MEMBRANE REACTORS FOR DEHYDROGENATION REACTIONS

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New and innovative methods for the conversion of alkanes to olefins and aromatics – April 13, 2021

Outlook

- Who we are
- Why Membrane reactors
- Bizeolcat membrane reactor
  - Experimental on membranes
  - Techno-economics

Our Lab(s)

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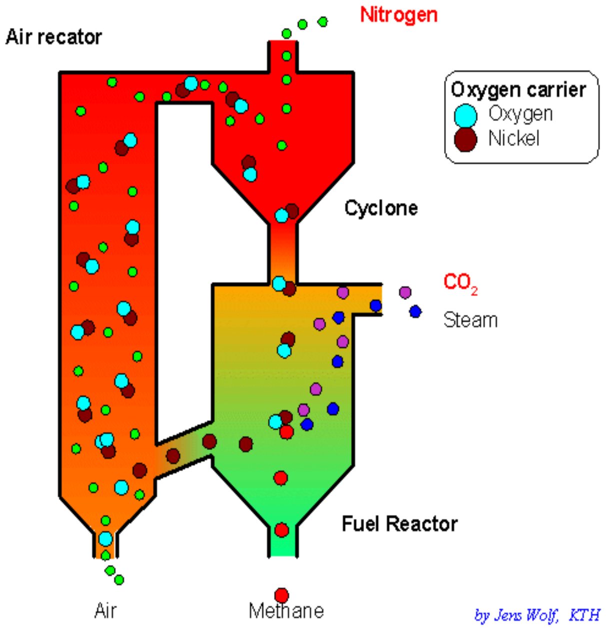
Research themes - SIR

- Novel intensified reactor concepts via:

➢ Integration <u>reaction</u> and <u>separation</u>
(membrane reactors, chemical looping)

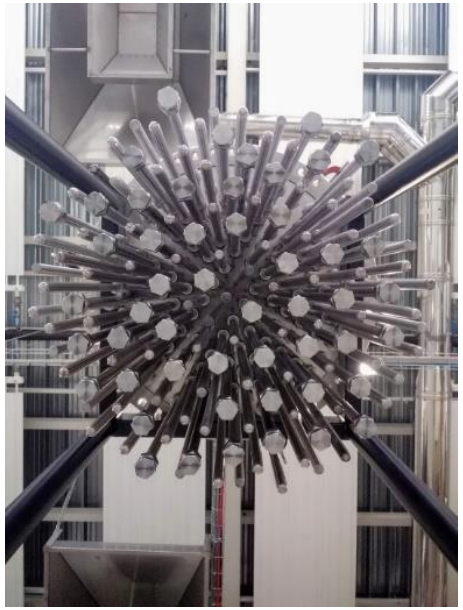
➢ Integration <u>reaction</u> and <u>heat/energy management</u>
(endo/exothermic, plasma systems)

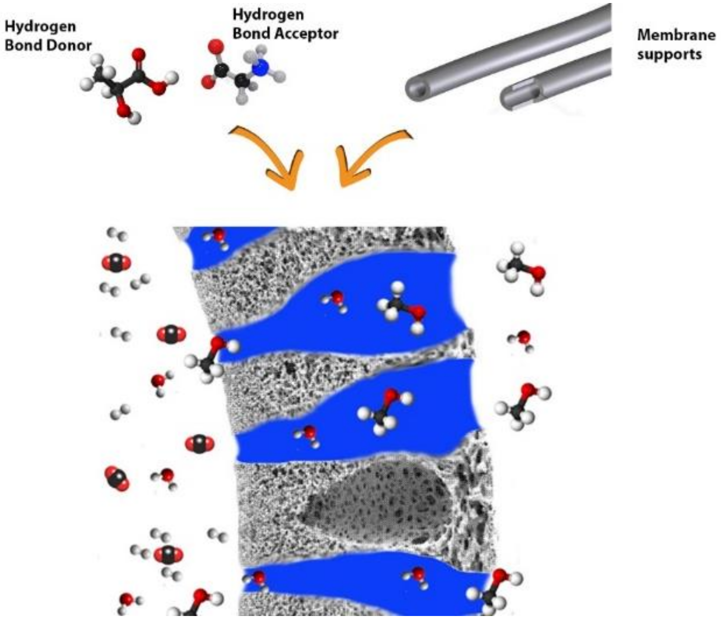


- **Research approach:** combination experimental PoC and modelling

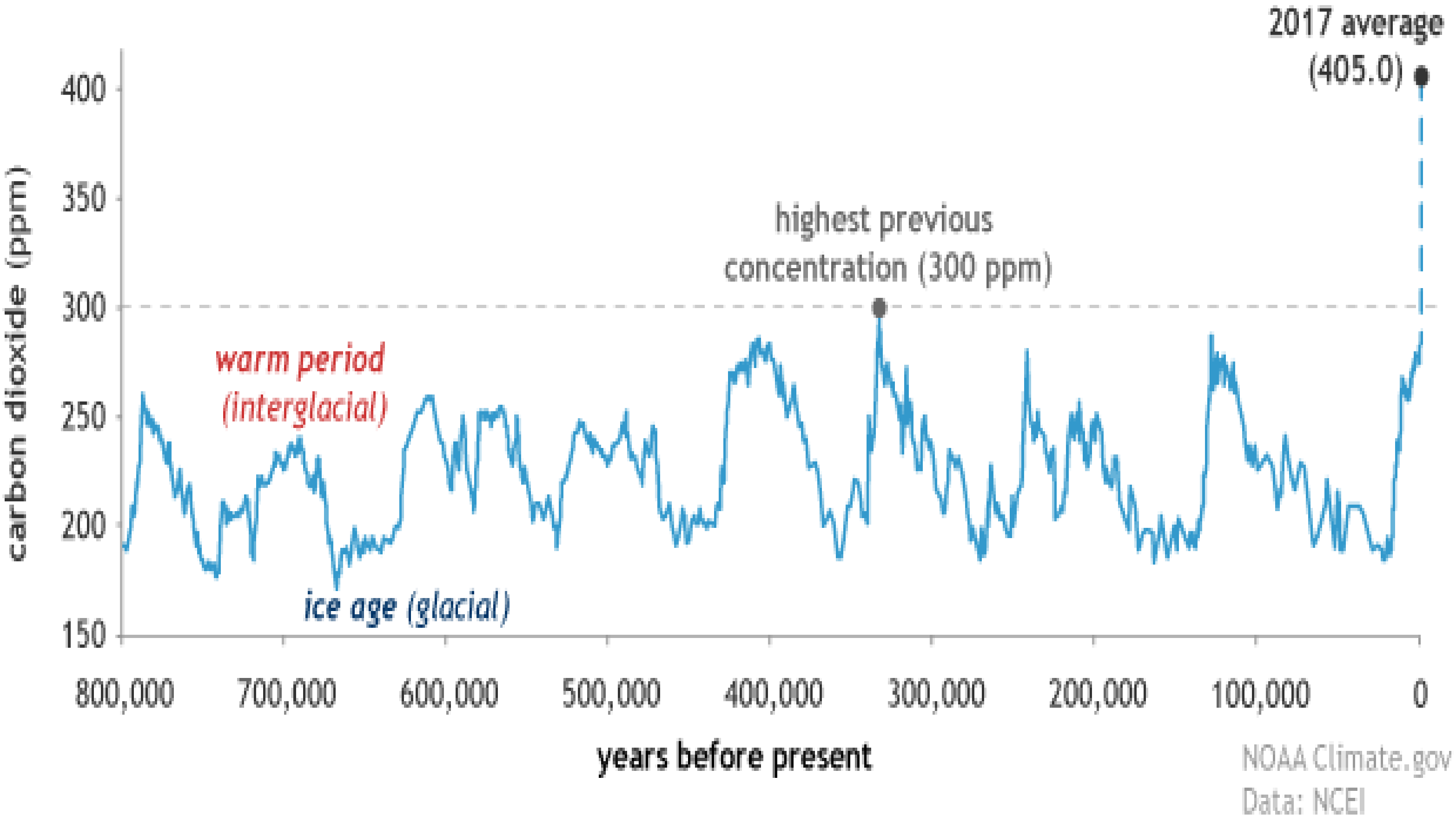
Research themes - SIR

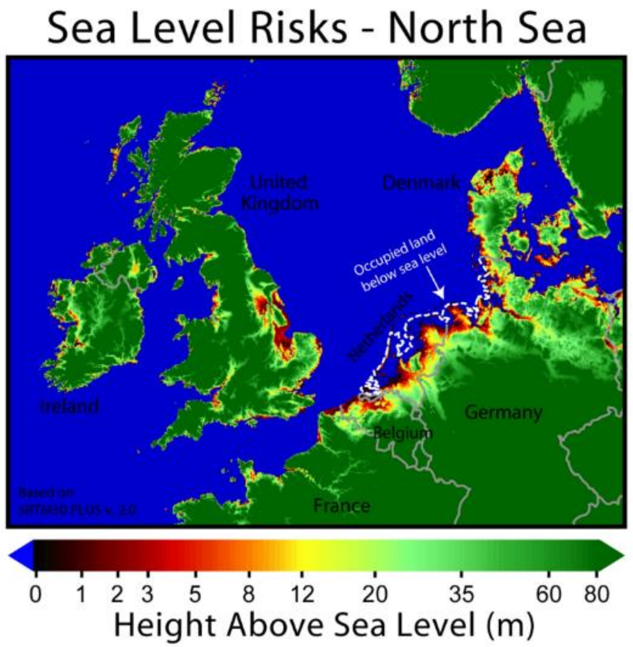
- Integration reaction + separation
- *Packed bed and fluidized bed membrane reactors*
  (H_2, syngas, oxidative dehydrogenations, partial oxidations)
  - Use membranes to improve fluidization and fluidization to improve membrane flux
  - Liquid supported membranes



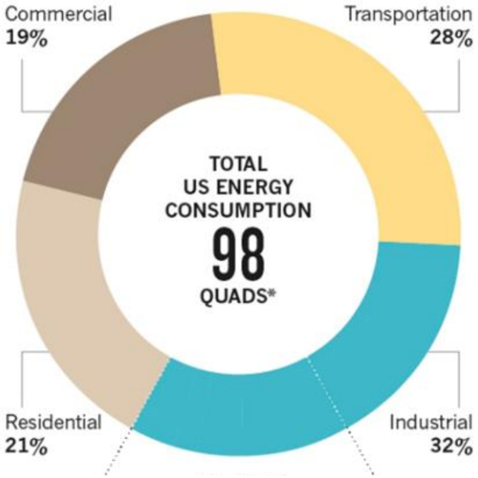


One of our challenges





A possible solution



*A quad is a unit of energy equal to 10^{15} British Thermal Units (1 BTU is about 0.0003 kilowatt-hours).

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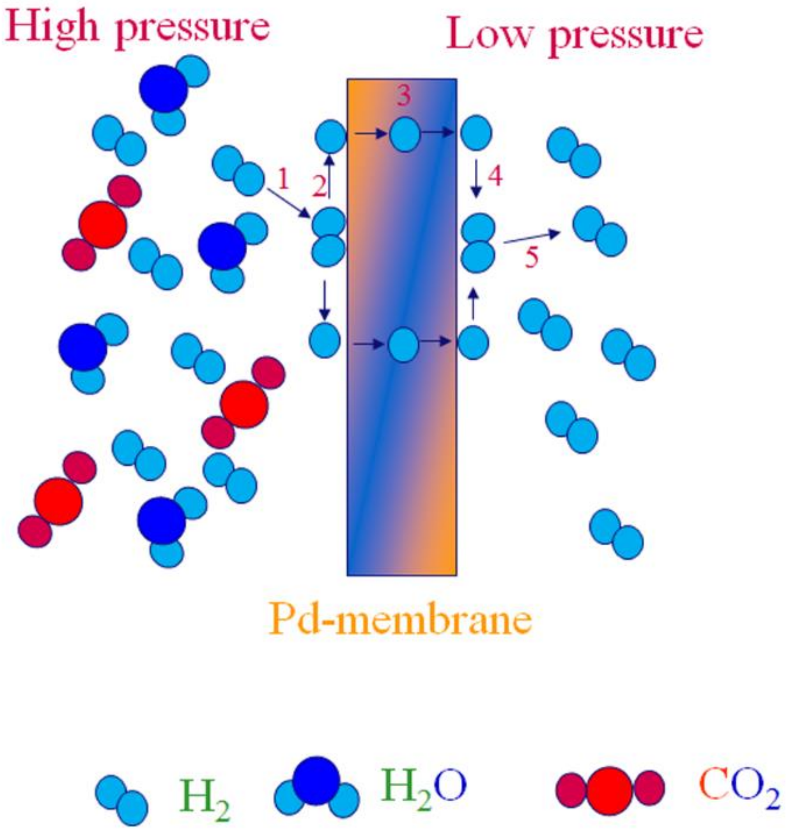
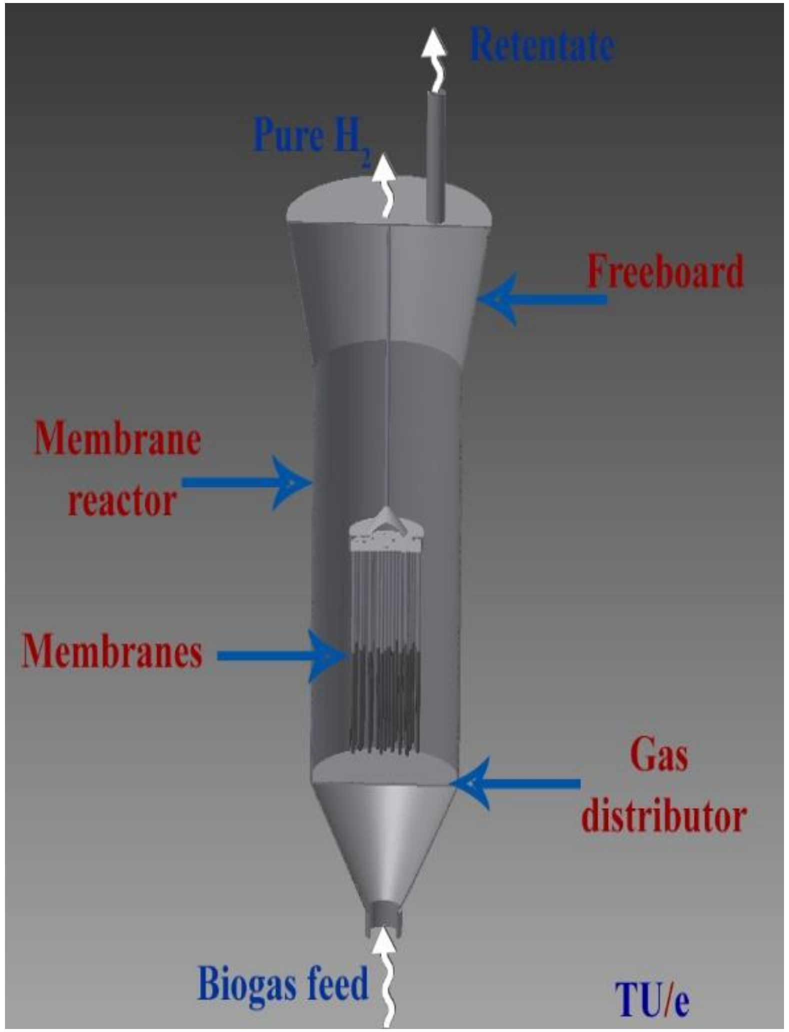
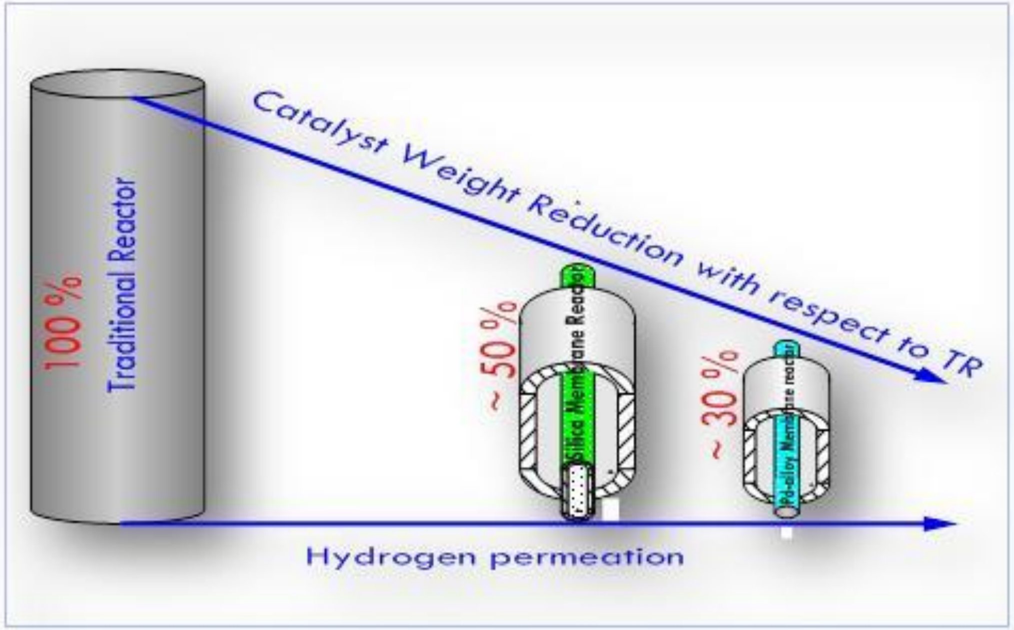


A membrane reactor

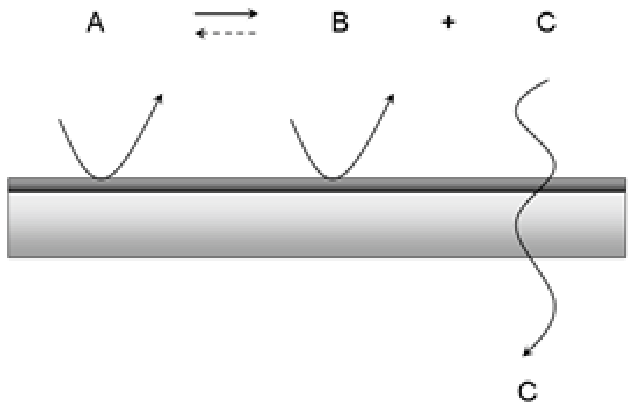


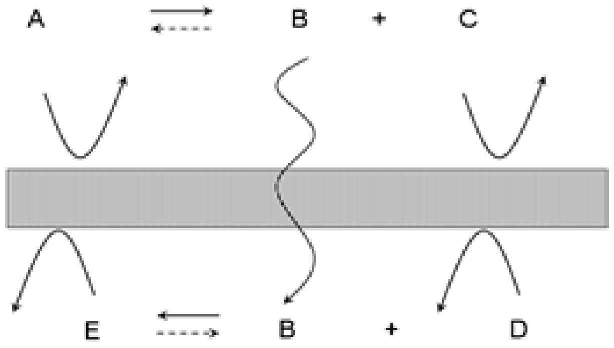


Brunetti A.; Caravella C.; Barbieri G.; Drioli E.; "Simulation study of water gas shift in a membrane reactor", *J. Membr. Sci.*, 2007, 306(1-2), 329-340

Why a membrane reactor?

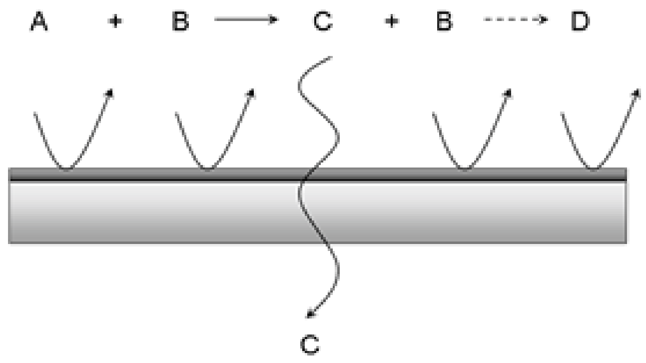
conversion enhancement by selective permeation of a reactant product of an equilibrium limited reaction

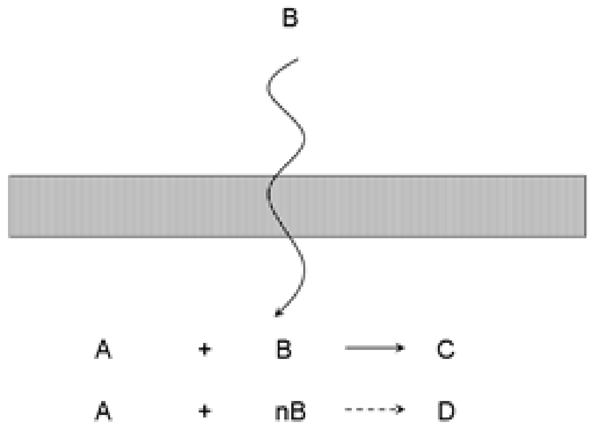




conversion enhancement by coupling of reactions

selectivity enhancement by selective permeation of an intermediate product

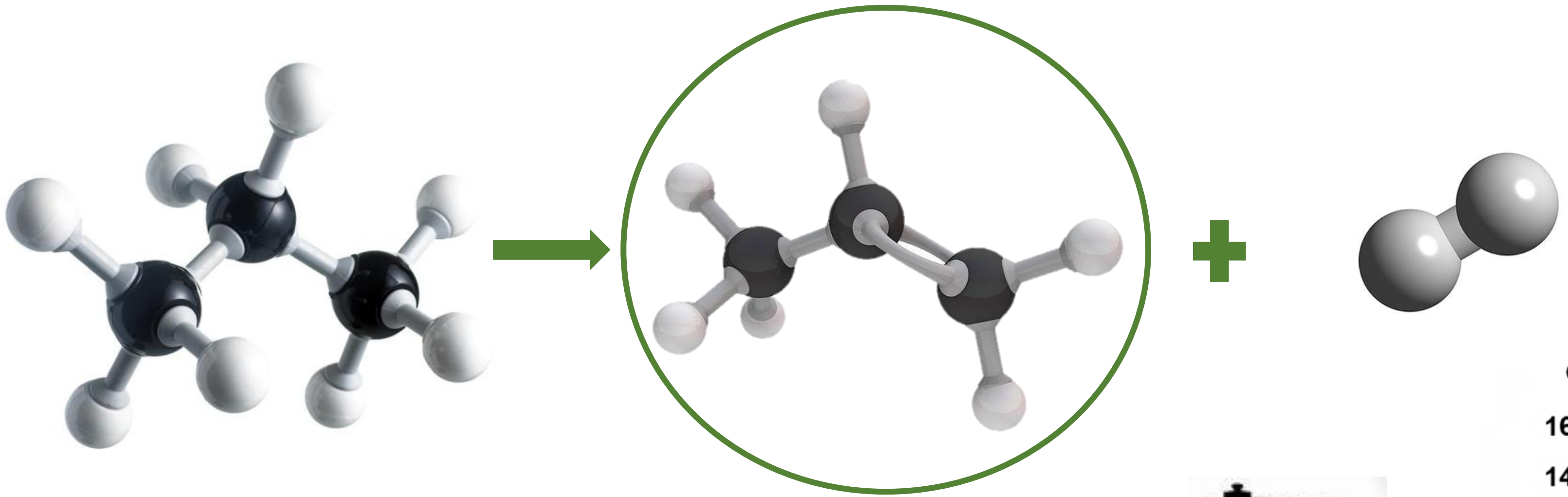




selectivity enhancement by dosing a reactant through the membrane

BIZEOLCAT why

Direct Dehydrogenation of Propane



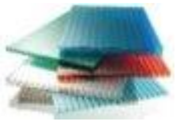
✓ Direct route for propylene production

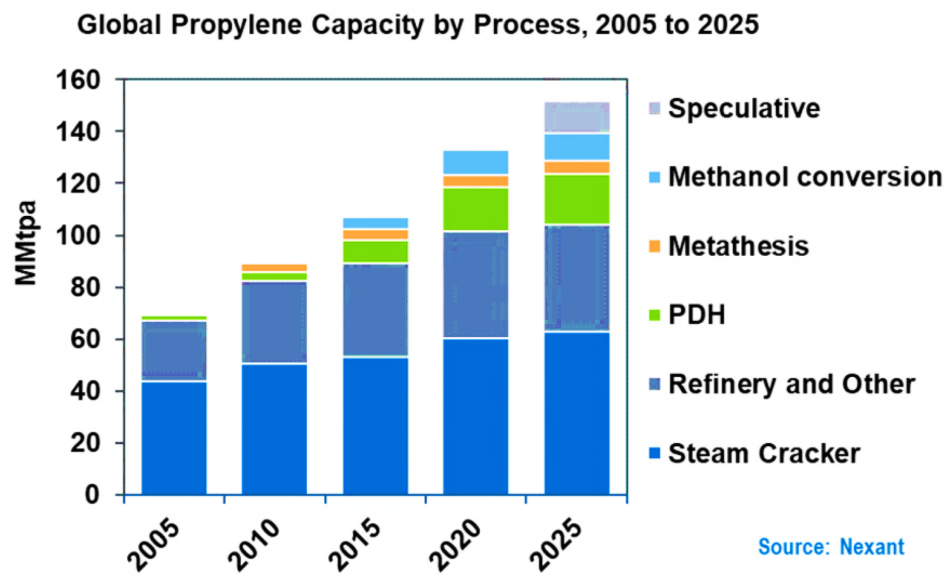
- Polypropylene
- Propylene Glycol
- Polyvinyl Butyral
- Acrylics

Fine chemicals

Monomers

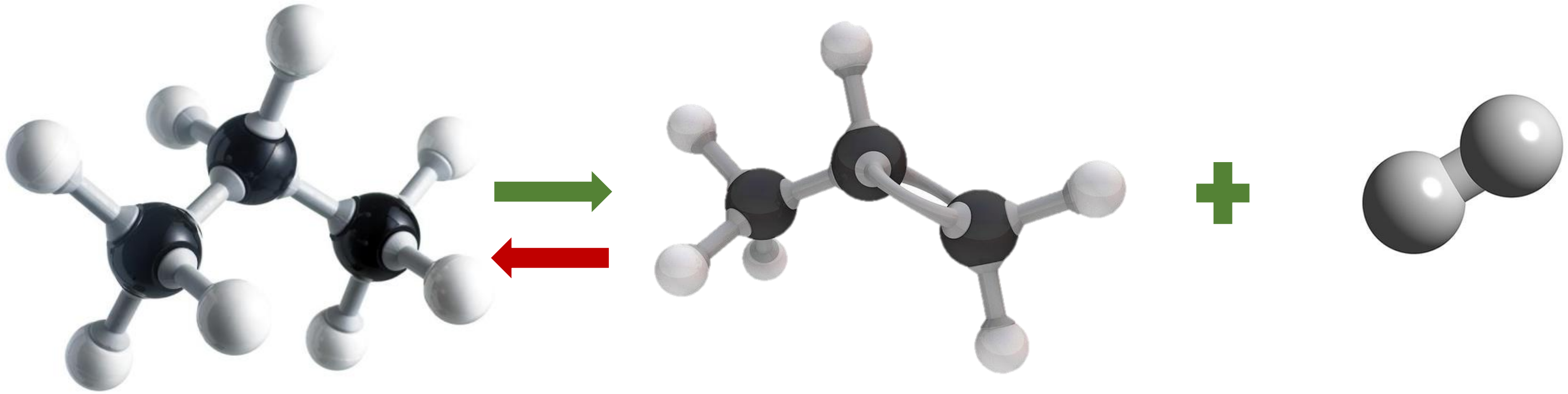
Materials (e.g. polymers)

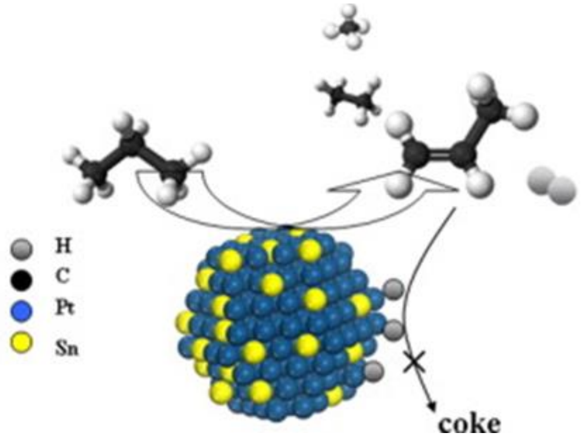




BIZEOLCAT why

Direct Dehydrogenation of Propane

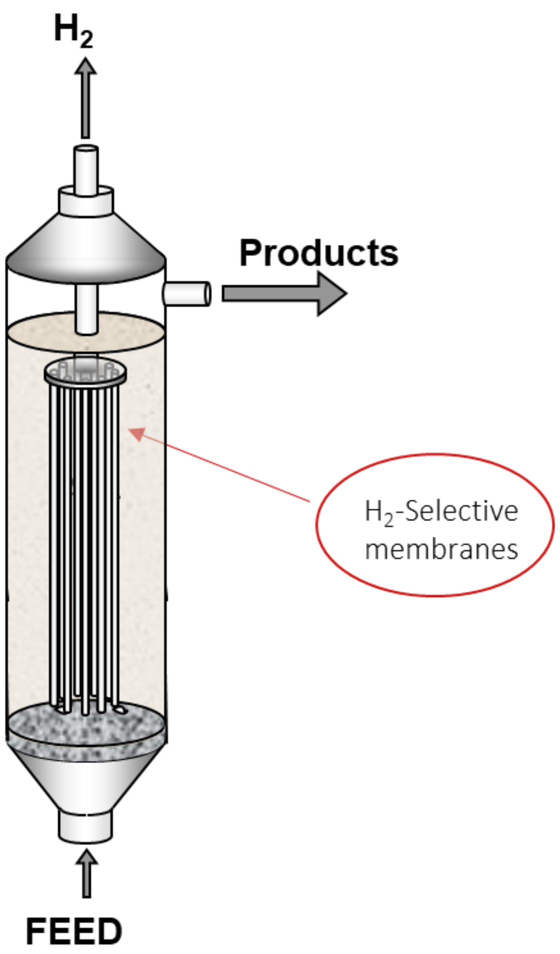


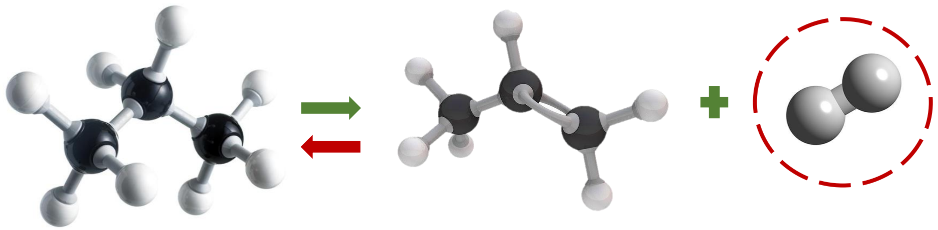


- ✓ Direct route for propylene production
- ✗ Limited by thermodynamic eq
- ✗ Highly endothermic $(\Delta H^0_{298K} = +120\,\frac{kJ}{mol})$
- ✗ Side cracking reactions → low product yield

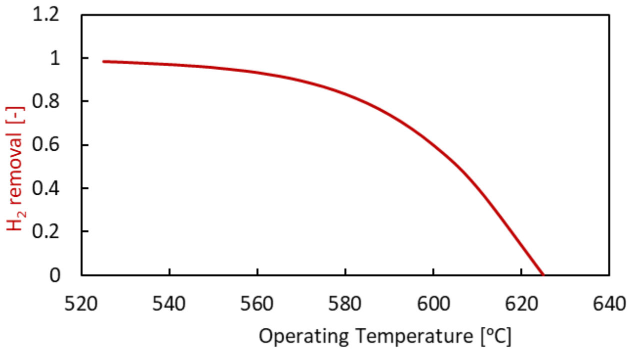
BIZEOLCAT how

Direct Dehydrogenation of Propane in H_2 Selective Membrane Reactors





- ✓ Continuous *in-situ* separation of H_2 shifts the equilibrium beyond thermodynamic restrictions (of conventional reactors)
- ✓ Milder operating conditions
- ✓ Higher product yields



Packed-Bed Membrane Reactors

Fluidized-Bed Membrane Reactors

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BIZEOLCAT how

H_2 Selective Membrane Materials

Requirements:

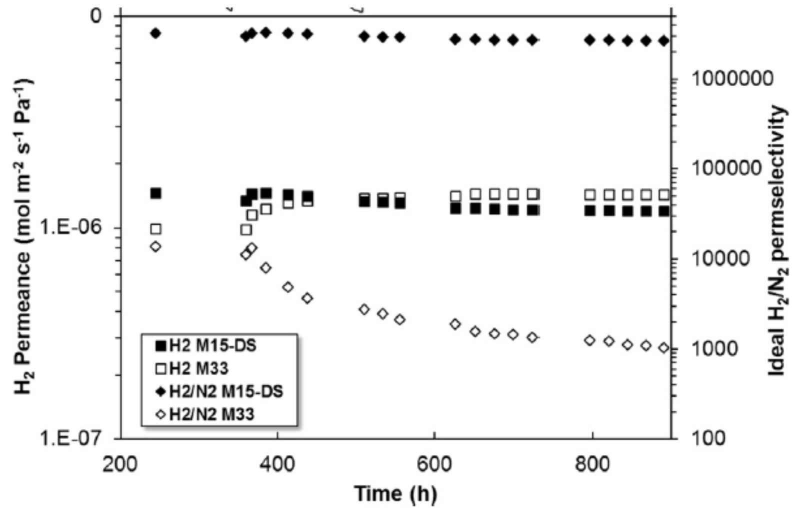
- High selectivity towards H_2
- High flux
- High chemical stability

  → against chemical interaction in catalytic beds
- High mechanical stability

  → against erosion in fluidized beds

Pd-based membranes

Novel Double-skinned PdAg membrane

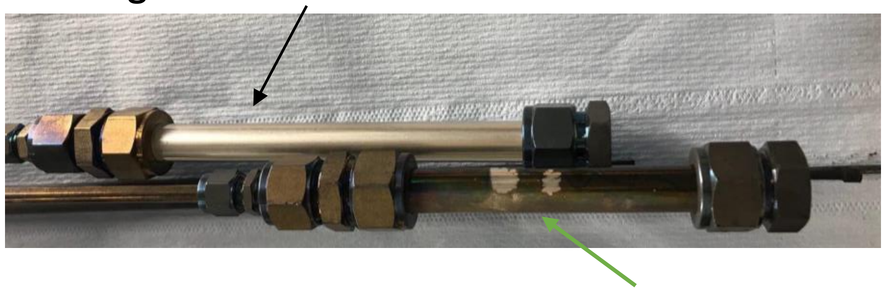


A. Arratibel, J.A. Medrano, J. Melendez, D.A. Pacheco Tanaka, M. van Sint Annaland, F. Gallucci, Attrition-resistant membranes for fluidized-bed membrane reactors: Double-skin membranes, J. Memb. Sci. 563 (2018) 419–426

Experimental Materials and Methods

- H_2 Selective Membranes

1. Double-Skinned Pd-Ag membrane (DS)
2. Conventional Pd-Ag membrane (C)



	DS-Membrane	C- Membrane
Asymmetric support	• Porous tubular substrates made of Al_2O_3 • Pore size of ~ 100 nm	
Selective layer	• Made of: $Pd_{93.33}Ag_{6.67}$ • Thickness: ~ **2-3 µm**	• $Pd_{95.67}Ag_{4.23}$ • ~ **3-5 µm**
Protective layer	• 50wt% YSZ- 50wt% γ-Al_2O_3 • Mesoporous: ~ 2-5 nm • Thickness: ~ **0.5 µm**	

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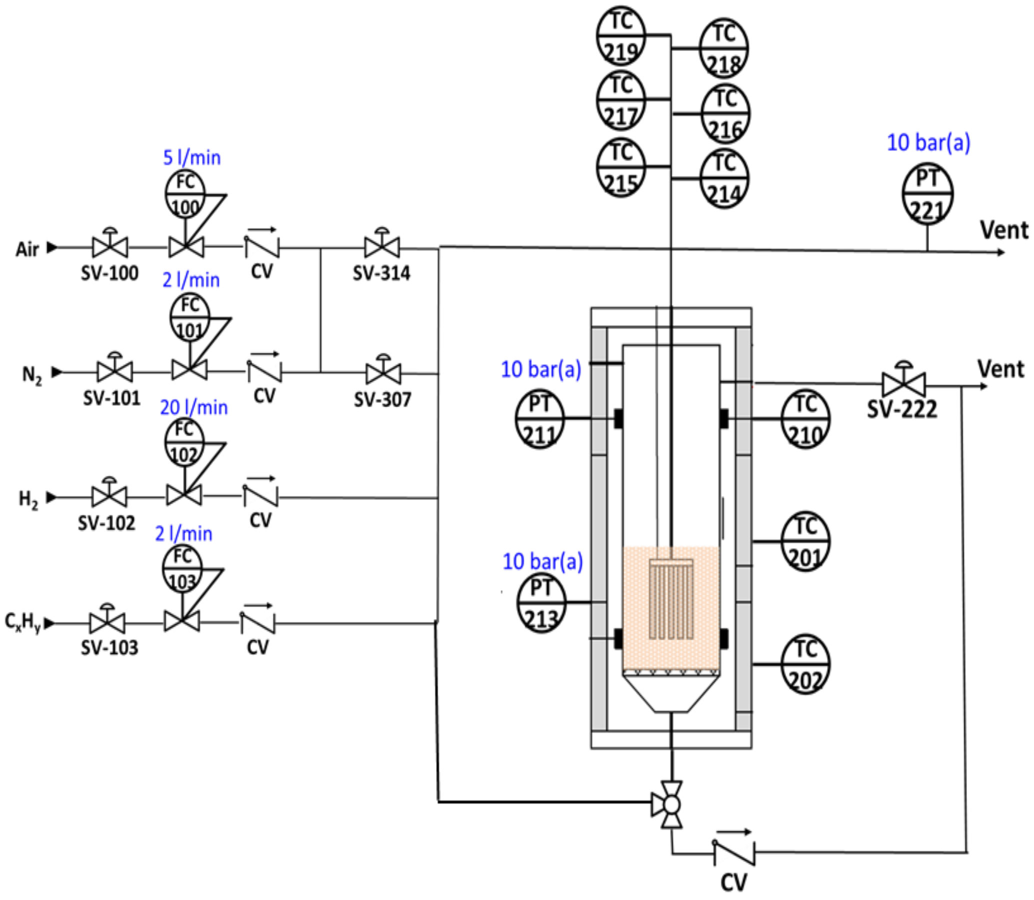
Experimental Materials and Methods

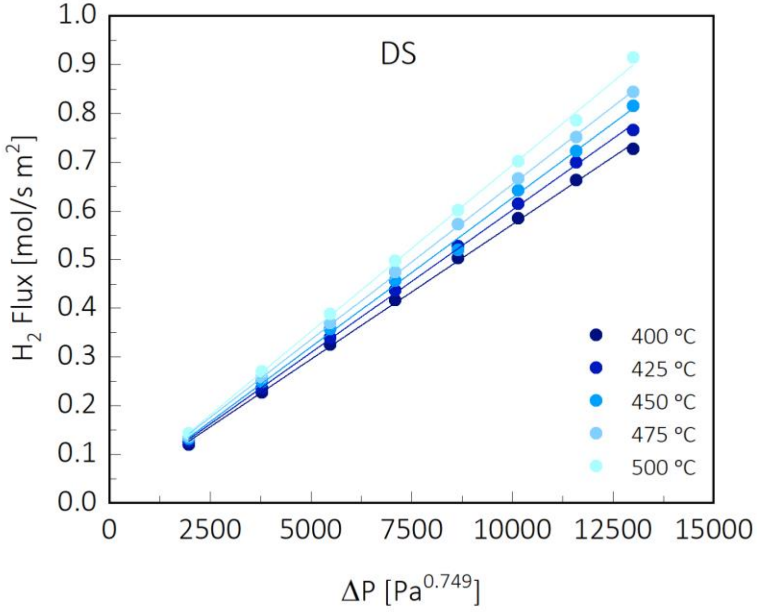
- <u>Experimental Tests</u>
  1. Membrane stability tests
     → Characterize membranes permeation properties
  2. H_2/N_2 mixture tests
     → Investigate the concentration polarization effect
  3. H_2/C_xH_y mixture tests
     → Investigate coke formation tendency
  4. SEM-EDX characterization post-mortem

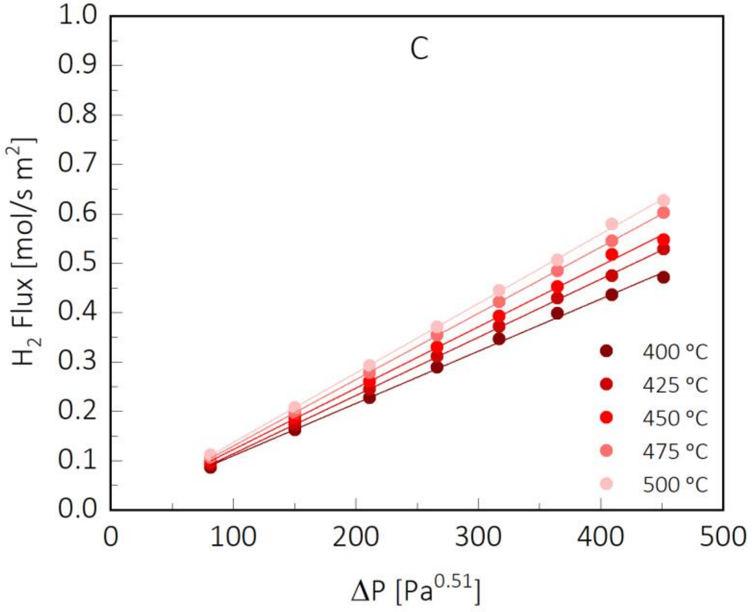


- <u>Operating Conditions</u>
  - T: 400-450 °C, ΔP: 2 bar, 90-60 vol% H_2
  - Cyclic exposure to pure H_2 and binary (H_2-N_2) and (H_2-C_xH_y) mixtures over time
  - Regeneration in diluted oxygen (25 vol% O_2 and 75 vol% N_2) for 2 minutes, at 400 °C

Experimental Results

- Membrane permeation properties: Single gas permeation tests





$P_0=4.373\cdot10^{-10}$ [$mol\cdot s^{-1}\cdot Pa^{-0.749}\cdot m^{-1}$]
$\delta=1.91\cdot10^{-6}$ [m]
E_{act} =7.8053 [kJ/mol]
n = 0.749 [-]

$P_0=2.79\cdot10^{-8}$ [$mol\cdot s^{-1}\cdot Pa^{-0.51}\cdot m^{-1}$]
$\delta=3.51\cdot10^{-6}$ [m]
E_{act} = 11.208 [kJ/mol]
n = 0.51 [-]

H_2 permeance
(T= 500 °C, ΔP= 4 bar):

$2.28\cdot10^{-6}$ $mol\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1}$

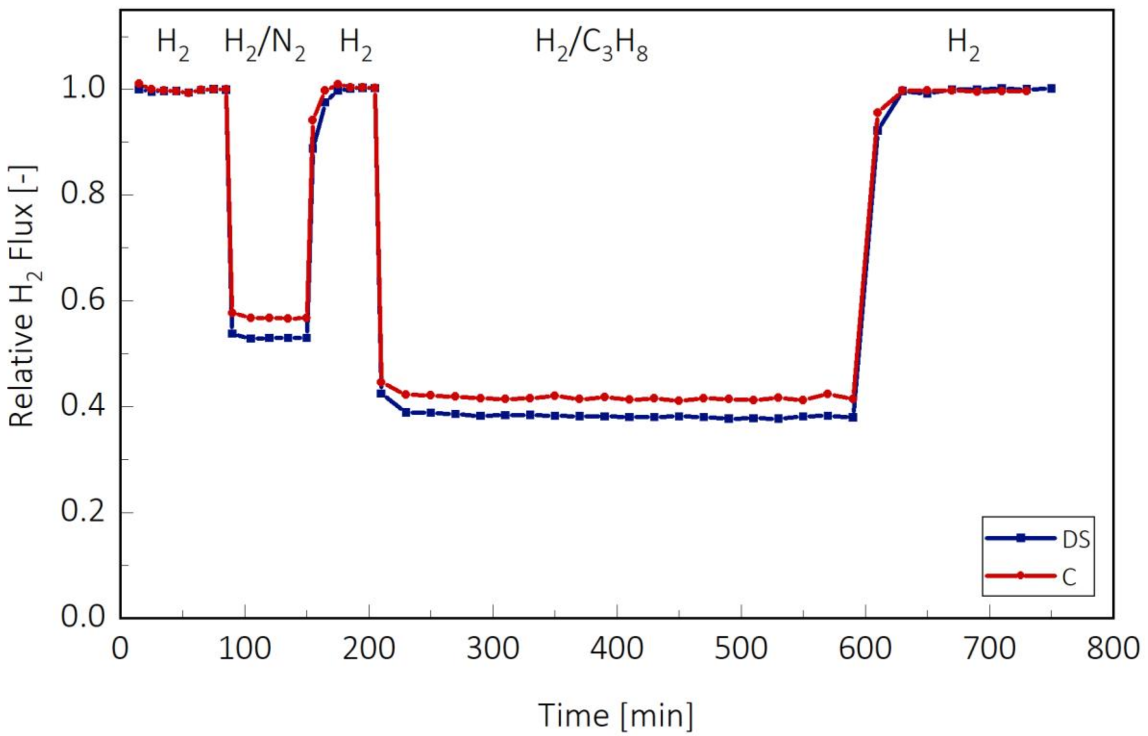
$1.56\cdot10^{-6}$ $mol\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1}$

Experimental

T= 400 °C, ΔP= 2 bar
$H_2/N_2 - H_2/C_xH_y$: 80/20 vol%

- Membrane performance in PDH conditions: exposure to alkanes/alkenes

PROPANE



- Immediate drop of H_2 flux to steady values under H_2/N_2
- Additional (15%) immediate drop of H_2 flux to steady values under H_2/C_3H_8
- Fast and complete recovery under pure H_2 exposure

Exposure to alkanes:
- Reversible interaction with Pd surface
- No major interaction with protective layer and no coke formation

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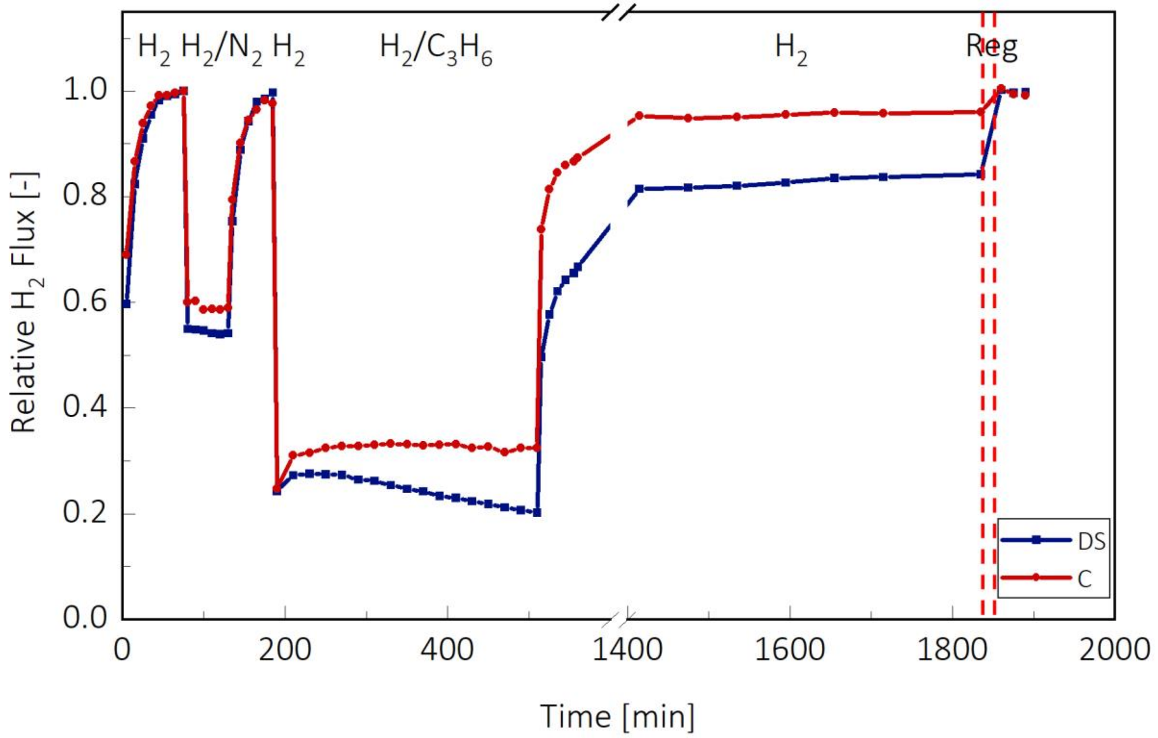
Experimental Results

T= 400 °C, ΔP= 2 bar
$H_2/N_2 – H_2/C_xH_y$: 80/20 vol%

- Membrane performance in PDH conditions: exposure to alkanes/alkenes

PROPYLENE



- Immediate drop of H_2 flux to steady values under H_2/N_2
- Severe transient decrease in H_2 flux under H_2/C_3H_6
- Uncomplete recovery under pure H_2 exposure (20h) → Air regeneration

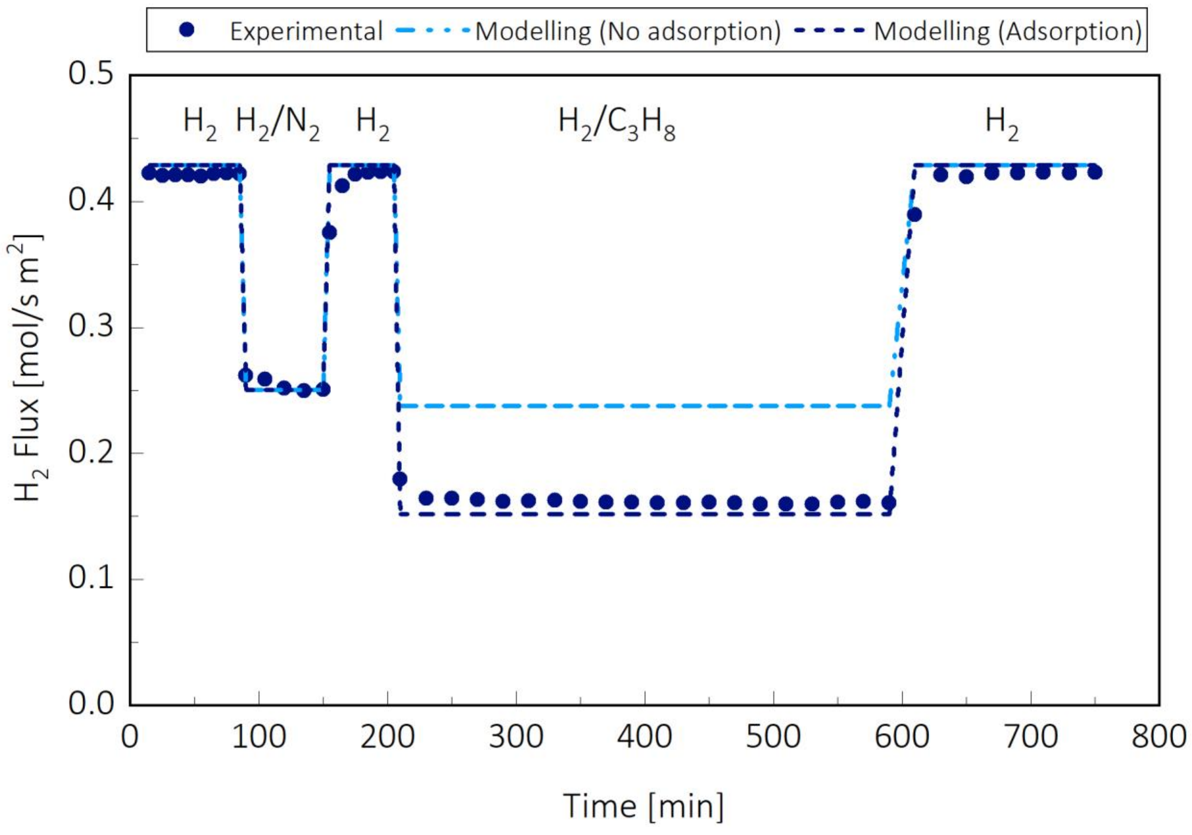
Exposure to alkenes:
- Inhibition of avalable Pd surface sites for H_2 dissociation

Experimental vs Modelling Results

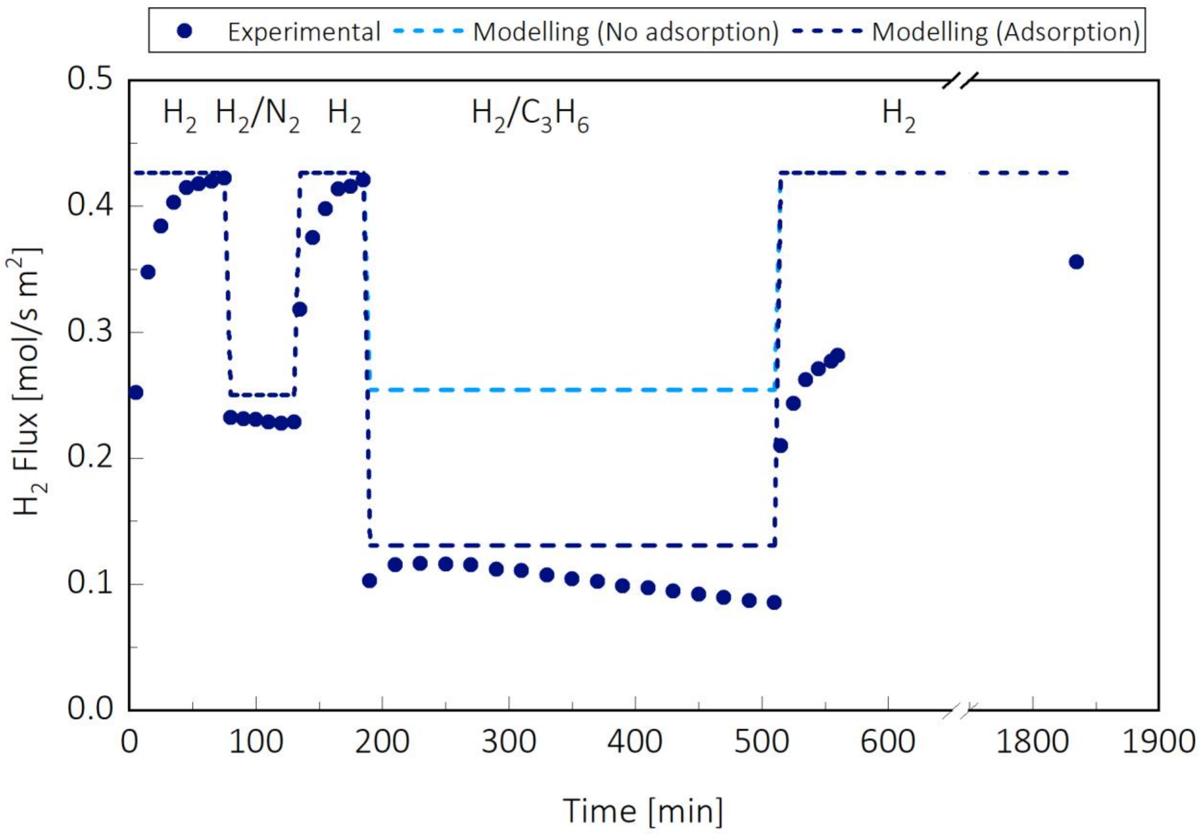
T= 400 °C, ΔP= 2 bar
$H_2/N_2 – H_2/C_xH_y$: 80/20 vol%

- Membrane performance in PDH conditions: exposure to alkanes/alkenes

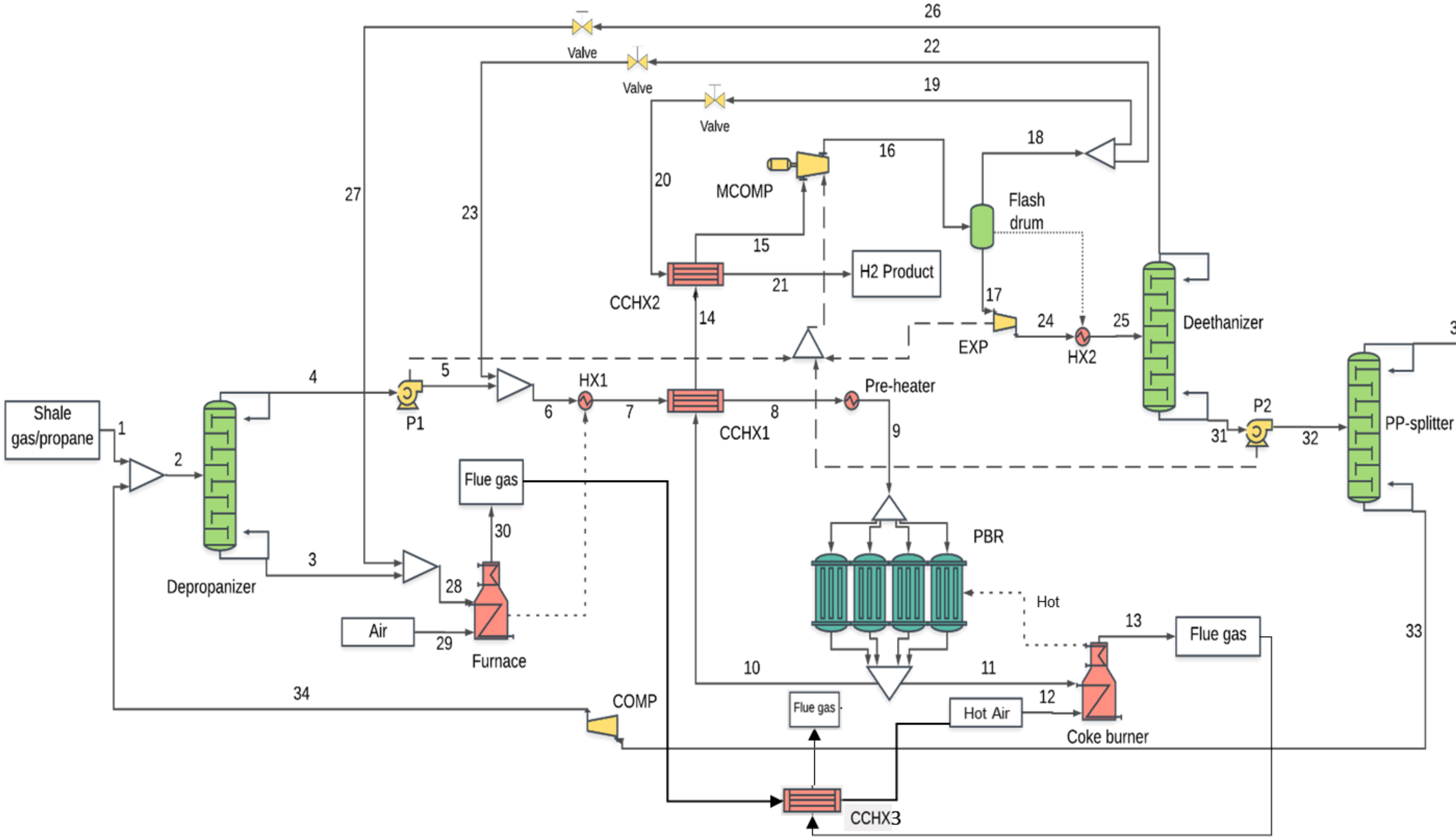
$$C_3H_8 + 3S \rightarrow C_3H_8 - S_3$$



$$C_3H_6 + 3S \rightarrow C_3H_8 - S_3$$



Process design: Benchmark PDH technology



- Benchmark technology:

  CATOFIN®

- Plant capacity:

  570,000 MTA

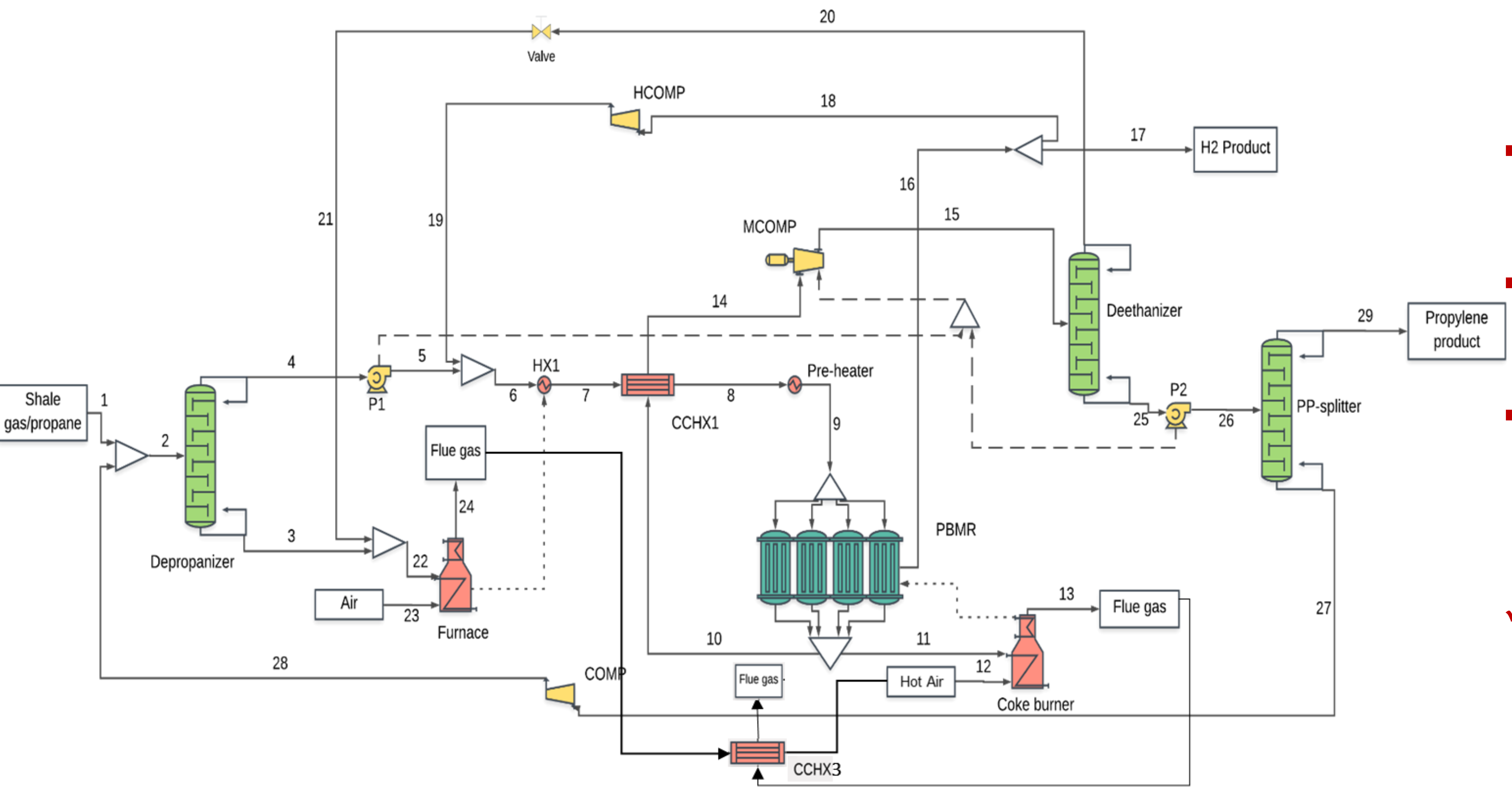
- Final propylene PG purity:

  99.80 wt%

- Reaction unit:

  PBR in parallel

Process design: Novel MR-assisted PDH technology



- Plant capacity:
  650,000 MTA
- Final propylene PG purity:
  99.96 wt%
- Reaction unit: **PBMR** in parallel with H_2-selective membranes

✓ **Simplified downstream product separation**

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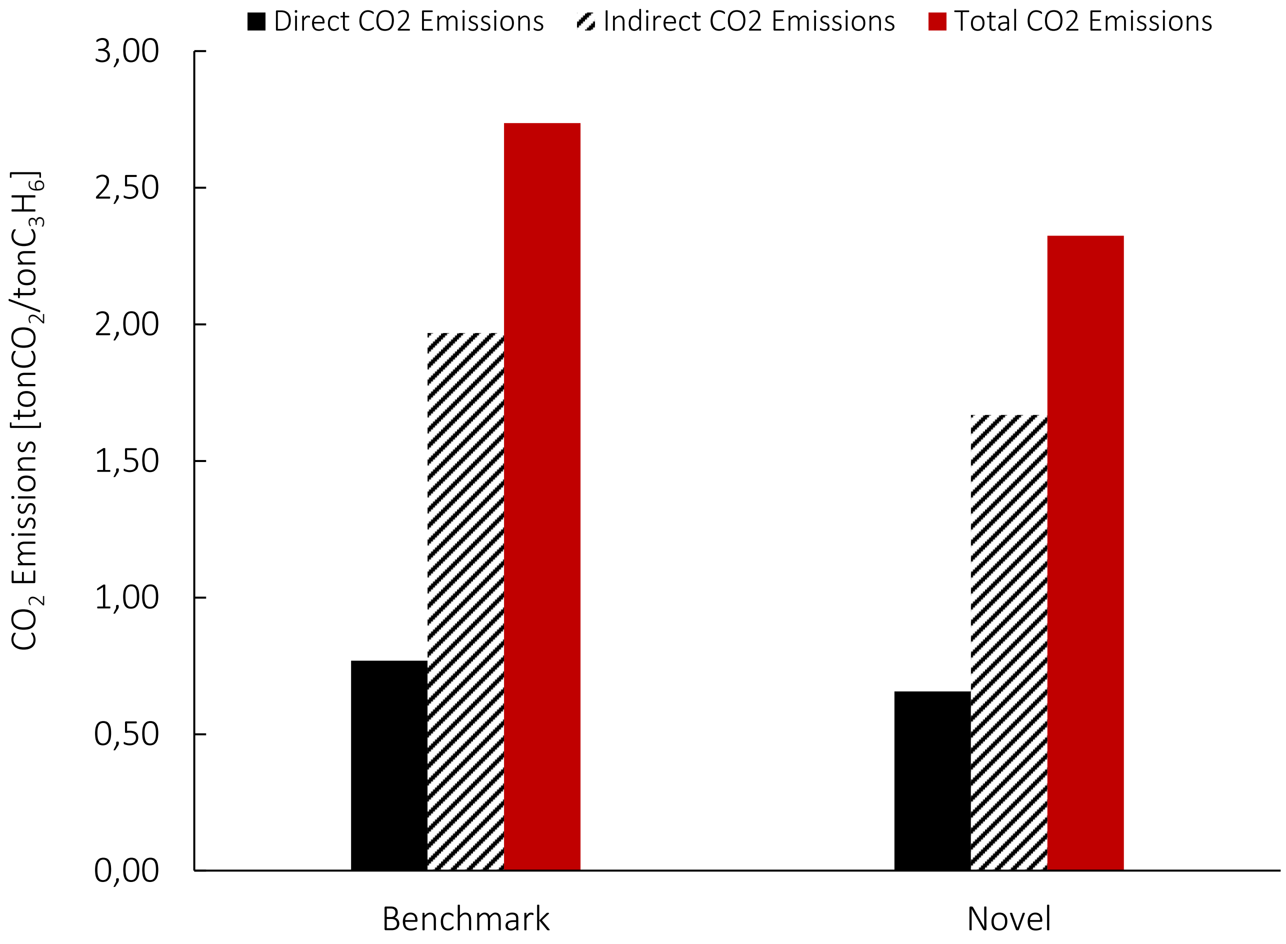
CO_2 Emissions



Benchmark Total CO_2 emissions:
2.7 ton_{CO2}/ton_{C3H6}

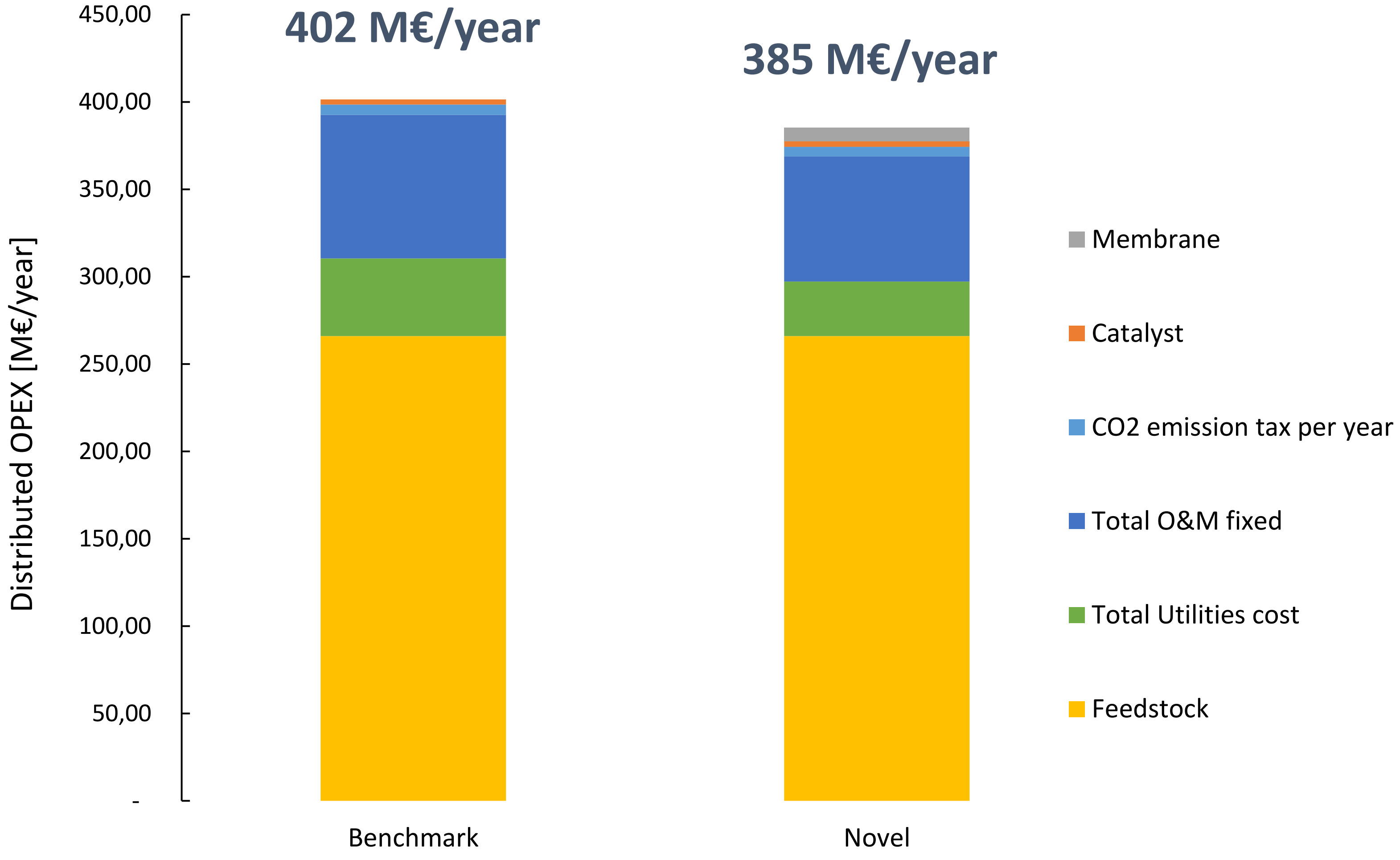
Novel Total CO_2 emissions:
2.3 ton_{CO2}/ton_{C3H6}

-15% CO_2 Emissions

Better Carbon Footprint

Economic Analysis

Operating Costs



4% reduced OPERATING costs in the novel technology

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Conclusions and Outlook

- ✓ First evaluation of a novel double-skinned membrane performance under typical dehydrogenation conditions
- ✓ The novel double-skinned membrane shows higher hydrogen fluxes than a conventional Pd-Ag membrane
- ✓ Experimental results well fitted by the model only under alkane exposure (mass transfer resistance + adsorption)
- ✓ Membrane coking experienced only under alkene exposure and confirmed by SEM-EDX characterization
- ✓ Extent of coke formation higher at higher T and alkene concentrations
- ✓ Economic analysis shows the benefit of using membrane reactors compared to standard technologies

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Inorganic Membranes & Membrane Reactors

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