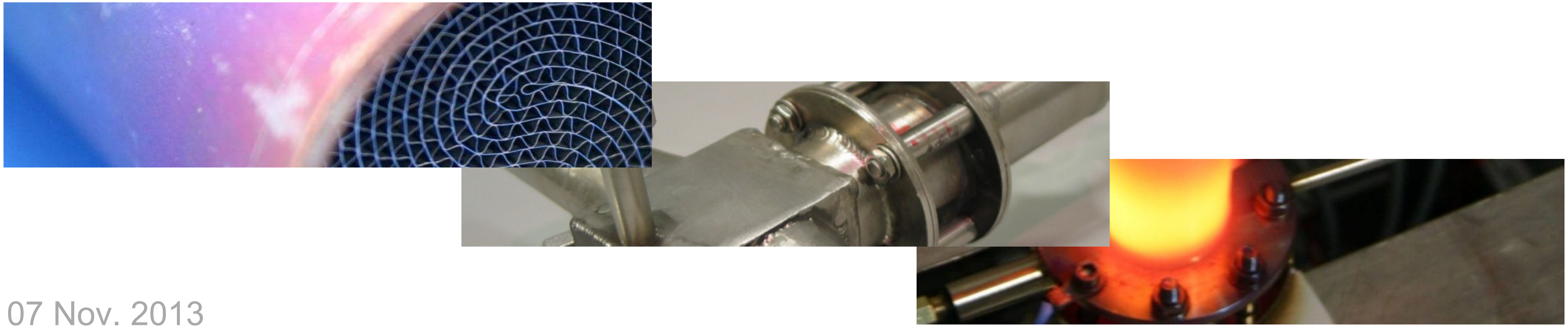
Zentrum für BrennstoffzellenTechnik GmbH

Design and Demonstration of an Ethanol Fuel Processor for HT-PEM Fuel Cell Applications

AIChE Annual Meeting 2013
Fuel Processing for Hydrogen Production



07 Nov. 2013

Overview

- Introduction
- Process Simulation
- Heat Integration Analysis
- Catalyst Selection
- Component Development
- Fuel Processor Demonstration
- Outlook

Introduction

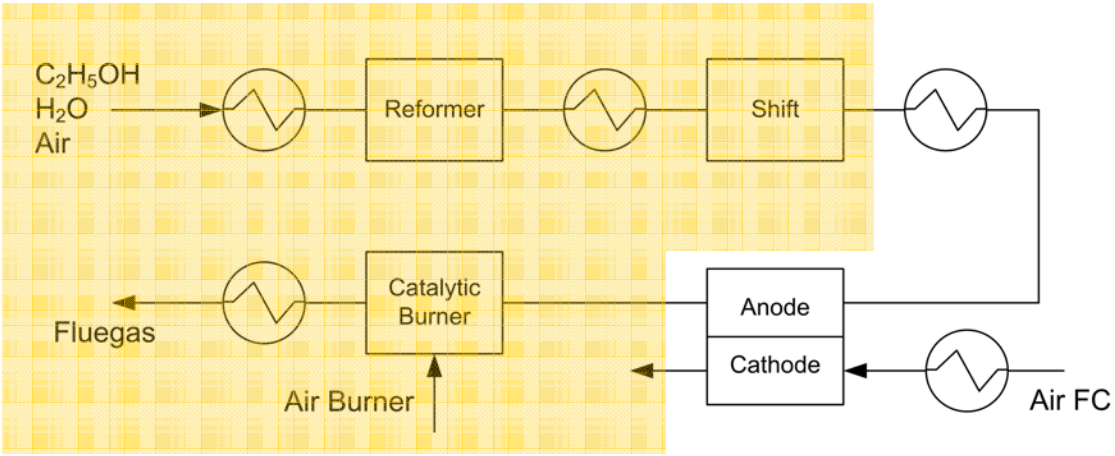
Application

- Hydrogen generation for small scale fuel cell systems (P_{el} = 200 – 500 W)
- HT PEM fuel cell
- Off grid stationary power supply
- Backup power
- Leisure and security markets

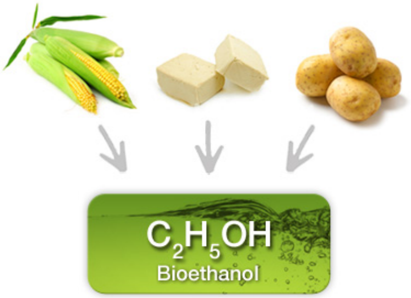
Fuel Bioethanol (C_2H_5OH)

- CO_2 neutral
- Good portability
- High energy density
- Good storage capability

Fuel processor boundary



Flow sheet of reformer fuel cell system



Source www.lacus.ch

Introduction

Requirements Fuel Processor

- P_{H2} = 600 – 1500 W
- HT PEM FC suitable reformate gas quality (CO ≤ 1 %)
- Fast start up
- High robustness
- Potential of low cost manufacturing
- Low pressure drop

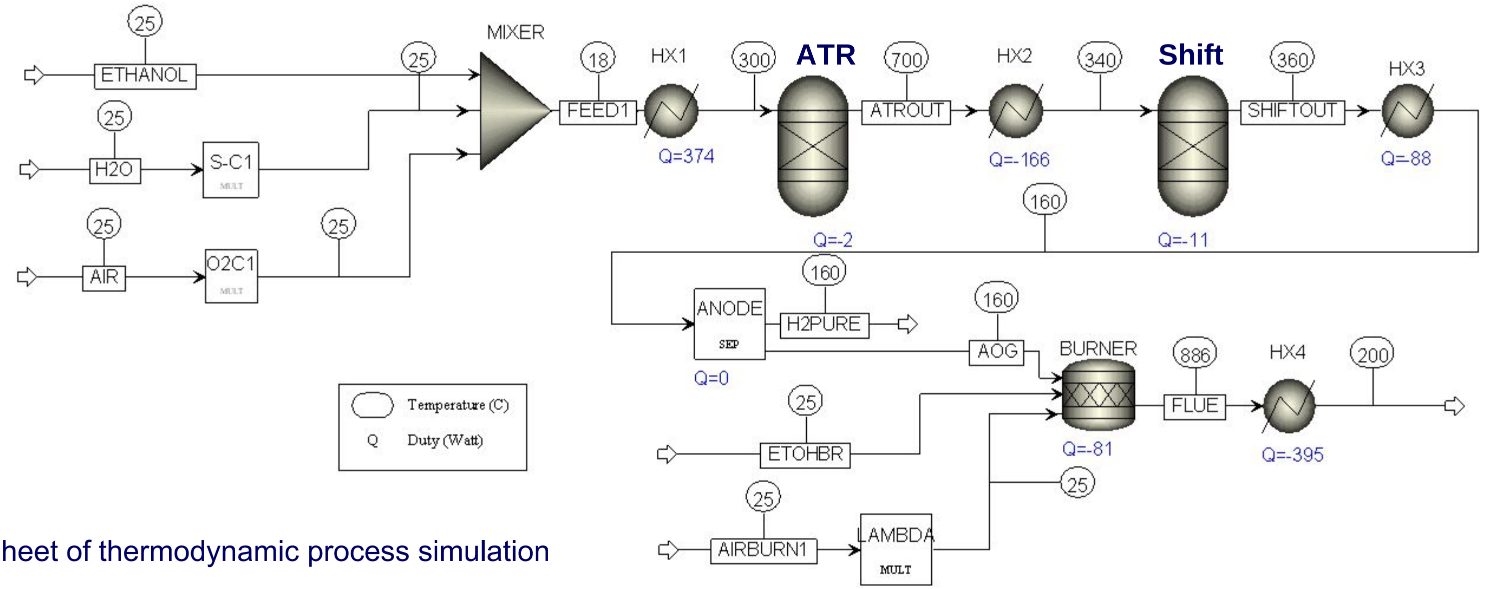
→ Autothermal Reforming of Bioethanol

Process Simulation

Approach

- Parameter variation
- Reformate gas composition
- Definition heat streams and heat demand
- Carbon and side product formation
- Definition of basic operation point

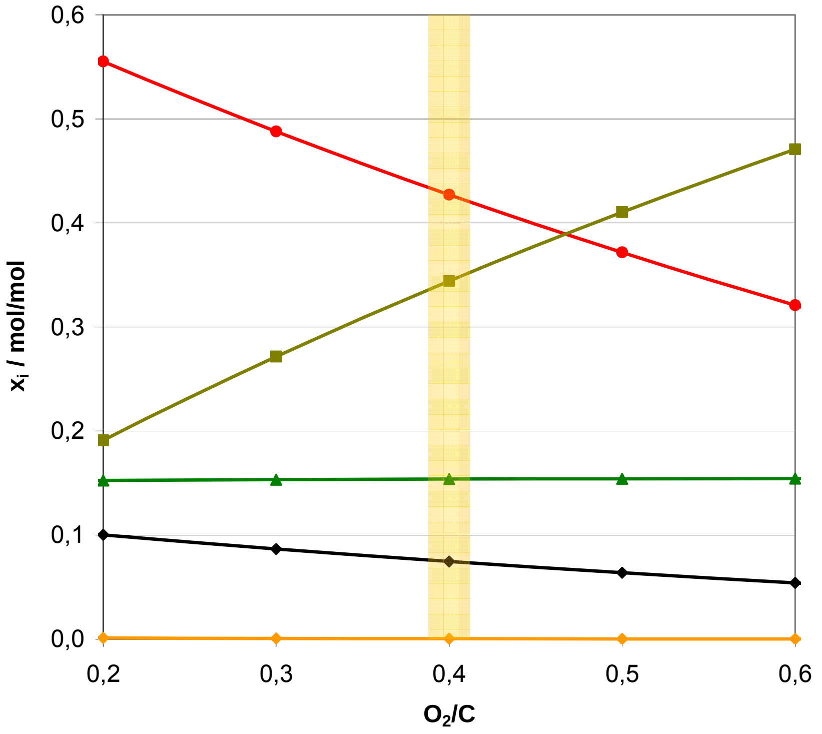
Parameter	Interval	Step	Basic Operation Point
T_{ATR} / °C	500 - 800	25	700
O_2/C / -	0 – 1.5	0.1	0.4
S/C / -	0 - 5	0.25	2.75
T_{Shift} / °C	200 - 400	25	300



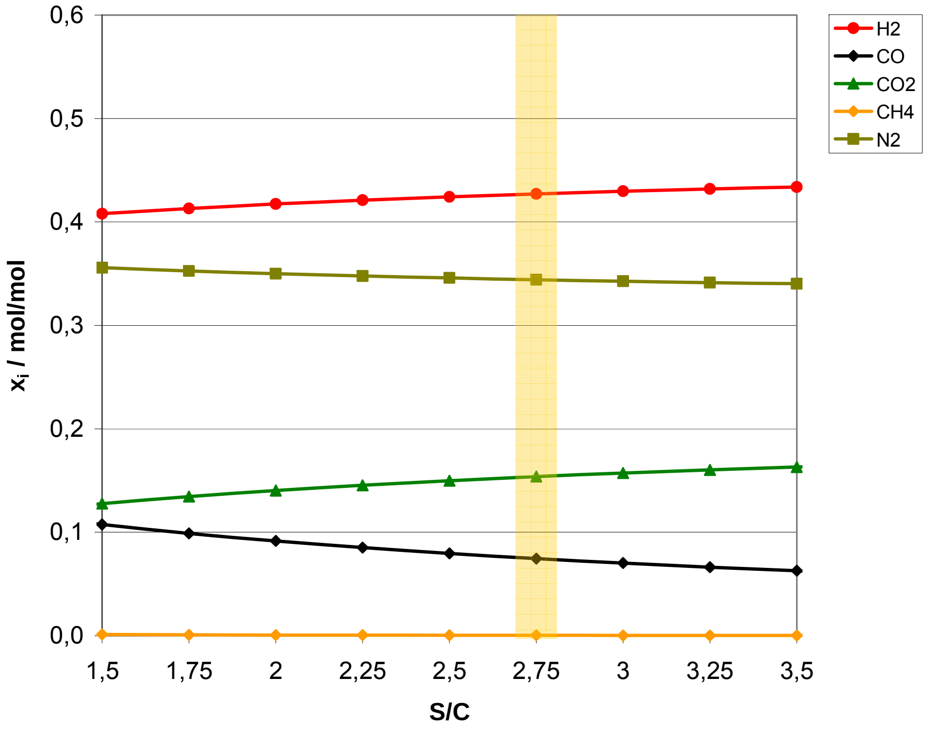
Flow sheet of thermodynamic process simulation

Process Simulation

Product gas composition (example ATR out)



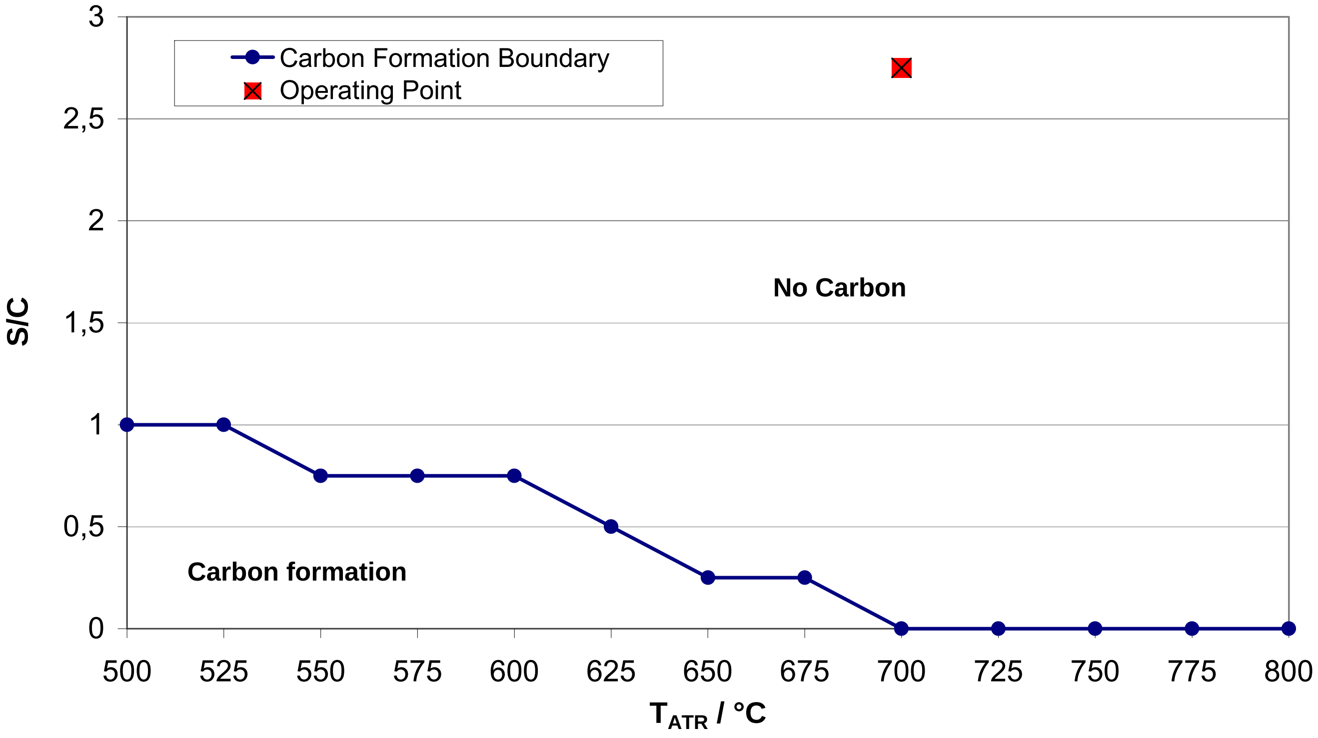
Equilibrium, T_{ATR} = 700 °C, S/C = 2.75



Equilibrium, T_{ATR} = 700 °C, O_2/C = 0.40

Process Simulation

Thermodynamic Potential of Carbon Formation

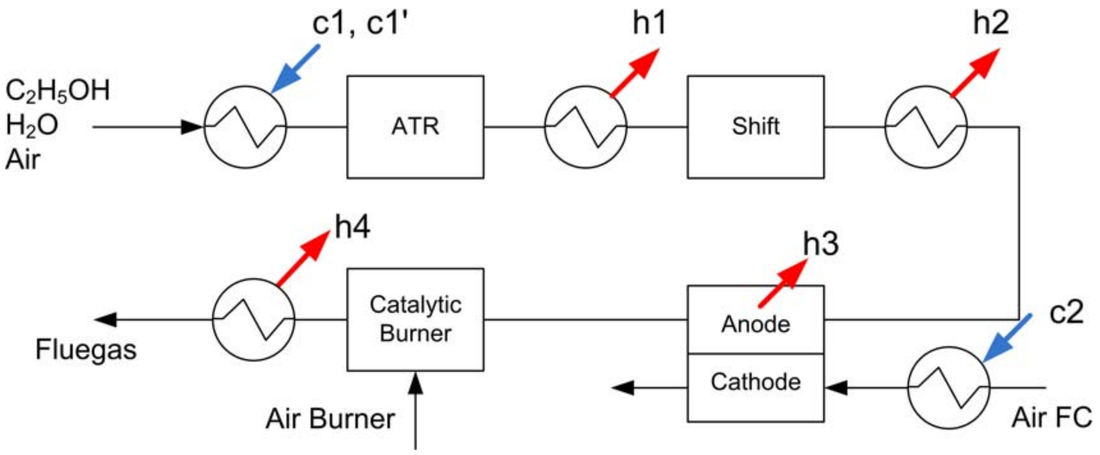


Carbon formation boundaries of EtOH reforming ($O_2/C = 0.4$)

Aspen settings for solid carbon

Parameter	**Setting**
Method	IDEAL
Stream Class	Mix CISLD
Reactor type	Gibbs-reactor (possible products gas phase **&** pure solid)
Consideration of carbon formation by homogeneous gas phase reaction	

Heat Integration Analysis



Approach

- Basic operation point
- Simulation results (heat streams, temperatures)
- Pinch Point Analysis

Main System Layout Targets

Minimization of

- Heat exchangers
- Heat exchangers with high thermal stress (> 500 °C)
- Heat exchangers with internal evaporation (mixing of educts)

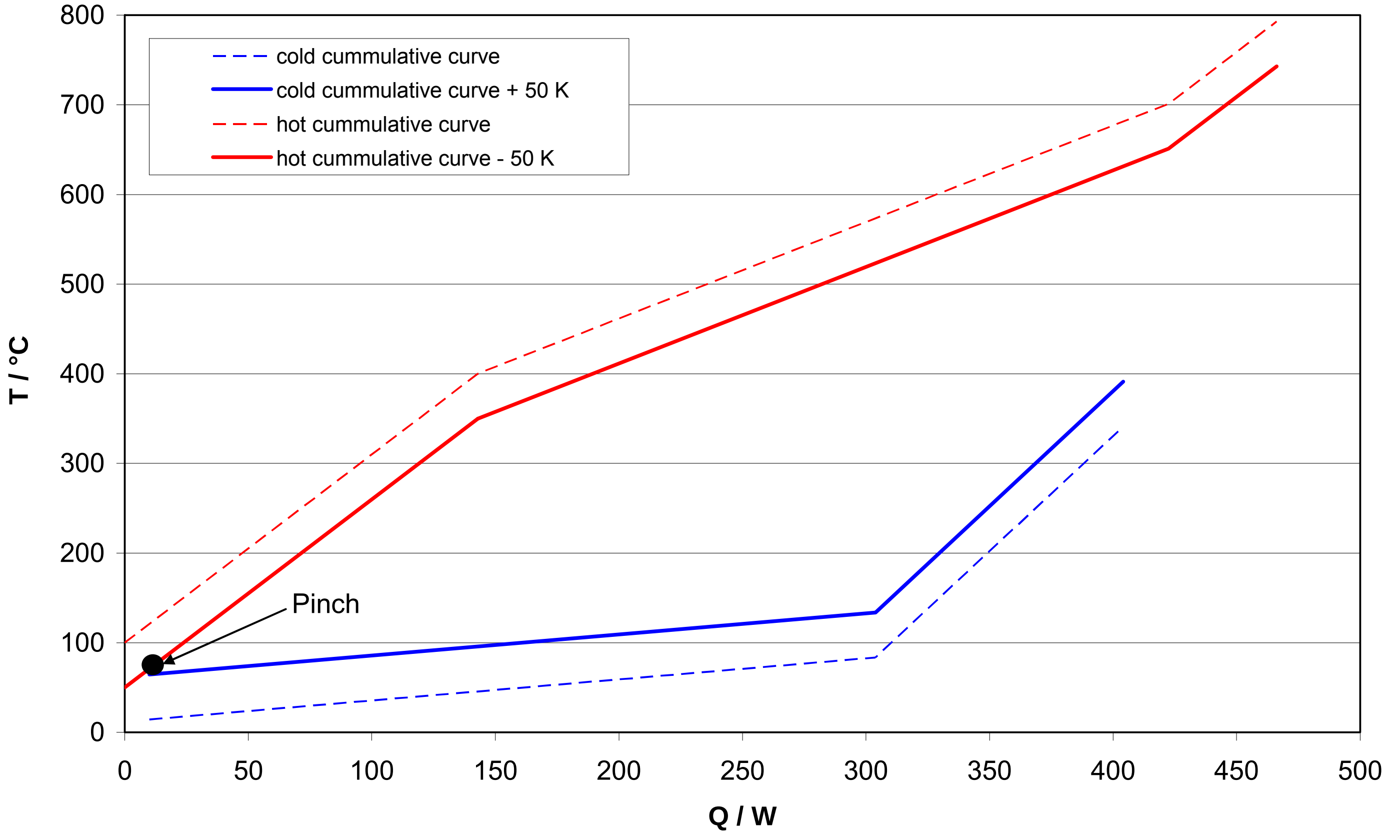
Maximization of

- Variance for setting of main temperatures
- Internal fulfilment of heat demand

Heat Integration Analysis

Pinch Point Analysis

for streams c1’, c1, h1 and h4



Cummulative curves of heat demand and supply

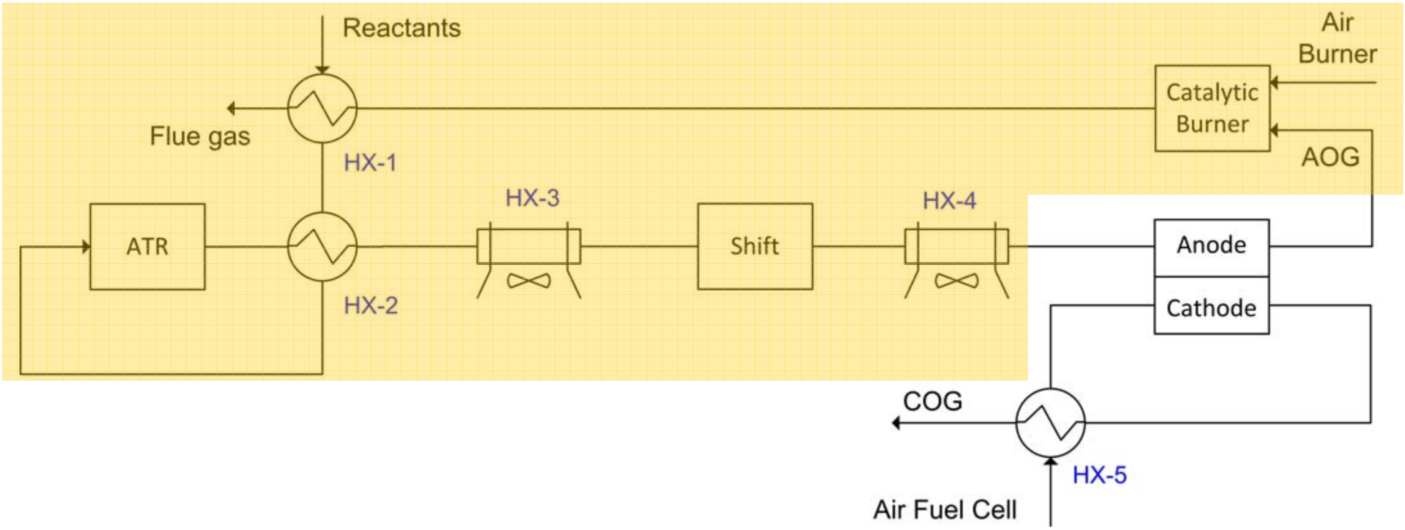
Stream	**T_{in} / °C**	**T_{out} / °C**	**Q / W**
c1’	14	84	294
c1	84	341	100
h1	793	100	-330
h4	700	400	-136

Heat Integration Analysis

Resulting System Flow Sheet

- Reactants (C_2H_5OH, H_2O, Air) completely premixed
- 4 heat exchangers (two coupled) for fuel processor
- $T_{Shift,in}$ and $T_{Anode,in}$ freely adjustable

Fuel processor boundary

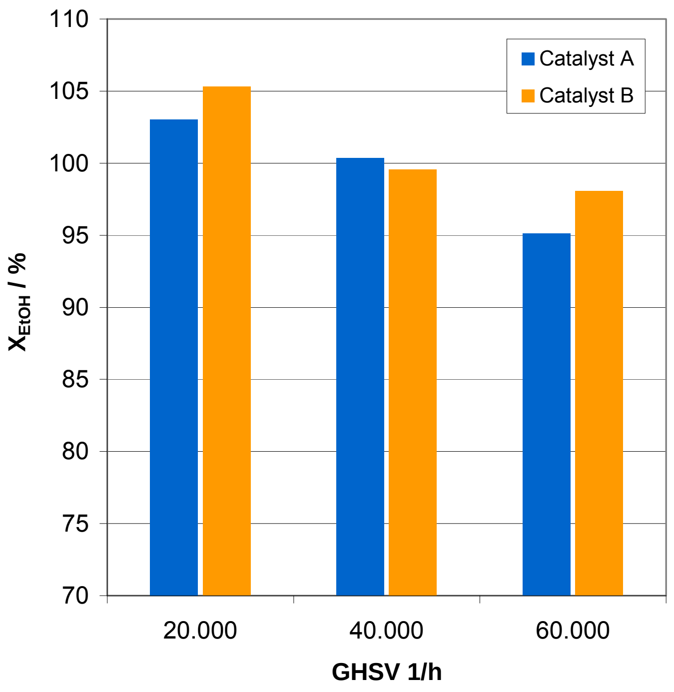


Flow Sheet Fuel Cell System

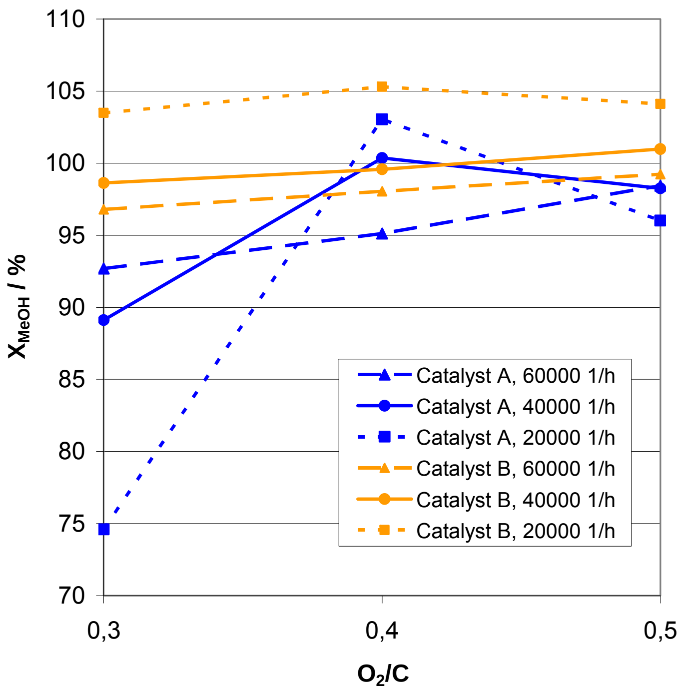
Catalyst Selection

Screening

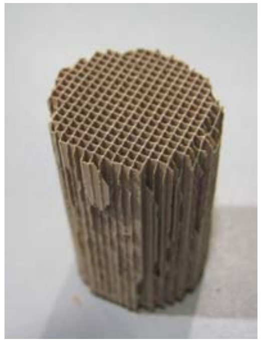
- Precious metal catalysts
- Ceramic monolith



EtOH conversion as function of GHSV (S/C = 2.75, O_2/C = 0.40)



EtOH conversion as function of O_2/C and GHSV (S/C = 2.75)



$$X_{EtOH} = \frac{\left(\dot{n}_{EtOH,out} - \dot{n}_{EtOH,in}\right)}{\dot{n}_{EtOH,in}}$$

$n_{EtOH,out}$ calculated by means of C-atom balance

Component Development

ATR

- Precious metal catalyst
- GHSV = 50,000 1/h
- Ceramic monolith (600 cpsi)
- Adiabatic reactor

Burner

- Precious metal catalyst
- GHSV = 25,000 1/h
- Ceramic monolith (600 cpsi)
- Electrical heater / glow plug (alternative)
- Evaporation zone with metal fibre structure
- Suitable for ethanol and AOG

Shift

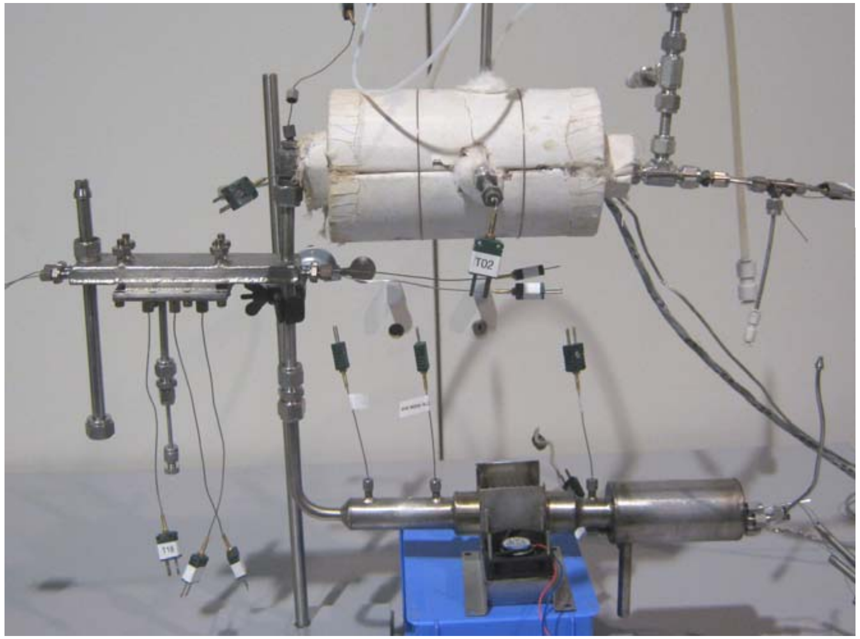
- Precious metal catalyst
- GHSV = 15,000 1/h
- Ceramic monolith (600 cpsi)
- Adiabatic reactor

Evaporator Superheater Unit

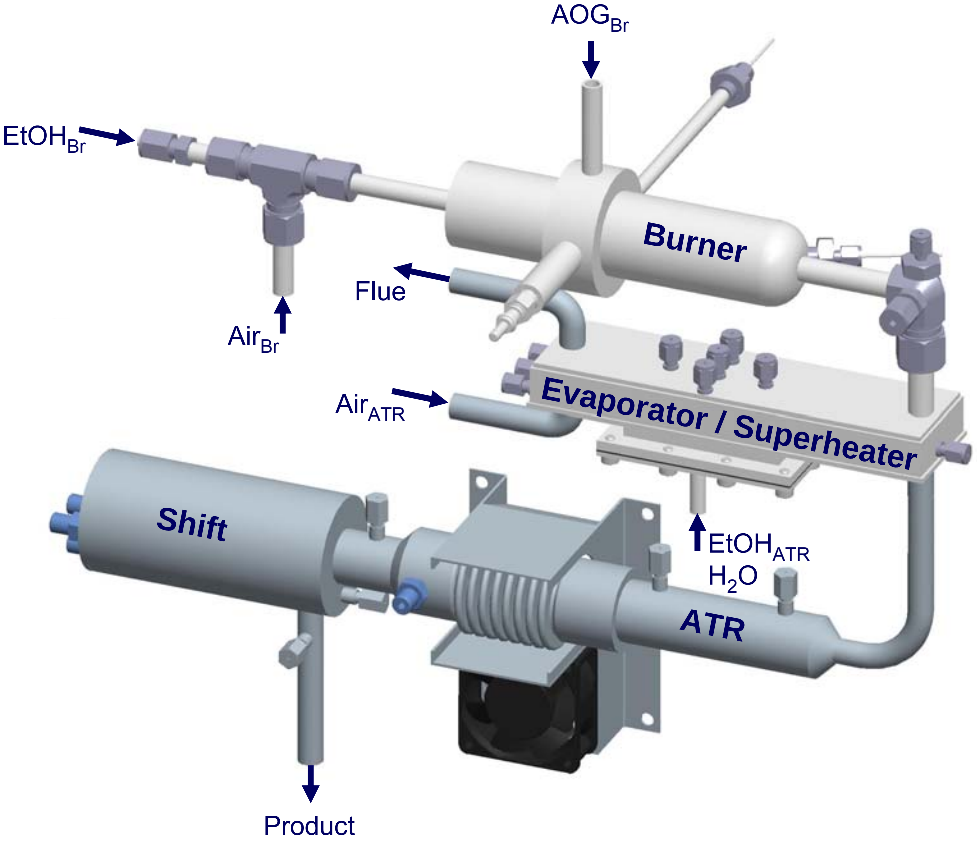
- Internal cooling fins
- Counter current flow
- Flue gas as heat source
- Evaporation zone with metal foam structure
- Superheating zone

Fuel Processor Demonstration

Laboratory Fuel Processor

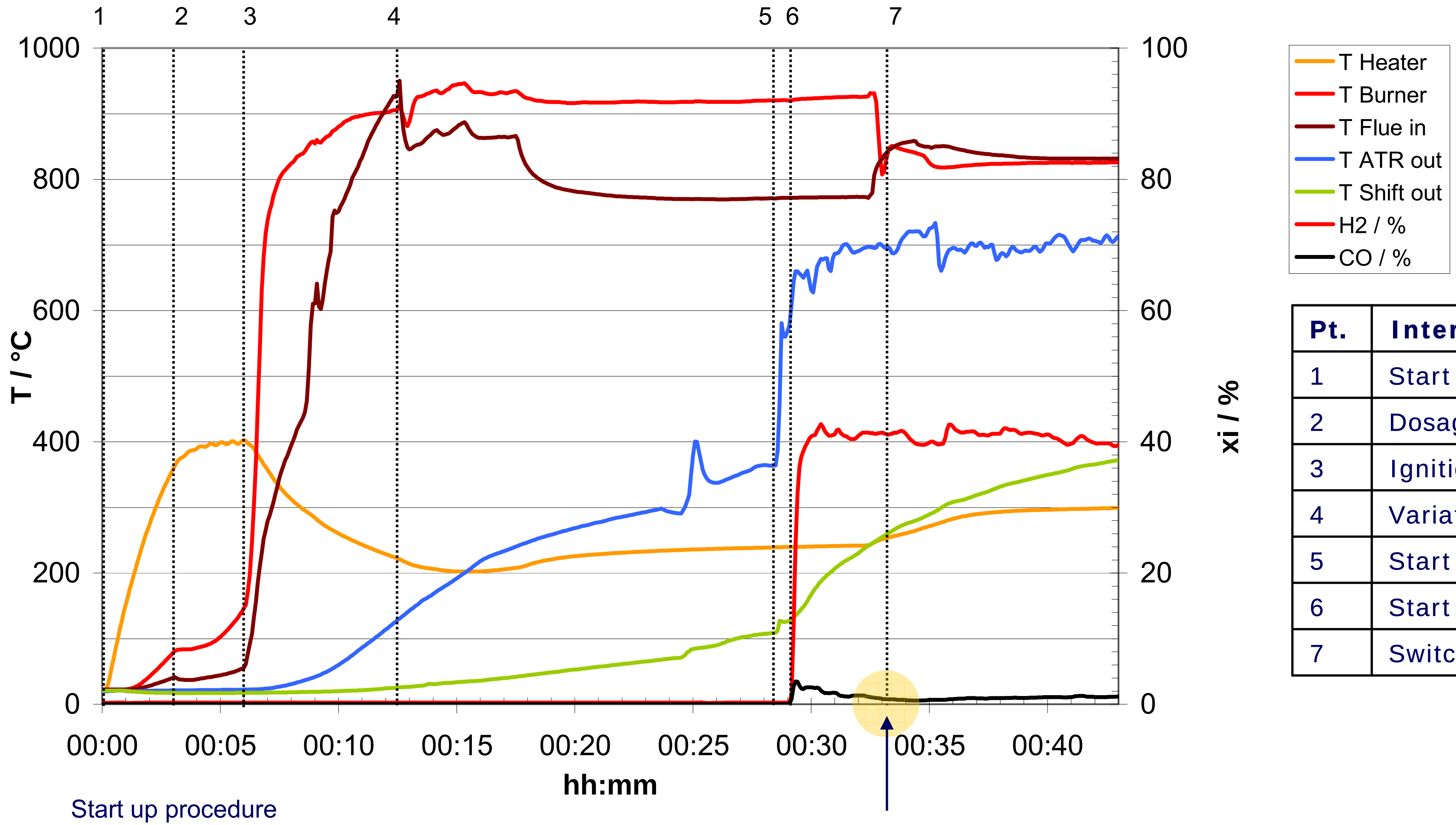


Fuel processor assembly equipped with thermocouples



Fuel Processor Demonstration

Start up process



Pt.	Interval
1	Start Heater
2	Dosage EtOH burner
3	Ignition burner
4	Variation load burner
5	Start H_2O dosage
6	Start reforming
7	Switch to AOG

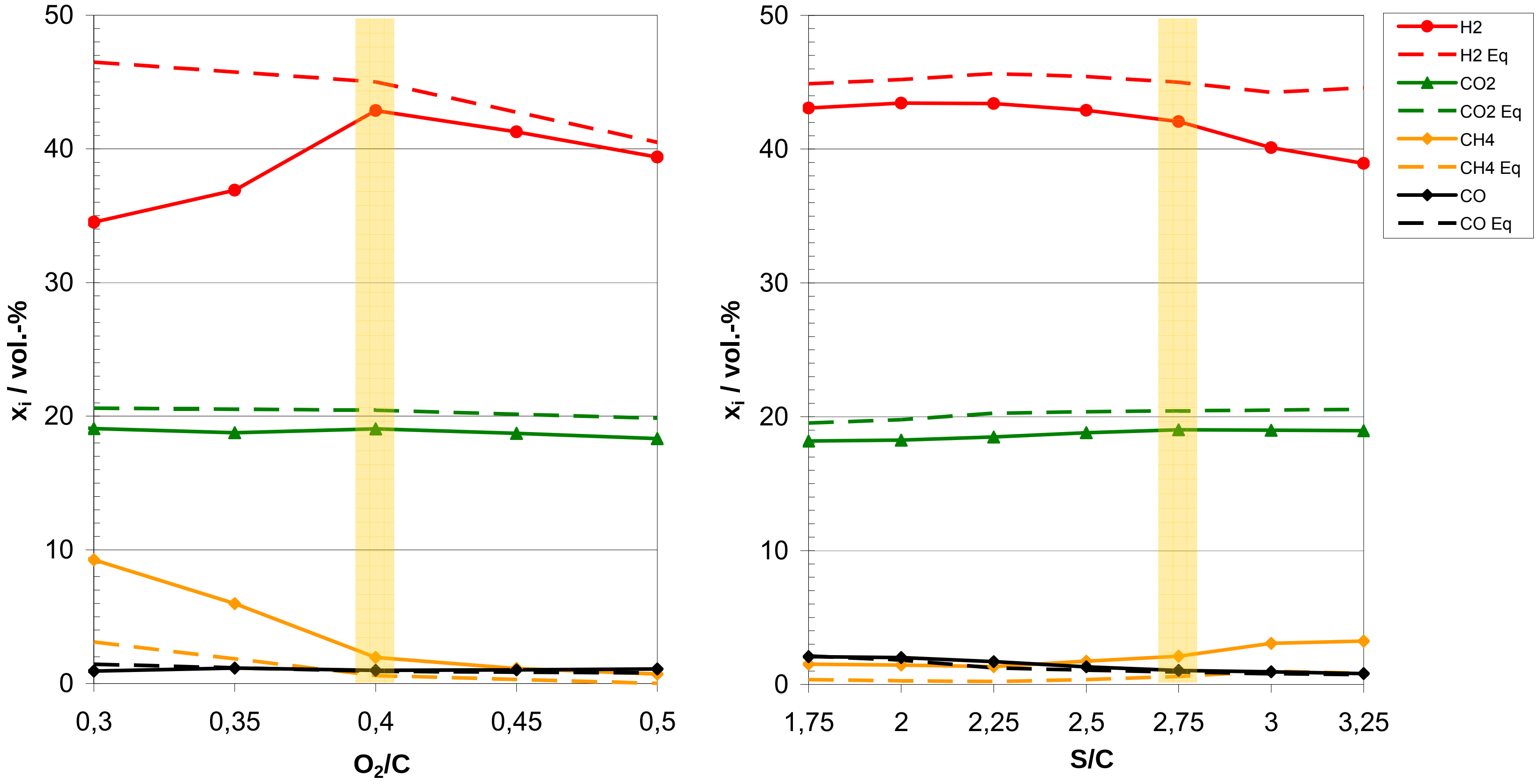
Start up procedure

$x_{CO} < 2$ %

Fuel Processor Demonstration

Gas composition shift out

- Variations of O_2/C and S/C



x_i as function of O_2/C (S/C = 2.75), measurement vs. equilibrium, dry

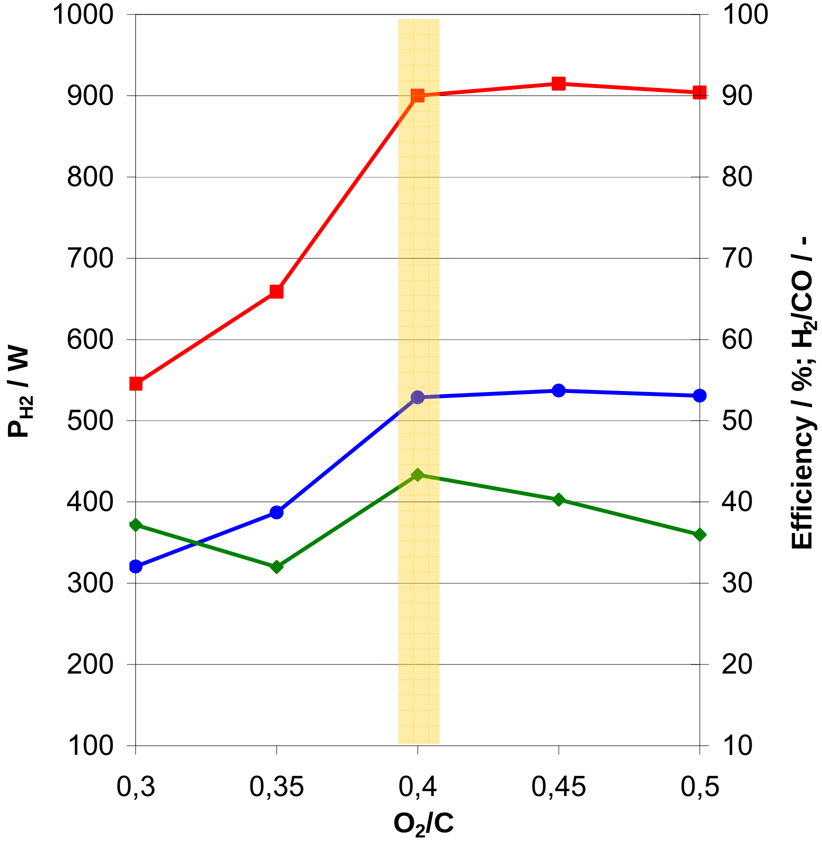
x_i as function of S/C (O_2/C = 0.4), measurement vs. equilibrium, dry

Fuel Processor Demonstration

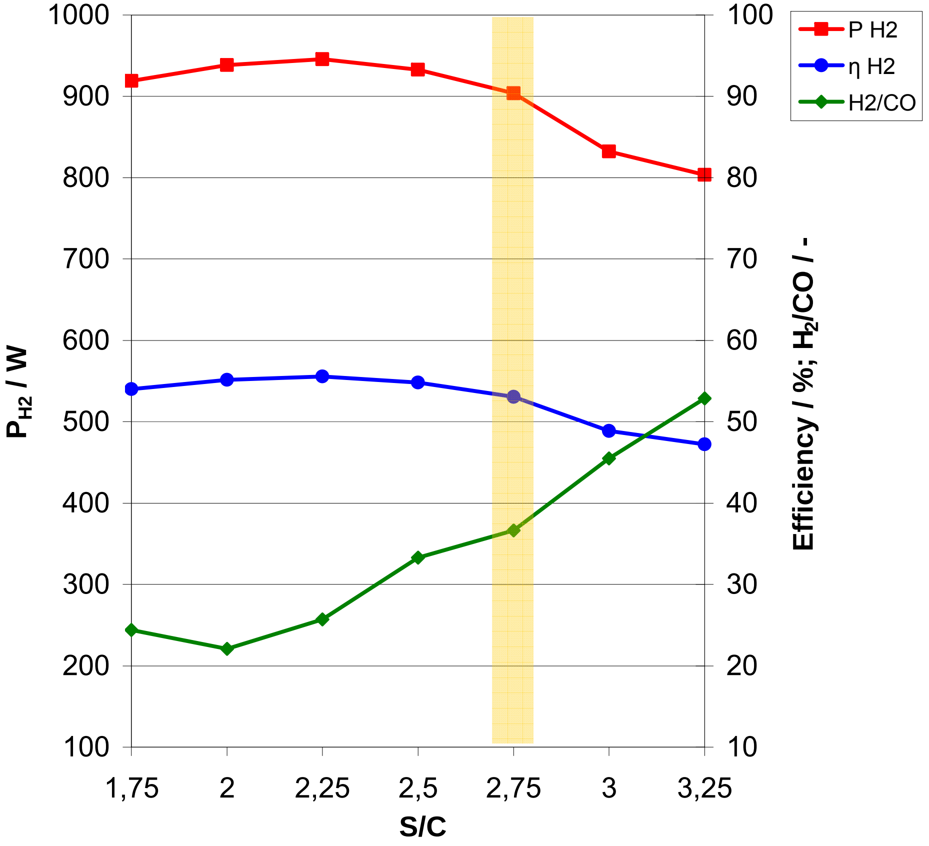
Power output / efficiency steady state

$$\eta_{H2} = \frac{P_{H2}}{P_{EtOH,ATR} + P_{Burn} + P_{AOG}}$$

P_{H2} calculated by means of N_2-atom balance



Performance data as function of O_2/C (S/C = 2.75)

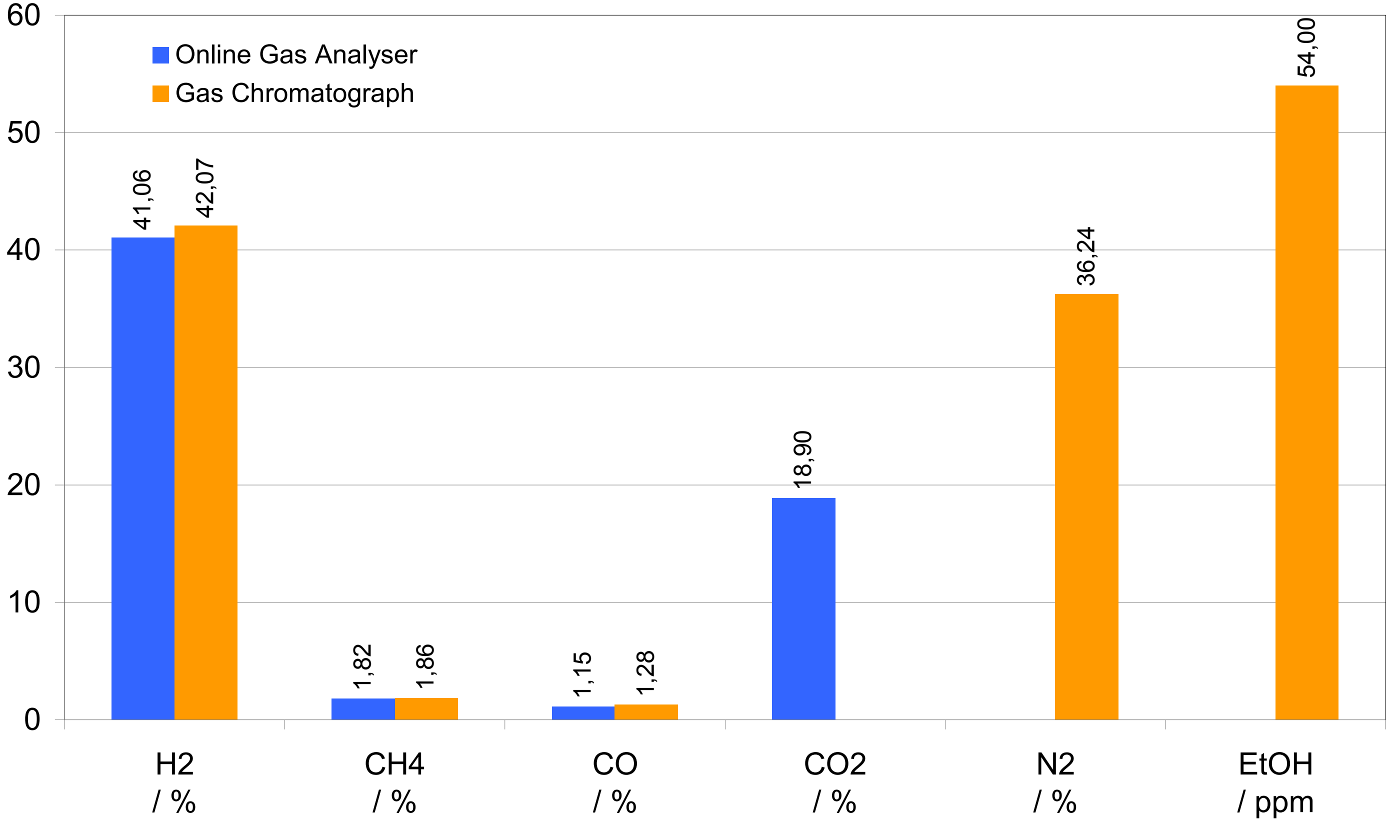


Performance date as function of S/C (O_2/C = 0.4)

Fuel Processor Demonstration

Gas composition shift out

- Comparison Online Gas Analyser (Rousemount Analytical NGA 2000, MLT 4) vs. Gas Chromatograph (Agilent Micro GC 3000A)



x_i of basic operation point (O_2/C, S/C = 2.75), online GA vs. GC, dry basis

Calibrated Components for GC

Comp.	Lower limit / %	Upper limit / %
He	0,356	1,663
H2	35,87	81,363
O2	0,051	20,5
N2	0,524	89,93
CH4	0,3195	88,2
CO	0,1972	49,3
Ethan	0,0104	14,0
Propan	0,0102	3,01
iso-Butan	0,0104	0,539
n-Butan	0,0099	0,803
N-pentan	0,0107	-
NH3	0,0487	1,044
N-Hexan	0,0107	-
C_2H_4O	0,0983	1,015
MeOH	0,165	-
EtOH	0,0103	0,098

Fuel Processor Demonstration

Development Status

Parameter	**Basic Operation Point**
m_{EtOH} / g/h	160
O_2/C / -	0.42
S/C / -	2.75
T_{ATR} / °C	650 – 700
T_{Shift} / °C	380 – 400
H_2 / %	42,0
CO / %	0,9
CO_2 / %	19,0
CH_4 / %	2,0
EtOH / ppm	54 (GC meas.)
N_2 / %	36,1 (calculated)

Performance Data	**Status**	**Target**
Power output P_{H2} / W	900	600 - 1500
Efficiency η_{H2} / %	55	70
X_{EtOH} ATR / % (calculated)	~ 100	100
Gasquality, CO / %	1.0 – 1.5	< 1.0
Start up time / Min	~ 30	< 15
Pressure drop / mbar	15 - 20	20

Outlook

Issues to be addressed

- Long term test
- Reduction start up time
- Optimization evaporator
- Enhancing efficiency
- Optimization temperature control shift
- Coupling with HT-PEM fuel cell

Acknowledgements

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