

# Coupling Detailed Heterogeneous and Homogeneous Kinetics with Mass and Heat Transfer in Catalytic Reforming of Conventional Fuels

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## Introduction

A considerable long term interest in hydrogen as a fuel in relation to the scarcity of fossil fuels and the associated pollution problems excites the development of systems using catalytic partial oxidation and steam reforming for the production of hydrogen-rich synthesis gas from conventional fuels. Two examples of such systems being currently of great technological interest are the Solid-Oxide Fuel Cell (SOFC) [1] when operated with non-pure hydrogen fuels, e.g. partially reformed logistic fuels, and short-contact time reactors for reforming gasoline and diesel fuels [2], e.g., as first stage of an on-board auxiliary power unit (APU). The non-linear coupling of complex homogeneous and heterogeneous chemical reaction kinetics with heat and mass transfer in such systems matters for reactor behavior, often even superimposed by transient modifications of the active catalytic phase, e.g. by oxidation and coking

In this work, we will present a modeling and simulation study on a catalytic reformer for the production of hydrogen-rich synthesis gas from the gasoline surrogate iso-octane. This example exhibits all features mentioned above: complex homogeneous and heterogeneous reaction schemes, mass and heat transfer effects, catalyst deactivation. Present work is related to the coupling of models of these phenomena, and their computational implementation to explain the impact of residence time on fuel conversion and hydrogen production and to optimize the reactor performance.

## Experimental and Modeling Methods

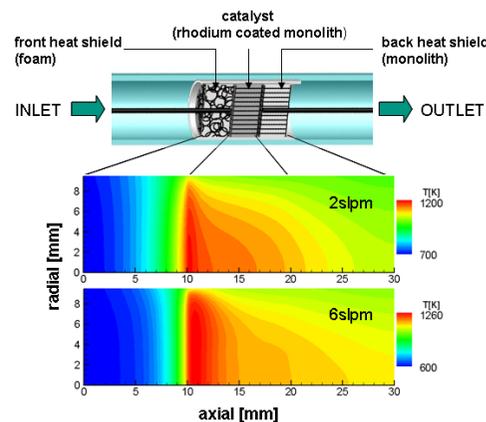
The model couples elementary-step based reaction mechanisms with a two-dimensional parabolic description of the flow field in a representative number of monolith channels and heat transport in the entire solid structure of the reactor including catalyst, heat shields, insulation, and reactor wall (Fig. 1). This approach is realized in the computer code DETCHEM<sup>MONOLITH</sup>, which uses the code DETCHEM<sup>CHANNEL</sup> for the simulation of the individual channels [3].

The concept is applied to analyze conversion, selectivity, and temperature profiles in partial oxidation of iso-octane, a gasoline surrogate, over a rhodium/alumina monolithic catalyst. Although more complex fuels have already been studied experimentally [4], data from our experimental study of a single-component reference fuel iso-octane (2,2,4-trimethylpentane) [5] are chosen as reference because detailed reaction mechanisms of CPOX of iso-octane over Rh has recently been developed and coupled with homogeneous reaction schemes [4, 6]. Both homogeneous and heterogeneous mechanisms are applied in the current study without further modifications.

## Results and Discussion

The numerical simulation predicts the two-dimensional temperature profile of the three monoliths of the reactor as function of axial and radial position as well as species profiles and product distribution in the single channel of monoliths for the different flow rates (2 – 6 slpm) studied at 0.8 and 1.0 C/O ratios.

It was found that the major objective of the reactor, i.e. production of high hydrogen yields at minimal formation of coke-precursors, can be achieved at C/O ratios close to 1.0 and sufficiently but not extremely high flow rates. The counter-intuitive flow rate effect on hydrogen yield is explained by the ratio of chemical heat release to physical heat loss. Coking propensity is related to the C/O ratio, the flow rate, and the occurrence of homogeneous fuel conversion.



**Figure 1.** Sketch of the catalyst section of experimental setup with two heat shields simulated (top) and numerically predicted steady-state monolith temperature at C/O = 1.0 and at flow rates of 2 slpm and 6 slpm (bottom). The symmetry axis of the monolith is at radial dimension of zero.

## References

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The implementation of detailed chemical kinetics in a two-dimensional parabolic flow model for individual monolith channels and the coupling with heat balances of the catalytic monolith as well as heat shields, insulation, and reactor wall provides a simulation tool that is able to analyze the behavior of structured CPOX reactors in great detail. The simulation can provide guidance to reactor design and optimization of the operating conditions such as flow rate and fuel/oxygen ratio.