PIN-NL

Dutch Process Intensification Network

Process Intensification Research and Development

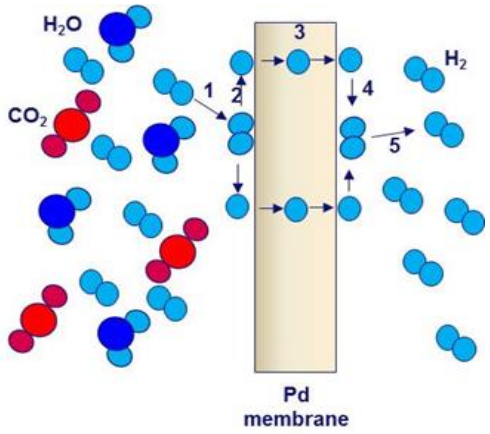
One of our PIN-NL objectives:
dissiminate and exchange PI knowledge and experience

PIN-NL / PSE-NL meeting 13 April 2017

Wikisheet
Membrane Reactors for Hydrogen Production

The mechanism of **selective hydrogen separation** involves a series of steps (at least 5 for thick membranes):

1. adsorption
2. dissociation
3. diffusion
4. re-association
5. desorption



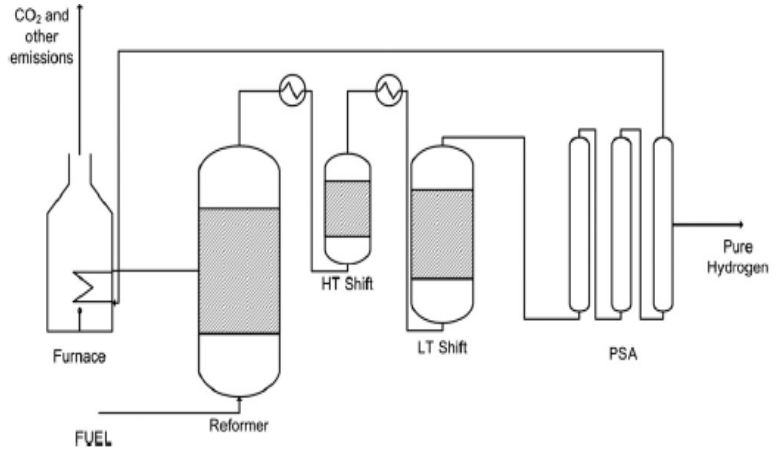
Chemistry and H_2 production

Traditionally hydrogen produced via steam reforming –SR- of hydrocarbons, e.g. CH4. naphtha, oil or methanol/ethanol.
Industrially >80% by SR of natural gas in multi-tubular fixed-bed reactors

Steam reforming: $CH4 + H2O \rightleftharpoons CO + 3H2$ ($\Delta H298\ K = +206$ kJ/mol)
Water-gas-shift: $CO + H2O \rightleftharpoons CO2 + H2$ ($\Delta H298\ K = -41$ kJ/mol)
Overall: $CH4 + 2H2O \rightleftharpoons CO2 + 4H2$ ($\Delta H298\ K = +165$ kJ/mol)

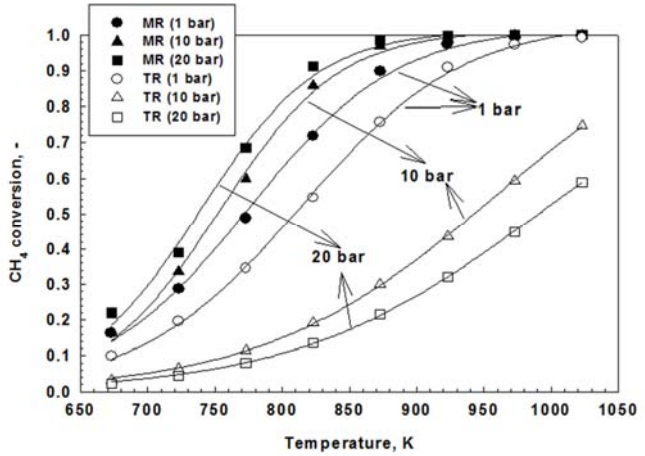
- All reactions equilibrium limited
- Endothermic reactions require combustion of part of CH4
- Gas product is a mixture

Conventional steam reforming to H2



High temperature reformer, HT and LT shift, separations

H2 perm-selective membranes = PI, basics



Increased conversion by H2 removal + positive P effect

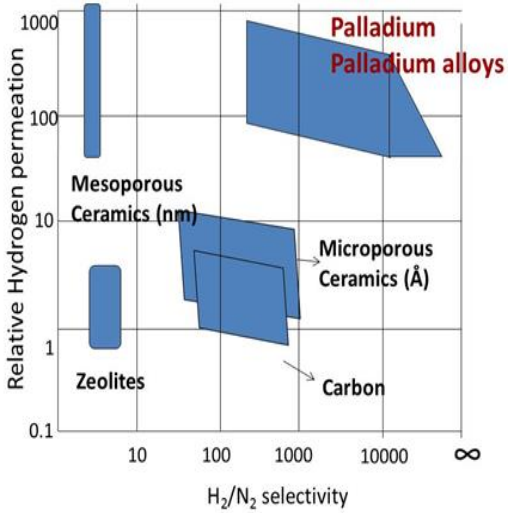
H2 perm-selective membranes = PI, needs

- Production of thin membranes with high H2 fluxes and H2 selectivities
- Design of innovative reactor concepts – reaction+separation+ heat exchange, reduction of mass and heat resistances, construction of membranes and sealing+housing

Membranes should have:
- High selectivity towards H2
- High flux
- Low cost
- Mechanical and chemical stability

R&D is ongoing to pilot scale process – near future

H2 permeation versus H2/N2 selectivity

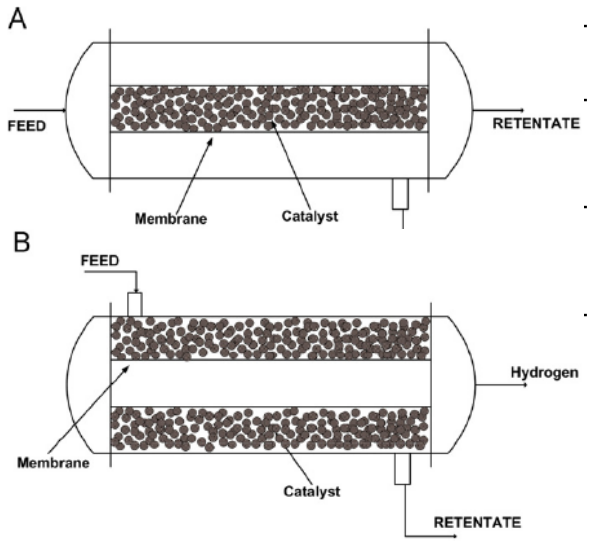


Pd alloys, thin layers 1-5 µm, supported by microporous ceramics

Unsupported, >50 µm, low H2 permeance

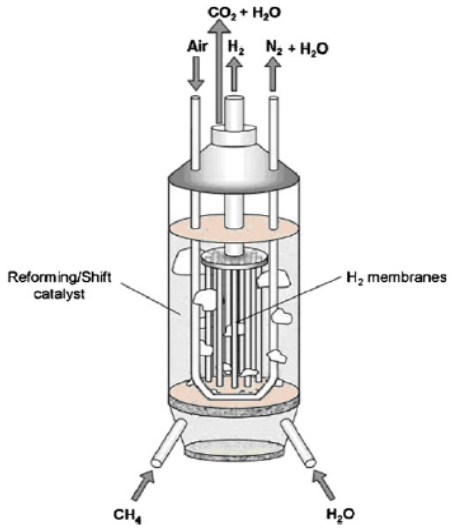
Inconsistency between publications

Membrane reactors – packed bed



- Catalyst in shell or in tube
- Cat can be poisoned by H2S or CO at T< 300°C
- Flux through membrane is often limiting step
- Heat management + T profiles-challenges endothermic reaction max T membrane, autothermal can give hot spot

Membrane reactors – fluidized bed, MAFBR



- For ultra pure H2
- Bundle H2-selective membranes in fluid bed
- Autothermal reforming →heat for endothermic reactions by burning H2 permeated in 2nd membrane
- Isothermal operation
- Low ΔP
- Exhaust CO2+steam only

Membrane assisted fluidized bed reactor

Membrane reactors – micro structured

- Improved mass and heat transfer owing to the reduction of the scale length in the micro-channels;
- Removal of mass transfer limitations (concentration polarization)
- High degree of process intensification by integrating different process steps in a small scale device.

Reactor:

- Micro-channels13 mm long and a section 1 mm x 1 mm,
- Membranes self- supported Pd-based thinner than 3 mm
- A 1.4 μm thick membrane can withstand a differential pressure >470 kPa.

Although there is a great interest in micro-reactors, the application of membrane micro-reactors is still limited.

Objective of this contribution: show participants examples of new developments in PI related R&D

Method applied:
Selection of PI R&D sources – literature and contacts

Basis: a 22 pages review and ~10 publications were selected
The support of Martin van Sint Annaland, TU/e, is appreciated:
"MBR merging to industrial application"

Open: **next topic to be discussed**

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