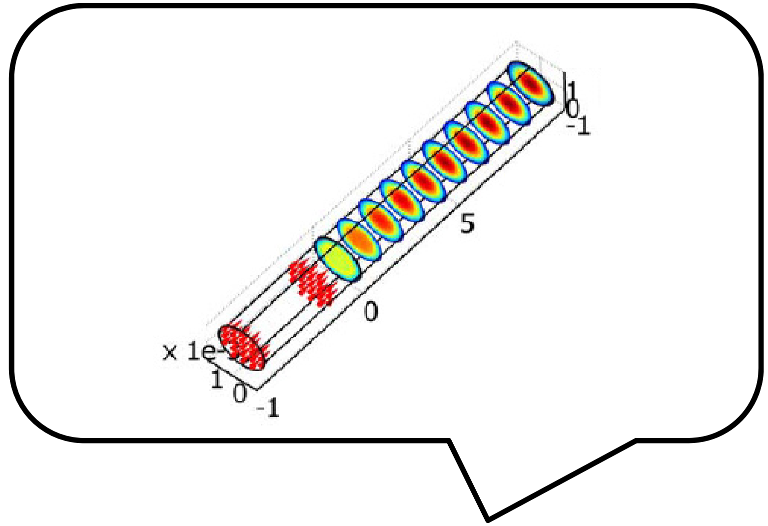
Presented at the COMSOL Conference 2009 Milan

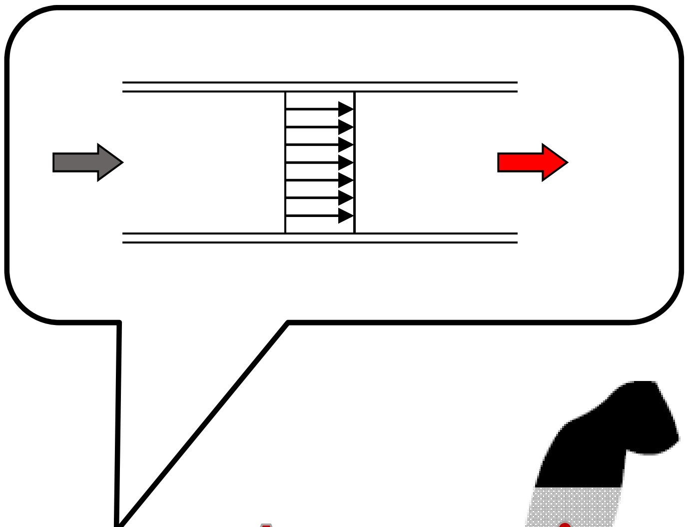
Providing an Entry Length in Heterogeneous Catalytic Reactors with Fast Diffusion

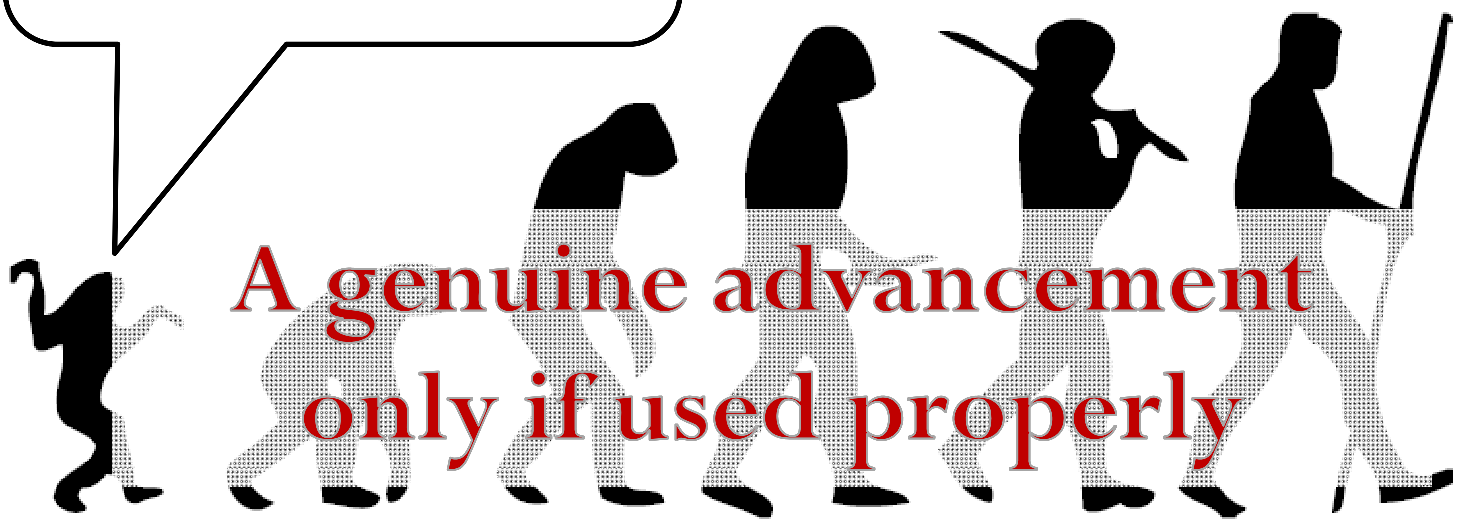
D. Dalle Nogare, P. Canu
University of Padova, Italy

to the CFD



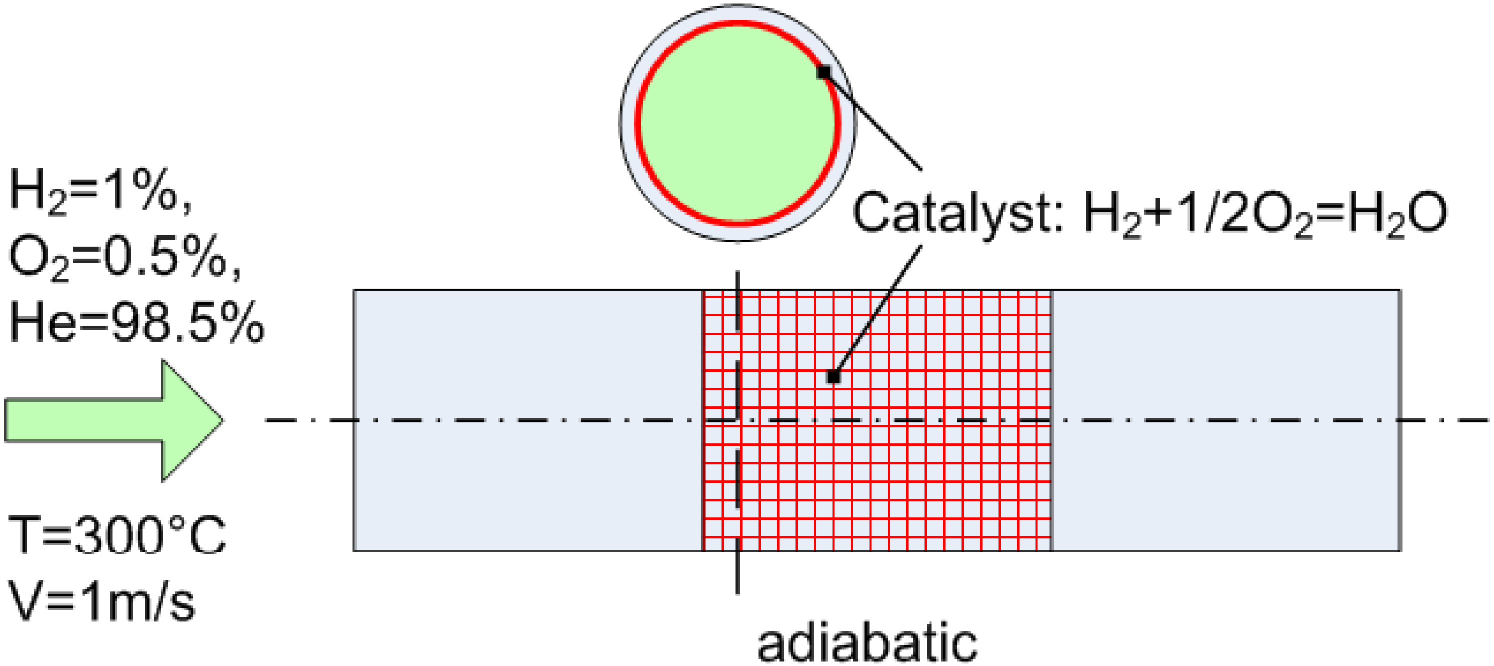
From the PFR





A genuine advancement only if used properly

Problem Definition



Model Definition (i)

- Equations:
  - convection and diffusion for H_2, O_2, H_2O, He
  - convection and conduction for T
  - weakly compressible Navier-Stokes for u,v in 2D **OR** $\rho \cdot v$=cost for u in 1D model
  - ρ form the ideal gas law

- Implementation of production rates
  - 1D: heat and mass source/sink are applied within the reactor domain (production rates * catalytic area per unit volume)
  - 2D: production rates of the gas species at the wall are fluxes at the boundary

Model Definition (ii)

- Heterogeneous kinetics[1]
  - 10 reactions in 3 gas species (H_2, O_2, H_2O) and 5 surface species (PT(S), H(S), H2O(S), OH(S), O(S))
  - ki kinetics constants have several functional forms ⇒ kinetics interpreter Cantera[2] (with Matlab interface)
  - species production rates in [mol/m^2/s] are defined per unit catalytic area

- Thermophysical properties:
  - Cp, Cv are polynomial function of the NASA coefficients
  - Viscosity, heat conductivity and diffusivities are calculated through the Lennard-Jones potential well depth, ε/k_B [K] and collision diameter σ [Å].

[1]O. Deutschmann, R. Schmidt, F. Behrendt, J. Warnatz,, *Symp. (Int.) Combust.*, ***26, 1747–1754*** (1996)
[2]D.G. Goodwin. In *Proc. CVD XVI and EuroCVD 14, M Allendorf, Maury, and F* Teyssandier (Eds.), Electrochemical Society, 155-162 (2005).

Use of COMSOL MPh (i)

- *Client / Server / Matlab… : Connect to Matlab*
- *Options, Functions…:*
  - Function name: "my_reactionH2";
  - Arguments: "c_H2, c_O2, c_H2O, c_He, T";
  - Expression: "prod_h2(c_H2,c_O2,c_H2O,c_He,T)"
- In "Subdomain settings" (1D model) or "Boundary settings" (2D model) insert the function: "my_reactionH2(c_H2,c_O2,c_H2O,c_He,T)"

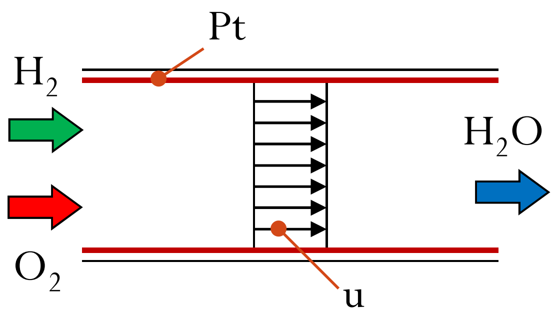
Use of COMSOL MPh

Species production rates and heat of reaction as Matlab functions:

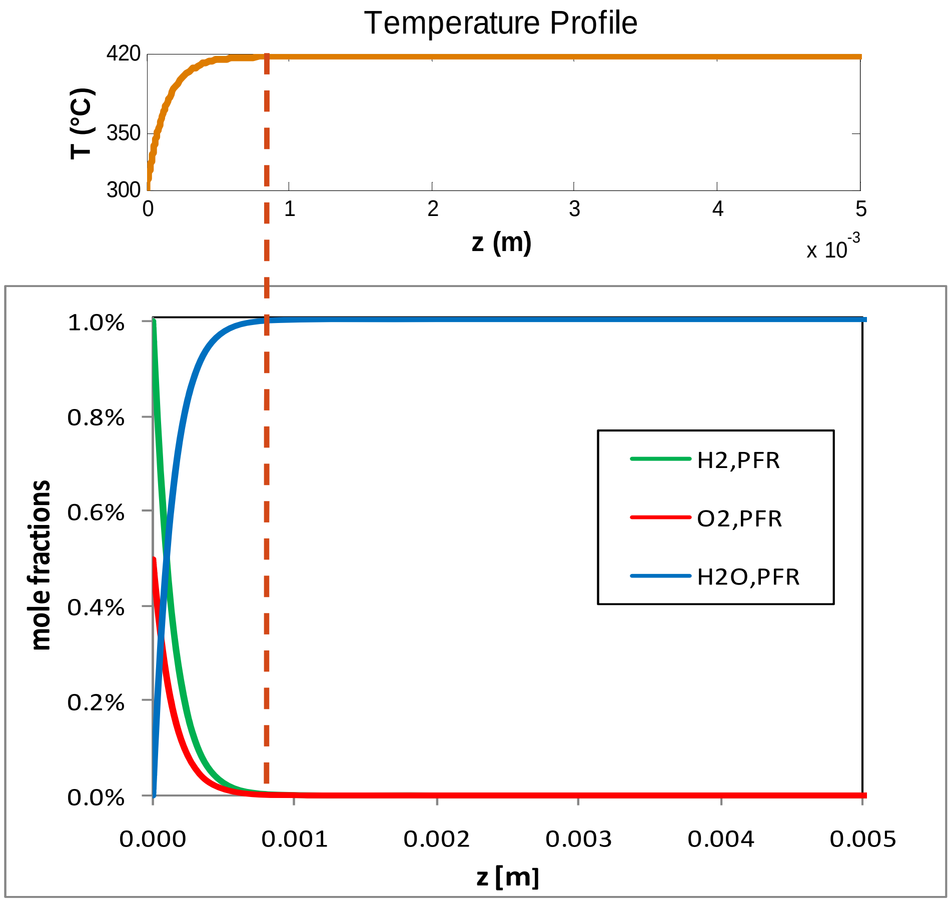
```
function pr_H2=prod_h2(h2,o2,h2o,he,T)

gas = importPhase('ptcombustH2.xml','gas');
surf = importInterface('ptcombustH2.xml','Pt_surf', gas);

for kz=1:length(h2)
    setMoleFractions(gas,[h2(kz),o2(kz),h2o(kz),he(kz)]);
    ...
    wdot = netProdRates(surf).*1000; %mol/m^2/s
    pr_H2(kz)=wdot(1);
end
```

Results
1. Plug Flow Reactor

- Axially segregated 1D model

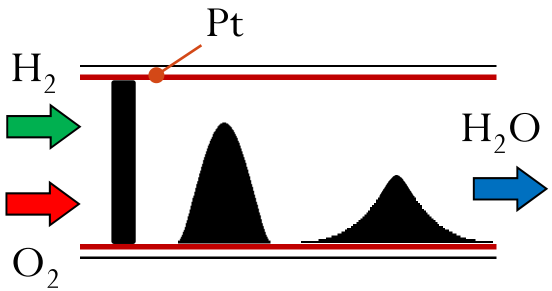


Full H_2 and O_2 conversion within 1mm



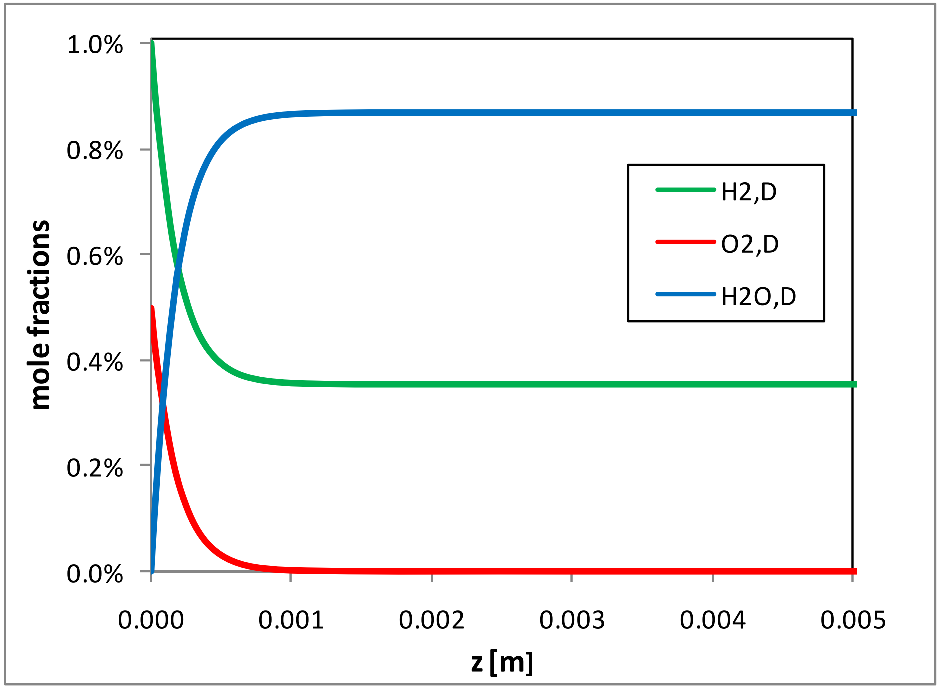
2. Dispersed Plug Flow Reactor

- Axially dispersed 1D model



Inlet: Dirichlet BCs on c_i and T

H_2 and O_2 are not in stoichiometric ratio

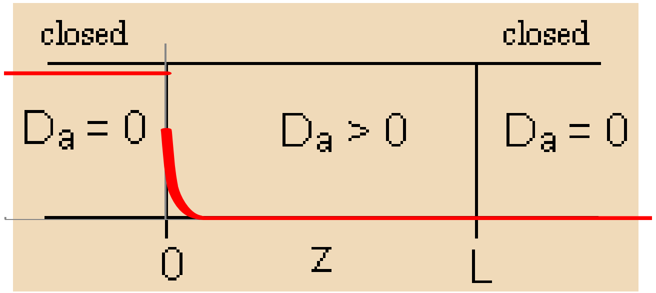


If H_2 and O_2 are given same Diffusivity, stoich. ratio is restored

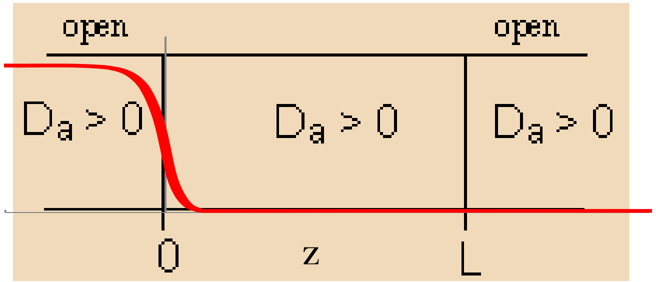
Open or closed vessel?

- Boundary Conditions for Dispersed Reactors

- Closed vessel (Closed-Closed BCs)

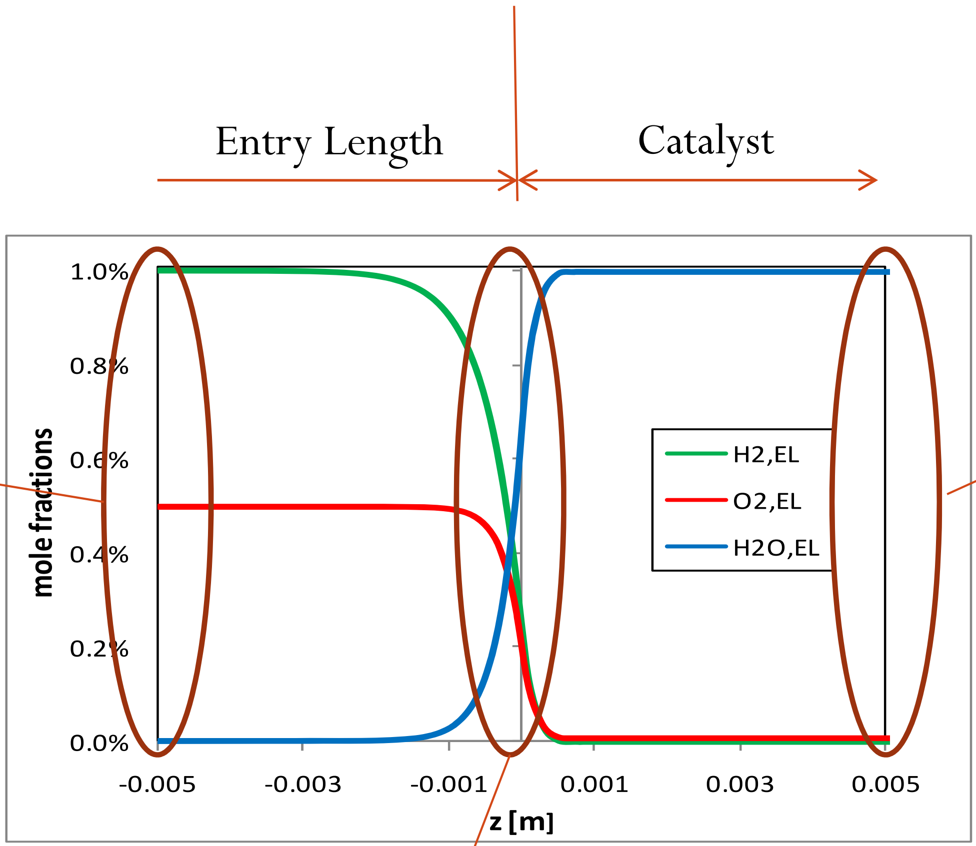


- Open vessel (Open-Open BCs)



- Low dispersion (large Pe) $\Rightarrow$ same solution <u>in output</u>
- High dispersion (small Pe) $\Rightarrow$ very different solutions

3. DPFR + Entry Length



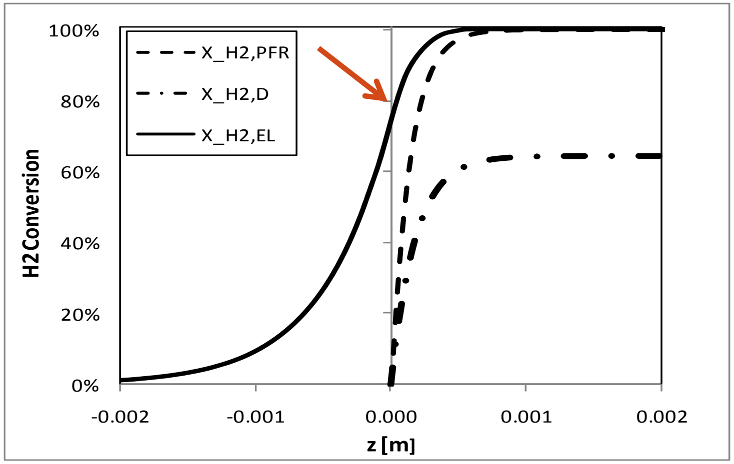
Zero gradients: Dirichlet condition applies

H_2 and O_2 again in stoich. ratio

H_2 and O_2 diffuse forward, H_2O diffuses backward

Summary of 1D models

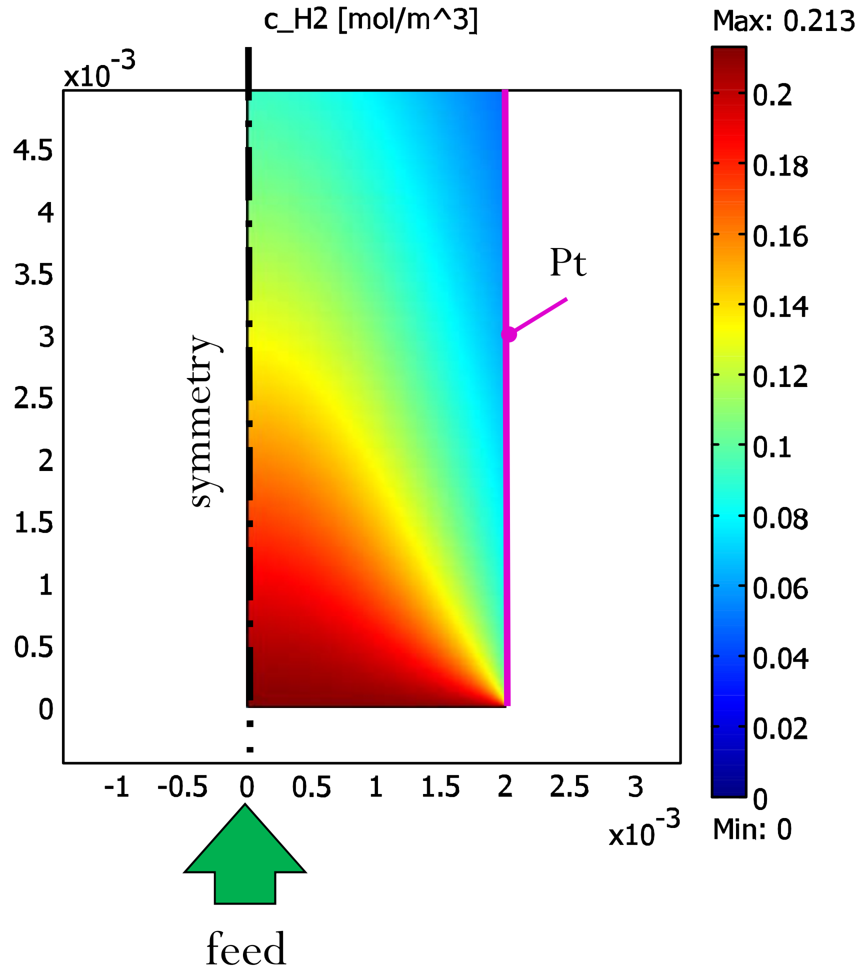
- PFR is correct but not physically accurate if dispersion is relevant
- DPFR accounts for axial diffusion
  - if Dirichlet BC is set at the inlet, the c° (and T°) set points are misundersood by the solver
  - The Entry Lenght allows the correct settings.
  - H_2 conversion at the inlet in a 1D model is X=80%, due to H_2 forward-diffusion



4. 2D model with Dirichlet BCs

- Axial symmetric model

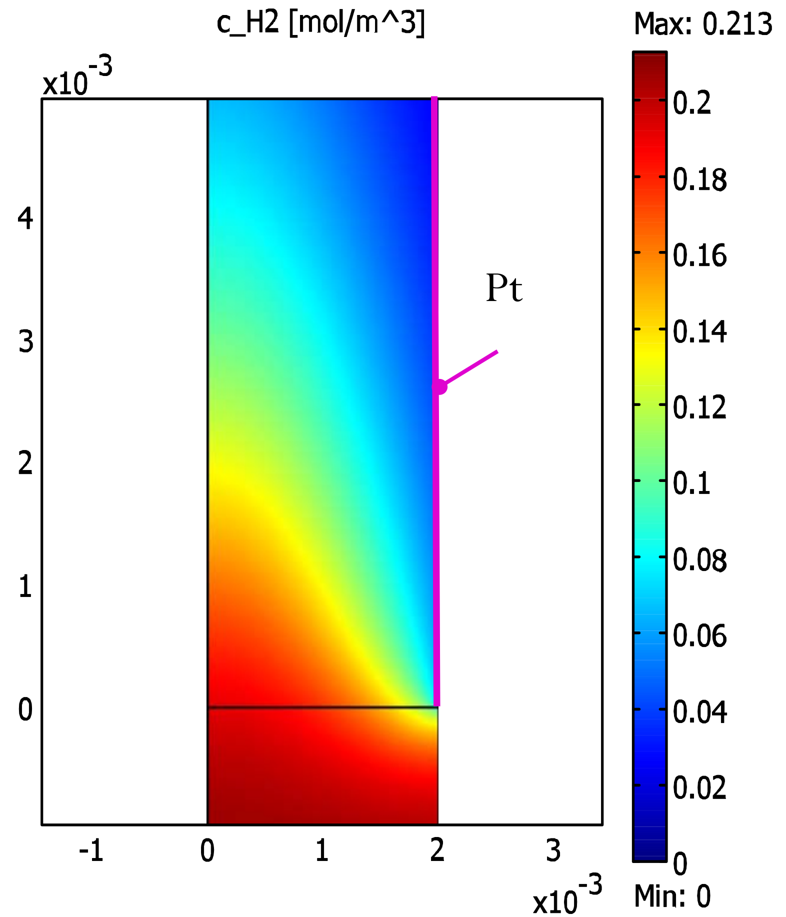
Strong gradients at the entrance near the catalytic wall are likely to give rise to diffusive fluxes.



5. 2D model with Entry Length

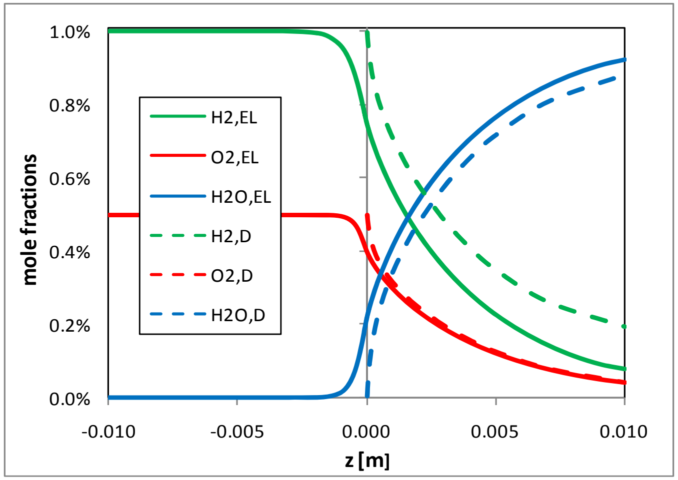
- Axial symmetric model

H_2 at the entrance is already low, therefore less strong gradients occur and the reacting conditions are milder



Summary of 2D models

- Conversion in 2D models is much lower, due to tranfer resistances
- if Dirichlet BC is set at the inlet, the c° (and T°) set points are misundersood by the solver
- H_2 conversion at the inlet in a 2D model is X=25%, due to H_2 forward-diffusion



Conclusions

- Heterogeneous kinetics was implemented linking the kinetics interpreter Cantera in its Matlab interface to COMSOL PMh
- A 1D analysis showed that with low Pe systems the Dirichlet BC at the inlet overestimates reagents mass fluxes
- The Open Vessel BC, implemented through an Entry Length, assures the correct BC settings
- The 2D description is required for a catalytic reaction in diffusion regime

Thank you for your attention.