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A numerical optimization study on the catalytic dry reforming of methane in a spatially resolved fixed-bed reactor

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ABSTRACT

Fixed-bed reactors with a small tube-to-particle diameter ratio are typically used for highly exothermic or endothermic reactions. Flow, temperature and species distribution as well as the reaction rates are affected by the effect of the confining wall. In this study we have investigated numerically a spatially resolved fixed-bed including a detailed reaction mechanism for dry reforming of methane (DRM). Operating conditions in terms of feed composition, feed and heating temperature and feed mass flow could be identified, where the deactivation of the catalyst due to coking is prevented but still a reasonable conversion of methane and carbon dioxide as well as a high hydrogen selectivity can be achieved. Finally the need of a spatially resolved simulation is shown. While a pseudo-homogeneous 2D simulation needs significantly less computation time, it over predicts the conversion by approx. 20% due to an overestimated heat transfer.

1. Introduction

Fixed-bed reactors are widely used in the chemical and process industry among others for heterogeneous catalysis. The packing can be either structured or randomly distributed. Typical particles are spheres, cylinders, Raschig-rings or even more complex shapes. The choice of tube diameter and particle dimensions has several constraints. On the one side, a reasonable pressure drop and a high volume flow constrain the particle diameter. On the other hand, in the case of highly exothermic or endothermic reactions, heat has to be transferred into (or out of) the reactor (Dixon, 1997). This leads to small tube-to-particle diameter ratio ($D/d < 10$). Especially for these reactor configurations the conventional description with a porous media based plug-flow model is at least questionable. The inhomogenities in the bed structure lead to significant wall effects, local backflows and, hence, to large axial and radial gradients of velocity, temperature and species distribution. This was shown experimentally by investigating the interstitial flow with particle image velocimetry (PIV) (Hassan and Dominguez-Ontiveros, 2008) and is confirmed by detailed computational fluid dynamics (CFD) simulations. Detailed CFD simulation means that each particle is resolved geometrically, resulting in an entire representation of the bed structure. Consequently, the velocity field between the particles can then be governed as well as the temperature and species distribution (Dixon and Nijemeisland, 2001; Eppinger et al., 2011; Freund et al., 2005; Shams et al., 2014). Obviously, these detailed simulations are more computational demanding than lumped models. But on the other hand there is no need for lumped parameters like dispersion coefficient or effective heat transfer properties to capture non-ideal behavior.

In chemical reactors there is also an interplay between the kinetics and transport phenomena. A proper determination of the temperature field is a requirement for an adequate prediction of the reaction rates and consequently also for the species profiles. Due to the Arrhenius formulation the kinetics is more influenced by the temperature than vice versa (Wehinger et al., 2014; Nogare et al., 2011).

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Several researchers have coupled lumped reaction mechanisms, i.e., Hougen–Watson–Langmuir–Hinshelwood type rate equations, with spatially resolved fixed-bed simulations (Dixon, 2012; Kuroki et al., 2009). However, such reaction mechanisms do not distinguish between adsorption, surface reaction and desorption. Thus, spatial and transient aspects are not taken into account. In some cases they even lead to erroneous predictions, as was shown by Korup et al. (2011) for the oxidative coupling of methane. A critical review of reaction mechanism modeling is given in Salciccioli et al. (2011). Consequently, first-principles-based multiscale modeling, as described by Dudukovic (2009), of heterogeneous catalytic fixed beds has to combine a detailed description of the flow field, i.e., spatially resolved bed structure, with a detailed description of the reaction mechanism, i.e., micro kinetics. In recent years, this rigorous modeling approach was applied among others for multi-channel catalytic monoliths (Hettel et al., 2013; Maffei et al., 2014), catalytic gauze (Quiceno et al., 2006) and catalytic foams (Nogare et al., 2008; Korup et al., 2013).

The global climate changes without any doubt and likewise is its anthropogenic contribution. Continued emissions of greenhouse gases will lead to further warming and changes in all aspects of the climate system. Constraining climate change will require serious and sustained reductions of greenhouse gas emissions (Climate Change, 2013). Carbon dioxide plays an outstanding role among greenhouse gases. Besides CO_2 sequestration and storage, several alternative approaches are available like algae cultivation with CO_2 or creating biochar (Hasse, 2013). On the contrary, catalysis and reaction engineering are asked to develop innovative technologies for CO_2 utilization (e.g., its conversion to alcohols or power-to-gas) (Vlachos and Caratzoulas, 2010). Processes which combine methane and carbon dioxide, both are greenhouse gases, are in the spotlight. Dry reforming of methane (DRM) is such a process, where CH_4 and CO_2 react to syngas:

$$CH_4 + CO_2 \Leftrightarrow 2H_2 + 2CO \quad \Delta H \approx 260\,\text{kJ/mol} \tag{1}$$

This endothermic reaction takes place at temperatures of 700–1000 °C with an adequate catalyst, e.g., noble metals or nickel (Rostrup-Nielsen and Hansen, 1993; Bradford and Vannice, 1999). However, coke formation at the catalyst surface is still the major drawback. The highly endothermic character of DRM demands a high energy input from outside the reactor resulting in a small tube-to-particle diameter ratio. This leads to inhomogenities of the bed structure and consequently to large gradients in the radial and axial coordinate. In commercially applied steam reforming of methane the heat input is realized by open-flame burners (Stitt, 2005). Typically, the tube-to-particle-diameter-ratio is small ($D/d < 7$). In previous works the rigorous modeling of a fixed-bed reactor for dry reforming of methane with spherical particles was presented. Besides meshing recommendations, special attention was paid toward boundary layers and their resolution for laminar and turbulent flows (Wehinger et al., 2015a). The fixed-bed modeling was then extended to non-spherical particles and a comparison of different particle shapes, i.e., spheres, cylinders and one-hole cylinders with dimensions typical for industrial applications was done. It could be shown that velocity, species and temperature distribution are influenced by the particle shape and subsequently also conversion and yield although the typical design parameters like catalytic surface area and hydraulic residence time are kept constant for all three particle shapes (Wehinger et al., 2015b). For both studies a detailed reaction mechanism for DRM by McGuire et al. (2011) was implemented.

Engineering problems are often optimization problems where a design should be as good as possible with respect to one or more goals although it is often not mentioned explicitly as an optimization problem. Optimization means to find a minimum or maximum in a solution space depending on one or more independent variables. But due to limitations in time, cost or manufacturing capabilities optimization is also used in the context of improving something in one or more aspects compared to a previous or benchmark design. There are numerous optimization algorithm available which can be roughly divided in local and global search algorithms. Local methods always converge more or less fast to a maximum or minimum value. Well-known methods are the gradient-based gradient descent and conjugate gradient method or the gradient-free Nelder–Mead method. Their major drawback is that it is not guaranteed that they find a global maximum/minimum. On the other side global methods are searching with a certain randomness for an optimal solution: typical representatives are evolutionary, genetic or particle swarm algorithms.

In this study the operating parameters heating temperature, feed mass flow and composition are investigated and optimized numerically using a commercial CFD software package by CD-adapco. The aim of this optimization is to minimize coke formation or carbon deposition on the catalytic surface while the conversion of the green house gases methane and carbon dioxide as well as the hydrogen selectivity is maximized. The optimization is done based on a 3 dimensional spatially resolved fixed bed reactor. This is finally justified by a comparison with the results of a less time consuming 2D simulation, which shows some significant differences in the distribution of species and temperature as well as in the total conversion and yield.

2. Modeling

All simulations were conducted with the finite volume code STAR-CCM+ version 10 by CD-adapco. DARS, a stiff ODE solver which is completely integrated into STAR-CCM+, was used to solve the surface chemistry. The optimization itself was carried out using Optimate+, which accesses HEEDS in the background. Since this investigation is based on previously published work (Eppinger et al., 2011; Wehinger et al., 2014, 2015a,b) only the modeling which has not been already described elsewhere is discussed in detail. Everything else is described shortly and the relevant references are given.

The reactor consists of a tube filled with 120 spherical particles. The tube-to-diameter ratio is $D/d = 4.5$ to ensure that sufficient heat can be transferred into the reactor. The length of the fixed bed is with a chosen value of $h \approx 8d$ pretty short to keep the computational time low. It is known that the upstream velocity profile is influenced by the bed and that the velocity profile is developing in the entrance region of the bed. Typically the flow field is fully developed after a distance of 3–4 particle diameter (Zobel et al., 2012). This indicates that entrance effects can have an influence on the results but this beyond the scope of this investigation.

The fixed-bed reactor is modeled three-dimensionally with geometrically resolved catalytic particles. The fixed-bed is generated with the discrete element method (DEM): 120 spherical particles are injected randomly into the reactor tube and settle due to gravity. When all particles are in a stable position a CAD description is created based on the position of each particle. This CAD model is then meshed with polyhedral cells and local refinement at the particle surface. Additionally the mesh is extruded at the inlet and outlet to reduce the influence of the boundary condition on the flow through the fixed-bed. At the particle–particle and the particle–wall contact points, the so-called caps or local flattening method is used. For all simulations the same polyhedral mesh was used with a resolution of the fluid domain of 1.9 M cells and the solid particles with 1.1 M cells. The solid cells are needed to model the heat conduction in the particle, which cannot be neglected. Details of the mesh settings are given elsewhere (Wehinger et al., 2015b) while Fig. 1 shows some details of the mesh.

For the gas flow ideal gas behavior was assumed. At the inlet a constant velocity and temperature varied according to Table 2 was specified. The same temperature as the inlet temperature was applied to the confining tube wall. At the outlet for all simulations a constant pressure of $p = 1$ bar was used. An overview of the reactor is shown in Fig. 2.

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