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Investigation of Pd-based membranes in propane dehydrogenation (PDH) processes

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Scale-up of Pd Membrane Technology
From Fundamental Understanding to Pilot Demonstration

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CARENA CO-FUNDED BY THE EUROPEAN UNION SEVENTH FRAMEWORK PROGRAMME

CARENA DEMCAMER RE4CELL New Energy World JU CoMETHy

Background

- **Propane dehydrogenation (PDH) to propylene**
  - Predominant industrial technology (Star, Catofin, Oleflex, and FBD) require regular catalyst regeneration due to coking
  - CARENA will demonstrate a PDH unit applying H_2-selective membranes allowing for a reduction in operation temperature
    - *avoiding the classic trade-off between selectivity and conversion*
    - *prevent coke formation on the catalyst*

- **Tasks of SINTEF in CARENA: to verify if Pd-based membranes have potential applicability in PDH processes**
  - Manufacturing and testing of H_2-selective membranes for C3-dehydrogenation reactors
  - Study of the effect of pressure and temperature on the H_2 flux obtained in mixtures representing the propane dehydrogenation process
  - Supporting the process design and simulation of the overall process

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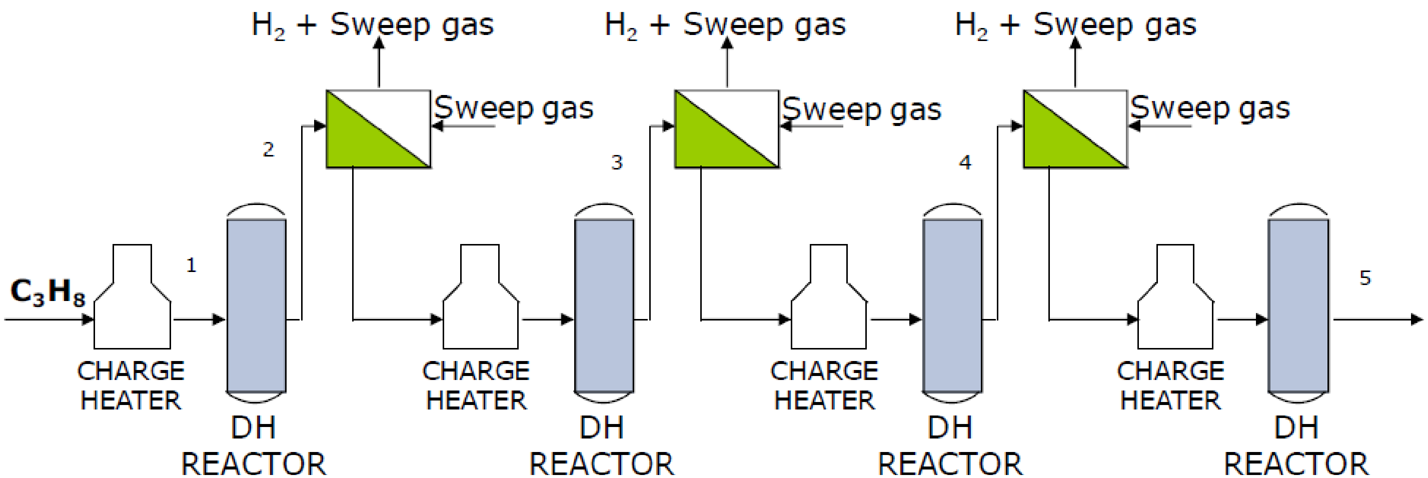
Background

- **Process design**
  - Non-integrated reactor/separator system

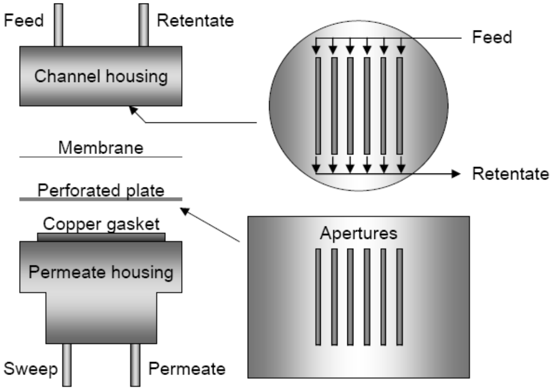


  - Typical envisioned operating temperature and pressure equal to 400 – 500 °C and 4-6 bars, respectively
  - Important to verify membrane performance to support the process design of the overall process – coke formation tendency

Experimental

- **Experiments performed**
  - Effect of propane/propene on H_2 permeation through Pd-alloy membrane
    - ✓ Effect of alloy composition
    - ✓ Effect of temperature
    - ✓ Effect of H_2/propene ratio
    - ✓ Addition of steam
  - Reduction of coke formation by membrane deactivation

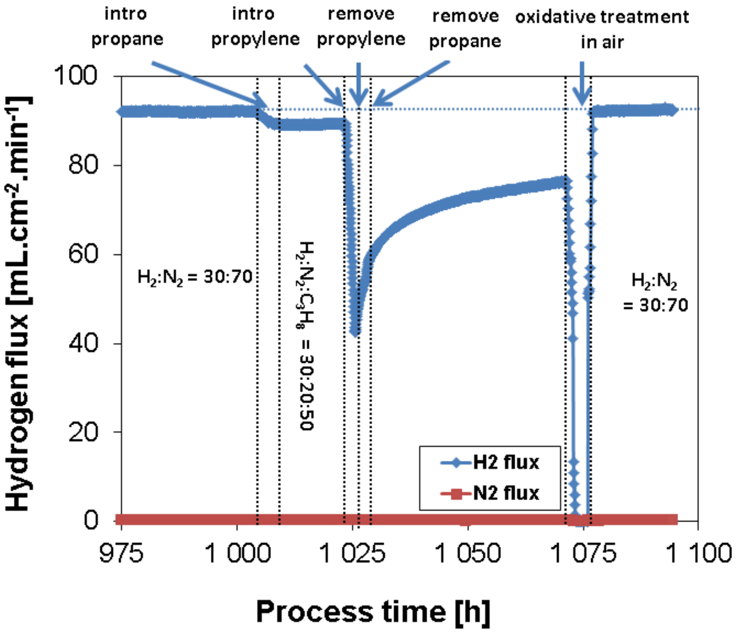
- **Membranes applied**
  - 10 micron-thick $Pd_{77}Ag_{23}$ films
  - Microchannel-configured membrane module
  - This configuration is very well-suited for the investigation of surface effects under different operating conditions



Results - effect of propane/propylene

- **Effect of propane/propene on H_2 permeation through $Pd_{77}Ag_{23}$ membrane**
  - Membrane thickness ~10 µm, T = 400 °C, 4 bars
  - $H_2:N_2:C_3H_8:C_3H_6$ = 30:10:50:10 at 1000 mL·min^{-1}, Ar sweep at 500 mL·min^{-1}

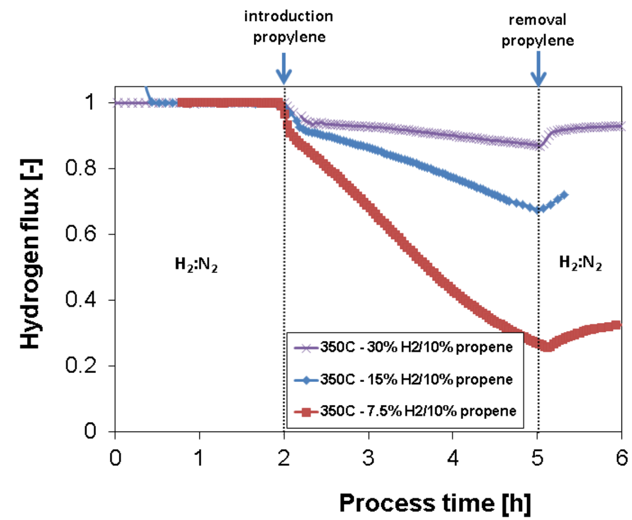
  - The tendency for coke formation in presence of propane is minimal
  - Propylene introduction leads to a fast decrease in H_2 flux
  - H_2 flux gradually recovers after propane and propylene removal
  - A simple exposure of the membrane surface to air at its operating temperature recovers the H_2 flux to its original value

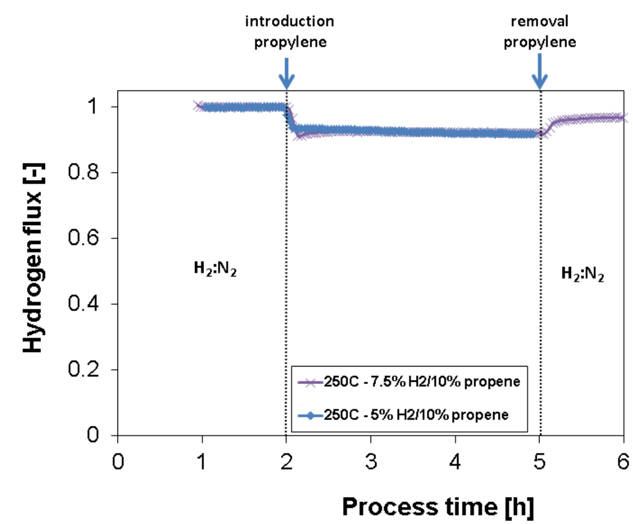


- **Subsequently, parameter investigation on coke formation kinetics performed**

Results – parametric study

- **Results – 400 °C**
  - Little difference between the $Pd_{80}Cu_{20}$ and the $Pd_{77}Ag_{23}$ alloy membrane
  - H_2/propene ratio has a large influence on the flux stability
  - Little effect of absolute H_2/propene concentration at a fixed H_2/propene ratio
  - Little difference of steam content on coke formation
- **Conclusions**
  - Flux-decreasing coke formation is limited at lower operating temperature
  - A decrease to at least 300 °C, or preferably, to 250 °C is required to obtain stable membrane operation
  - A 50% H_2 recovery factor results in H_2/propene ratio down to 0.5





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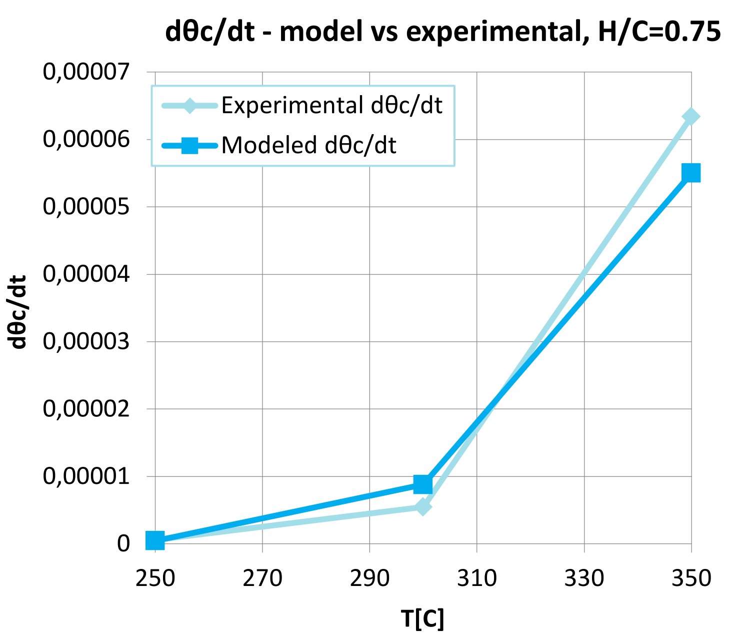
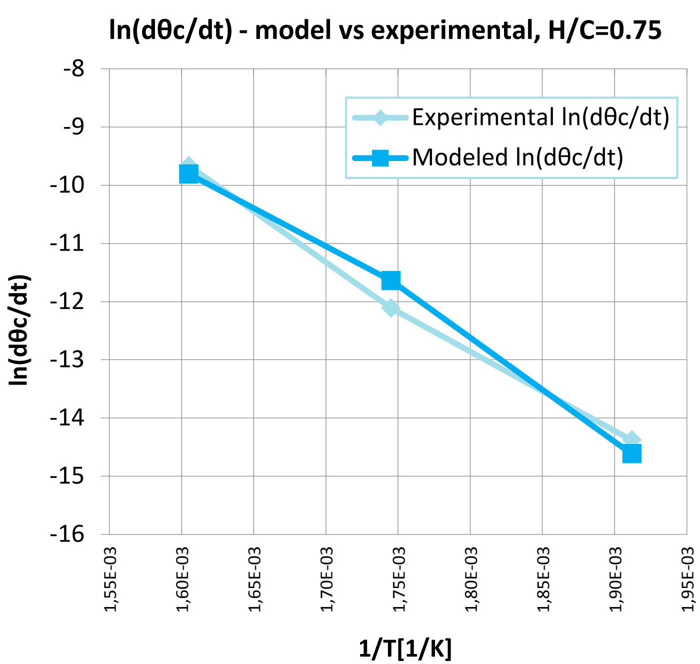
Model of membrane deactivation

- **Coking rate expression parameters were calibrated to experimental results using reference temperature = 350 °C**

$$\frac{d\theta_C}{dt} = \theta_C P_{C_3H_6} k^*_{C,350C} \exp\left(\frac{-E_C}{R}\left(\frac{1}{T} - \frac{1}{623K}\right)\right) - \theta_C P_H k^*_{r,350C} \exp\left(\frac{-E_r}{R}\left(\frac{1}{T} - \frac{1}{623K}\right)\right)$$





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Coke formation on Pd-based membranes

- *Effect of operating conditions*
- *Reduction of coke formation by membrane deactivation*

Combined membrane and catalyst experiments applying a non-integrated membrane reactor system

Background / hypothesis

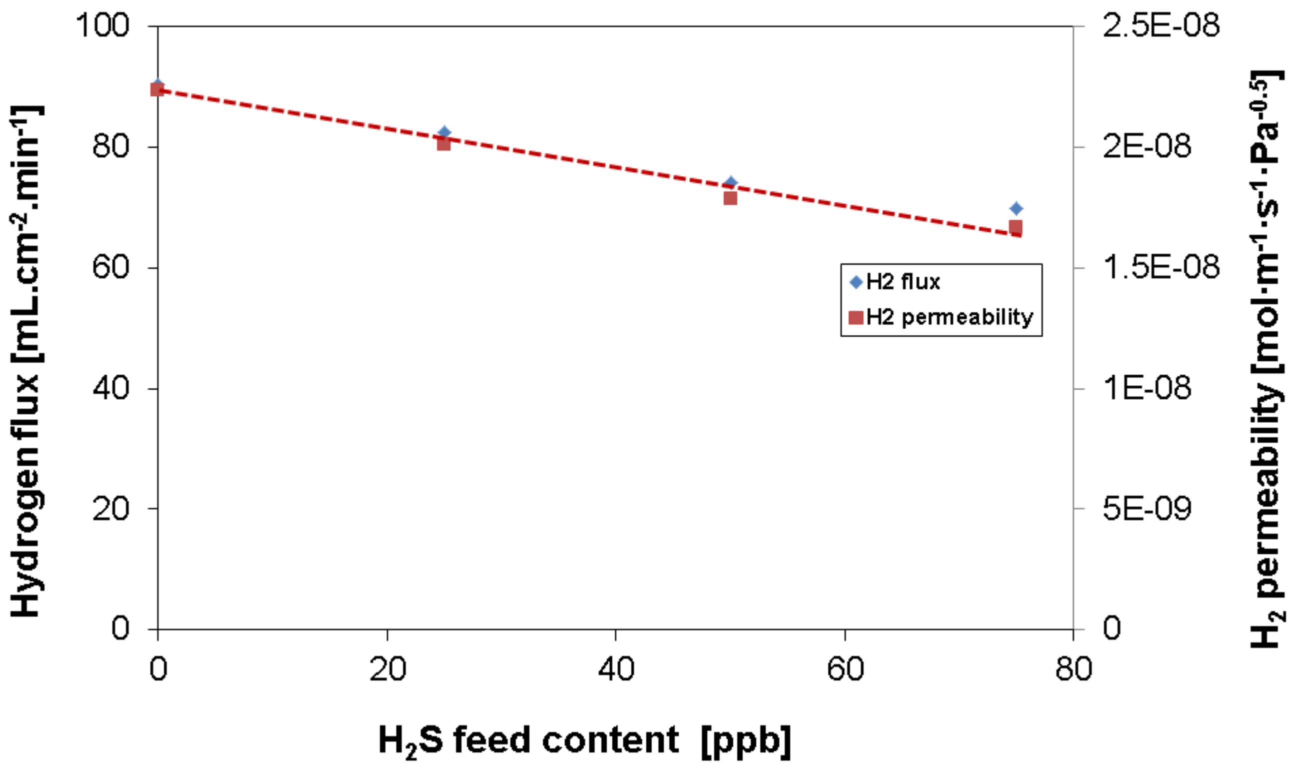
- **Coke formation**
  - Occurs on the most active sites of the Pd-alloy membrane surface
  - Coke formation can be prevented by a selective deactivation of these most active surface sites

- **Deactivation of Pd-alloy membranes by H_2S**
  - Even a trace amount (< 1 ppm) of H_2S in a membrane feed is known to reduce the H_2 flux due to strong surface adsorption
  - First at higher concentrations, a complete deterioration of the membrane is caused by formation of bulk Pd_4S

- **Aim and description of performed work**
  - Verify the effect of trace amounts of H_2S (ppb level) on membrane permeability
  - Investigate the presence of H_2S on coke formation kinetics

Results – H_2S inhibition of H_2 permeability

- **H_2 permeation through $Pd_{77}Ag_{23}$ membrane**
  - Membrane thickness ~10 µm, temperature equal to 400 °C and pressure of 4 bars
  - $H_2:N_2$ = 30:70 at 1000 mL·min^{-1}, Ar sweep at 500 mL·min^{-1}



Results – H_2S effect on coke formation

- **H_2 permeation through $Pd_{77}Ag_{23}$ membrane**
  - Membrane thickness ~10 µm, temperature equal to 400 °C and pressure of 4 bars
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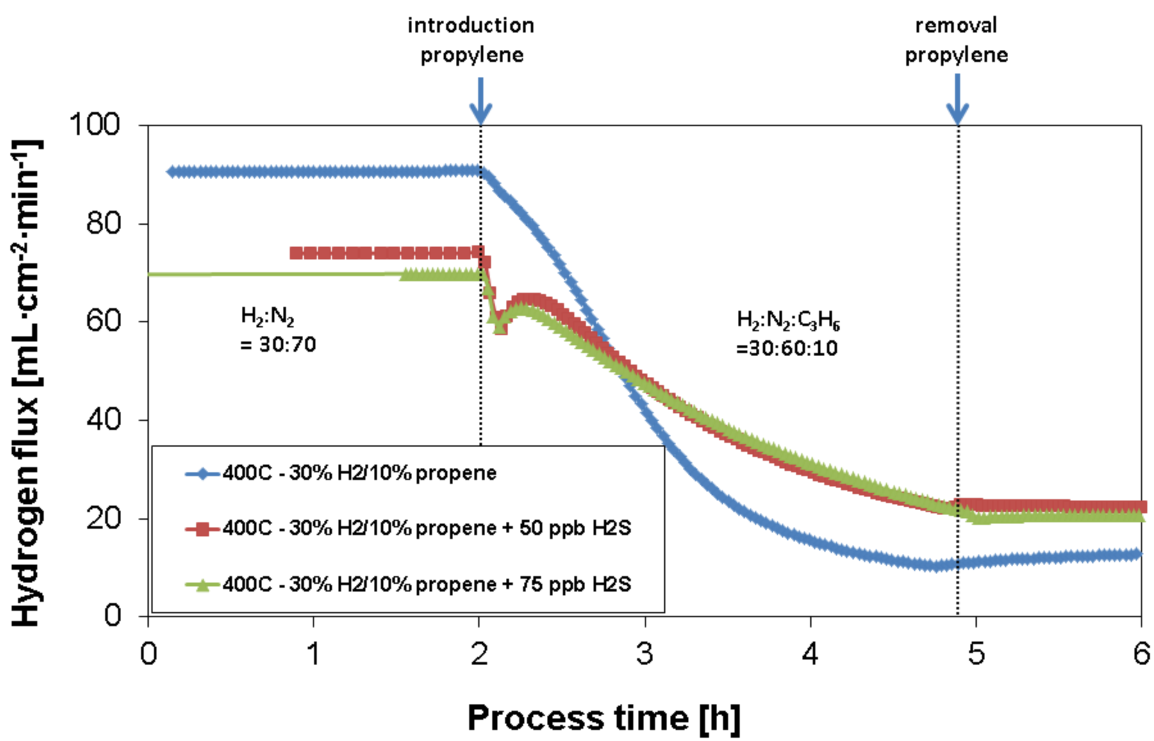
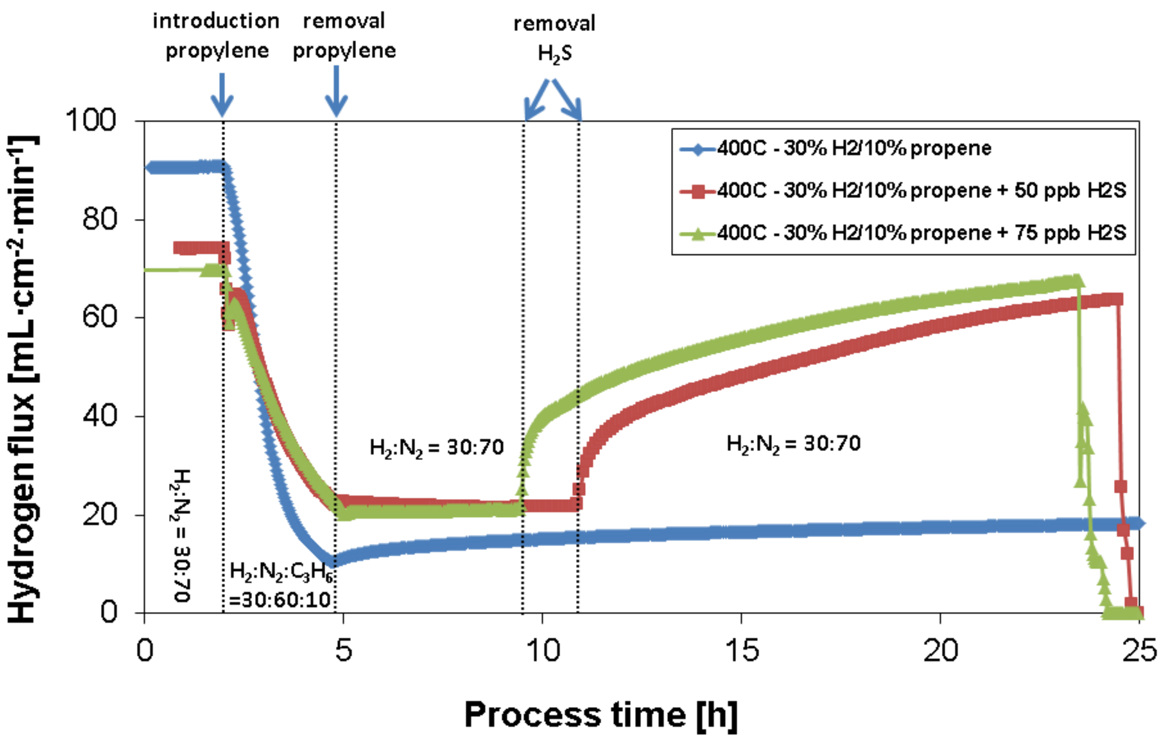


- Previously shown flux decrease due to coke formation after propene exposure
- Less rapid flux decrease during propene exposure in the presence of H_2S
- Larger absolute flux in the presence of propene already is obtained after 1 hour of propene exposure

Results – H_2S effect on H_2 flux recovery

- **H_2 permeation through $Pd_{77}Ag_{23}$ membrane**
  - Membrane thickness ~10 µm, temperature equal to 400 °C and pressure of 4 bars
  - $H_2:N_2$ = 30:70 at 1000 mL·min^{-1}, Ar sweep at 500 mL·min^{-1}



- Little to no H_2 flux recovery after removal of propene from gaseous feed
- No H_2 flux recovery after propene removal, but rapid recovery after H_2S removal
- Formation of organo-sulfur components?

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Coke formation on Pd-based membranes

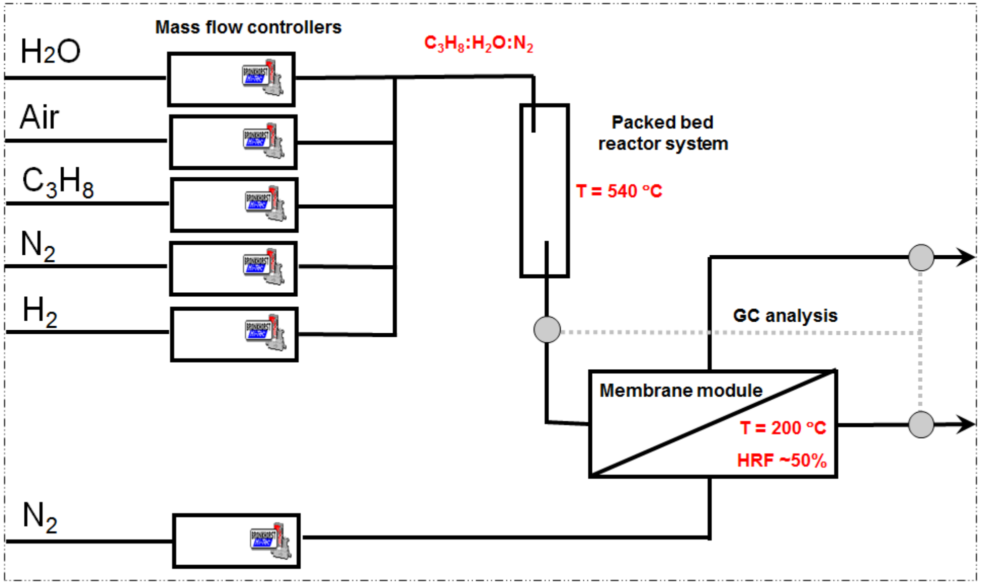
- *Effect of operating conditions*
- *Reduction of coke formation by membrane deactivation*

Combined membrane and catalyst experiments applying a non-integrated membrane reactor system

Investigation of non-integrated reactor/membrane design

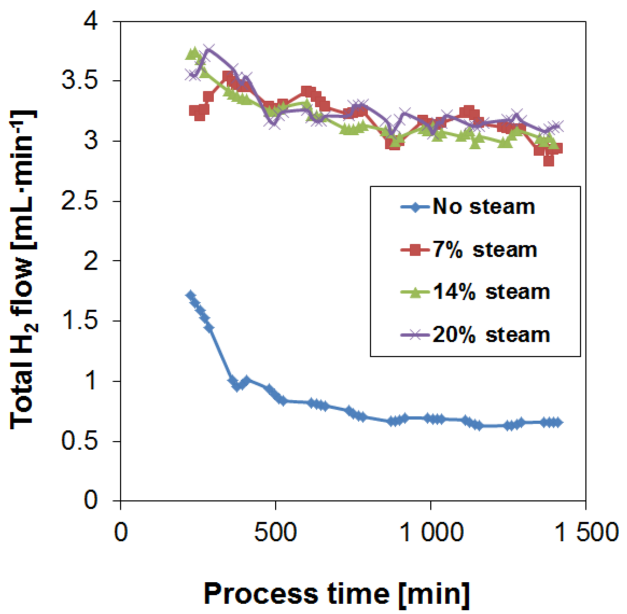
- **Mass flow & pressure controlled reactor test station**
  - Catalyst and membrane temperature of 540 and 300/200 °C, respectively
  - Run at atmospheric pressure
  - Gas analysis on a dry basis with GC

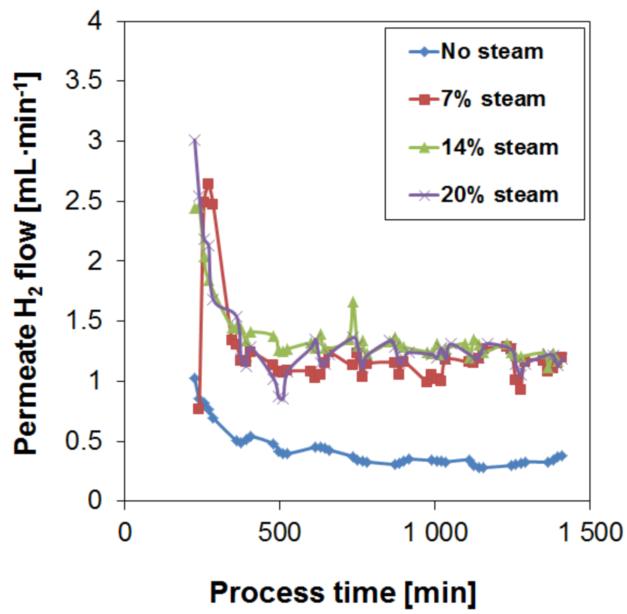
- **Experimental runs**
  - Sequential analysis of membrane retentate and permeate stream
  - Regeneration between separate experiments by air



Investigation of non-integrated reactor/membrane design

- **Effect of steam content**
  - Catalyst operation at 540 °C and membrane operation at 200 °C: $C_3H_8:N_2$ = 14.9:1





- Steam is required to obtain a good conversion
- Produced H_2 independent on steam content
- Appropriate catalyst stability obtained
- Stable membrane performance obtained at HRF varying from 38-50%

Conclusions

- **Investigated the use of Pd-based membranes in propane dehydrogenation (PDH) processes**
  - Studied the effect of pressure and temperature on the H_2 flux obtained in representative PDH mixtures
  - Supporting the process design and simulation of the overall process
- **Coke formation**
  - Flux-decreasing coke formation is limited at lower operating temperature
  - A decrease to at least 250-300 °C is required to obtain stable membrane operation
  - Membrane stability in feed originating from PDH catalyst needs further attention
- **Membrane deactivation by H_2S**
  - Less rapid flux decrease during propene exposure in the presence of H_2S
  - Larger absolute flux is obtained after 1 hour, combined with a more rapid H_2 flux recovery
  - Formed deposits are of a different chemical nature compared to those formed in the absence of H_2S - organosulfur components

Acknowledgements

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