

An aerial night photograph of the TU/e campus in Eindhoven, showing modern glass-walled buildings with interior lights glowing, surrounded by trees and city lights in the background.

MEMBRANE REACTORS FOR DEHYDROGENATION REACTIONS

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Outlook

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

Our Lab(s)



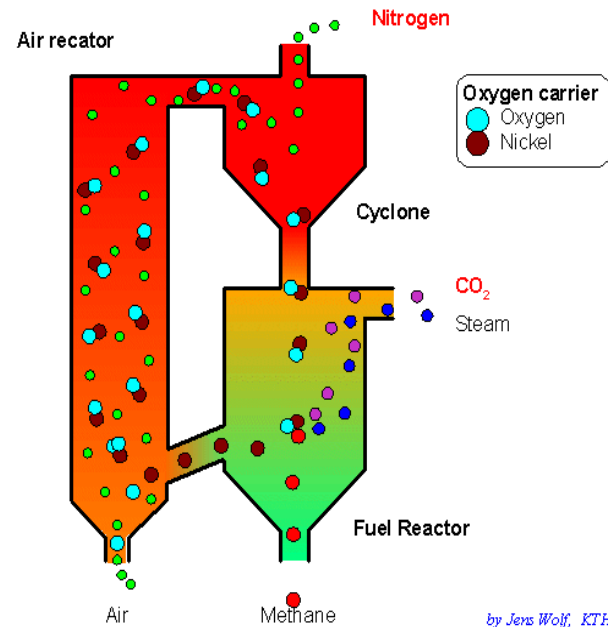
TU/e

tecnalia



Research themes - SIR

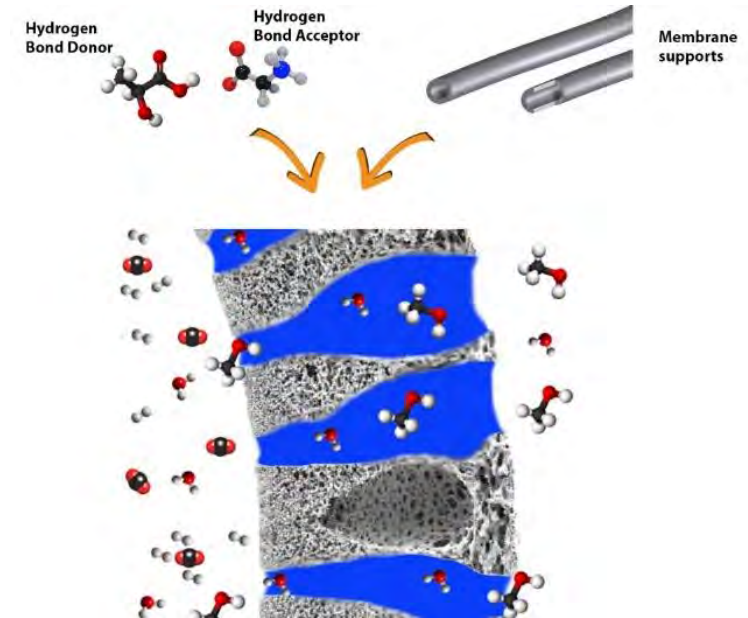
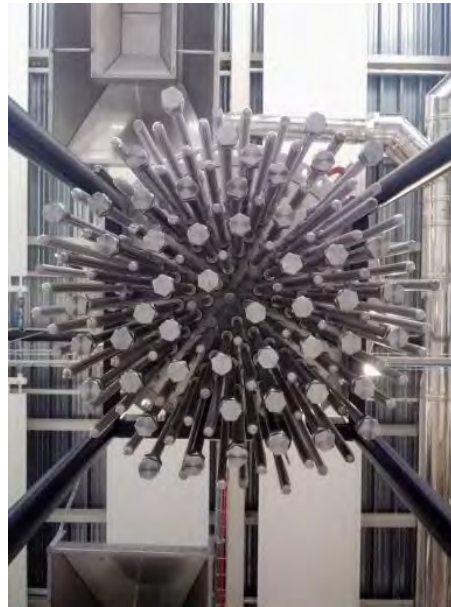
- Novel intensified reactor concepts via:
 - Integration reaction and separation (membrane reactors, chemical looping)
 - Integration reaction and heat/energy management (endo/exothermic, plasma systems)



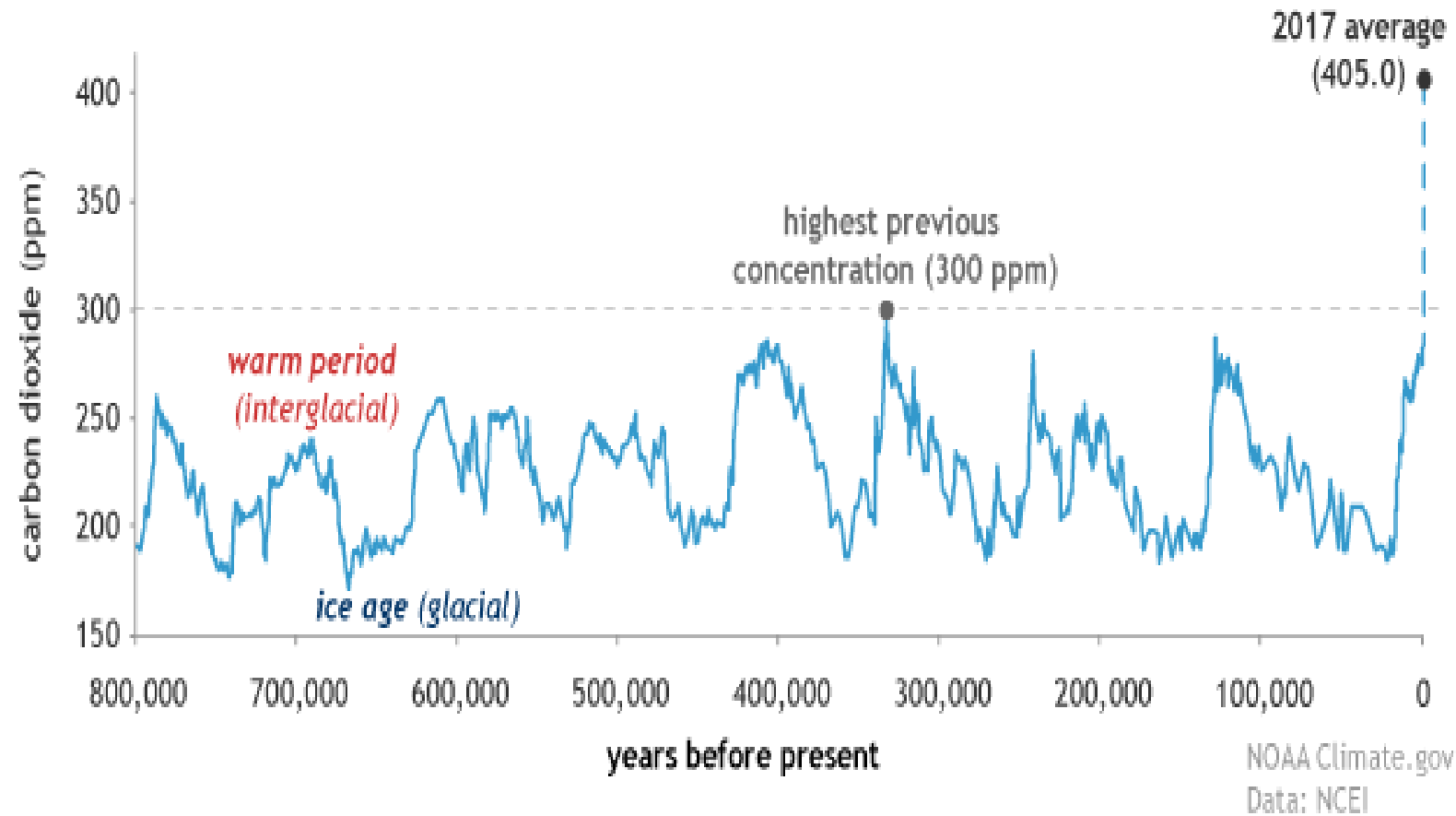
- **Research approach:** combination experimental PoC and modelling

Research themes - SIR

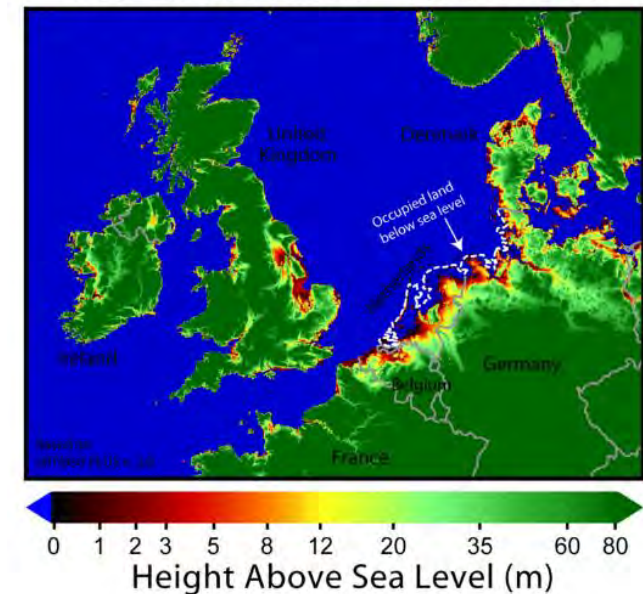
- Integration reaction + separation
- *Packed bed and fluidized bed membrane reactors*
(H_2 , syngas, oxidative dehydrogenations, partial oxidations)
 - Use membranes to improve fluidization and fluidization to improve membrane flux
 - Liquid supported membranes



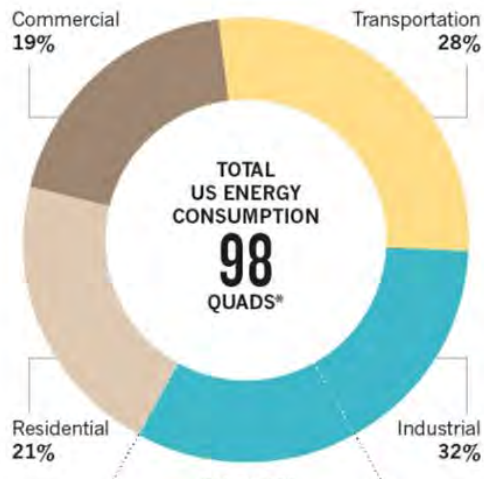
One of our challenges



Sea Level Risks - North Sea

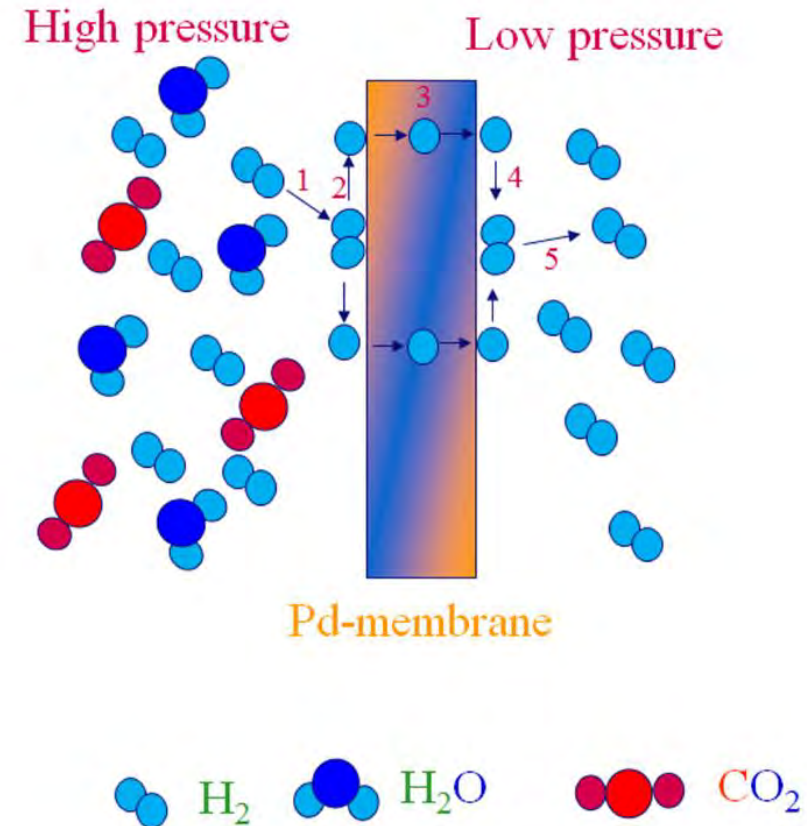


A possible solution

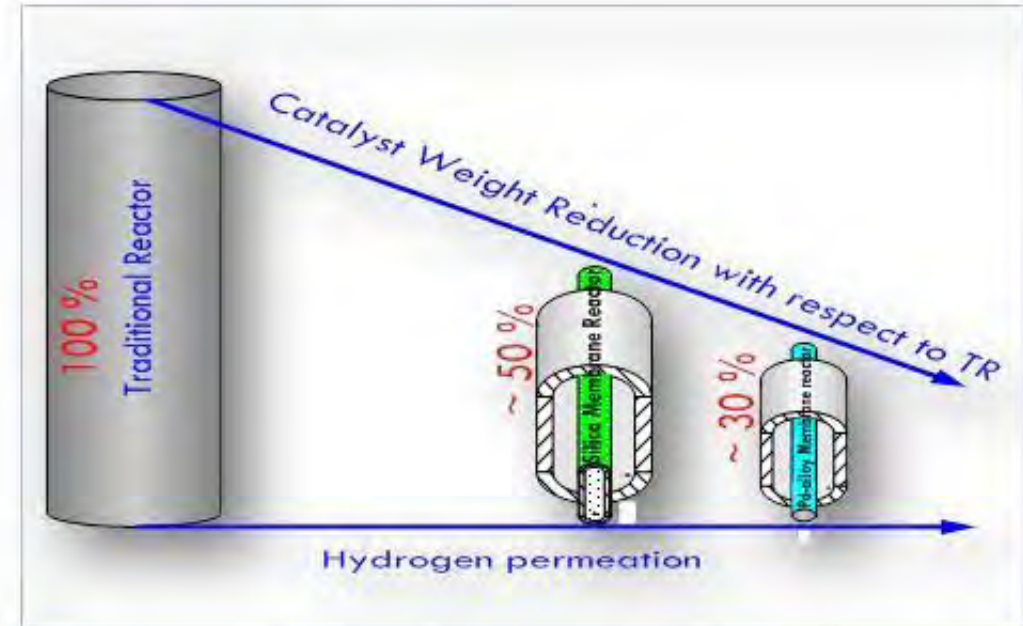
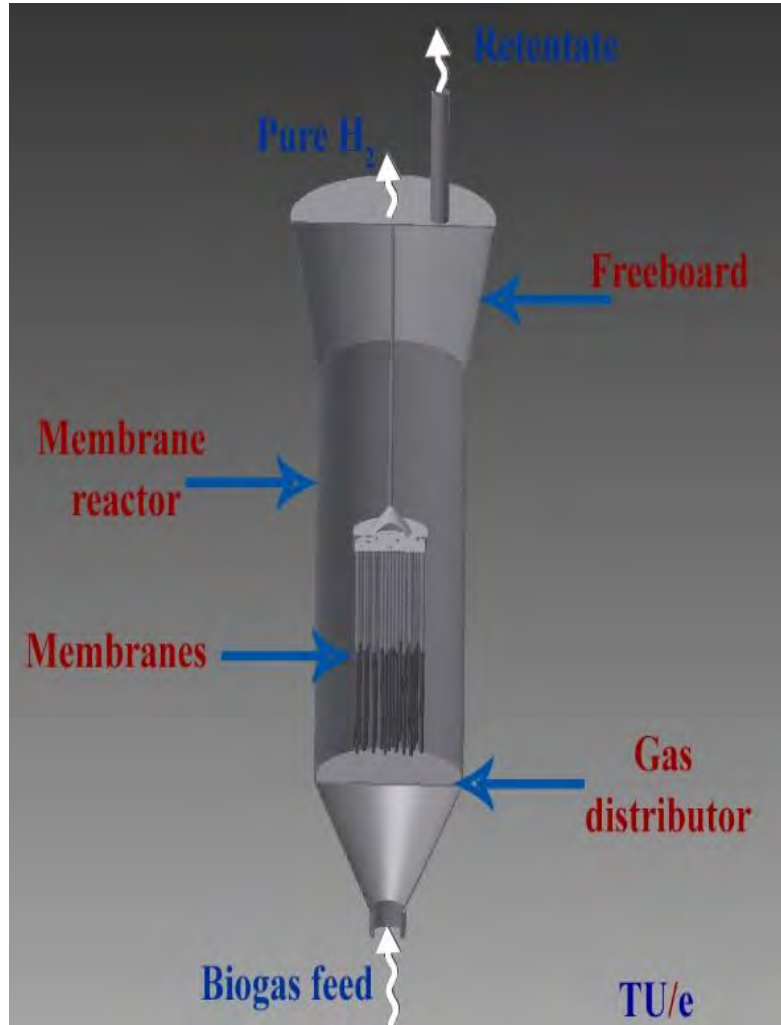


*A quad is a unit of energy equal to 10^{15} British Thermal Units (1 BTU is about 0.0003 kilowatt-hours).

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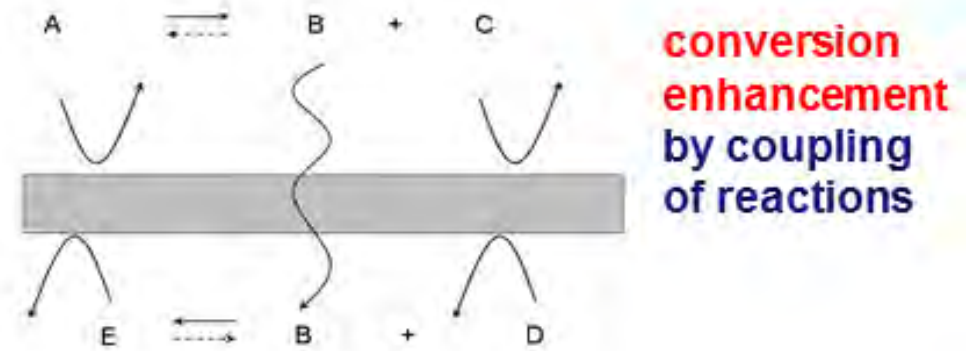
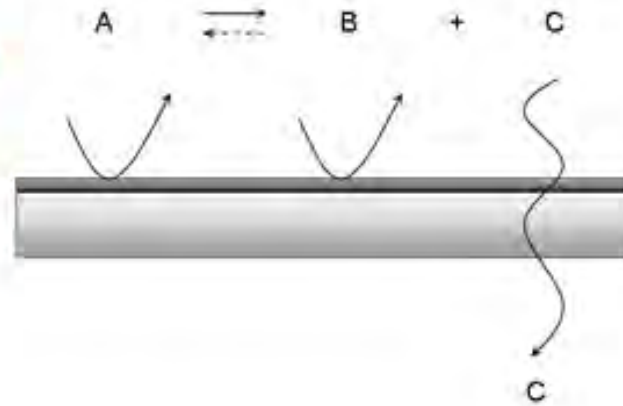
A membrane reactor



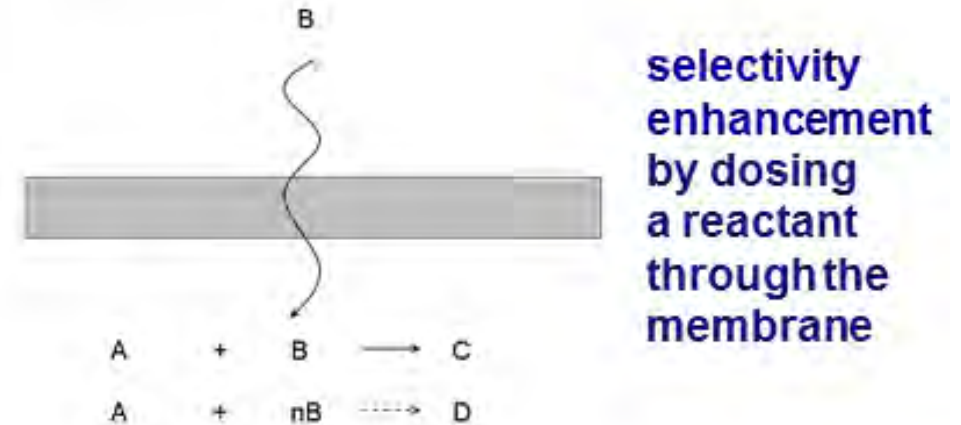
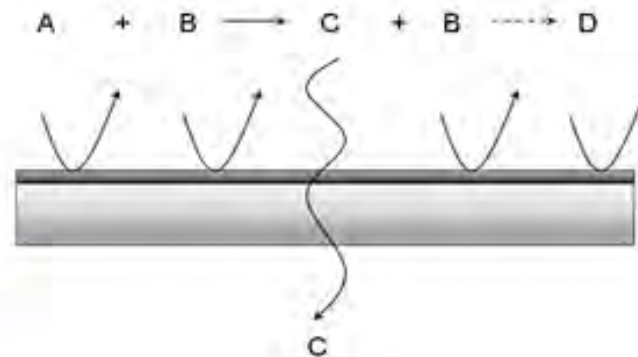
Brunetti A.; Caravella C.; Barbieri G.; Drioli E.; "Simulation study of water gas shift in a membrane reactor", *J. Membr. Sci.*, 2007, 306(1-2), 329-340

Why a membrane reactor?

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

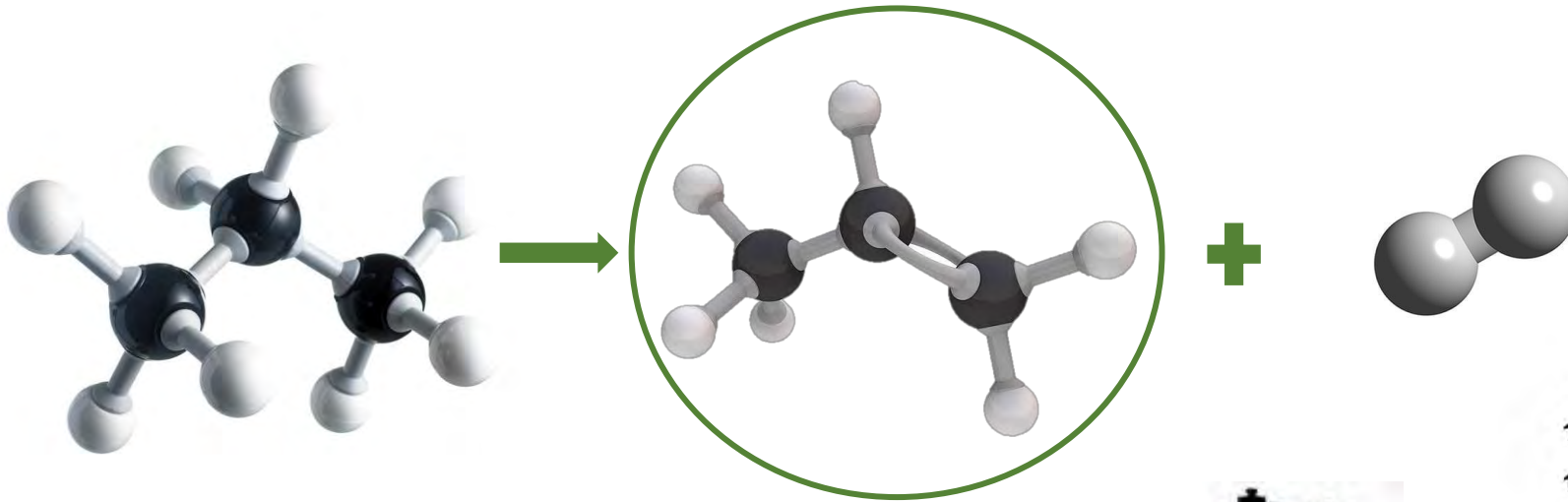


**selectivity
enhancement
by selective
permeation of an
intermediate product**



BIZEOLCAT why

Direct Dehydrogenation of Propane



✓ Direct route for propylene production

- Polypropylene
- Propylene Glycol
- Polyvinyl Butyral
- Acrylics

Fine chemicals



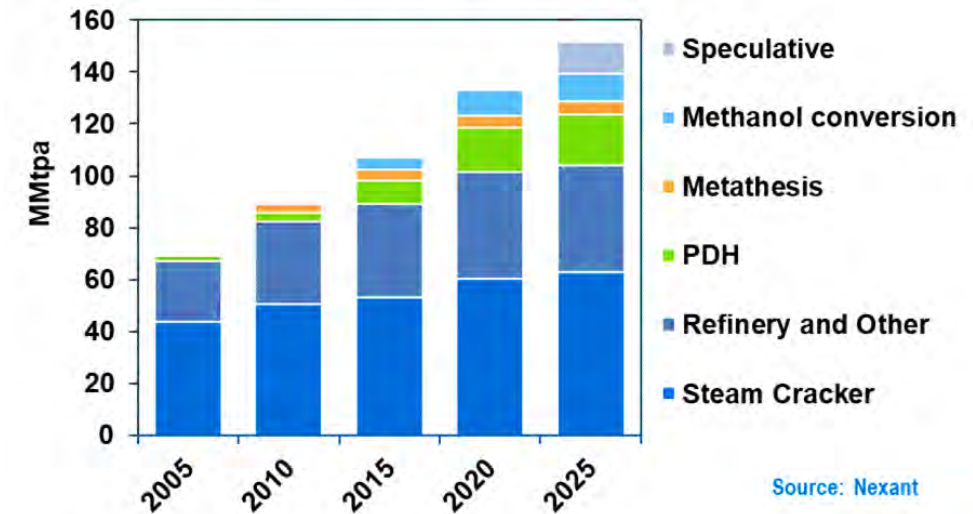
Monomers



*Materials
(e.g. polymers)*



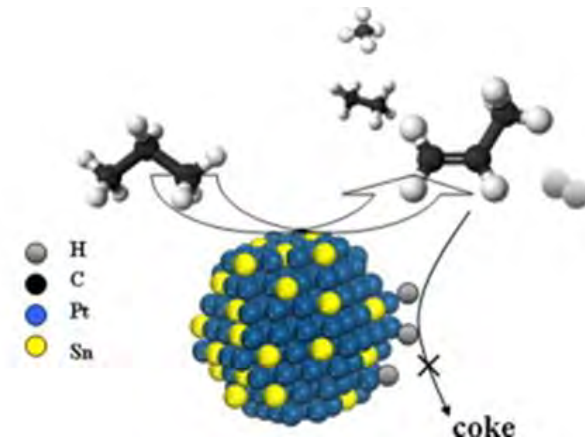
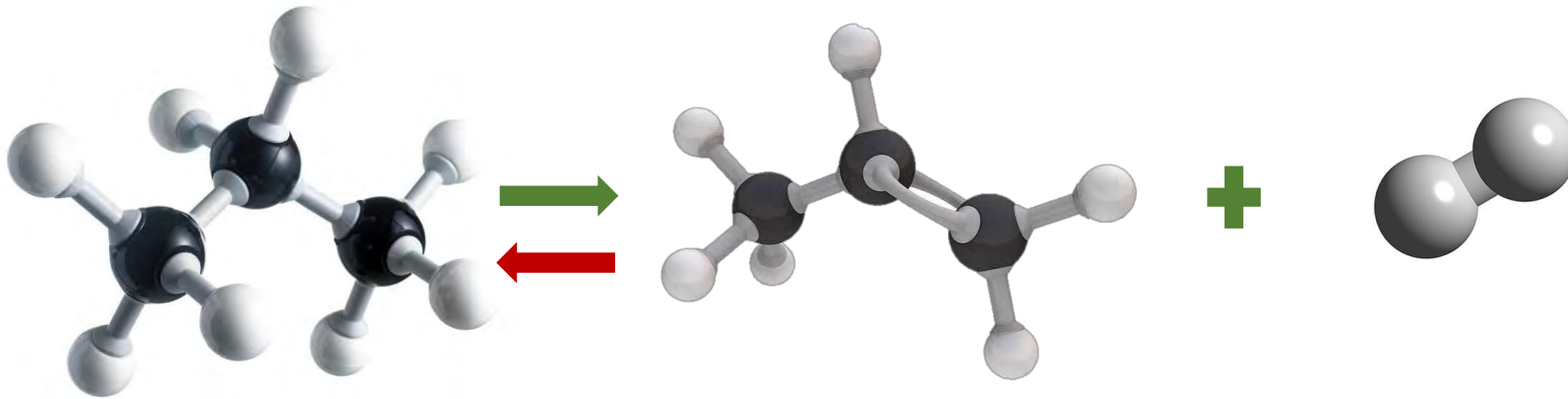
Global Propylene Capacity by Process, 2005 to 2025



Source: Nexant

BIZEOLCAT why

Direct Dehydrogenation of Propane



✓ Direct route for propylene production

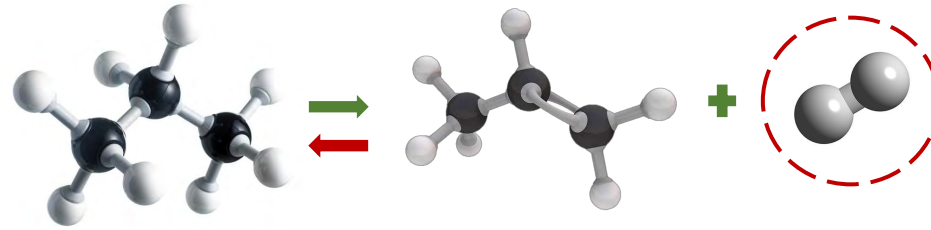
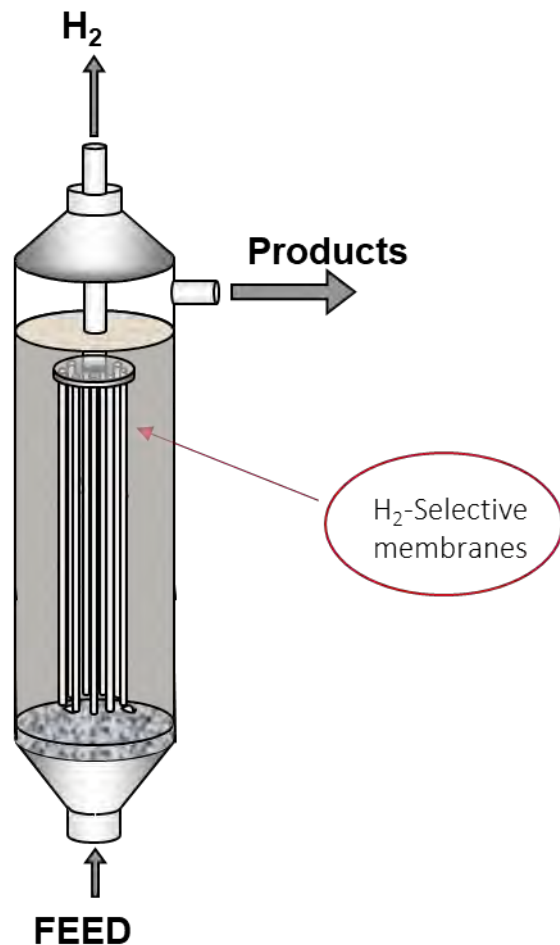
✗ Limited by thermodynamic eq

✗ Highly endothermic
($\Delta H_{298K}^0 = +120 \frac{kJ}{mol}$)

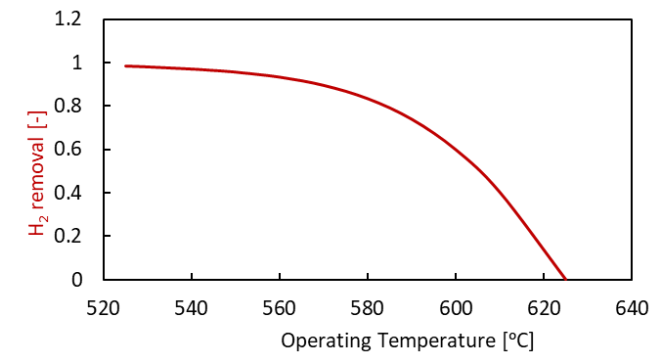
✗ Side cracking reactions
→ low product yield

BIZEOLCAT how

Direct Dehydrogenation of Propane in H₂-Selective Membrane Reactors



- ✓ Continuous *in-situ* separation of H₂ shifts the equilibrium beyond thermodynamic restrictions (of conventional reactors)
- ✓ Milder operating conditions
- ✓ Higher product yields



Packed-Bed Membrane Reactors

Fluidized-Bed Membrane Reactors

BIZEOLCAT how

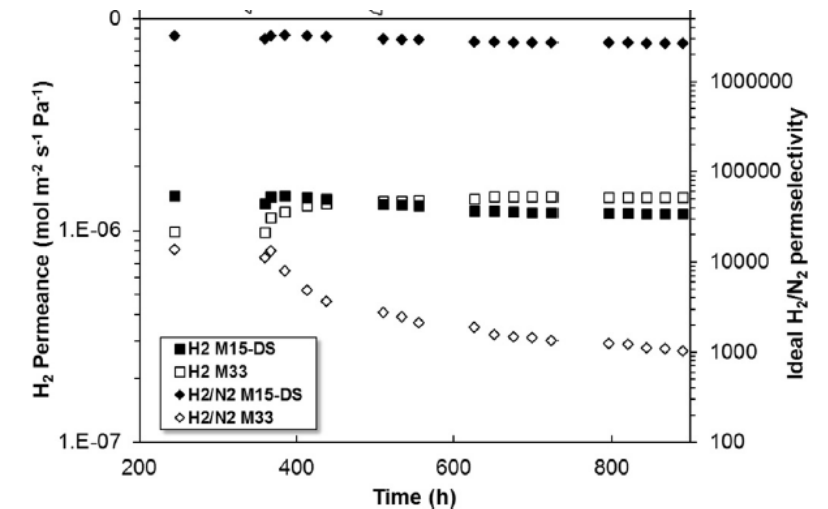
H₂ Selective Membrane Materials

Requirements:

- High selectivity towards H₂
- 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

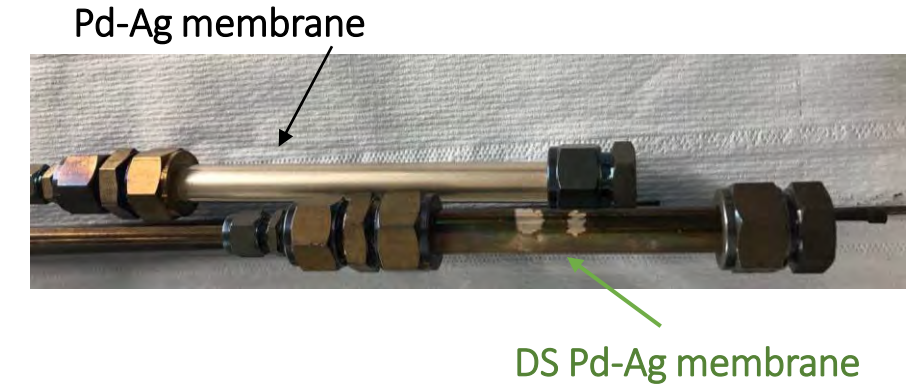


A. Arratibel, J.A. Medrano, J. Melendez, D.A. Pacheco Tanaka, M. van Sint Annaland, F. Gallucci, Attrition-resistant membranes for fluidized-bed membrane reactors: Double-skin membranes, J. Memb. Sci. 563 (2018) 419–426

Experimental Materials and Methods

■ H₂ Selective Membranes

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



	DS-Membrane	C- Membrane
Asymmetric support	<ul style="list-style-type: none">• Porous tubular substrates made of Al₂O₃• Pore size of ~ 100 nm	
Selective layer	<ul style="list-style-type: none">• Made of: Pd_{93.33}Ag_{6.67}• Thickness: ~ 2-3 μm	<ul style="list-style-type: none">• Pd_{95.67}Ag_{4.23}• ~ 3-5 μm
Protective layer	<ul style="list-style-type: none">• 50wt% YSZ- 50wt% γ-Al₂O₃• Mesoporous: ~ 2-5 nm• Thickness: ~ 0.5 μm	

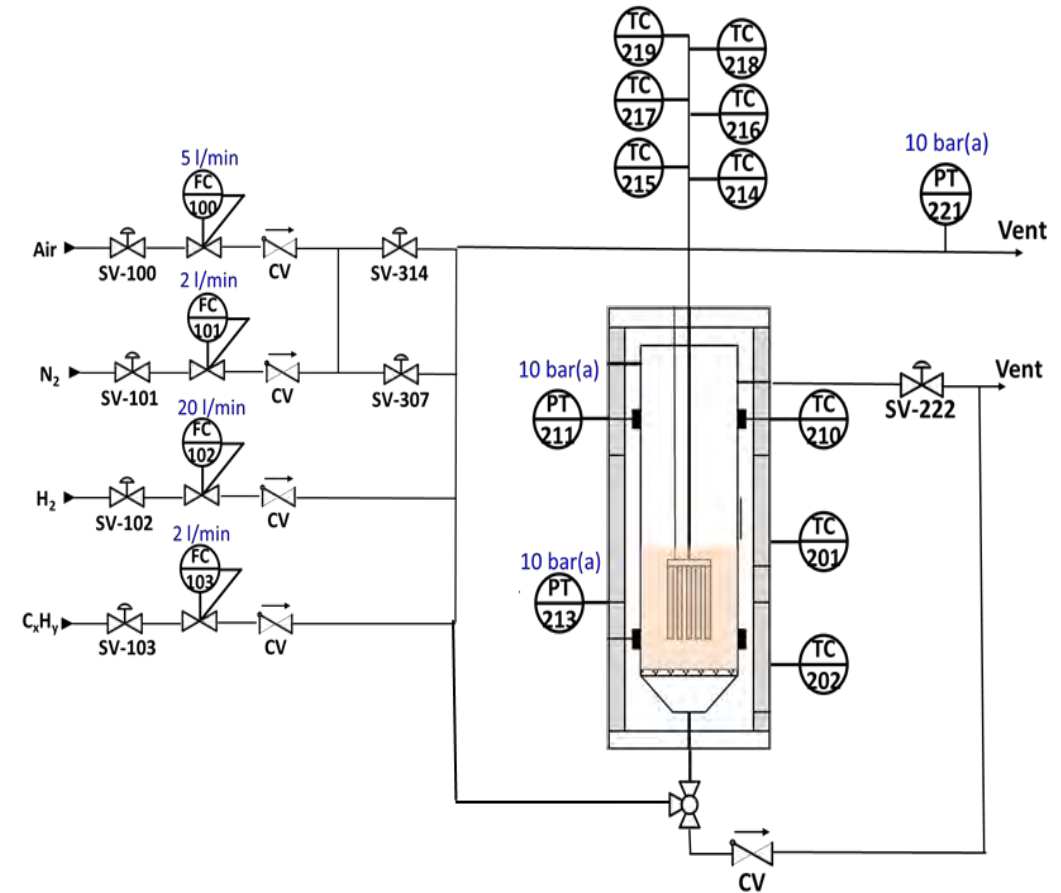
Experimental Materials and Methods

■ Experimental Tests

1. Membrane stability tests
→ Characterize membranes permeation properties
2. H_2/N_2 mixture tests
→ Investigate the concentration polarization effect
3. $\text{H}_2/\text{C}_x\text{H}_y$ mixture tests
→ Investigate coke formation tendency
4. SEM-EDX characterization post-mortem

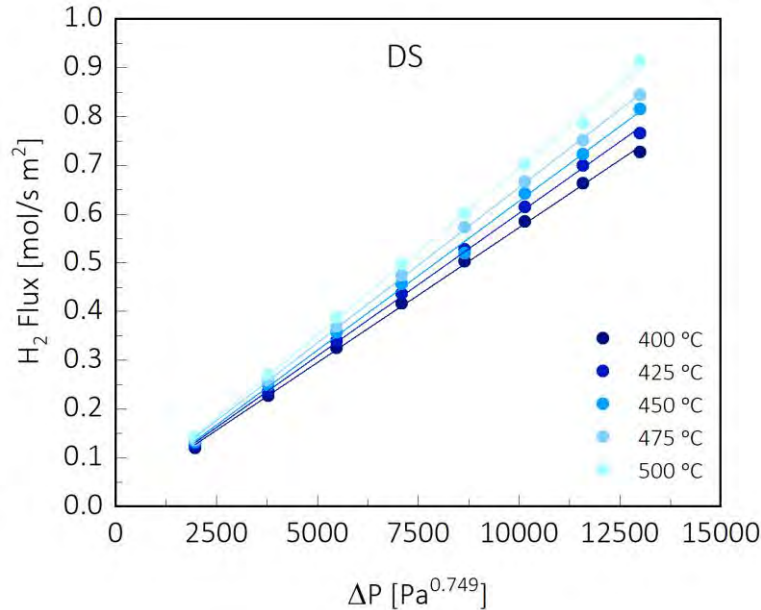
■ Operating Conditions

- T: 400-450 °C, ΔP : 2 bar, 90-60 vol% H_2
- Cyclic exposure to pure H_2 and binary ($\text{H}_2\text{-N}_2$) and ($\text{H}_2\text{-C}_x\text{H}_y$) 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



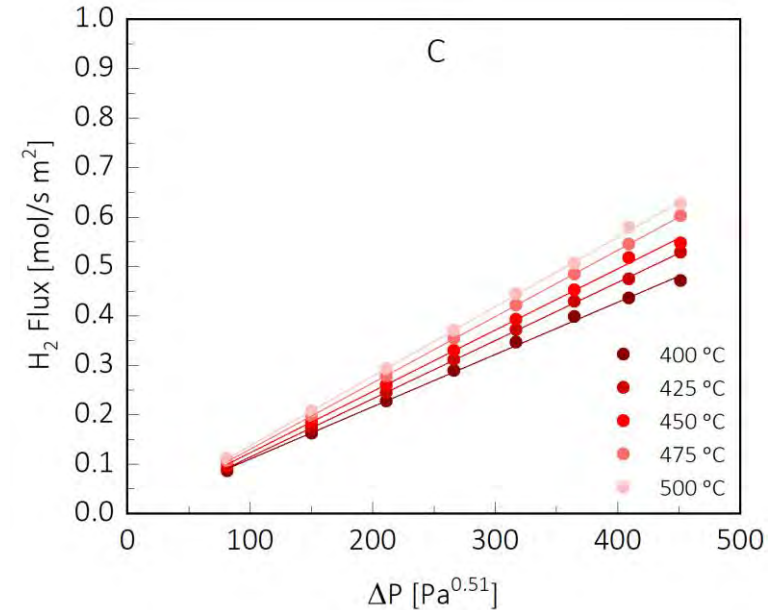
$$P_0 = 4.373 \cdot 10^{-10} \text{ [mol} \cdot \text{s}^{-1} \cdot \text{Pa}^{-0.749} \cdot \text{m}^{-1}]$$

$$\delta = 1.91 \cdot 10^{-6} \text{ [m]}$$

$$E_{\text{act}} = 7.8053 \text{ [kJ/mol]}$$

$$n = 0.749 \text{ [-]}$$

H₂ permeance
(T= 500 °C, ΔP= 4 bar): $2.28 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$



$$P_0 = 2.79 \cdot 10^{-8} \text{ [mol} \cdot \text{s}^{-1} \cdot \text{Pa}^{-0.51} \cdot \text{m}^{-1}]$$

$$\delta = 3.51 \cdot 10^{-6} \text{ [m]}$$

$$E_{\text{act}} = 11.208 \text{ [kJ/mol]}$$

$$n = 0.51 \text{ [-]}$$

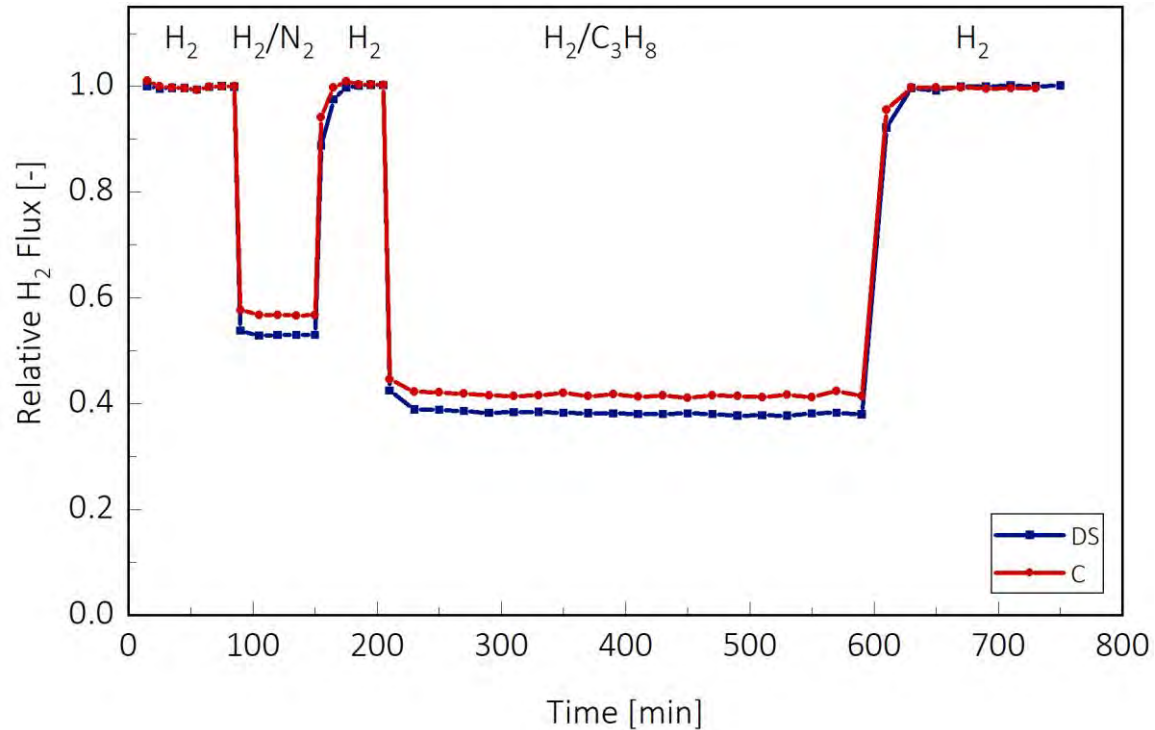
$1.56 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$

Experimental

$T = 400\text{ }^{\circ}\text{C}$, $\Delta P = 2\text{ bar}$
 $\text{H}_2/\text{N}_2 - \text{H}_2/\text{C}_x\text{H}_y : 80/20\text{ vol\%}$

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

PROPANE



- Immediate drop of H₂ flux to steady values under H₂/N₂
- Additional (15%) immediate drop of H₂ flux to steady values under H₂/C₃H₈
- Fast and complete recovery under pure H₂ exposure

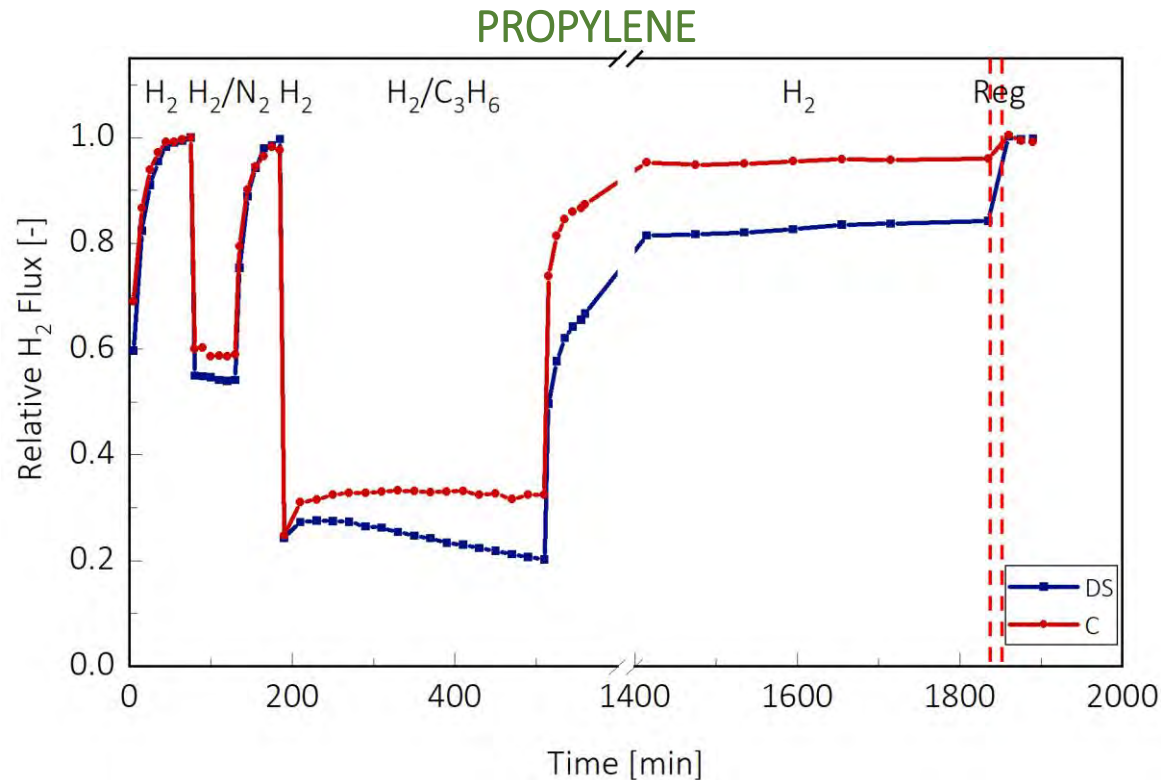
Exposure to alkanes:

- Reversible interaction with Pd surface
- No major interaction with protective layer and no coke formation

Experimental Results

$T = 400\text{ }^{\circ}\text{C}$, $\Delta P = 2\text{ bar}$
 $\text{H}_2/\text{N}_2 - \text{H}_2/\text{C}_x\text{H}_y : 80/20\text{ vol\%}$

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



- Immediate drop of H₂ flux to steady values under H₂/N₂
- Severe **transient decrease** in H₂ flux under H₂/C₃H₆
- Uncomplete recovery** under pure H₂ exposure (20h) → Air regeneration

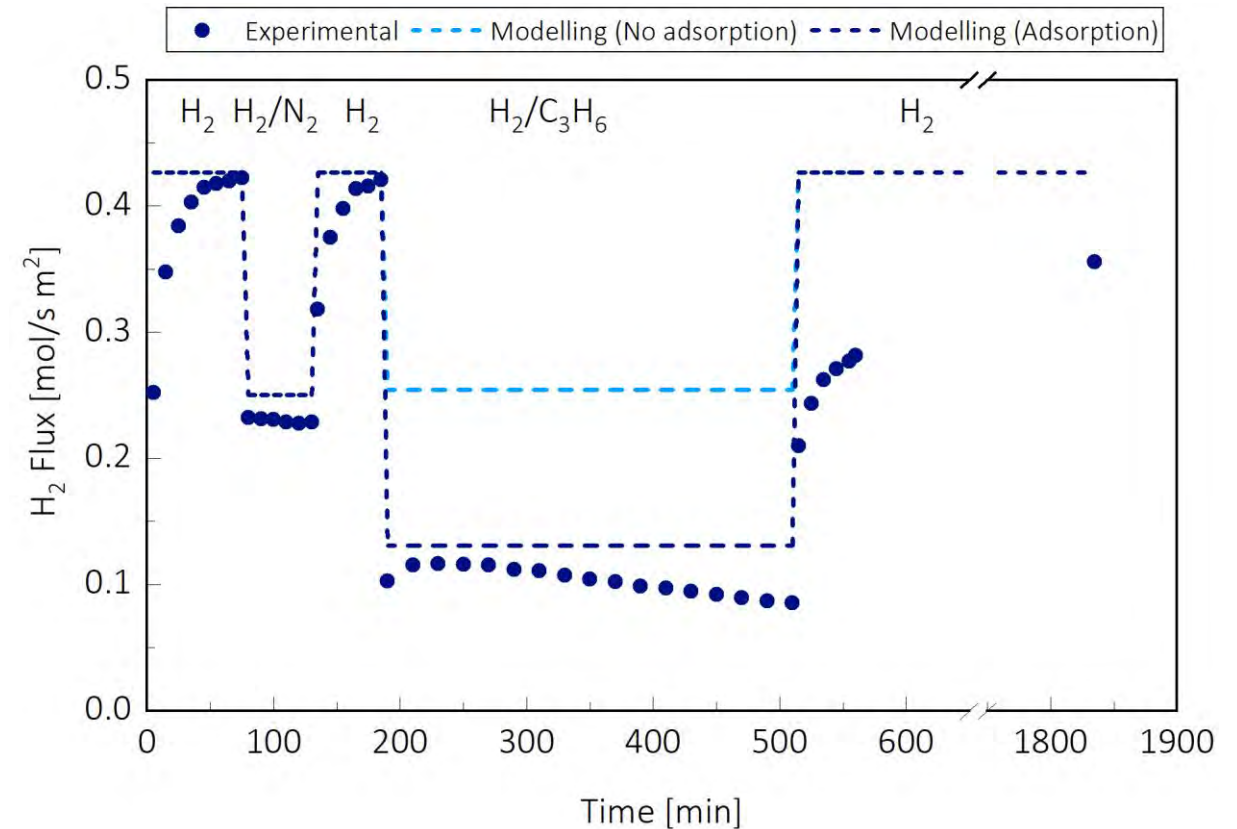
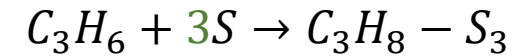
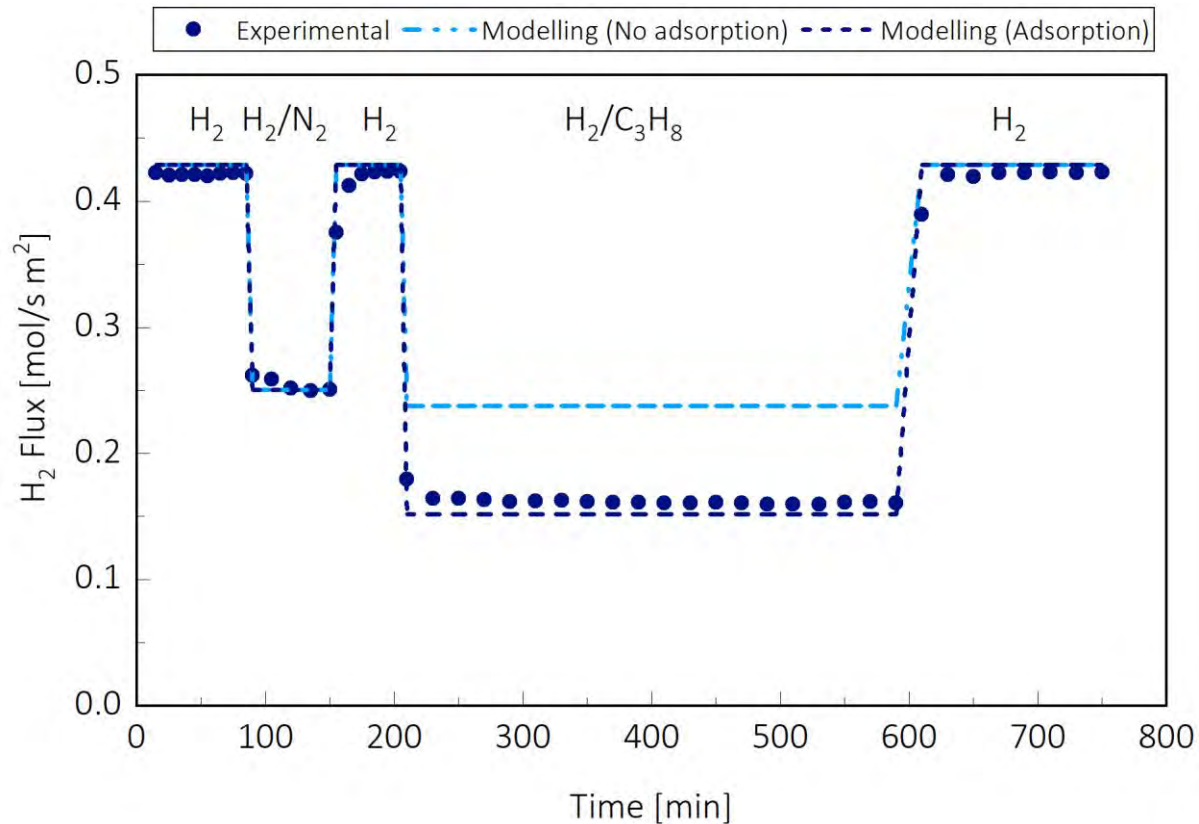
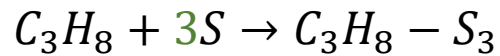
Exposure to alkenes:

- Inhibition of available Pd surface sites for H₂ dissociation

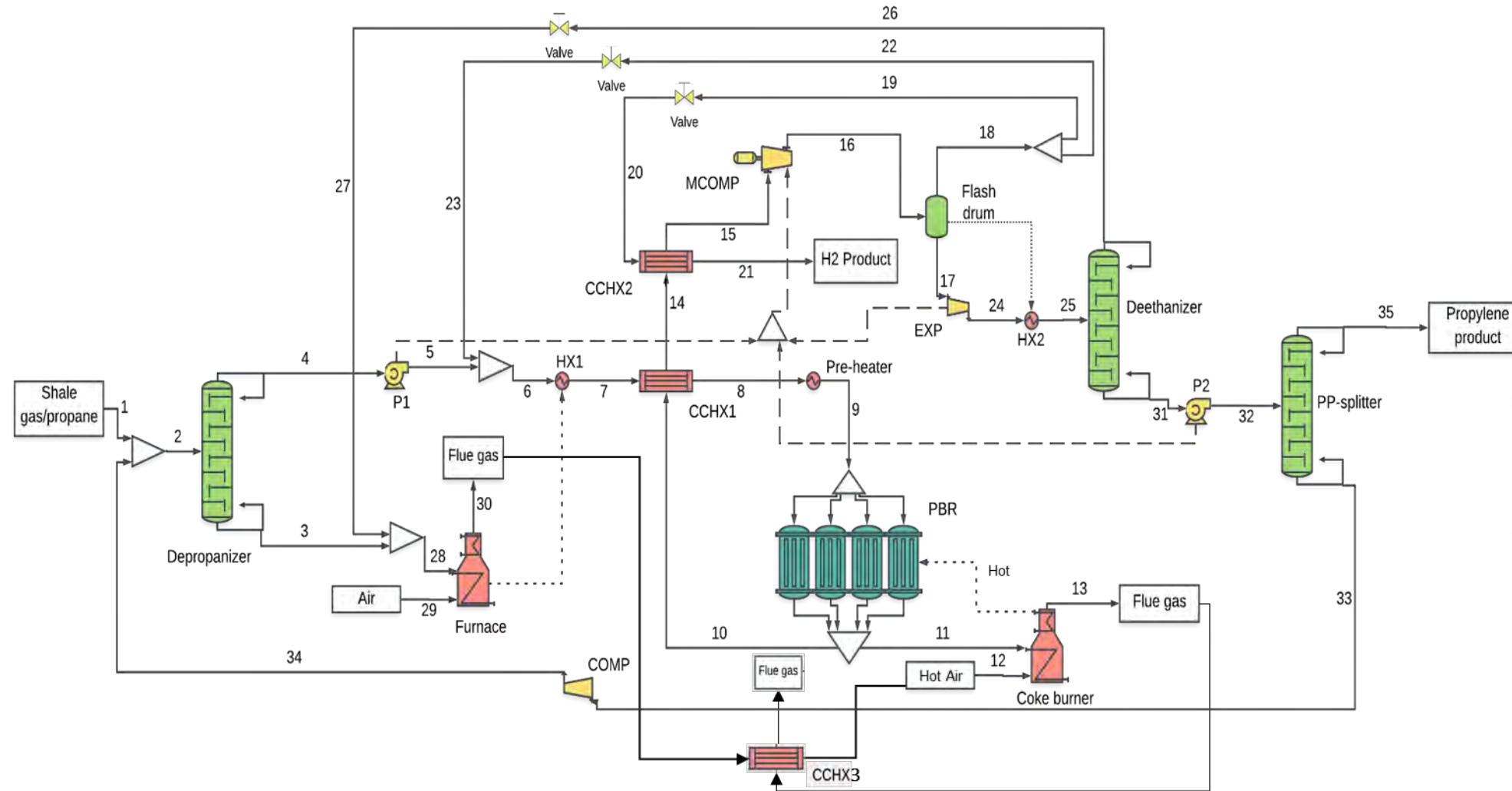
Experimental vs Modelling Results

$T = 400\text{ }^{\circ}\text{C}$, $\Delta P = 2\text{ bar}$
 $\text{H}_2/\text{N}_2 - \text{H}_2/\text{C}_x\text{H}_y$: 80/20 vol%

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

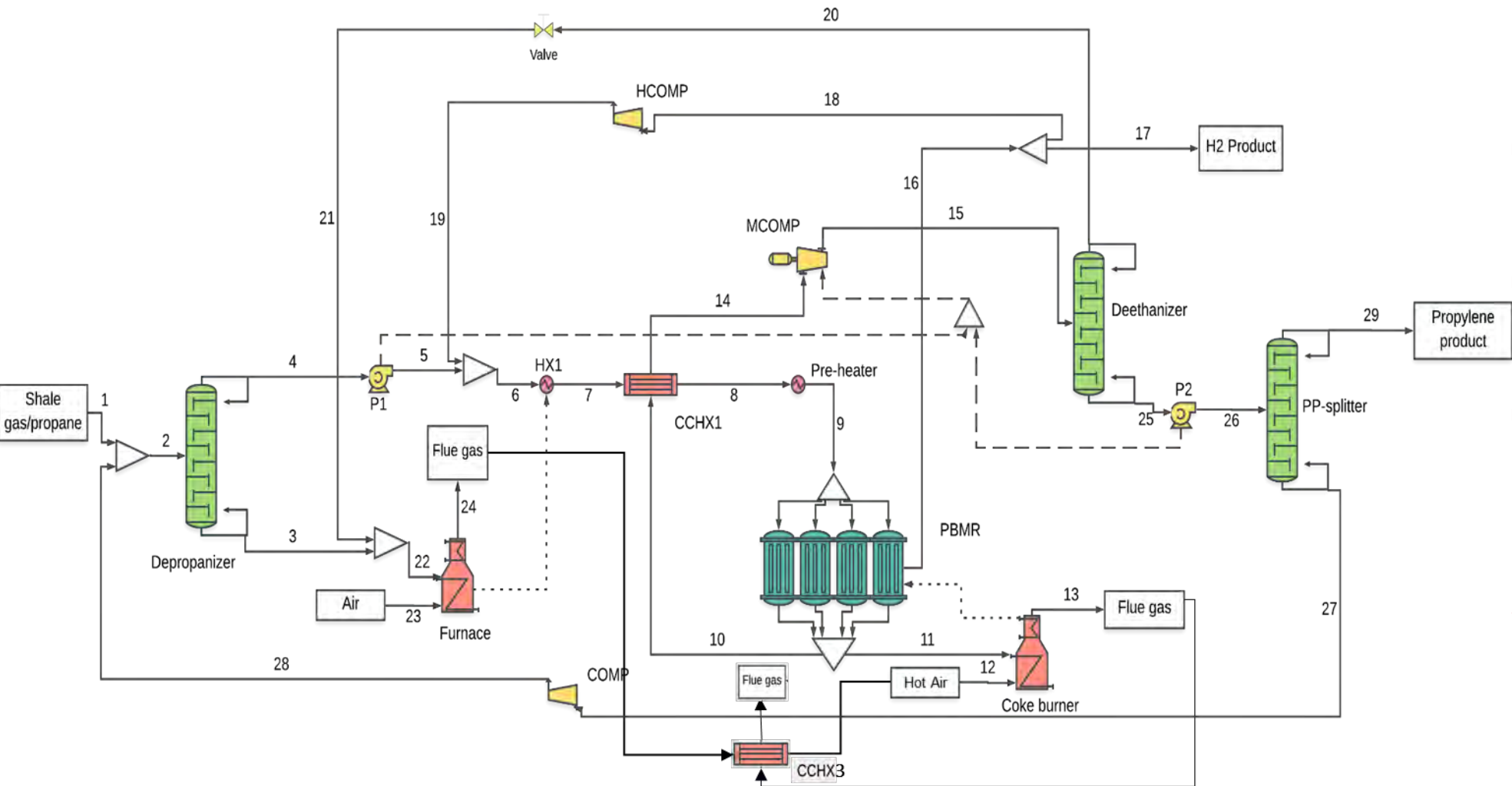


Process design: Benchmark PDH technology



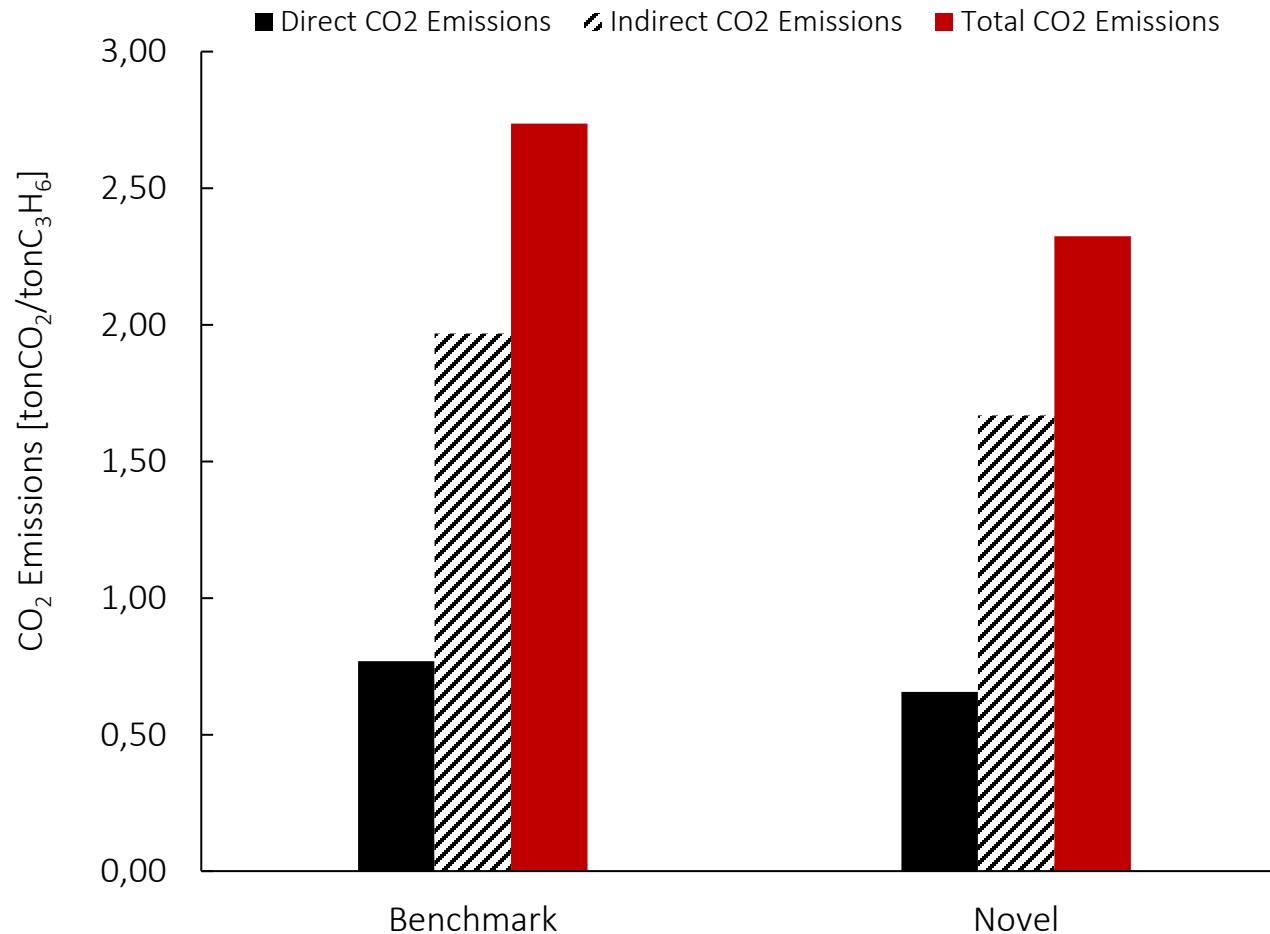
- Benchmark technology:
CATOFIN®
- Plant capacity:
570,000 MTA
- Final propylene PG purity:
99.80 wt%
- Reaction unit:
PBR in parallel

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 H₂-selective membranes
- ✓ **Simplified downstream product separation**

CO₂ Emissions



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

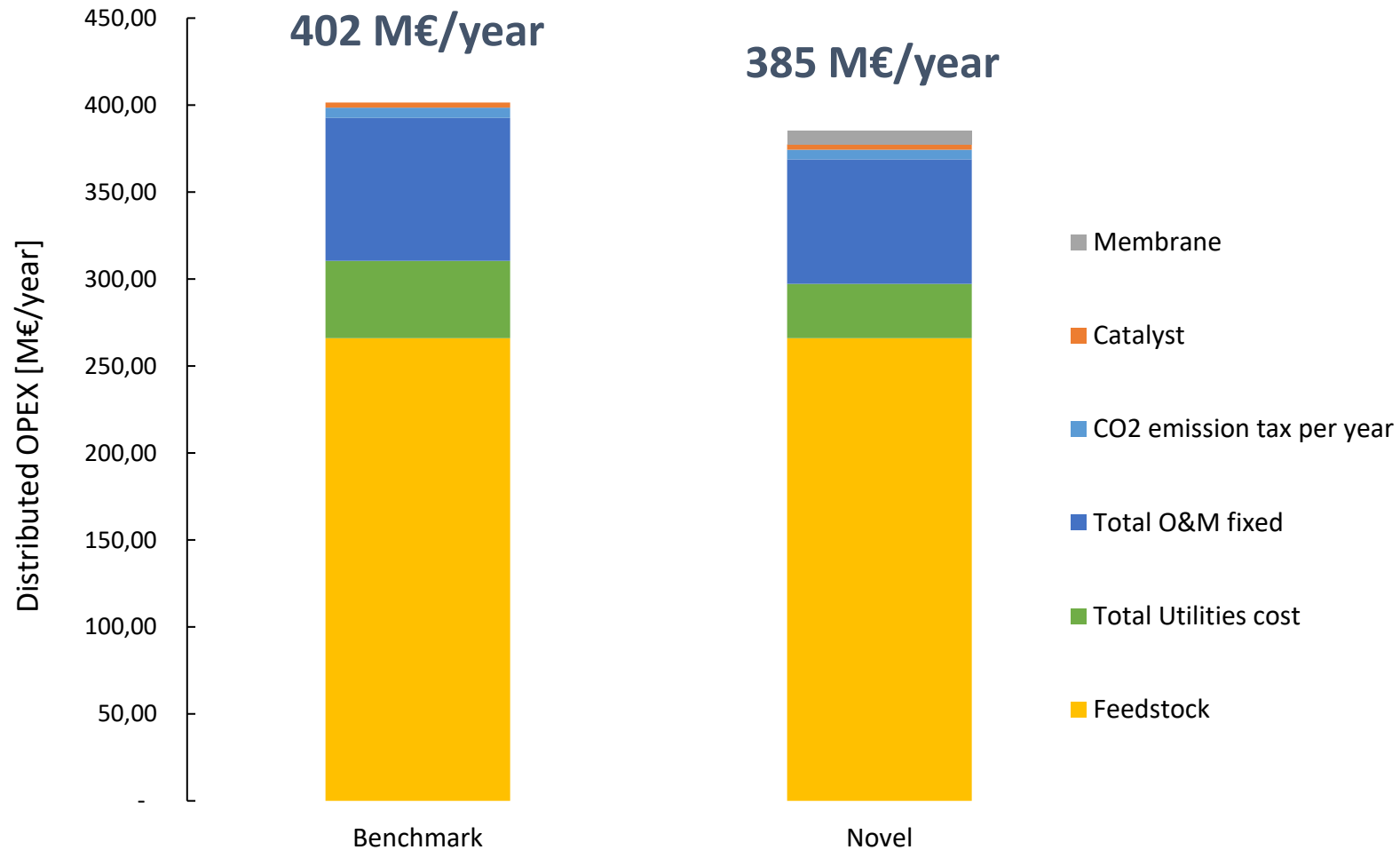
Novel Total CO₂ emissions:
2.3 ton_{CO₂}/ton_{C₃H₆}

-15% CO₂ Emissions

👍 Better Carbon Footprint

Economic Analysis

Operating Costs



4% reduced OPERATING costs in the novel technology

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



Inorganic Membranes
& Membrane Reactors

*Thank
you*



BiZeolCat 

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