Membrane reactors for the chemical industry

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ECN

Energy research Centre of the Netherlands

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Energy research Centre of the Netherlands (ECN)

ECN develops high-level knowledge and technology for a sustainable energy system and transfers it to the market

- Non-profit non-governmental organisation
- (Inter)national co-operation with companies, universities and research institutes
- Number of people 680
- Annual turn over 80 M€
- 8 Programmes related to energy RD&D

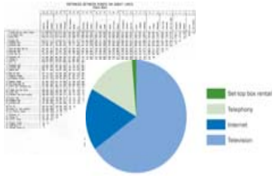
ECN

The EUROPEAN ROADMAP **for** PROCESS INTESIFICATION

Instruments created by the Taskforce PI

1. **Quick Scan:** Helping industry identify PI possibilities in their own process, focus on SME's

2. **Facts and Figures:** Collecting and evaluating data from experts and vendors on what is happening



3. **Roadmap:** Identifying potential and barriers for PI technologies, ranking and designing development routes

4. **Skyline team:** Identifying long-term break-throughs

Outcome roadmap PI:
11 Program lines making up the research program

Program lines

PI THRUST AREAS

1. Alternative energy- based operations
2. Membrane-based hybrid separation or chemical conversion
3. Integration of separation and chemical conversion (non-membrane based)
4. Transport-limited processes
5. Preservation
6. Energy efficient separations (incl. water)

PI ENABLING TECHNOLOGIES

7. PI process analysis tools
8. PI process modeling & control
9. PI manufacturing tech. & piloting

PI SPECIAL THEMES

10. Open theme
11. Skyline Team

Barriers for implementation of PI common to all sectors

Technical / equipment

- Fundamental research
- Building track-record
- Knowledge vested current process
- Piloting possibilities
- Retrofitting PI technologies

Economic

- Pay-back period new process Technology
- Reliable/known suppliers are lacking

Culture / organization

- Lack of PI knowledge and know
- Lack of chain vision
- IP issues during R&D/development

Roadmap Process Intensification

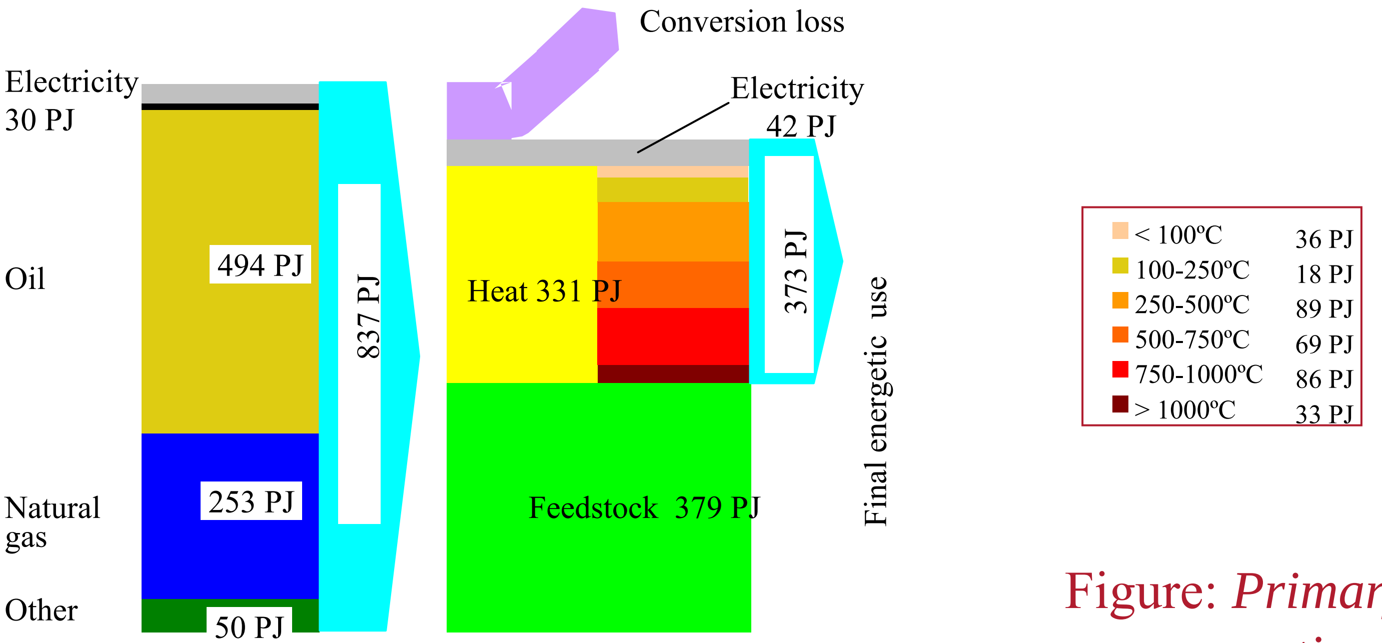
Main points:

- Public private partnership with industry, institutes and universities as active members
- Membrane reactors perceived (by industry) as key area
- General barriers for process intensification are valid for MR's.

MEMBRANE REACTOR APPLICATIONS in the CHEMICAL INDUSTRY

Relevance chemical industry to the Dutch energy system

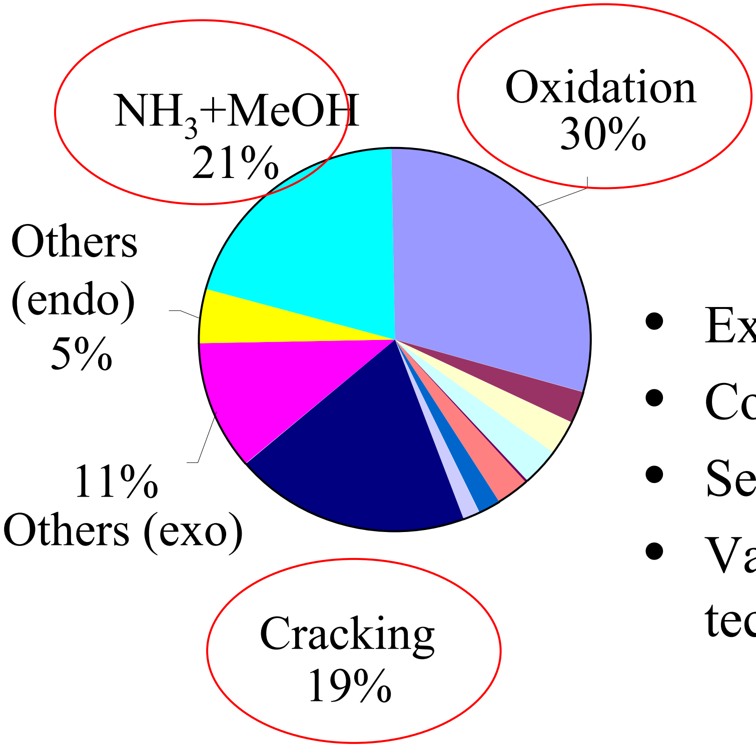
Chemical & refining = 30% of primary energy (including feedstock)



Total NL= 3051 **Total NL= 2518**

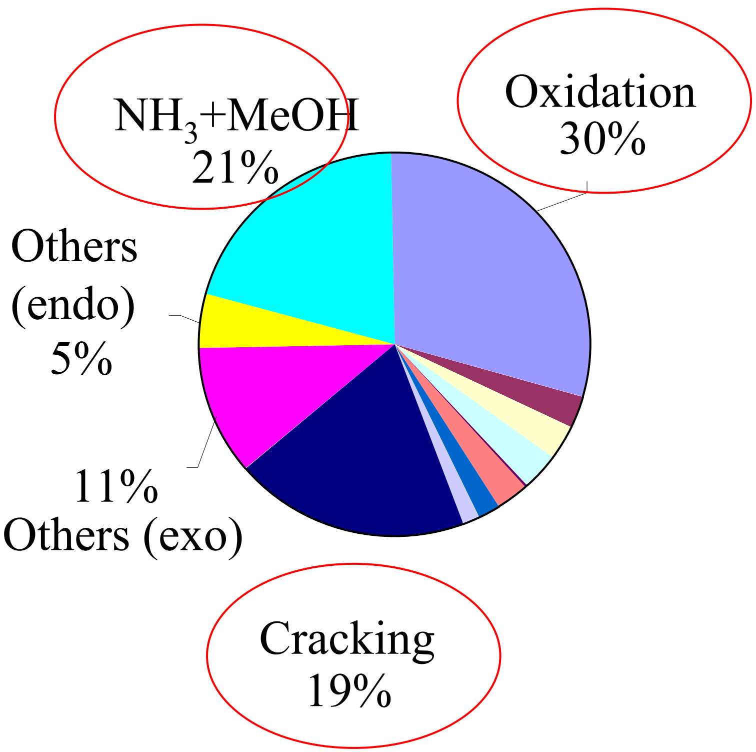
Figure: *Primary and final energy consumption of the Dutch chemical & refining industry (data 2000)*

Analysis of energy use in Dutch chemical industry



- Extensive database of Dutch chemical processes
- Covers to 100+ of processes (energy use)
- Searchable on specific aspects
- Valuable tool for analysis of potential of technologies

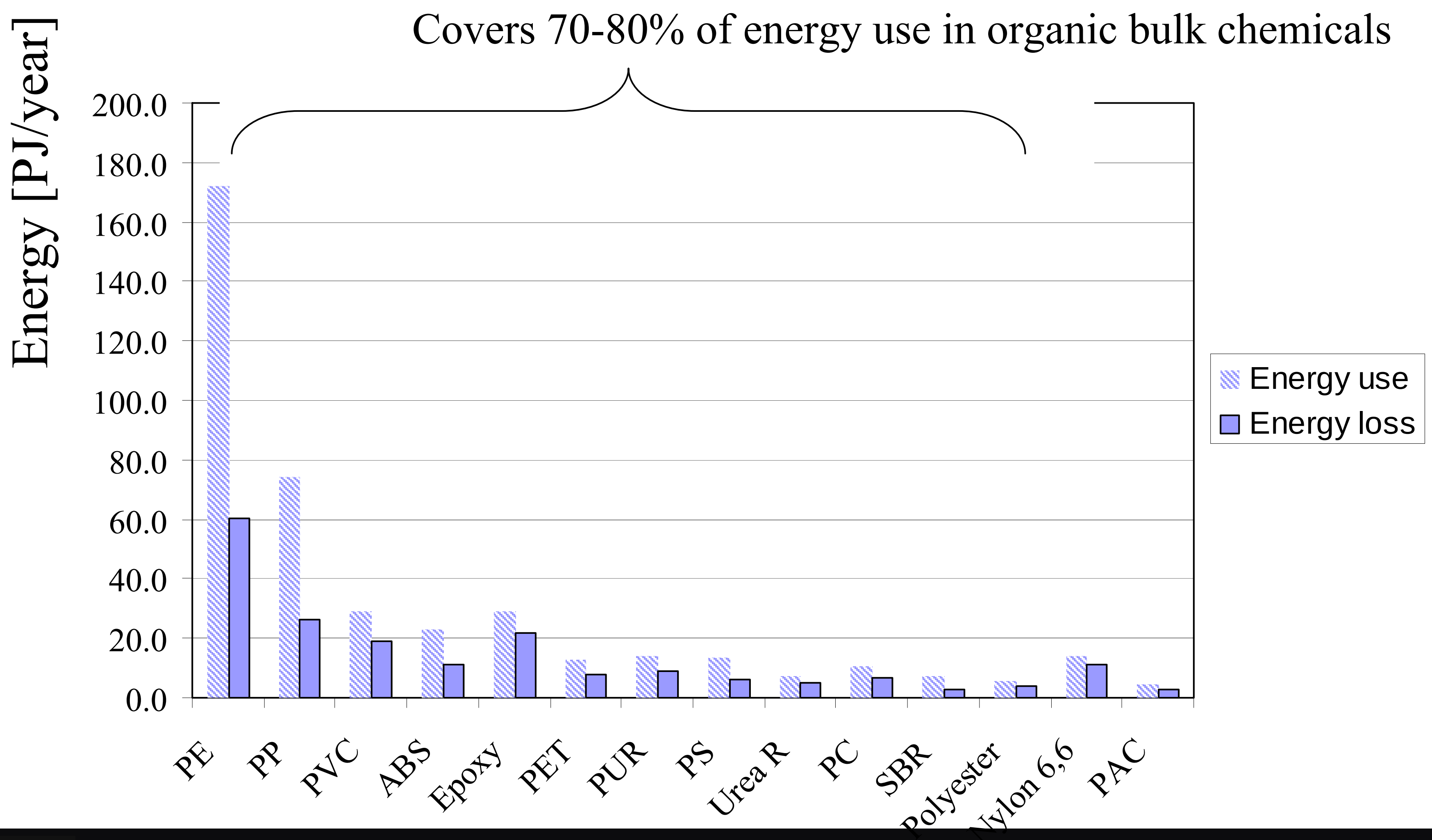
Analysis of energy use in Dutch chemical industry



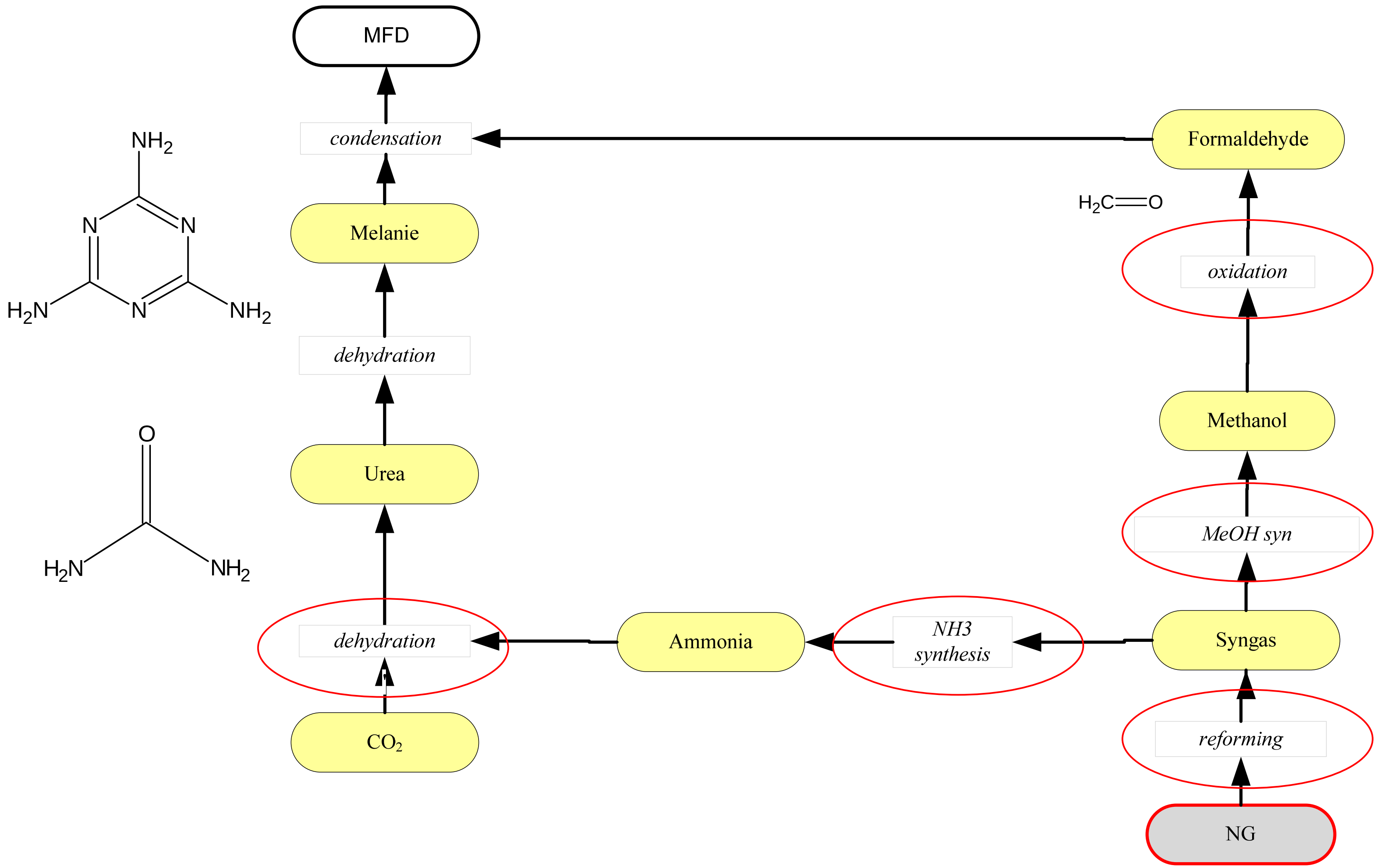
Analysis based on final products:

- Organic bulk chemicals (polymers)
- Inorganic bulk chemicals
- Future trends chemical industry

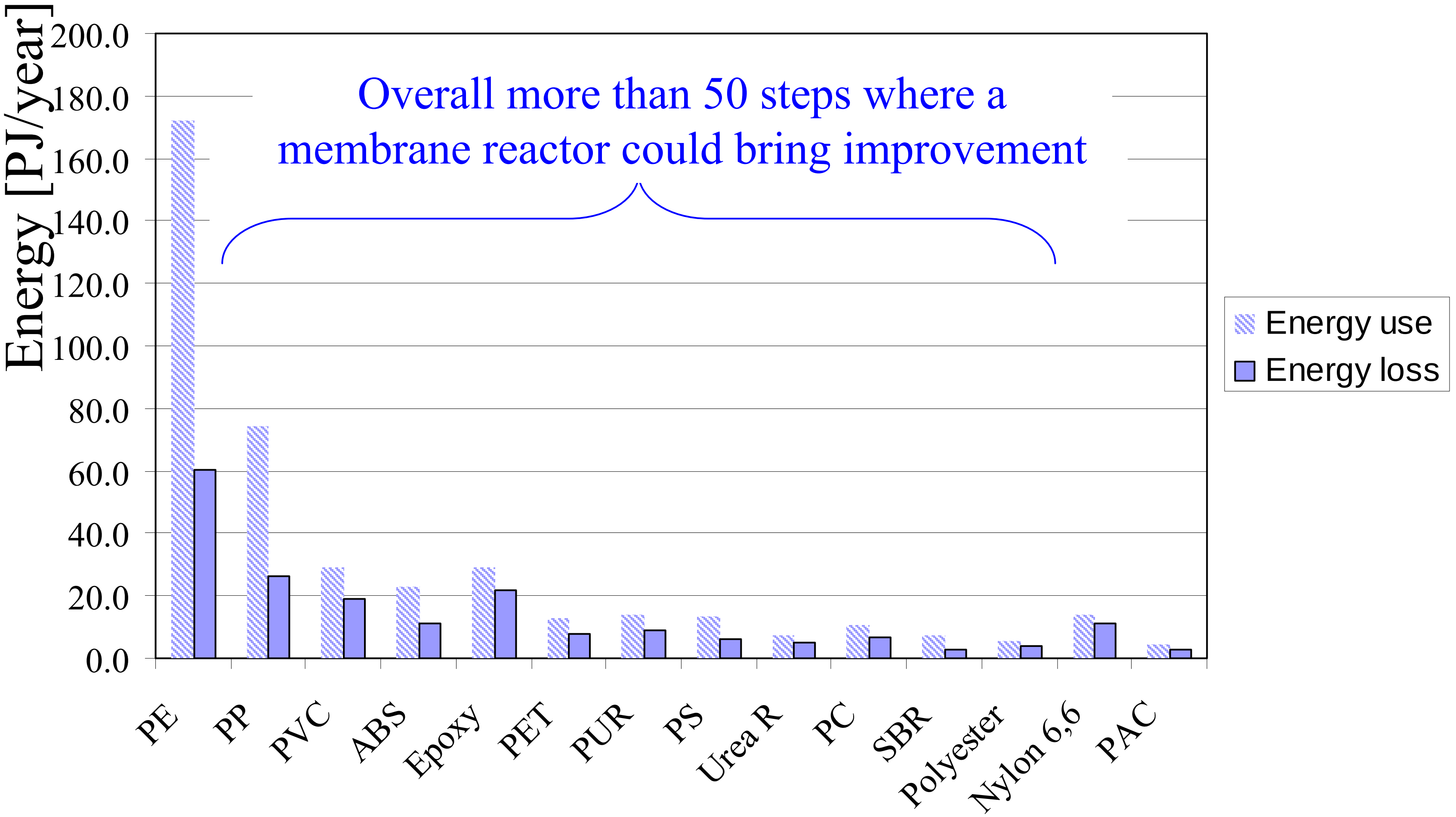
Energy use and loss in the production of polymers



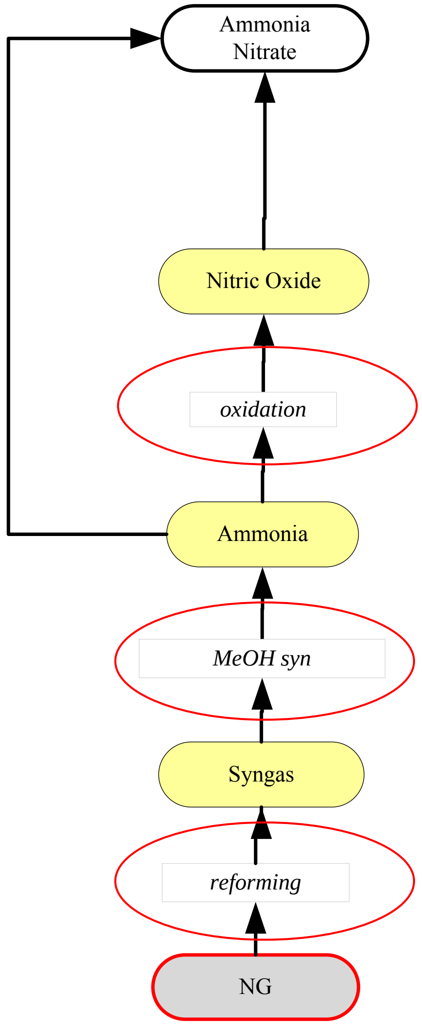
Potential application of MR's in production of UFR



Energy use and loss in the production of polymers



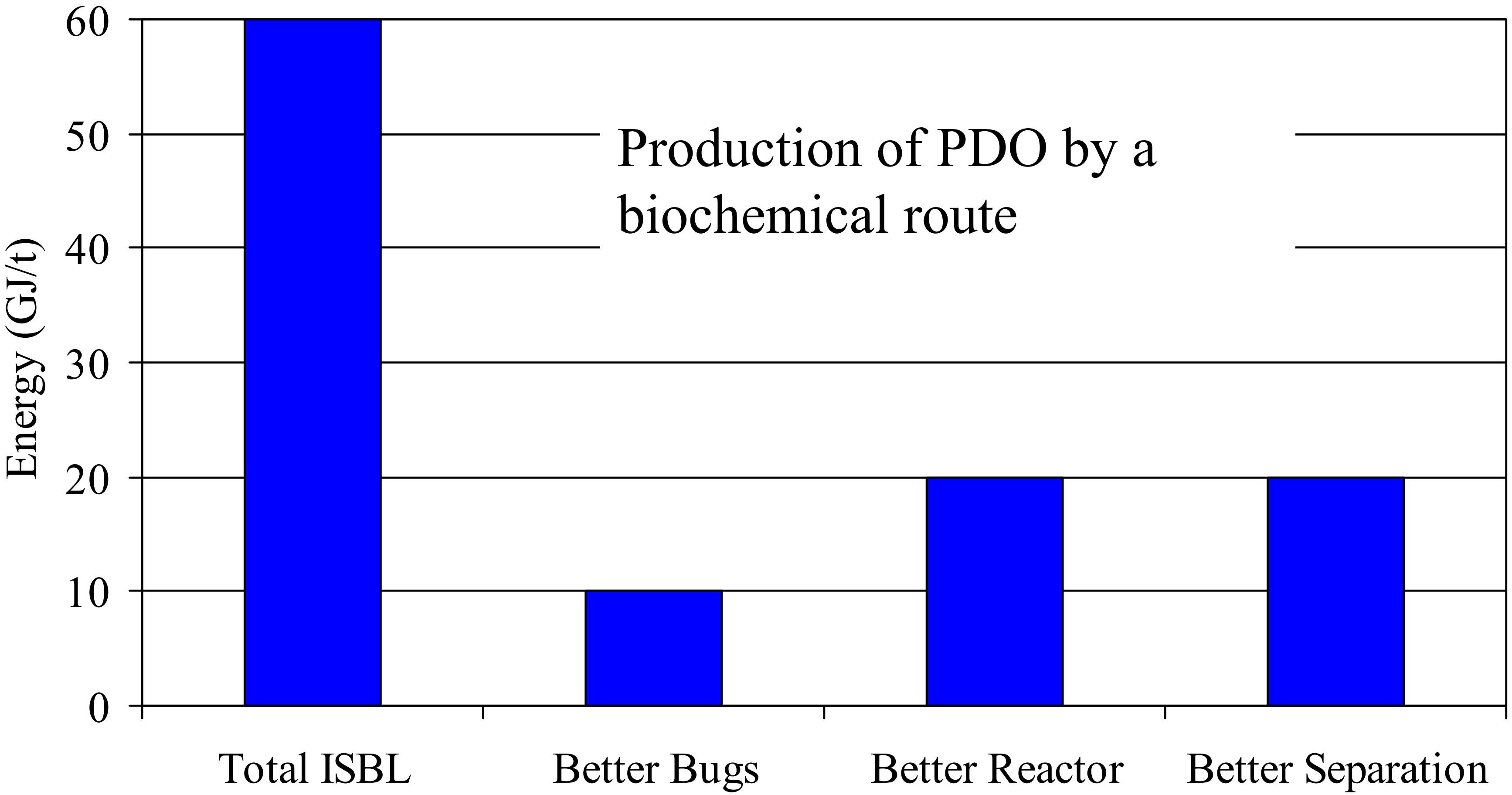
Potential application of MR’s in production of Ammonia Nitrate



Trends for the Future Chemical Industry

- C1 chemistry
  - Methanol-to-olefins
  - Fischer-Tropsch
  - Methane activation
- Replacing alkenes by alkanes as feedstock
- Biochemical routes

Potential ways to save energy in a bio-based processes
(BREW study, 2005)



Applications of MR's in chemical industry
conclusions

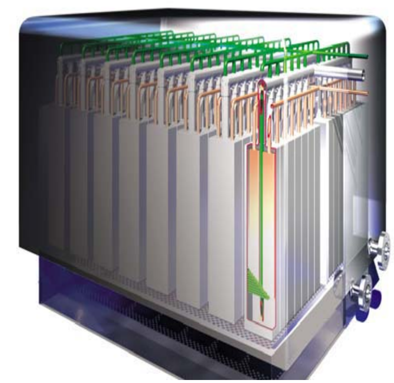
- For all important (energy-intensive) routes membrane reactor based processes could lead to increased efficiency
- Both in current and in future chemical industry
- Wide variety of membrane and principles

Pd based MEMBRANE REACTORS for steam reforming

Hydrogen membrane reactors

- Hydrogen production from natural gas
- Equilibrium-limited process
- High temperature needed to achieve sufficient conversion
- Applications:
  - Mostly produced in very large systems (100 000 Nm3/h) for industrial applications
  - On-site production market (500 – 5000 Nm3/h) much smaller
  - Much research interest in combination with fuel cells

Status of hydrogen membrane reactors
Tokyo Gas / Mitsubishi



Achievements
- 40 Nm3/h
- Fully integrated
- High efficiency (>80%)

Focus further development
- Lower investment cost
- Lower S/C
- Increase conversion with large membrane area
- Decrease auxiliary power consumption

Status of hydrogen membrane reactors MRT/BOC

Characteristics:

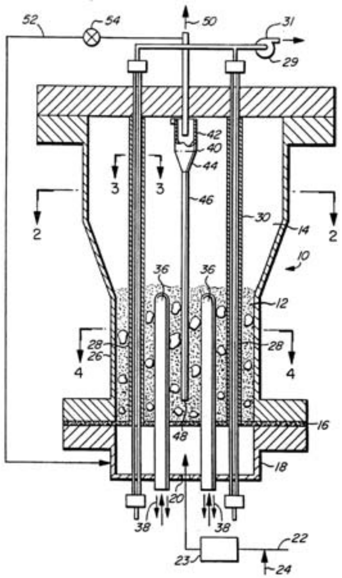
- Fluidized bed reactor
- Flat-plate membranes

Achievements:

- Fully integrated system
- 15 Nm3/h
- No detrimental effect of catalyst on membrane

Focus on:

- Optimisation of membrane cost vs. performance/lifetime
- Cost of mechanical design

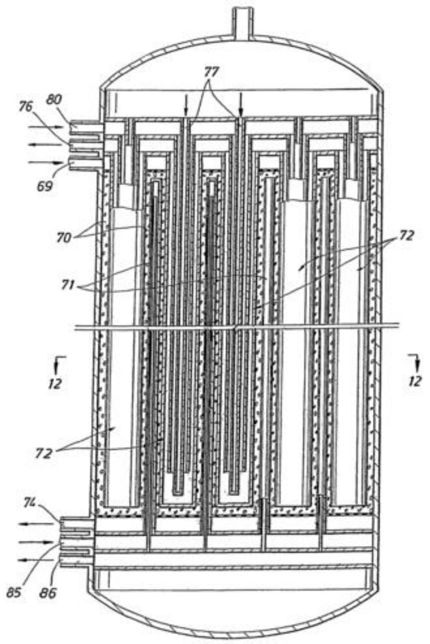


Status of hydrogen membrane reactors SHELL/CRI

Characteristics:
- Pd and Pd alloy membranes on tubular porous metallic support
- Patents in different reactor concepts

Achievements:
- Membranes scaled up to L = 120, D = 5 cm
- High conversion in reformer, long life-time as separator

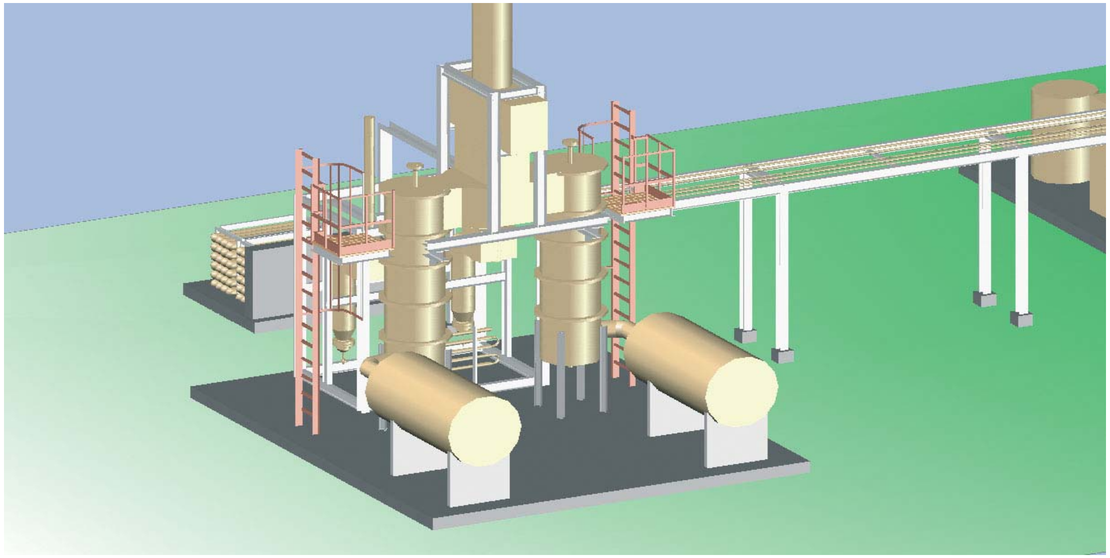
Focus:
- Improving and commercializing membranes



Status of hydrogen membrane reactors KTI/membrane developers

Characteristics:

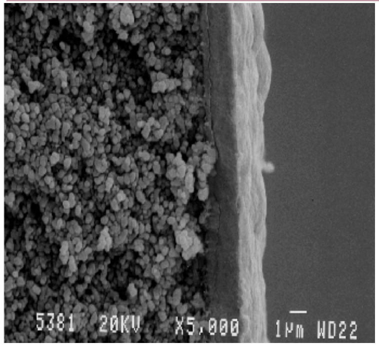
- Development of hydrogen generator with partial integration
- Building 20 Nm^3/h unit
- Different membrane suppliers



Status of hydrogen membrane reactors ECN

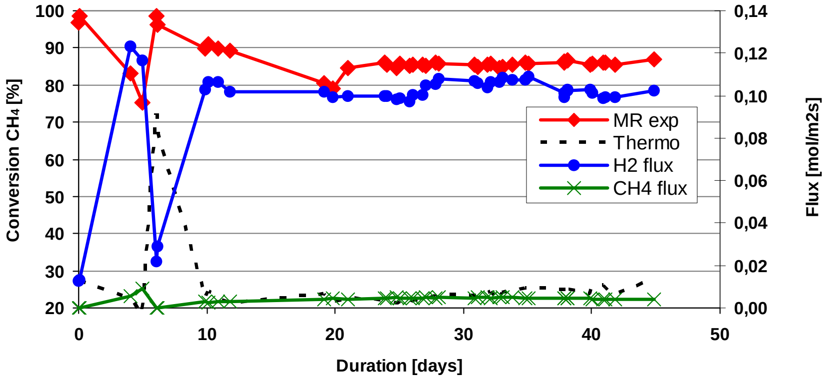
Applications:

- Large-scale industrial hydrogen production
- Carbon capture energy production
- On-site hydrogen production
- Dehydrogenation



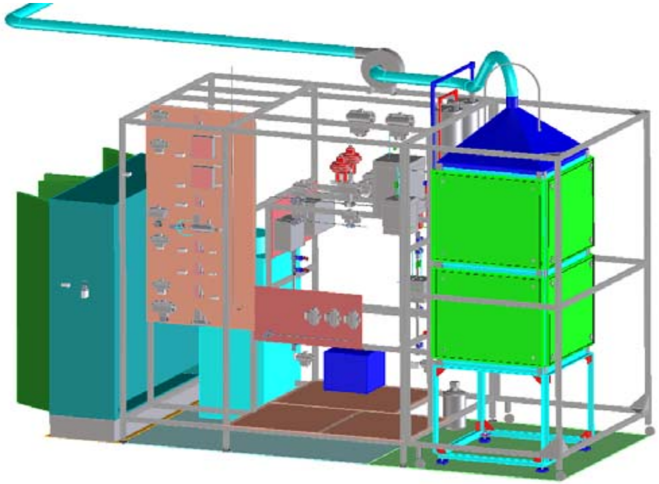
Thin (3-5 μm) defect-poor Pd or Pd alloy layer on a (inexpensive) porous ceramic support

Status of hydrogen membrane reactors ECN



Steam reforming reactor tests

→ poster Yvonne van Delft (S06-P202)



Status of hydrogen membrane reactors

- Significant progress has been made by a number of consortia in scaling-up from lab to systems
- Key technical and economical challenges remain to be resolved, for example:
  - Membrane and catalyst lifetime
  - Improving economic reactor and process design
  - Creating a chain-of-supply for membranes and catalyst
  - Financing scale-up (valley-of-death)

Key challenges

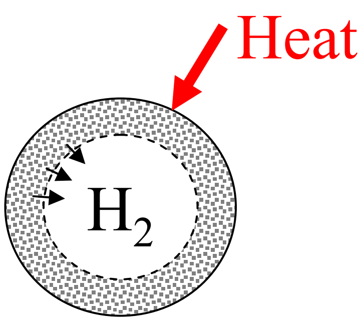
Challenges in reactor design:
Operating window

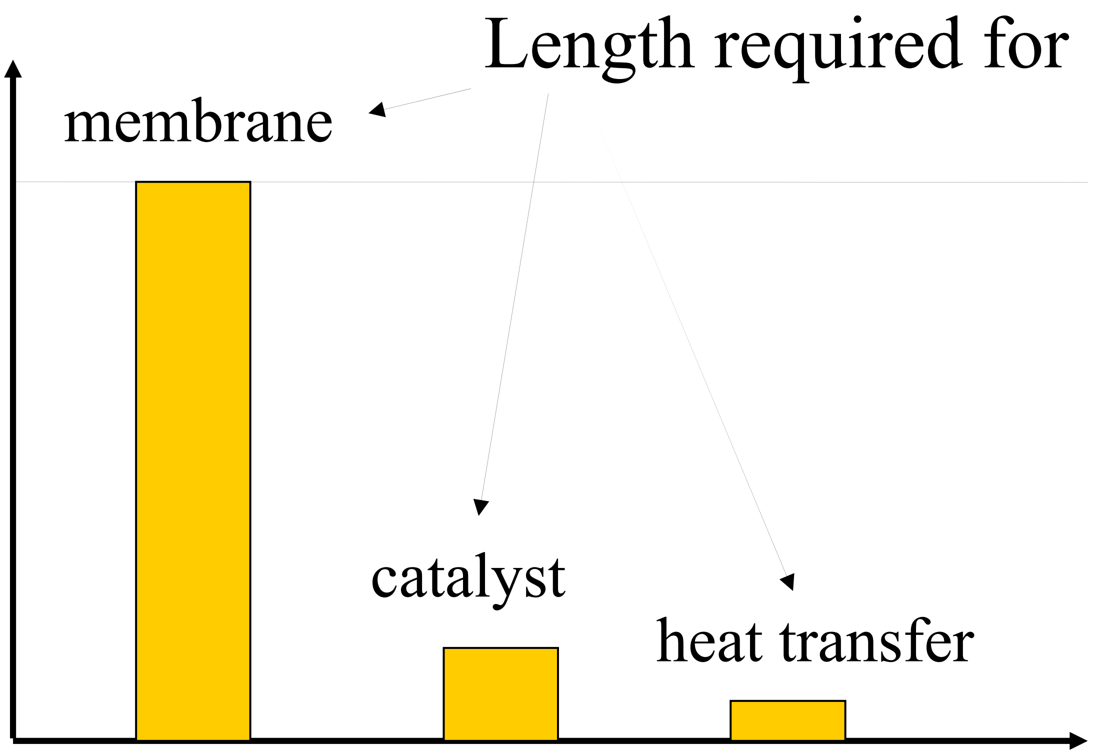
Matching reaction and separation

- Understanding interactions between catalyst and membrane
- (Undesired) catalytic activity of membrane
- Operating catalyst and/or membrane at different conditions

- Schembecker, G.; Tlatlik, S. (2003) *Process synthesis for reactive separations*, CEP, 42.
- Stitt, E. H. (2006) *Multifunctional reactors? "Up to a point lord Copper"*, IchemE, Feb 2004

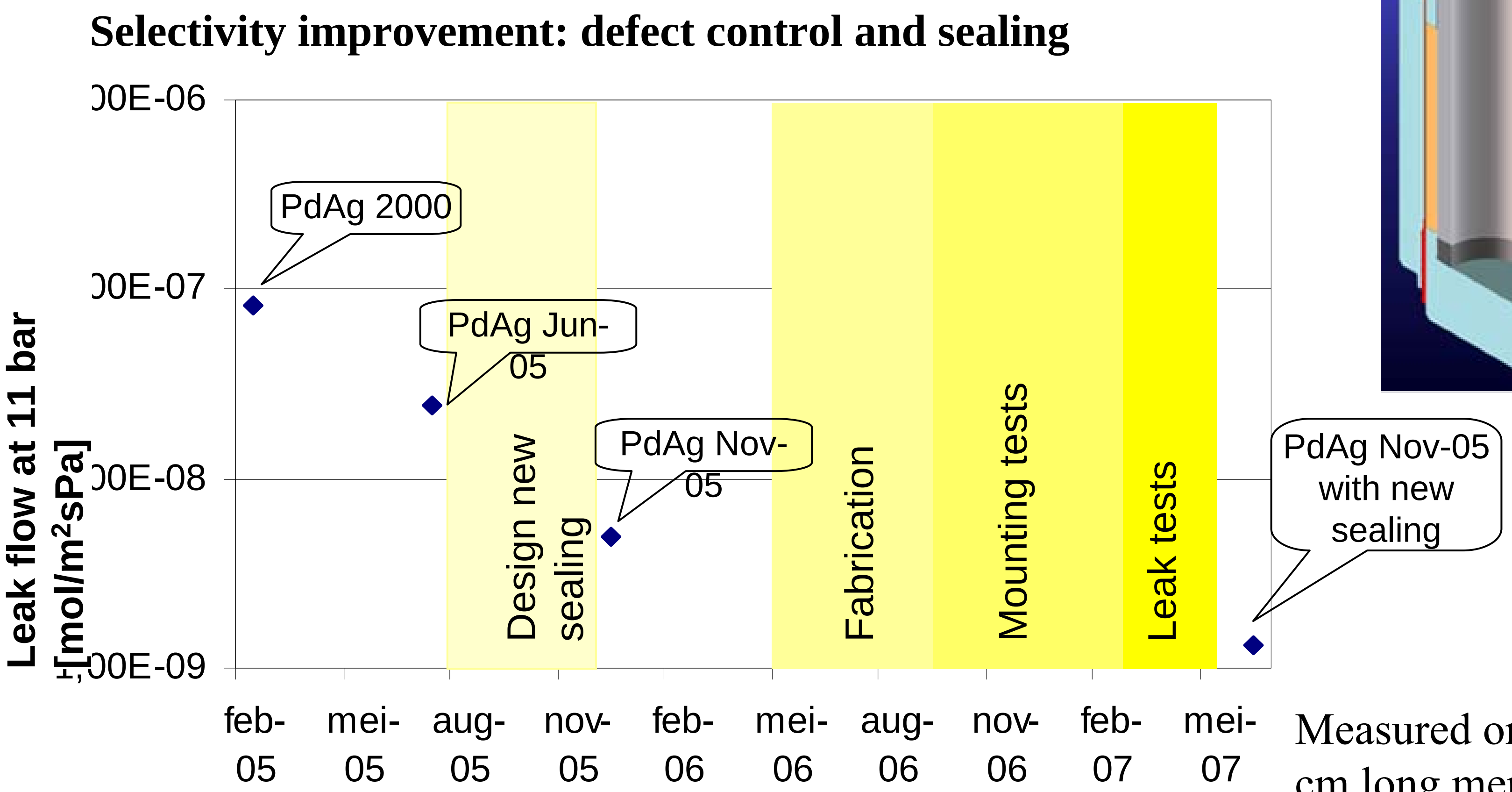
Challenges in reactor design:
Multi-functional and economic

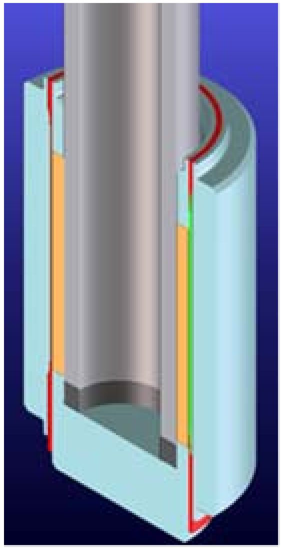




How to match for an economic reactor design?

Challenges in reactor design:
Sealing





Measured on 90 cm long membranes

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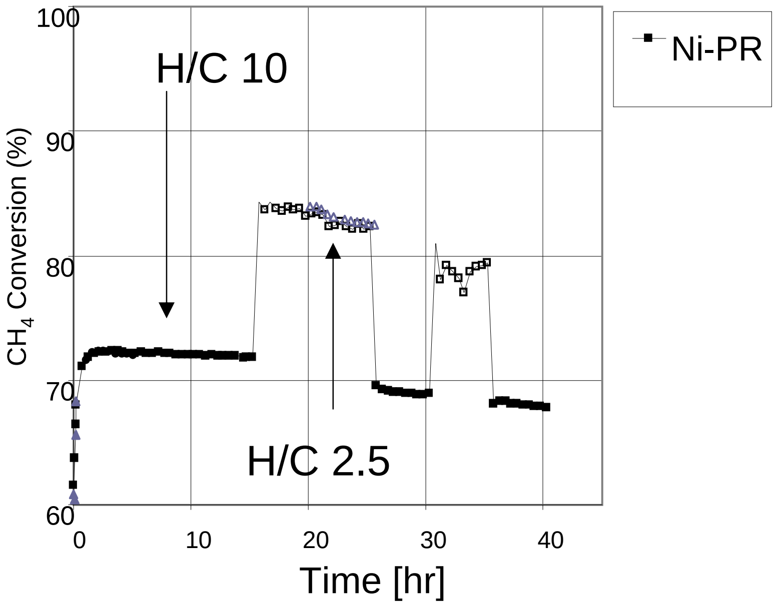
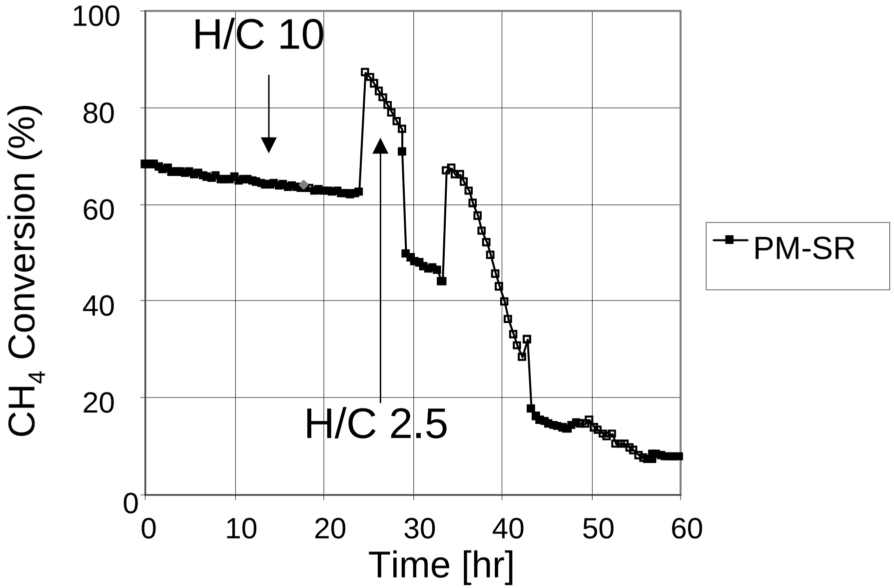
Challenges in membrane development:
Lifetime issues

Jean-Pierre Pieterse (S7-O32, this afternoon)

Catalyst issues:
- Activity at lower temperature
- Lifetime at other conditions

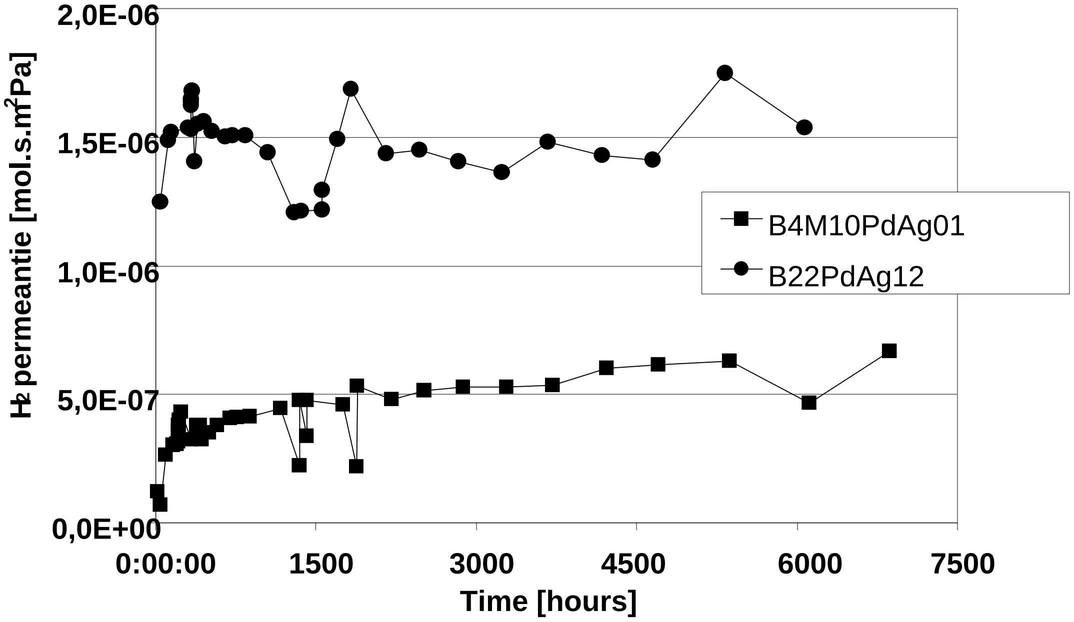




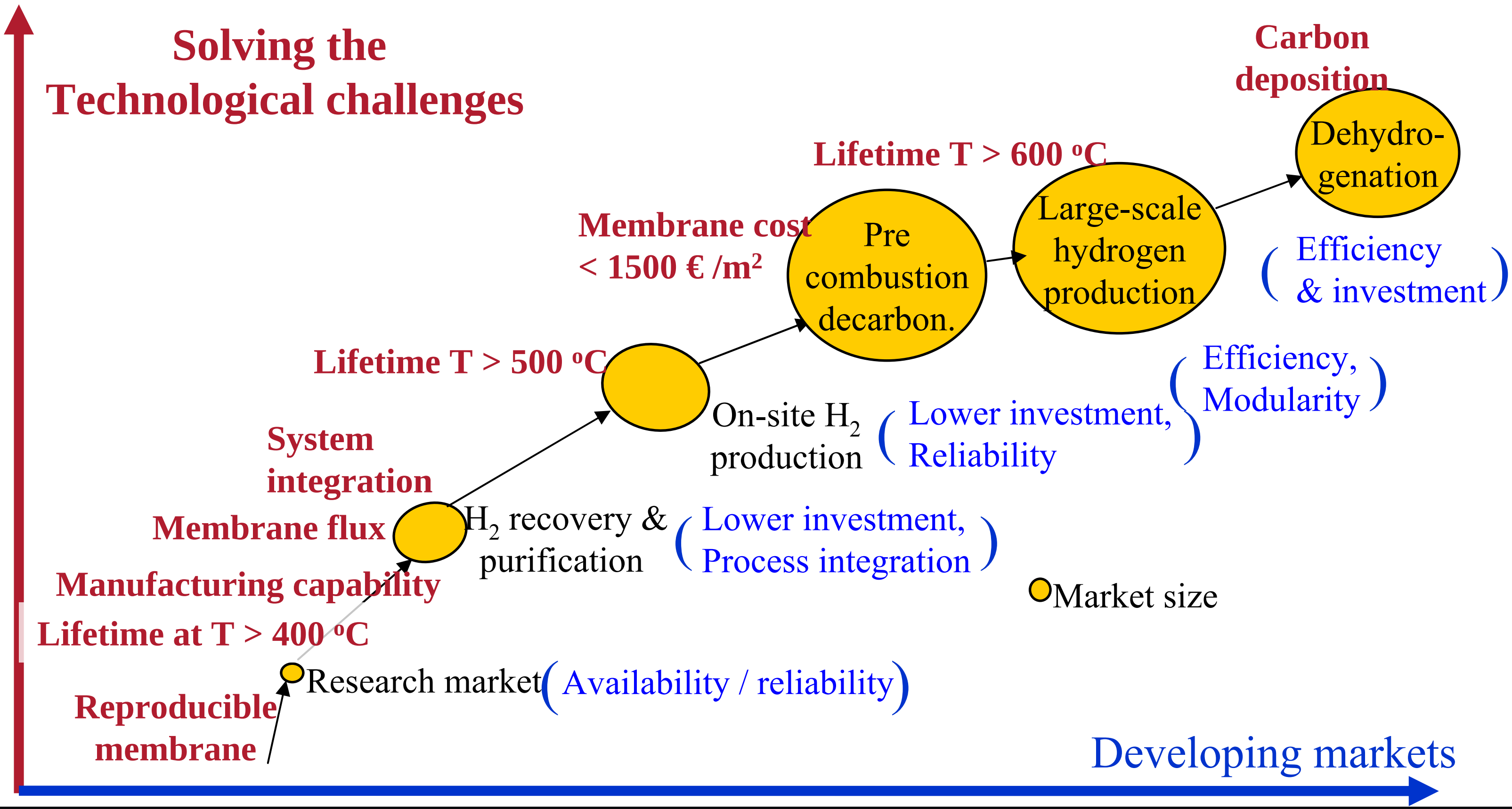
Challenges in membrane development:
Lifetime issues

Many different membrane developers have shown lifetimes several 1000's of hours at temperature (350-500 ^oC)

Lifetime >500 ^oC is issue



Challenges in membrane development:
Creating the chain of supply for membranes



Challenges in membrane development:
Creating the chain of supply for membranes

First step: provide separation modules to third parties

Objectives:

- Accelerate learning process by partnering
- Create partnerships for membrane fabrication

Partners:

- CRL Energy (New Zealand)
- University of the Basque Country (Spain)
- Technip KTI (Italy)
- N-GHY (France)

Challenges in membrane development:
Creating the chain of supply for membranes

HYSEP®
Hydrogen Separation Modules

Prototype hydrogen separation modules:

- Single or multi tube
- Hydrogen flow: 0.15 - 6 Nm^3/h
- Up to 25-70 bars

www.hysep.com

Challenges in membrane development:

Creating the chain of supply for membranes

Challenges in membrane development: Involving industry

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Acknowledgements

- Sponsors: SenterNovem, EU (different projects)

- Partners
  - Hygear, Continental Engineers
  - BP, Sintef, Dalian, PDC, NTUA

CONCLUSIONS AND RECOMMENDATIONS

- Membrane reactor potential in the chemical industry
- Key challenges
- Creating a common agenda with industry
- Many consortia bringing technology from lab to implementation

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Thank you for your attention!