

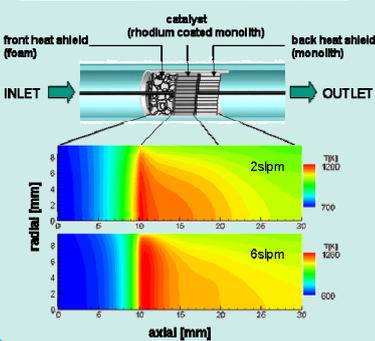
# Interaction of heterogeneous and homogeneous kinetics with mass and heat transfer in catalytic reforming of logistic fuels

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## Introduction

Today, in the discussion of alternative fuels and green-house gases, devices are discussed, which use 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.

## Modeling approach



### CPOX of gasoline on rhodium (*i*-octane as a reference fuel)

- detailed gas phase reaction mechanism consists of 690 reactions among 130 species
- detailed surface reaction mechanism for C1-C3 surface chemistry: 111 reactions, 31 surface species.

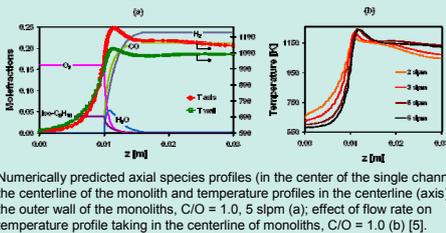
### Software DETCHEM<sup>MONOLITH</sup> [3]:

- 2D transient simulation of the thermal behaviour of the whole monolith (including catalyst and heat shields)
- provides inlet and boundary conditions for single channel simulations

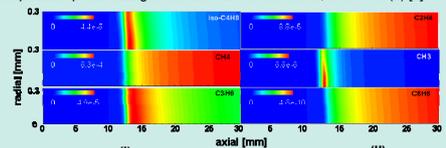
### Software DETCHEM<sup>CHANNEL</sup> [3]:

- 2D parabolic description of the laminar flow in the single channel of monolith catalyst
- coupled with the detailed surface chemistry models and transport phenomena

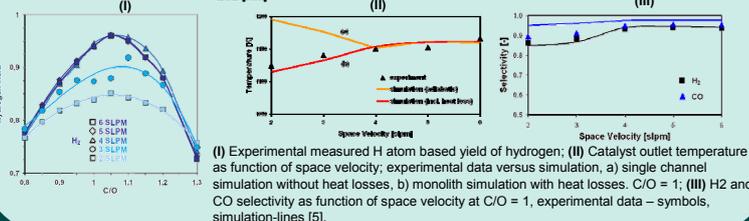
## Results



Numerically predicted axial species profiles (in the center of the single channel) in the centerline of the monolith and temperature profiles in the centerline (axis) and at the outer wall of the monoliths, C/O = 1.0, 5 slpm (a); effect of flow rate on temperature profile taking in the centerline of monoliths, C/O = 1.0 (b) [5].



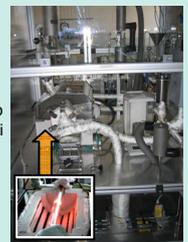
2D profiles of gas-phase temperature and mole fraction of species in the catalytic channel at C/O = 1.0 and 5 slpm. The symmetry axis of the channel and the gas-wall interface are at radial position of 0 and 0.3 mm, respectively.



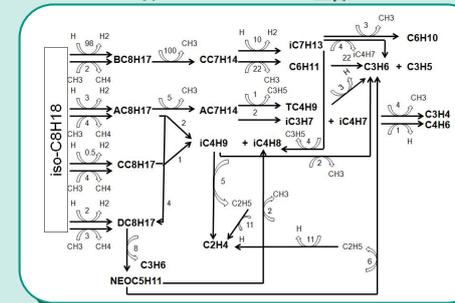
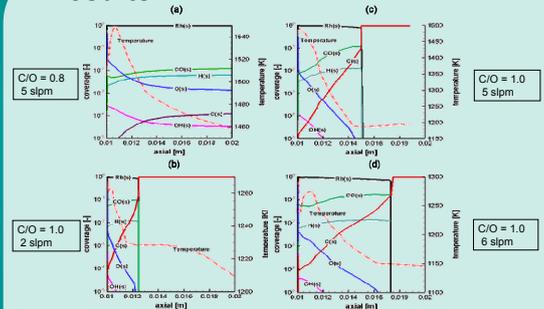
(I) Experimental measured H atom based yield of hydrogen; (II) Catalyst outlet temperature as function of space velocity; experimental data versus simulation, a) single channel simulation without heat losses, b) monolith simulation with heat losses. C/O = 1; (III) H<sub>2</sub> and CO selectivity as function of space velocity at C/O = 1, experimental data – symbols, simulation-lines [5].

## Experiments

- iso-octane/air mixture, C/O = 0.8 – 1.3, 2 – 6 SLPM
- 900 cpsi Rh coated (1.41 mg/cm<sup>3</sup>) honeycomb monolith catalyst; upstream heat shield: 85 ppi uncoated foam (γ-Al<sub>2</sub>O<sub>3</sub>); downstream heat shield: 600 cpsi uncoated honeycomb
- time-resolved monitoring of product species, FT-IR, MS, paramagnetic GC [4]



## Results



Reaction rate flow analysis for pyrolysis of iso-octane 1010 K, residence time of 42 ms. The time-integrated values given are scaled in a way that the maximum molar production rate of an individual reaction occurring of all reactions is set to be 100. Note that only major paths are shown [5].

[1] Hecht, E.S., Gupta, G.K., Zhu, H.Y., Dean, A.M., Kee, R.J., Maier, L., Deutschmann, O. *Appl. Catal. A. General* 295, 40 (2005).  
[2] Thormann, J., Maier, L., Pfeifer, P., Kunz, U., Deutschmann, O., Schubert, K. *Int. J. Hydrogen Energy* 34, 5108 (2009).  
[3] Deutschmann, O., Tischer, S. et al. DETCHEM version 2.3 (2010) [www.DETCHEM.com](http://www.DETCHEM.com)  
[4] Hartmann, M., Maier, L., Deutschmann, O. *Appl. Catal. A: General* doi:10.1016/j.apcata.2010.08.051. (2010).  
[5] Maier, L., Hartmann, M., Tischer, S., Deutschmann, O., Combustion and Flame, accepted (08.11.2010).