# Simulation of Surface Chemical Reactions in a Monolith Channel for Hydrogen Production

N. Pacheco[*,1], D. Pavone[1] , K. Surla[1], J.L. Houzelot[2] and E. Schaer[2]
[1]IFP-Lyon, [2]ENSIC
*Corresponding author: IFP-Lyon, BP3, 69360 Solaize, France, nuno-manuel.pacheco-magalhaes@ifp.fr

**Abstract:** This paper intends to show a model of a monolithic reactor for the autothermal reforming process (ATR). This process uses hydrocarbons (fossil fuels or biofuels) to produce $H_2$. The ATR chemical reactions take place on the surface of monolith channels coated with a catalyst. The isothermal ATR reactor is modeled using 42 catalytic surface chemical reactions that involve 13 solid species and 7 gas species. To solve the model, two numerical techniques are compared: the Surface Model using weak form equations (SM) and a standard thin Volume Model (VM). This paper shows that the surface modeling (SM) is the better way to calculate the monolith catalytic reactions. Because this simulator is a preliminary version not yet experimentally validated, and in order to verify the simulator result consistency, results are compared with thermodynamic equilibriums calculated by COMSOL. The conclusions are that the results given by the dynamic simulator are in agreement with the thermodynamic equilibriums.

**Keywords:** Autothermal Reforming, Monolith, Methane, Hydrogen, Surface Chemical Reaction, Weak Form, Thermodynamic Equilibrium

## 1. Introduction

IFP has been developing economic and clean processes for hydrogen production for several years.[1] Two main sources are considered: hydrocarbons and biomass.

The hydrogen is nowadays considered as a promising energy source for the future. It appears as an interesting way to limit the use of fossil fuels and it could reduce the emissions of greenhouse gases. However, the hydrogen is not a primary source of energy and therefore it must be produced hence, the hydrogen production itself must use low emissions of $CO_2$ techniques.

One efficient way to produce $H_2$ is via Autothermal Reforming (ATR). This process is mainly based in three chemical reactions:

$$CH_4 + H_2O \xrightleftharpoons{} CO + 3H_2 \tag{1}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \tag{2}$$

$$CO + H_2O \xrightleftharpoons{} CO_2 + H_2 \tag{3}$$

However, this chemical reaction system needs to be catalyzed for the process optimization. To hold the catalyst, IFP decided to use monoliths in the reactor (Figure 1).

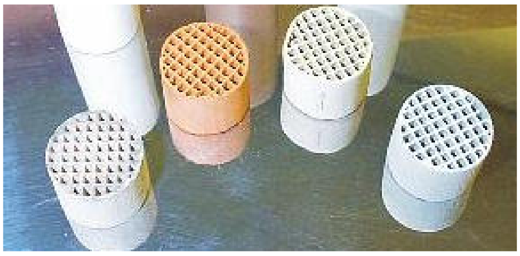

**Figure 1.** Monolith examples

From a process point of view, the monolith offers advantages like low pressure drop and no fine particle production. In addition, from a research point of view, the monolith channel geometry is well-known and hence can be perfectly described in COMSOL, which is not the case for random loading in packed beds.

## 2. Objective

The aim of this work is to build an ATR monolith reactor simulator using COMSOL. It will take multiphysics into account, mainly mass balances including a surface chemical reaction mechanism involving 42 chemical reactions, 7 gas species and 13 adsorbed species.

The monolith considered in this work has deposited over its walls a washcoat impregnated with catalyst sites. This chemically active region will be modeled considering it numerically as a surface (SM) or as a thin volume (VM). The objective is to use the best numerical way to simulate such a thin section of catalyst.

In addition, the thermodynamic equilibriums will be calculated in COMSOL to be compared with the numerical simulation as an alternative to the experimental data that are not yet available.

Finally, this simulator will be helpful to improve the performance of the main process, to choose the right geometry for the monolith channels and to derive knowledge about surface chemical reactions and mass/energy transfer between gas and solid.

The simulator benefits from previous modeling research developed at IFP.[2]

## 3. Monolith Model Description

### 3.1 Geometry

A monolithic reactor is modeled considering only one channel. To simplify calculations, this channel is assumed to be a cylindrical tube. Therefore, an axial symmetric geometry is employed.

The catalytic layer is modeled using the two approaches presented in Figure 2: one models catalyst as a surface (SM) while the other one a thin volume (VM).

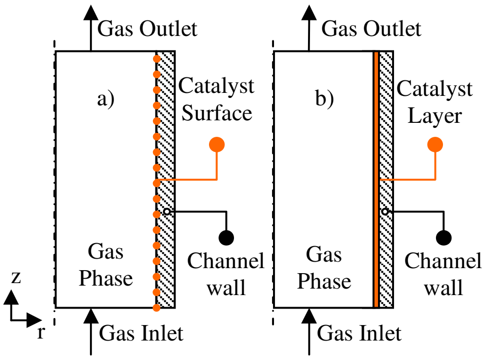

**Figure 2.** Two monolith channel geometries: catalytic layer as a surface (a) or as a thin volume (b).

The geometric parameters are presented in Table 1:

**Table 1.** Geometric parameters

| | |
|---|---|
| Channel radius | 0.567 mm |
| Washcoat thickness | 0.056 mm |
| Length | 200 mm |

### 3.2 Mass Transport

In the gas phase, the convection and diffusion of all the 7 gas species ($N_2$, $H_2$, $O_2$, $CO$, $CO_2$, $H_2O$ and $CH_4$) are considered, hence the *"Convection and Diffusion"* application of *"Chemical Engineering"* module is used (4). For the gas species, the diffusion coefficient is assumed to be constant and equal to $10^{-5} m^2/s$. Only catalytic reactions are considered, therefore any chemical reaction occurs between gas species.

In the solid phase, the model considers the chemical reactions and the diffusion for the 7 gas species. No convection exists in the solid phase. The Deutschmanns [3] mechanism is used with 42 surface chemical reactions, involving 13 surface adsorbed species and the 7 gas species. The 13 surface adsorbed species are: $H_2Os$, $OHs$, $Hs$, $Os$, $Cs$, $COs$, $CO_2s$, $CH_4s$, $CH_3s$, $CH_2s$, $CHs$, $HCOs$ and $Ni$. No porosity effects are considered in this work.

The mass balance equation is defined as:

$$\frac{\partial C_k}{\partial t} + \nabla.\left(-D\nabla C_k + C_k u\right) = R \qquad (4)$$

Where $C_k$ represents the concentration of the specie $k$, $R$ is the source term defined as:

$$R = \sum \nu_i r_i \qquad (5)$$

$$r_i = k_i \prod C_j^{\nu j} \qquad (6)$$

Where $\nu_i$ is the stoichiometric coefficient, $r_i$ is the transformation rate, $k_i$ is the kinetic constant and $C_j$ is the concentration of the specie $j$.

### Solid catalytic modeling

Depending on the way the geometry is modeled (SM or VM), two different COMSOL applications are used for the mass balance equation in the solid phase: "*Boundary Weak Form*" or "*Diffusion*".

For the catalytic surface modeling (SM), the "*Boundary Weak Form*" from the "*PDE Modes*" is used, where the mass balance equation for the solid phase in weak form is:

$$\text{weak} = \text{c\_test} * \text{R} \qquad (7)$$

$$\text{dweak} = \text{c\_test} * \text{c\_time} \qquad (8)$$

For the standard modeling of catalysts as a thin volume (VM), the "*Diffusion*" application form "*Chemical Engineering Module*" is employed. Here, the diffusion coefficient is 0 for adsorbed species.

The surface reaction mechanism is converted to a volume reaction mechanism conserving the total number of catalytic sites. Therefore, all the kinetic constants are divided by the catalyst thickness.

### 3.3 Boundary Conditions

The boundary conditions for the gas phase are shown in Figure 3**.** In the case of the surface modeling (SM) the source term for the surface is converted into flux boundary condition for the gas phase. In the other modeling case (VM) boundaries are obvious.

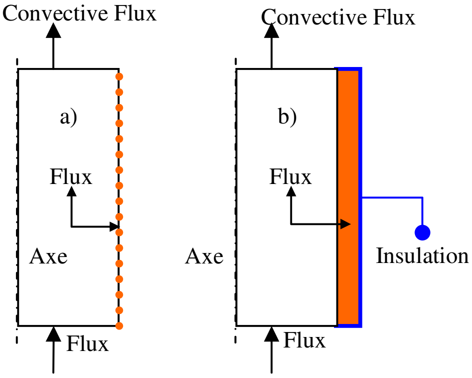

**Figure 3.** Boundary conditions for gas phase in the surface case (a) and continuities for the volume case (b).

### 3.4 Other Considerations

For the hydrodynamics, the model uses the well known solution for laminar Navier-Stokes equations i.e. the parabolic profile. Consequently, the velocity field is:

$$\begin{cases} u_r = 0 \\ u_z = 2v_{inj}\left[1-\left(\frac{r}{R}\right)^2\right] \end{cases} \tag{9}$$

Where, $v_{inj}$ is 0.8 m/s, $r$ is the radial coordinate and $R$ the internal channel radius.

The model is solved using the direct UMFPACK method in the time dependent mode, considering that all initial values are equal to 0.

## 4. Thermodynamic Equilibrium

The thermodynamic equilibriums are helpful to compare with numerical solutions when experimental data is not available because the thermodynamic imposes the chemical conversion limits.

The calculation obeys to:

1. the atomic mass balance (four atoms then, four atomic mass balances (10) - (13))
2. to the minimum of Gibbs energy (equilibrium condition (14) and (15))
3. the assumption that oxygen is totally converted

$$2F_{in}(N_2) = 2F_{out}(N_2) \tag{10}$$

$$2F_{in}(O_2) + F_{in}(H_2O) = 2F_{out}(CO_2) + F_{out}(CO) + F_{out}(H_2O) \tag{11}$$

$$2F_{in}(H_2O) + 4F_{in}(CH_4) = 2F_{out}(H_2O) + 4F_{out}(CH_4) + 2F_{out}(H_2) \tag{12}$$

$$F_{in}(CH_4) = F_{out}(CH_4) + F_{out}(CO_2) + F_{out}(CO) \tag{13}$$

$$K_{eq}(1) = \frac{P_{CO} P_{H_2}{}^3}{P_{CH_4} P_{H_2O}} \tag{14}$$

$$K_{eq}(3) = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \tag{15}$$

The equilibrium constants are temperature dependant (16).The parameters in equation (16) are presented in Table 2 for the reactions.

$$K_{eq} = \mathrm{e}^{\left(\frac{\mathrm{a}}{\mathrm{T}} + b + \mathrm{c.log(T)} + \mathrm{d.T} + \mathrm{e.T}^2 + \mathrm{f.T}^3\right)} \tag{16}$$

This calculation is set as "*Global Equations*" in COMSOL.

**Table 2.** Equilibrium coefficients

| Coefficient | Reaction (1) | Reaction (3) |
|---|---|---|
| a | -22843.958 | 4873.196 |
| b | -23.147 | 0.466 |
| c | 7.620 | -1.087 |
| d | -3.380E-3 | 3.260E-3 |
| e | -1.174E-7 | -9.408E-7 |
| f | 9.795E-11 | 1.244E-10 |

However, this equation set can have multiple solutions especially ones with negative concentrations. To avoid this problem and to get only one solution set, we switched the COMSOL unknowns from *C* (concentrations) to *log(C)*. Hence, when we get the solution, we are certain that $C = \exp(\log(C))$ is positive. This technique works very well and has the advantage to give rise to homogeneous unknown scaling.

## 5. Results

### 5.1 Surface (SM) and Volume Modeling (VM) comparison

To simplify, the simulation presented here just involves $O_2$. $O_2$ reacts along the surface and produces two adsorbed Os. The final simulation time is 1s, short enough to catch the front in the middle of the channel.

For these two cases (SM and VM), Figure 4 exhibits similar profiles of oxygen concentration in the gas phase. This proves that the two models are equivalent. However, a slight delay between oxygen front waves can be observed. It is due to the catalyst gas porosity that is not simulated in the SM case but acts as a sink in the volume case (VM). Because the porosity gas volume in the catalyst is very low, the discrepancy in the two kinds of simulation is light.

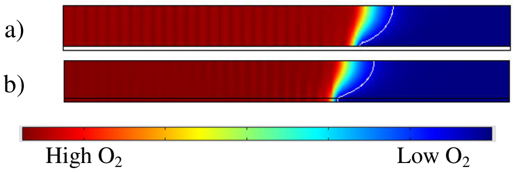

**Figure 4.** Oxygen concentration profile in the surface case (a), and in the volume case (b). (White line represents 10% of $O_2$ injection value)

From global simulation point of view, under the same conditions, the thin volume case (VM) takes much more time to calculate the solution than the surface one (SM). Further more, whenever using the whole chemical reaction set the simulator becomes numerically instable leading to very long simulation times. Consequently, the original surface modeling case (SM) will be used for the next calculations.

### 5.2 ATR Reactor Model Results

These results were simulated in a dynamic mode until achieves the stationary state (about 100s). The following conditions were taken into account:

**Table 3.** Injection Conditions

| Gas Total Flow | 2.692E-07 $m^3/s$ |
|---|---|
| Molar Fraction | |
| $O_2$ | 0.0588 |
| $CH_4$ | 0.1176 |
| $H_2O$ | 0.5882 |
| $N_2$ | 0.2353 |

The mesh used is quadrangular with 100 cells in *z* direction and 5 cells in *r* direction with an element ratio of 5 from the wall towards the *z* axis. The concentration profiles and the outlet concentrations are shown in Figure 5.

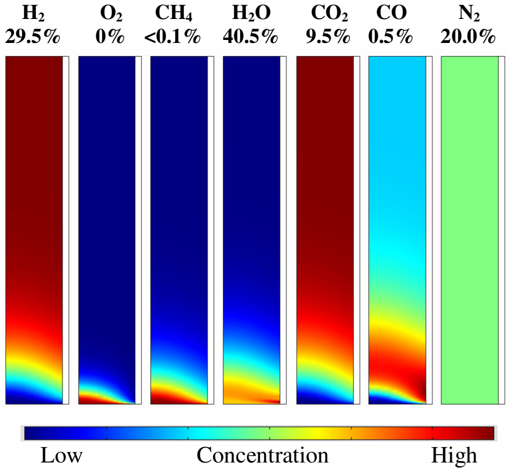

**Figure 5.** Concentration profiles in the monolith channel.

Almost all of the conversion can be observed in the very beginning of the reactor.

Looking at the $O_2$ profile, we can say that oxygen conversion (2) is fast and total. This fact, plus the increase of $H_2O$ and CO prove that the combustion is the fastest reaction. This was expected because the combustion is more spontaneous than steam reforming (1) or water gas shift (3).

The methane conversion is completed latter in the channel by steam reforming reaction (Eq 1), producing $H_2$. Finally, the water gas shift reaction occurs through the entire reactor, producing more $H_2$ and consuming the unwanted CO.

The Figure 6 presents the surface molar fraction for the three main species, the other species are not shown because they are less than 1%.

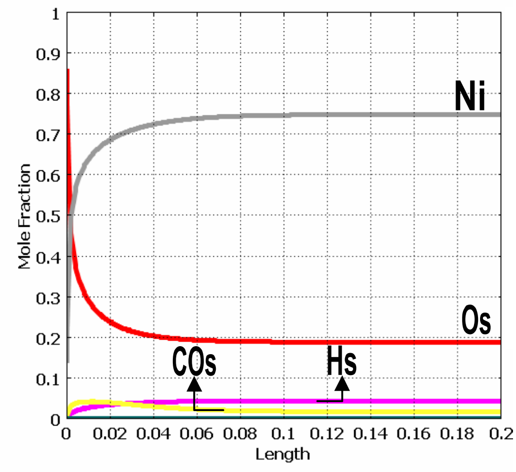

**Figure 6.** Mole fraction of adsorbed species in the solid phase

From numerical result we can observe that more than 50% of catalytic sites are free. In terms of coverage ratio, the most significant species are the *Os,* the *Hs* and the *COs*. Consequently, it can be said that all reactions where these species are involved are very significant.

### 5.3 Thermodynamic equilibrium comparison

The thermodynamic equilibriums are calculated to be compared with simulation results. Thermodynamic equilibriums can be calculated in COMSOL, as explained in paragraph 4. We have verified these results with commercial software to ensure that the equilibriums are well calculated.

The reactor reaches the equilibrium state at the reactor first half, which means that only 10cm are necessary to obtain the maximum conversion.

The results from the simulation agree with the thermodynamic equilibrium calculations.

## 6. Conclusions

From the modelling point of view, it can be concluded that the surface modelling (SM) that uses weak form equations, gives good results.

The monolithic ATR reactor in isothermal condition seems to be correctly described using a chemical reaction mechanism of 42 reactions and involving 20 different species. More over the equation set leads to conversions that are close to the thermodynamic equilibriums.

Finally, the thermodynamic calculation reveals to be a useful tool since it can be quickly compared with the simulation results, while waiting for experimental data. However, some numerical tricks need to be taken to easily implement this kind of calculation in COMSOL.

## 7. Acknowledgments

The authors thank ANRT for the financial support. Nuno Pacheco is grateful to IFP and ENSIC for providing a doctoral grant.

## 8. Reference

1. IFP - Hydrogen Production and Transportation, http://www.ifp.com/axes-de-recherche/carburants-diversifies/production-et-transport-de-l-hydrogene, (01/09/08)

2. Pavone, CO2 capture by means of chemical looping combustion, Comsol Multiphysics Conference, 293-301, (2005)

3. Deutschmann, O., Tischer, S., Schaedel, B., and Maier, L., Surface reactions: Reforming and oxidation of methane on nickel, http://www.detchem.com/mechanisms/nickel.html, (01/03/06)