Membranes integrated in conversion processes as a way to process intensification

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CPAC Satellite Workshop
Rome, March 21 – 24, 2011
Membranes integrated in conversion processes as a way to process intensification

» Introduction about process intensification and microreactor technology

» The VITO approach

» VITO demonstrators
  » Algae recovery
  » In situ Product Recovery
  » Catalyst immobilisation
  » Functionalised membranes
  » Catalytic Membrane Reactors

» FMMC
Green chemistry: Giving each molecule the same processing history

- Tank Reactor
- Batch process
- Tubular Reactor
- Continuous process
Future challenges in MicroReactor Technology

According to Norbert Kockmann (Lonza AG):

» Scale up and robustness
  » Single and multiphase flow including solids;
  » Mixing, residence time, and plugging;
  » Heat transfer and reaction control;
  » Chemically stable and corrosion resistive.

» Catalyst integration
  » Flexible and versatile;
  » Rapid screening and scale-up.

» Cost efficient devices
  » Simple, robust, and combination with periphery.

» Work-up steps and process design
  » Consistent and robust scale-up strategy
  » Complete plant integration;

整合分离和净化过程
Green chemistry: Maximizing effectiveness of intra- and intermolecular events

**CHALLENGE:**
- Control of the geometry of approach and mutual orientation of molecules at the moment of collision.
- The most efficient way of supplying energy (form and transfer mechanism) to let reactants molecules selectively overcome this barrier.
- Control of energy distribution amongst the reaction products.

**Catalysis**
- Less energy
- Higher specificity
Maximizing synergistic effects from partial processes

Example: membrane reactor (reaction + separation)

- Equilibrium limited reaction
- Enhancing selectivity, in situ product removal (NINA)
- Purification of a reactant

(R. Reintjens)

In situ product recovery
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Objective 1: Process intensification

From batch to continuous

Integration of conversion and separation technology
Objective 2: From fossil-based to biomass-based chemistry
From reaction + purification to integration of reaction and separation

- Chemical Reaction(s) → Purification → Manufacturing → Product
- Substrate → Fermentation → Downstream processing → Manufacturing → Product
- Substrate → Enzymatic process → Downstream processing → Manufacturing → Product
- Substrate → Reaction / conversion process → Separation → Manufacturing → Product
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Algae production – recovery – with integrated water treatment

- Continuous recovery of algae from production system by VITO membranes
- Better quality in production system
- Less energy needs for algae harvest
- Allows better water treatment
CO₂ / NOₓ conversion in algae biomass: downstream processing

CO₂ → harvesting → extraction → purification
NOₓ → harvesting 
water → harvesting
O₂ → harvesting

Algae → biomass → Cells → Sc CO₂ extraction → lipids
Sc CO₂ extraction → proteins
Sc CO₂ extraction → polysaccharides
Sc CO₂ extraction → dyes
Sc CO₂ extraction → chemicals
...
Integration of conversion and membrane separation to improve overall efficiency
Orghanolphilic pervaporation (OPV) membrane

» Mixed matrix membranes for OPV at VITO

✓ PVDF or PAN support membrane on non-woven PE
✓ Thin layer of silica-filled PTMSP
Integration of conversion and membrane separation to improve overall efficiency

*Fig. 3*: Schematic of a butanol fermentation process integrated with a pervaporation process. Arrows show the direction of liquid flow.
In situ alcohol recovery by organophilic pervaporation

- Continuous fermentation operational
- Coupled to PV system → continuous operation
» **Proof-of-concept** for coupling of fermentation and pervaporation:
  » Pervaporate concentration from 60 – 180 g/L
  » Productivity enhancement of 87%
  » Use of concentrated feedstocks


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» **Direct future:**
  » Use of in-house developed mixed-matrix composite PTMSP membrane
  » Optimizing continuous conversion
Wastewater + waste transformation into chemicals

- Fermentation
  - Acids / Alcohols
  - Acid/alcohol Conversion
    - Acid Separation
      - Acetate
      - Butyrate
  - Alcohol Separation
    - Ethanol
    - Butanol
Functionalized membranes: reactive membranes

- **Nano Activated membranes (NAM)**
  - Ag, TiO$_2$ (desinfection)
  - Pt, Pd, Fe, Au (catalysis, oxidation-reduction)

- **Biocatalyst Activated membranes (BAM)**
  - Enzyme immobilisation
  - Bioplasma (Patent)
  - Zirfon® (Patent)
  - Co-factor immobilisation?

**Diagram**: Reactor Membraan → Permeaat → Reagentia → Geïmmobiliseerd enzyme → Retentaat

**Images**: Covalent technology, ~ 100ng/cm²
Immobilization of enzymes on membranes
Membrane electrode assemblies

- (Bio)chemical reactions by
- Catalysts (inorganic, enzymes, bacteria) on electrodes
- Linked to a membrane (MEA)
- Where the electrochemical voltage improves the efficiency of the reaction
- Whereas simultaneous electron transfer is transformed into electric current via an external circuit

- E.g. acetate oxidation by *Geobacter*
- *E.g. CO2 reduction to formic acid, butyric acid*
- E.g. Hydrogenation of NO to NH2OH
- E.g. Dehydrogenation of nitrobenzene to aniline
(Bio)electrochemical cells

» VITOs highlights
  » Microbial fuel cell working on acetate
  » Enriched microbial community
  » PTFE layered carbon electrode with current collector
  » Zirfon® (ion permeable membrane) coated on carbon electrode (thin; less O2 permeability, less biofouling potential than Nafion® or Fumasep® (PEM)
  » Separator and fuel cell expertise
  » Electrochemical expertise
  » Porous gas electrode development
  » Future stack development
  » 1600 mW/m² (Pt-electrode Penn State)
  » 1220 mW/m² (VITO-electrode Penn State)
  » 2720 mW/m² (Pt-electrode best ever)
Affinity separations in OSN

OSN is more complicated than filtration in water

Potential for affinity separation with functionalised/grafted membranes

- Hydrophobic or functional group

~ 1 nm
Membrane functionalization at VITO/UA

Post-modification based on organometal chemistry: \textit{grignard reaction} (patent)

\[ \text{M} \rightarrow \text{OH} \rightarrow \text{M} \rightarrow \text{R} \]

| direct, covalent bond | highly stable |

Compatible with a \textit{wide variety of functional groups}

Opens path to:

- affinity separations
- membranes tailored to separation

Status: reproducible hydrophobic membrane at lab-scale

2011: optimization hydrophobization + 1st functionalization
Catalyst recovery

» Homogeneous catalyst modification and membrane modification in order to recover catalysts from reaction mixtures
  » Pharmaceuticals
  » Fine chemicals
  » Biomolecules
  » Polymers
  » Removal of impurities, reaction compounds,…

\[ \text{cata} + \text{Membrane} \rightarrow \text{Increase of selectivity} \]
\[ \text{cata} + \text{Modified membrane} \rightarrow \text{R} \]
Catalytic Membrane Reactors
Dehydrogenation of ethane

Approximate temperature window for
Membrane material ion conductivity
Reaction thermodynamics
Catalyst operation

Useful T - window

Temperature (°C)

Legend
- HF membrane wall
- Cat layer or bed

H₃C

CH₃

H₂C═CH₂ + H₃C

CH₃

sweep
sweep + H₂

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Concept of MIEC hollow fiber membrane reactor for dehydrogenation reactions

$C_2H_6 \rightarrow \text{MIEC material} \rightarrow \text{catalyst} \rightarrow \text{H}_2 \rightarrow \text{C}_2\text{H}_4$

$\text{CH}_3\text{-CH}_3 \leftrightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2$

$\text{H}_2 = 2\text{H}^+ + 2e^-$

(high pH$\text{H}_2$ (reaction side))

(low pH$\text{H}_2$ (sweep side))

$2\text{H}^+ + 2e^- = \text{H}_2$
Concept of MIEC hollow fiber membrane reactor for oxidative coupling of methane

\[ \text{CH}_4 + \text{O}_2 \leftrightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

- **High pO\(_2\)** (air)
- **Low pO\(_2\)** (reaction side)

2\( \text{O}_2^{-} = \text{O}_2 + 4 \text{e}^{-} \)

MIEC material

catalyst
Concept of MIEC hollow fiber membrane reactor for dehydrogenation/cracking reactions

C_4H_{10} \leftrightarrow 2 \text{CH}_2=\text{CH}_2 + \text{H}_2

H_2 = 2 H^+ + 2 e^-

H_2 = \text{H}_2 (reaction side)

low pH_2 (sweep side)

MIEC material

catalyst

V_H

2 H^+ + 2 e^- = H_2

high pH_2 (reaction side)
How do we operate?

Individual integrated approach

Guidance to full-scale implementation
Pilot-scale testing
Lab-scale testing
Theoretical studies

R&D

National and European research projects
Strategic co-operation and partnerships
Own developments (new products, concepts)
Our references
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“A government funded initiative to stimulate the development and integration of microfluidic applications in Flemish industry by knowledge diffusion and partner matching”
Project leaders:

Funding:

In line with:

Flanders' Initiative for Sustainable Chemistry
“A government funded initiative to stimulate the development and integration of microfluidic applications in Flemish industry by knowledge diffusion and partner matching”

Activities:

- Competentiation-inventorisation
- Partnermatching → starting innovative projects between members
- Informing proactively through newsletters and website
- Organizing seminars, workshops and bilateral contacts
FMMC after 8 months

> 20 members from Flemish industry & Academia