Influence of gas-phase reactions on catalytic reforming of isooctane

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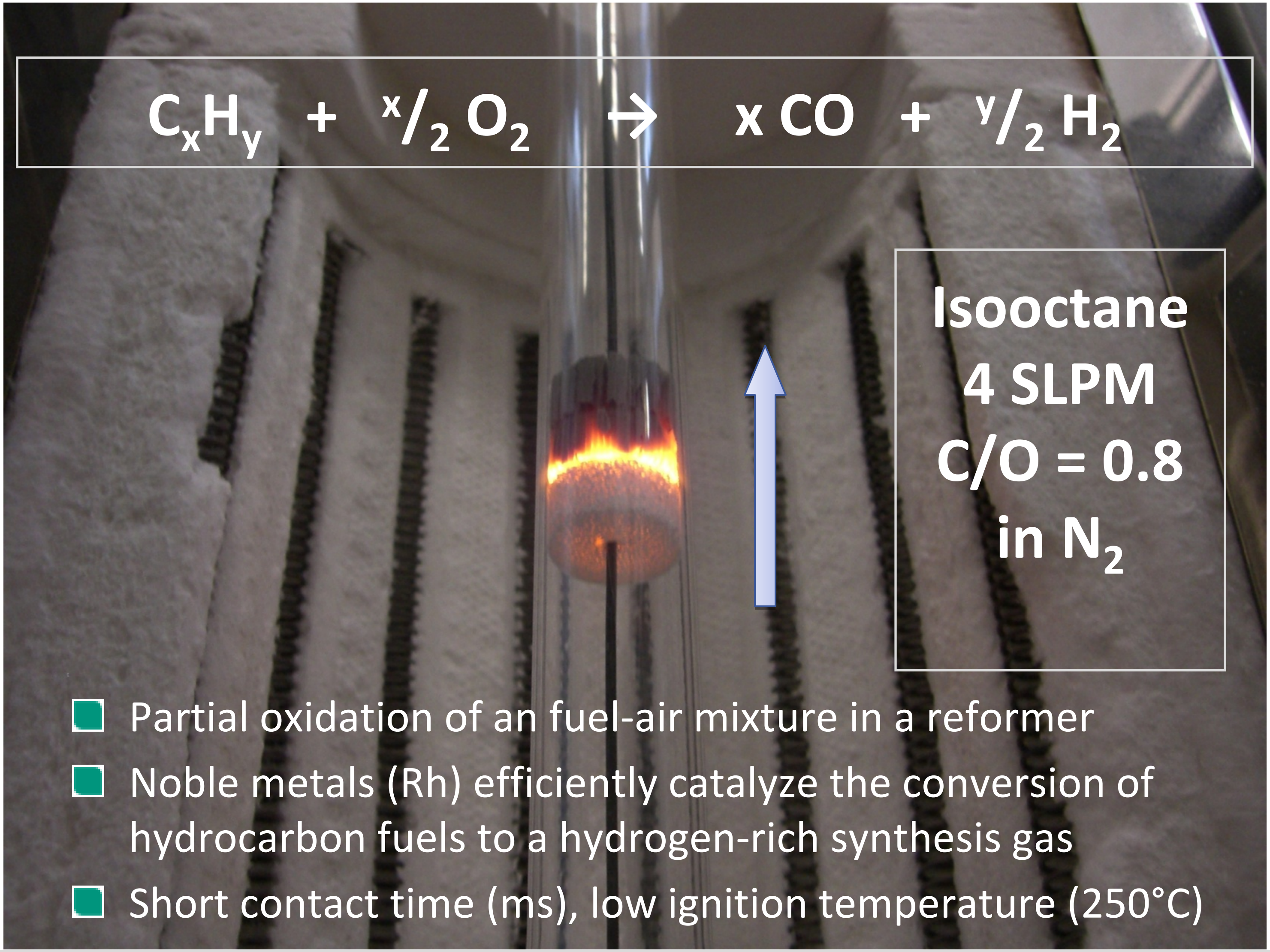
Institute of chemical technology and polymer chemistry

Introduction

CPOX of higher hydrocarbons



$$C_xH_y + {}^{x}/_{2}\, O_2 \rightarrow x\, CO + {}^{y}/_{2}\, H_2$$

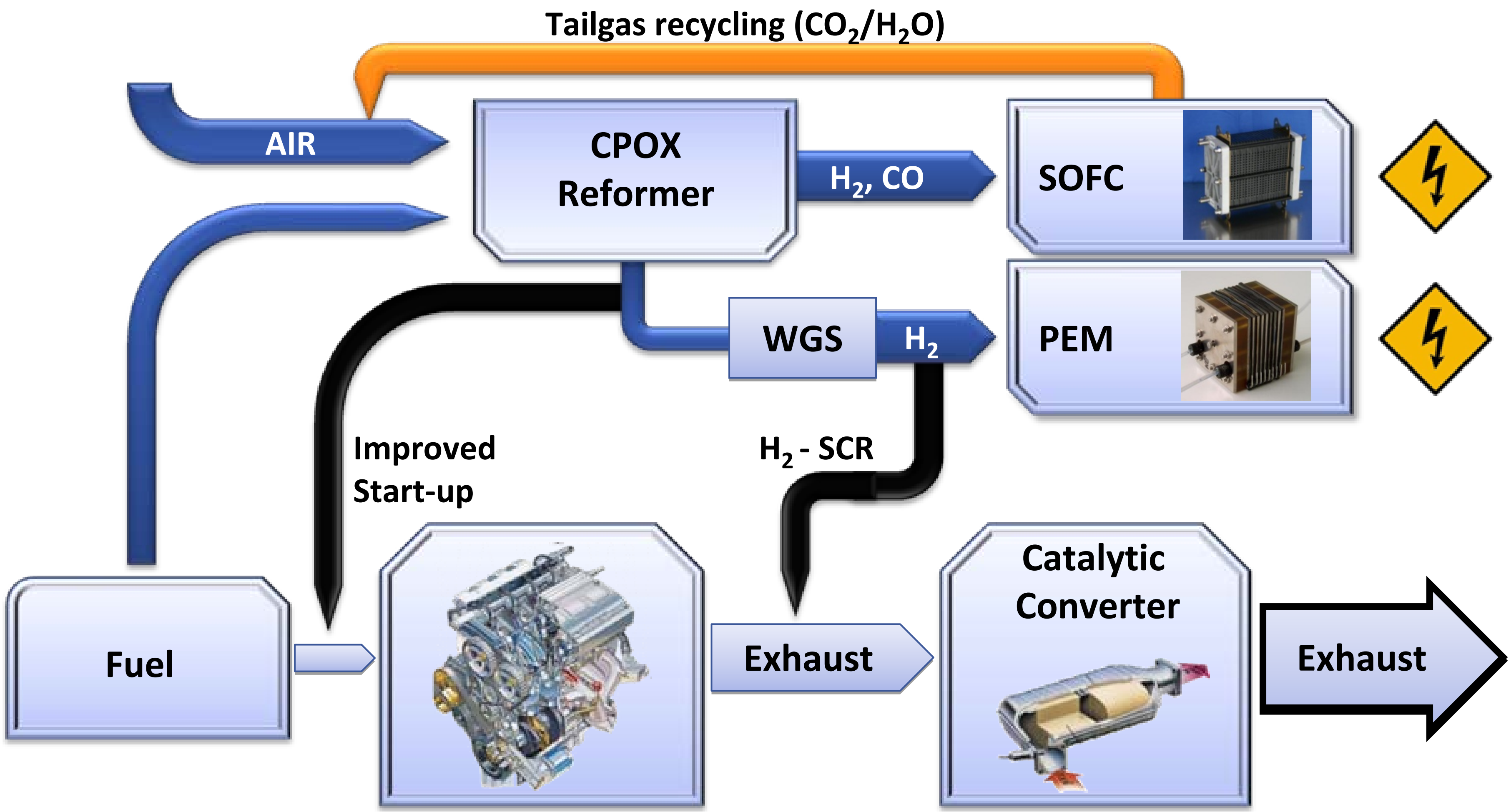
Isooctane
4 SLPM
C/O = 0.8
in N_2

- Partial oxidation of an fuel-air mixture in a reformer
- Noble metals (Rh) efficiently catalyze the conversion of hydrocarbon fuels to a hydrogen-rich synthesis gas
- Short contact time (ms), low ignition temperature (250°C)

Motivation

On-board fuel processing as future technology

- Compact autothermal reformers for onboard electricity supply (APU)

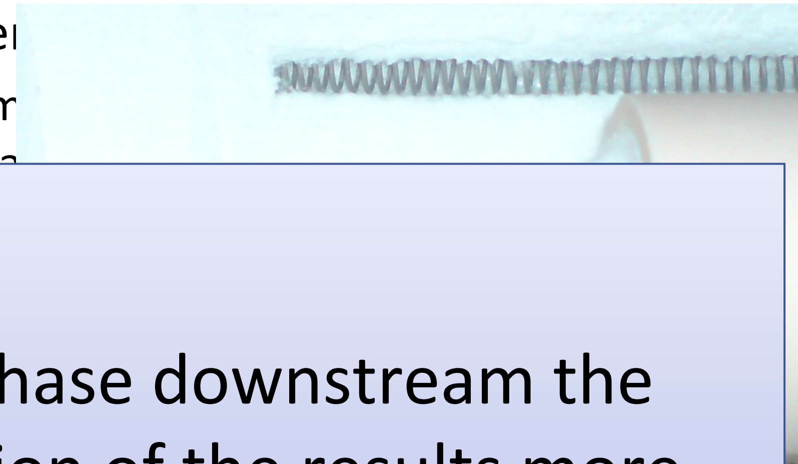


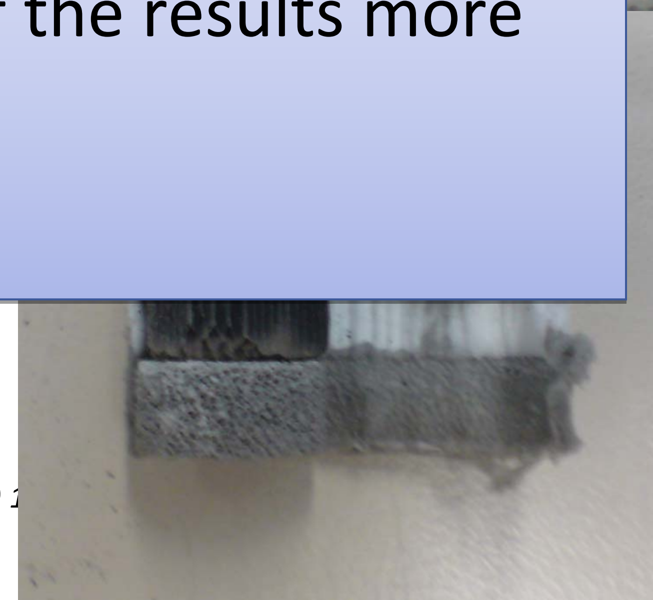
Motivation

Challanges in CPOX of higer HCs

- High-temperature oper
  - Beside surface chem
    chemistry is importa
  - C_1-C_3 precursors

N. Burke, D. Trimm, React. Kinet. Catal. Lett. 84 (2005) 1

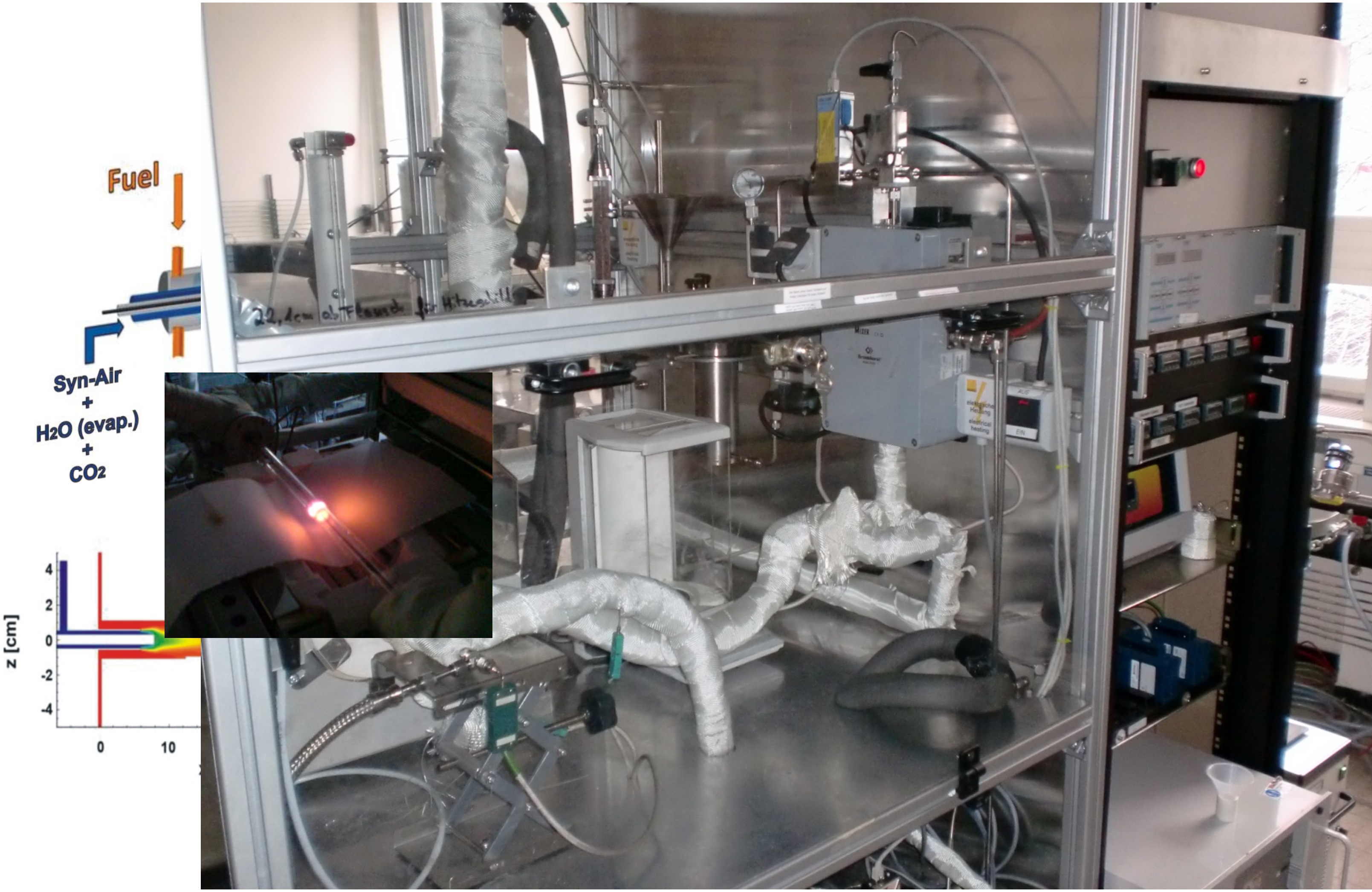




Post-reactions in the gas-phase downstream the catalyst make interpretation of the results more complicated

Experimental Setup

Rapid mixing below autoignition temperature



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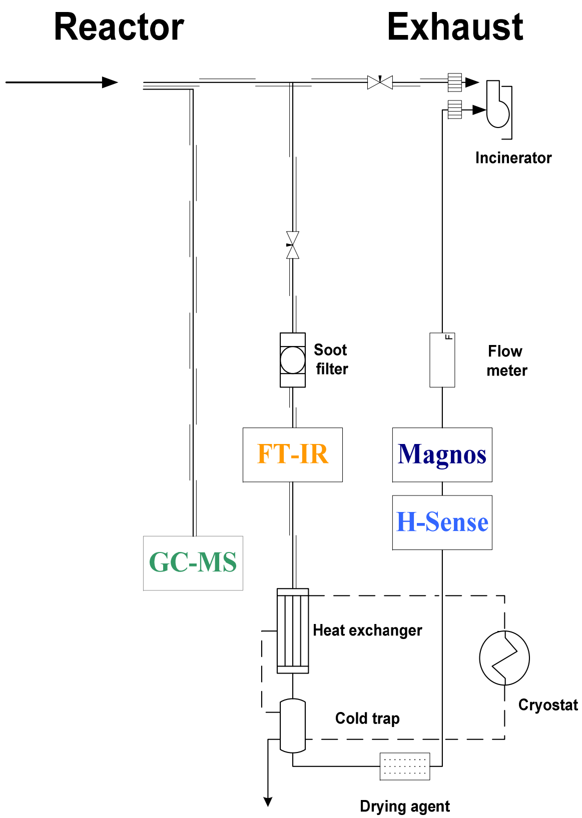
M. Hartmann, Sven Lichtenberg, Nicole Hebben, Dan Zhang, O. Deutschmann, Chemie Ingenieur Technik 81 (2009), 909-919

Experimental Setup

Product gas processing and analysis



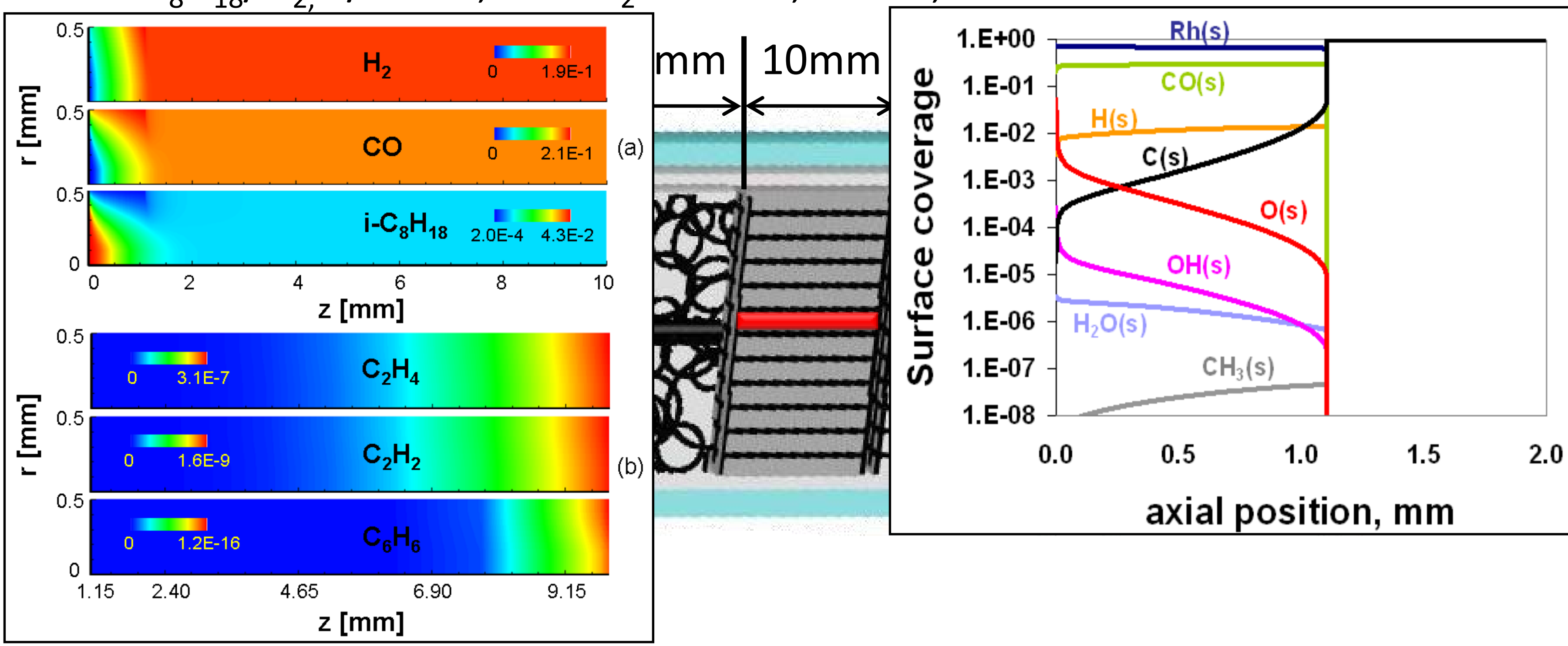
Total flow determination via internal standard methods and drycal® technology

M. Hartmann, Sven Lichtenberg, Nicole Hebben, Dan Zhang, O. Deutschmann, Chemie Ingenieur Technik 81 (2009), 909-919

Conversion with catalyst

Surface and gas-phase reactions

Iso-C_8H_{18}/O_2, C/O=1.1, 80% N_2 dilution, 1080K, 4 SLPM

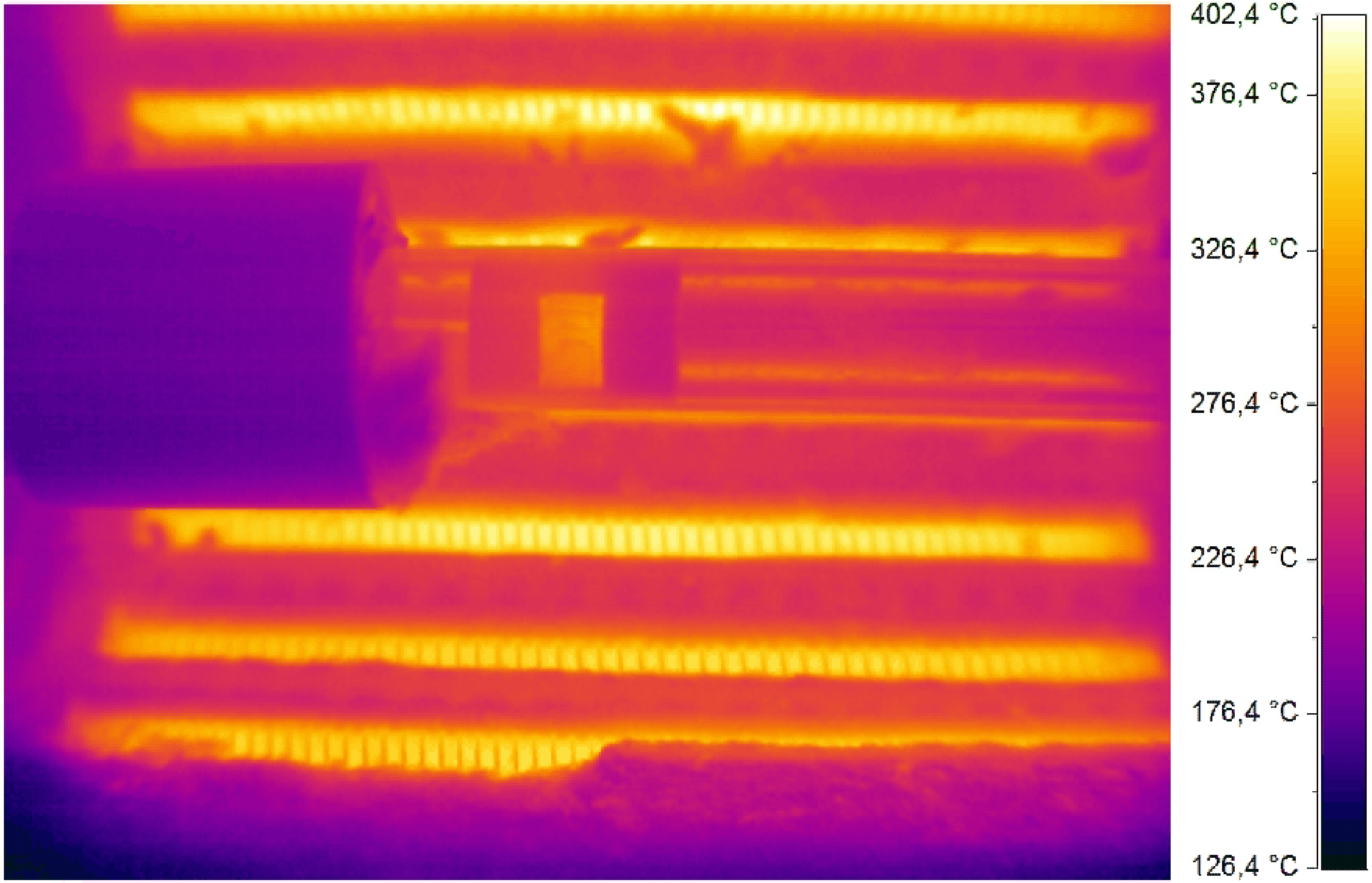


2D species distribution (molar fractions) along the catalyst. The symmetry axis of the channel and the gas-wall interface are at r = 0 and 0.5 mm, respectively.

M. Hartmann, L. Maier, H. D. Minh, O. Deutschmann, Combust. Flame 157 (2010) 1771-1782.

Catalytic experiment

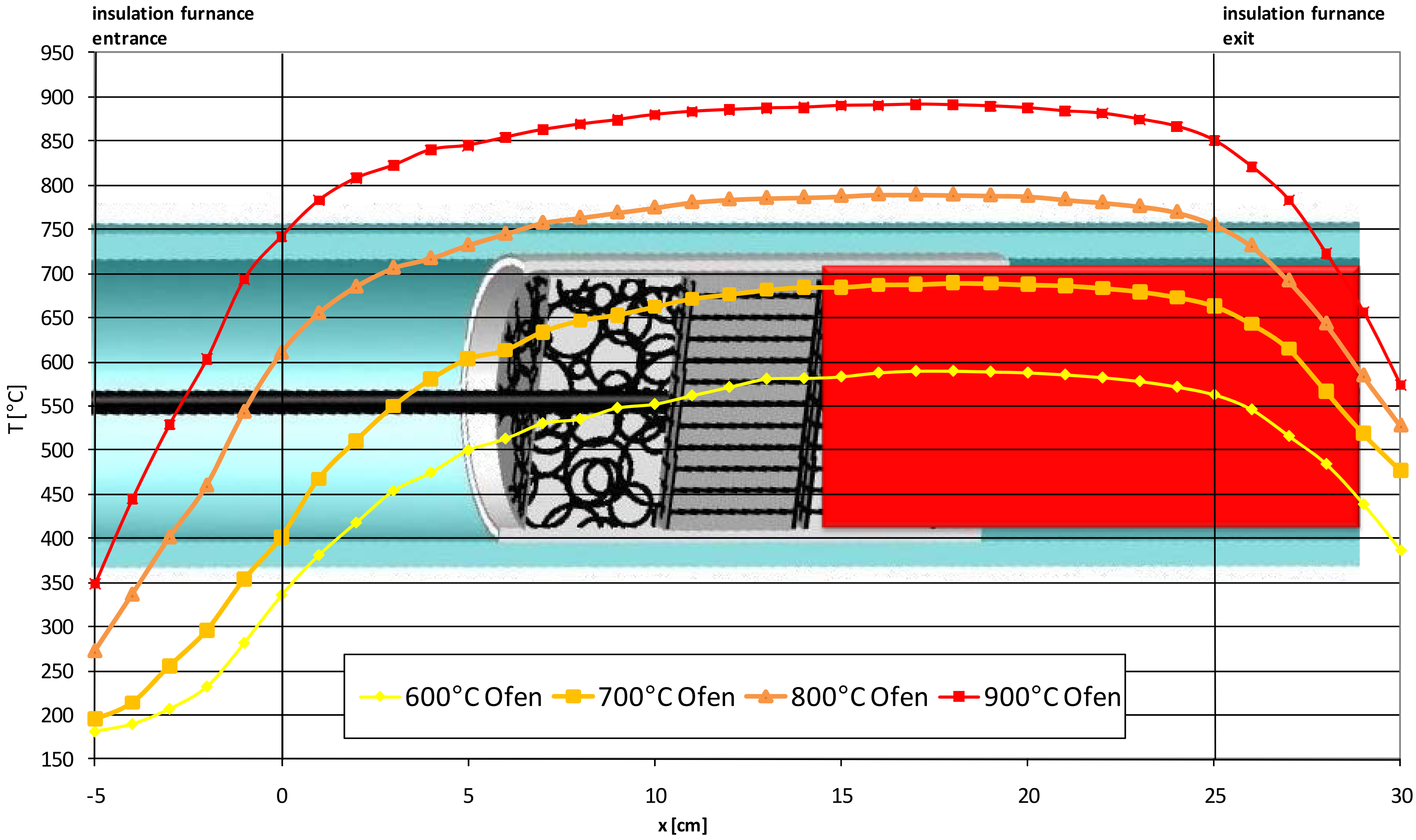
Ignition behaviour



Conversion without catalyst

Non-catalytic gas-phase experiment

Post-catalyst regime for gas-phase reactions



Non-catalytic gas-phase experiment

Inlet conditions in non-catalytic case taken from catalytic case

C/O	1	1.3	1.6	2
x CO	0.2014	0.1821	0.1681	0.1652
x H2	0.2316	0.2294	0.2120	0.1947
x CO2	0.0110	0.0118	0.0141	0.0191
x H2O	0.0147	0.0087	0.0134	0.0213
x Ethyeln	0.0000	0.0005	0.0004	0.0002
x i-octane	0.0001	0.0028	0.0077	0.0032
x nitrogen	0.5412	0.5648	0.5843	0.5963

Non-catalytic gas-phase experiment

1D steady state plug-flow simulation

DETCHEM^{PLUG} : isothermal, length 25.5 cm, radius 1cm, flow 0.318 m/s

MECHANISM M1: **Westbrook-Kalghatgi** gas phase chemistry:
1082 species, 8927 reactions

detailed *n*-heptane/*iso*-octane mechanism from LLNL

H.J. Curran, P. Gaffuri, W.J. Pitz, C.K. Westbrook, Combust. Flame 129 (3) (2002) 253–280

and detailed toluene mechanism from Dagaut

P. Dagaut, G. Pengloan, A. Ristori, Phys. Chem. Chem. Phys. 4 (2002) 1846–1854.

were merged.

Johan Andrae, David Johansson, Pehr Björnbom, Per Risberg, Gautam Kalghatgi,Combustion and Flame 140 (2005) 267–286

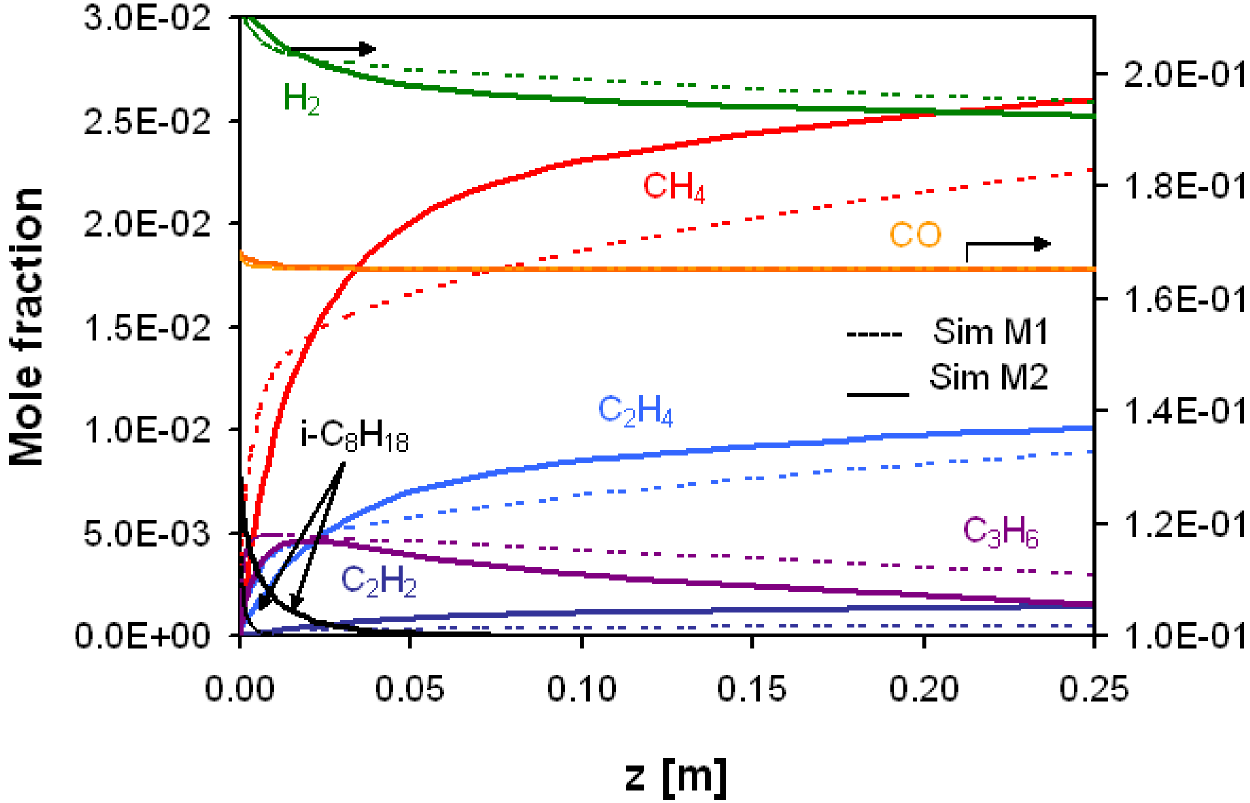
MECHANISM M2: **based on work of Dean et al** gas phase chemistry:
420 species, 3611 reactions, PAH pathway

C.A. Mims, R. Mauti, A.M. Dean, K.D. Rose, J. Phys. Chem. 98 (50) (1994) 13357–13372

K.M. Walters., A.M. Dean, H. Zhu, R.J. Kee, Journal of Power Sources 123 (2003) 182–189

Results

Numerically predicted axial product profiles

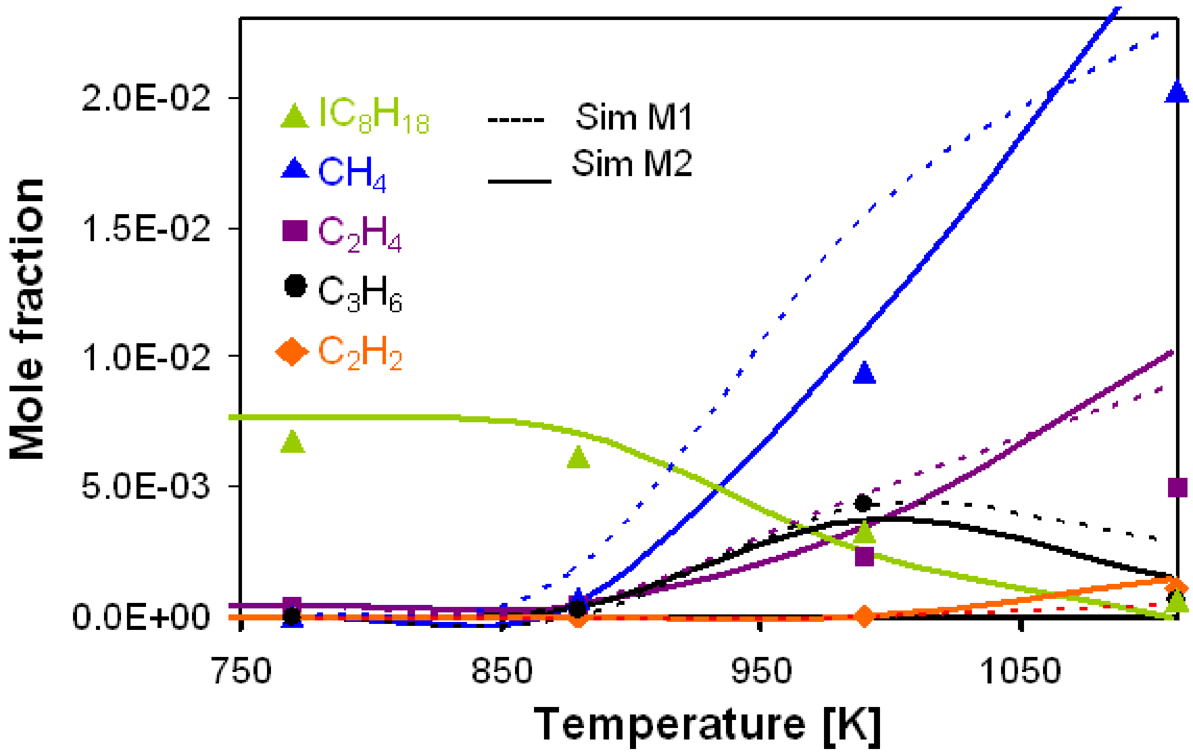


C/O = 1.6, 1108 K, 6 SLPM

- C_8 completely converted for z ≥ 5 cm
- H_2 and CO decrease
- HCs increase
- Thermal cracking leads to decreasing $HC_{>3}$ for z ≥ 3 cm
- 10% H_2 conversion
- H_2O, CO_2 increase due to WGS and hydrogenation reactions

Results

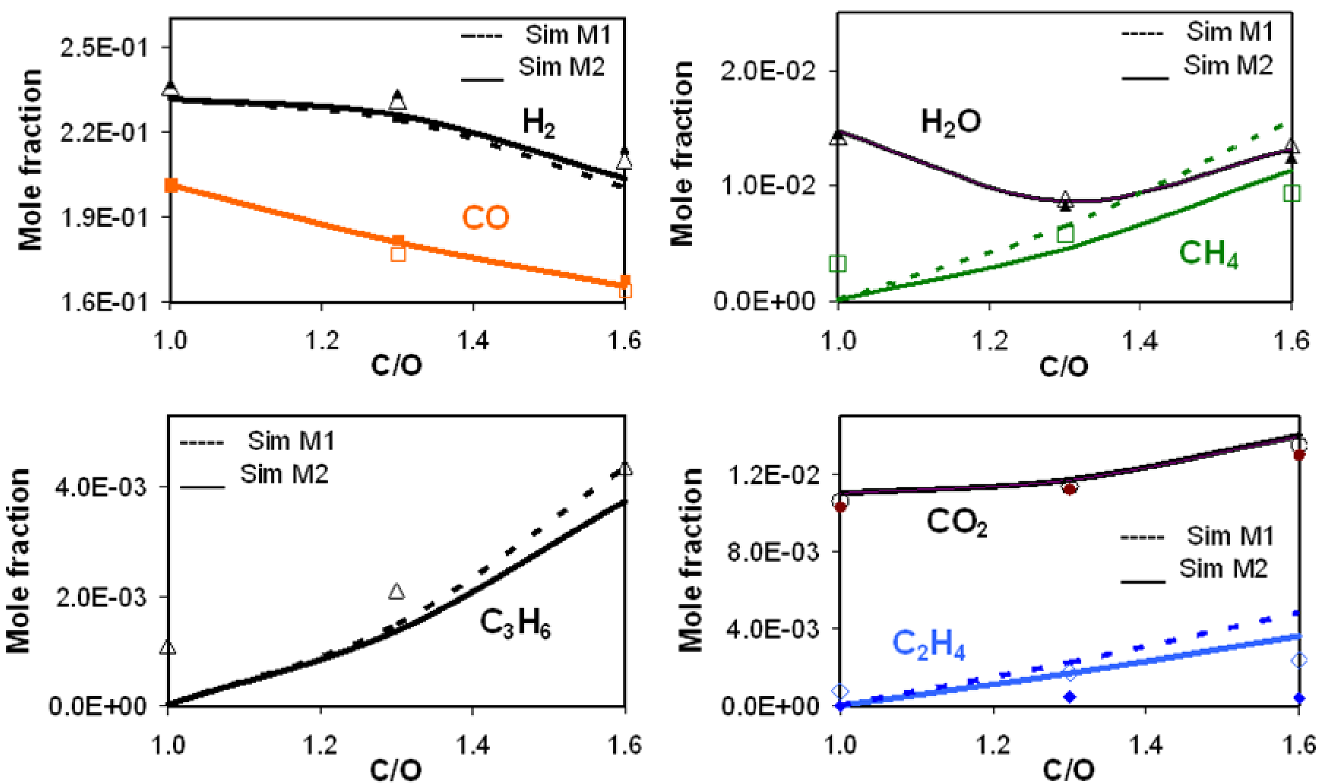
Product distribution as function of temperature



- Minimum T is required
- C1-C3 observed at T > 850 K
- No C8 conversion below T < 850 K
- Max. conversion of 87.5% at 1108 K
- M2 predictes less C1-C3 than M1 due to PAH formation
- C3 decreases for T > 990 K because of higher formation enthalpy of ethylene and acetylene

C/O = 1.6, 6 SLPM, symbols = experiment

Main- and side-products

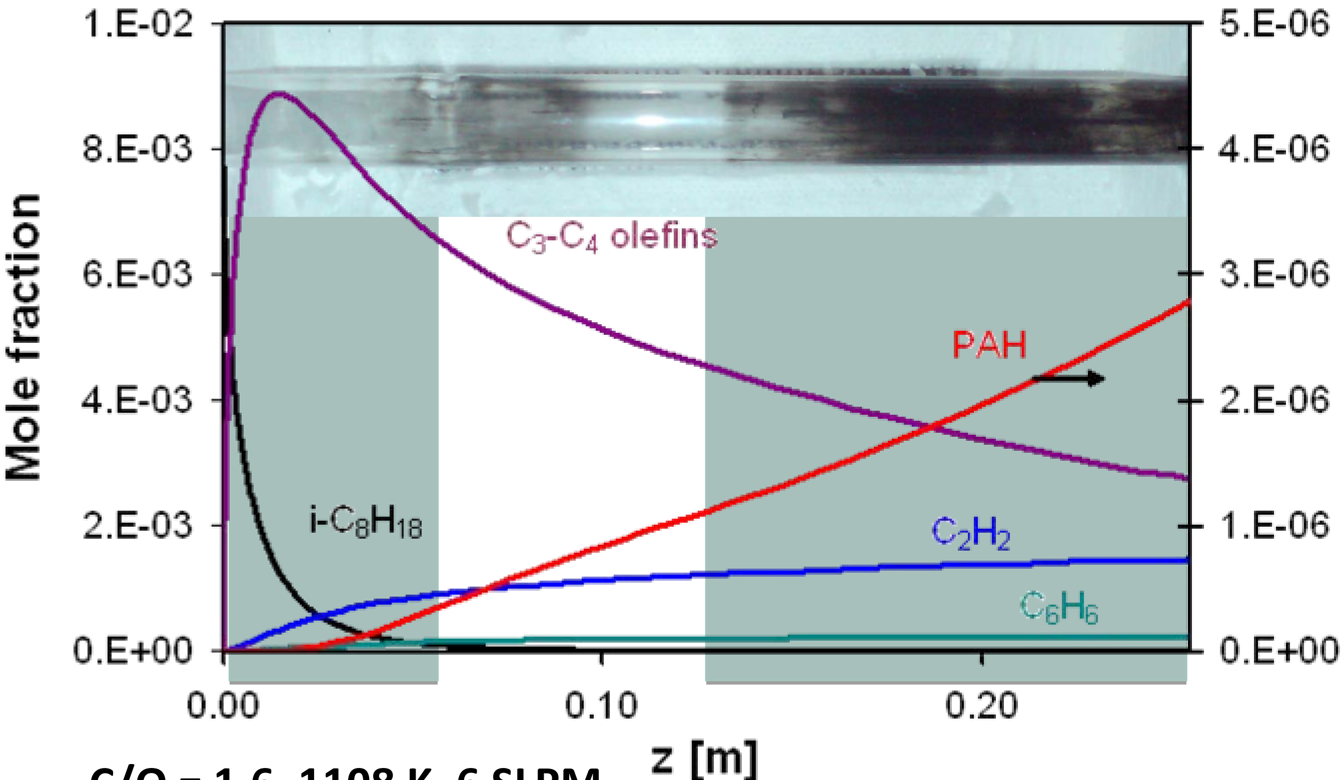


- With rising C/O:
  - More soot precursor formation
  - Slight Syngas consumption
- Consumption of H_2O points to WGS for C/O < 1.3
- Consumption of H_2 for C/O > 1.3 points to methantion reactions

993 K, 6 SLPM, open symbols = experiment, <u>filled symbols = inlet</u>

Results

Carbon Precursor Distribution along the Reactor



C/O = 1.6, 1108 K, 6 SLPM

- C3-C4 directly formed at reactor entrance
- Two zones of coke deposition expected

Entrance Zone:

alternative pathways compared to PAH (polyyne model, C_2H_2 pyrolysis, carbon cluster formation)

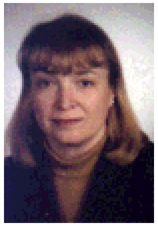
Center and Downstream:

PAH formation

Conclusions

- Catalyst is covered with C downstream the position at which all O_2 is consumed at fuel rich conditions
- gas-phase plays important role in the conversion of the remaining fuel
- Gas-phase reactions are responsible for coke formation when unconverted fuel leaves the HT oxidation zone of the catalyst
- Cracking of remaining fuel increases concentrations of by-products and as a consequence of C-deposition
- Gas-phase reactions have to be considered in HT CPOX reformers especially in fuel-rich operation mode

Acknowledgment



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