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Operational behavior and reforming kinetics over Ni/YSZ of a planar type pre-reformer for SOFC systems

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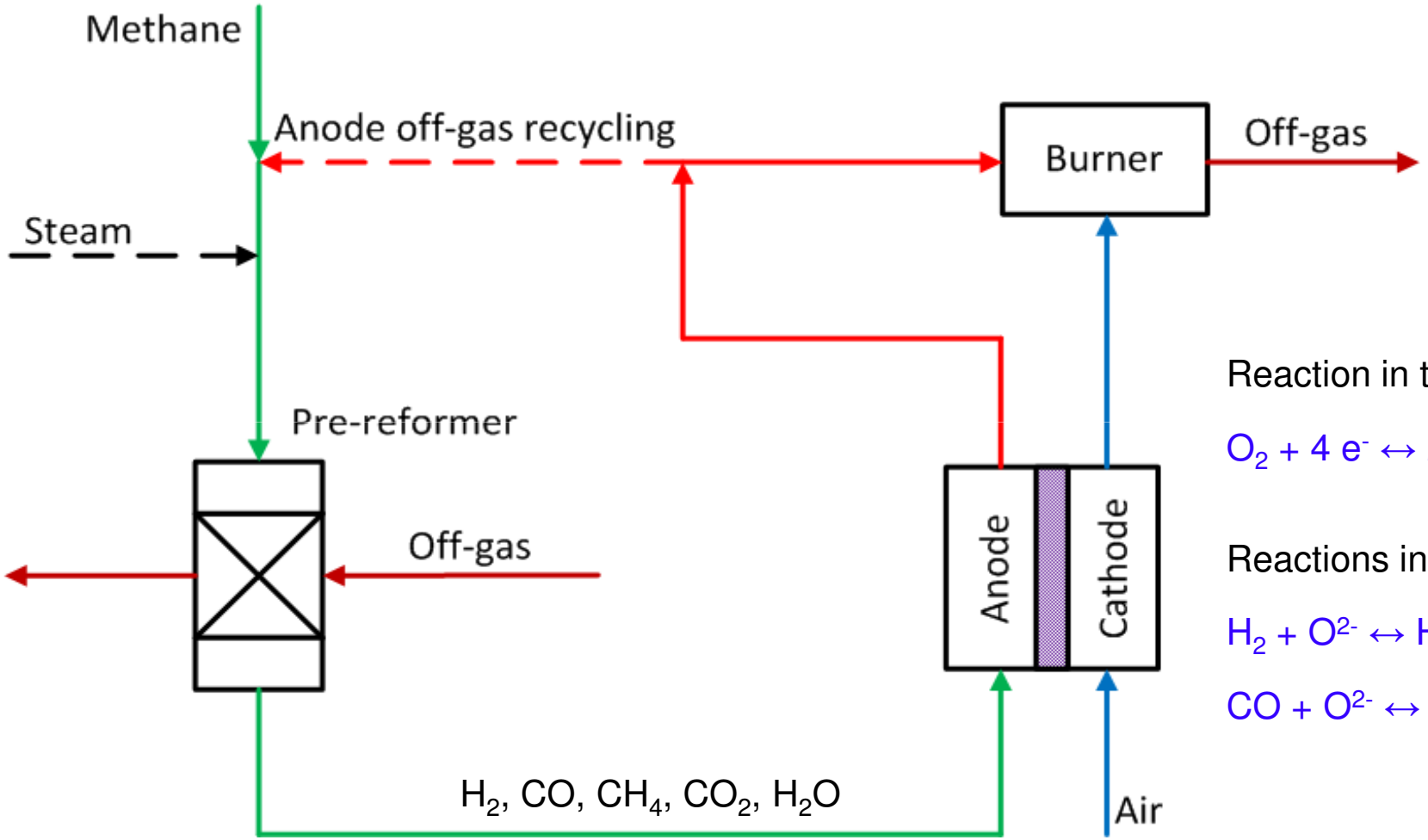
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Outline

- Introduction
- Global reaction kinetics
- Experimental setup
- Results
- Modeling
- Conclusions

Basic layout of the SOFC system



Reaction in the Cathode:

$O_2 + 4\ e^- \leftrightarrow 2\ O^{2-}$

Reactions in the Anode:

$H_2 + O^{2-} \leftrightarrow H_2O + 2\ e^-$

$CO + O^{2-} \leftrightarrow CO_2 + 2\ e^-$

Steam reforming reactions of methane

Reaction		-ΔH (25 °C) [kJ/mol]
R1	$CH_4 + H_2O \leftrightarrow CO + 3\ H_2$	-206
R2	$CH_4 + 2\ H_2O \leftrightarrow CO_2 + 4\ H_2$	-165
R3	$CH_4 + CO_2 \leftrightarrow 2\ CO + 2\ H_2$	-247
R4	$CO + H_2O \leftrightarrow CO_2 + H_2$	41
R5	$CH_4 \leftrightarrow C + 2\ H_2$	-75
R6	$2\ CO \leftrightarrow C + CO_2$	172
R7	$CO + H_2 \leftrightarrow C + H_2O$	131

Models for global reaction kinetics

1) Arrhenius type

$$r_{r,\,Arr} = F \cdot p_{CH_4}^{\alpha} \cdot p_{H_2O}^{\beta} \cdot \exp\left(\frac{-E_a}{R \cdot T}\right)$$

2) Langmuir-Hinshlewood type

$$r_{r,\,Lang} = k \frac{p_{CH_4} \cdot p_{H_2O} \cdot K_{CH_4} \cdot K_{H_2O}}{\left(1 + p_{CH_4} K_{CH_4} + p_{H_2O} \cdot K_{H_2O}\right)^2}$$

3) Equilibrium approach

$$r_{r,\,eq} = k \cdot p_{CH_4} \cdot p_{H_2O} \cdot \left(1 - \frac{p_{CO} \cdot p_{H_2}^3}{K_{e,STR} \cdot p_{CH_4} \cdot p_{H_2O}}\right)$$

4) Water shift reaction approach

$$r_s = k_s \cdot p_{CO} \cdot \left(1 - \frac{p_{CO\,2} \cdot p_{H_2}}{K_{e,s} \cdot p_{CO} \cdot p_{H_2O}}\right)$$

Global reaction kinetics (Arrhenius type)

$$r_{r,\,Arr} = k \cdot p_{CH_4}^{\alpha} \cdot p_{H_2O}^{\beta}$$

where $$k = F \cdot \exp\left(\frac{-E_a}{R \cdot T}\right)$$

Literature data review: inconsistent results of kinetics *

α: 0.85 – 1.4 (α=**1** was used very often)

β: negative and positive values

Ea : 42 - 208 kJ/mol

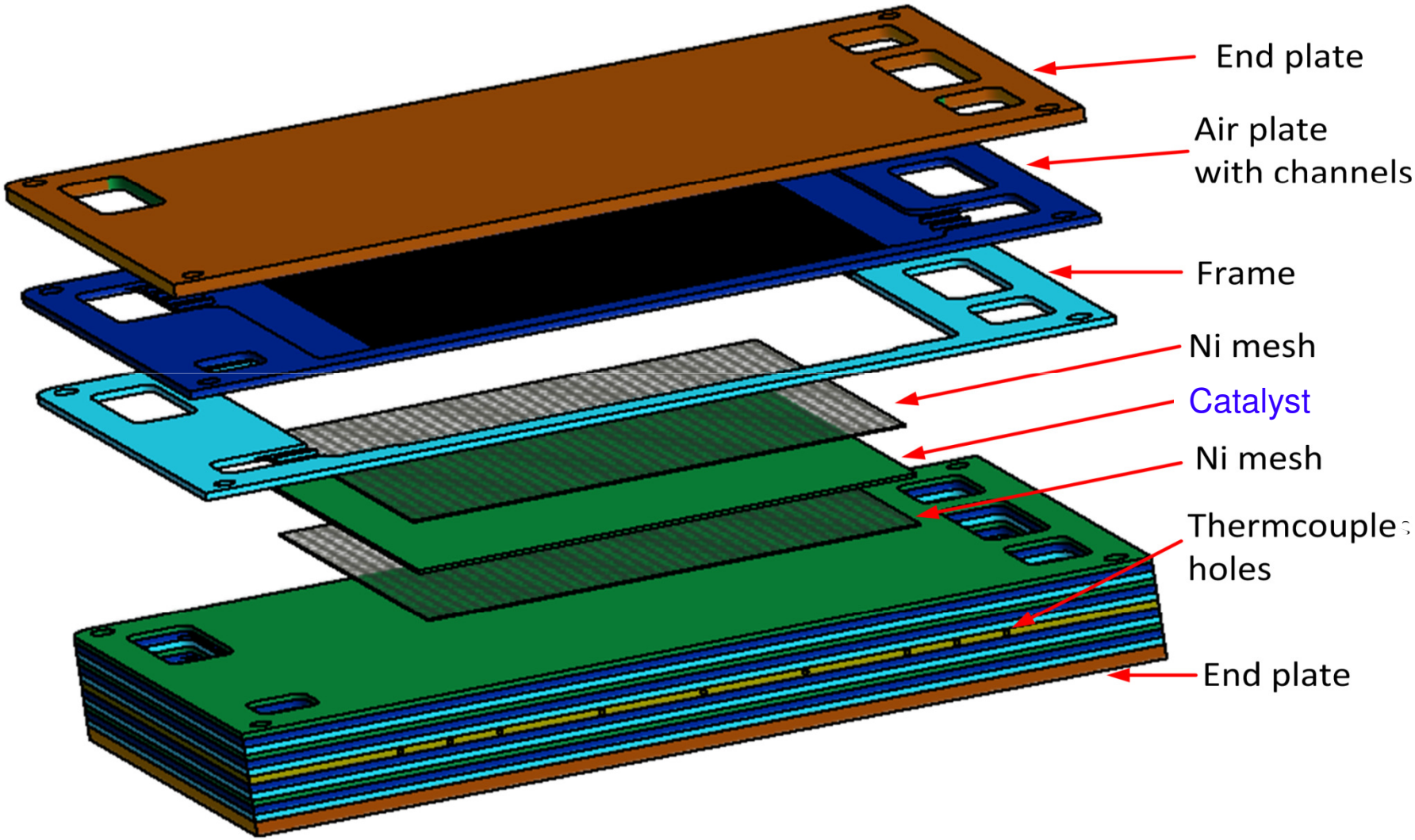
* Andersson M, Yuan J, Sunden B, Applied Energy 2010; 87:1461

Motivation:

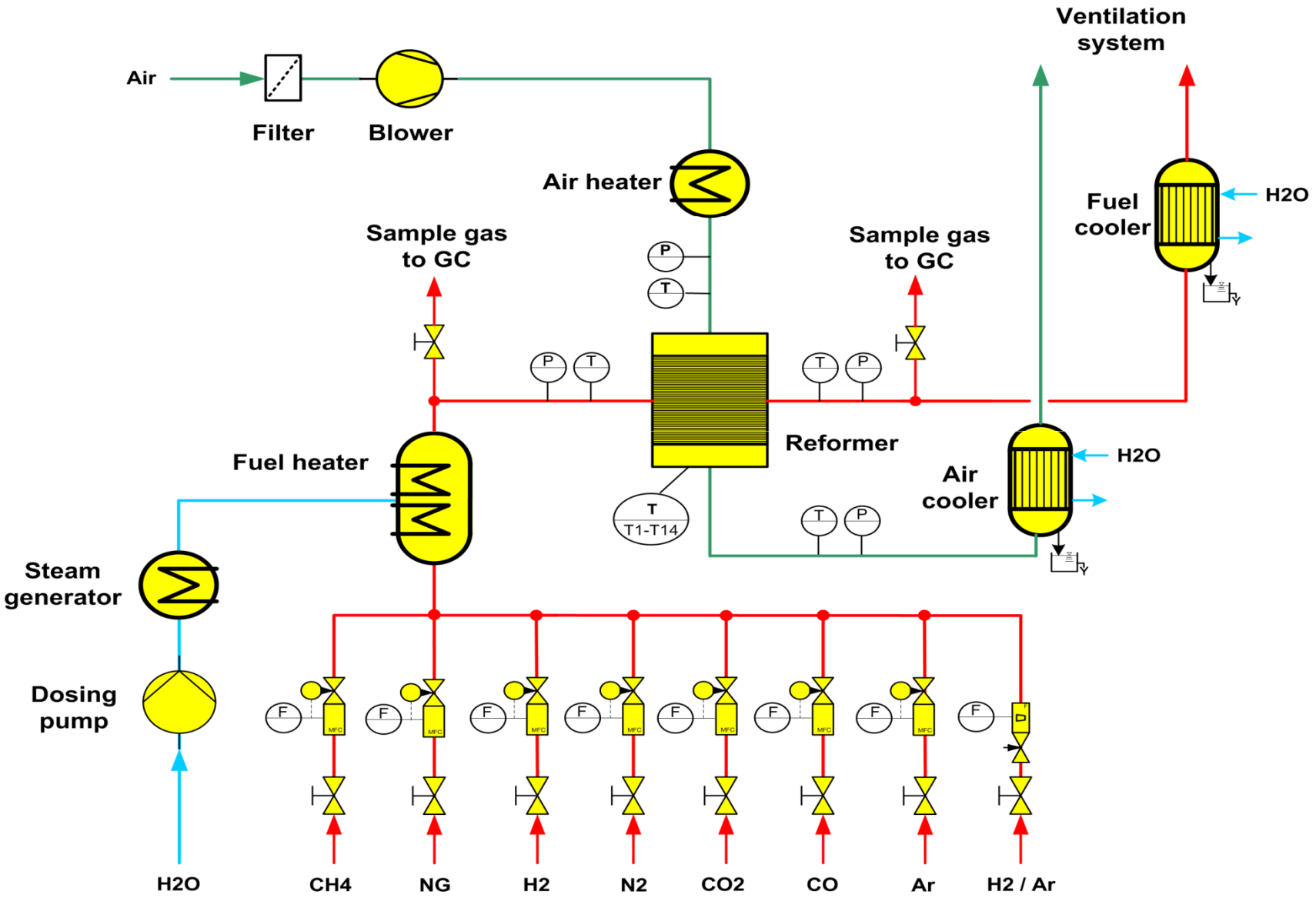
- **Find the ”real” global kinetics of steam reforming reactions**
- **Optimization of pre-reformer for SOFC-system**

Design of a 5-layer pre-reformer using air heater

Catalyst: Ni/YSZ (Ni + 8 mol% Y_2O_3-stabilized ZrO_2)

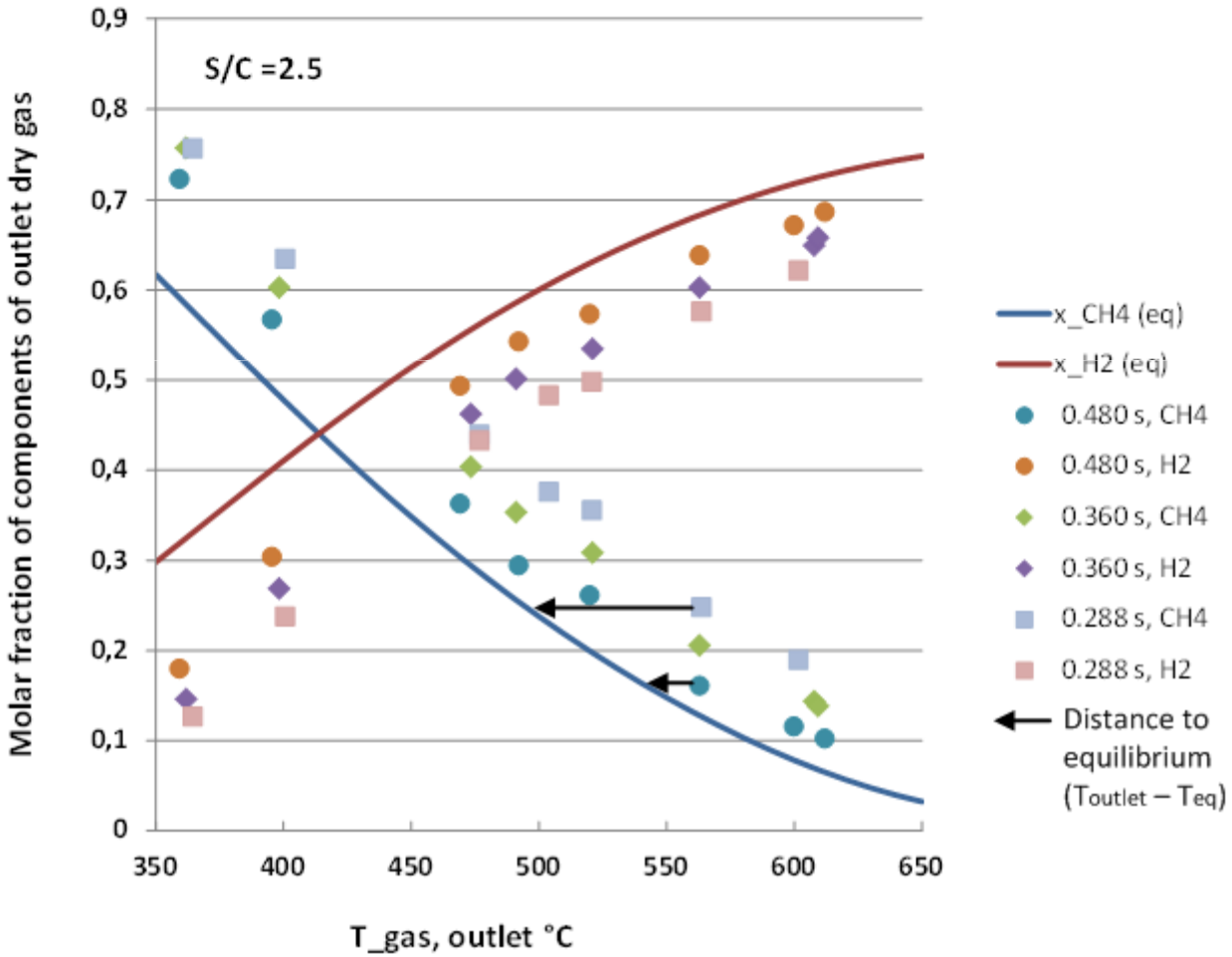


Flow scheme of the experimental setup



Results

The comparison between the compositions for equilibrium and measurement as function of temperature and space-time



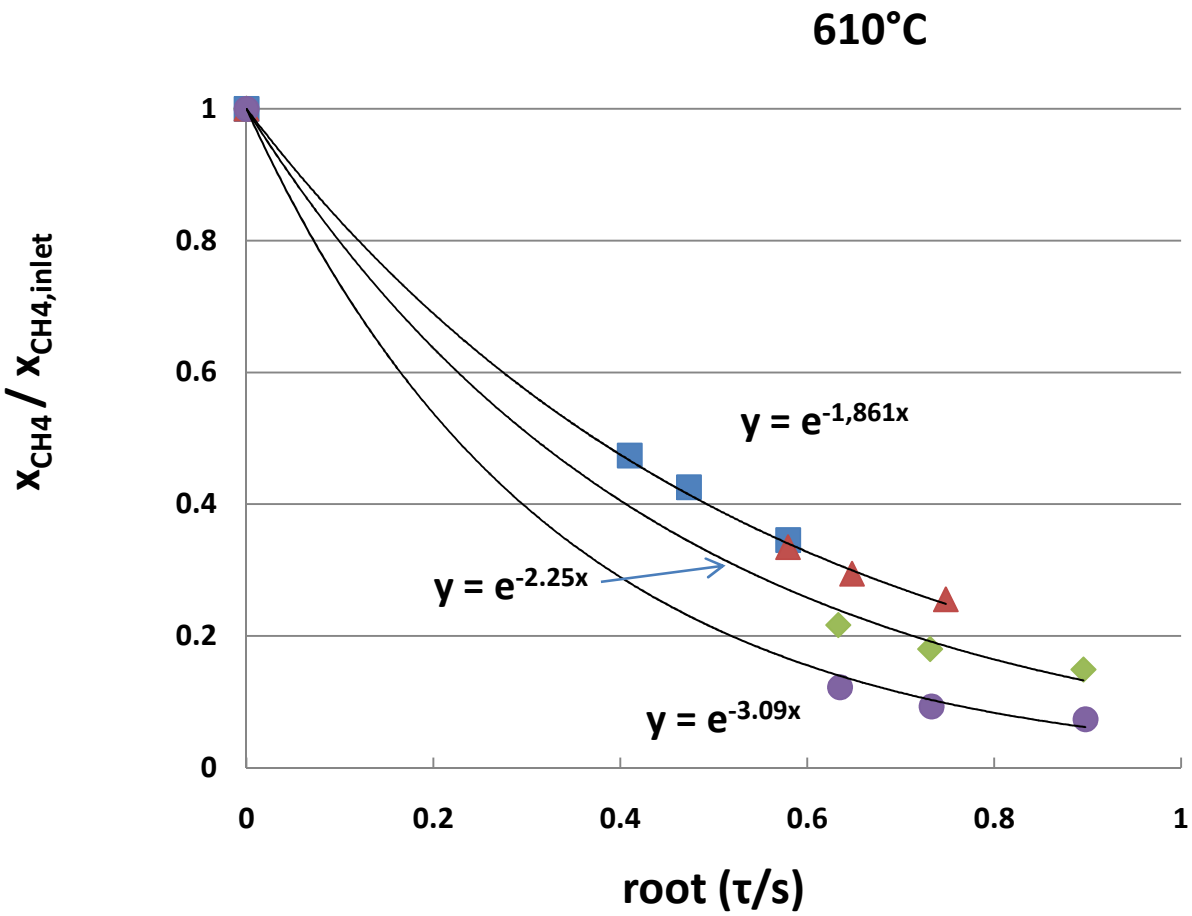
Analytical methods

- dew-point-measurement
- gas-chromatographic method

$$\tau = \frac{V}{v_o} = \frac{\text{reactor volume}}{\text{volumetric feed rate}}$$

Graphs of concentration versus space time

The experimental data fit not first order kinetics for methane concentration

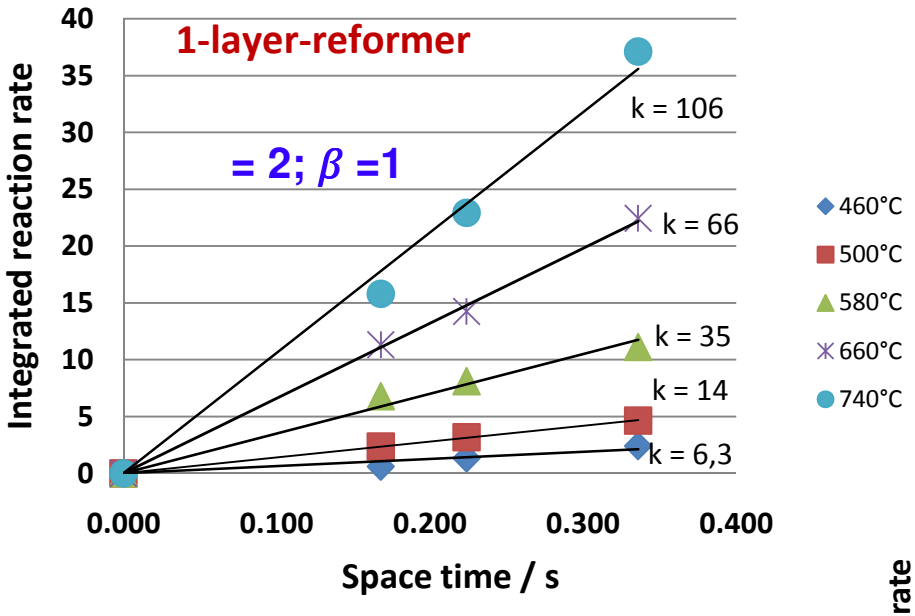


S/C=2, k = 46
70% AOGR, k = 155
80% AOGR, k = 372

- 1-layer-reformer, S/C=2
- 5-layer-reformer, S/C=2
- 70% Recycle
- 80% Recycle

$$\tau = \frac{V}{v_o} = \frac{\text{reactor volume}}{\text{volumetric feed rate}}$$

Modeling (Arrhenius type)



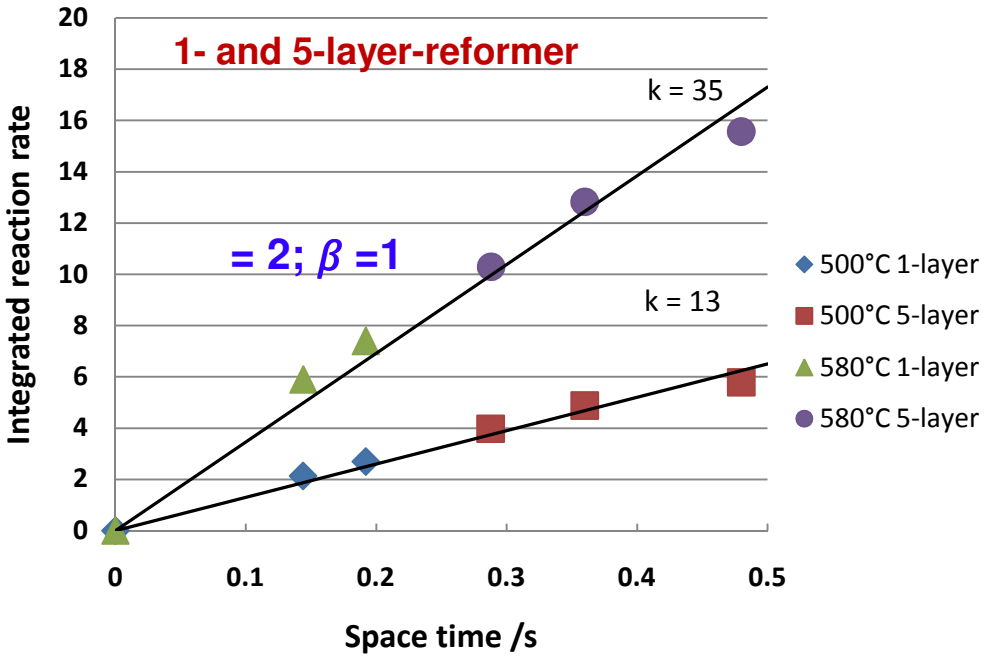
$$\tau = \frac{V}{v_o} = \frac{\text{reactor volume}}{\text{volumetric feed rate}}$$

$$-\int_0^{\tau} \frac{dx_{CH4}}{x_{CH4}^2 \cdot x_{H2O}} = k \cdot \tau$$

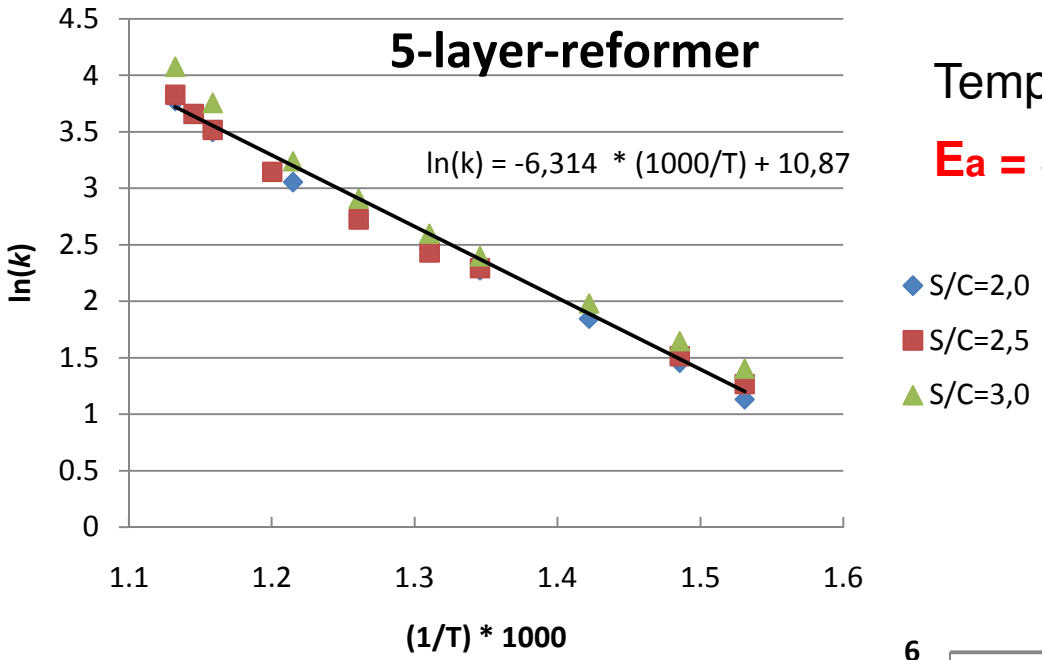
$$\int_0^{\tau} \frac{d(\xi)}{\left(x_{0,CH_4} - \xi\right)^2 \cdot \left(x_{0,H_2O} - \xi\right)} = k \cdot \tau$$

ξ: Progress variable of reforming reaction

Integrated reaction rates from exp. data of the both reformers



Temperature dependency of reaction rate



Temperature: 350 °C – 620 °C

E_a = 53 kJ/mol*

* Nguyen,V.N., Blum, L., Peters, Ro., Int. J. Hydrogen Energy (2014) **39**: 7131

E_a = 50 kJ/mol**

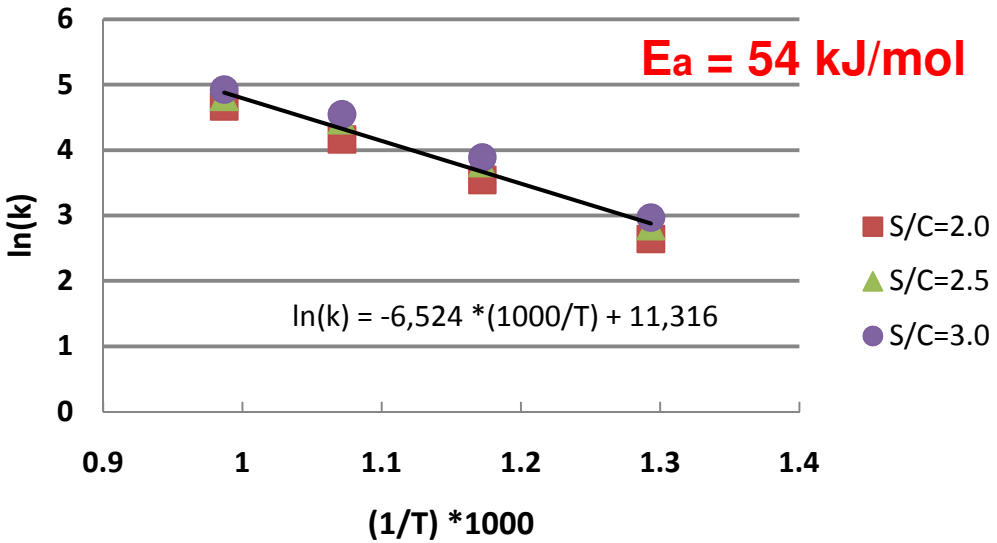
** Drescher I. Kinetik der Methan-Dampf-Reformierung. Diss RWTH Aachen 1999.

E_a = 38.5 - 62 kJ/mol***

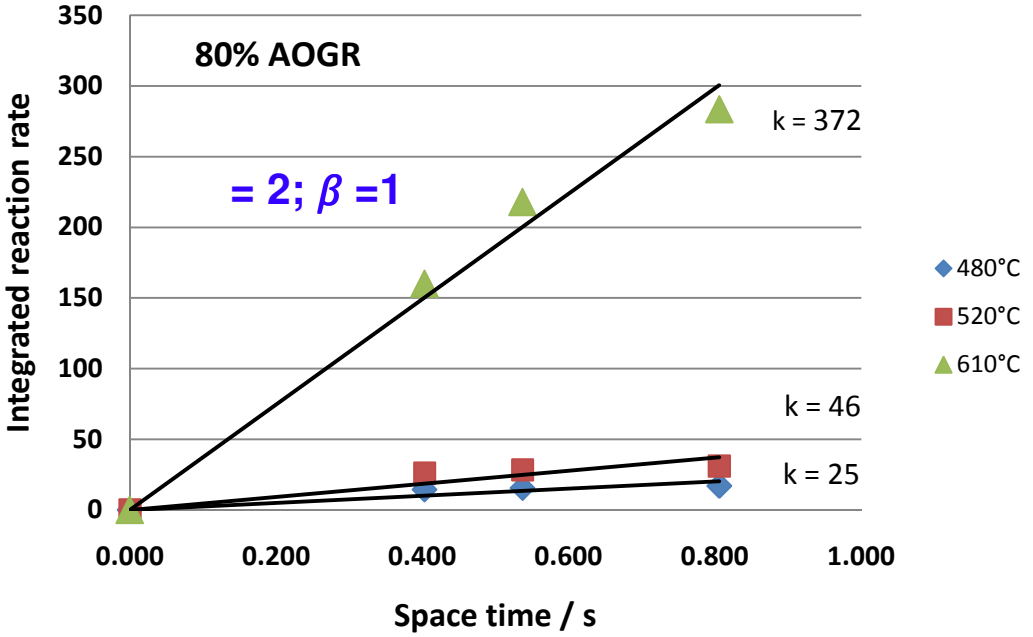
*** Liu, K., Song, C., Subramani, V. (Eds.) Wiley & Sons Publication; 2010.

Temperature: 460 °C – 740 °C

1-layer-reformer



Effect of anode off-gas recycling (AOGR)



$$-\int_0^{\tau} \frac{dx_{CH4}}{x_{CH4}^2 \cdot x_{H2O}} = k \cdot \tau$$

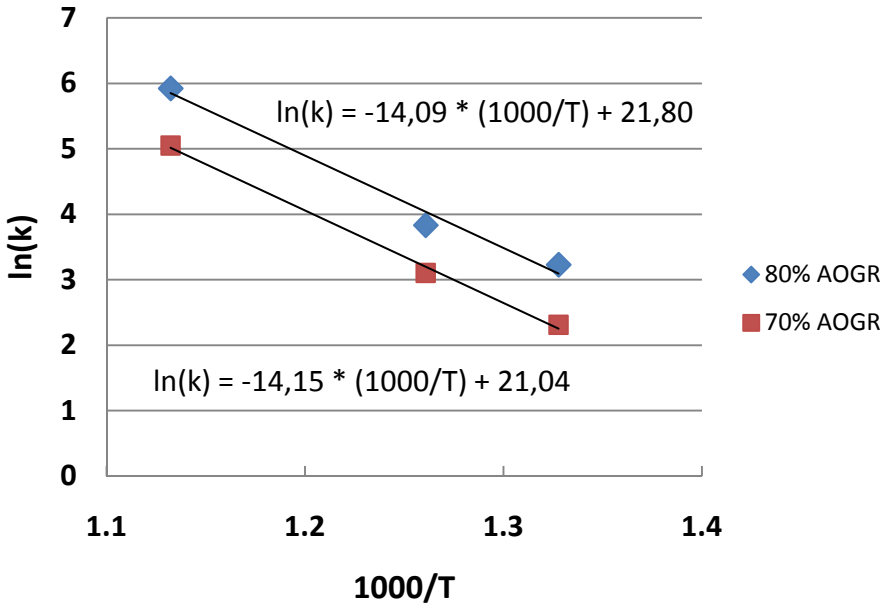
$$\int_0^{\tau} \frac{d(\xi)}{(x_{0,CH_4} - \xi)^2 \cdot (x_{0,H_2O} - \xi)} = k \cdot \tau$$

ξ: Progress variable of reforming reaction

AOGR at 70% fuel utilization

Example at 610 °C:
Without AOGR, k = 46
70% AOGR, k = 155
80% AOGR, k = 372

Ea = 117 kJ/mol



Conclusions

- Two different planar pre-reformers containing Ni/YSZ catalyst were tested for operational behavior and kinetics of methane steam reforming reactions in a temperature-range of 350 °C - 740 °C.
- Experimental results for the two reformers are close to each other.
- The developed kinetic expression of Arrhenius type (second order with respect to mole fraction of methane and first order with respect to mole fraction of water) gives a good agreement with the experimental results.
- This kinetic expression (**= 2; β =1**) is universally applicable for different steam to carbon ratios and also for the case of anode off-gas recycling (AOGR).
- In the case of anode off-gas recycling the reaction rate constant is larger than that without AOGR.
- Understanding of the methane steam reforming reactions is expected to be of significant importance for the further development of SOFC systems.

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Thank you for your attention!