

Providing an Entry Length in Heterogeneous Catalytic Reactors with Fast Diffusion

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Abstract: This work investigates the effects of boundary conditions on the species profiles in heterogeneous catalysis, with low Peclet systems. Hydrogen combustion in Helium was chosen because of the high diffusivities. Furthermore, already at $T=300^{\circ}\text{C}$ over a Pt catalyst, kinetics is very fast and the composition gradients at the inlet extremely steep. The issue is analyzed with 1D models, showing the difference between Plug Flow and Dispersed Plug Flow, the latter with Dirichlet BCs or with an Entry Length that reproduces the open-open vessel boundary condition. The same circumstances are also analyzed with 2D models. The gradients in the mean cross section profiles are lower, due to the transfer resistances, but local gradients are stronger, giving rise to larger diffusive fluxes. Both in the 1D and in the 2D problem, the application of Dirichlet is proved to arise non conservative BCs with large diffusive fluxes at the inlet.

Keywords:

Heterogeneous catalysis, detailed kinetic mechanism, Robin boundary condition, low Peclet number, hydrogen combustion.

1. Introduction

In catalytic reactors, steep axial concentration and temperature gradients can be observed at the inlet, in case catalyst is very active at the operating temperature. The effect calls for particular attention to select physically consistent boundary conditions while modeling.

A monolithic reactor behaves as an open-open (O-O) vessel, since the same mixing conditions apply to both the catalyst and the duct upstream, where a fast diffusing product can be experimentally detected. Nonetheless, it could be modeled with closed-closed (C-C) boundary conditions (BCs) in case of high Pe values (convection prevailing on dispersion) without significant errors. On the contrary, with low Pe these two BCs (O-O or C-C) lead to very different solutions (1). In spite of the well settled

theory (both the O-O and the C-C problems had analytical solutions more than 50 years ago for a simplified 1D problem), the applications to 2D seem to ignore the issue. Indeed, quite often the monolithic reactor is being modeled in literature with a computational domain restricted to the actual reactor geometry, with a Dirichlet BC at the inlet (2-5), with few exceptions (6).

This work applies the 1D Dispersed Plug Flow model (DPF) to a low Pe case, showing the errors due to a wrong choice of BCs. It also compares a full 2D model with either Dirichlet BCs at the inlet or O-O BCs, obtained through an Entry Length (EL) in the form of an extra duct length in front of the catalyst. The case study is H_2 combustion in He. The application is quite critical because diffusivities in He are strongly enhanced, doubling those in air. Furthermore, H_2 diffuses twice as fast as O_2 , which highlights the effects of backward diffusion at the inlet. The reactor geometry is very simple, a tubular reactor with a catalyst coating on the tube wall. Platinum is chosen as the catalyst; above 300°C its activity is so high that the total conversion is achieved with very short contact time, except for transfer limitations. Nonetheless, kinetics are handled with great detail, being described through a well established multi-step surface mechanism, the Deutschmann- CH_4 combustion (7), a subset of which is also suitable for H_2 combustion. The kinetics interpreter of choice is the Cantera library (8), an object oriented software for reacting flows. Cantera is used in its Matlab interface and is coupled with COMSOL MultiPhysics through Matlab interface, providing the species production rates and the heat of reactions.

2. Problem Definition

The model describes an adiabatic tubular reactor ($L=10\text{mm}$, $\varnothing=4\text{mm}$) in which a stoichiometric mixture of H_2 and O_2 ($\text{H}_2:1\%$, $\text{O}_2:0.5\%$), at high dilution in He, flows and reacts at the catalytic wall, ultimately yielding H_2O .

The feed flows at $v=1\text{ms}^{-1}$. Its temperature is 300°C .

The equations to solve are four “convection and diffusion” mass balances, one for each molecular species (H_2 , O_2 , H_2O , He), the “convection and conduction” gas energy balance and the “weakly compressible Navier-Stokes” momentum balance in the 2D problem, while the continuity equation ($\rho \cdot v = \text{const}$) constrains the velocity in the 1D model. Heat conduction in the solid is neglected for sake of simplicity. Density ρ is always calculated by the ideal gas law.

The homogeneous kinetics can be neglected in comparison with the heterogeneous ones, at atmospheric pressure. Therefore, the species production rate is only the heterogeneous term, s [$\text{mol}/\text{m}^2/\text{s}$], and is defined per unit catalytic area. The kinetic mechanism consists of 10 reactions in 3 gas species (H_2 , O_2 , H_2O) and 5 surface species ($\text{PT}(\text{S})$, $\text{H}(\text{S})$, $\text{H}_2\text{O}(\text{S})$, $\text{OH}(\text{S})$, $\text{O}(\text{S})$). The kinetics constants are either in the modified Arrhenius or the sticking coefficients form and can be function of the surface coverage. The reaction order can be different from the stoichiometric coefficient and the rate constants can depend on the coverage in several functional forms (9). Because of all these features, the kinetics is handled by an interpreter, which reads the mechanism written in standard CHEMKIN format and returns the calculated production rate and the heats of reaction at local temperature and composition. Cantera was chosen as kinetics interpreter because of its Matlab interface with COMSOL MPH.

In the 2D model, the production rates of the gas species at the wall are implemented as fluxes at the boundary, as explained in the BCs definition, in section 5. In contrast, the 1D model assumes uniform concentration radial profile (no transfer resistances); then, heat and mass source/sink are applied within the whole reactor subdomain (and not on the boundaries), correcting the production rates s with the catalytic area per unit volume, A_V .

The specific heat at constant pressure, as well as the ratio of specific heats, is introduced as a *global expression*, and calculated as a polynomial function of the NASA coefficients for pure He. The transport properties are calculated through the Lennard-Jones potential well depth, ε/k_B [K] and collision diameter σ [\AA] (9). Viscosity and heat conductivity are referred

to the inert carrier (He), as well as all the species binary diffusion coefficients.

3. Use of COMSOL Multiphysics

The heterogeneous reactor model has two peculiarities in COMSOL MPH. Firstly, the Chemical Engineering Module “convection and diffusion” application mode, unlike its homologous in the general module, allows vectorial definition of concentration, which is useful in the subsequent linking with Matlab. Secondly, the heterogeneous kinetics can be handled by an external interpreter called through Matlab functions.

Steps in implementing a Matlab function are the following:

1. From menu *File*, select the *Client/Server/Matlab... : Connect to Matlab*. This opens Matlab and export the fem to it. Note that the use of COMSOL with Matlab must have been selected during installation.
2. In menu *Options, Functions...*: add the definition of the function to use in Matlab. Note that the function and the expression names must be different, e.g. Function name: “MyFunction”; Arguments: “c, T”; Expression: “MyFunction_ML(c,T)”. Accordingly, the external Matlab function is named “MyFunction_ML.m”, with arguments (c,T) that are vectors and should give vector results.
3. In “Subdomain settings” (1D model) or “Boundary settings” (2D model) the function “MyFunction(c,T)” can be specified just like a user defined variable.

In this model, concentrations are named c_{H_2} , c_{O_2} , $c_{\text{H}_2\text{O}}$ and c_{He} , and T is the temperature. In the 1D model the production rate of H_2 is defined in the “Subdomain settings” form as $R = A_V \cdot \text{ProductionRateH2}(c_{\text{H}_2}, c_{\text{O}_2}, c_{\text{H}_2\text{O}}, c_{\text{He}}, T)$ [$\text{mol}/\text{m}^3/\text{s}$]. In the 2D model the production rate is defined in the “Boundary settings” form as a flux = $\text{ProductionRateH2}(c_{\text{H}_2}, c_{\text{O}_2}, c_{\text{H}_2\text{O}}, c_{\text{He}}, T)$ [$\text{mol}/\text{m}^2/\text{s}$]. The function “ProductionRateH2” is a Matlab function which in turn calls Cantera routines.

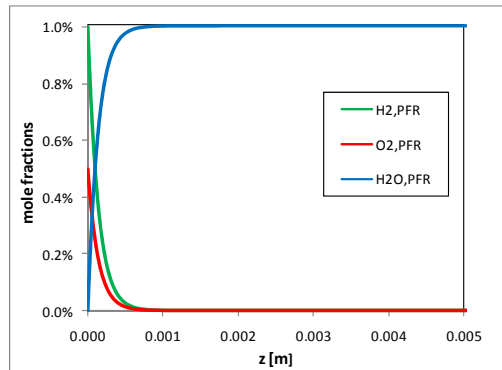


Figure 1. Species profiles in a PF model.

4. 1D model

4.1 Plug Flow

The Plug Flow (PF) model assumes axially segregated flow and no transfer resistances from the bulk to the catalytic surface. It was solved integrating the PF mass and energy balances with MATLAB, calling the interpreter Cantera. It predicts complete H_2 conversion in less than 1mm (Figure 1), at $T > 300^\circ C$. Note that, being the reactants fed stoichiometrically for combustion, their concentrations at the outlet are both zero.

4.2 Dispersed Plug Flow – Dirichlet BC

The Dispersed Plug Flow (DPF) model allows axial dispersion but it still assumes a flat radial profile, as in the PF model. It can be solved with a 1D model in COMSOL MPh, using the kinetics as homogeneous, as described in the previous sections. Different Boundary Conditions may apply to this model. At first, Dirichlet BCs are used at the inlet. Due to the lack of transfer resistances in the radial direction and to the fast kinetics, the conversion is again complete in less than 1mm (Figure 2), slightly downstream than in the PF.

It can be noticed from the figure that the model is not conservative. Even if the feed is stoichiometric, O_2 is completely consumed while H_2 consumption is only 60%. This means the boundary condition is not correctly set. As a proof, all species diffusivities were put equal to He's and the DPF_D turned out to convert both reactant completely. This demonstrate that if H_2 and O_2 had the same diffusivities, the

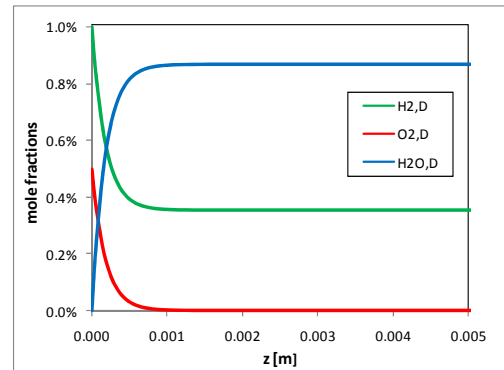


Figure 2. Species profiles in a DPF model with Dirichlet BCs at the inlet.

stoichiometric ratio would be maintained even with the Dirichlet BCs, but since they do not, this means the Dirichlet are the wrong BCs in a back-diffusing system.

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In actual experiments, the concentration profiles in z direction have been measured for a similar case. The concentration axial profiles shows a bend well before $z=0$, because the reactant diffuses forward driven by the strong gradient at the inlet. Therefore, the concentration at $z=0$ (c^o) is sensibly lower than the concentration in the feed (c^*), far upstream the catalyst. If the reactor is modeled only in its strict domain, the boundary condition $c^o=c^*$ at the inlet is understood by the solver as if the feed concentration were higher than c^* , in proportion to the diffusivity of the species. For example, if in the real world the difference between c^* (feed) and c^o (cat. inlet) is 10%, the correct Dirichlet boundary condition at the inlet would be $c^o=0.9c^*$. If we put $c^o=c^*$, then the solver assumes that the feed composition is $c^{**}=1.1c^*$, which is not our intent and makes the mass balance wrong in excess. Since H_2 diffusion is approximately twice the O_2 diffusion, the mass

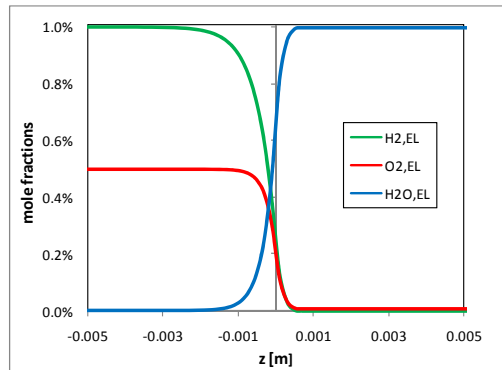


Figure 3. Species profiles in a DPF model provided with an Entry Length.

balance on H_2 is more affected by this error than that on O_2 . The situation that turns out is depicted in Figure 2: even though the feed we meant to assign was stoichiometric, O_2 conversion is 100%, while H_2 is 60%, because the solver, quite correctly, interprets the c° BCs as the results of the convection-diffusion phenomena that play their role at the inlet and introduces more H_2 than the stoichiometric.

If we tried to impose the inlet BCs as fluxes, with the Neumann BCs, we might introduce an analogous error, but now with an underestimation of the H_2 in the inlet. If we imposed a convective flux at the inlet, the solver would interpret it as a sum of diffusive and convective fluxes and therefore would underestimate the net H_2 flux.

In the attempt to describe this problem as a closed-closed vessel, the correct BC to apply to keep the model conservative would be a combination of Dirichlet and Neumann's, also known as Robin type-BC. Summarizing, the C-C BCs are suitable for a high Pe system, while it gives wrong results in output for low Pe systems, for which an O-O BCs is to use.

4.3 Dispersed Plug Flow – Entry Length

A more rigorous BC at the inlet of the catalytic reactor is the O-O vessel, particularly with low Pe systems. It correctly assumes that there could be some variation in the composition also upstream the catalyst. Therefore, some length of piping before the actual reactor is to be included in the model. In this work, this is called Entry Length (EL) and is conservatively set equal to the reactor length. The condition to

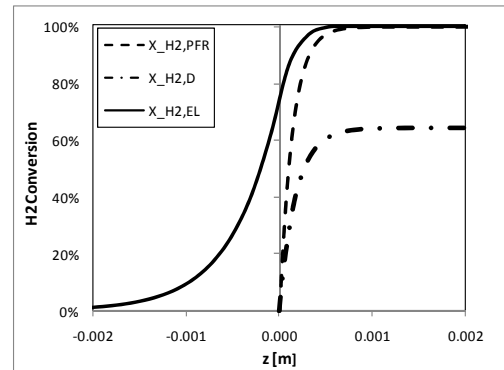


Figure 4. Comparison among the H_2 conversion in the three models: PF, DPF_D with Dirichlet BCs and DPF with Entry Length.

fulfill is the zero gradient at the inlet of the EL, such that the Dirichlet BC applies.

The simple 1D model is effective in showing the importance of considering back-diffusion, particularly with the smallest species. The composition of the gas reaching the inlet of the catalyst is not that of the feed, but it is poorer in the reactants and includes some products. This aspect is important in optimizing the reactor. For example, in distributing unevenly the load of the catalyst on the monolith, such to obtain the desired working condition, it is important to consider the “real” composition and not to suppose the composition to behave like a PF before the catalyst. In addition, the hot spot in the temperature profile (not shown) is highly smoothed, leading to milder conditions in the catalyst operation.

To compare the three 1D models presented so far, the H_2 conversion is shown. PF and DPF_D produce analogous slopes in $z=0$, but the second fails in reaching $X_{H_2}=100\%$. On the other hand, the DPF_EL predicts a X_{H_2} around 80% already before the reactor, representing a high extent of back-diffusion into the upstream gas.

5. 2D Model

The 2D model is needed to correctly predict the species and temperature profiles in the heterogeneous reactor, particularly with such strong kinetics, that imply there might be a predominant diffusion regime controlling the conversion. The radial profiles are expected to be nonuniform, implying that mass and heat transfer rates can limit the reactivity.

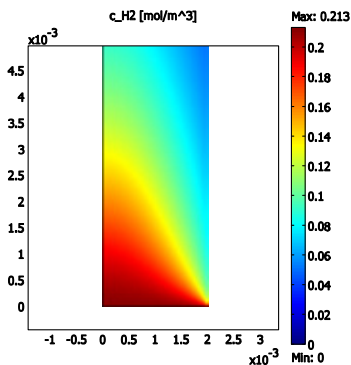


Figure 5. H₂ profile in a 2D model with Dirichlet BCs at the inlet. The gas flows upstream. The catalytic wall is at r=2mm.

Boundary Conditions

Inlet (both with and without EL): Dirichlet BCs for all the variables: v , T , c_{H_2} , c_{O_2} , c_{H_2O} , c_{He} . Outlet: pressure outlet and convective flux for the mass and energy balances. Symmetry axis ($r=0$): symmetry. “Entry” Wall: slip condition on velocity and insulation for concentration and temperature. “Reactor” Wall: the basic assumption of “no accumulation” in catalysis states that the coverage of the active site should not change in a steady state problem, thus s for the surface species equals zero. It is therefore possible to evaluate the coverage as a function of the local gas composition near the catalytic wall. For this reason, the boundary conditions at the catalyst wall are functions of the compositions of all the gas species and of the temperature, as follows:

c_{H_2} :
 $\text{flux} = \text{ProductionRateH2}(c_{H_2}, c_{O_2}, c_{H_2O}, c_{He}, T)$
 c_{O_2} :
 $\text{flux} = \text{ProductionRateO2}(c_{H_2}, c_{O_2}, c_{H_2O}, c_{He}, T)$
 c_{H_2O} :
 $\text{flux} = \text{ProductionRateH2O}(c_{H_2}, c_{O_2}, c_{H_2O}, c_{He}, T)$
 c_{He} : insulation
 T :
 $\text{heat flux} = \text{HeatOfReaction}(c_{H_2}, c_{O_2}, c_{H_2O}, c_{He}, T)$

These Matlab functions call the “netProdRates” subroutine from the Cantera’s “Kinetics” module and the “enthalpies_RT” subroutine from the “ThermoPhase” module. Results without the EL and with a Dirichlet BC at the inlet are shown in Figure 5. The H₂ concentration at the inlet is uniform and equals its composition in the feed. As soon as it reaches the catalytic surface, the H₂ concentration drops to ½ after $1 \cdot 10^{-4}$ m. Local concentration gradients

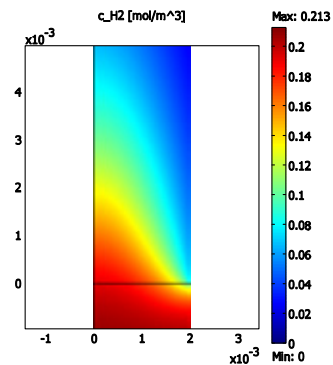


Figure 6. H₂ profile in a 2D model with EL. The reactor inlet is at z=0. The catalytic wall is at r=2mm.

are about $10 \text{ (mol/m}^3\text{)}/\text{mm}$ at $z=0$. Under these circumstances, it is hard to figure out that no diffusion occurs upstream, unless a distributor is present.

In figure 6 there is the analogous problem, solved with the EL. It is clear that the gas reaches the catalyst (at $z=0$, $r=2\text{mm}$) already at higher dilution and big gradients are no more present.

The comparison between the two 2D models with different BCs is shown in Figure 7 where average cross-section mole fractions are calculated by the species and total flow rates across each section. Adding the transfer resistances leads to an even lower reactivity at the wall, with the net result that the mean concentration at the inlet reflects a conversion of only 25% instead of the 80% of the 1D model.

Again, we notice the Dirichlet BCs leads to a non conservative model. The O₂ decrease is the same in both the models, while the H₂ left in the system is higher than the stoichiometric ratio.

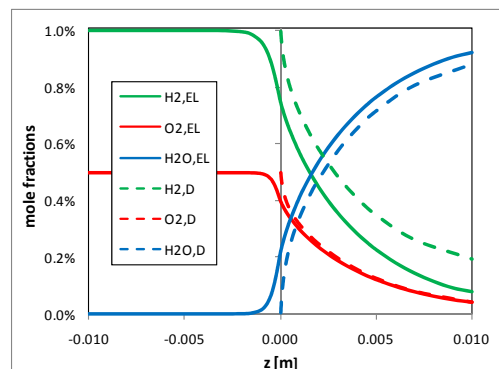


Figure 7. Composition profiles in the 2D model, with and without EL, evaluated as mole flows mean in the cross section.

Besides providing the correct solution, another benefit of the EL is that, since the reactant on the catalyst is much more diluted, the mesh can be looser at the inlet and the extended domain does not require more computational resources than the strictly catalytic domain.

6. Conclusions

Heterogeneous catalysis applications can be challenging because of the sharp concentration gradients, which generate strong diffusive fluxes, particularly with low Pe systems. It occurs frequently, e.g. where H₂ is among the reactants or products or if He is the carrier, the velocities are low or the geometry is particularly narrow, as in micro-fluidic applications. The most effective solution is accounting for an Entry Length (EL) before the inlet of the reactor, to gain the zero gradients condition, which allows Dirichlet BCs. Otherwise, the calculated profiles do not reproduce correctly the experimental and, possibly, the mass and heat balances may be not fulfilled.

Three 1D models are presented. A Plug Flow, for which no transfer resistances occur, gives complete conversion in the shortest length. A Dispersed Plug Flow, with Dirichlet Boundary Conditions at the inlet, is not conservative due to the strong gradients near the inlet that cause diffusive fluxes at the inlet, not taken into account by the Dirichlet BCs. A DPF with EL evidences a large variation of concentrations in the upstream fluxes.

A 2D model is also shown, with the two different BCs. The transfer resistances slow down the reactivity, reducing the wall concentrations with respect to 1D models. Nonetheless, large concentration gradients develop at the inlet, close to the catalytic wall, and back diffusion is still an important feature of the model. Again, the model with Dirichlet BCs is proved to be non conservative.

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8. Acknowledgements

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