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AACHENER VERFAHRENSTECHNIK

Model Development and Implementation of a Membrane Shift Reactor

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Membrane Shift Reactor - The Basic Idea

- Membrane Shift Reactor is part
  of an Auxiliary Power Unit
  for heavy duty trucks
- The APU system consists of a proton exchange membrane fuel cell (PEM fuel cell) that generates electricity for vehicle needs
- PEM fuel cells use hydrogen as fuel
- To avoid an additional hydrogen tank, hydrogen contained in the diesel fuel can be used
- Steam reforming of diesel fuel in fuel processor yield hydrogen rich reformate stream

$$C_nH_m + n\,H_2O \longrightarrow n\,CO + \frac{n+m}{2}H_2$$

Fuel processor

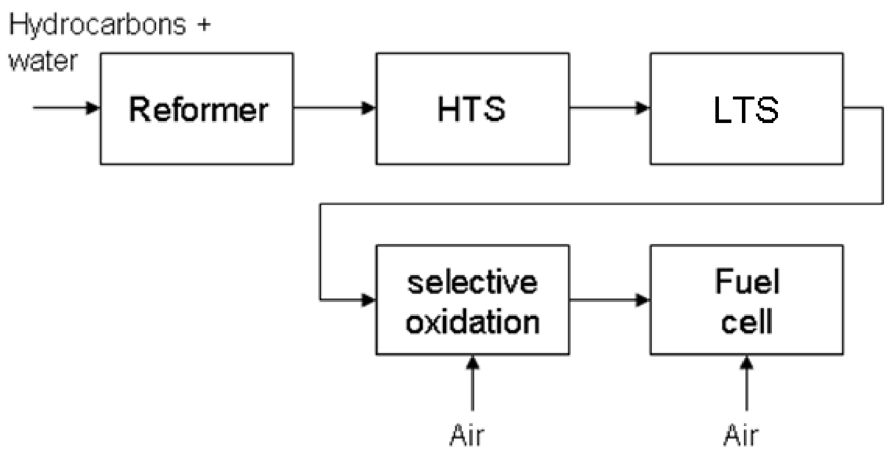
- PEM fuel cells require CO content in fuel gas below 10 ppm
- Conventional fuel processor: several reactors to reduce CO content in reformate gas
  - Water Gas Shift reaction

    $$CO + H_2O \longleftrightarrow H_2 + CO_2$$

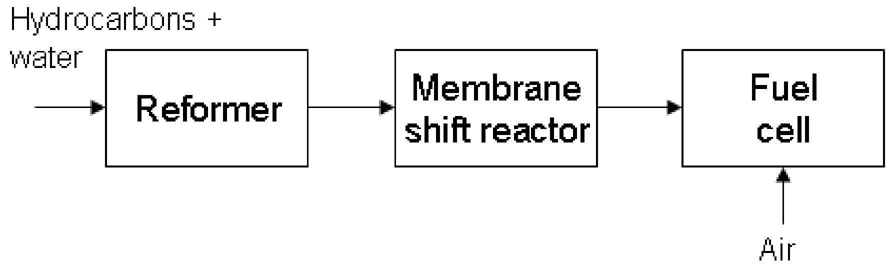
  - selective Oxidation

    $$CO + \frac{1}{2} O_2 \longrightarrow CO_2$$

- Membrane Shift Reactor: purification of hydrogen rich reformate stream by selective hydrogen permeation across palladium membrane



fuel cell with conventional fuel processor



fuel cell with membrane shift reactor

Advantage of Membrane Shift Reactor

- very pure hydrogen stream to fuel cell (> 99.95%)
  - no catalyst poisoning
  - dead end operation of fuel cell possible, leading to higher efficiency
- favorable influence on water gas shift and methane steam reforming equilibria through hydrogen removal from reactor
  - higher CO and methane conversion

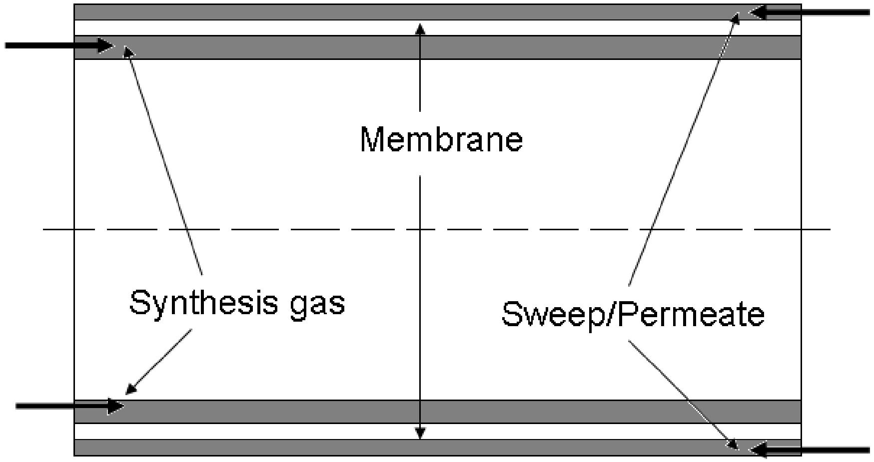
$$CO + H_2O \longleftrightarrow H_2 + CO_2$$

$$CH_4 + H_2O \longleftrightarrow 3\,H_2 + CO$$

- Metallic composite membrane: dense palladium layer on porous sinter metal support
- highly hydrogen selective
- driving force for permeation: difference in hydrogen partial pressures

Membrane Shift Reactor

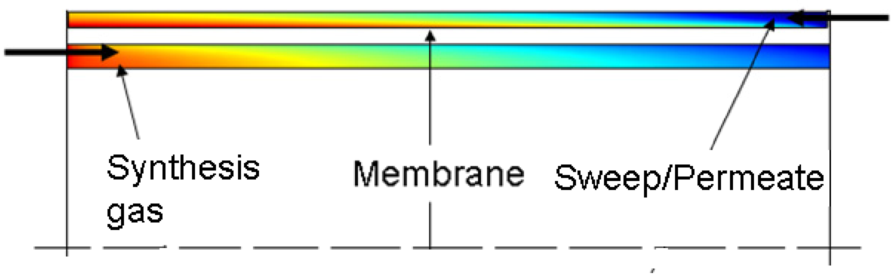
- Double annulus reactor, separated by the membrane
  - inner annulus is filled with catalyst
  - WGS and methane steam reforming reaction take place
  - in outer annulus steam is introduced as sweep gas to reduce hydrogen partial pressure
- Temperature ca. 600°C
- designed for 0.06 kg hydrogen per hour or 2 kW thermal energy



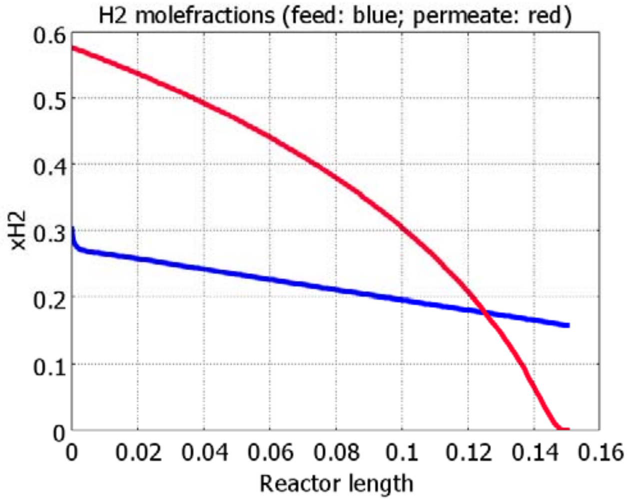
COMSOL Model

- two-dimensional steady state model
- two subdomains for the two annulus'
- several transport phenomena are considered
  - momentum transport
  - mass transport
  - heat transport
  - transport across the membrane
- two equilibrium reactions are considered with literature data
  - Water Gas Shift Reaction
  - Methane Steam Reforming Reaction
- strongly coupled multiphysics model
  - large damping
  - long calculation time

Model results

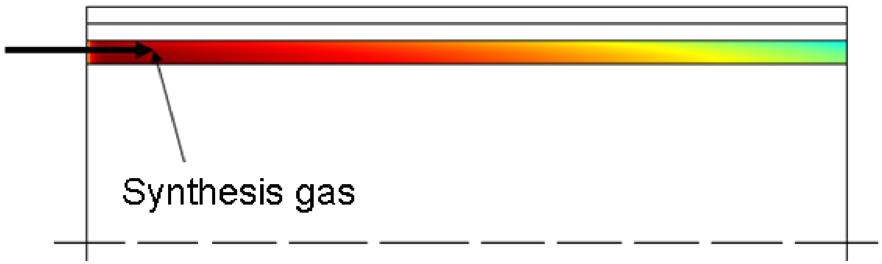


hydrogen concentration profile

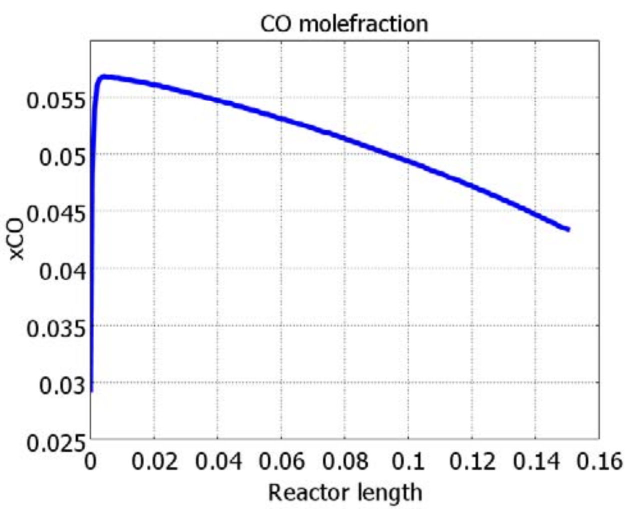


- Hydrogen concentration profiles show transport of hydrogen from the inner annulus (feed stream) to the outer annulus (sweep / permeate stream)
- two dimensional model shows a concentration polarization effect
  - lower hydrogen concentration at membrane than in the bulk feed stream
  - higher hydrogen concentration at membrane than in bulk sweep / permeate stream
  - resulting in lower driving force and lower permeation

Model results



CO concentration profile



- The concentration of carbon monoxide decreases along the reactor length
  - increased CO conversion due to selective hydrogen removal
  - enhanced hydrogen recovery by Water Gas Shift reaction in Membrane Shift reactor

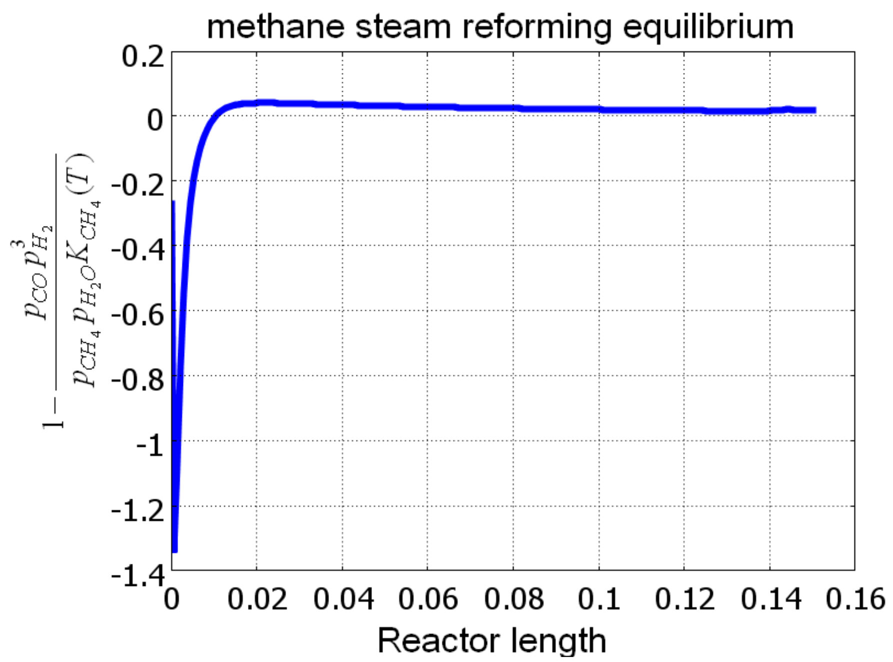
Evaluation of Model Results

	Feed	Residue	Sweep	Permeate
one-dimensional model				
H2O	0.614	0.450	0.201	0.201
H2	0.044	0.021		0.060
CO	0.060	0.061		
CO2	0.393	0.591		
CH4	0.102	0.031		
COMSOL model				
H2O	0.579	0.575	0.190	0.190
H2	0.046	0.017		0.033
CO	0.045	0.066		
CO2	0.397	0.392		
CH4	0.097	0.088		

streams in kg/hr

- Results of two-dimensional COMSOL Model with reaction rates are compared to results of a one-dimensional equilibrium model by Matthias (2009)
  - COMSOL Model predicts hydrogen product stream of 0.033 kg/hr
  - one-dimensional Model predicts product stream of 0.06 kg/hr
- predicted CO content in residue stream comparable for both models
- predicted methane conversion is significantly higher using the one-dimensional equilibrium model

Evaluation of model results



Distance from reaction equilibrium

- Slight positive deviation from methane steam reforming equilibrium along reactor length
- Reaction rate for methane steam reforming in the order of magnitude of hydrogen permeation across membrane
  - The equilibrium is not entirely reached in reactor
  - Smaller methane conversion predicted than in one-dimensional equilibrium model

Conclusion

- Results of COMSOL model are expected qualitatively
- Quantitative comparison with one dimensional model shows lower hydrogen recovery
  - lower recovery was expected due to incorporation of diffusion and concentration polarization effects into the two-dimensional model
  - differences between the two models in hydrogen recovery and methane conversion are much larger than expected
- Comparison with experimental results needed
- Model results can be fitted to experimental results by adjusting the expressions for the reaction rates or the reaction equilibrium constants

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Thank you

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