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COMSOL Multiphysics® Model of an Industrial Top-Fired Steam Methane Reforming Reactor

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Abstract
A first-principle fully-coupled multi-scale model is developed for a typical top-fired, packed-bed multi-tubular steam methane reforming (SMR) reactor. The model makes it possible to account for the effects of the catalyst features, on the one hand, and the operating conditions of the furnace, on the other. The model results demonstrate very good agreement with reference literature experimental and modeling data, also regarding the temperature profiles obtained in the furnace, validating the approach proposed in this study. The model provides a detailed study of the phenomena occurring inside the SMR reactor, paving the way for further detailed investigations, such as for example coke deposition.
Keywords: Multi-scale modeling, Steam methane reforming (SMR).

Introduction
Nowadays, the hydrogen economy proposed by Lawaceck, Appleby and Bockris in the early 1970s [1] is still far from being realized. Nevertheless, hydrogen is already widely used in the chemical industry, mainly in refineries and in the production of ammonia and methanol. In this context, hydrogen is typically produced through steam reforming (SR) of hydrocarbons, especially methane. The chemical reactors implementing this process are thus an established technology. Nevertheless, they still suffer of some unresolved issues, for example the deposition of the carbon contained in the fuel, which can cover the active sites of the catalyst, inhibiting its activity and hindering gas diffusion through the catalytic bed. In order to gain a better insight in the functioning of these reactors, several models have been developed. A review can be found in a previous paper [2]. Although several studies have been developed since the early 1970s, all the models reported in the literature contain many adjustable parameters, and for none of them has predictive capability been demonstrated. In this work, a multi-physics model is presented, containing only one adjustable parameter. To the best of the authors' knowledge, this is the first multi-physics model realized for SMR chemical reactors.

SMR Reactor
Figure 1 shows a scheme of a typical SMR reactor. The burners are located in the ceiling of the furnace, and the combusting gas then flows towards the bottom. The packed-bed tubes contain two adjacent catalytic sections, filled with NiO supported on calcium aluminate commercial catalysts. As represented in Figure 1 the catalysts have a cylindrical-quadrilobe shape. The tubes are fed from the top, and flow direction is from top to bottom, in co-current with the combusting gas.

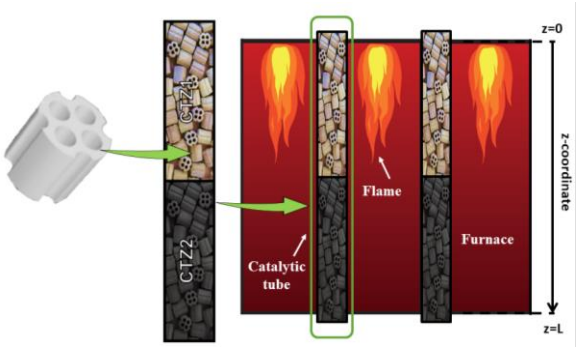

Figure 1. Scheme of a typical SMR reactor. Left: Catalytic pellet. Middle: Detail of a catalytic tube. Right: Scheme of the furnace with the catalytic tubes.

Reaction Scheme
The general formulation of the endothermic SR reactions of hydrocarbons is:

$$C_nH_m + nH_2O \rightleftarrows nCO + \left(n + \frac{m}{2}\right) H_2$$

In the case of SMR, this becomes:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

An additional reaction occur together with SMR, i.e. the slightly exothermal water gas shift (WGS):

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Theory
A multi-scale model is presented for a top-fired industrial SMR reactor, featuring a fully coupled simulation of the catalyst pellets inside the reactor tubes, the tubes themselves, and the furnace accommodating the tubes. All tubes are supposed to be identical and operated in identical conditions, and therefore only one tube is simulated. At each level, the model is based on a rigorous first-principle approach, including the appropriate microscopic balance equations coupled to transport equations and constitutive laws. In particular, for the furnace, a novel methodology is proposed, based on rigorous mass and energy balances

coupled to simplified linear kinetics rate laws for the combustion reactions that develop in the flame. Further details can be found in [2].

Governing Equations

Figure 2 shows the scheme of the COMSOL model, displaying the modules and physics interfaces used. The basic COMSOL modules are used to define the geometry (Geometry module), the basic model parameters (Definitions module), and the chemical reactions (Chemistry module).

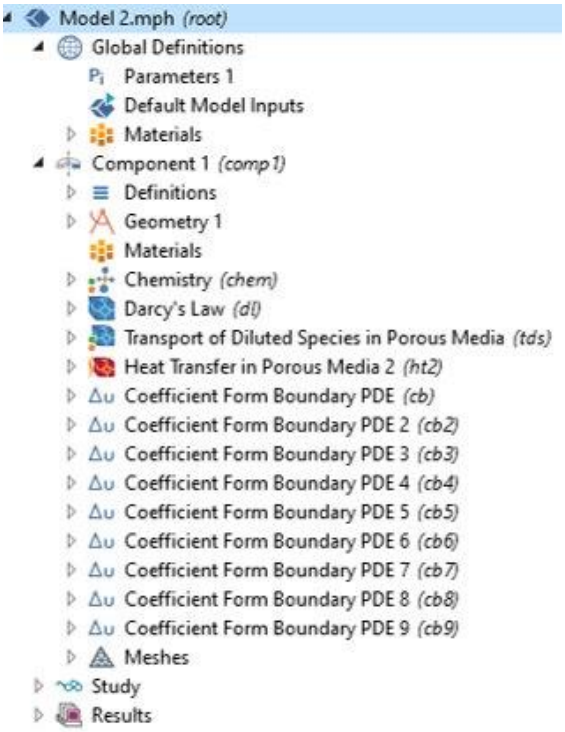

Figure 2. Scheme of the SMR reactor model implemented in COMSOL.

The 'Reacting Pellet' module is used to evaluate mass transport associated with multicomponent diffusion inside the catalyst pellet. This is coupled to the 'Transport of Diluted Species in Porous Media' module, which is used to implement mass and energy balances in the catalytic bed. The 'Darcy's Law' module calculates pressure distribution inside the catalytic bed. Finally, the 'Coefficient Form Bounday PDE' is used to implement mass and energy balances for the furnace. Further details of the model equations can be found in [2].

Simulation Results

In the SMR reactor, many thermal effects take place, mainly the exothermal combustion in the furnace, and the endothermal SMR process inside the tube. This triggers heat transfer from the furnace to the tube. The heat passes through the thickness of the tube wall by conduction and is subsequently transferred through the catalytic bed towards the center of the tube. Consequently, the process-gas temperature is constantly higher close to the wall than at the tube axis, as shown in Figure 3. Therefore, the temperature profiles display a clear deviation from the ideal plug-flow behavior, with significant radial temperature gradients, up to 26.4K/cm. This maximum radial temperature gradient is located in the upper part of the furnace, in correspondence with the peak of furnace temperature.

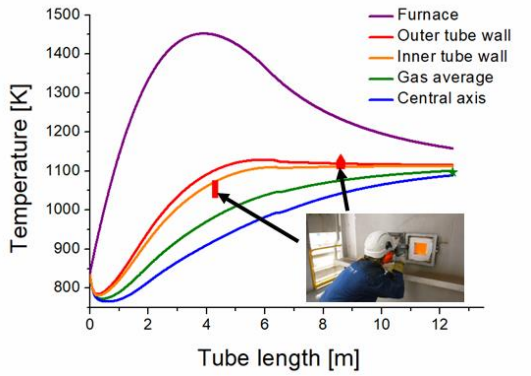

Figure 3. Temperature distribution along the furnace and the catalytic tube. Lines: simulation. Symbols: experimental data.

The temperature profile of the process-gas along the axial coordinate is reported in Figure 3. At the entrance of the reactor, this temperature shows an abrupt decrease of nearly 70.4K, due to the endothermal effect of the fast SR reactions, in particular of the higher hydrocarbons. Thereafter, the higher hydrocarbons are completely consumed within a short distance, and therefore the endothermal effect becomes smaller. The heat released by the furnace combustion exceeds that required by the SMR reaction and, as a result, both the furnace and the process-gas temperatures increase along the axial coordinate, as illustrated in Figure 3. Then, after the middle of the reactor, the SMR reaction slows down significantly, and the temperature profile is almost flat, demonstrating that thermal equilibrium is reached, where the heat required by the SMR reaction is practically equivalent to that transferred from the furnace.

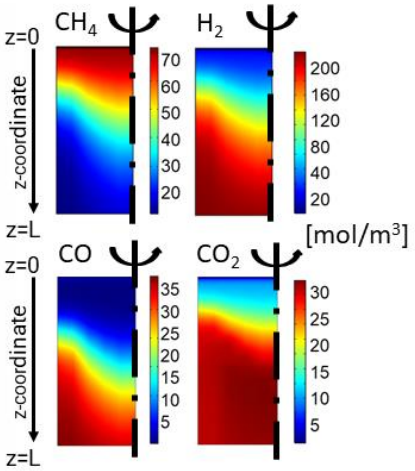

Figure 4. Concentration of chemical species along the tube.

Figure 3 also shows some experimental data collected from an industrial reactor operating under the same conditions used for the simulations. The agreement between simulated and experimental results is very good. A more extensive experimental validation is demonstrated in [2].
Figure 4 shows the concentrations of chemical species along the tube. At the inner tube wall, where the temperature is higher, reaction rates are faster, and higher H_2 production and CH_4 consumption are predicted by the model. It is visible that moving down along the axial coordinate (z-coordinate) of the tube, the composition tends to become more uniform, corresponding to the attainment of thermodynamic equilibrium.

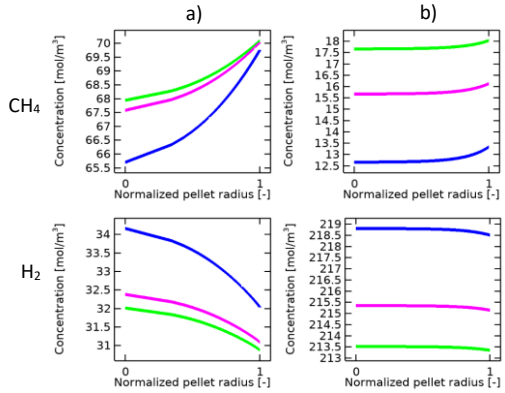

Figure 5. Simulated concentration profiles of CH_4 and H_2 in catalyst pellets at different positions along the tube: a) z=0.6 m (minimum temperature); b) z=12.43 m (outlet). Radial position: tube axis (green line), middle of radius (magenta line), and inner tube wall (blue line).

Regarding the results at the microscale level of the catalyst, Figure 5 shows the composition profiles of CH_4 and H_2 within the catalytic pellets, at different positions in the catalytic bed. As expected, the graphs shows that H_2 increases between the surface and the center of the catalyst pellet. It is worth noting that concentration gradient of H_2 between the surface and the center of the catalytic pellet at the same axial position are more significant on the inner tube wall and decrease moving towards the axis of the tube. This is due to the temperature profiles in the tube.
It is visible that moving down along the axial coordinate of the tube, the composition profiles in the interior of the catalyst pellets tend to flatten, corresponding to the attainment of thermodynamic equilibrium.

Conclusions

A reliable prediction of temperature distribution inside the SMR reactor tube is fundamental to obtain a correct evaluation of the physical-chemical variables in the reactor and to identify possible critical conditions. This emphasizes the strength of the multi-scale SMR reactor model, providing a fully coupled simulation of the catalyst pellets, the SMR tube, and the furnace. Despite its complexity, the model features only one adjustable parameter i.e., the length of the flame in the furnace (L_f). The predictive capability of the model is demonstrated by comparing the modeling results with experimental data obtained from an industrial-scale SMR reactor, with good results. The model provides a detailed study of the phenomena occurring inside the steam methane reforming reactor, paving the way for further detailed investigations, such as for example coke deposition.

References

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