Integration of Reaction and Separation: Perspectives and Drawbacks

Maryam Ghadrdan[1]

[1]Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway

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Contents:

Motivation

- More than 30000 specialty chemicals are produced industrially.

- The performance of reactors suffers from several limitations (Thomas2001):

Problem 1   The rates of reactions leading to desired products are often too low to establish economically attractive processes.

Problem 2   The conversion of many reactions of interest is thermodynamically limited

Problem 3   The energy efficiency of endothermal and exothermal reactions performed industrially is often not satisfactory.

Problem 4   In reaction networks the selectivities and yields with respect to a certain target product are limited.

Motivation

Solution 1 Developing new catalysts (Bhaduri2000 & Ertl2008)

Solution 2 New reactor concepts & integration of reaction with separation

Solution 3 New reactor concepts, e.g. reverse flow reactor (Matros1996) and loop reactor (Sheintuch2005)

Solution 4 Catalysis is the main tool

The focus of this presentation is on the second approach

Conventional approach

$$A + B \leftrightarrows C + D$$
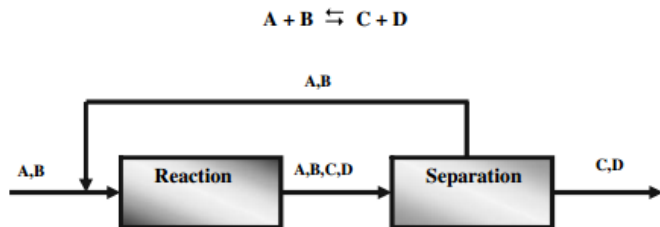
(Schmidt2006)

- The process must include the separation of mixtures and recycling of the reactants
- The number of seapration steps depend on the number of products,catalysts, solvents and reactants which are not converted
- Higher costs are involved

Reactive Separation

In some cases, integration helps to have more efficient separation

A chemical separation typically involves changing the chemical composition of one of the solutions so that new physical properties of one part are reached while leaving the rest alone

Example: Reactive Absorption or Adsorption

Integration of Reaction and Separation
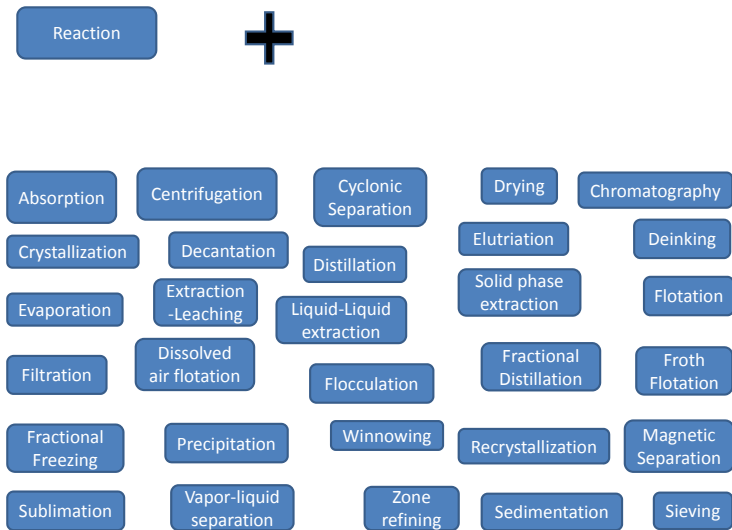
Guidelines to select separation units (Schembecker1998)

- Separate phases already exist: decanter, sedimentation

- For phase creation, prefer the input or the removal of energy condensation and crystallization) over using auxiliary components (e.g. extracting agents) to avoid additional separations steps

- Prefer single stage processes

- When additional component is needed for separation (extraction, azeotropic distillation, adsorption), prefer components which are already in the process over external components

Different Separation Options

Example (Krishna2002)

> Carboxylic acid + Alcohol ↔ Ester + Water

Option 1 **Reactive Distillation**
Option 2 **Membrane pervaporation reactor (Zhu1996)**
- carried out in a tubular reactor with ceramic support impregnated in polyetherimide to selectively permeate water through membrane

Option 3 **Pulsed chromatographic reactor (Sardin1992)**
- Mixed alumina and cation exchange resin in acidic form used as catalysts
- A pulse containing the feed mixture in stoichiometric proportions is injected to reactor. The solvent is fed continuously

Option 4 **Continuous moving bed adsorber-reactor (Carr2001)**
- Amberlyst-15 is used as adsorbent and catalyst. Water is adsorbed
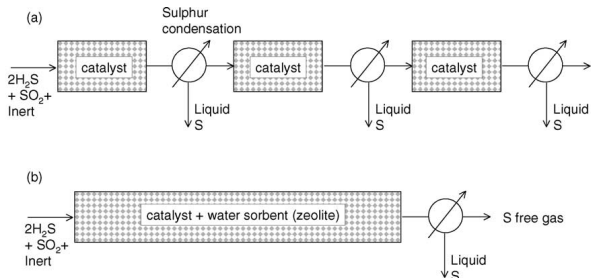
To obtain pure ester, a further distillation step is required.
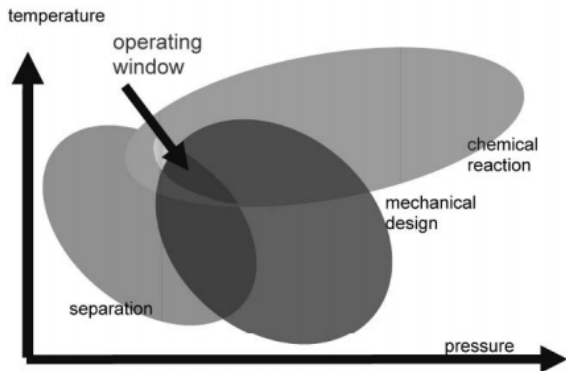
Which product to separate?

Example

$$2H_2S + SO_2 \leftrightarrow \tfrac{3}{8}S_8 + H_2O$$

- Any of the products can be removed (Agar1999)

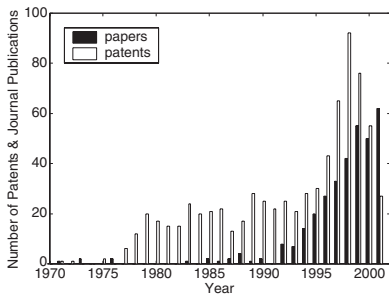## The operating window of an integrated system is narrower

(Schmidt-Gorak2006)

Reactive Distillation

## Reactive Distillation
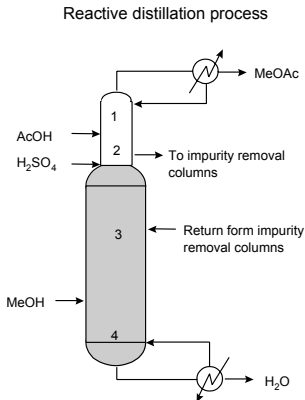
Advantage:

- Chemical equilibrium limitations can be overcome

- The heat of reaction can be used in-situ for distillation

- Azeotropic or close-boiling mixtures can be handled easier

- Higher selectivities can be achieved

History

History:

- 1860s: Ammonia recovery in Solvay process
- 1980s: MTBE
- 1980s: Eastman-Kodak condensed the plant for methyl acetate to an RD unit
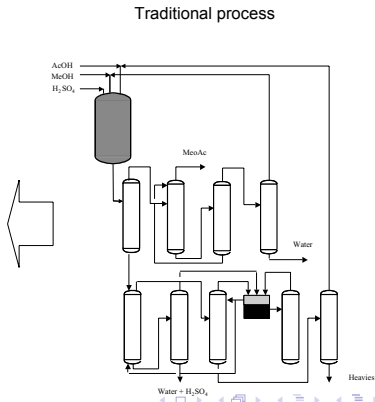
Applications

Industrially important reactions, implemented in commercial or lab scale using RD

Reaction	Remarks	Ref
Etherification (Methanol+isobutene↔ MTBE)	Enhance conversion	Quang1989
Esterification (Acetic Acid + M-Ol↔MA+Water)	overcomes azeotrope formation	Agreda1990
Hydrolysis (Acrylonitrile to Acrylamide)	less side product formation	Kim1992
Acetalization (Ethylene glycol + formaldehyde)	better recovery of formaldehyde	Chopade1997
De/Hydration (Ethylene oxide + water↔ E glycol)	MEG selectivity, avoid forming DEG	Ciric1994
Alkylation (Benzene + Propylene ↔ Cumene)	use of exotherm rxn, purer cumene	Shoemaker1987
Isomerizaion (n-paraffins↔iso-paraffins)	higher Octane, surpass equil.	Krill1999
Chlorination (dichlorobenzene to trichlorobenzene)	increase selectivity	Barnum1995
Transestrification (AA + V strearate ↔ stearic A+VA)	improve yield	Geelen1965
Hydrogenation of isophorone to TMP	simul. separation of TMP	Schmitt1966

and many more...
Sharma et al. also introduced some candidate reactions for RD

Reactive Distillation

$$A_1 + A_2 \leftrightarrow A_3 + A_4$$

Assuming stoichiometric inputs, with volume correction term taking into account the distillation, the conversion equation is:

$$U_1 = \tau \frac{k_1 c_1 c_2 - k_2 c_3 c_4}{c_{10}}$$
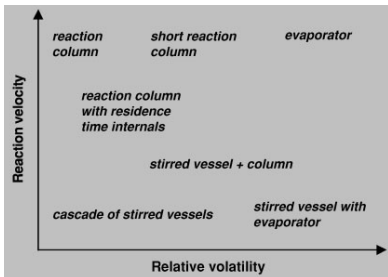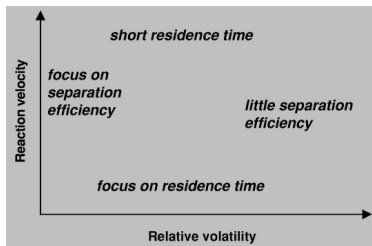
Fact

Suppression of the reverse reaction influences conversion only up to a certain limit
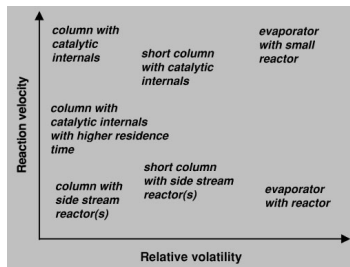
Two operating conditions:

- '**Controlled by distillation**': Conversion is influenced by the concentration of the component to be separated.

- '**Controlled by reaction**': Conversion is influenced by residence time.
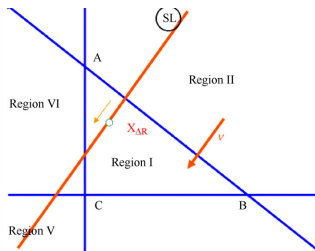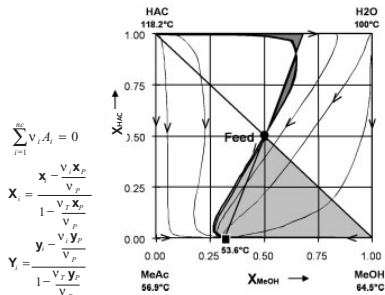
Design of RD systems (Jones1991)

homogeneous catalysis

heterogeneous catalysis

Process Synthesis

- RD lines: used to study the feasibility (Sundmacher2002)

- SYNTHESISER: Software to sketch RD lines

- DESIGNER: Software, from feasibility to rigorous simulation

- Reactive Column Profile Map (RCPM): based on the concept of scalar/vector difference point (Mulopo2008)

Rate-based or Equilibrium-based modeling?

Equilibrium-based modeling

Assumption: vapor-liquid equilibrium at each stage
The departure from equilibrium is accounted for by tray efficiency (tray columns) or HETP (packed columns)

Rate-based models

Assumption: the vapor-liquid equilibrium occurs only at the interface and Maxwell-Stefan equation is used to describe the mass transfer between the phases

- When the number of sections in rate-based model are equal to the number of theoretical stages and V-L interfacial area is increased, the two models get closer
- It is suggested to use the solution from Equilibrium-based model as the initial guess for rate-based model (Peng2002)

Example:$A_1 \leftrightarrow A_2$, A_1 has higher boiling point
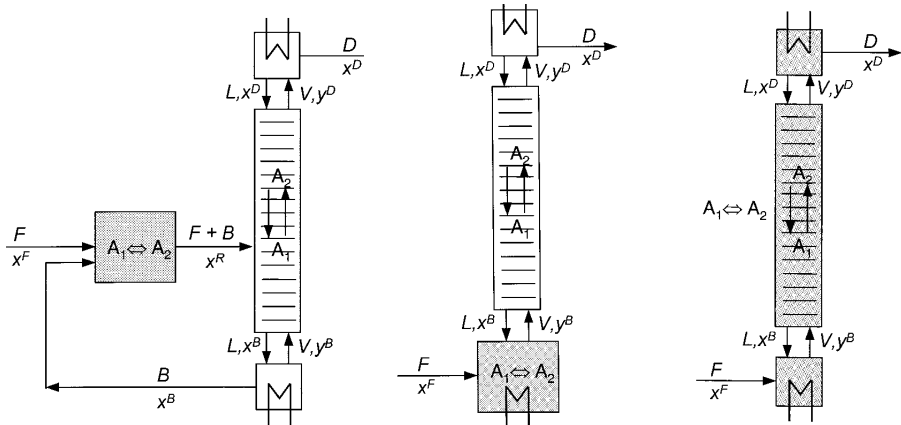
(Sundmacher2002)

- Design variables: Size of reactor ($Da \equiv \frac{kV_x}{F}$), number of theoretical stages
- (∞,∞)-Analysis and (∞, N_{min})-Analysis are used for conceptual design
  - (∞,∞)-Analysis: With infinite reflux ratio and number of stages, x_R,x_B and x_D, critical recycling ratio (ϕ) and critical Damköhler number are calculated
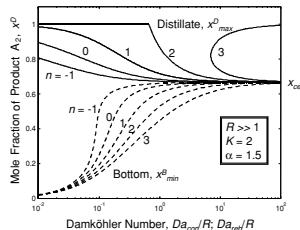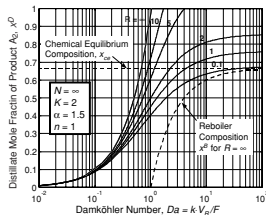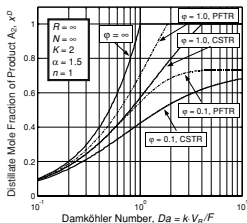
(Sundmacher2002)

Optimal Design (based on superstructure)

- Choice of the superstructure is based on problem-specific knowledge
- Ciric et al.(Ciric1994)
  - The existence of optional parts as binary variable
  - Non-existing trays cause zero flow rates and numerical problems (Grossmann2005)
  - Solved using Generalized Benders Decomposition (GBD) algorithm
- Frey and Stichlmair 2001
  - Reaction and separation are performed in consecutive blocks
  - Existence of column tray is modeled by variable position of reboiler
- Jackson and Grossmann 2001
  - Used geenralized disjunctive programming (GDP) to formulate process superstructure
  - Modeled the existence of column trays by boolean variables which deactivate a subset of model constraints for non-existing trays

Hardware differences

- For reactive trays, we need to increase the liquid holdup and so the preferred regime of operation is the bubbly flow or froth regime;

- The weir heights used for reactive trays need to be significantly higher than those for conventional distillation.

- Hardware design poses considerably more challenges in heterogeneously catalysed RD columns. Particle sizes larger than 1-3 mm lead to intra-particle diffusion limitations.

Scale-up problem

The separation performance and the ratio of separation
performance / reaction performance should be maintained.

To achieve this:

- Reaction with heterogeneous catalyst in the downcoming stream or
  side-reactors
- Reference columns on an industrial scale

Definitions

Separation performance: Intensity of product removal in a reaction column
Reaction performance: property of converting the starting materials

Some remarks

- The combination of distillation and reaction is possible only if the conditions of both operations can be combined (reasonable conversions at T, P levels that are compatible with distillation

- The combination of reaction and distillation might lead to the formation of reactive azeotropes.

  - Example: A mixture of acetic acid, isopropanol, isopropyl acetate and water exhibits three two-component azeotropes, one three-component azeotrope but no four-component azeotrope; the last appears only under equilibrium reaction conditions. (Song1997)

Some Remarks

- The catalyst selection should be done wisely.
- Data lab scale packing may differ from packing applied on industrial scale. e.g. Sulzer Katapak-S has ca. 3 theoretical stages per meter on lab and 1-1.5 on the industrial scale

- Most of the reactions carried out in RD columns are kinetically controlled and they can affected by the limitations of inter- and intraphase mass- and energy transport resistances. (Sundmacher2002)

- Multiplicity, Oscillatory behavior and Nonlinear wave propagation are some of the dynamic issues

- Most of the control studies focus on processes that are operated close to chemical equilibrium

Reactive Absorption

Reactive absorption: Integration due to Separation imperfection

- Methods to capture gaseous components:
  - absorption
  - adsorption
  - permeation through membrane
  - chemical conversion to another compound
  - condensation

- Chemical absorption is also known as Reactive absorption

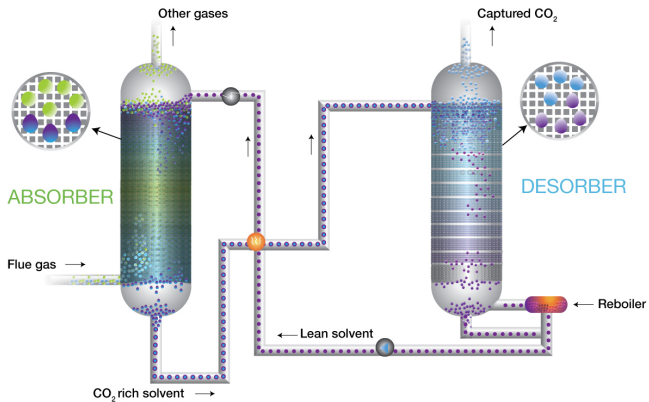|	
The gas industry	Gas dehydration
	Removal of CO_2 and H_2S
	Selective absorption of H_2S
Refineries	Hydrocarbon absorbers for lean oil etc.
	H_2S absorbers
	Various types of stripping columns
	Sour water strippers
The petrochemical industry	Synthesis gas processing
	Gas saturation
	Ethylene oxide absorption
	Acrylonitrile absorption
The chemical industry	Synthesis gas processing (CO_2 removal)
	Chlorine drying
	HCl and ammonia absorption
	Absorption of nitrous gases
The cellulose industry	Sulphur dioxide absorption
	Chlorine dioxide absorption
	Flue gas scrubbing with sulphur recovery
Food processing	Stripping various components producing odours
	Processing fatty acids
	Hexane absorption and stripping
The metal and packaging industries	Absorption of triethylamine (in foundries)
	Absorption of lube and cooling oils
	Absorption and recovery of solvent vapours
Exhaust air scrubbing	Removal of acid components (wet- and dry-scrubbing of SO_x and NO_x)
	Removal of base components
	Removal and recovery of organic solvents
Wastewater/sewage treatment and pollution control	Air stripping of chlorinated hydrocarbons
	Desorption and recovery of ammonia
	Effluent neutralization
	Deaeration of seawater

(Chattopadhyay 2007)

Gas Sweetening

- Gas sweetening is one of the well-known and well-developed examples

- Carbon dioxide, hydrogen sulfide, and other contaminants are often found in natural gas streams.

- Gas sweetening: Removing acid gas from natural gas

- $CO2 + water \rightarrow carbonic acid$ is corrosive.

- CO2 reduces the BTU value of gas and in concentrations of more that 2% or 3% the gas is unmarketable.

- H_2S is extremely toxic gas and tremendously corrosive to equipment.

CO2 capture from stack gas

- Intention: Global warming

- Storage of stack gas is not economic

- In the case of capture from stack gas, pressure is too low, that physical dissolution is not considerable

- Physical solvent are used for high pressure systems

  1. **Selexol process**: dimethyl ether of polyethylene glycol

  2. **Fluor solvent process**: propylene carbonate

  3. **Purisol**: N-methylpyrrolidone

- An enhancer for dissolving process is needed

Typical RA process

Reaction set for MEA case

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

$$CO_2 + 2H_2O \Leftrightarrow H_3O^+ + HCO_3^-$$

$$HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3{}^{2-}$$

$$2MEA + CO_2 \Leftrightarrow MEAH^+ + MEACOO^-$$

$$MEA^+ + H_2O \Leftrightarrow MEA + H_3O^+$$

$$MEACOO^- + H_2O \Leftrightarrow MEA + HCO_3^-$$
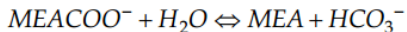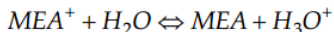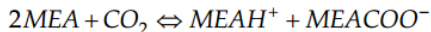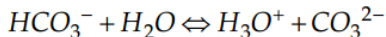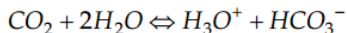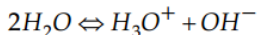
- Forward direction: Low temperature (Absorber)

- Backward direction: High temperature (Desorber)

Reactive absorption

- Rate-based approach: Most reliable method (Yildirim2012)

- The two film parameters: to describe mass-transfer (Kenig2003)

- Solvents must be chosen depending on (Mondal2011)
  1. Required purity of cleaned gas stream
  2. Composition of feed gas
  3. Utility requirements, process costs
  4. Corrosion and solvent degradation

- Each solvent has pros and cons
  1. Reaction rate of primary amines is higher than tertiary amines leading to high solvent circulation rates of tertiary amines
  2. Primary amines are more corrosive
  3. Loading increases from primary to tertiary amines

* Loading describes the capability of one mole solvent to absorb one mole acid gas components

Developing Solvents for Reactive Absorption

- Simple and well-known amines: Monoethanolamine(MEA), Diethanolamine(DEA), 2-amino-2-methyl-1-propanol(AMP)

- Mixture of amines: One with high capacity(with drawback of low reaction rate), and the other with high reaction rate(but low capacity); AMP-Piperazine

- Mixture of amines that after absorption splits to 2 phases(one with higher loading of CO_2 and the other with low loading of CO_2): 2-(diethylamino)-ethanol (DEEA) / 3-(methylamino)-propylamine (MAPA)

- Mixture of an amine with an enzyme

Activities in the field of RA

Important research programs world-wide:,

- Luminant Carbon Management program

  - University of Texas at Austin

  - Research on CO_2 rate kinetics and solubility measurements, degradation of solvents, system modeling, pilot plant testing

- International Test Center (ITC) for CO_2 capture

  - Multi-purpose pilot unit (1 ton of CO_2 per day)

  - a semi-commercial (4 ton of CO_2 per day) recommissioned in 2000

Activities in the field of RA

- Technology Center Mongstad, Norway

  - Designed to capture about 100,000 tonnes per year of CO_2, the project will be the largest demonstration of CO_2 capture technologies to date.

- NTNU & SINTEF

  - +20 projects on Solvent & packing characterization, thermodynamic modelling, Process simulations

- CASTOR, CAPRICE, CESAR, NZEC, CO2CRC, and more (see Wang2011)

Some remarks

- A major application of RA is removal of CO_2 and/or H_2S from various industrial streams

- Reduce energy consumption by developing new solvents and heat integration

- Process Intensification (Wang2011, Lin2007)

  - Lower installation factors and reduced capital costs.

  - Residence times are reduced

  - The improvement in heat/mass transfer coefficients and thermodynamic efficiency.

Reactive Adsorption

Reactive Adsorption

- A widely used separation tool in almost every sector
- Example: Drying air, water treatment, air purification, removal of odor, separation of components from mixtures
- To increase the retention forces two approaches can be taken: (Petit2010)
  - The presence of highly porous structure with pores similar to the size of adsorbate
  - The presence of functional groups reacting with adsorbate to enable its strong retention on adsorbent structure
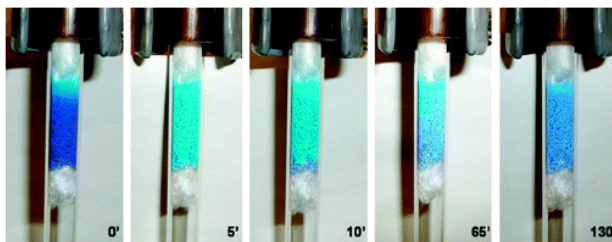
Modified adsorbents used for Reactive adsorption (Sharma2012)

Process	Adsorbate	Adsorbent	Modification procedure	Remarks	Ref.
Wastewater treatment	Penicillin G	Activated carbon modified with nitric acid (20%)	Wet Oxidation and Thermal Treatment	The surface characteristics of modified carbon promote the reactive adsorption of Penicillin. Acid activated carbon posses low adsorption capacity and high rate of degradation. While it is vice-versa for basic carbon	Ania et al. (2010)
desulfurization	Dibenzothiophene (DBT)	Modified activated carbon	Chemical modification by H_2SO_4 at 150–270 °C	The modified AC exhibits high adsorption capacity for large molecules but acts negatively for small molecules as compared to conventional AC	Jiang et al. (2003)
gas phase reactive adsorption	Ammonia	Modified activated carbon	Incipient wetness impregnation with metal salts followed by calcination at 300 °C	The nature of metal deposits, surface functionalities, moisture and acidity of adsorbent determines the adsorption capacity. Highly acidic nature is required for the reactive adsorption of NH_3	Le Leuch and Bandosz (2007)

Adsorption Reactor Configurations

- Fluidized bed: difficult solid handling
- Fixed bed combined with regeneration cycles are the common choices

- Regeneration strategies: (Schmidt-Gorak2006)
  - Pressure swing
  - concentration swing
  - temperature swing
  - reactive regeneration
  - displacement regeneration
  - combinations
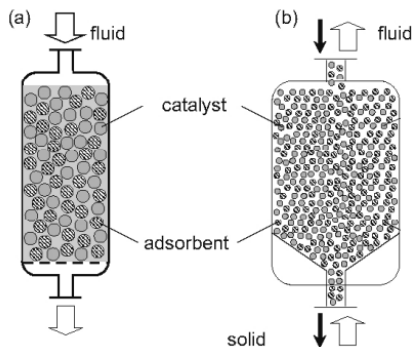
Some remarks

- For an effective reactive adsorption, adsorbent modification is recommended.

- The selection criteria of an adsorbent for a particular adsorbate species depend upon the nature of adsorbate.

- An extensive research is required for the selection and regeneration of reactive adsorbent to make reactive adsorption economically feasible.

- Parametric analysis of reactive adsorption is required in order to optimize the design of a reactive adsorber.

- Evaluation of the performance of reactive adsorbents for continuous large scale applications is also a potential area.

Membrane Reactors

Membranes for MRs

Classification 1 Nature
- I Biological
  - Limited operating T and pH range
  - Susceptible to microbial attack
  - difficulties with cleaning
- II Synthetic
  - Organic (polymeric): operates between $100 - 300°$
  - Inorganic (Metal, Ceramic, Carbon, Zeolite)
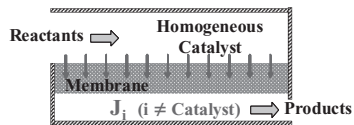
Classification 2 Separation regime
- Dense
- Porous
- Ion exchange
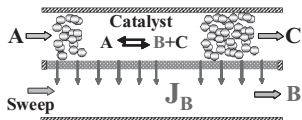
Classification 3 Geometry
- Planar
- Tubular (tubes, capillaries and hollow fibers)

MR Concepts

Retainment of homogeneous catalysts (Cheyran1986)

Extractor (Pfefferie1966)

Selectivity enhancement through withdrawal of a product (Kölsch2002)
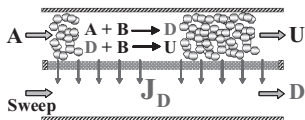
Contactor (Miachon2003)
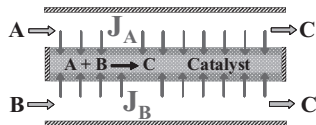
Energetic coupling (Gryznov1974)
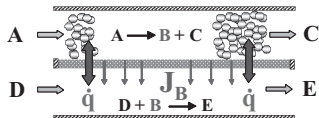
Selectivity enhancement through optimized reactant dosing (Mallada2000)
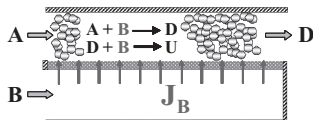
Membrane reactors for H2 production

Membranes and membrane reactors for pure H2 production are widely investigated, because of

- important application areas of hydrogen
- mechanically and chemically stable membranes with high perm-selectivity towards hydrogen are available

Comparison of membrane types for hydrogen separation

Depending on the operating conditions and feed gas composition, a wide variety of membrane materials can be selected (Kluiters2004,Liu2010)

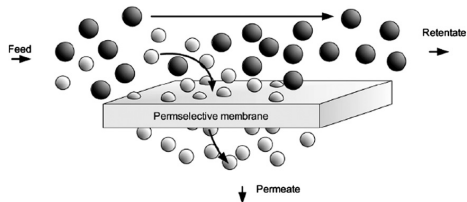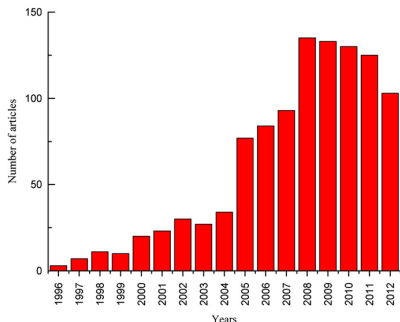| Membrane type	Polymeric	Microporous ceramic	Porous carbon	Dense metallic	Photon conducting dense ceramic
Materials	Polymers: Polyimide, cellulose acetate, ploysulfone, etc	Silica, alumina, zirconia, titania, zeolites, MOF	Carbon	Palladium alloys	Perovskite
Temperature (c)	<100	200-600	500-900	300-700	600-900
H2 selectivity	Low	5-139	4-20	>1000	>1000
H2 flux (10^{-3} molm^{-2}s^{-1}) at DP=1bar	Low	60-300	10-200	60-300	6-80
Transport mechanism	Solution-diffusion	Molecular sieving	Surface diffusion, Molecular sieving	Solution-diffusion	Solution-diffusion
Stability issues	Swelling, compaction, mechanical strength	Stability in H2O	Brittle, oxidizing Strong adsorbing vapors, organics	Phase transition(causes embrittlement)	Stability in CO2
Poisoning issues	HCl, Sox, CO			H2S, HCl, CO	H2S
Cost	Low	Low	Low	Moderate	Low

Membrane reactors

- Packed-bed reactors
  - Most studied configuration for H2 production

  - PBMR is used in different studies to produce H2: methane reforming (Galluchi2006), POX of methane (Tan2009), reforming of alcohols (Tosti2009), autothermal reforming (Simakov2009)

  - Limitation: Low membrane area per unit volume

  - Limitation: pressure drop along the reactor, which dictates the size of catalysts

  - Reactions are quite endothermic (reforming) or exothermic (CPO). So, temperature control is important

  - A decrease in temperature leads to decrease of hydrogen flux through membrane while an increase of temperature could result in crack on the membrane surface

Membrane reactors

- Fluidized bed reactors

  - More complex fluid dynamics compared to packed-bed MR

  - Bundle of hydrogen-selective membranes immersed in a catalytic bed operated in the bubbling or turbulent regime.

  - Negligible pressure drop, which allows using small particle sizes resulting in no internal mass and heat transfer limitations.

  - (Virtual) isothermal operation.

  - Flexibility in membrane and heat transfer surface area and arrangement of the membrane bundles.

- Membrane microreactors

  - Improved mass / heat transfer owing to reduction of scale length in micro-channels

  - High degree of process intensification

  - By comparing the performance of the same membrane in different configurations, it is concluded that in micro-channel MR configurations the concentration polarization effect can be neglected

Membrane Reactors

- Membrane bio-reactors

  - Environment friendly

  - The biological processes for H2 production can be summarized as (Das2008)

    - Biophotolysis of water using algae and cyanobacteria.

    - Photodecomposition of organic compounds by photo-synthetic bacteria.

    - Fermentative hydrogen production from organic compounds

    - Hybrid systems using photosynthetic and fermentative bacteria.

  - The membranes used for these biological processes are typical (polymeric) membranes already commercially applied to water treatments

Optimal design

Optimal structure can be obtained from superstructure model
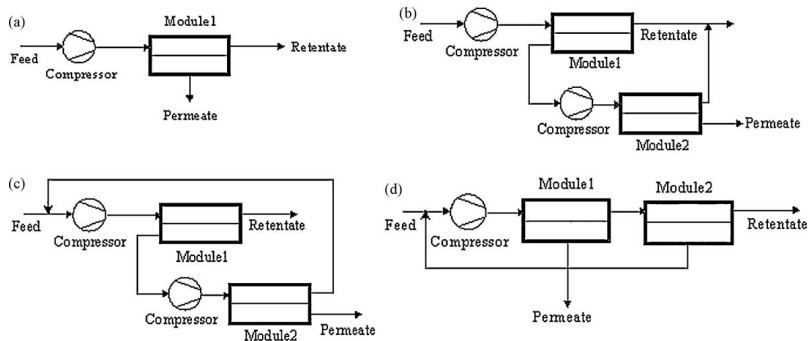
(Deng2010)

some remarks

- The most widely studied membrane materials for H2 production are dense metal membranes and among them the Pd-based membranes are closer to the market (Gallucci2013)

- Dense metal membranes are commercialized by: CRI/Criterion (owned by Shell), ECN, Eltron Research Inc., Green Hydrotec

- Industrial type of MRs will most likely be based on fluidized bed configuration and/or micro-structured reactors

- Based on the reviews, the first membrane reactors operated at large scale will be probably based on natural gas reforming or bio-ethanol reforming (Gallucci2013)

Summary

- Reactive separations are generally regarded as "new" technology. Developing a new technology includes higher costs and risks

- The overlap in process conditions required to provide acceptable reaction and separation performance is quite narrow

- Application of reactive separations are custom tailored to the problem to be addressed. Solutions might not work in a similar situation

- Extensive equipment design is often required to address the details of how the reaction and separation phenomena are coupled in one vessel

- The development of reactive separation processes generally leads to increased complexity of process operations and control

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