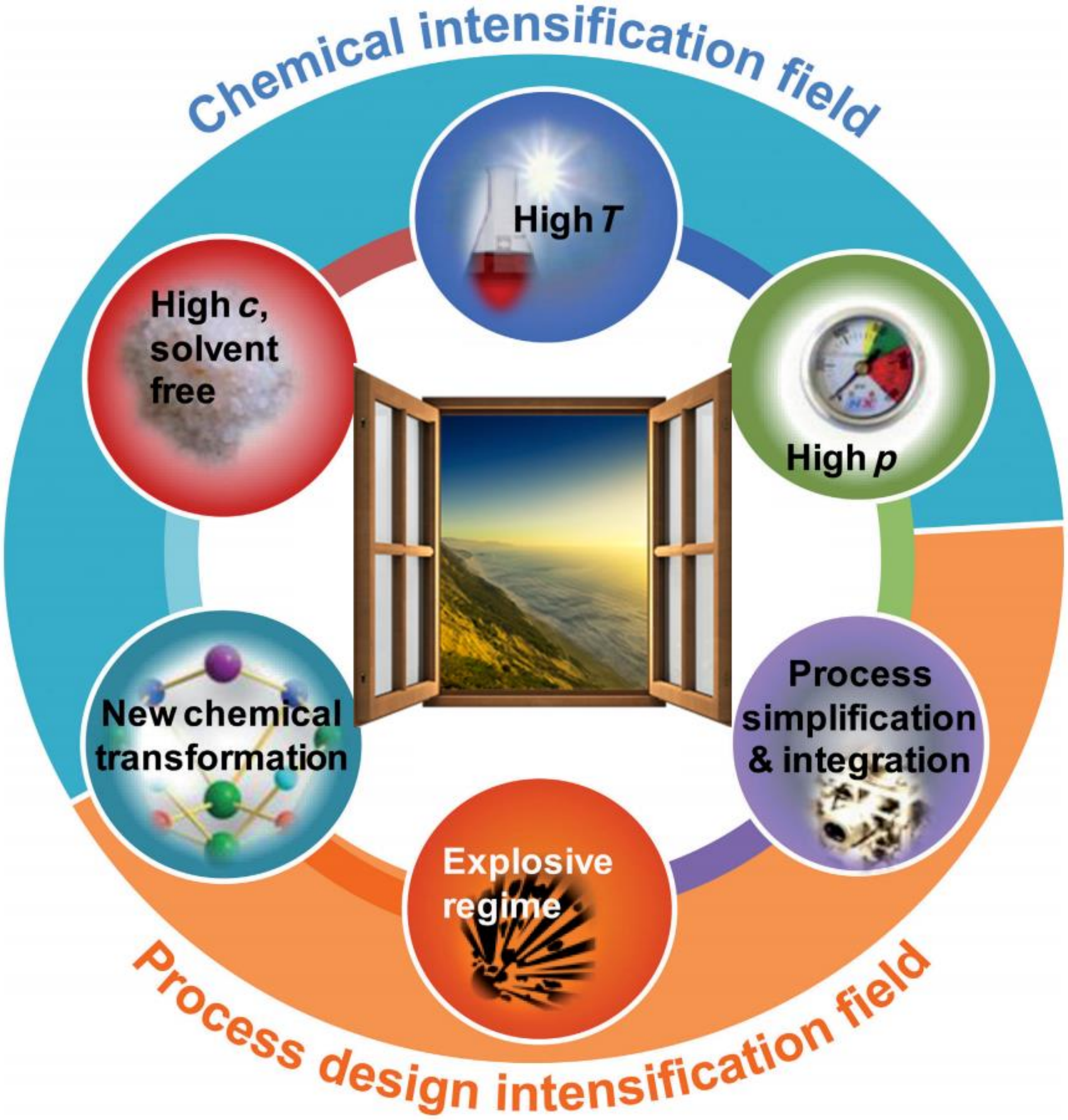
Engineering

Intensified Process

Product

Low residence times, minimal effluent separation, energy efficiency, zero wastes, limited supply, improved intrinsic safety, process flexibility or specification adaptability, fast answer to market, improved controls, just in time production on order.

Schematic representation of Novel Process Windows.



from Hessel et al. ChemSusChem, 2013, 6, 746–89

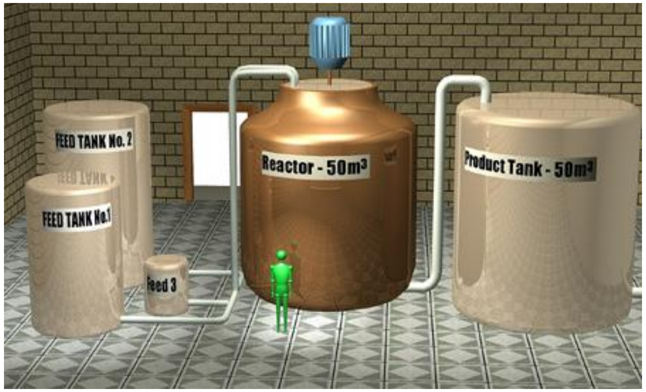
Process Intensification.

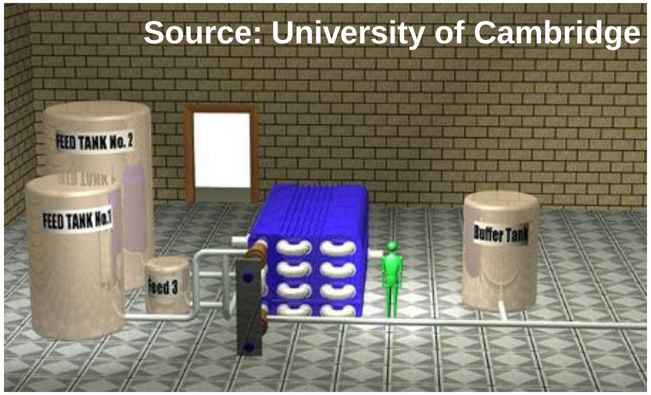
Definition:

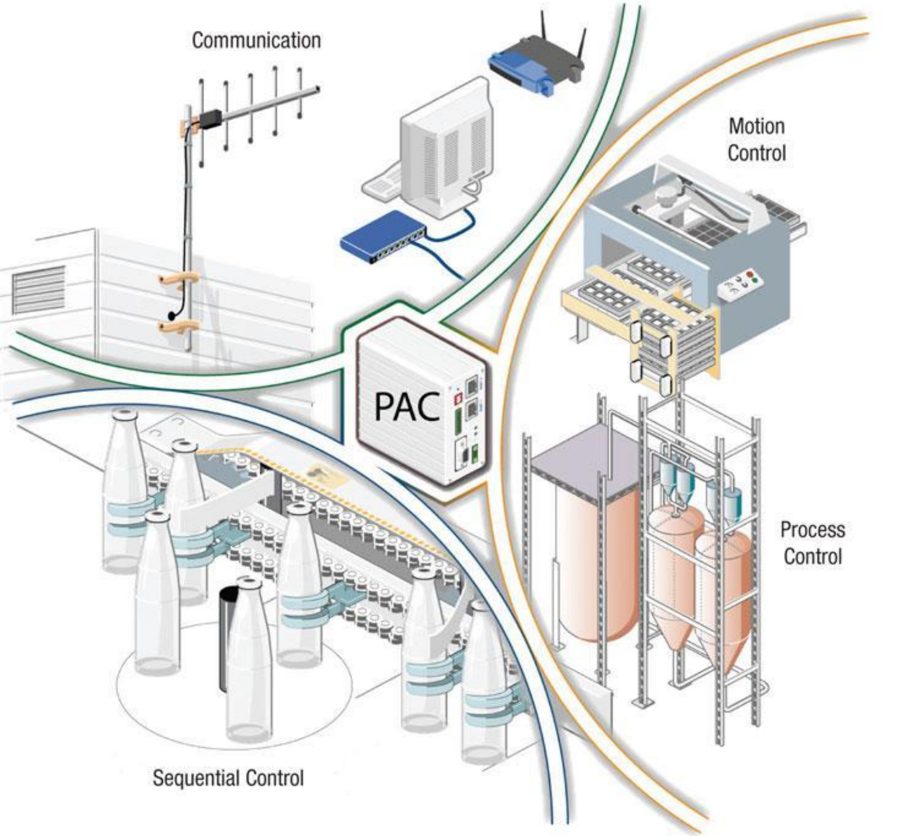
> “IP provides radically innovative principles (“paradigm shift”) in process and equipment design which can provide significant (> 2) benefits in terms of process and chain efficiency, capital and operating expenses, quality, wastes, process safety and more”.
>
> (European Roadmap of Process Intensification 2007)

- Develop new compact devices and improved techniques of production processes
- Require all unit operations must be intensified, i.e. reactors, heat exchangers, distillation columns, separators, ….
- Use multifunctional modules for various functions
- Use compact design joining classical unit operations
- Can use non conventional energy sources (ultrasounds, microwave, visible and ultraviolet light, electric current, etc.).

Volume Reduction and Process Integration.

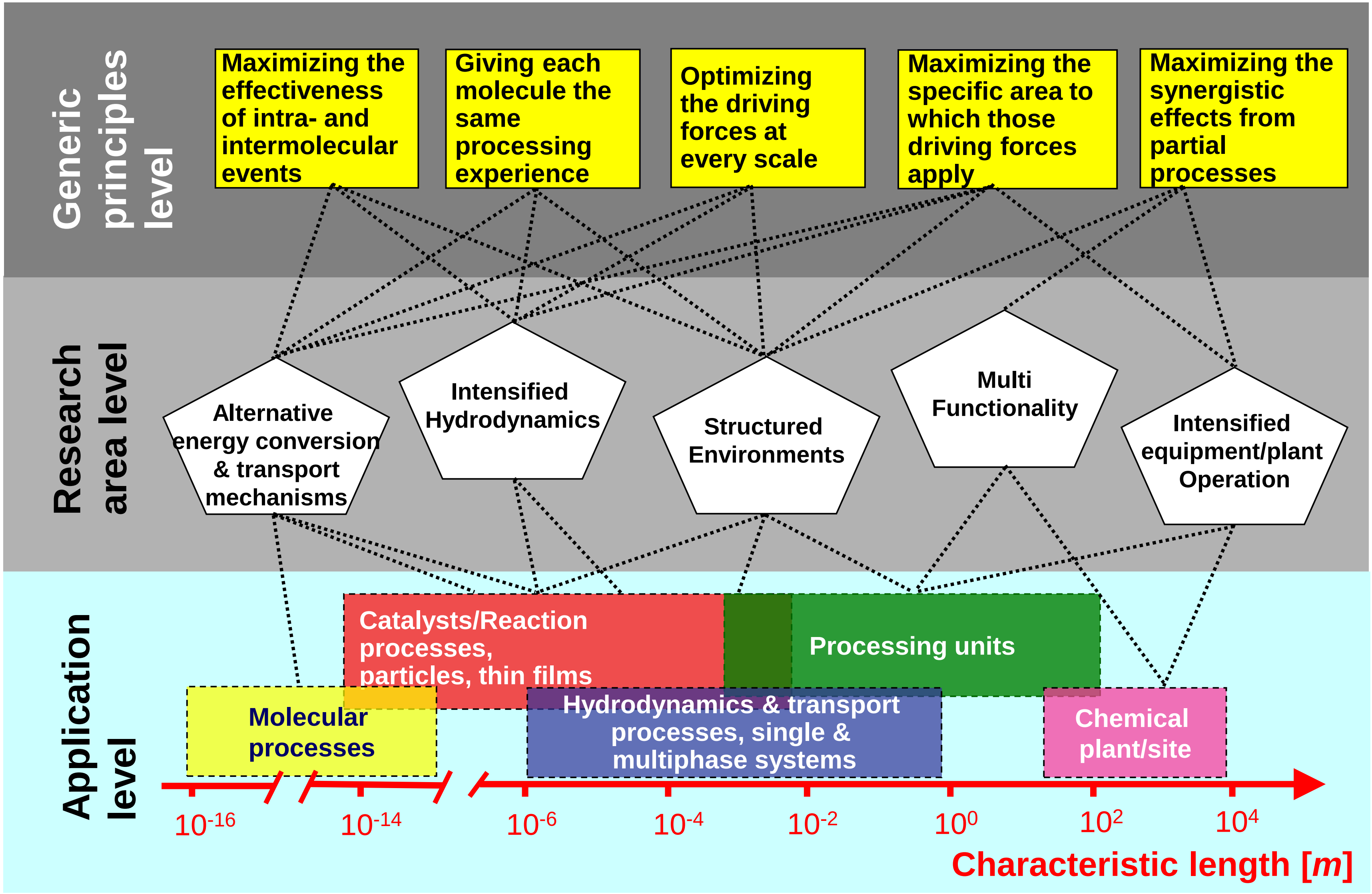



Source: University of Cambridge

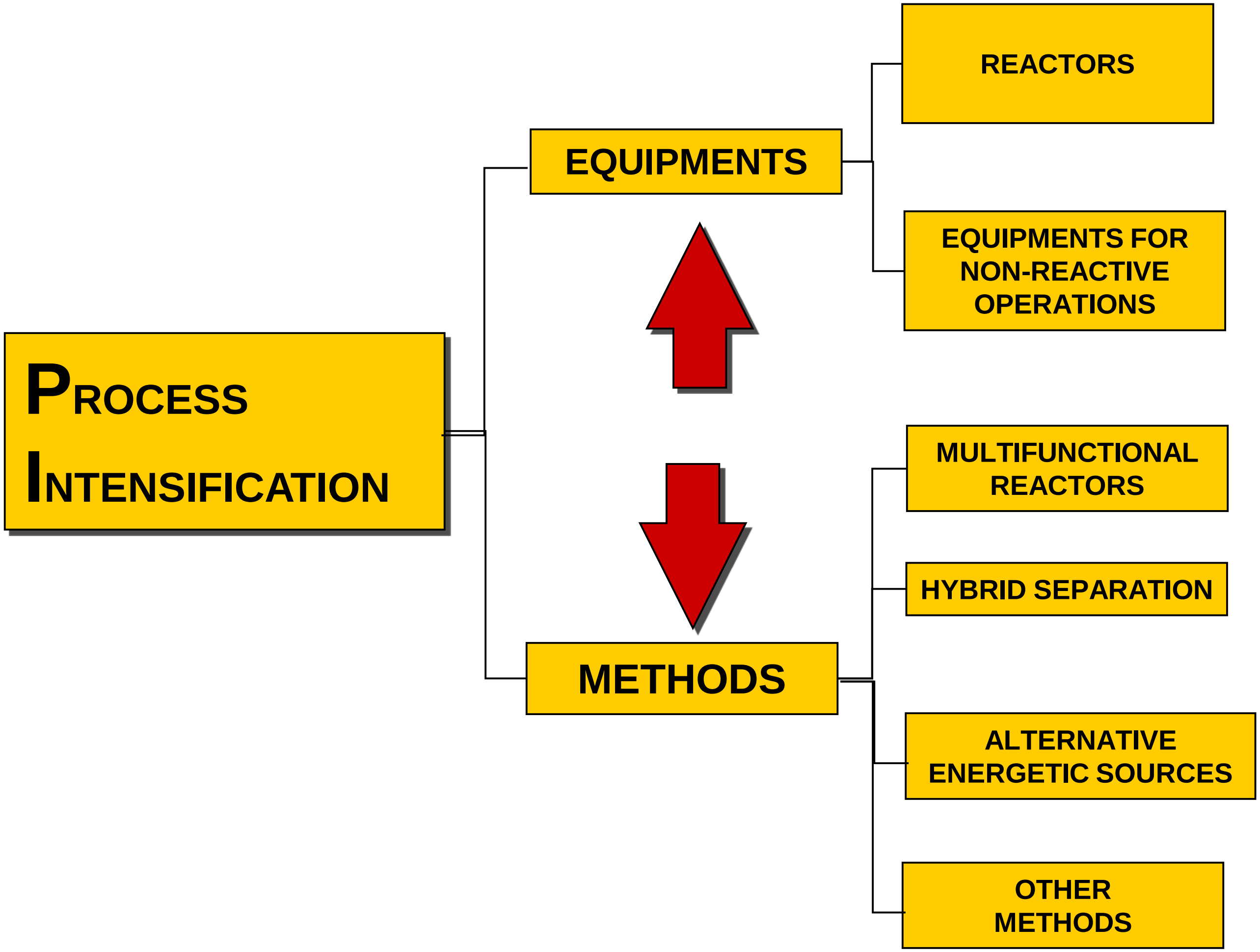


- Shift from i batch to continuous processes
- Use technologies with high mixing rates and heat transfer rates instead of conventional stirred tanks
- Consider the opportunity to improve the process technology and in meantime the chemical bases
- Use 'Plug and play' process technology to afford flexibility in a multiproduct environment
- In line Analytical control to prevent deviation from settings.

Process Intensification – a Set of New Principles and Research Areas…



Elements of Process Intensification.



EXAMPLES:

PROCESS INTENSIFICATION

EQUIPMENTS

REACTORS
- Spinning disk reactor
- Static mixing reactor
- Monolithic reactor
- Micro reactor

EQUIPMENTS FOR NON-REACTIVE OPERATIONS
- Static mixer
- Compact heat exchanger
- Spinning packed bed
- Centrifugal absorption

METHODS

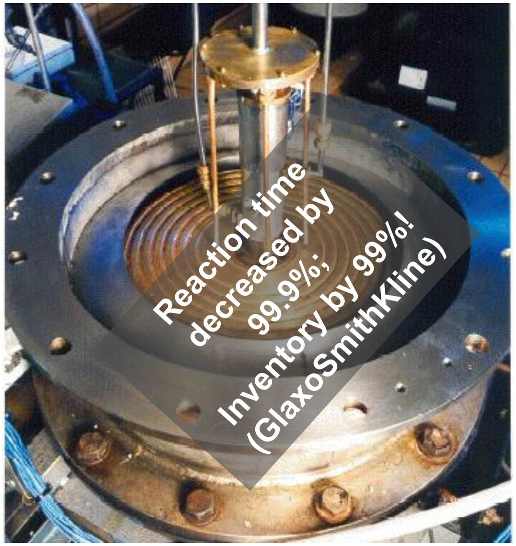
MULTIFUNCTIONAL REACTORS
- Integrated heat reactors
- Reactive separations
- Reactive milling
- Reactive extrusion
- Fuel cells

HYBRID SEPARATION
- Membrane Absorption
- Membrane distillation
- Absorptive distillation

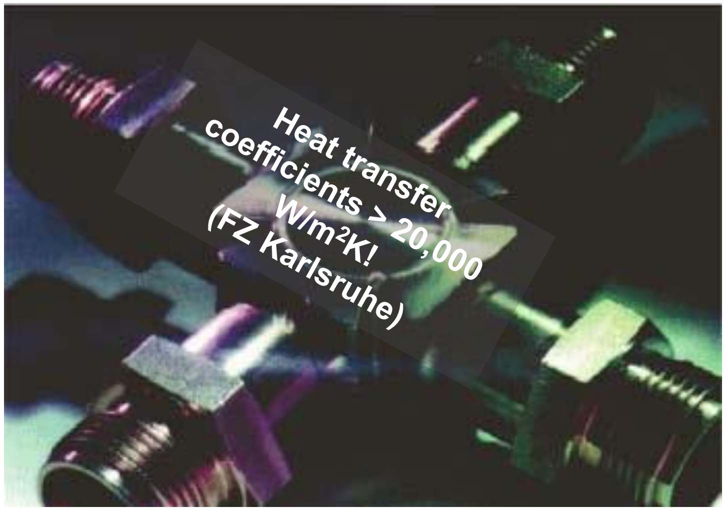
ALTERNATIVE ENERGETIC SOURCES
- Centrifugal fields
- Ultrasounds
- Solar energy
- Microwave
- Electrical fields
- Plasma technology

OTHER METHODS
- Supercritical fluids
- Dynamic Operation
- Cavitation

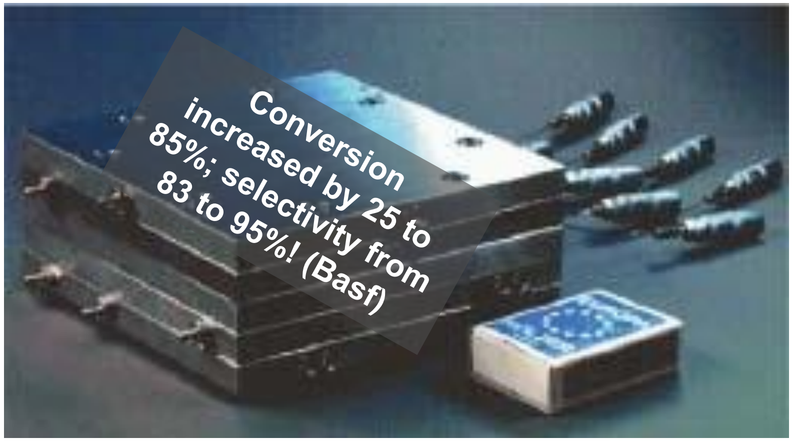
Some Examples of Intensified Equipment.



Reaction time decreased by 99.9%; Inventory by 99%! (GlaxoSmithKline)



Heat transfer coefficients > 20,000 W/m^2K! (FZ Karlsruhe)



Conversion increased by 25 to 85%; selectivity from 83 to 95%! (Basf)

Reaction time decreased from 18 hours to 15 min! (Hickson & Welch)

Design Considerations and Stages of Process Intensification.

Process is based on batch or continuous technology?

- Identify the rate limiting steps (mass, heat transfer, mixing, etc.) in all equipment in the production units
- *Line Balance :* temporal cycles of all equipment evaluated in a batch plant.
- *Understand well the base chemistry of the process and know how monitor it*
- Identify appropriate equipments/modules/intensification concepts
- Eliminate, if possible, the solvents; use supported catalysts where possible, reduce pressure/temperature gradients, and increase the transport rate
- *Mathematical modeling:* mathematical analysis of single equipment and of all plant to understand the transport process rate to evaluate performances.
- Reduce the number of stages through multifunctional modules
- *Multifunctional Equipments:* used to perform different operations in one unit.
- *Process intensification Equipments:* are designed to improve productivity, selectivity, energetic efficiency.
- *Alternative energy sources.*

Characteristics of an Intensified Process.

- Provide each molecule the same working sequence
- Make equal mixing and transport rate to reaction rate
- Optimize mass and heat transfer rate
- Push the reaction to its rate not to the plant rate.
- Improve selectivity and yield
- Improve the product quality and validation
- A fast cleaning allows a rapid change of production
- Fast answer to the values of assigned variables
- In same cases, lab scale is just sufficient (volume typically is the range of 250-1000 mL).

Nitroglycerine – Process Intensification.

Slow mixing

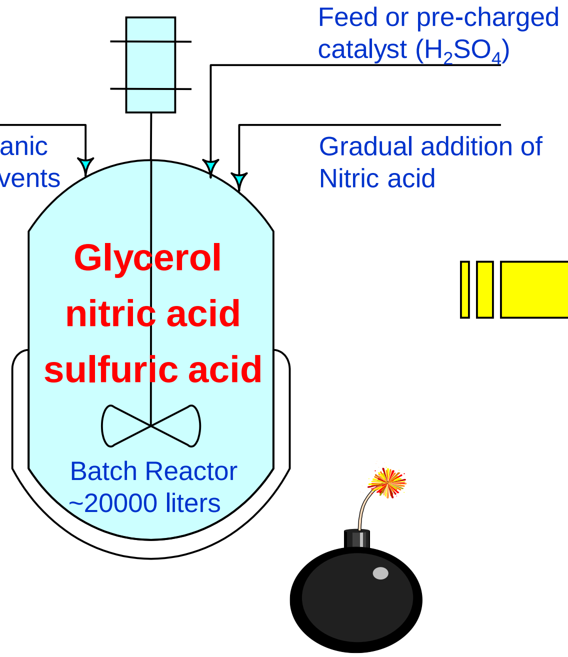
Reaction time 2 *h*

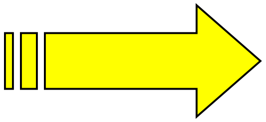
Inventory 1 *ton*

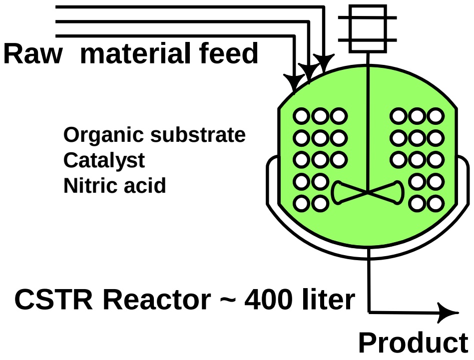
Rapid mixing via pumping

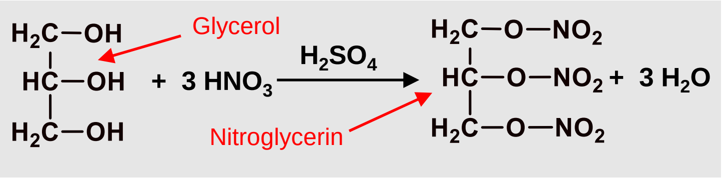
Reaction time 7 *min*.

Inventory 60 *Kg*







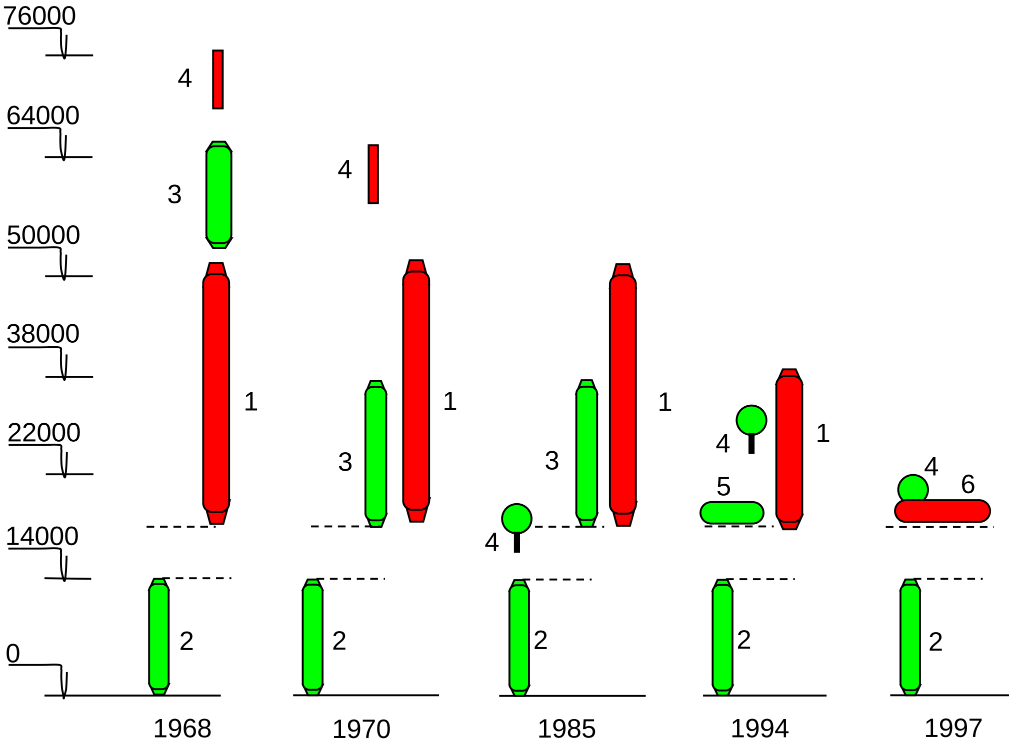


$$\begin{array}{l} H_2C-OH \\ HC-OH \\ H_2C-OH \end{array} + 3\ HNO_3 \xrightarrow{H_2SO_4} \begin{array}{l} H_2C-O-NO_2 \\ HC-O-NO_2 \\ H_2C-O-NO_2 \end{array} + 3\ H_2O$$

Possible alternatives:

- **Mixing – reagent contact**
- **Mass transfer – from aqueous phase (HNO_3) to organic phase**
- **Heat removal**

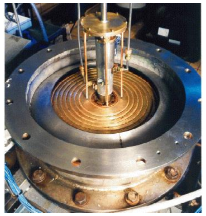
DSM Urea 2000plus Technology.

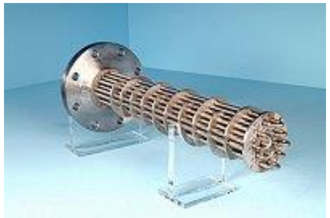


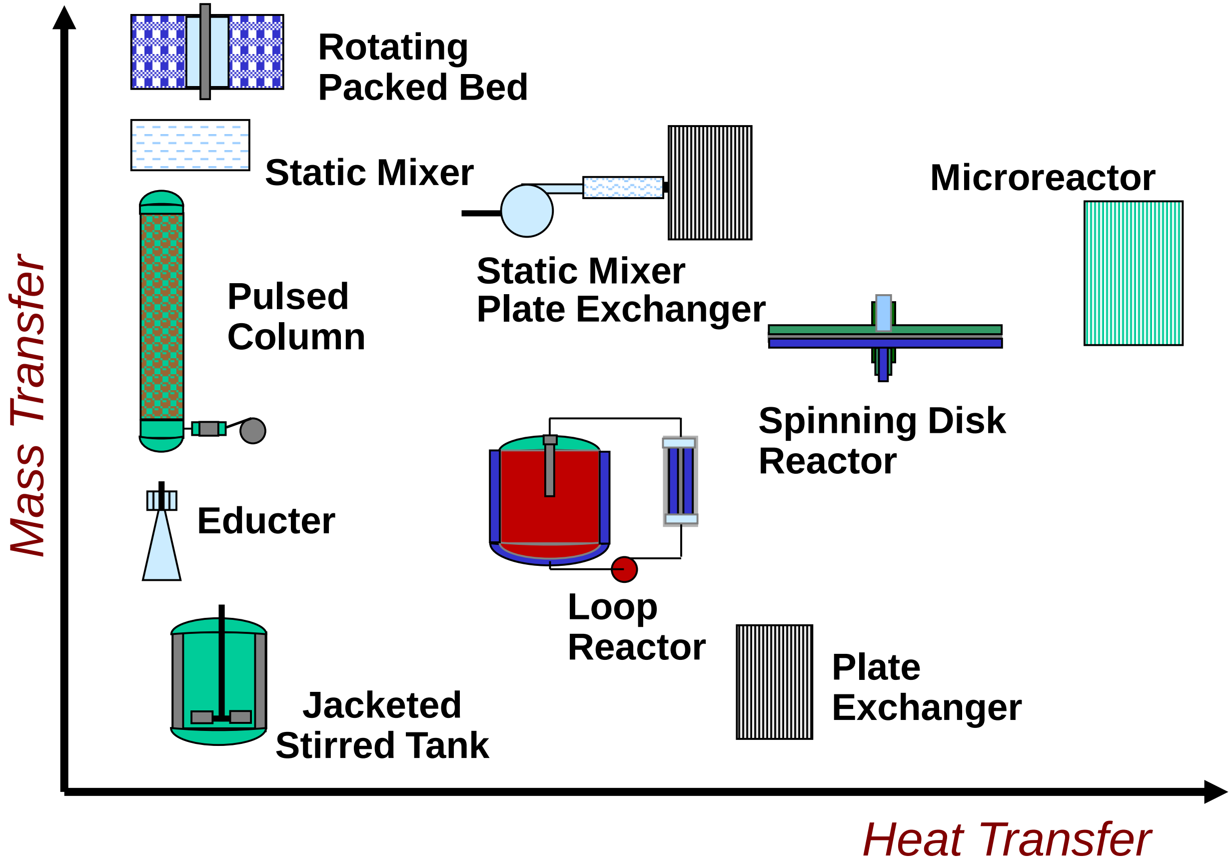
1. Reactor
2. Stripper
3. Condenser
4. Scrubber
5. Pool condenser
6. Pool reactor

Simple lay-out *** reduced piping *** less structural steel

Equipment Characterized by E & m Transfer Performances.







Rotating Packed Bed

Static Mixer

Pulsed Column

Educter

Jacketed Stirred Tank

Static Mixer Plate Exchanger

Loop Reactor

Spinning Disk Reactor

Plate Exchanger

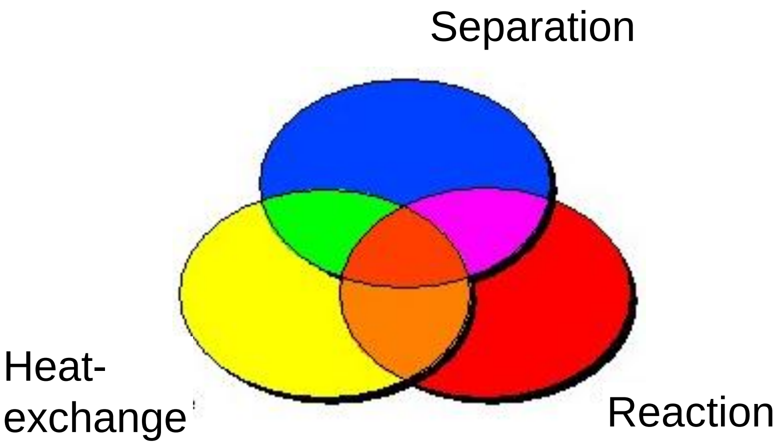
Microreactor

Mass Transfer

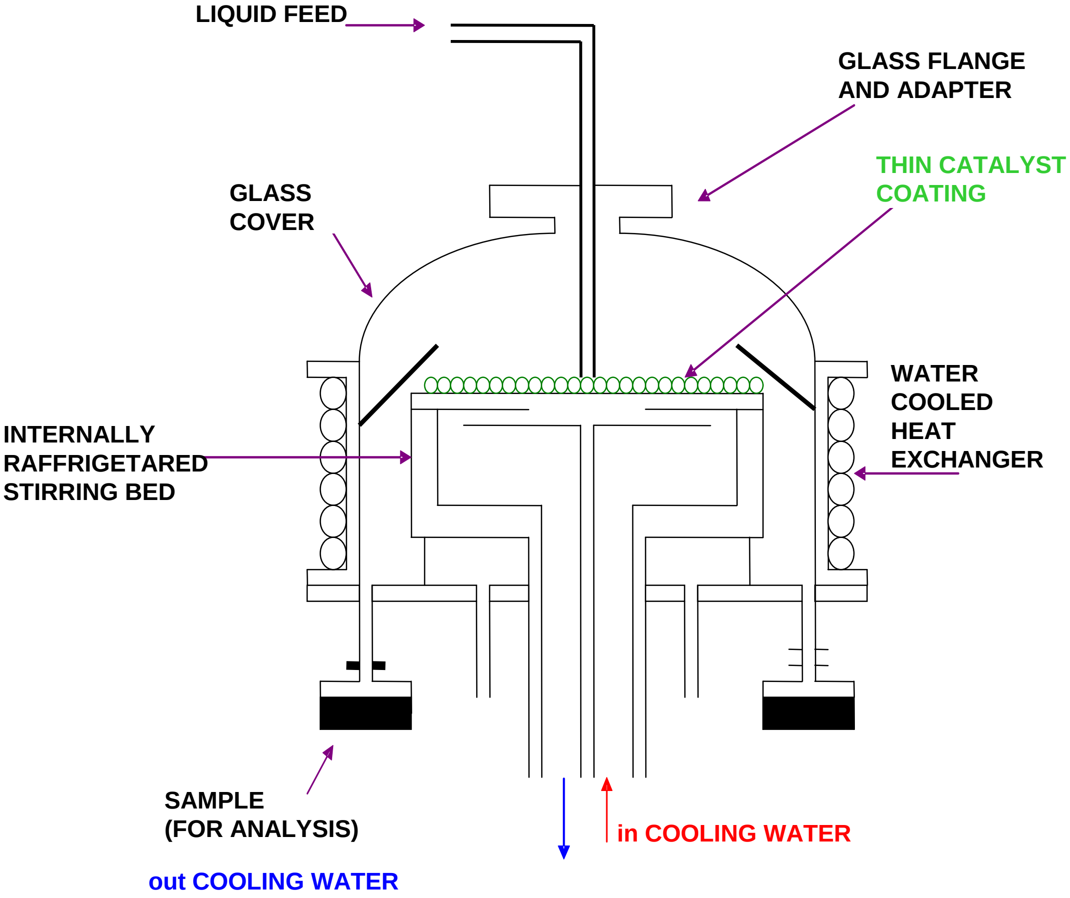
Heat Transfer

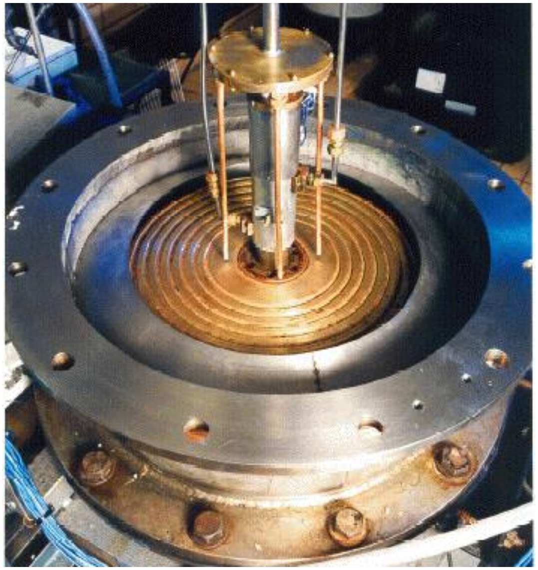
Areas for Process intensification (UO Gathering).

- Reaction-separation: membrane reactors, reactive distillation
- Reaction-heat exchange
- Separation-heat exchange: Deflemmators or heat integrated distillation
- Reaction-separation-heat exchange: reactors with isothermal membrane.



Stirring Bed Catalytic Reactors (SDR).





SDR Reactor Peculiarities.

- In a SDR, a liquid is feed at the center of a rotating disk and, as the liquid moves toward the edge, intense waves are formed which interfere under the influence of centrifugal force. This allows to obtain very high heat transfer coefficients between the disk and the liquid, but also an high mass transfer between the liquid and upper gas. Waves produce also an intense local mixing.

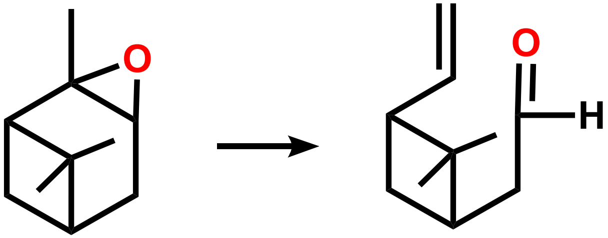
- The liquid flow imply a limited retro-mixing and therefore a nearly pure flow arises. The residence time is small, typically 50 seconds. The liquid film height is 500 *mm* and high viscosity is supported.

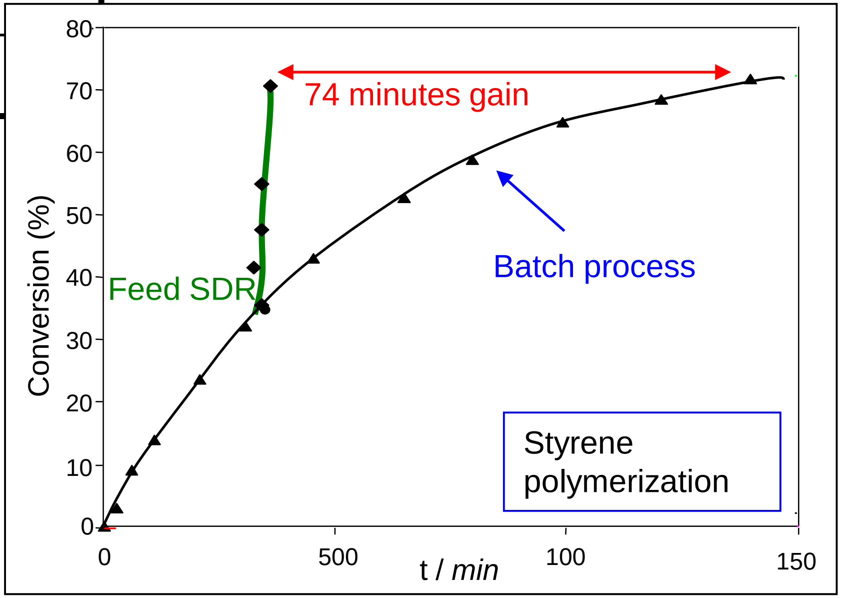
- The reactor manages a low liquid volume (near 10 *mL* for a batch equivalent of 5 m^3) and is easily installed also in restricted places.

Protensive

Catalytic SDR Performances.

α-Pynene oxide rearrangement to campholenic aldehyde	Batch reactor	Catalytic SDR
Feed	100 *ml*	100 *ml*
Conversion	50%	95%
Yield	42%	71%
Working time	900 *s*	17 *s*

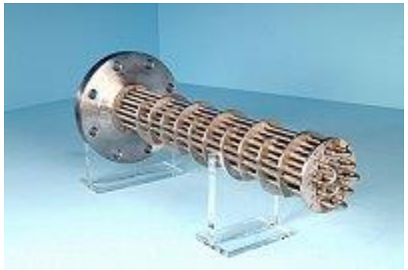




Flex Reactor.

FlexReactor represents a family of reactors designed to cover a wider spectrum of transport capacity, heat transfer rate, and mixing intensity.

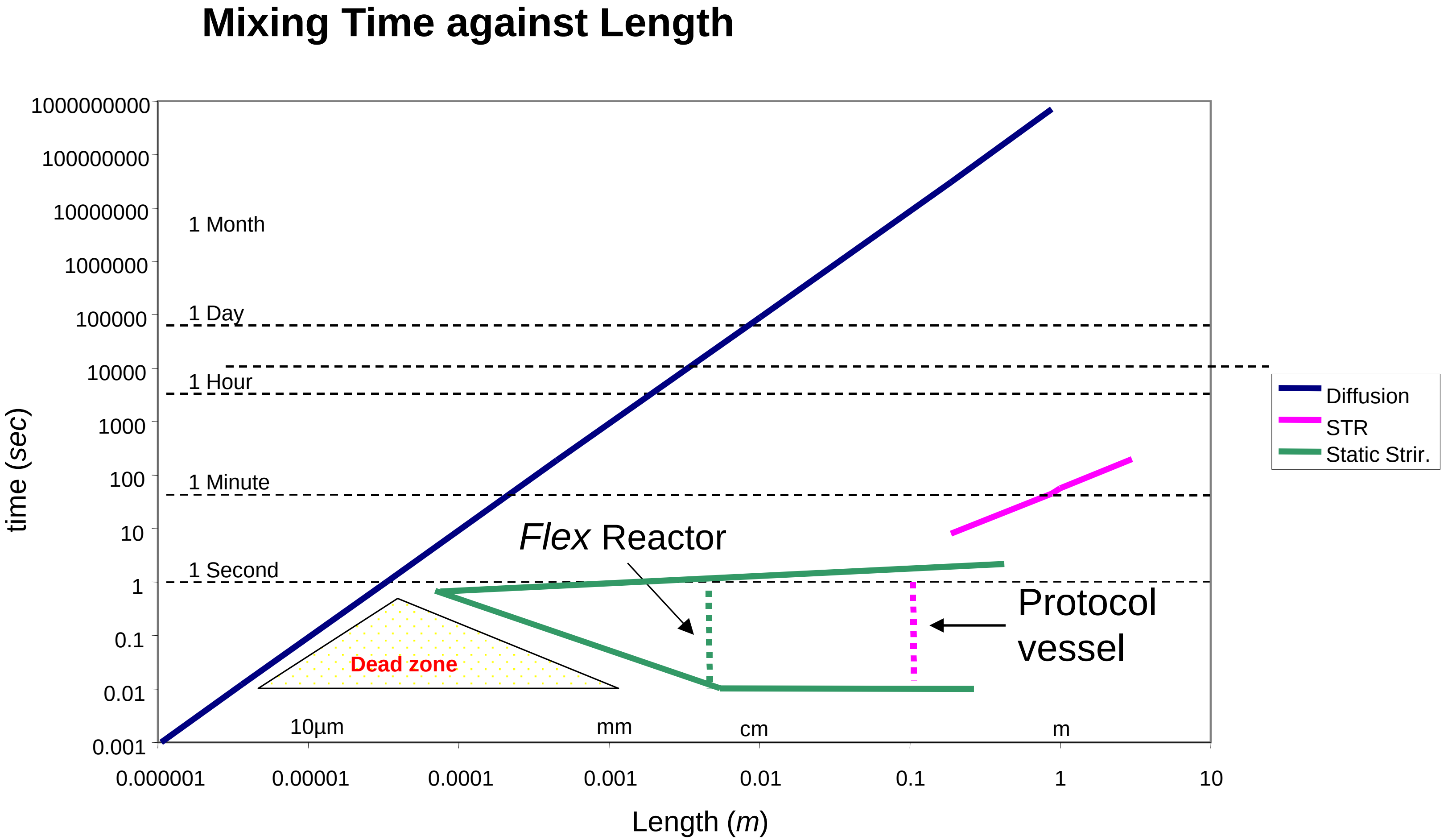
1. multiple feeding of reagents (in series or in parallel)
2. Sensors in the reactor (e.g. T, FT-IR, etc.) to follow the reaction course and to collect critical kinetic data.



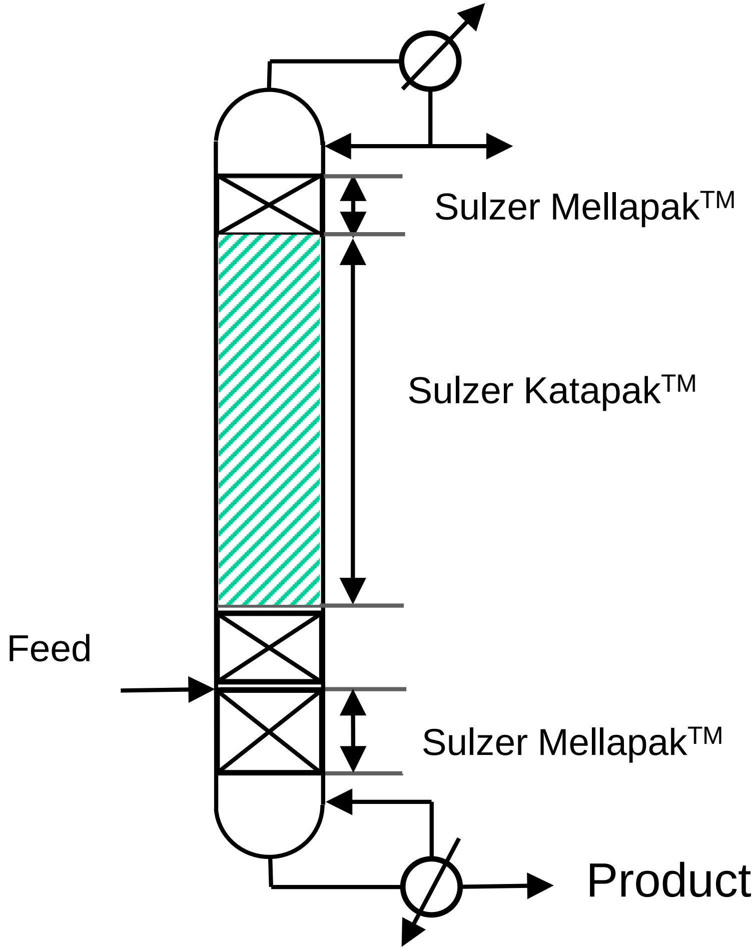
Incorporation of other functionalities between piping (e.g. separation, further heat transfer)

- Flexible and robust design with reconfigurable connectors to one end
- Otherwise to both ends.
- Laboratory, pilot or productive scale unit,

Flex Reactors.

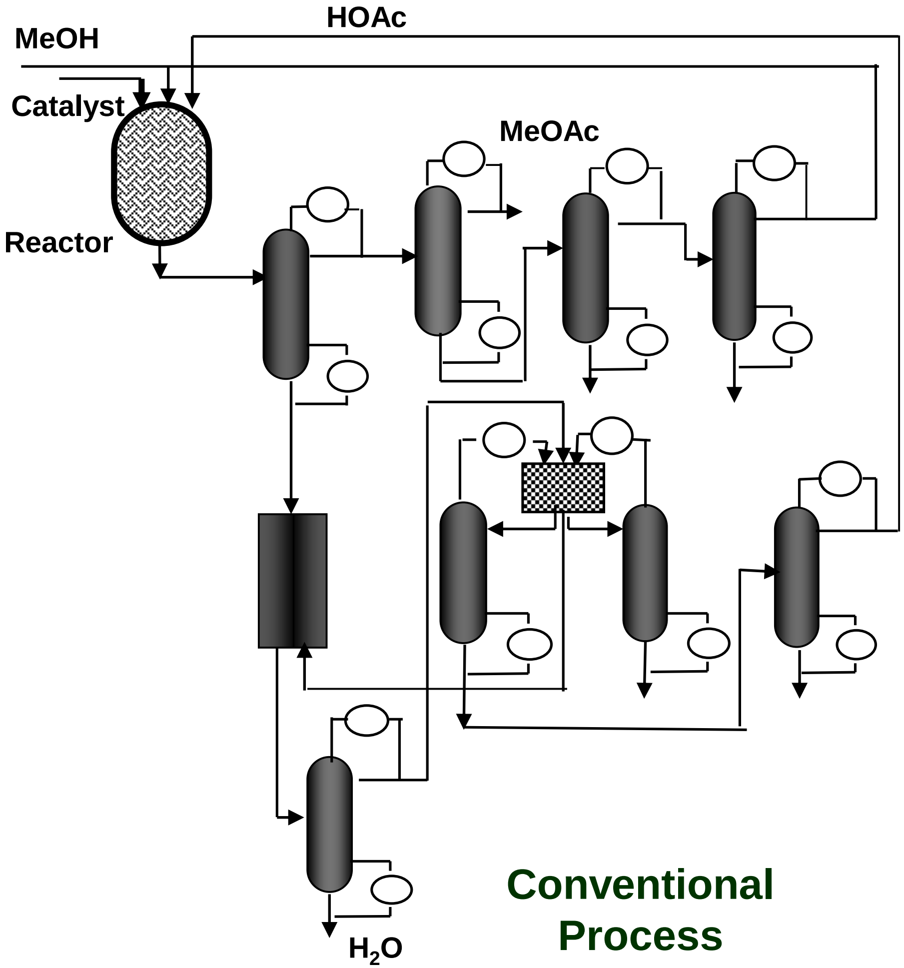


Reaction-Separation Technologies:
Catalytic or Reactive Distillation.

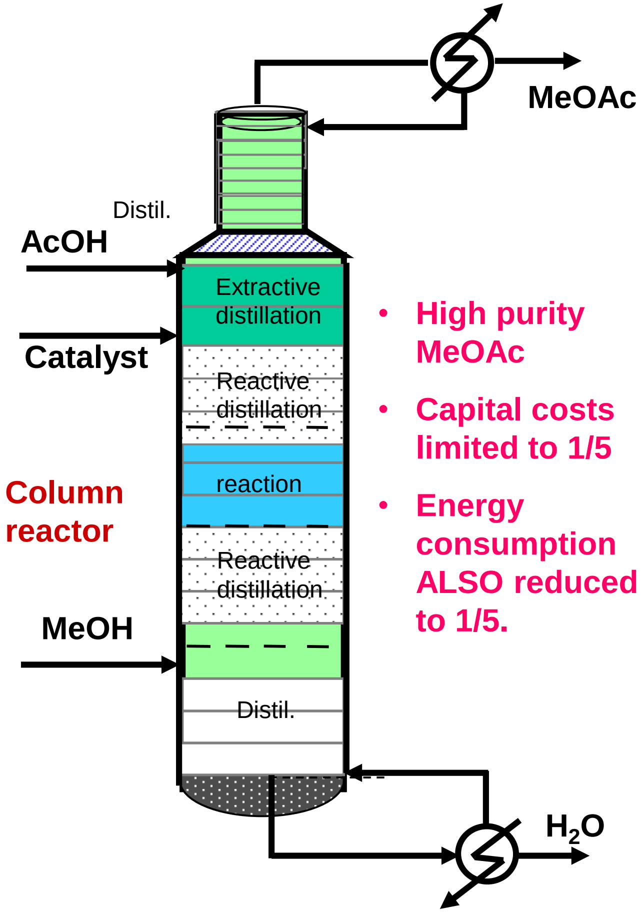


Catalyst: strong acid
or Amberlist 15 Resin
(catalytic esterification).

Reactive Distillation: Synthesis of Methyl Acetate.



Conventional Process



- High purity MeOAc
- Capital costs limited to 1/5
- Energy consumption ALSO reduced to 1/5.

Eastman Chemical Co (1990)

Non Trivial Simplification.

- Lower number of vessels
- Less pumps
- Less flanges
- Less equipments
- Less valves
- Less piping
- ......

but

- Reactive distillation column is quite more complex
- In the same vessel multiple unit operations occur
- More complex to design
- More difficult to control and manage

Reaction-Separation Technologies: Membranes.

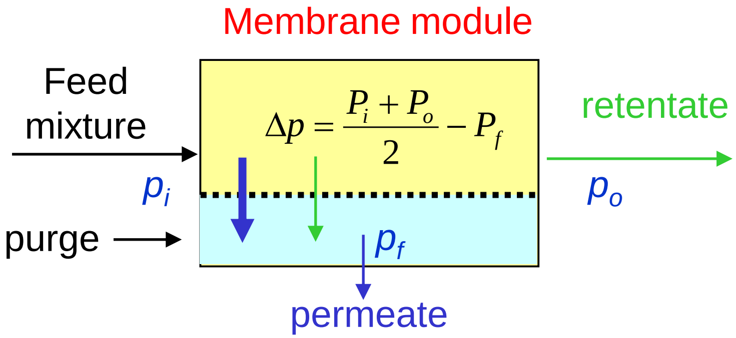
Synthetic membranes represent a growing area for gas, liquid, metal and microorganisms separations. These potentialities combine with big energy save, a low cost modular construction and high selectivity for separated materials. Membrane based processes are quite widespread.

In general, membranes have reached a commercial success in few applications (biotechnology). The total word market is however expected in expansion to more than 2.7 billions € in next years.

$$J_v = \frac{\varepsilon_m d_p^2 \Delta P}{32 \mu l_p}$$

J_v = permeate flow
ε_m = membrane porosity
d_p = mean pore diameter
ΔP = trans-membrane pressure
μ = viscosity
l_p = mean pore length

In membrane processes the feed steam is divided in two streams, one the retentate or concentrate and the other the permeate.



Membrane module

$$\Delta p = \frac{P_i + P_o}{2} - P_f$$

Membrane Separation Processes.

Definition: The term membrane most commonly refers to a thin, film-like structure that separates two fluids. It acts as a selective barrier, allowing some particles or chemicals to pass through while leaving others behind.

- This selectivity is utilized for separation.

- The selectivity is due to:
  - Size
  - Shape
  - Electrostatic charge
  - Diffusivity
  - Physicochemical interactions
  - Volatility
  - Polarity/solubility

- The Driving Force is due to:
  - Trans-membrane pressure (TMP)
  - Concentration gradient
  - Chemical potential
  - Osmotic pressure
  - Electric field
  - Magnetic field
  - Partial pressure
  - pH gradient

Membrane Separation Processes: Applications.

- Product concentration, i.e. removal of solvent from solute/s
- Clarification, i.e. removal of particles from fluids, a special case being sterilization which refers to remove of microorganisms from fluids
- Removal of solute from solvent, e.g. desalting, desalination, demineralization, dialysis
- Fractionation, i.e. separation of one solute from another
- Gas separation, i.e. separation of one gas from another
- Pervaporation, i.e. removal of volatiles from non volatiles (usually solvents)

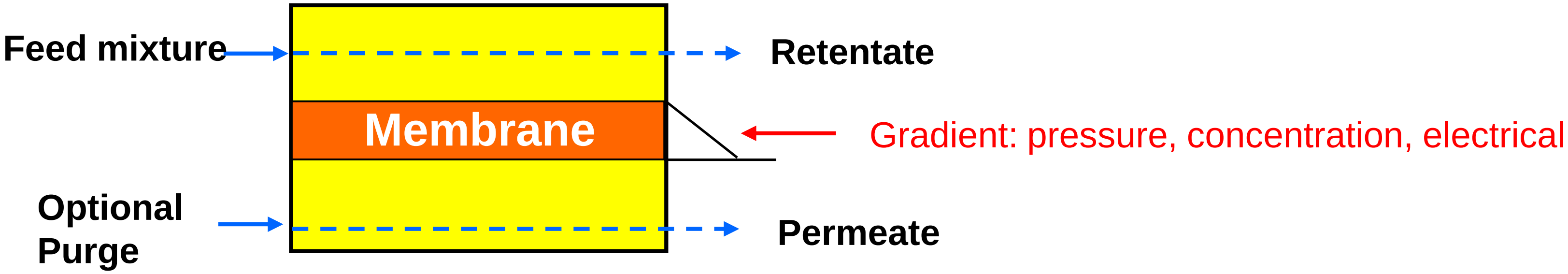
Membrane Separations:

- Are pervasive in biotechnological and pharmaceutical industries
- Are often used by biological systems
- Are one of the fastest developing areas in separations
- Are often highly selective, compact, inexpensive and easy to operate
- Overall throughput is generally low and often must be run in parallel.

Membrane Separations.

Three main driving forces are used for membrane separations:

- Pressure
- Concentration
- Electrical Potential



Reverse Osmosis: Desalination
Dialysis: Hemodialysis
Electrodialysis: Table salt from sea water, proteins from precipitation salts
Microfiltration: Purification of antibiotics
Ultrafiltration: Preconcentration of milk, recovery of vaccines form fermentation broth
Pervaporation: Removal of water from organic solvents
Gas Permeation: Recovery of helium
Liquid membranes: Recovery of Ni from electroplating solutions

Membrane Processes.

Advantages

- No heat generation
- No phase change
- Low energy requirements
- Easily automated
- High levels of containment
- Specific size separation

Limitations

- Membrane blockage
    - Fouling
    - Gel polarisation
- Membrane affected by the conditions of pH, ionic strength, etc.
- Cleaning and maintenance
- Product adsorption
- Not generally steam sterilisable
- Pore size distribution.

Membrane Materials.

Organic Polymers

Polysolfone (PS)
Polyethersulfones (PES)
Tetrafluoroethylene (Teflon)
Cellulose triacetate (CA)
Regenerated cellulose
Polyamides (PA)
Polyvinylidedefluoride (PVDF)
Polyacrylontrile (PAN)
Polyisoprene (PI)
Polycarbonates (PC)
Polyimides (PIM)

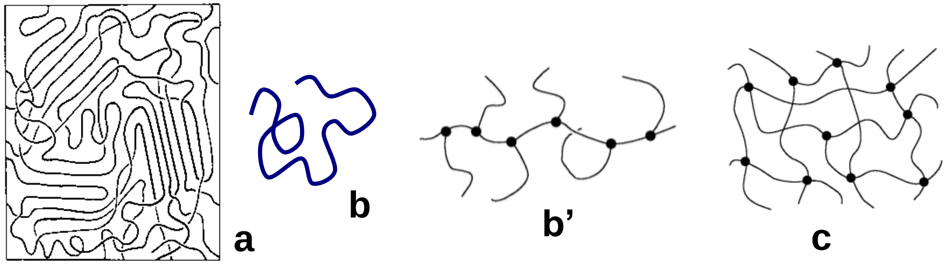
Inorganics

γ-Alumina
α-Alumina
Borosilicate glass
Pyrolyzed carbon
Zirconia/stainless steel
Zirconia carbon

Polymer Membranes.

Polymers:

a) Glassy or Crystalline
b) Straight or Branched
c) Porous or Non-porous
d) Cross-linked or Non-crosslinked



To be a good membrane material a polymer should have:

- a high Permeance (to increase throughput, and reduce the need for parallel stages)
- a high Permeance Ratio for 2 species being separated (to increase the separation factor).

$$N_i = \left(\frac{P_{M_i}}{I_M}\right) \times force = \overline{P}_{M_i} \times force$$

Driving force: pressure gradient, concentration gradient, coulombic force, etc.

The molar flux N_i across the membrane is equal to the permeance times the driving force. The permeance is the permeability divided by the membrane thickness.

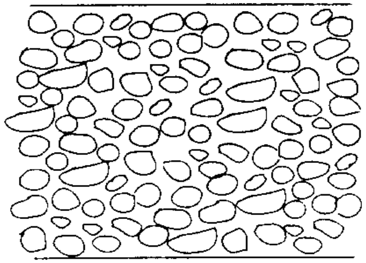
In other words, the permeability is the ratio of the molar flux N_i per unit of driving force times the thickness l_M of the membrane.

Membranes can be dense or microporous.

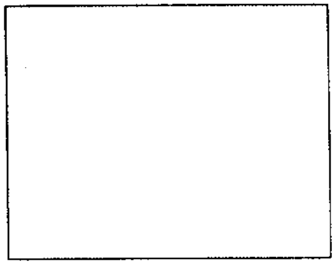
Membrane Structure and Morphology.

Symmetrical

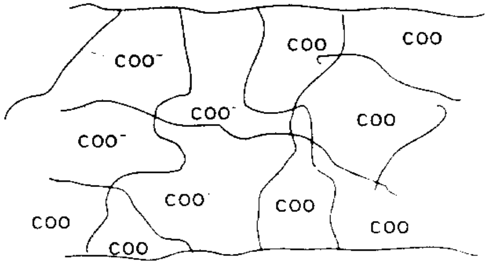
Isotropic microporous membrane



Nonporous dense membrane

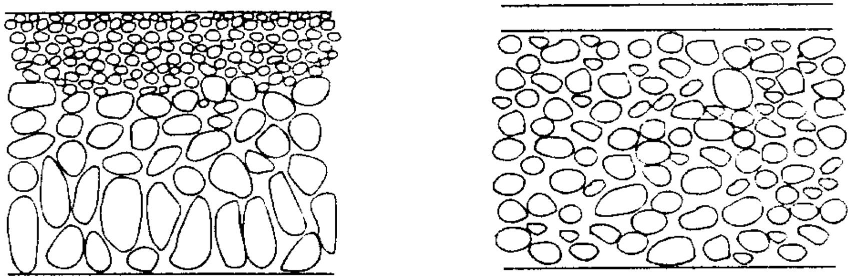


Electrically charged membrane

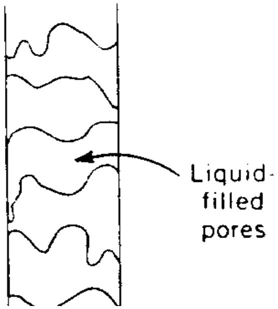


Asymmetrical

Asymmetric membranes



Supported liquid membrane



Membrane Preparation.

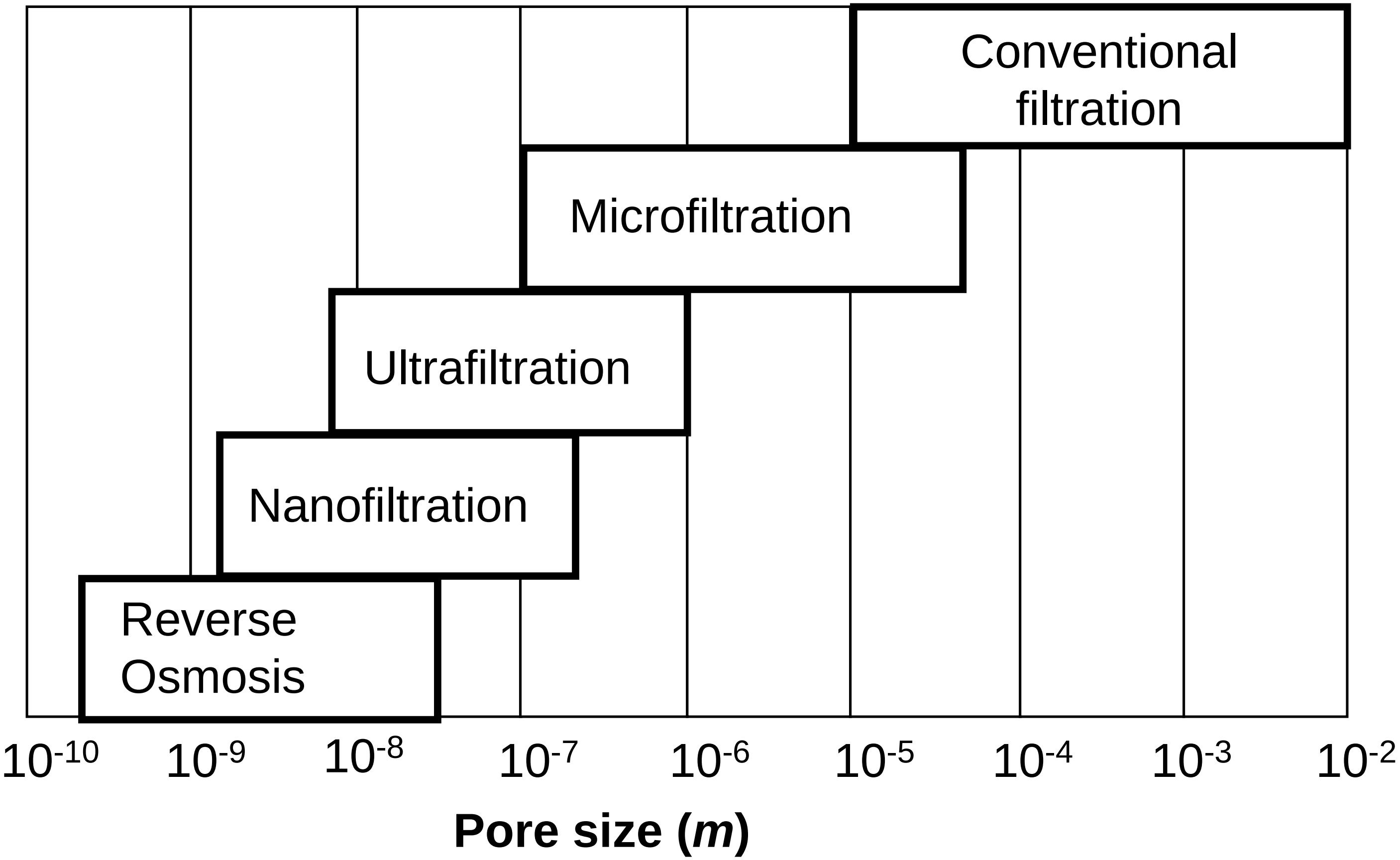
Polymer casting:

- Precipitation from vapour phase
- Precipitation by evaporation
- Immersion precipitation
- Thermal precipitation

Other methods:

- Stretching
- Sintering
- Slip casting
- Leaching
- Track etching

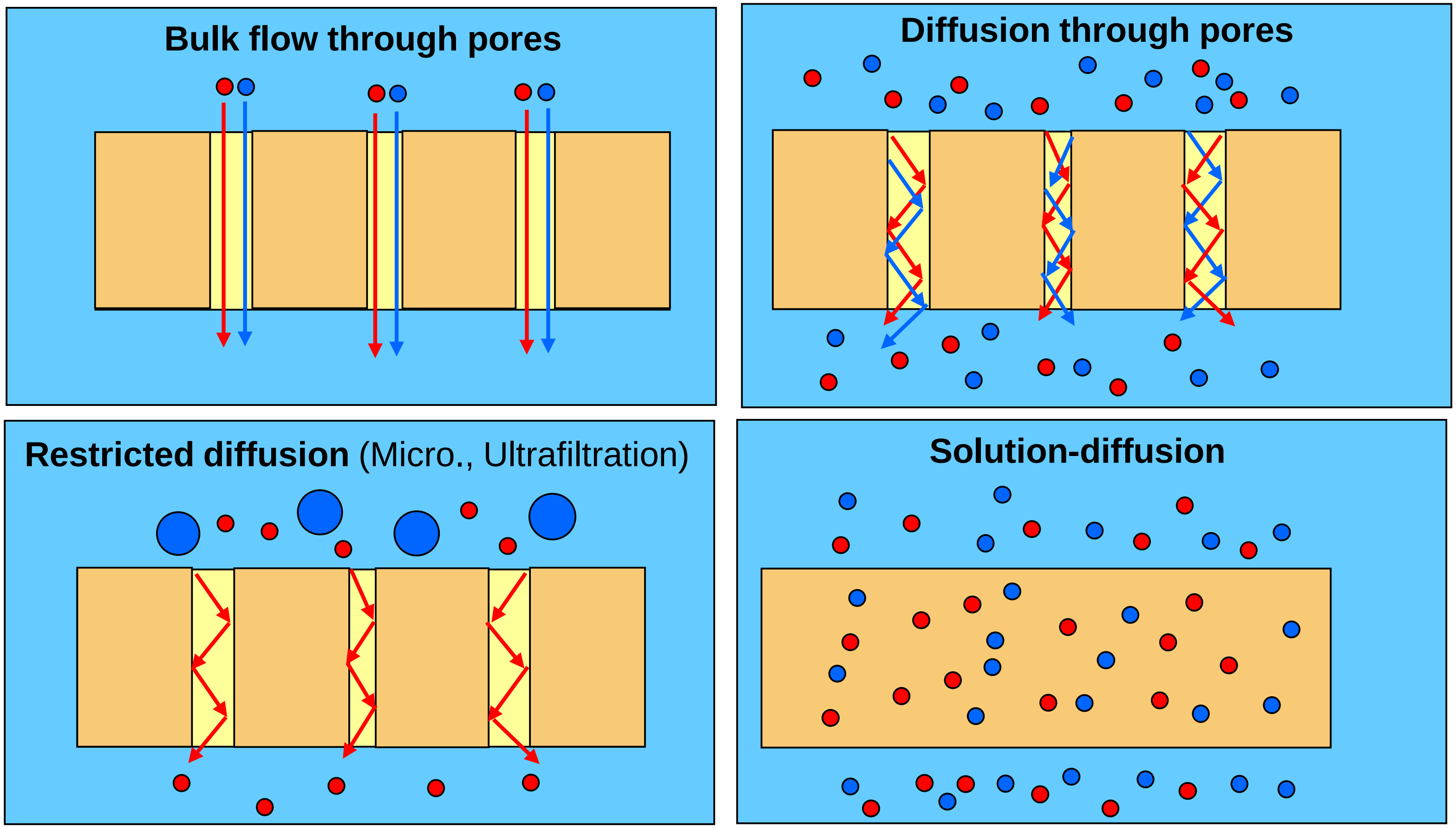
Classification of Membrane Processes Based on Pore Size.



Range	Ionic	Macromolecular	Micron	Fine particles	Coarse particles

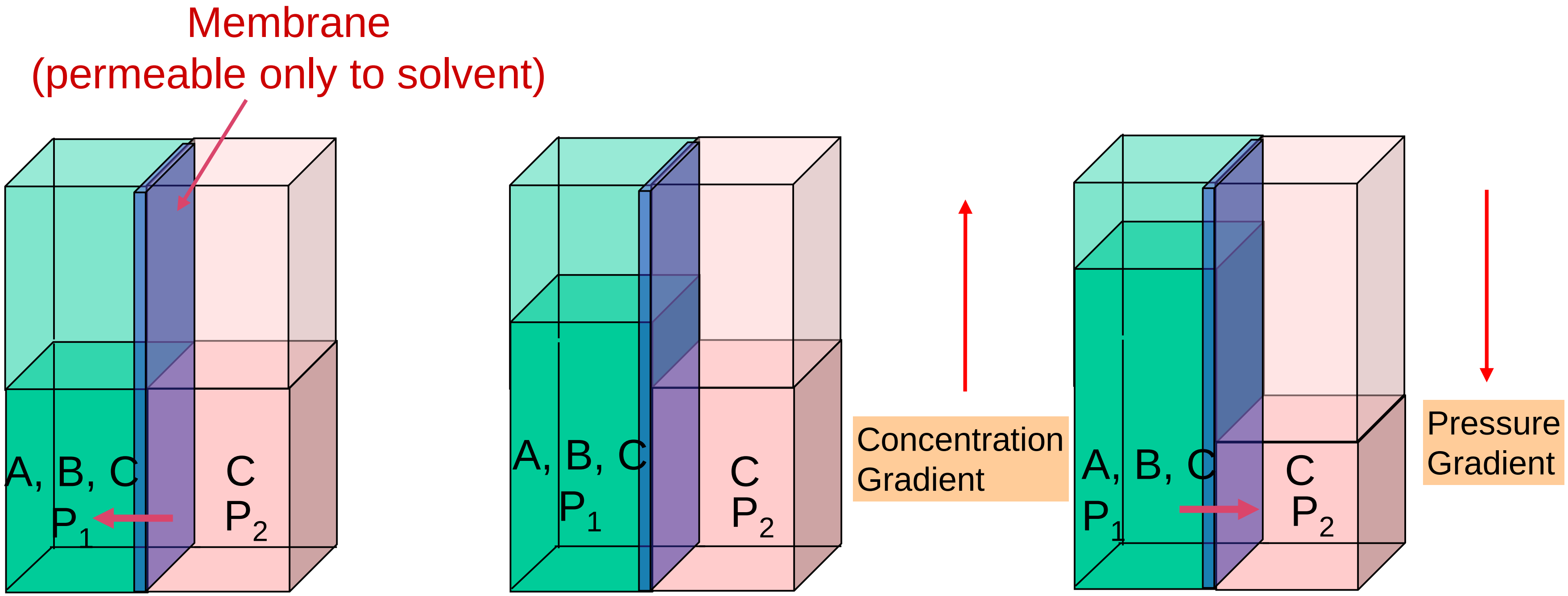
Transport Mechanisms Through Membranes.

- Bulk flow through pores (microporous with pores larger than the mean free path).
- Diffusion through pores (large enough for diffusion, but small relative to the MFP).
- Restricted diffusion through pores (large enough for some species, but not others).
- Solution-diffusion (Diffusion through dense Ms with diffusant dissolved in polymer matrix).



Osmosis and Reverse Osmosis.

In reverse osmosis a pressure gradient is used to push solvent through a membrane which is not permeable to the solute. This pressure must be greater than the osmotic pressure.



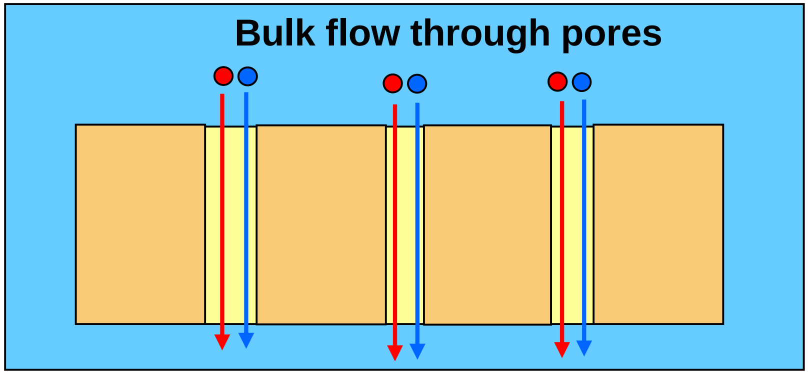
Initial condition (equal pressures)

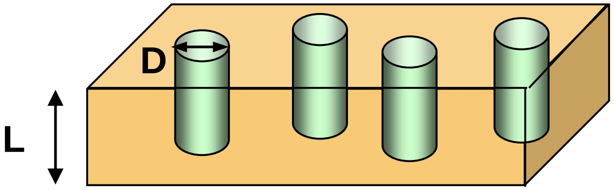
Equilibrium condition (pressure difference maintained by osmotic P)

Reverse osmosis (Transport against concentration gradient if pressure above osmotic P)

Bulk Flow Through Membranes.

Bulk flow through pores (if M is microporous with pores larger than the mean free path):





If flow is in the laminar regime then the Reynolds Number N_{Re} (which is related to the pore and fluid properties) is less than 2.100:

$$N_{\mathrm{Re}} = \frac{D\upsilon\rho}{\mu} < 2,100$$

Then the bulk flow velocity, v, depends on the P drop, (P_0-P) across the M, the pore diameter D, the viscosity of the fluid, μ, and the length of pore, L, as in the Hagen-Poiseuille Law:

$$v = \frac{D^2}{32\mu L}(P_0 - P)$$

Similar to Darcy's Law

$$\varepsilon = n\pi\frac{D^2}{4}$$

The void fraction (porosity) epsilon ε of the membrane is related to the pore diameter *D* and *n*, the number of pores per cross sectional area *A*:

Bulk Flow Through Membranes (2).

Combining:

$$v = \frac{D^2}{32\mu L}\left(P_0 - P\right)$$

Velocity

$$\varepsilon = n\pi \frac{D^2}{4}$$

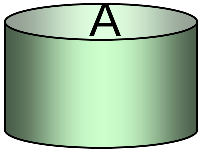
Porosity

$$N = v\varepsilon\rho$$

Density

Flux (molar or mass)

Note that the porosity gives the total cross-sectional area of the flow perpendicular to the flow direction:



$$N = v\varepsilon\rho = v(nA)\rho = \dot{V}\rho$$

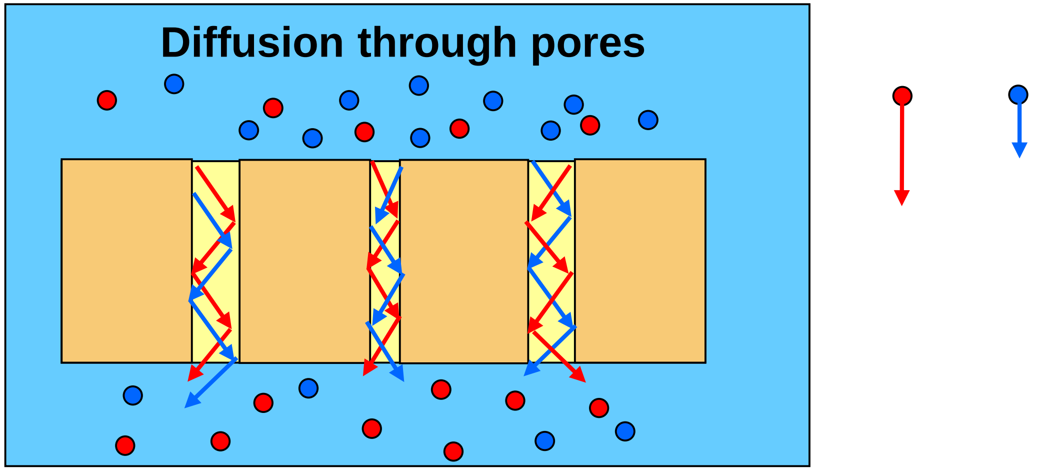
Volumetric
flow rate

$$N = \frac{\varepsilon\rho D^2}{32\mu L}\left(P_0 - P\right) = \frac{n\pi\rho D^4}{128\mu L}\left(P_0 - P\right)$$

If the pores are not straight or cylindrical then we must modify this equation by factors that describe the tortuosity and specific surface area.

Diffusion Through Membranes.

If the pressure on either side of a porous membrane is equal, but the concentration of species different, then there will be diffusion of species across the membrane, but no bulk flow. If species diffuse at different rates, then a separation occurs due to the differential transport of species across the membrane:



If the species shown in blue diffuses faster than the species shown in red, the faster moving species will have a higher average velocity and flux and the permeate side of the membrane becomes enriched in the faster diffusing species.

If the feed is a liquid, then the diffusion of species across the membrane is described by a modified form of Fick's Law:

Flux through the pore:

$$N_i = \frac{D_i}{l_m}\left(c_{i0} - c_{iL}\right)$$

Effective diffusivity

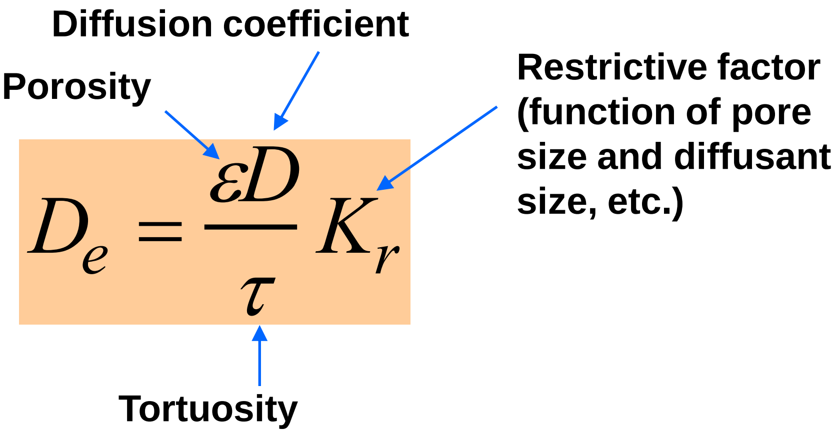
Length of the pore

Concentration gradient across membrane

Liquid Diffusion Through Membranes.

The effective diffusivity can be expressed as a function of the ordinary diffusion coefficient, the porosity, the tortuosity and the restrictive factor as:

The effective diffusivity is necessary because this diffusion occurs through pores in a membrane, and not just down a bulk concentration gradient.



Diffusion coefficient

Porosity

Restrictive factor (function of pore size and diffusant size, etc.)

$$D_e = \frac{\varepsilon D}{\tau} K_r$$

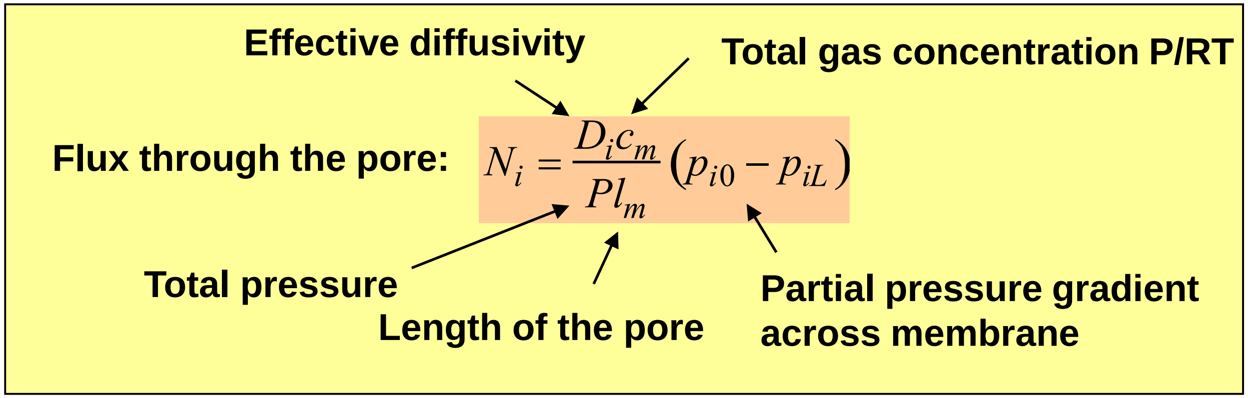
Tortuosity

We can write the flux then as:

$$N_i = \frac{\varepsilon D}{l_m \tau} K_r \left(c_{i0} - c_{iL} \right)$$

Gas Diffusion Through Membranes.

If instead of a liquid there is a gas on either side of the membrane then:



Effective diffusivity

Total gas concentration P/RT

Flux through the pore:

$$N_i = \frac{D_i c_m}{P l_m}\left(p_{i0} - p_{iL}\right)$$

Total pressure

Length of the pore

Partial pressure gradient across membrane

Compare to the liquid case:

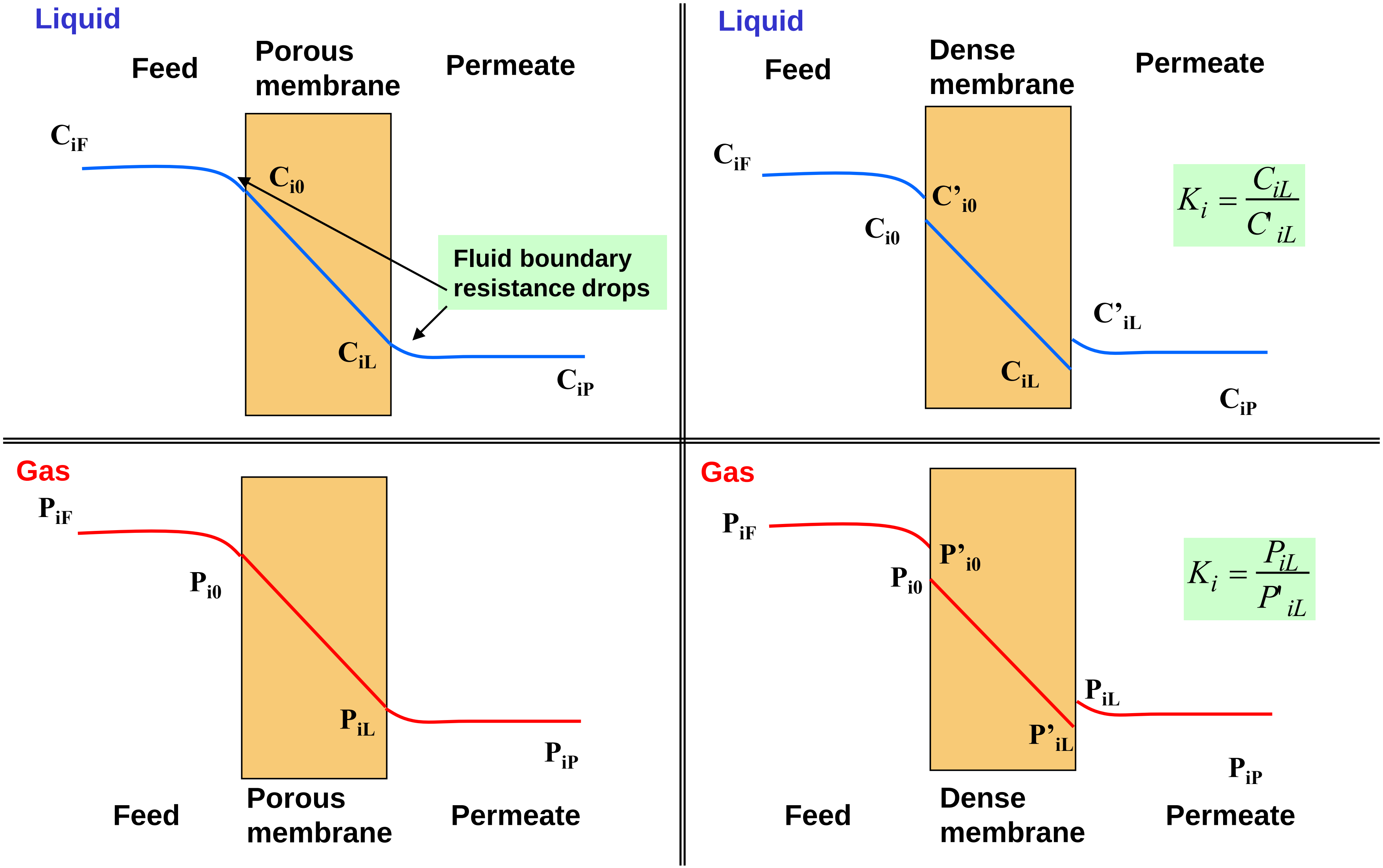
$$N_i = \frac{D_i}{l_m}\left(c_{i0} - c_{iL}\right)$$

If the pore is small relative to the mean free path, then diffusion occurs by ordinary diffusion in parallel with Knudsen diffusion. The diffusivity becomes:

$$D = \frac{\varepsilon}{\tau}\left(\frac{1}{1/D_i + 1/D_k}\right)$$

Compare to resistivity of parallel resistors.

Species Concentration Profiles.



Fluid boundary resistance drops

$$K_i = \frac{C_{iL}}{C'_{iL}}$$

$$K_i = \frac{P_{iL}}{P'_{iL}}$$

Separation of a Gas Mixture in a Dense Membrane.

The degree of separation, or the Separation Factor for a membrane separation definition is similar to the definition of relative volatility in distillation:

$$\alpha_{A,B} = \frac{K_A}{K_B} = \frac{y_A / x_A}{y_B / x_B}$$

The concentration at the membrane interface is proportional to the partial pressure adjacent to the membrane (assuming no equilibrium) by a Henry's Law constant:

$$H_{i0} = \frac{c_{i0}}{p_{i0}}$$

The membrane flux then becomes:

$$N_i = \frac{D_i c_m}{P l_m}(p_{i0} - p_{iL}) \longrightarrow N_i = \frac{H_i D_i}{l_m}(p_{i0} - p_{iL})$$

Partial pressures at the membrane surface.

If the external mass-transfer boundary layer resistances are small (no cake forms) then:

$$N_i = \frac{H_i D_i}{l_m}(p_{iF} - p_{iP})$$

Partial pressures far from the membrane surface.

Separation of a Gas Mixture in a Dense Membrane (2).

For a binary gas mixture the fluxes are:

$$N_A = \frac{H_A D_A}{l_m}\left(x_A P_F - y_A P_P\right)$$

$$N_B = \frac{H_B D_B}{l_m}\left(x_B P_F - y_B P_P\right)$$

and:

$$\frac{N_A}{N_B} = \frac{H_A D_A}{H_B D_B}\frac{\left(x_A P_F - y_A P_P\right)}{\left(x_B P_F - y_B P_P\right)}$$

When no sweep gas is used the ratio of the fluxes is equal to the ratio of the concentrations in the permeate:

$$\frac{N_A}{N_B} = \frac{y_A}{y_B} = \frac{H_A D_A}{H_B D_B}\frac{\left(x_A P_F - y_A P_P\right)}{\left(x_B P_F - y_B P_P\right)}$$

If the downstream pressure is much lower than the upstream (feed) pressure:

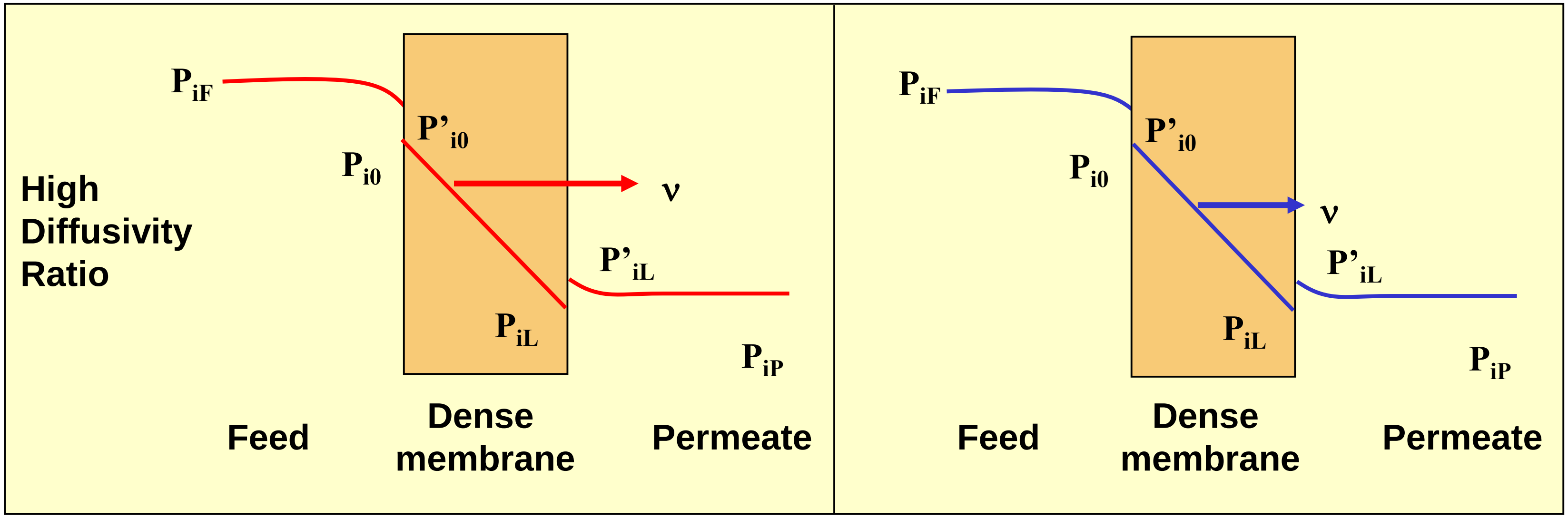
$$\frac{N_A}{N_B} = \frac{y_A}{y_B} = \frac{H_A D_A}{H_B D_B}\frac{\left(x_A P_F\right)}{\left(x_B P_F\right)} = \frac{H_A D_A}{H_B D_B}\frac{x_A}{x_B}$$

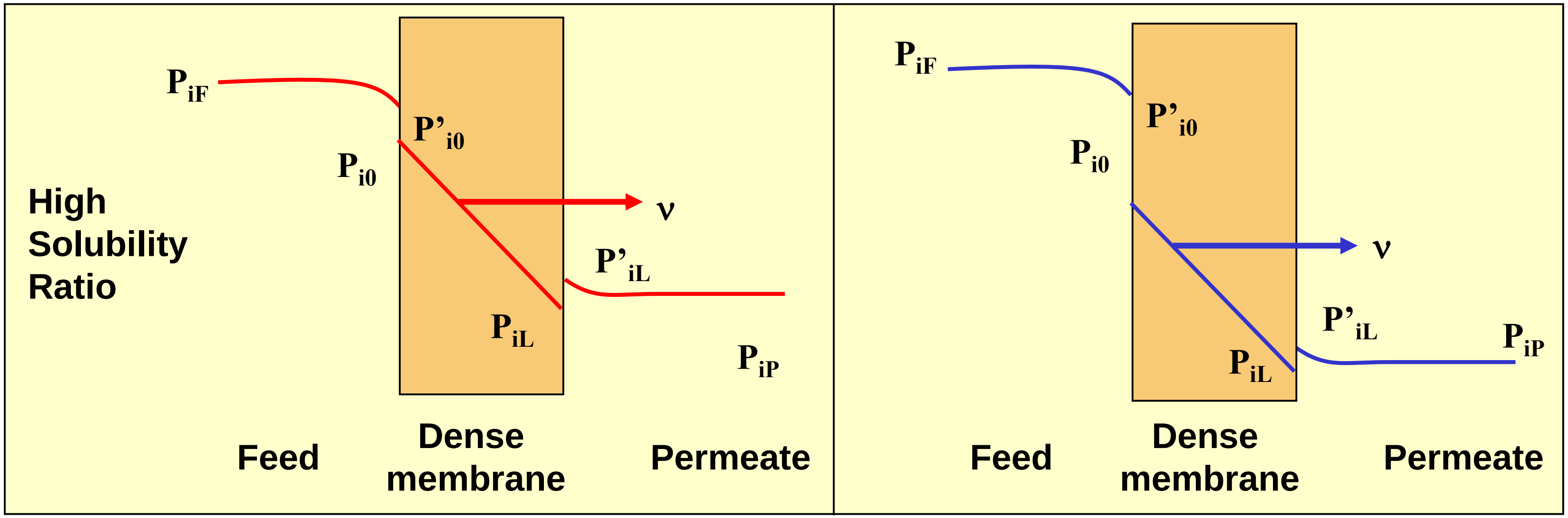
We rewrite this expression to get the Ideal Separation Factor:

$$\alpha_{A,B} = \frac{y_A / x_A}{y_B / x_B} = \frac{H_A D_A}{H_B D_B}$$

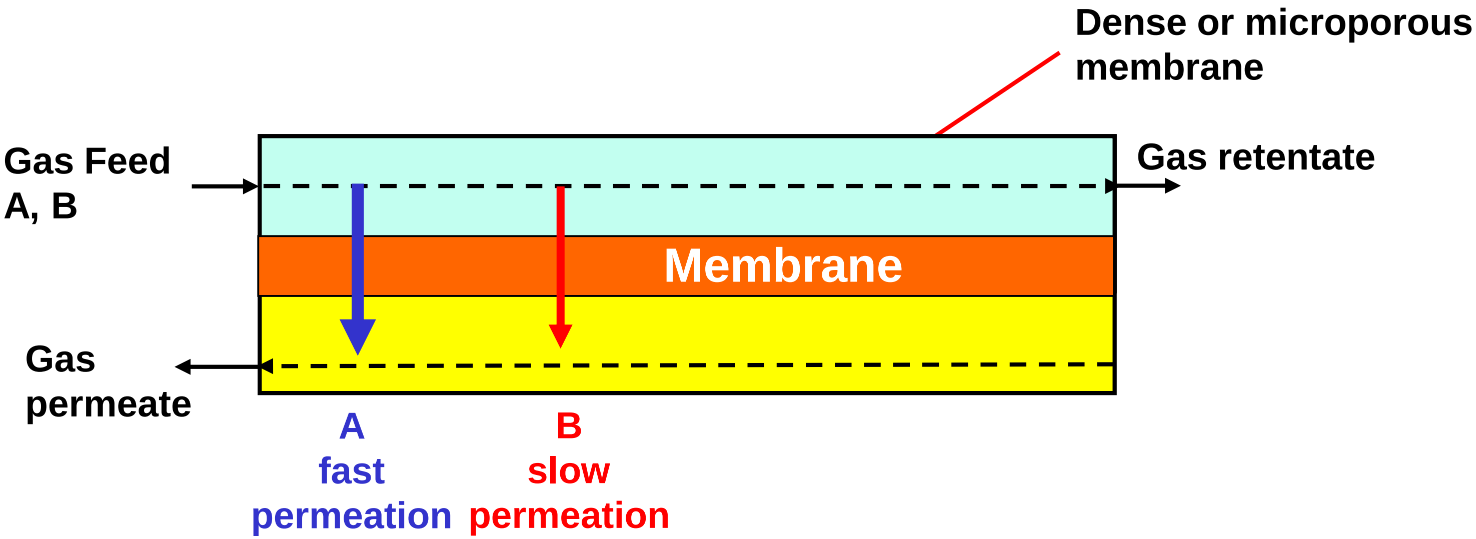
Thus, a large Separation Factor can be achieved either with a large diffusivity ratio or with a large solubility ratio or both.

Separation of a Gas Mixture in a Dense Membrane (3).



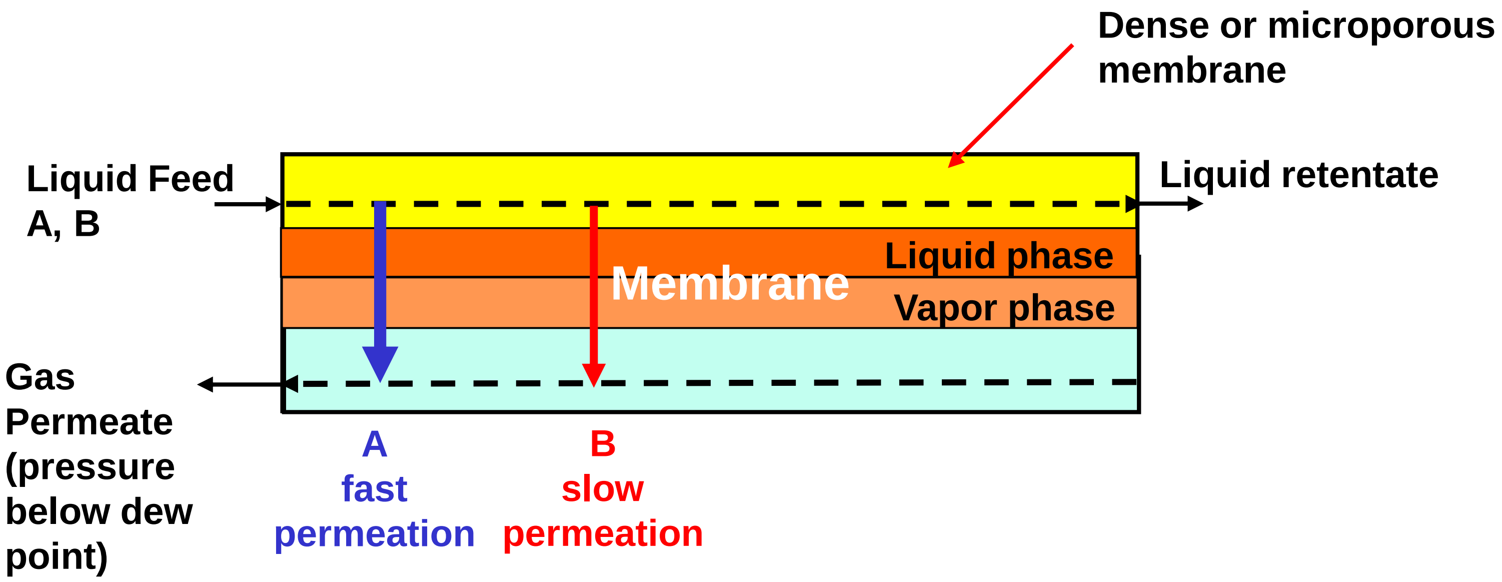


Gas Permeation.



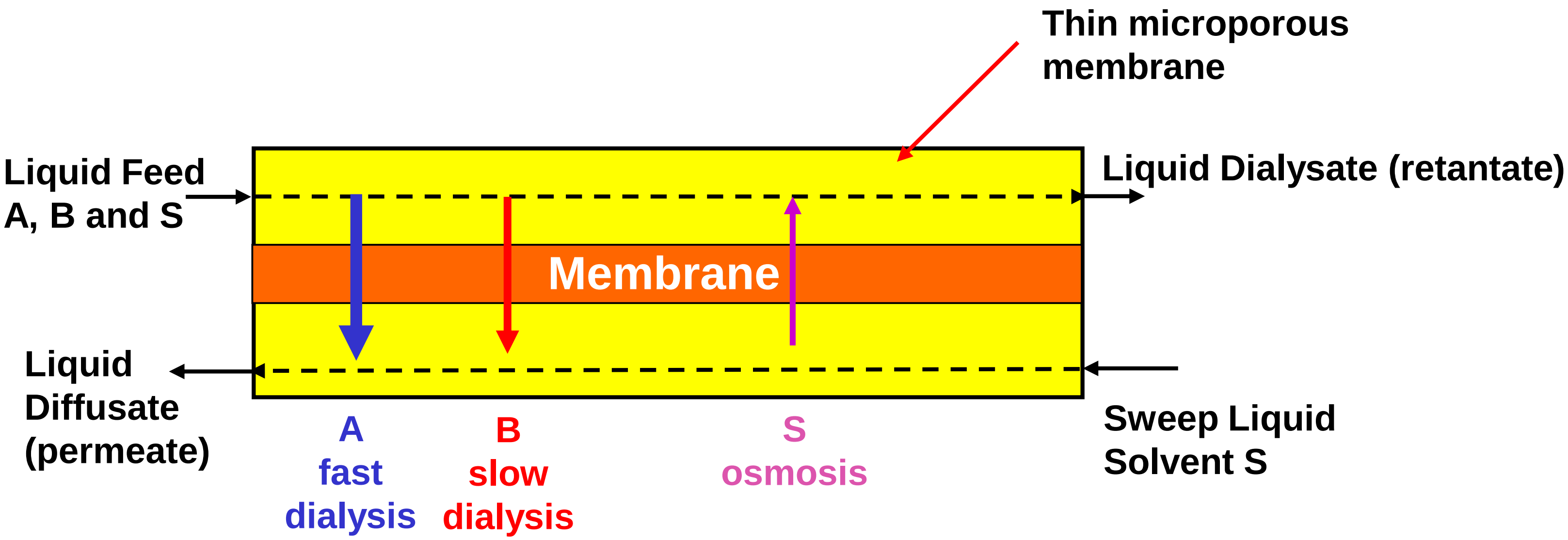
- Molecule A passes through the membrane down the concentration gradient.
- Permeation of molecule B is restricted or not allowed.
- No sweep is usually used. Permeate pressure is much lower than feed pressure.
- Membrane is chosen to be permselective; It preferentially transports one of the feed species.
- Applications include:
  - *Separation of H_2 from CH_4*
  - *O_2 enrichment of air*
  - *N_2 enrichment of air*
  - *Collection of He*

Pervaporation.



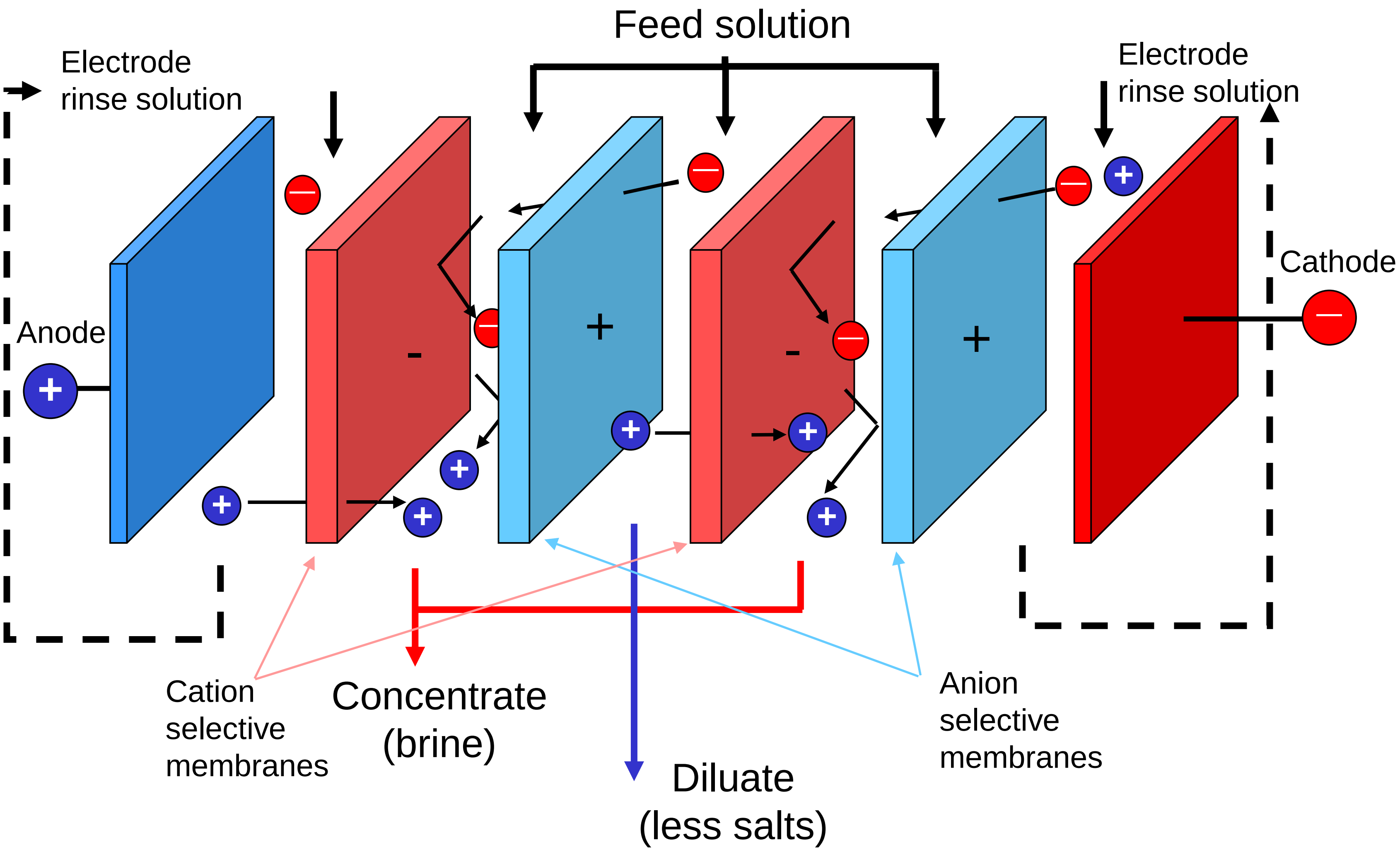
- Molecule A passes through the membrane down the concentration gradient.
- Permeation of molecule B is lower than A.
- No sweep is usually used. Permeate pressure is below dew point pressure.
- Feed pressure is above Bubble point pressure (including concentrations where A is depleted)
- Membrane is chosen to be permselective; It preferentially transports one of the feed species.

Dialysis.



- Solute A passes through the pores of the membrane down the concentration gradient.
- Solute B either cannot pass or its transport is greatly restricted.
- Solvent transports to the dialysate down a concentration gradient unless the pressure of the feed is increased above the osmotic pressure.
- Dialysis is most attractive when concentration differences between main diffusing species is large and when permeability differences between the solutes is large.
- Membranes are usually hydrophilic, less than 50 µm thick, and with pore diameters of 15 to 100Å.

Electrodialysis.



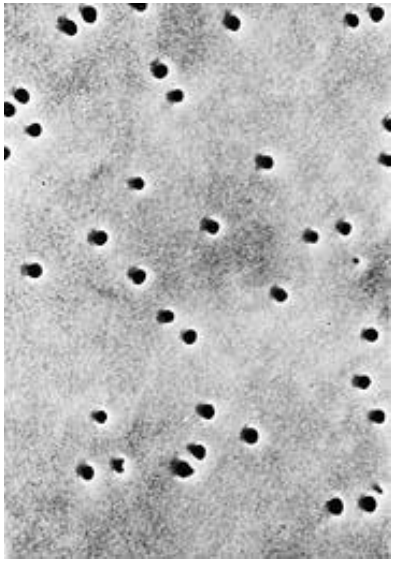
Characteristics of Membrane Processes.

Membrane process	**Feed**	**Permeate**	**Motive power**
Micro-filtration (MF)	liquid	liquid	Pressure (0.5-5 bar)
Ultra-filtration (UF)	liquid	liquid	Pressure (2-10 bar)
Nano-filtration (NF)	liquid	liquid	Pressure (5-20 bar)
Reverse osmosis (RO)	liquid	liquid	Pressure (10-80 bar)
Gas separation (GS)	gas	gas	Pressure (partial)
Facilitated transport (FT)	gas	gas	Chemical Ads. and Pres.
Vapor Permeation (VP)	vapor	vapor	Pressure (partial)
Perevaporation (PV)	liquid	vapor	Pressure (partial)
Electrodialysis (ED)	liquid	liquid	Electrical potential

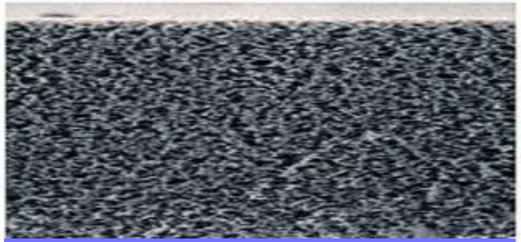
Typical Operative Conditions of Membrane Processes.

Features	Reverse Osmosis	Nanofiltration	Ultrafiltration	Microfiltration
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Symmetrical Asymmetrical
Wall Thickness	150 *mm*	150 *mm*	150-250 *mm*	10-150 *mm*
Film thickness	1 *mm*	1 *mm*	1 *mm*	various
Pore size	<0.002 *mm*	<0.002 *mm*	0.02-0.2 *mm*	0.2-5 *mm*
Rejects	HMWC, LMWC, Sodium, Chloride, glucose, amino acids, proteins	HMWC, mono-, di-, and oligo-saccharides, polyvalent anions	Macromolecules, proteins, polysaccharides, virus	Particulates, clay, bacteria
Membrane module	Tubular, spiral-wound, plate & frame	Tubular, spiral-wound, plate & frame	Tubular, hollow-fiber, spiral-wound, plate & frame	Tubular, hollow-fiber, plate & frame
Material	CA, TFC	CA, TFC	CA, TFC, Ceramic	CA, TFC, Ceramic, PVDF, Sintered
Pressure	15-150 *bar*	5-35 *bar*	1-10 *bar*	<2 *bar*
Flow	10-50 $l \cdot m^{2} \cdot h^{-1}$	10-100 $l \cdot m^{2} \cdot h^{-1}$	10-200 $l \cdot m^{2} \cdot h^{-1}$	50-1000 $l \cdot m^{2} \cdot h^{-1}$

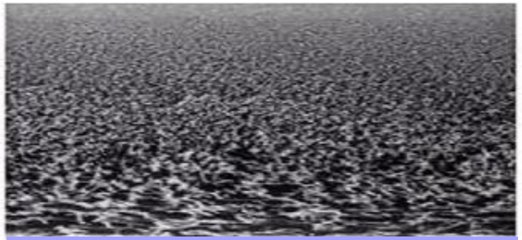
Some Membrane Types.



RO Reverse Osmosis

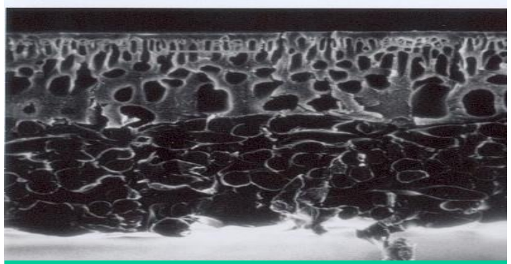


Traditional MF



Asymmetrical MF

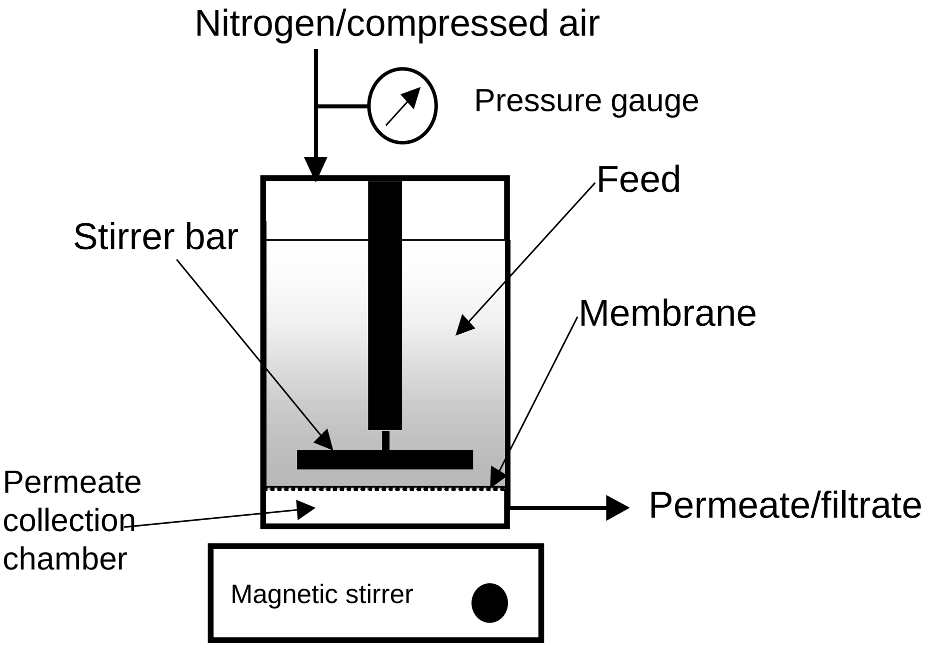
Very asymmetrical MF



Ultrafiltration UF

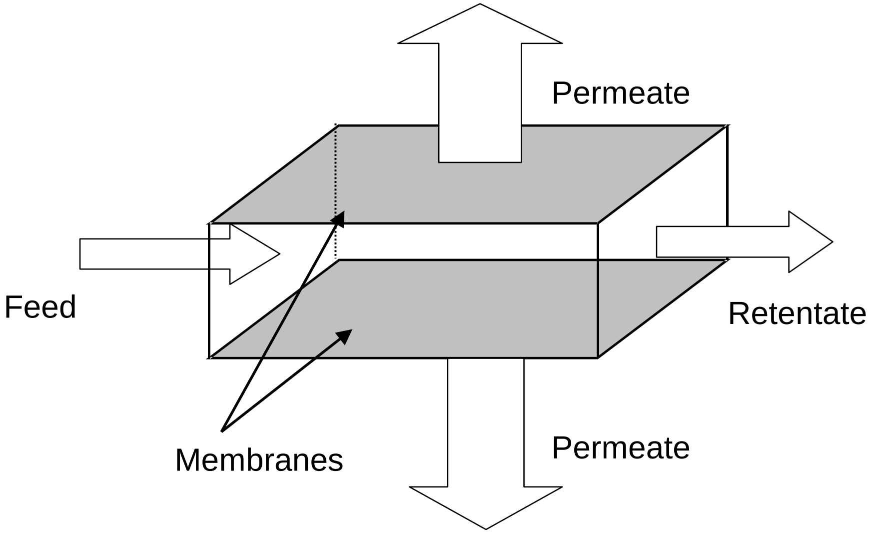
‘Basic Principles of Membrane Technology’, Mulder, M., 2nd. Edt., Kluwer Academic Publishers, 1996

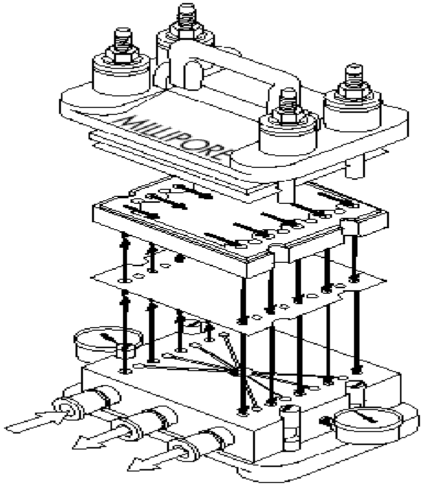
Some Membrane Modules (Stirred Cells).



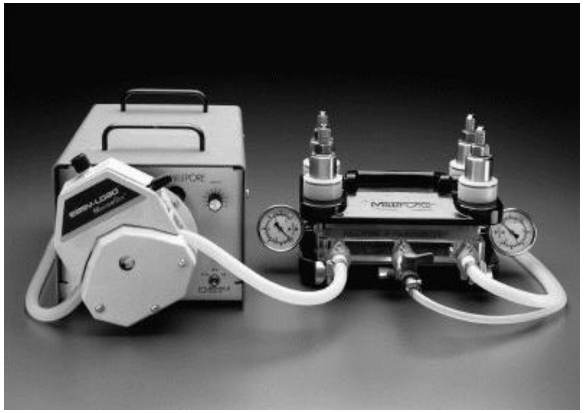
- Research and small-scale manufacturing.
- Used for microfiltration and ultrafiltration.
- Excellently suited for process development work.

Flat Sheet Tangential Flow Module.

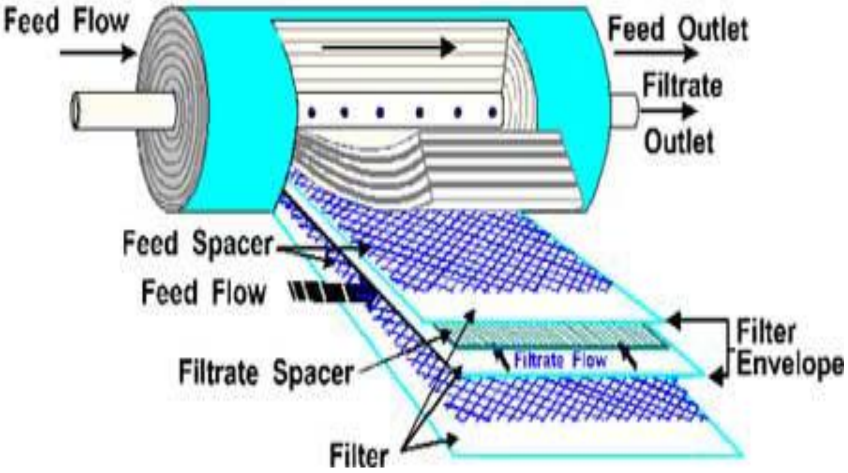




- Similar plate and frame filter press.
- Alternate layers of membranes, support screens and distribution chambers.
- Used for microfiltration and ultrafiltration.

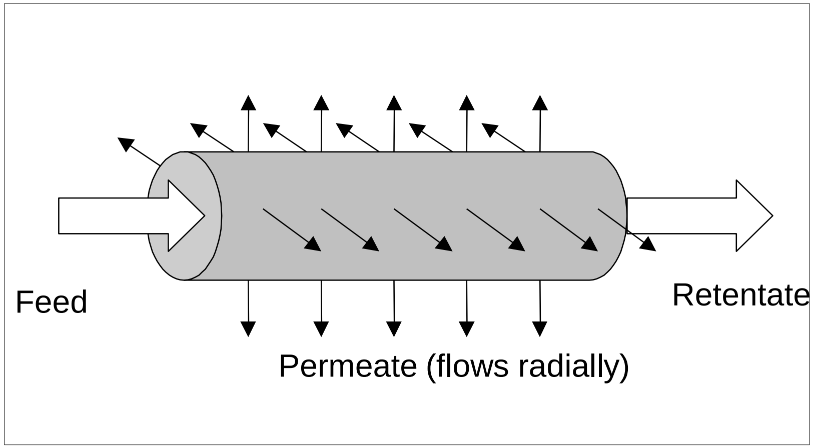


Spiral Flow Membrane Module.

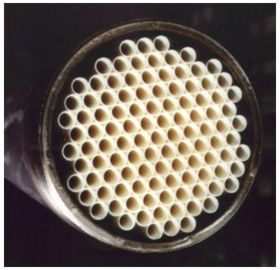


- Flat sheet membranes are fused to form an envelope.
- Membrane envelop is spirally wound along with a feed spacer.
- Filtrate is collected within the envelop and piped out.

Tubular Membrane Module.

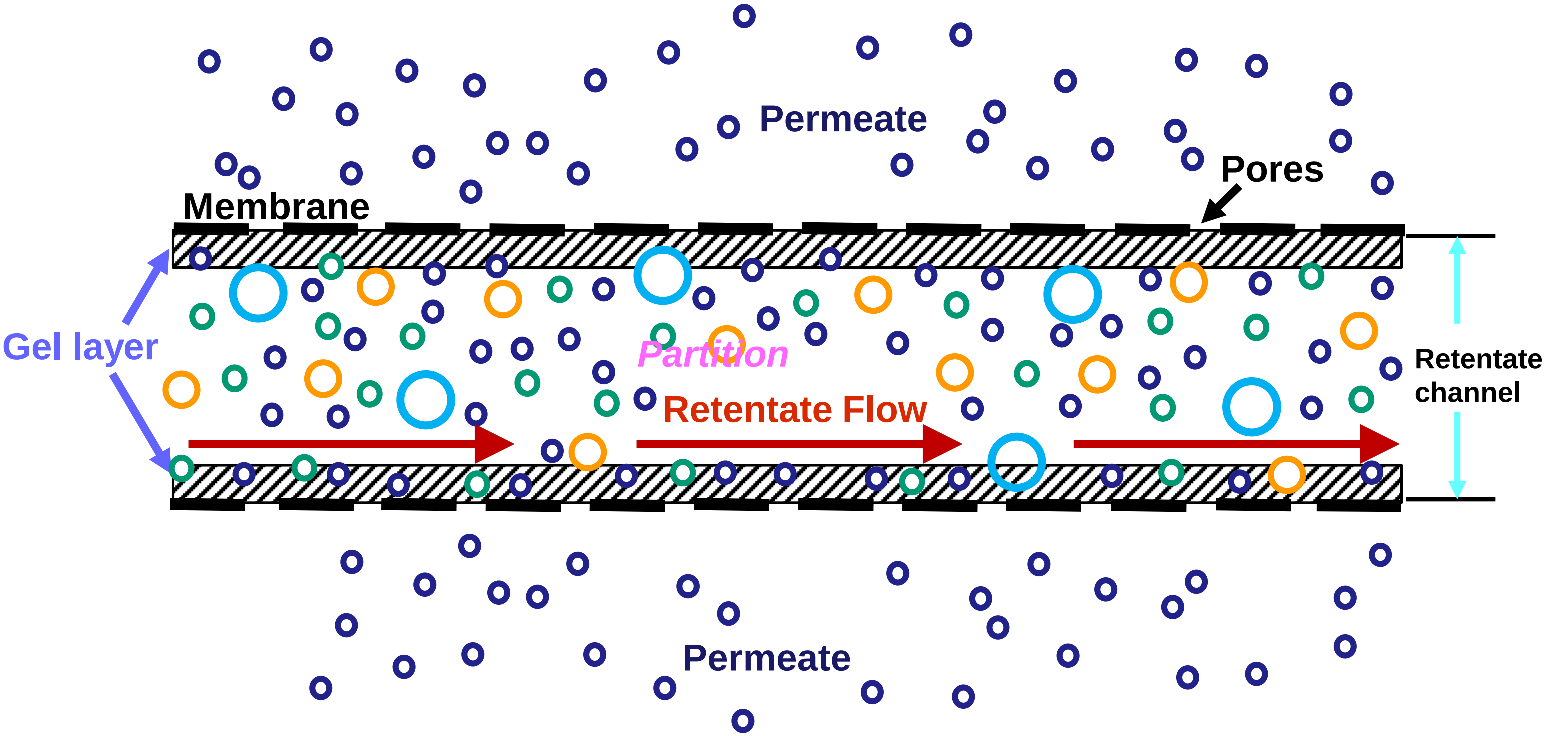


- Cylindrical geometry; wall acts as the membrane;
- Tubes are generally greater than 3 mm in diameter;
- Shell and tube type arrangement is preferred;
- Flow behaviour is easy to characterise.

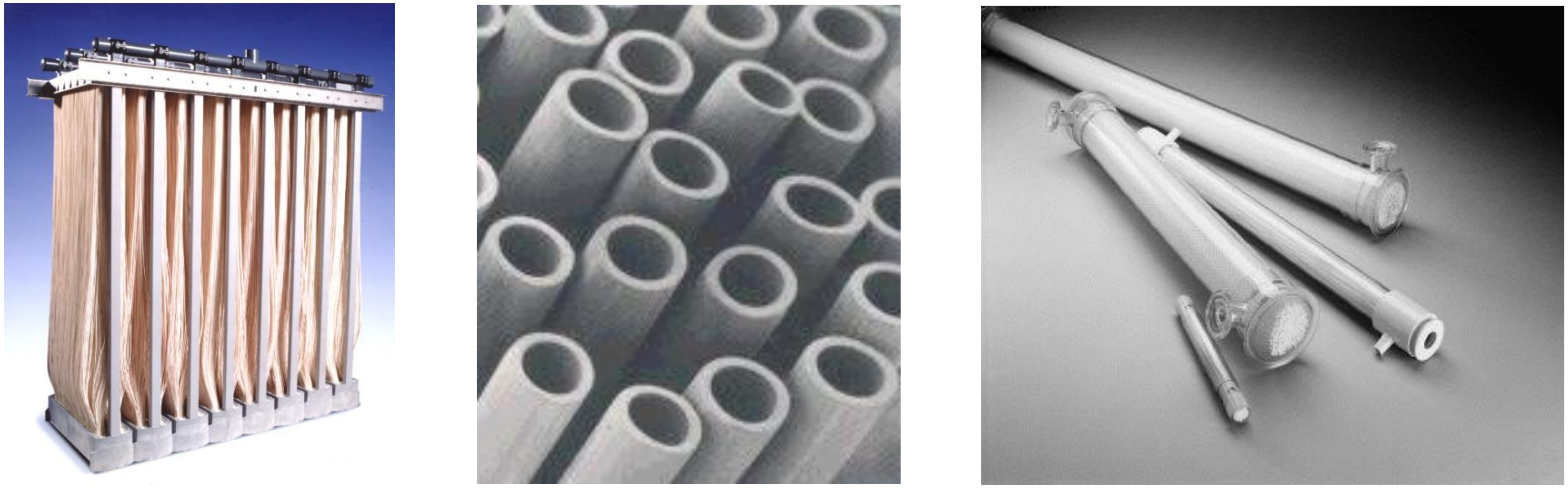


Tangential Flow Filtration.

Tangential flow filtration (TFF) (also Cross-flow filtration) is a separation process widely used in bio-pharmaceutical and food industries. It differs from other filtration systems in that the fluid is passed parallel to the filter, rather than being pushed through a membrane perpendicularly which can clog the filter media. The advantages are continuous filtration and reproducible performance.



Hollow Fibre Membrane Module.

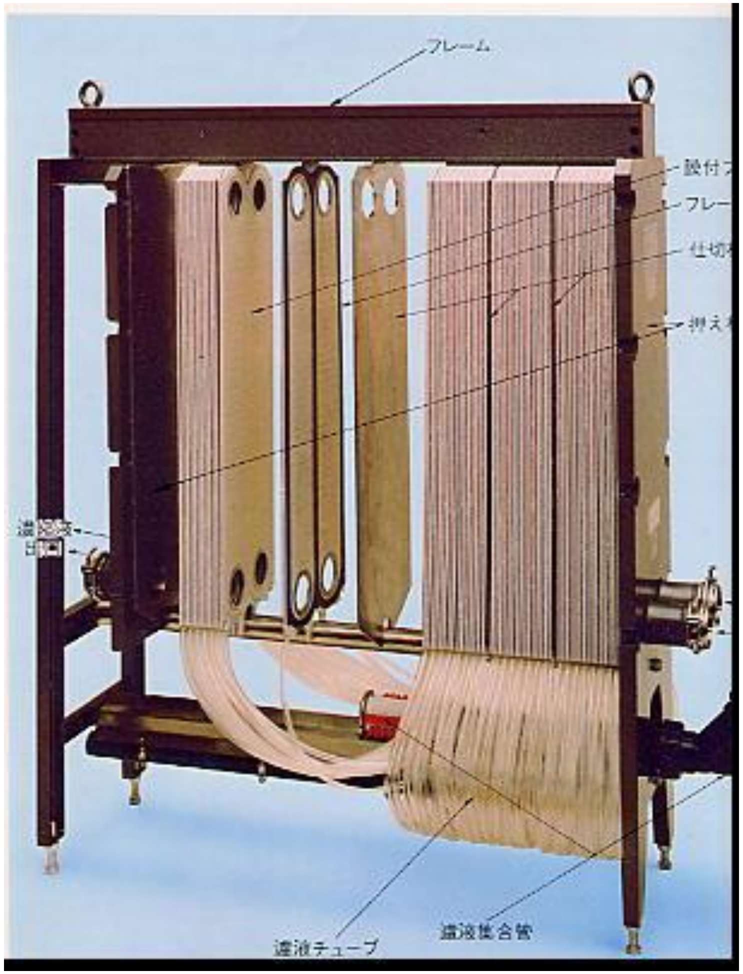


- Similar to tubular membrane module
- Tubes or fibres are 0.25 - 2.5 *mm* in diameter
- Fibres are prepared by spinning and are potted within the module
- Straight through or U configuration possible
- Typically several fibres per module.

Side-stream Ceramic Modules.

Made in permeable inorganic material worked in order to obtain hollows with inside several pores of variable forms and sizes.

Plate and Frame Module.



UF

Polyacrylonitrile (PAN)

Polyvinylidenefluoride (PVF)

Polysulfone (PS)

Sulfonated Polysulfone(SPS)

Building scale wastewater reclamation

Food processing

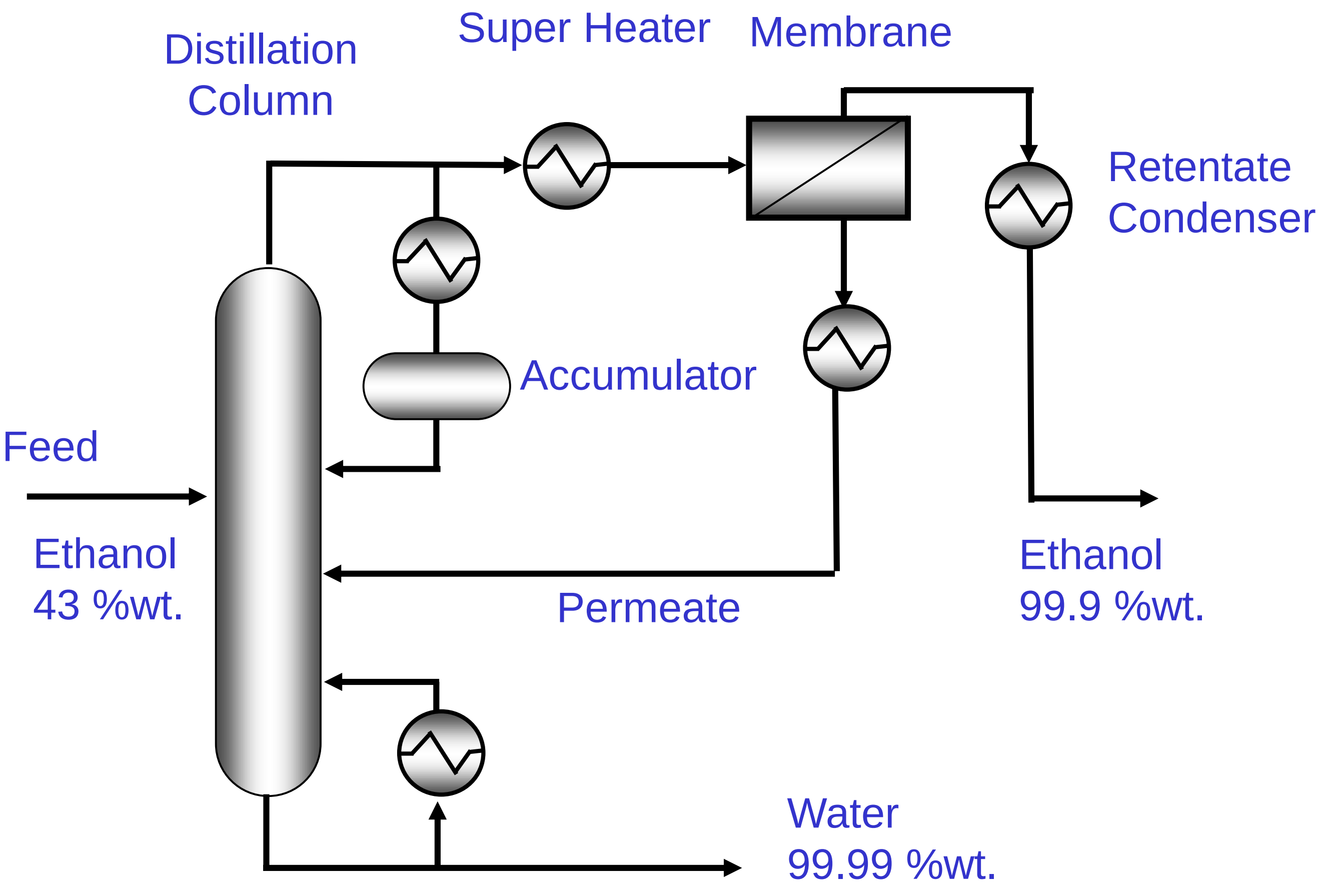
From Mitsui Petrochemical Catalogue

Typical Operative Conditions of Membrane Modules.

	Module Type			
Characteristic	**Flat plate**	**Spiral Wound**	**Shell and Tube**	**Hollow Fibre**
Packaging density ($m^2 \cdot m^{-3}$)	Moderate (200-400)	Moderate (300-900)	Low (150-300)	High (9000-30000)
Fluid management	Good	Good	High pumping costs	Good
Suspended solids capability	Moderate	Poor	Good	Poor
Cleaning	Sometimes difficult	Sometimes difficult	Facile	Backlashing possible
Replacement	Sheets or cartridge	Cartridge	Tubes	Cartridge

Combining Ceramic Membranes with Distillation.

Development of an industrially viable bio-ethanol dehydration process



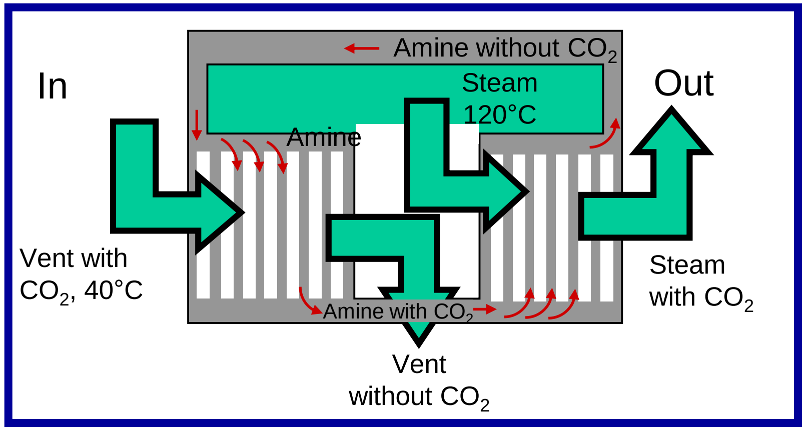
Advantages of Membrane Separations.

Conventional Process

Kvaerner process for the separation/capture of CO_2 from exhausted turbine gases.

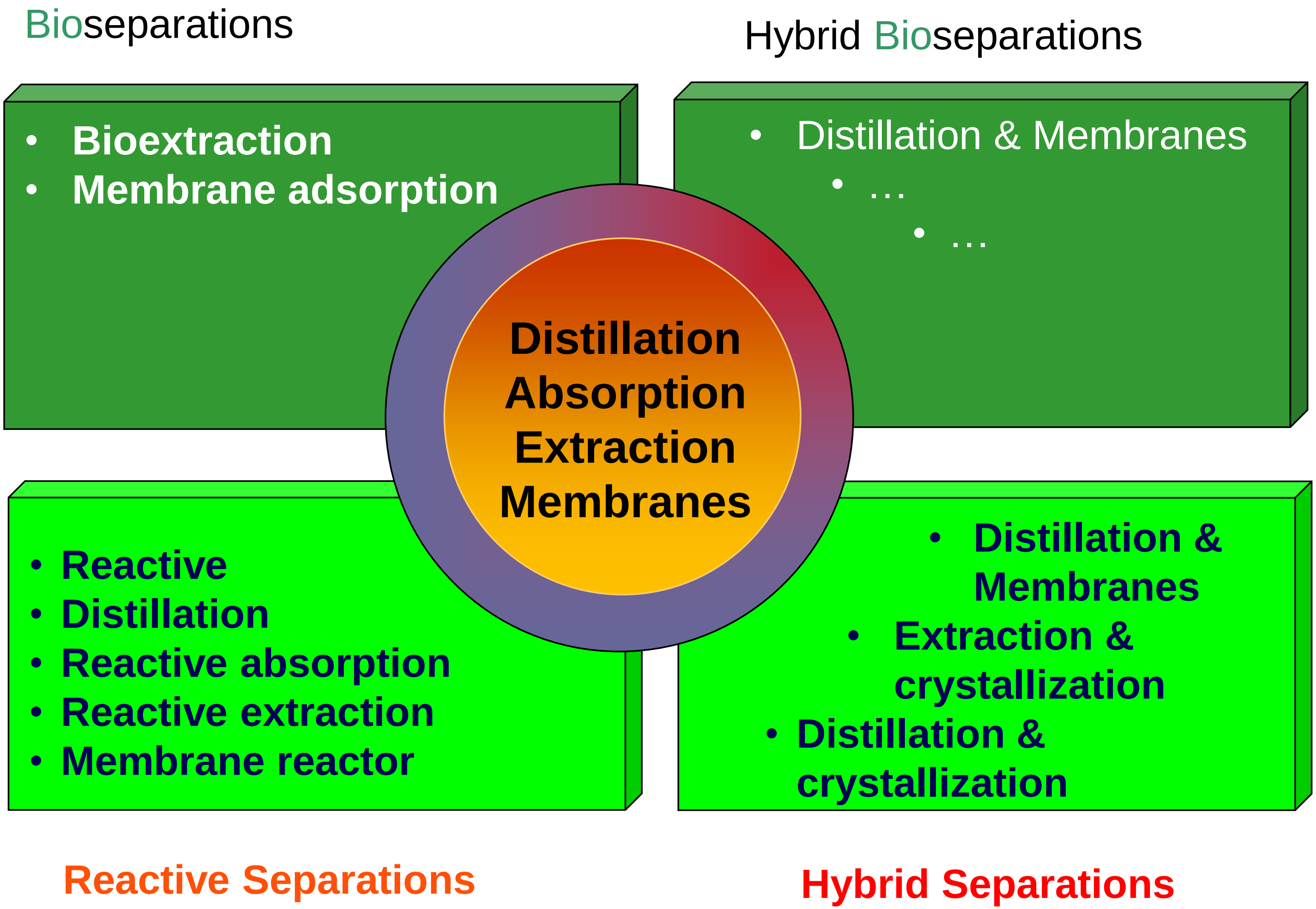
75% weight reduction;
65% size reduction

Membrane Process



Kværner

Reactive, Hybrid and Bio-separations.



Bioseparations

- Bioextraction
- Membrane adsorption

Hybrid Bioseparations

- Distillation & Membranes
  - …
    - …

Distillation
Absorption
Extraction
Membranes

- **Reactive**
- **Distillation**
- **Reactive absorption**
- **Reactive extraction**
- **Membrane reactor**

- **Distillation & Membranes**
- **Extraction & crystallization**
- **Distillation & crystallization**

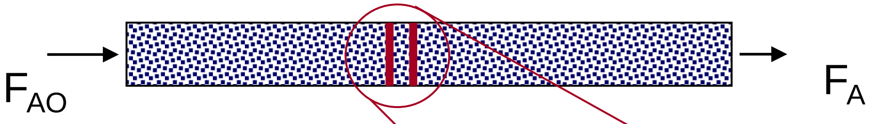
Reactive Separations

Hybrid Separations

Catalytic Reactions: Packed Bed Reactor.

Advantages

- No loss of catalyst
- Ensure high surface area for reaction
- High conversion and selectivity possible
- Wide range of operating conditions
- Enhance mixture between reagents



(Input – Output) + Gen = Accretion

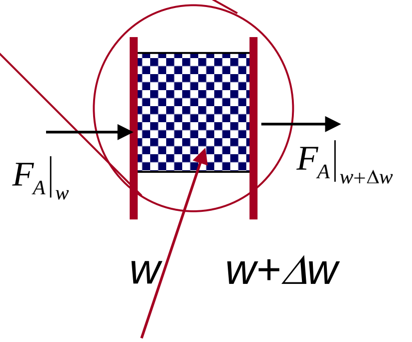
$$F_A|_w - F_A|_{w+\Delta w} + (r_A^{'})\Delta w = 0$$

$$\frac{F_A|_w - F_A|_{w+\Delta w}}{\Delta w} = -(r_A^{'})$$

$$-\frac{dF_A}{dw} = -(r_A^{'})$$

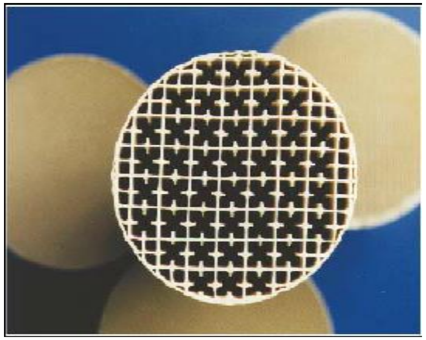
$$\boxed{F_{AO}\frac{dX}{dw} = -(r_A^{'})}$$

$$\boxed{w = F_{A0}\int_{X=0}^{X=X}\frac{dX}{(-r_A^{'})}}$$



Catalyst mass = Δw

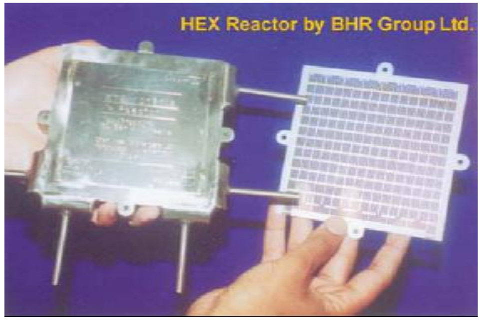
Structured Packing and Catalysts.

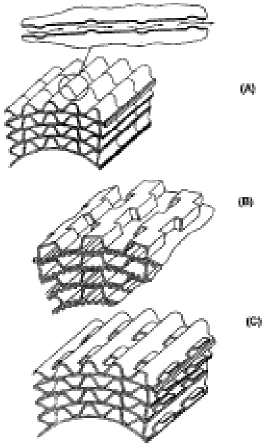


Internally finned monolith
TUD/Corning

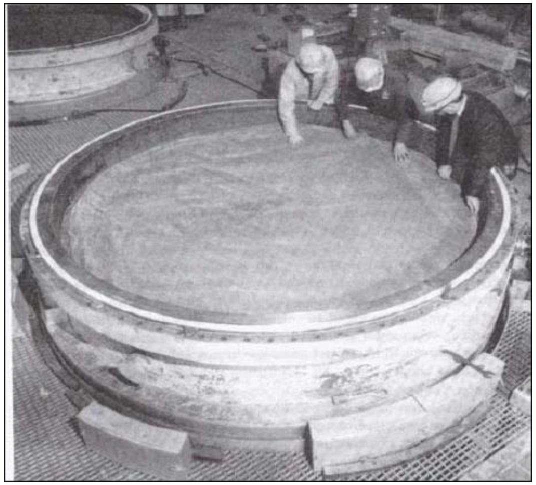
KATAPAK-S Sulzer

Microreactors
Process-on-a-chip
Platelet with integrated mixer, reactor and heat exchanger



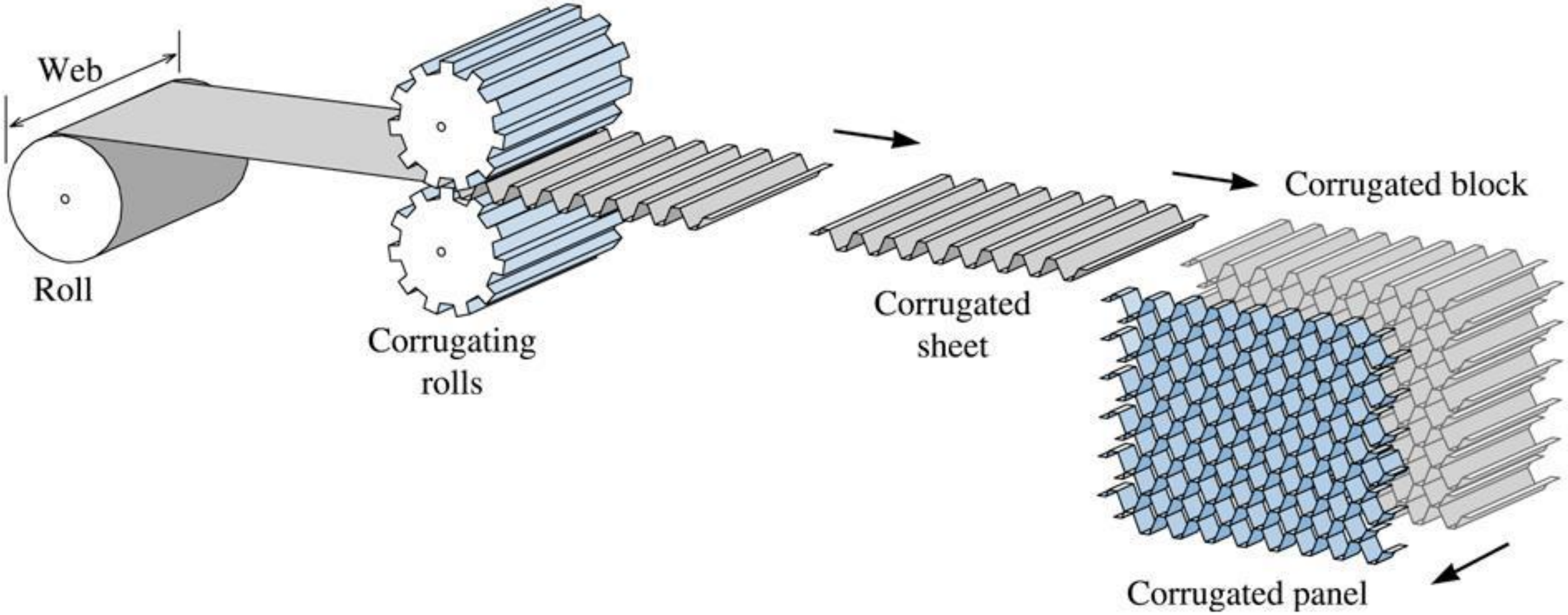


“Metal Monoliths”
Increased Turbulence



Gauzes

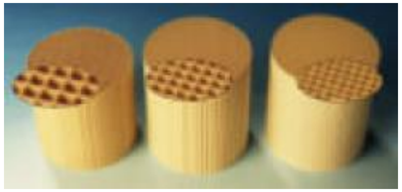
Metallic Monolith Reactor.



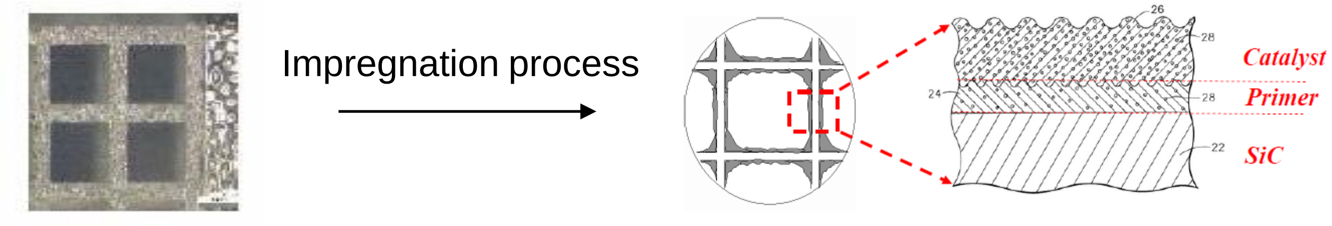
In the corrugation method for producing a honeycomb core, the material (such as aluminum) is corrugated between two rolls. The corrugated sheets are joined together with adhesive and then cut to the desired thickness.

Ceramic Monolith.

- Long and reliable lifetime
- High resistance to temperature and pressure
- High stability to organic media
- Rigid with no creep or deformation
- Stable over a wide pH range
- Corrosion and abrasion resistant
- Insensitive to bacterial action
- Can be repeatedly sterilised by stem or chemical
- Grater void area per unit area of filtration surface
- Consistent pore size
- Can process highly viscous fluids
- Possibility of regeneration after fouling
- Membrane bonded to substrate by strong ceramic bonds

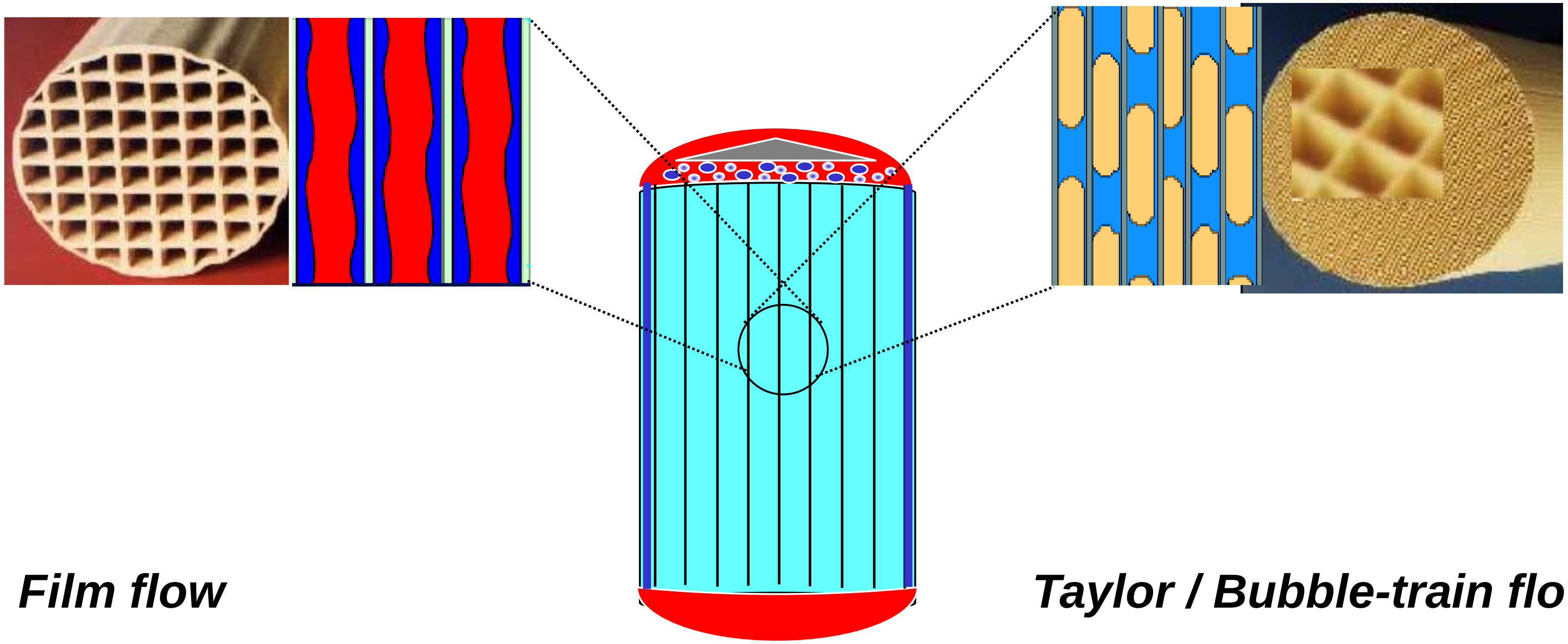


SiC; Cordierite



Impregnation process

Monoliths: Efficient Multi-phase Reactors Film Flow versus Taylor Flow.



Film flow

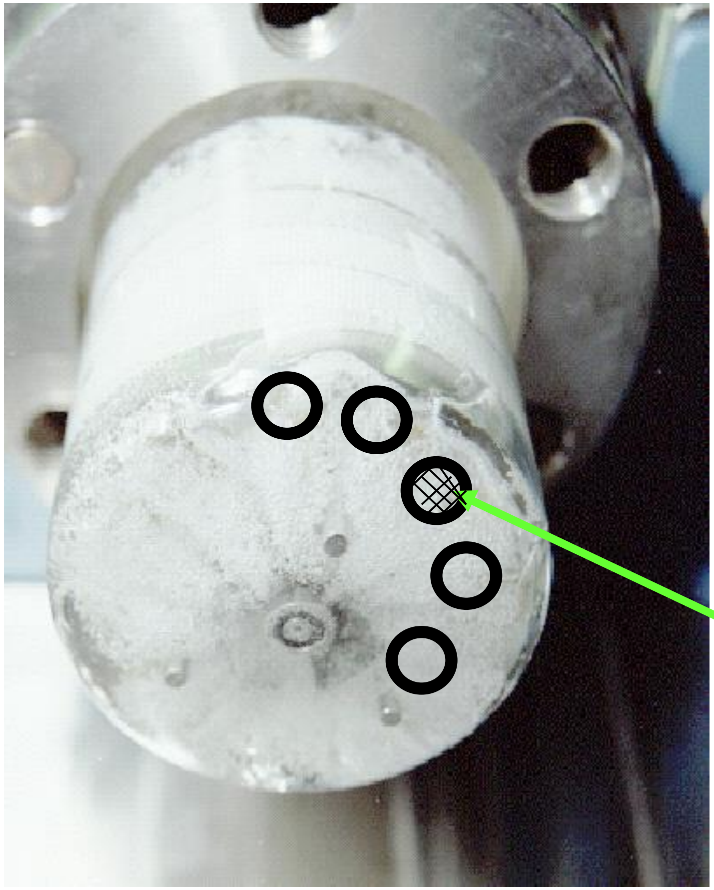
- Channels: 2 - 5 mm
- u_{LS} = 0.005 - 0.03 m·s^{-1}
- counter- and co-current

Taylor / Bubble-train flow

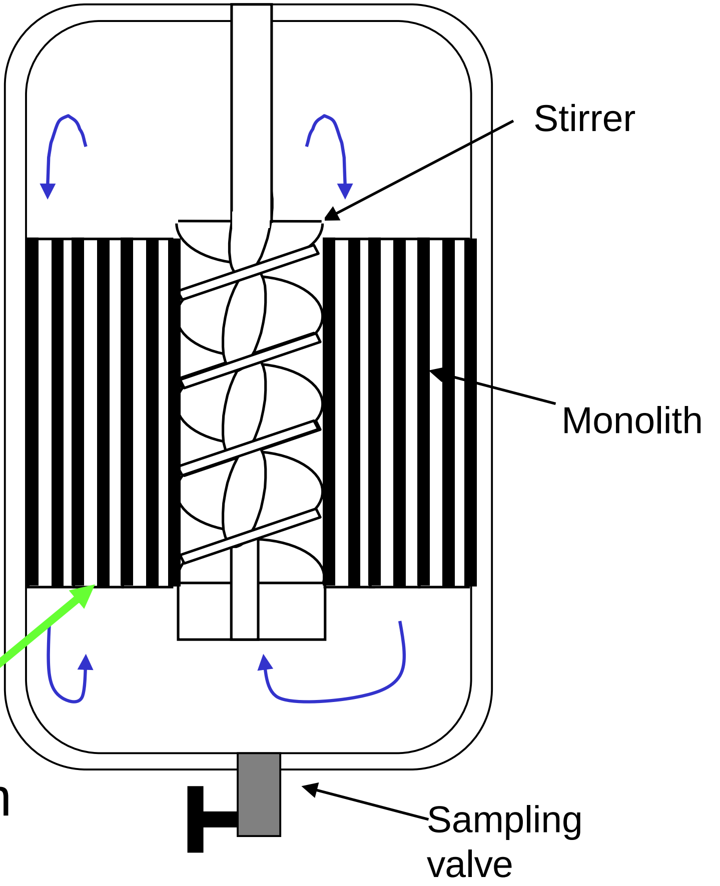
- Channels: 1 - 2 mm
- u_{LS} = 0.05 - 0.15 m·s^{-1}
- co-current down

Catalytic distillation, stripping **Process Intensification** **High rates**

SISR – Screw Impeller Stirred Reactor.



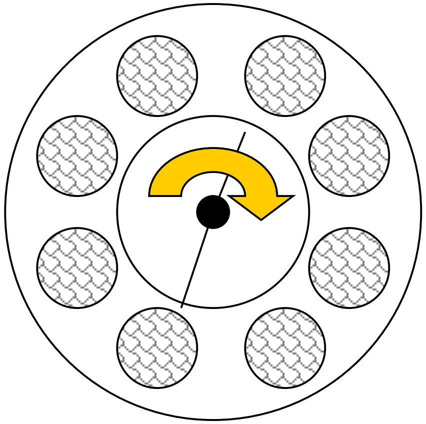
Monoliths
12 pc.
10 × 50 mm

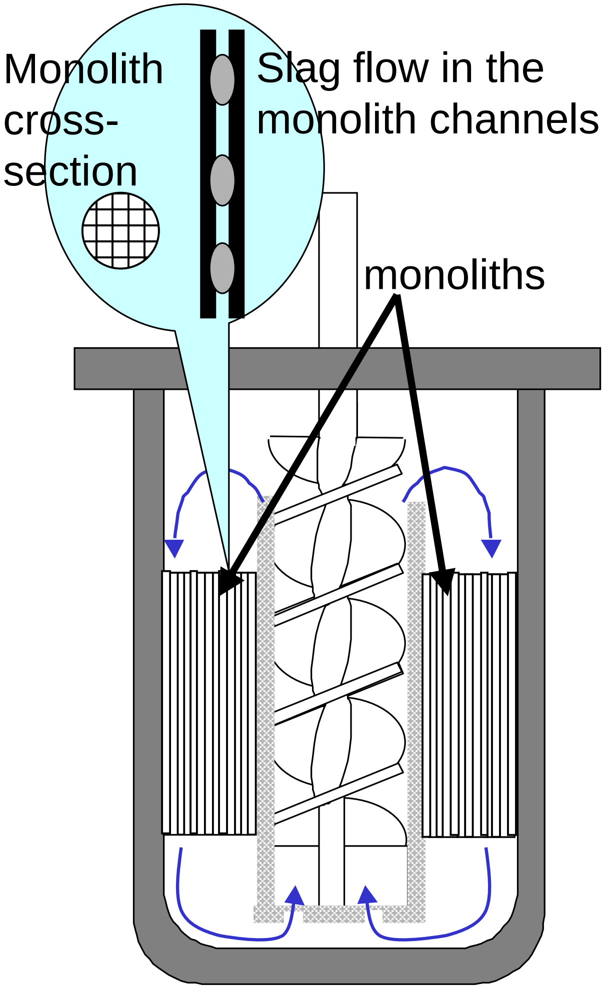


Slag Flow.

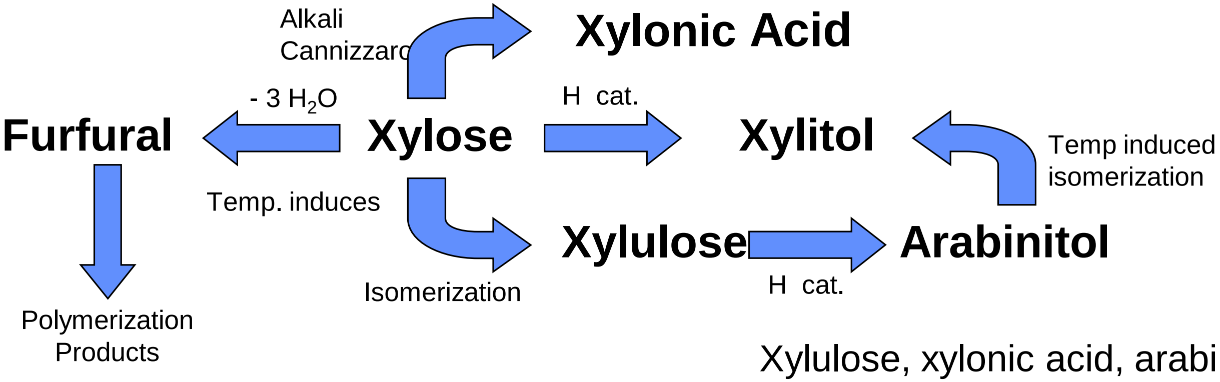
Recirculation within the liquid slug
→ enhanced mass transfer

The liquid film has a varying thickness and is alternatively exposed to the gas or liquid with different concentrations





D-Xylose to Xylitol.



Alkali Cannizzaro

Xylonic Acid

- 3 H_2O

Furfural

Xylose

H cat.

Xylitol

Temp induced isomerization

Temp. induces

Xylulose

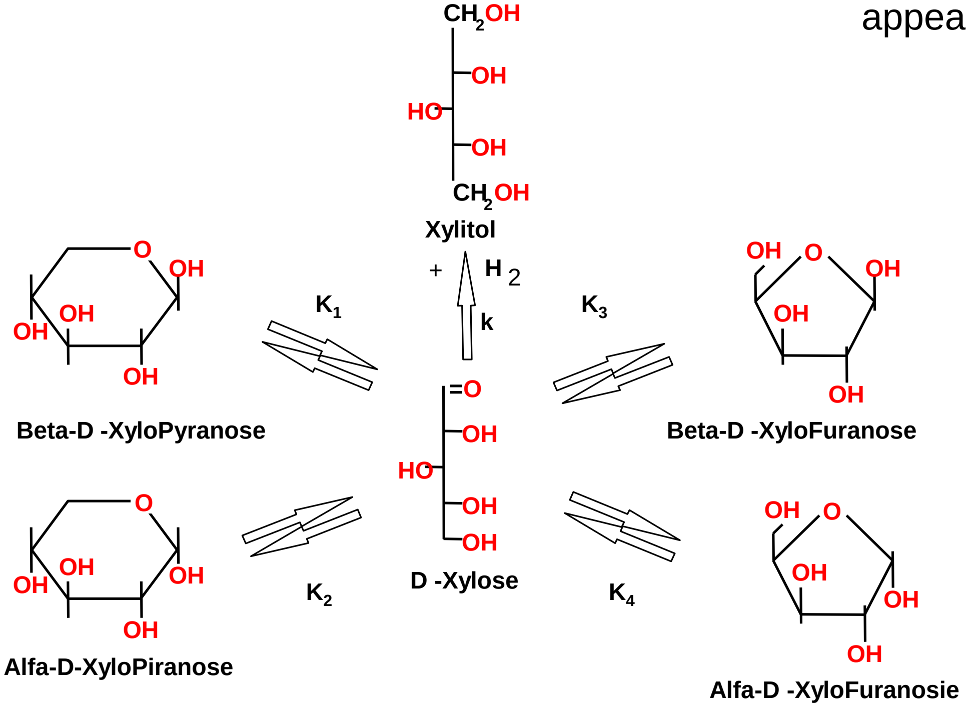
Arabinitol

Isomerization

H cat.

Polymerization Products

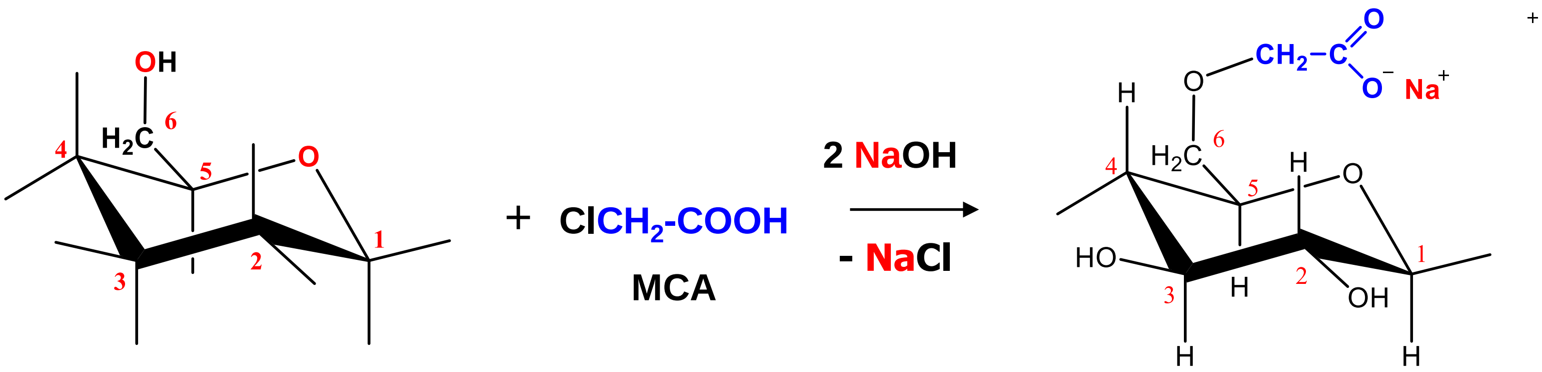
Xylulose, xylonic acid, arabinitol and furfural appear as by-products in low quantities.



The sugar equilibria

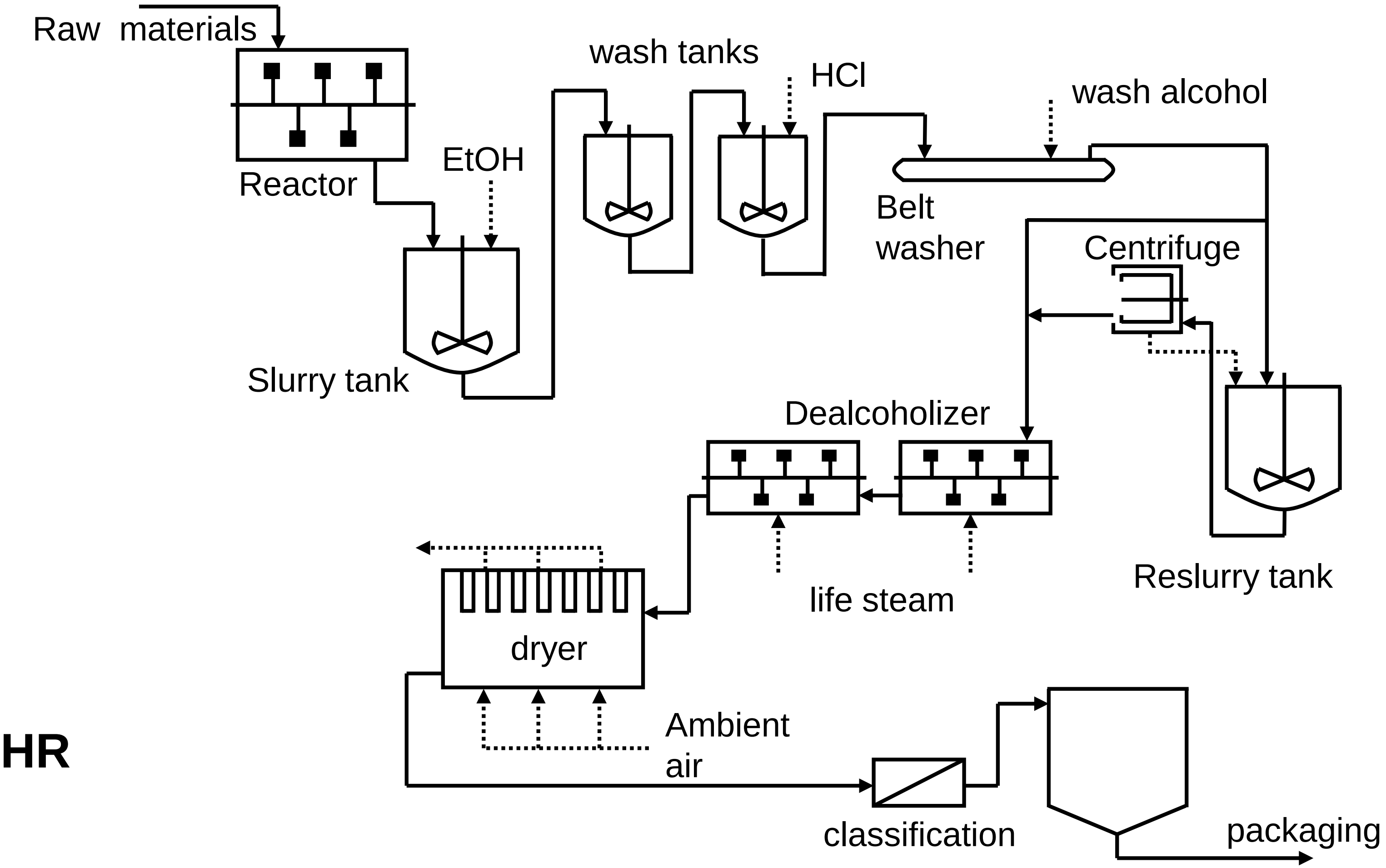
Carboxymethyl Cellulose Process.

- **CMC = carboxymethyl ether of cellulose, a polymer produced from cellulose and MCA, using both NaOH and EtOH or i-PrOH.**



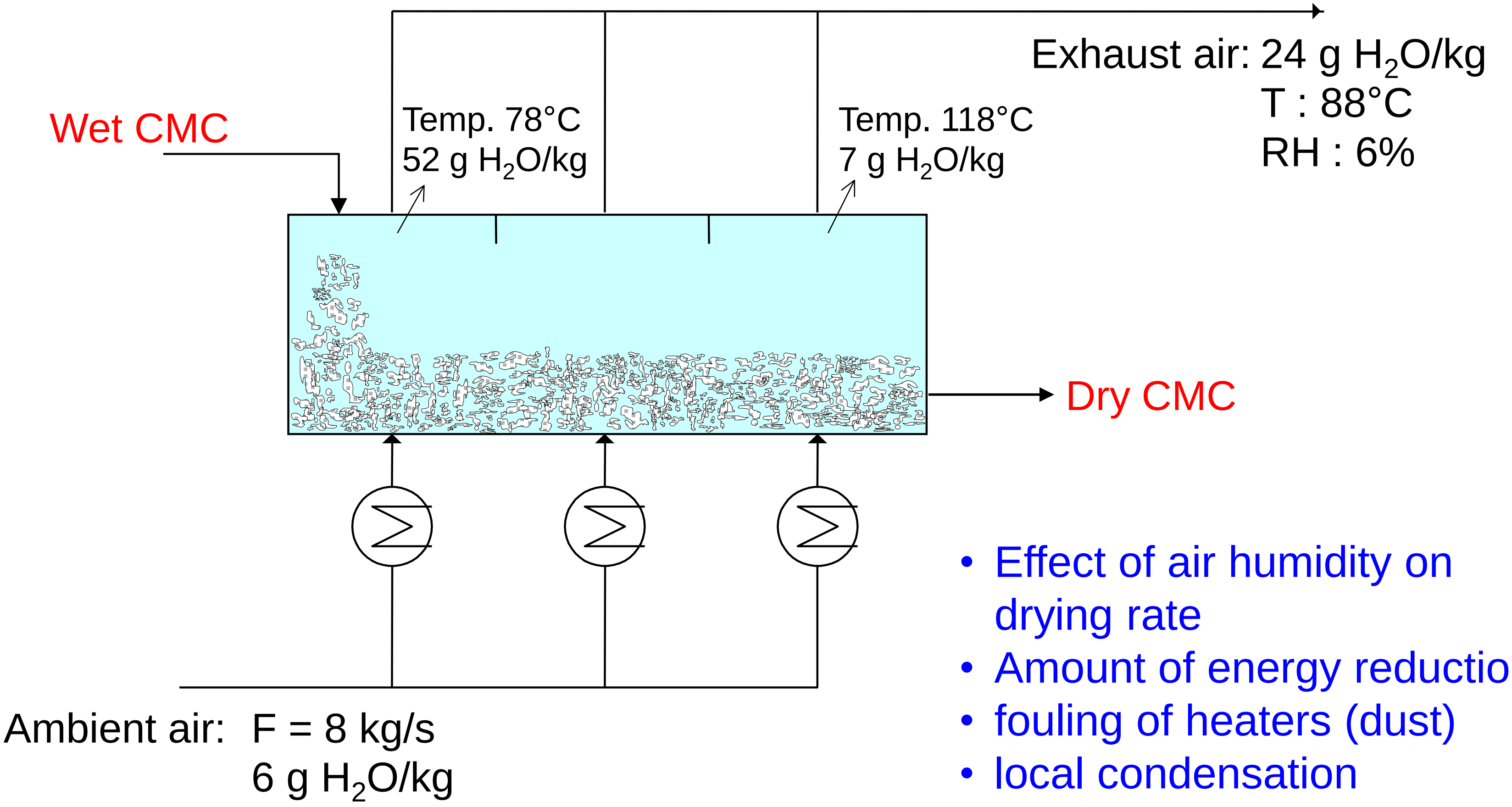
- **Different grades, depending on type of cellulose, degree of substitution, purity, etc.**
- **Wide variety of applications (food, detergents, drilling).**

CMC (simplified) Process Scheme.



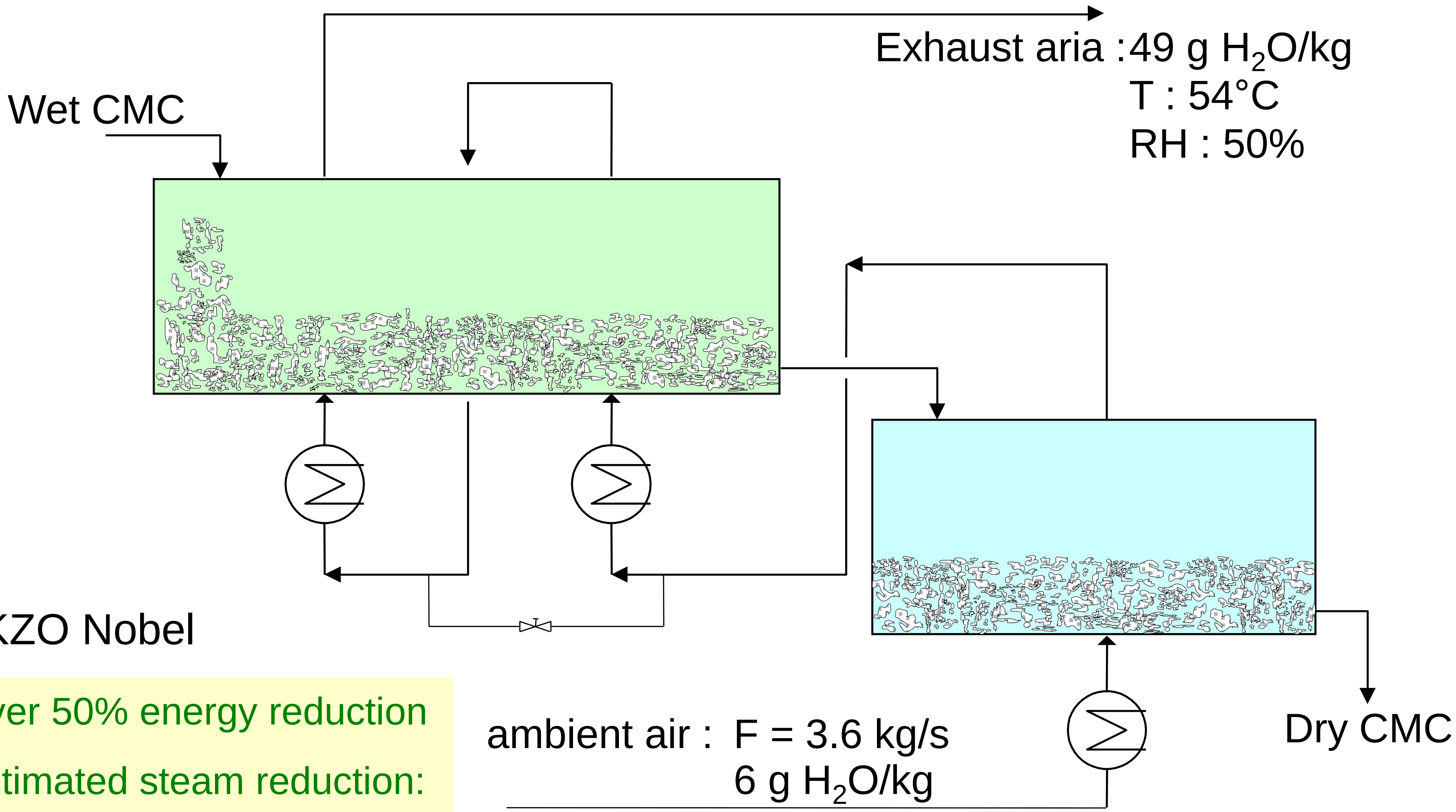
BHR

(Original) CMC Dryer.



- Effect of air humidity on drying rate
- Amount of energy reduction
- fouling of heaters (dust)
- local condensation
- valid for all types of CMC
- controllability of the system

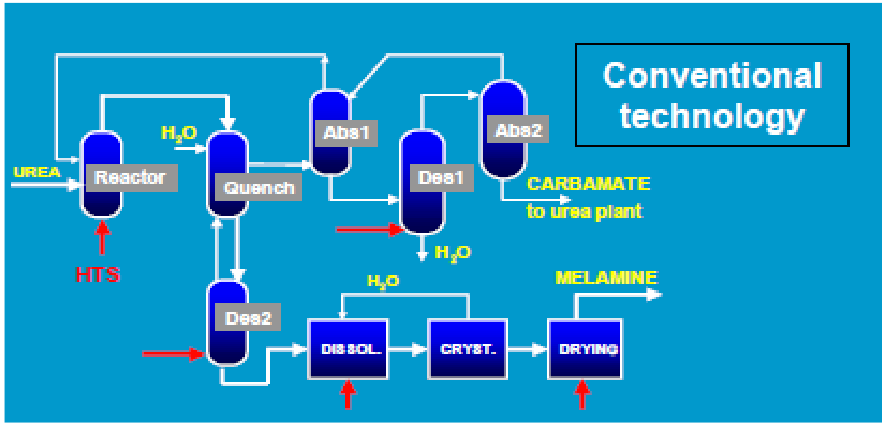
Modified CMC Dryer



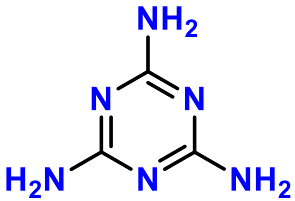
AKZO Nobel

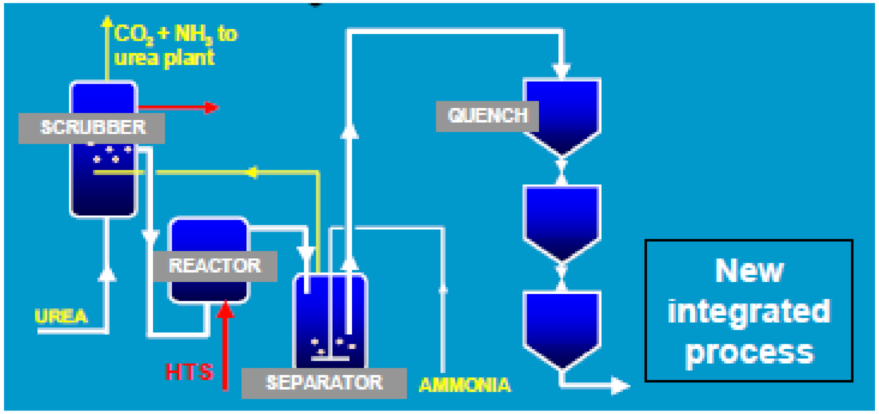
- Over 50% energy reduction
- Estimated steam reduction: 10.000 ton/year

DSM Melamine Technology



$$6\ (NH_2)_2CO \rightarrow C_3H_6N_6 + 6\ NH_3 + 3\ CO_2$$





Utilities (per ton of Melamine):

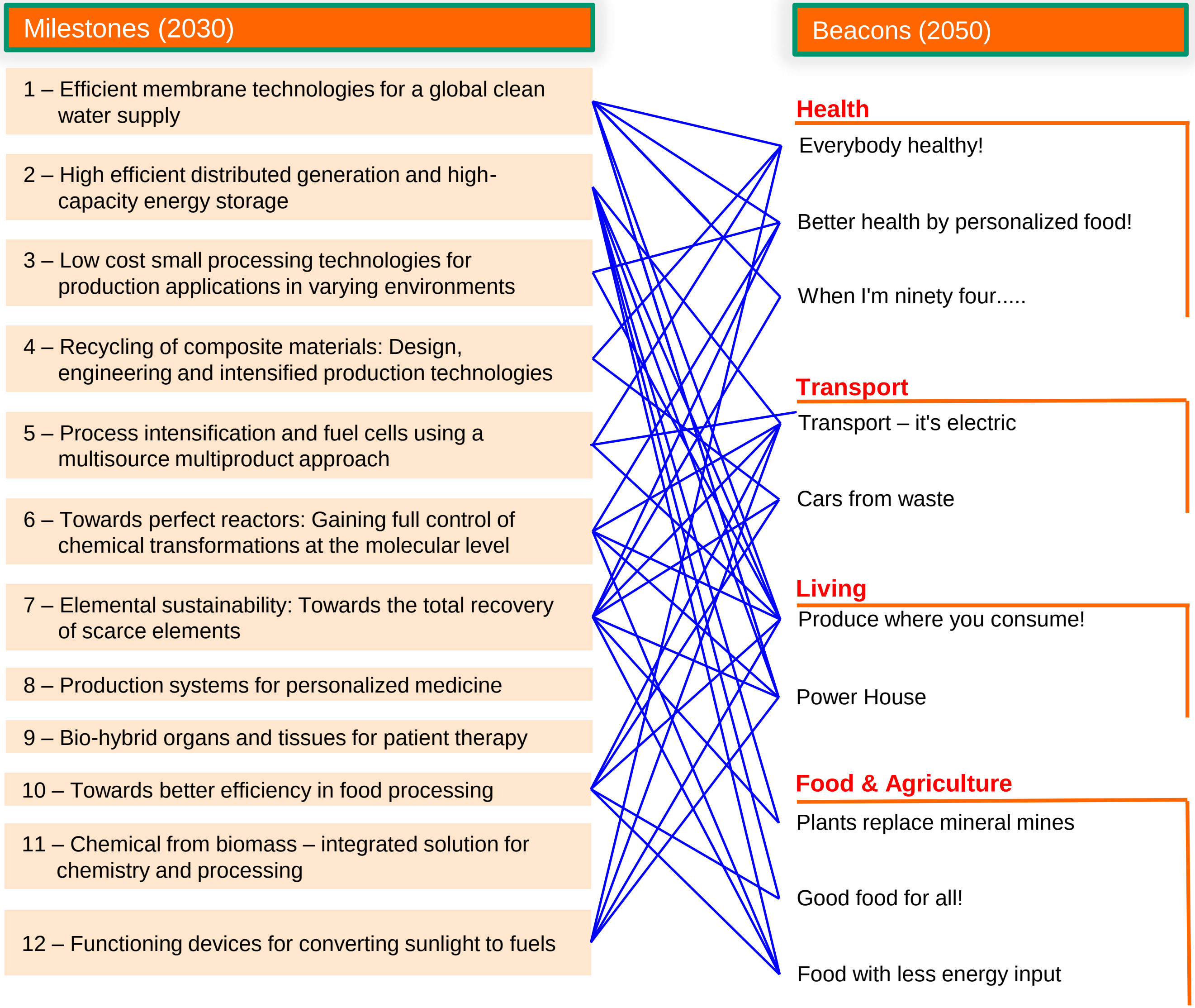
- Natural gas: ***7 GJ*** (reactor) (- 30 %)
- Steam: ***< 1 ton*** (- 85 %)
- Electricity: ***< 0.4 MWh*** (- 0 %)
- Cooling water: ***< 400 ton*** (- 40 %)

Major energy savings
Major plant size reduction

Some Caveats.

- Process modification is non-trivial for the chemical industry.
- Some strategies tend to shift risks, rather than reduce them:
  - e.g., reducing inventories may increase transportation
- Even if all risk could be eliminated from chemical manufacturing facilities, other targets exist:
  - only 18% of facilities required to report under RMP were chemical manufacturing facilities!
  - underscores importance of moving towards safer *products*, not just safer *processes*
- The "risk vs. efficiency" equation has implications for sustainability:
  - beware of "easy answers!"

PI Milestones for 2030.



Milestones (2030)

1 – Efficient membrane technologies for a global clean water supply

2 – High efficient distributed generation and high-capacity energy storage

3 – Low cost small processing technologies for production applications in varying environments

4 – Recycling of composite materials: Design, engineering and intensified production technologies

5 – Process intensification and fuel cells using a multisource multiproduct approach

6 – Towards perfect reactors: Gaining full control of chemical transformations at the molecular level

7 – Elemental sustainability: Towards the total recovery of scarce elements

8 – Production systems for personalized medicine

9 – Bio-hybrid organs and tissues for patient therapy

10 – Towards better efficiency in food processing

11 – Chemical from biomass – integrated solution for chemistry and processing

12 – Functioning devices for converting sunlight to fuels

Beacons (2050)

Health

Everybody healthy!

Better health by personalized food!

When I'm ninety four.....

Transport

Transport – it's electric

Cars from waste

Living

Produce where you consume!

Power House

Food & Agriculture

Plants replace mineral mines

Good food for all!

Food with less energy input

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