Multifunctional Microstructured Reactors as Fuel Processor Components for Mobile Fuel Cell Systems

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IMM- Centre of Excellence in Microtechnology

We are...

...an application oriented R&D institute

...some 150 employees with mainly academic background

...a non-profit company owned by the federal state of Rheinland-Pfalz

Main Fields of R&D work:	**<u>Focus on Chemical Process Technology and Microfluidics</u>, Micro Precision Engineering Thin Film Technology**
Energy echnology and: Catalysis Department (15 people)	**Development of Complete Micro-structured Fuel Processors (Reactor Design & Construction, Development of Catalyst Coatings, Catalyst / Reactor / System Testing), Liquid hydrogen technology**

Motivation for the Application of Microtechnology in Fuel Cells / Fuel Processors

- **Improved heat and mass transfer**
- **Catalyst coating techniques similar to automotive exhaust clean-up**
- **Low pressure drop (laminar flow regime)**
- **Systemintegration – integrated heat-exchanger reactor design**
- **Compactness – miniaturised heat-exchangers and evaporators**
- **Improvement of system dynamics – fast start-up**
- **Safety issues (microchannels act as flame arresters)**

Kolb G., Hessel V, Review
Chem. Eng. J. 98, 1-38 (2004)

Hessel V., Löwe H., Müller, A., Kolb G., 2005
'Chemical Micro Process Engineering-
Processing, Applications and Plants', Wiley, Weinheim
p.281 ff.

The Three Different Types of Reforming – Example Octane

Octane steam reforming (705°C):

$C_8H_{18} + 8\ H_2O \rightarrow 17\ H_2 + 8\ CO \quad \Delta H_{978} = +\ 1355\ kJ/mol$

Autothermal (= Oxydative Steam) Reforming of Octane (705°C):

$3\ C_8H_{18} + 8\ O_2 + 8\ H_2O \rightarrow 35\ H_2 + 24\ CO \quad \Delta H_{978} \approx +\ 124\ kJ/mol$

Partial Oxidation of Octane (705°C)

$C_8H_{18} + 4\ O_2 \rightarrow 9\ H_2 + 8\ CO \quad \Delta H_{978} \approx -\ 615\ kJ/mol$

Side Reactions of Reforming

Water-gas Shift (705°C)

$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H_{978} \approx -34$ kJ/mol

Methanation (705°C):

$CO + 3\,H_2 \rightarrow CH_4 + H_2O$ $\Delta H_{978} \approx -229$ kJ/mol

Catalytic Reformate Purification (CO-clean-up)

10% - 1% CO: Water Gas Shift (WGS):

$$CO + H_2O \rightarrow CO_2 + H_2$$

(Methanation: $CO + 3\ H_2 \rightarrow CH_4 + H_2O$)

≤ 1% CO: Preferential (or Selective) Oxidation (PrOx):

$$2\ CO + O_2 \rightarrow 2\ CO_2$$

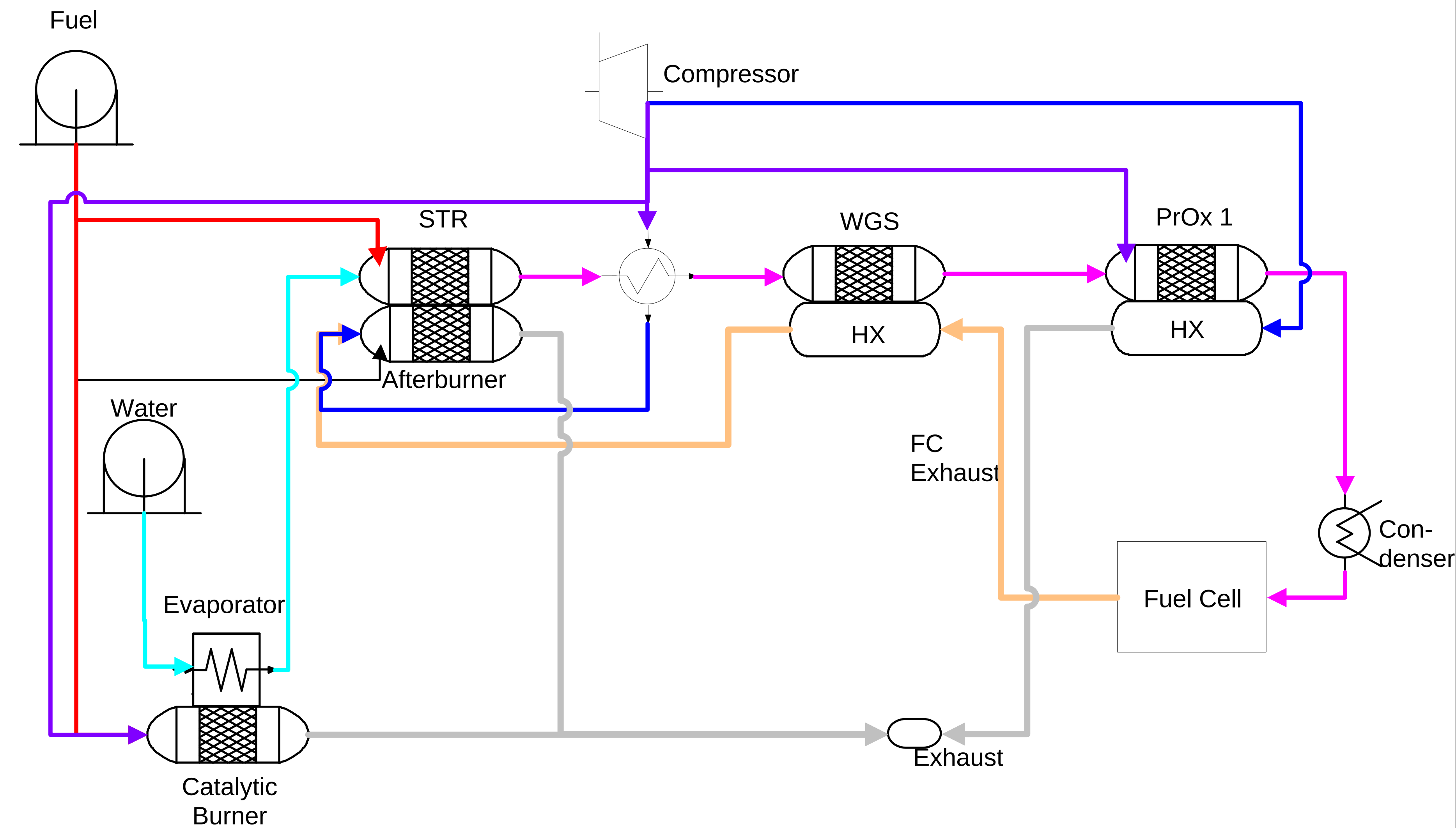
(Unselective Hydrogen Oxidation:

$$H_2 + O_2 \rightarrow H_2O)$$

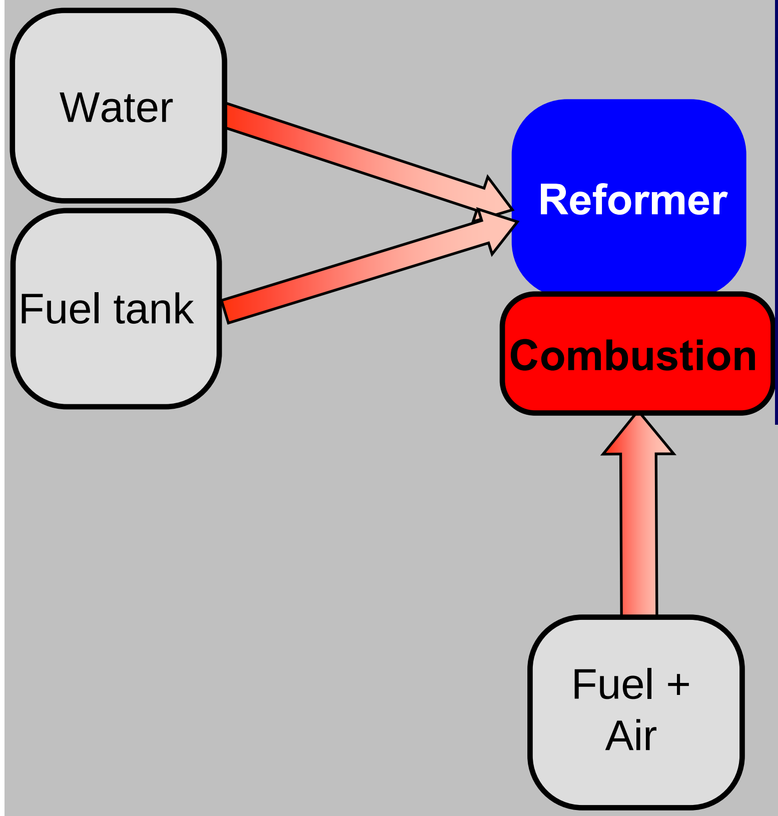
≤ 1% CO: Methanation:

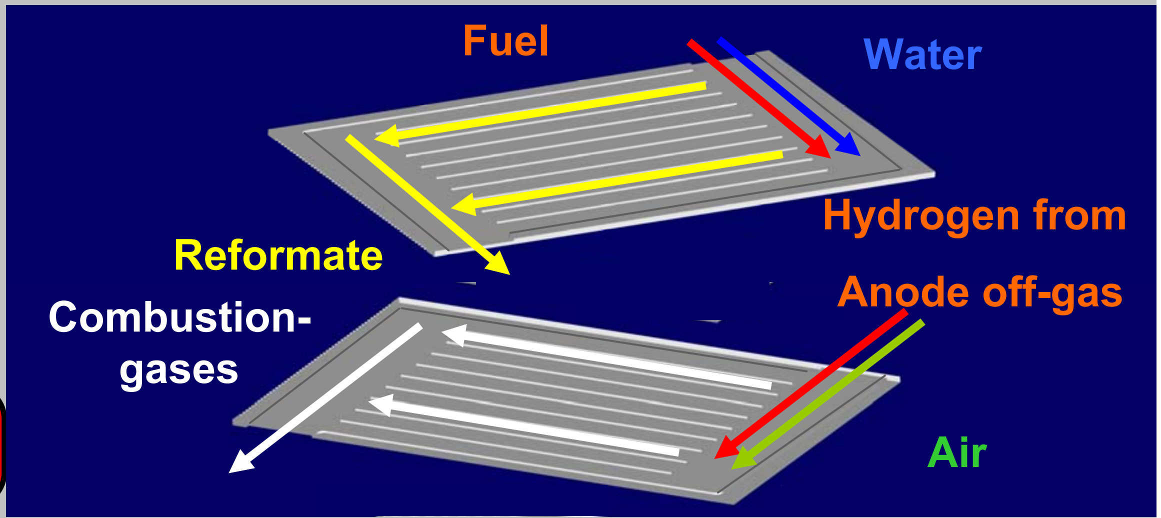
$$CO + 3\ H_2 \rightarrow CH_4 + H_2O$$

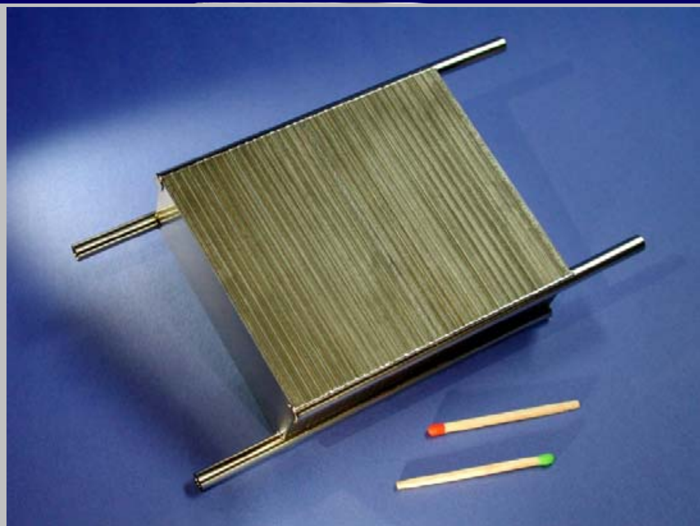
Fuel Processing in Microstructured Reactors – Exemplary Process Scheme: Steam Reforming



Steam Reforming in Integrated Microstructured Heat-Exchanger Reactors

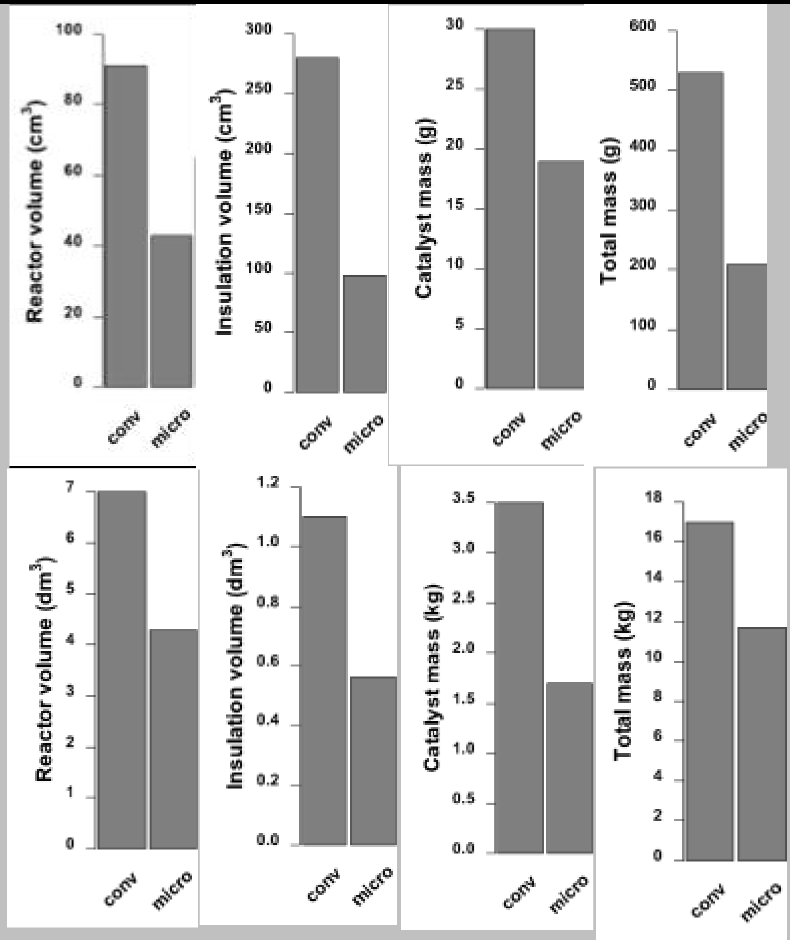






Demonstrated for Methanol (A.Renken et al.; T < 300°C), LPG, Ethanol and Diesel (IMM; T ≥ 750°C)

Comparison between conventional fixed bed technology (conv) and a combined micro-structured plate heat-exchanger/ catalytic afterburner (micro)



100 W

5 kW

E.R. Delsman, B.J.P.F. Laarhoven, M.H.J.M. de Croon, G.J. Kramer, J.C. Schouten,
Comparison between conventional fixed-bed and microreactor technology for a portable hydrogen production case,
Chem. Eng. Res. Design 83 (A9) (2005) 1063-1075

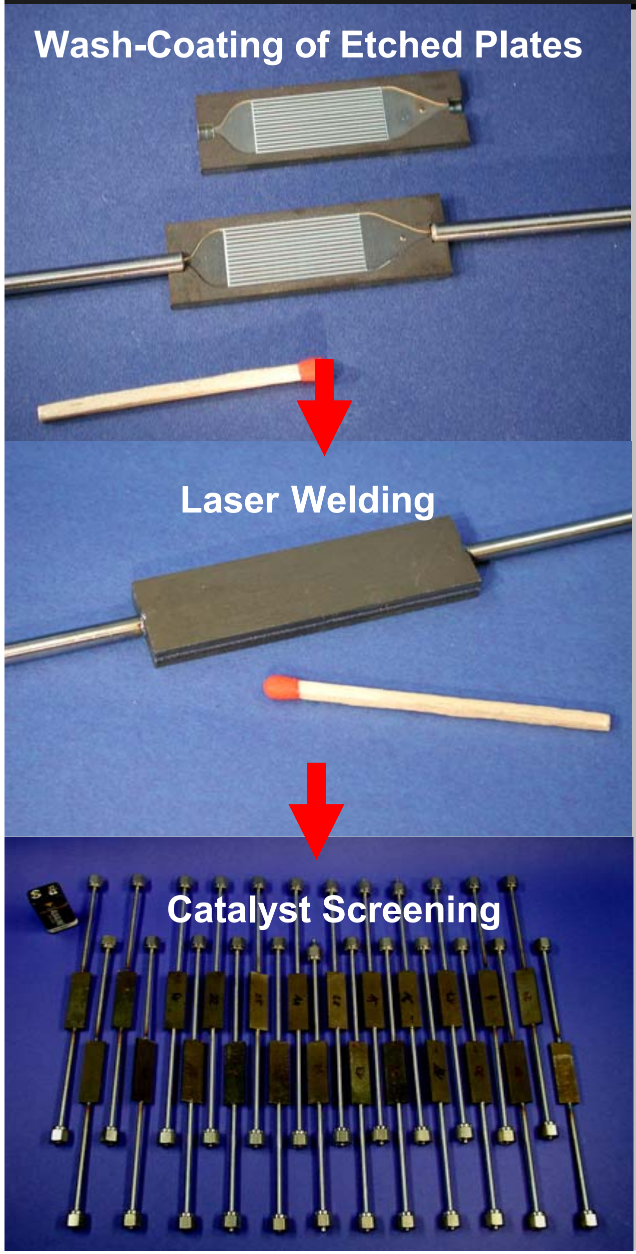
Requirements for Catalyst Coating Performance

Activity (100% conversion)

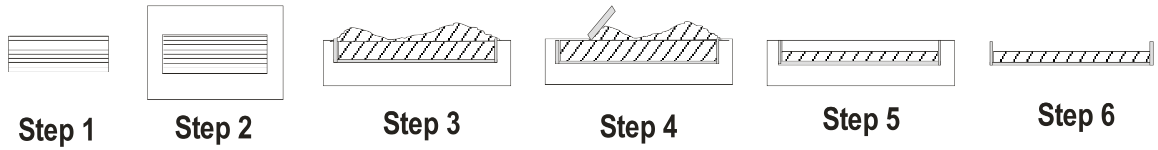
Selectivity (no other by-products than CO and CH_4)

Durability (at least 1,000 hours)

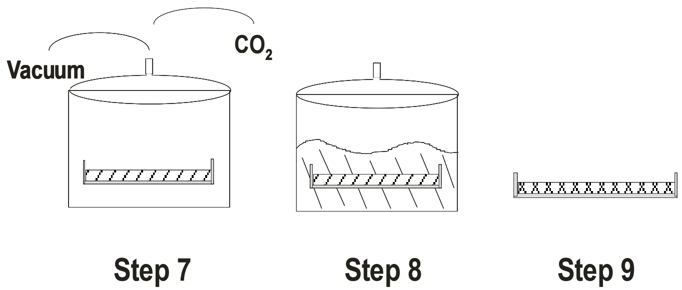
Sandwich Reactor Applied for Catalyst Screening and Testing



Process A: washcoating/wet impregnation



Suspension: 20wt.% Al2O3; 5wt.% PVA; 1wt.% acetic acid



Step 1: cleaning & thermal pre-treatment
Step 2: positioning & masking
Step 3: channel filling with suspension
Step 4: wiping-off excess suspension
Step 5: drying
Step 6: calcination
Step 7: pre-treatment of porous wash-coats (evacuation & pore filling with CO_2)
Step 8: impregnation
Step 9: drying & calcination

Process B: washcoating of commercially available catalyst powders (step 1 - 6)

Channel Dimensions: length 41 mm, width 500 µm, depth 2 x 400 µm

14 Channels per plate

Zapf, R.; Becker-Willinger, C.; Berresheim, K.; Holz, H.; Gnaser, H.; Hessel, V.; Kolb, G.; Löb, P.; Pannwitt, A.-K.; Ziogas, A., *Trans IChemE* A **81** (2003) 721-729

R. Zapf et al., CET, (2006), 29, 1509

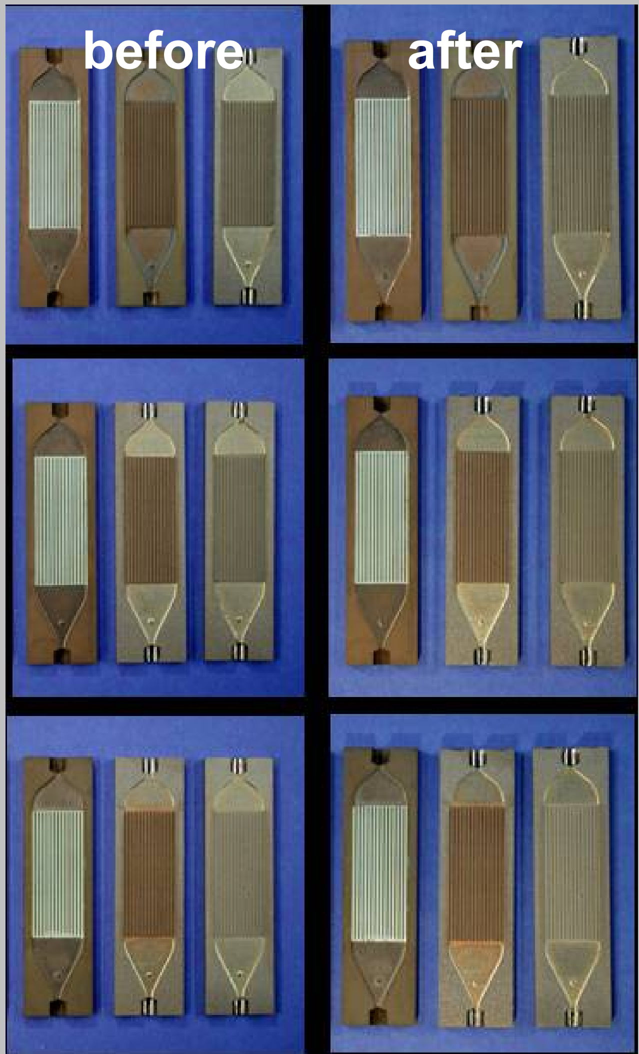
Catalyst Coating Stability Tests

Temperature Cycling to 750°C

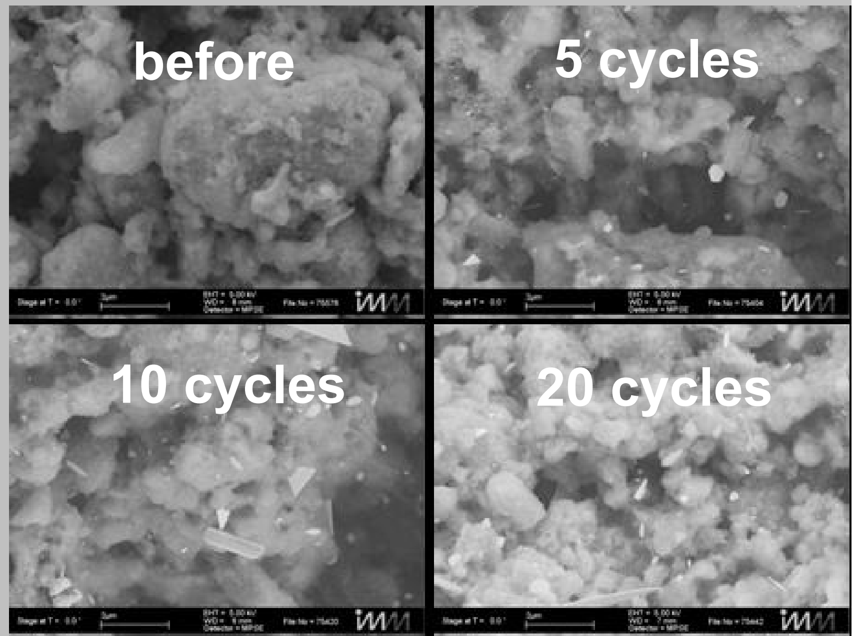
5 cycles

10 cycles

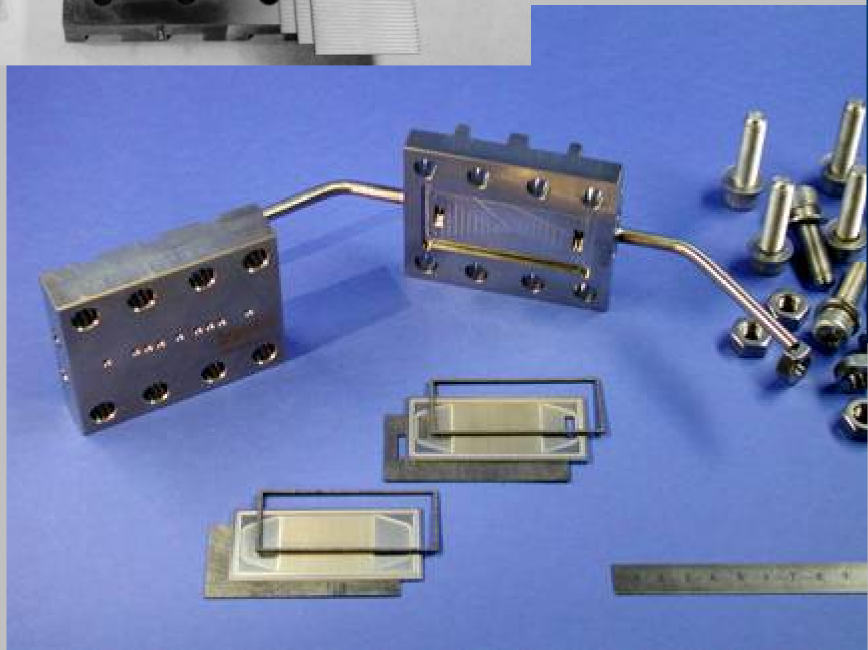
20 cycles

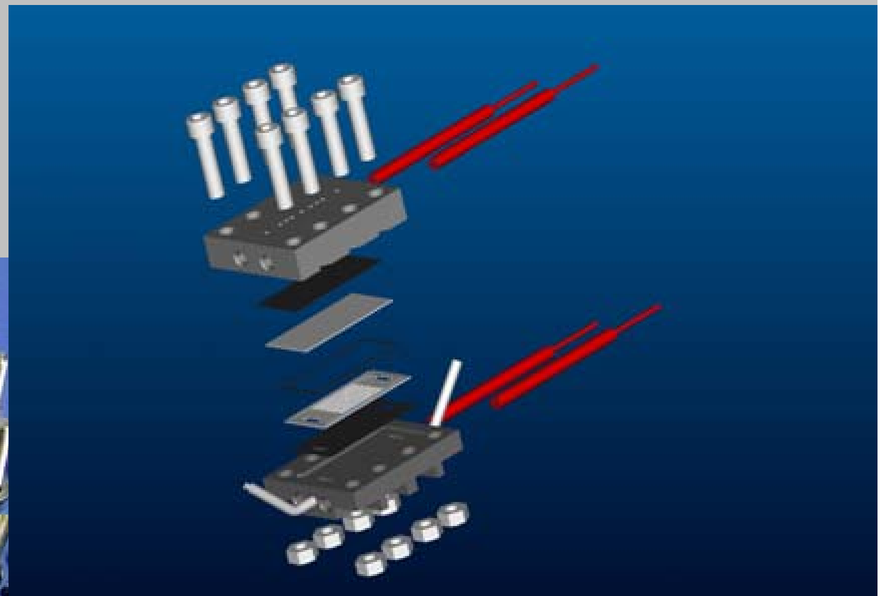


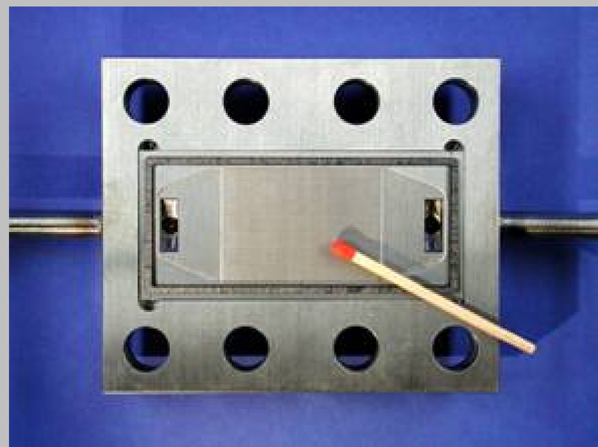
Drop Test:



Test Reactors



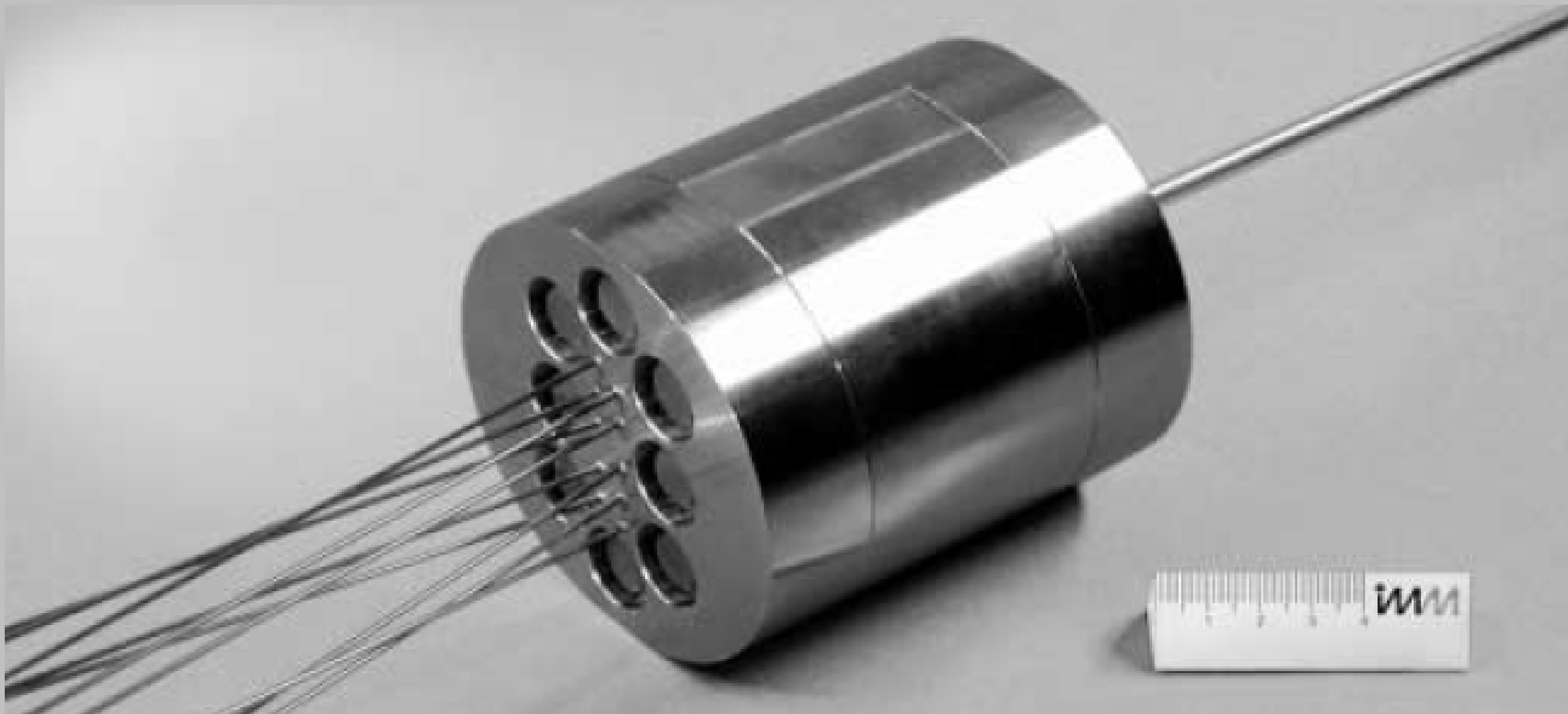




Too bulky for practical system,

mass of housing more than 95% of plate stack

Screening Reactor (up to 800°C; 100 bar) (SOLEMIO)



Methanol Steam Reforming

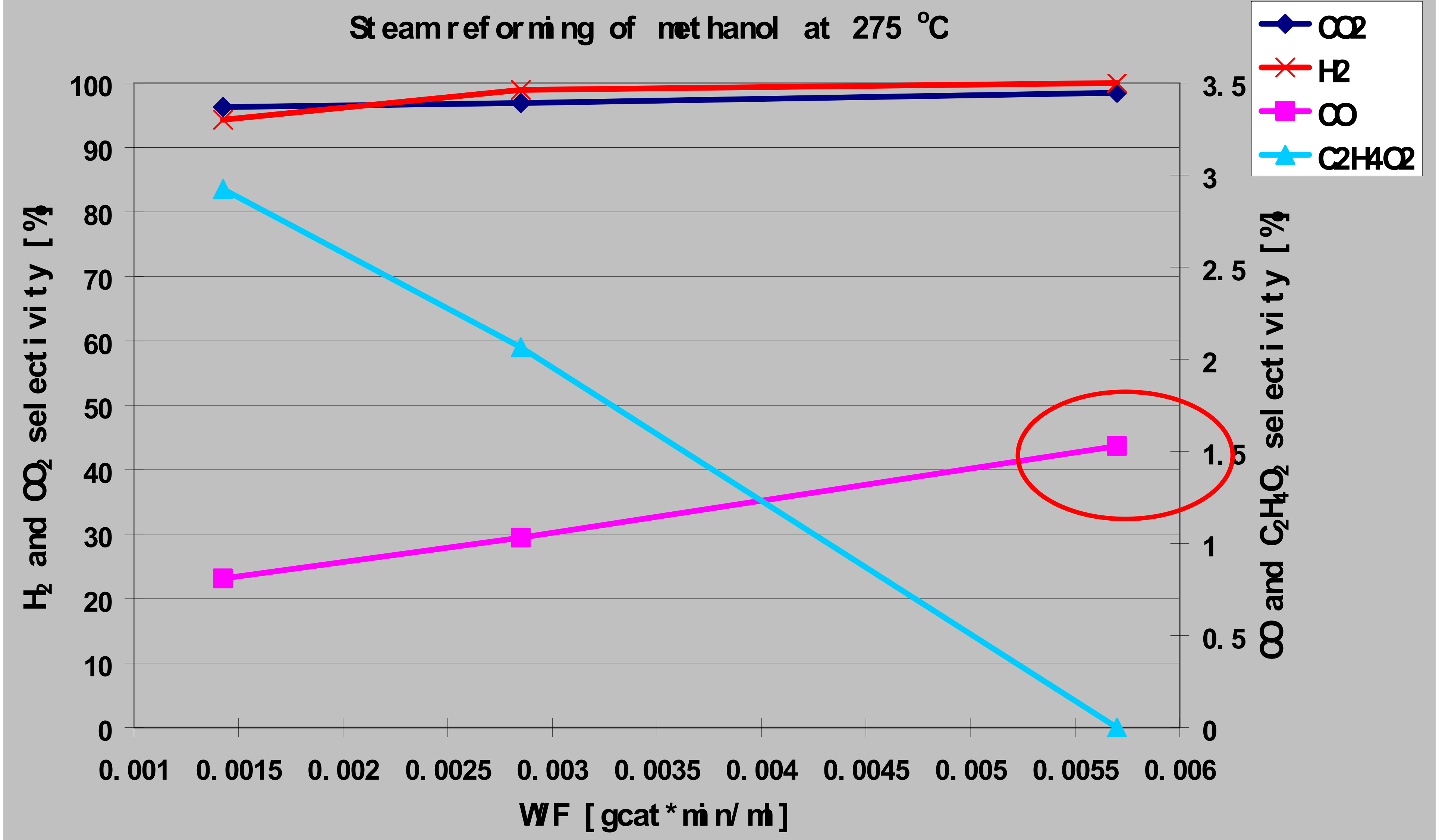
Application:

Small Scale Power Generation

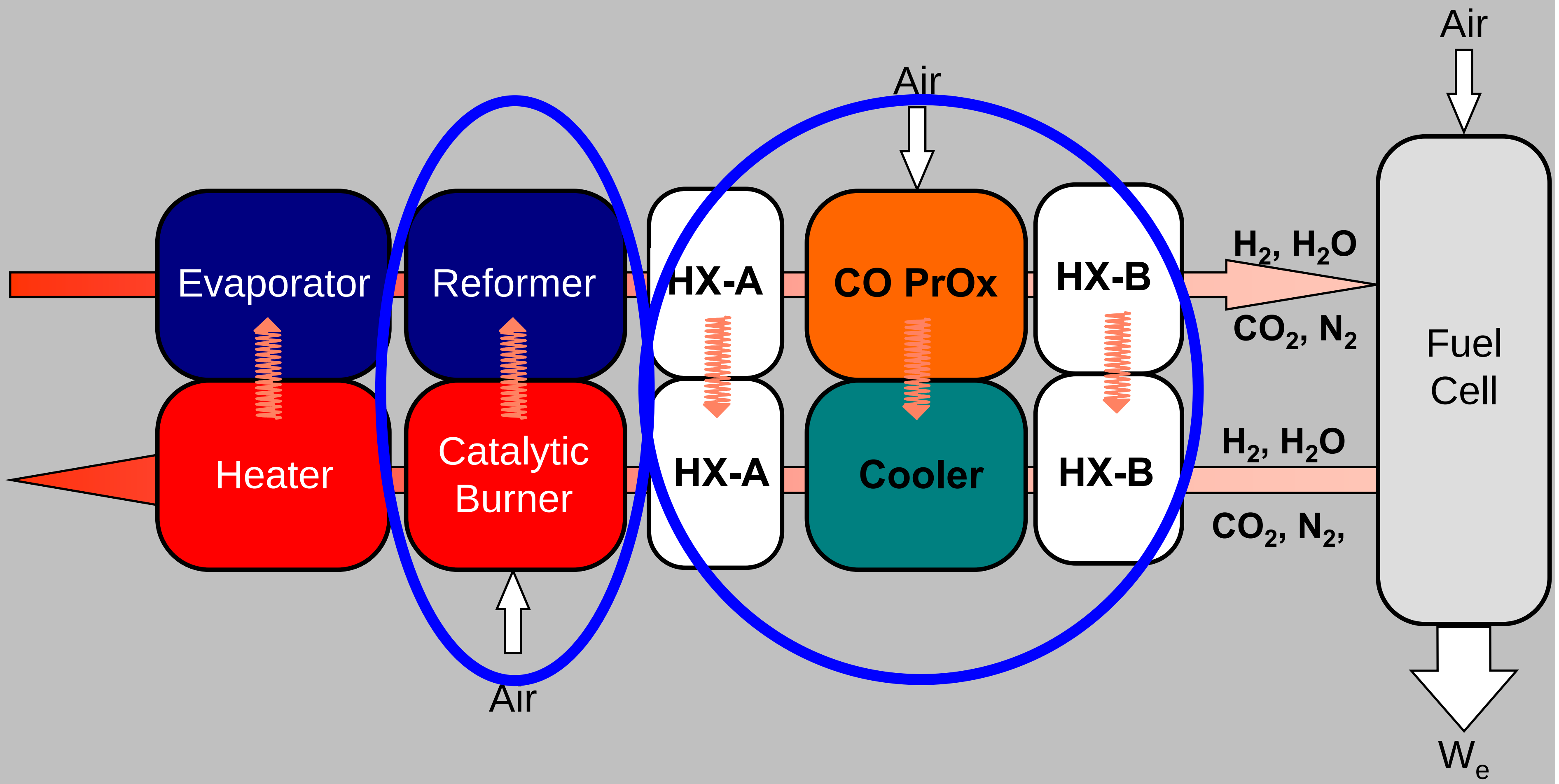
<100 W_{el} Lap-Top Charger

Y. Men, et al. Catal. Com. (5) (2004) 671-675. Y. Men et al. Appl. Catal. A 277 (2004) 83-90.
Y. Men et al. Int. J. Hydrogen Energy (2007) accepted for publication.

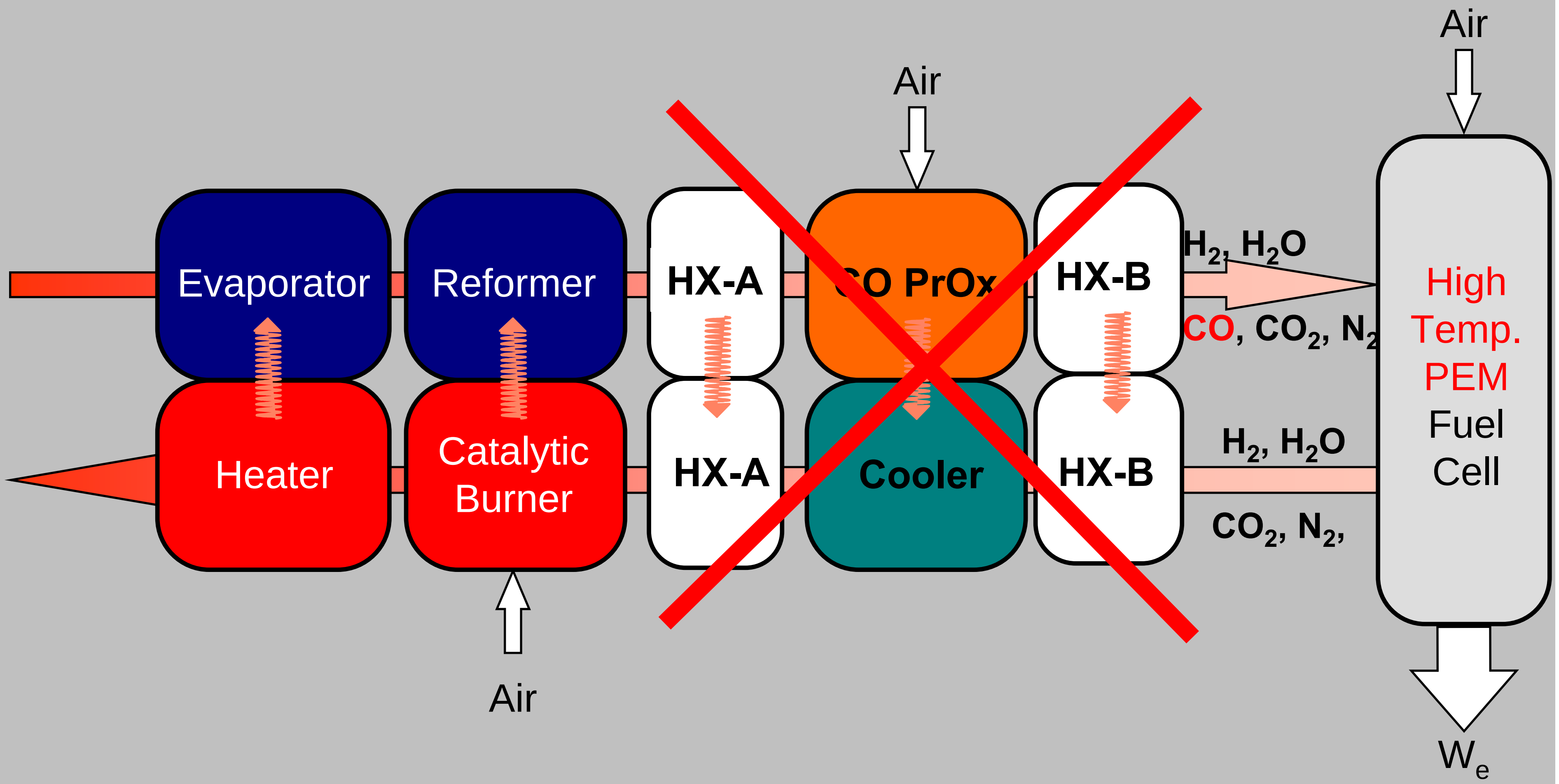
Complete Microstructured Fuel Processor for Methanol Steam Reforming – Running for 5 Days at Hannover Fair 2005



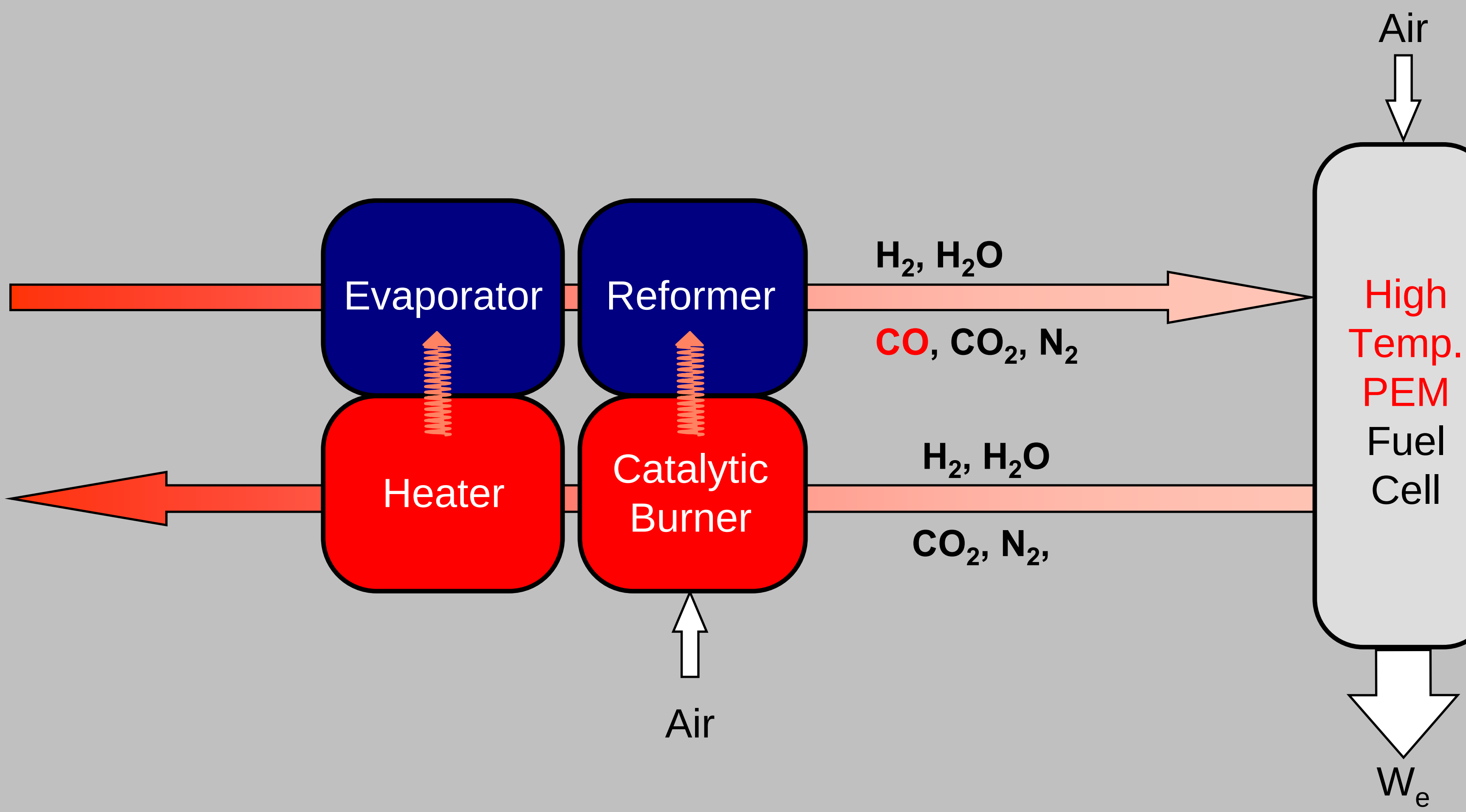
SYSTEM INTEGRATION – METHANOL REFORMING (100 W)



SYSTEM INTEGRATION – METHANOL REFORMING (100 W)



SYSTEM INTEGRATION – METHANOL REFORMING (≤100 W)



The smaller the system, the simpler it has to be!

Ethanol Steam Reforming

Application:

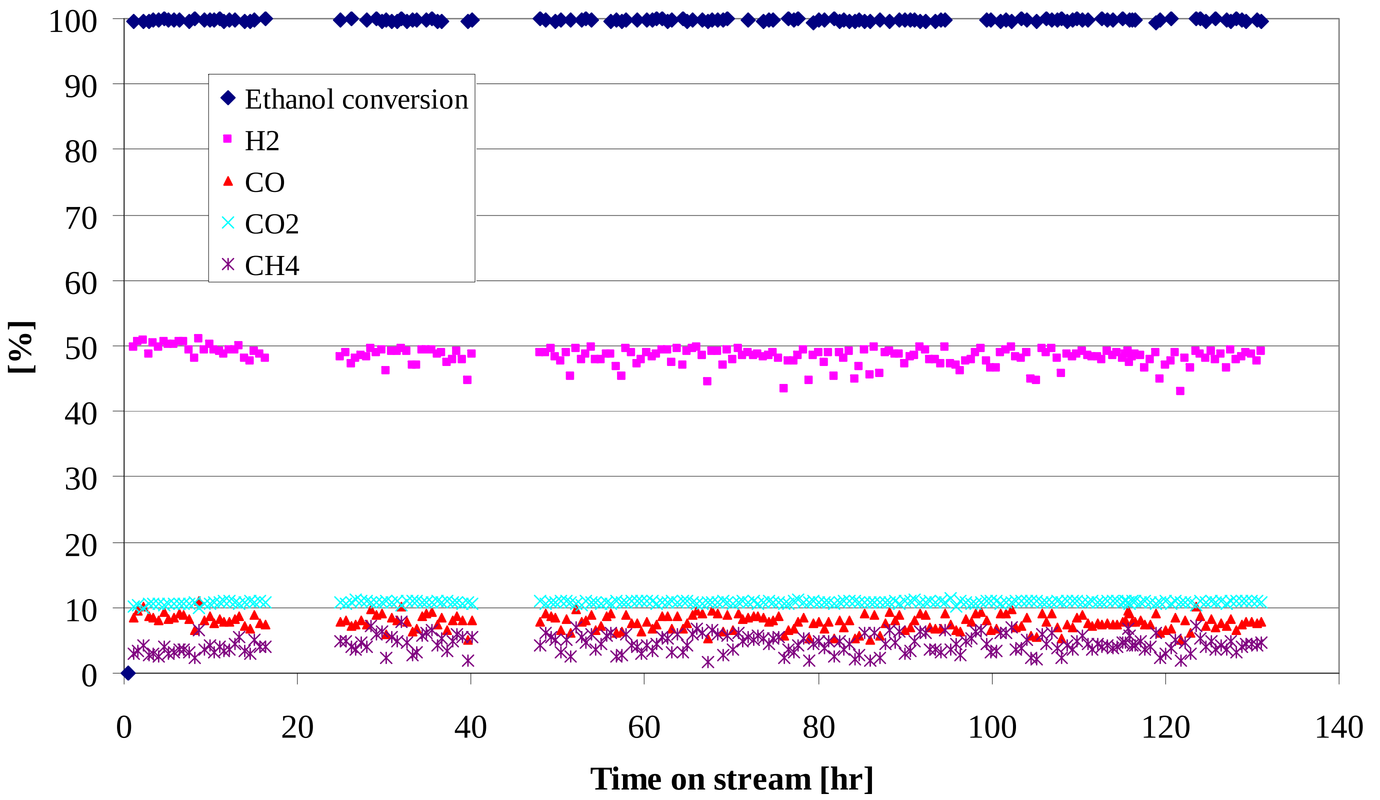
Portable Power Supply

< 1 kW_{el}

Summary of Tested Catalysts

Catalysts	Metal loading [wt.-%]	Surface area [m^2/g]
Co/Al_2O_3	10	161
Co/SiO_2	10	165
Co/MgO	10	177
Co/ZnO	10	12
Ni/Al_2O_3	10	156
Ni/MgO	10	70
Rh/Al_2O_3	5	149
Rh/MgO	5	58
Ru/Al_2O_3	5	149
$Rh/Ni/Al_2O_3$	5/10	125
$Rh/Ni/CeO_2/Al_2O_3$	5/10/15	170
$Rh/Co/Al_2O_3$	5/10/15	164

Durability Test of Rh/Co/Al_2O_3 Catalysts



➢ **Stable for 130 hrs 650 °C**

Integrated Ethanol Steam Reformer/ Catalytic Burner (250 W)

Propane(LPG) Steam Reforming

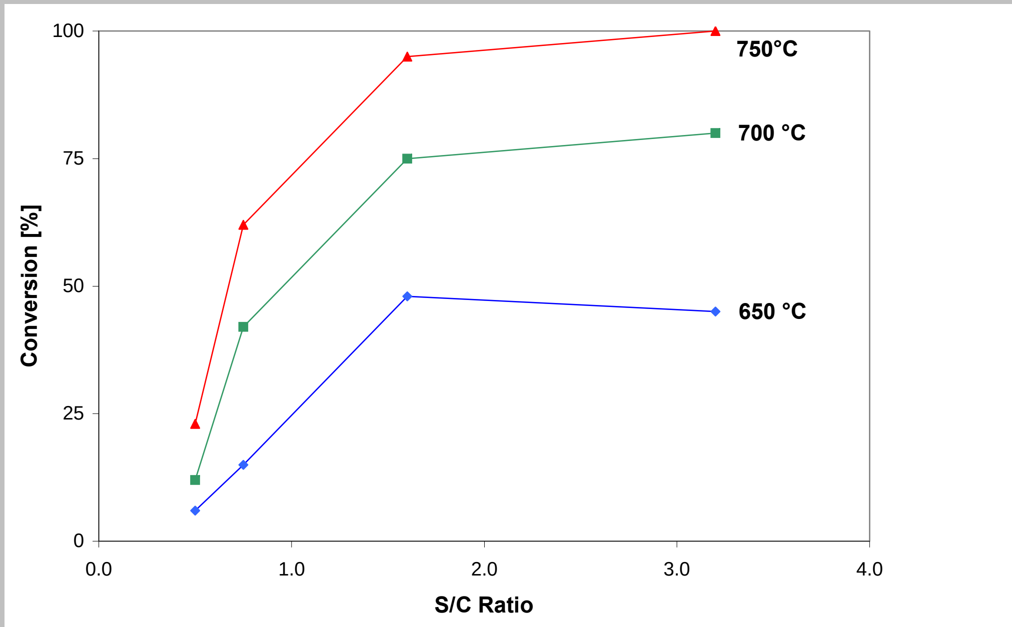
Application:

Power Supply for Caravans and Yachts

< 1 kW_{el}

Kolb, G.; Zapf, R.; Hessel, V.; Löwe, H., 2004, Appl. Cat. A: General 277, 155.

Propane Steam Reforming in Microstructured Reactors



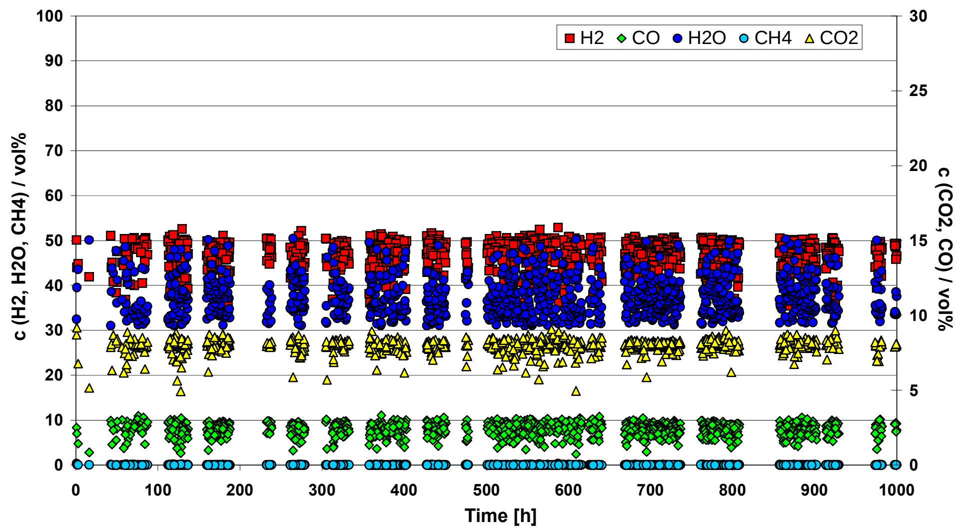
Conditions of Testing

Catalyst:	**4 wt.% Rh 4 wt.% Pt**
	24 wt.% CeO_2
	on γ-alumina
Feed:	**80 Vol.% N_2;**
	20 Vol.% C_3H_8/H_2O
$WHSV_{feed}$:	**375 Ndm³/(h g_{cat})**
Pressure:	**Ambient**

1000 Hours Durability Testing

Catalyst: Proprietary

Feed:	**C_3H_8/H_2O**
S/C:	**4.0**
$WHSV_{feed}$:	**375 Ndm³/(h g_{cat})**
Temp.:	**750°C**
Pressure:	**Ambient**



Application: The TRUMA Fuel Cell System – Joint Development

Truma Geraetetechnik GmbH & Co. KG

www.truma.de

Europe‘s largest manufacturer in the field of liquid gas heaters for leisure vehicles and boats.

Fuel Processor from IMM

250 W,

Fuel: LPG

Truma received the f-cell award in silver 2007

Truma VeGA converts LPG into electricity!

“Truma is developing a fuel cell system that is specifically for the recreational vehicle area. With a view to the environment and efficient usage, we have put our faith in liquid gas as a fuel supply.“

Octane Autothermal Reforming

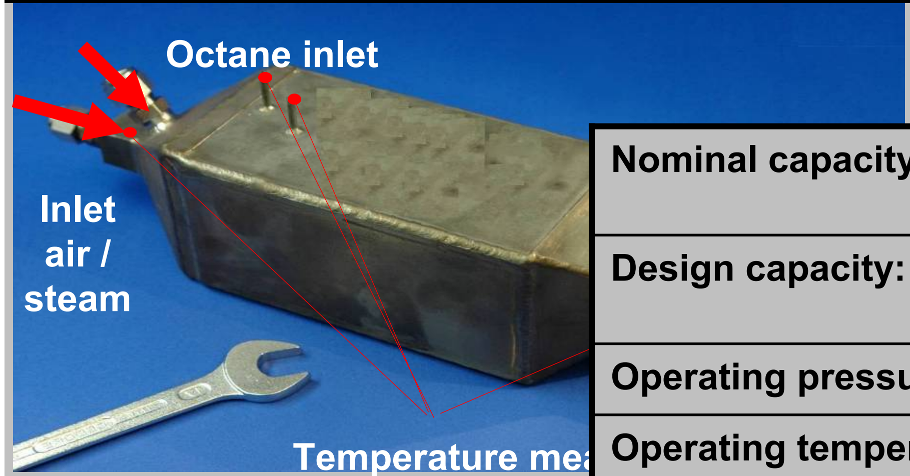
Application:

5 kW_{el} Auxiliary Power Unit (APU)

for Cars

G. Kolb et al. Chem. Eng. J. 137 (2008) 653-663.

Autothermal Microstructured Reformer for Iso-Octane

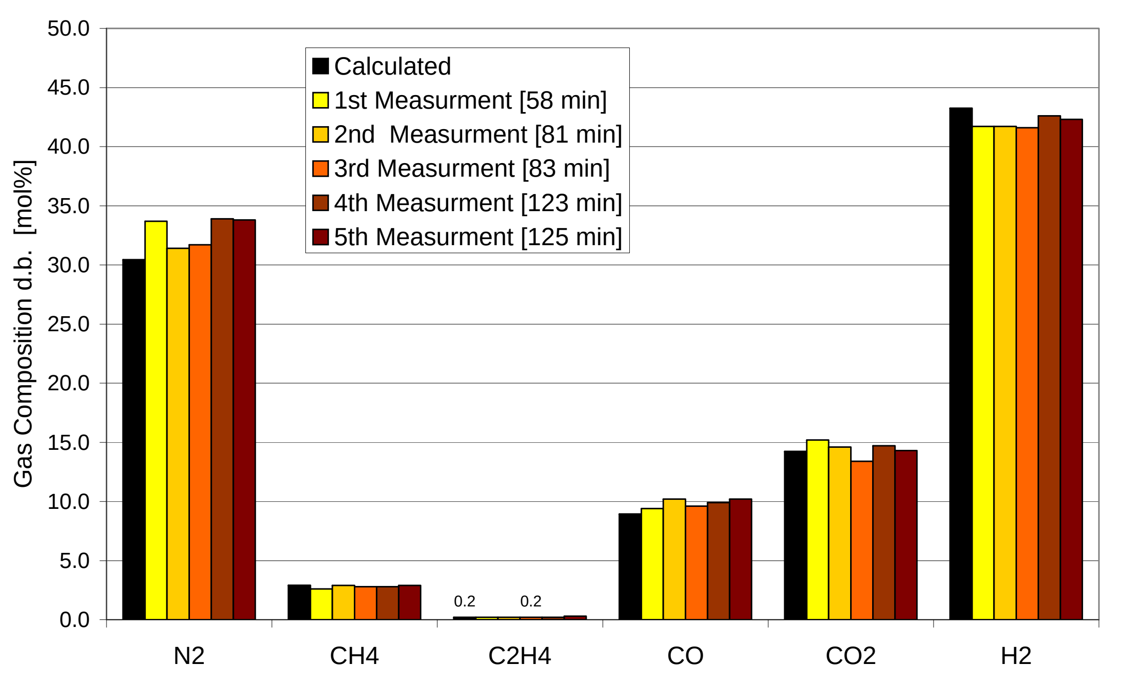


Nominal capacity:	Hydrogen production for a 5 kW_{el} fuel cell
Design capacity:	Hydrogen production for a 20 kW_{el} fuel cell (safety factor 4)
Operating pressure:	Max. 4 bar
Operating temperature:	Max. 800°C
Reactor dimensions:	80 x 80 x 150 mm^3; 200 stainless steel foils (0.4 mm)
Channel dimensions:	400 x 250 $µm^2$ 2520 channels / in^2 25000 channels
Coated channel surface:	2.6 m^2
Catalyst:	1% Rh on Al_2O_3-sol basis (developed by LIKAT/ CIRIMAT Toulouse)
Total catalyst mass:	19.5 g (0.2 g Rh)
WHSV:	330 $Ndm^3/(h\ g_{cat})$

G. Kolb et al. Chem. Eng. J. 137 (2008) 653-663.

Gas Composition – ATR Product

		calculated [100% Conversion]			experimentally determined				
		feed ATR	product ATR	product ATR [d.b.]	product ATR [d.b.]				
Test Duration	[min]	-	-	-	58	81	83	123	125
H_2O	[mol %]	67.3	40.4	0.0	-	-	-	-	-
N_2	[mol %]	23.4	18.1	30.4	33.7	31.4	31.7	33.9	33.8
O_2	[mol %]	6.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_8H_{18}	[mol %]	2.5	0.0	0.0	-	-	-	-	-
CH_4	[mol %]	0.0	1.7	2.9	2.6	2.9	2.8	2.8	2.9
C_2H_4	[mol %]	0.0	0.1	0.2	0.2	0.2	0.2	0.2	0.3
C_3H_6	[mol %]	n.d.	n.d.	n.d.	[0.03]	[0.05]	[0.06]	[0.02]	[0.02]
CO	[mol %]	0.0	5.3	8.9	9.4	10.2	9.6	9.9	10.2
CO_2	[mol %]	0.0	8.5	14.2	15.2	14.6	13.4	14.7	14.3
H_2	[mol %]	0.0	25.8	43.3	41.7	41.7	41.6	42.6	42.3



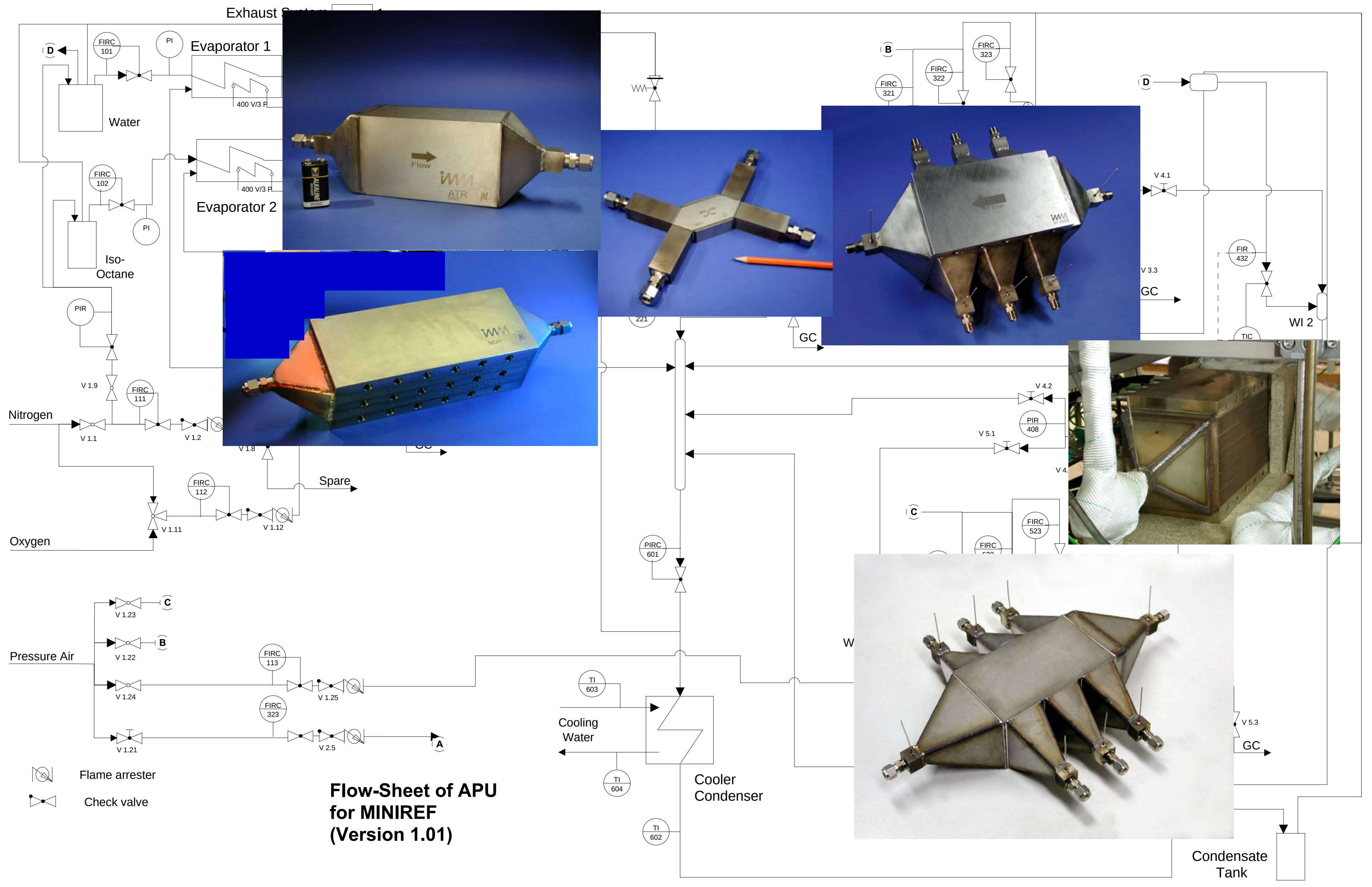
Conversion:

Determined by Adsorption and GC Analysis: >95%

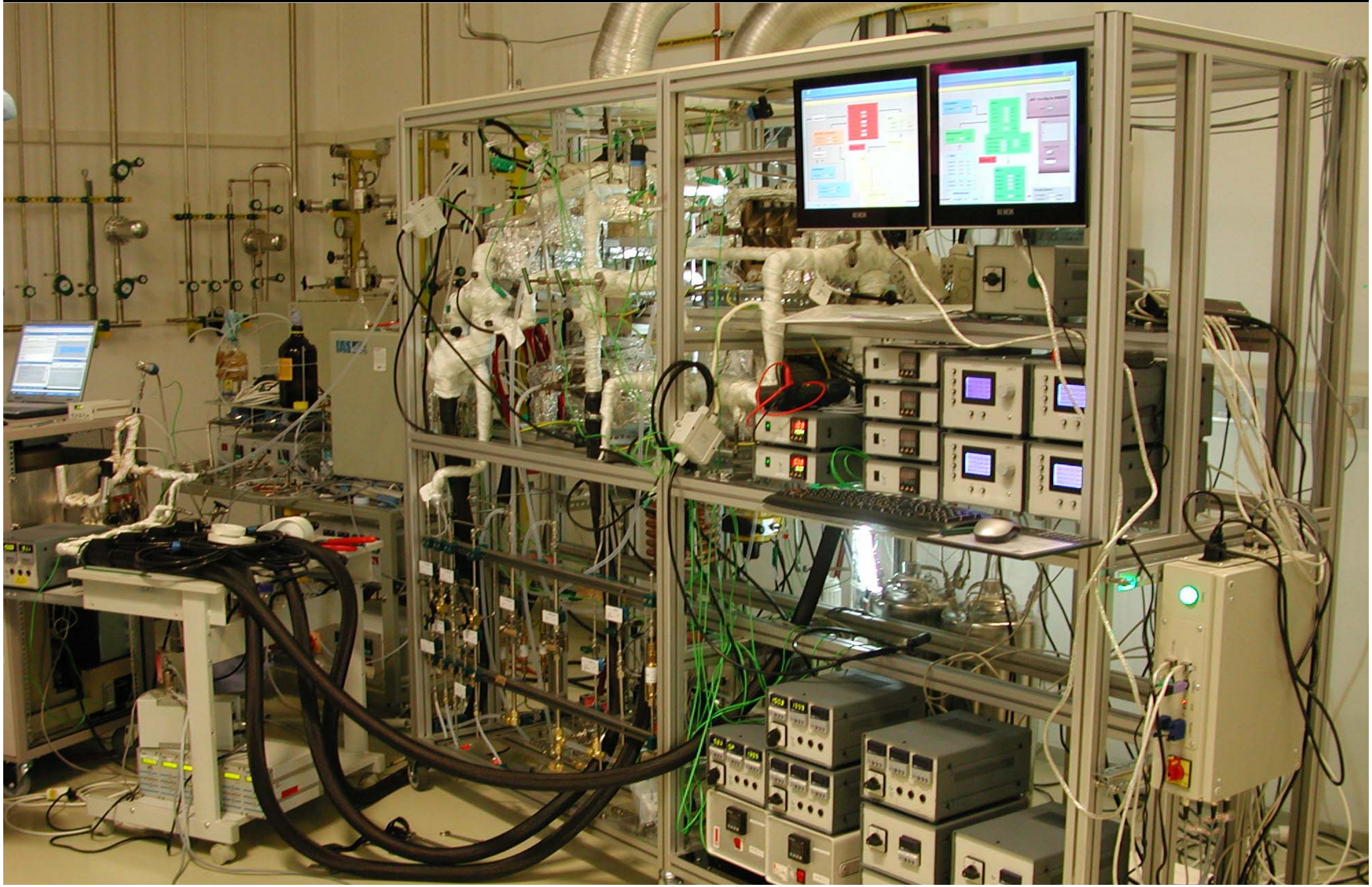
Determined by FT-Cyclotron-MS: > 99%

G. Kolb et al.,Chem. Eng. J. 138 (2008) 474-489

System Integration – Octane Reforming (5000 W_{el})

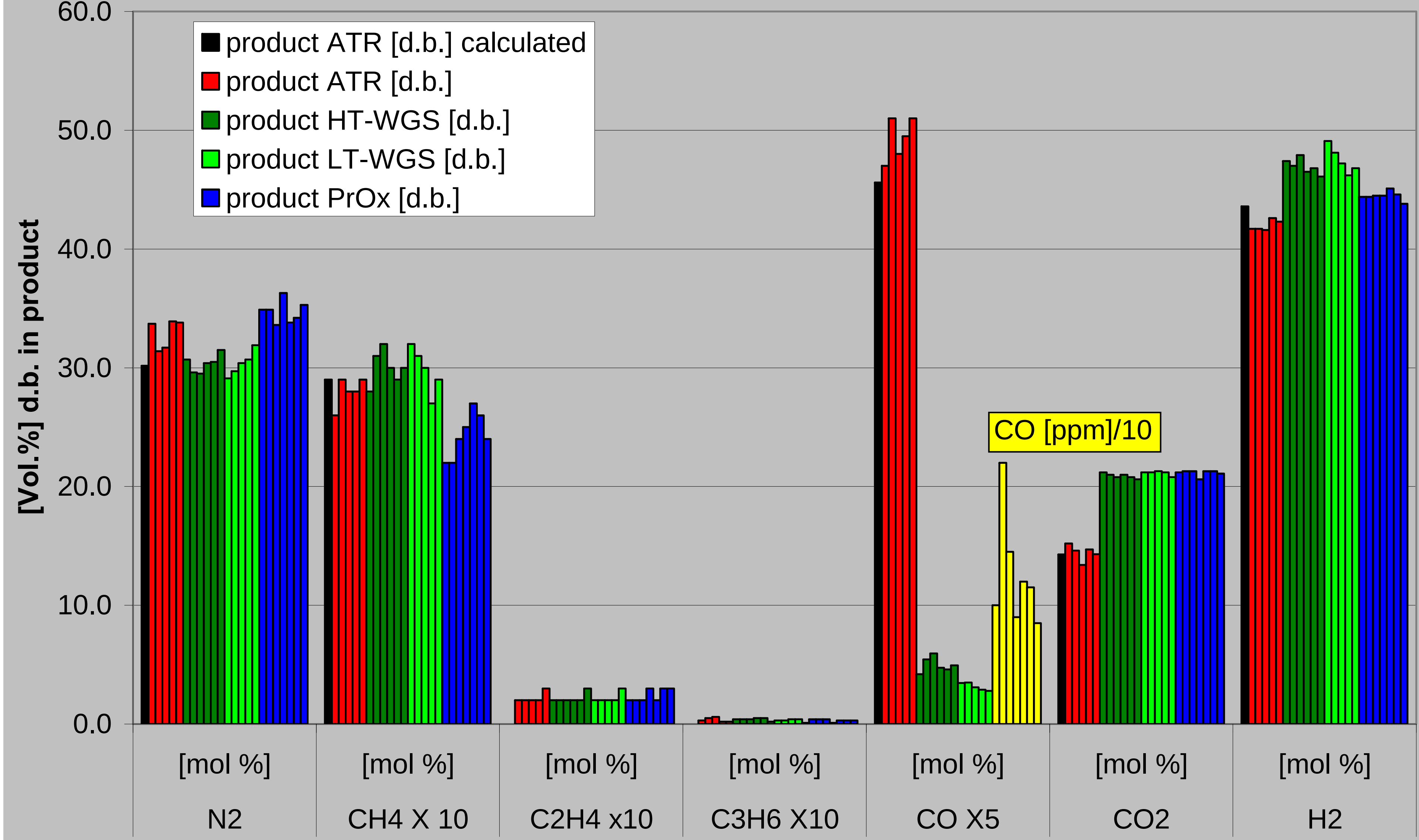


System Integration – Octane Reforming (5000 W_{el})



G. Kolb et al.,Chem. Eng. J. 138 (2008) 474-489

Gas Composition – Fuel Processor Products



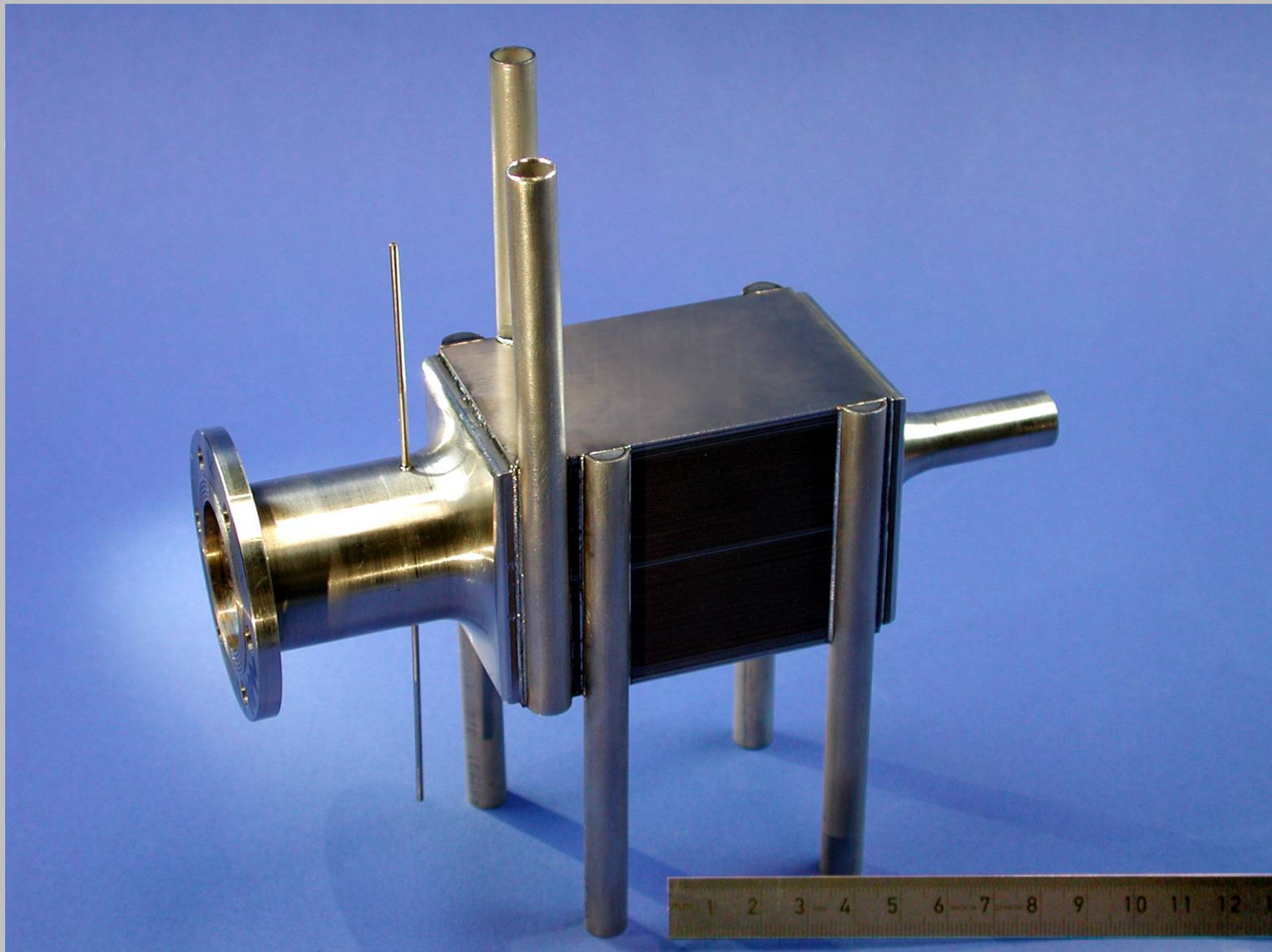
Diesel Steam Reforming

Application:

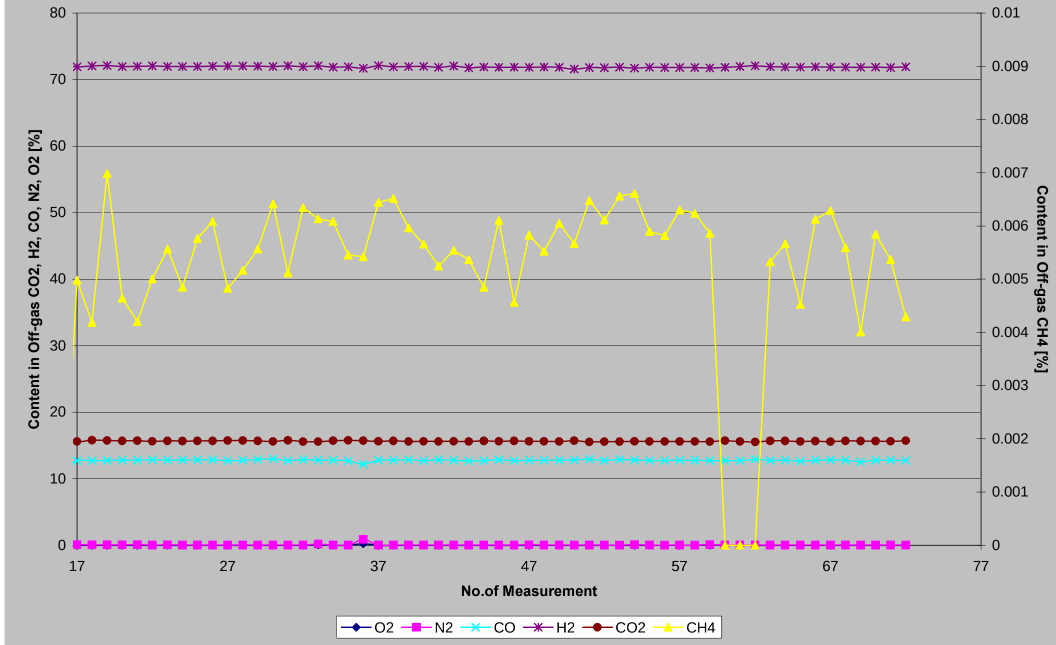
5 kW_{el} Auxiliary Power Unit (APU)

for Trucks

STR/AFB prototype (Explosion view)



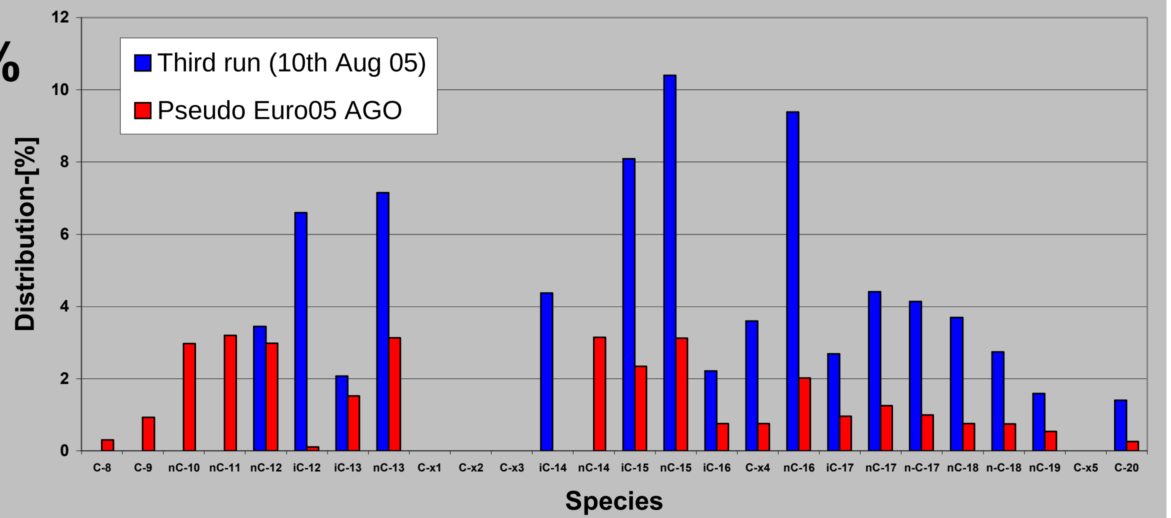
Diesel Steam Reforming (2 kW) – GC/GC-MS Analysis



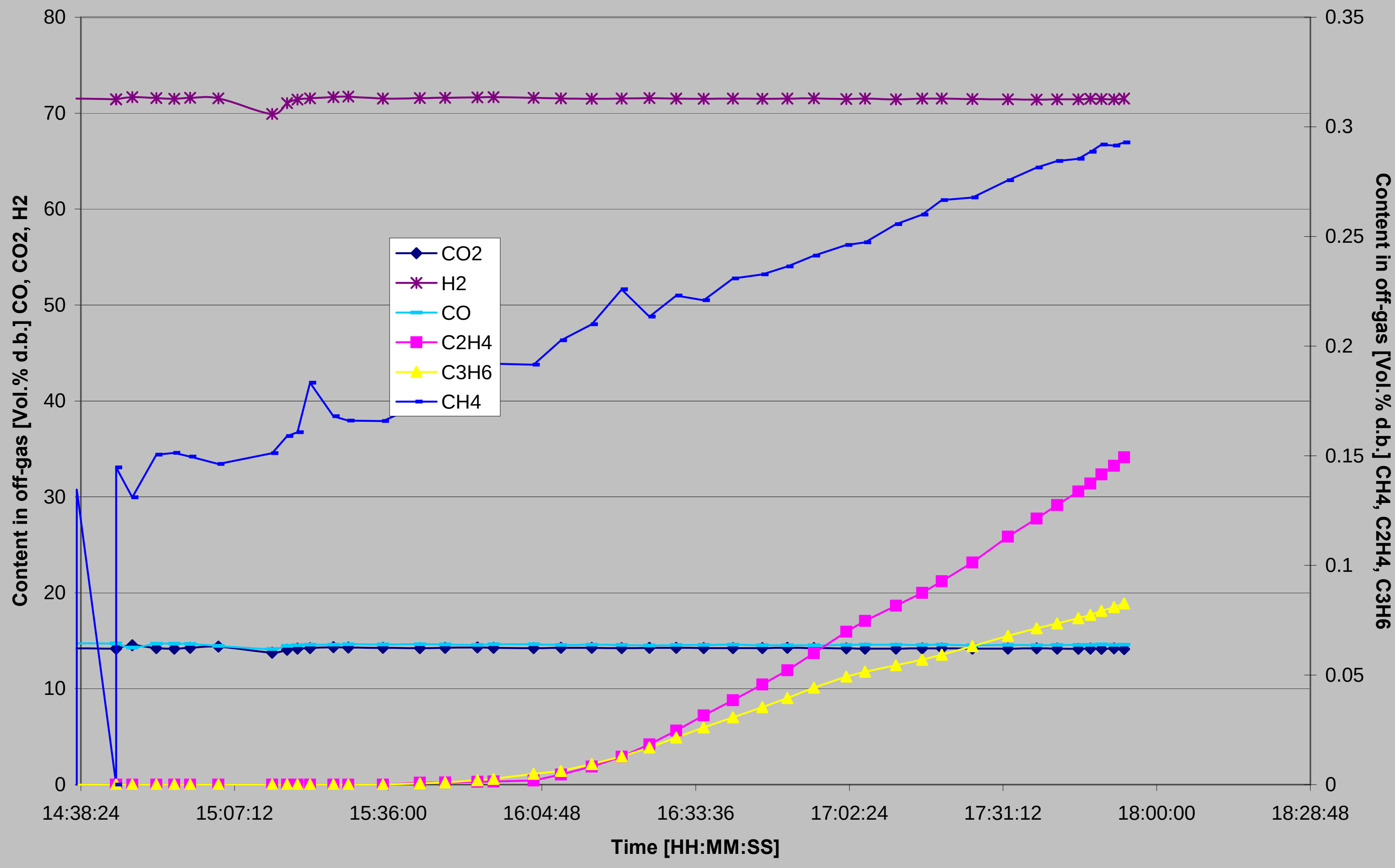
40 h stable operation

Conversion > 99.9%

S/C 4.6; O/C = 0

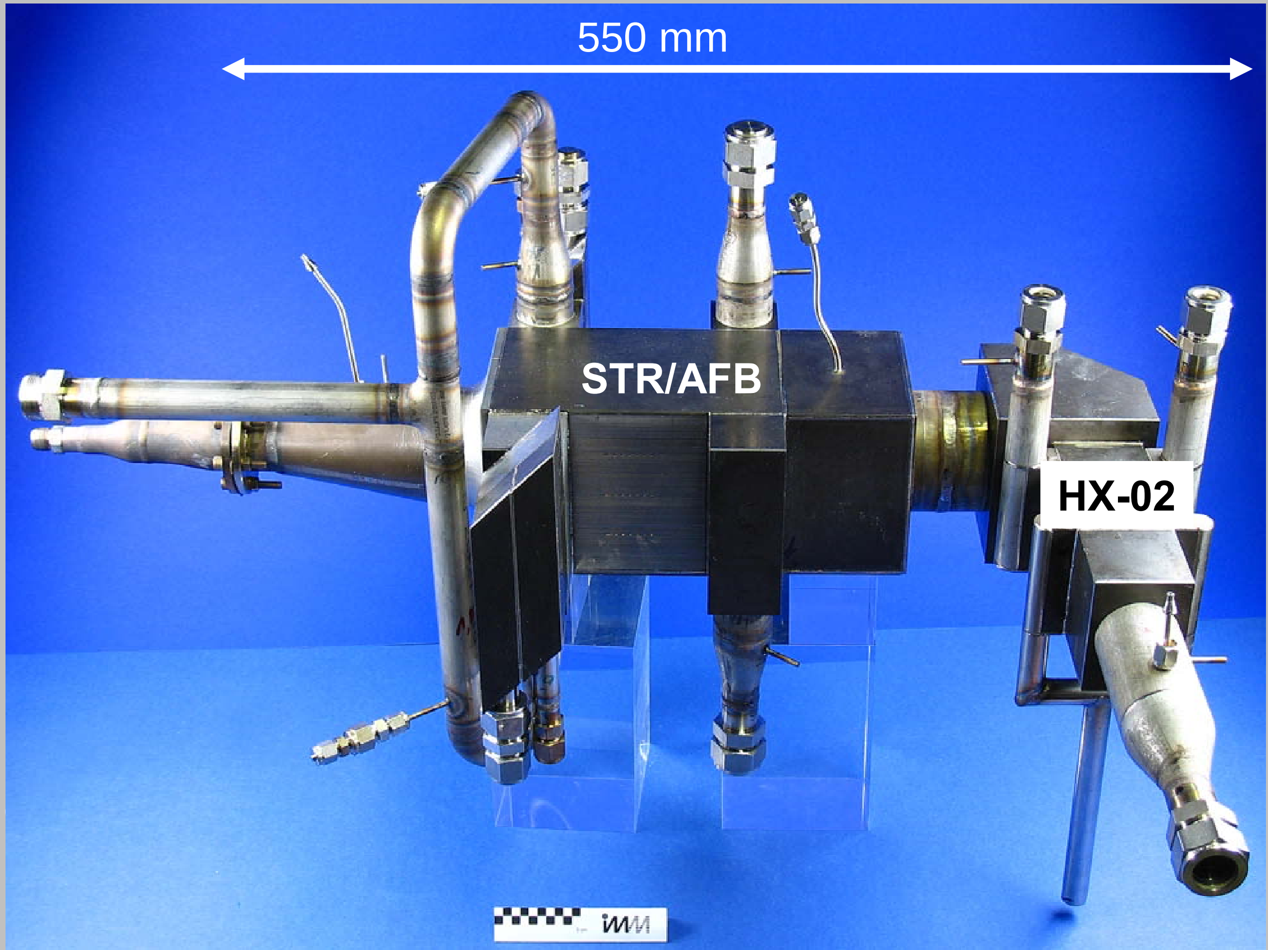


Diesel Oxydative Steam Reforming



Conversion > 99.9% S/C 3.6; O/C = 0

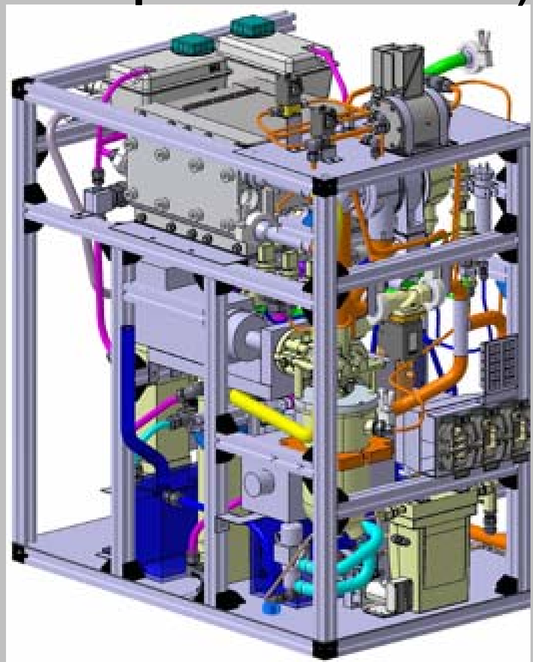
Diesel STR/AFB 5 $kW_{el, net}$ prototype



Total: 6.5 kW_{el}; >10 kW_{th}

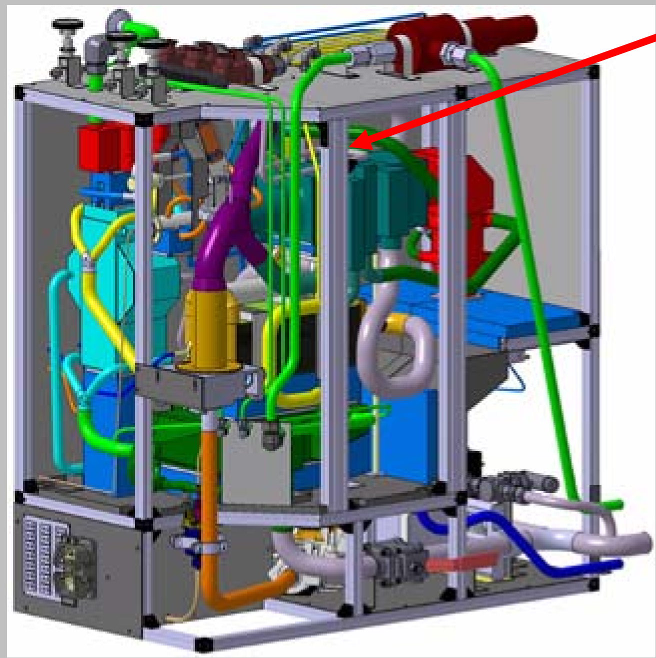
5 kW APU (System Integration by Tenneco)

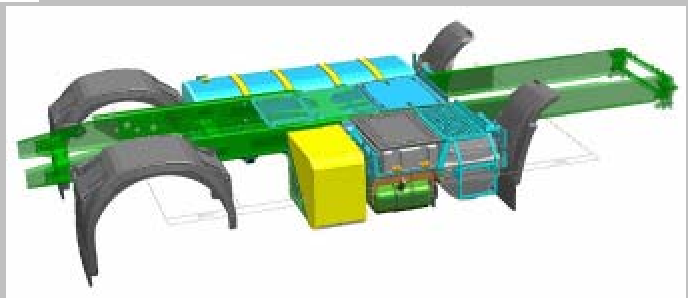
Cold Part (Fuel Cell, Compressor and BoP)



Hot Part (Fuel Processor)

Steam Reformer





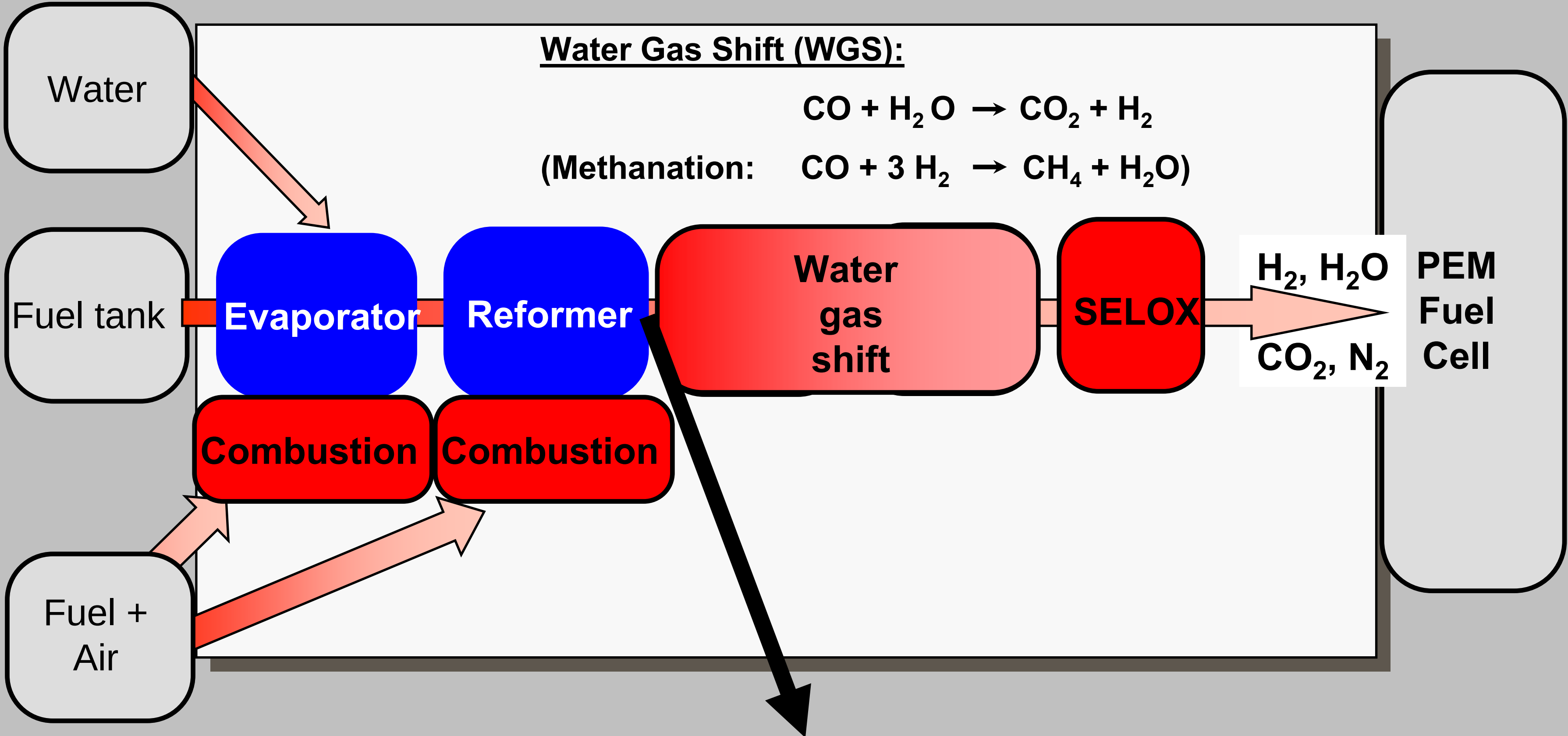
(Truck Chssis CAD model: Courtesy of DAF)

CO-Clean-up:

Water –Gas Shift

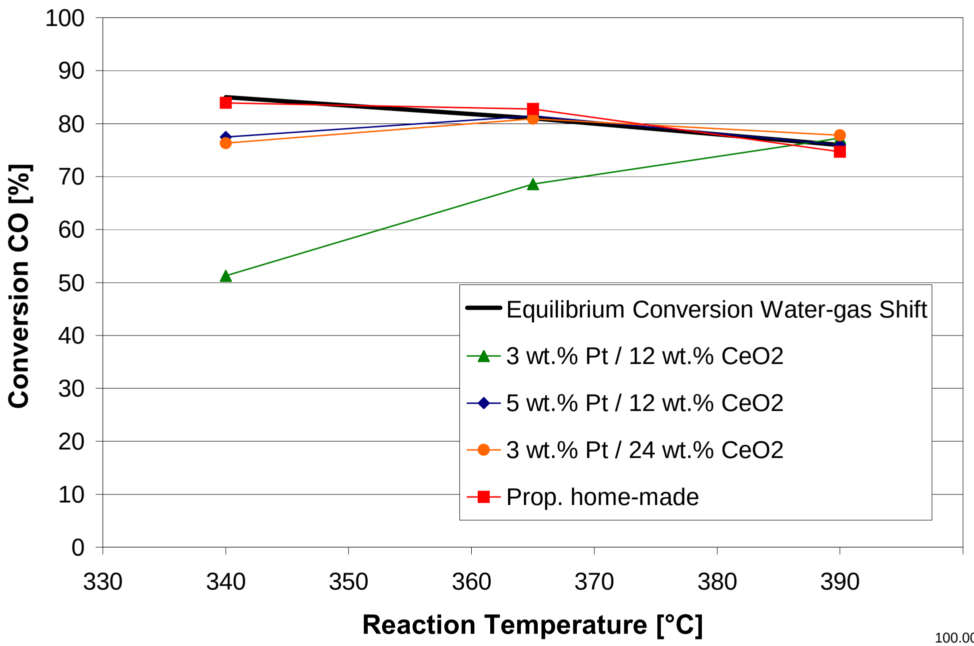
Kolb G., Pennemann H., Zapf R., Catal. Today 110 (2005) 121

Feed Composition for High Temperature Shift



Gas Composition HTS [mol%]	H_2 46.1	CO_2 8.8	CO 8	H_2O 37.1
Equilibrium Conditions HTS				
Reaction Temperature	[°C]	340	365	390
Eq. Conversion	[%]	85	81	76
CO_{eq}	[mol %]	1.2	1.5	1.9

Water-gas Shift – Home-Made Catalysts



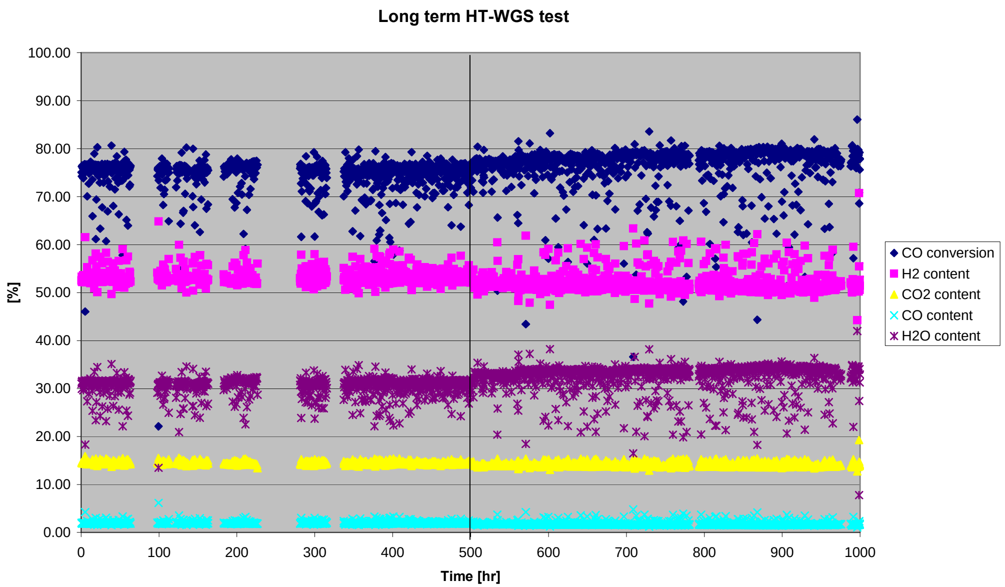
Self-developed Pt/CeO_2 Catalysts

WHSV$_{feed}$: 220 Ndm³/(h g$_{cat}$)

Pressure: Ambient

1000 Hours Durability Testing

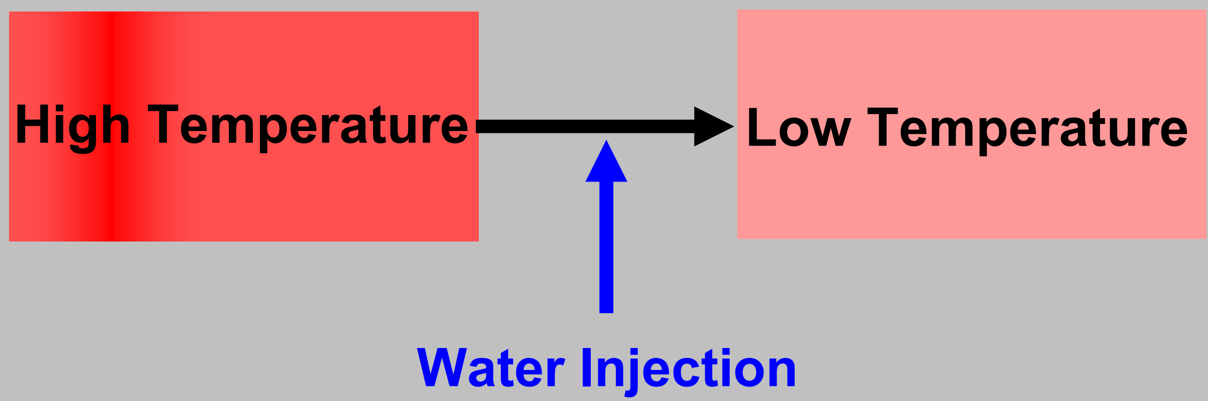
Catalyst:	**Self-developed; Proprietary**
WHSV$_{feed}$:	**220 Ndm³/(h g$_{cat}$)**
Temp.:	**400°C**
Pressure:	**Ambient**



Comparison of 'Conventional' (Monolithic) and Internally Cooled Water-gas shift

Conventional

2 stage:

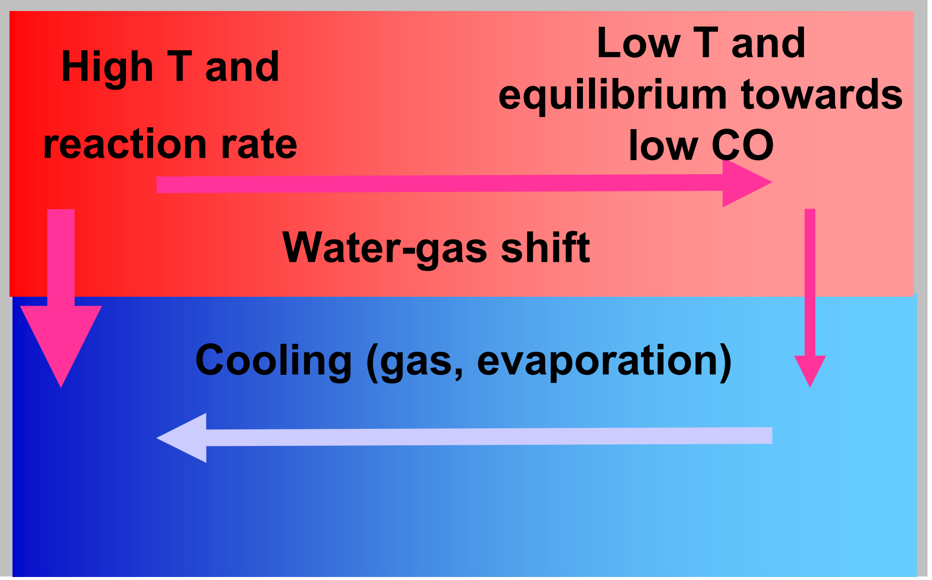


Microstructured Plate heat-exchanger

Idea first published

by Te Grotenhuis et al.:

TeGrotenhuis, W.E. King, D.L., Brooks, K.P., Holladay B.J., Wegeng, R.S. 6th International Conference on Microreaction Technology, 2002, AIChE, NY, 2002, p. 18



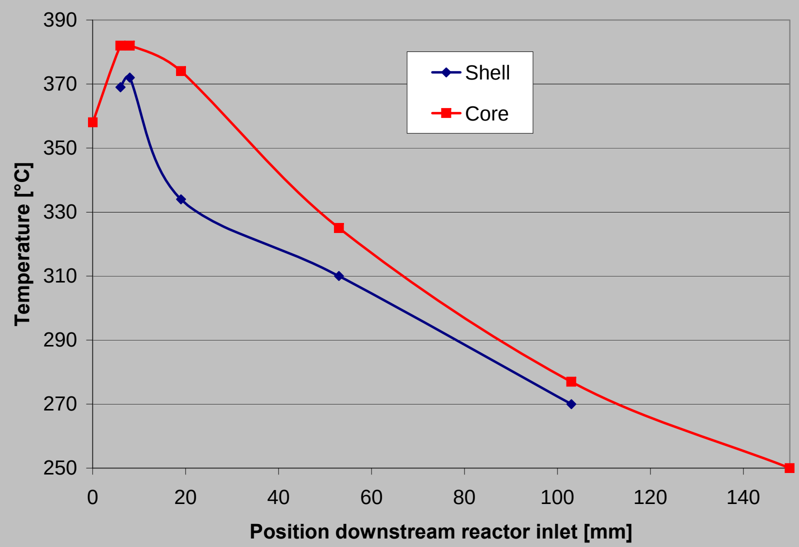
Internally Cooled Water-gas shift

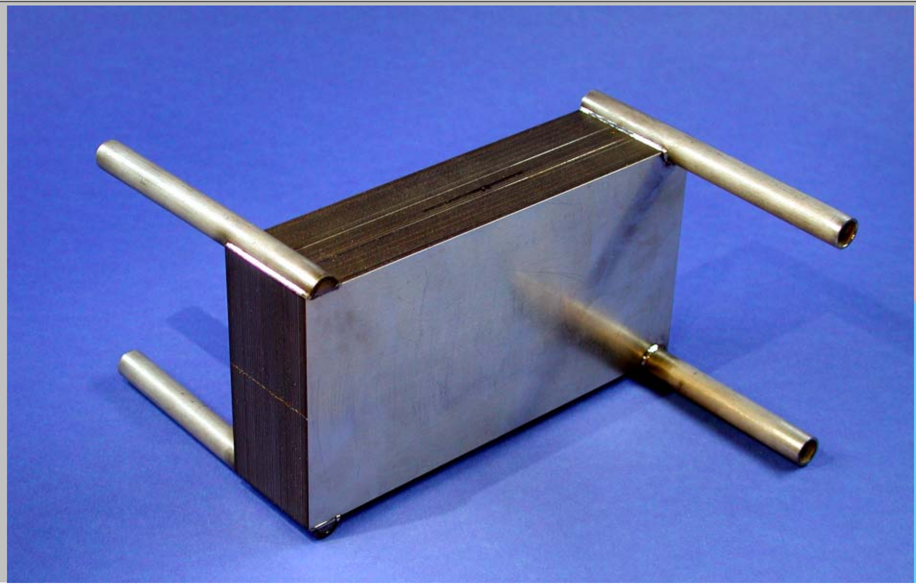
10.6% CO

1.05 % CO

Demonstration

in the 2 kW size range:





CO-Clean-up:

Preferential Oxidation

Experimental Protocol Long-term Testing PrOx – Self Developed Catalyst Formulation

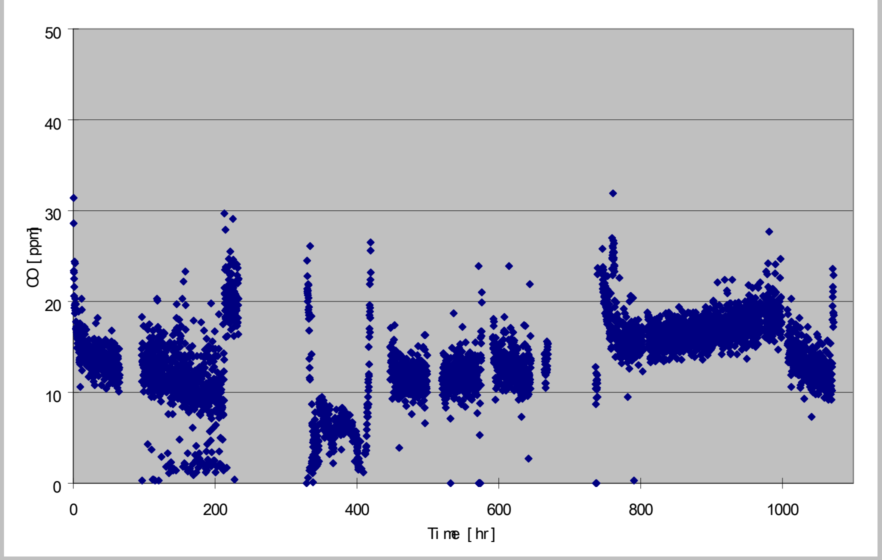
- **Pressure:** **Ambient**
- **Flow Rate:** **30 Nml / min**
- **Catalyst Mass:** **10 mg**
- **WHSV:** **3.0 Ndm³ / (min g_{Kat})**
  = 180 Ndm³ / (h g_{Kat})

- **Feed (Long Term Testing):** **λ (O/CO): 3**

H_2 [mol%]	H_2O [mol%]	CO_2 [mol%]	CO [mol%]	N_2 [mol%]	O_2 [mol%]
64.6	0.0	23.8	1.2	8.5	1.9

PrOx 1000 h Long Term Testing and Kinetics

Self-developed Pt/Rh/Al_2O_3-Formulation:
$\lambda(O/C)=3$; WHSV= 180 Nl/(min g_{cat});
$c_0(CO)$= 1.1 Vol.%



Kinetics Determined after 1000 h long term test in a microstructured gradientless recycle reactor with external recycle loop:

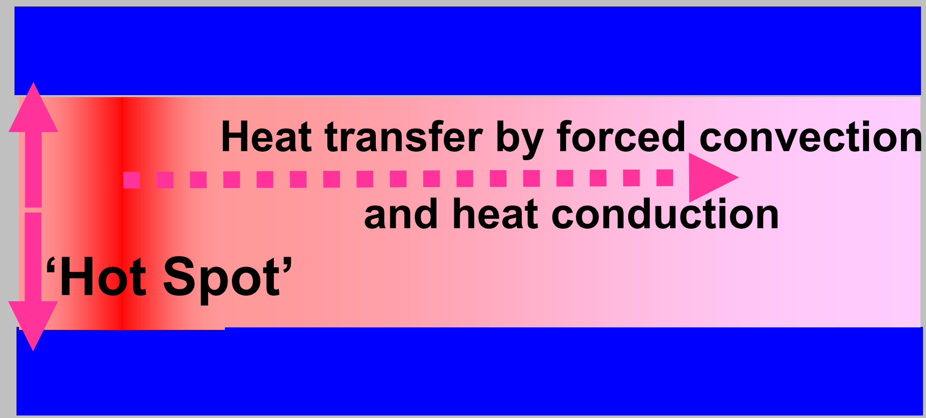
$$r_{CO} = k_0\, E_a\, [CO]^{-0.63}\, [O_2]^{0.71}\, [CO_2]^{-0.02}$$

$$k_0 = 2.62\ 10^{11}$$

$$E_a = 91\ \text{kJ/mol}$$

Comparison of ‘Conventional’ (Monolithic) and Internally Cooled Selective Oxidation

Conventional:



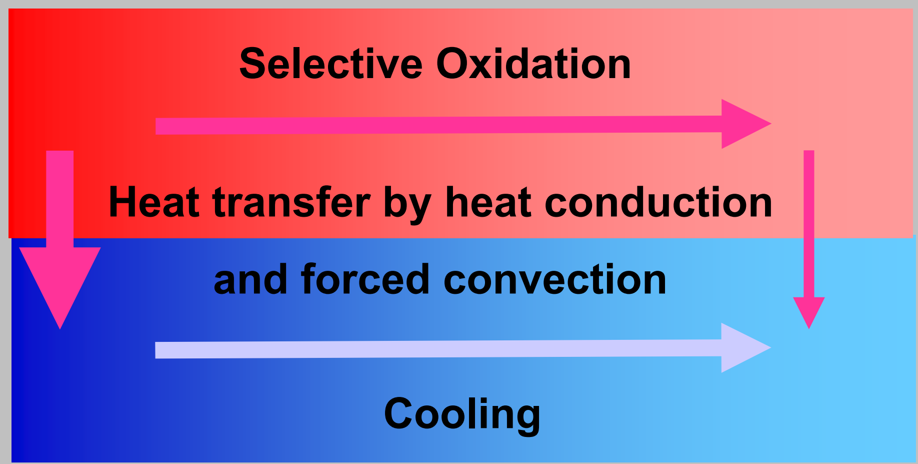
Multistage solutions (up to 7 stages) required for dynamic operation

Microstructured

Plate heat-exchanger

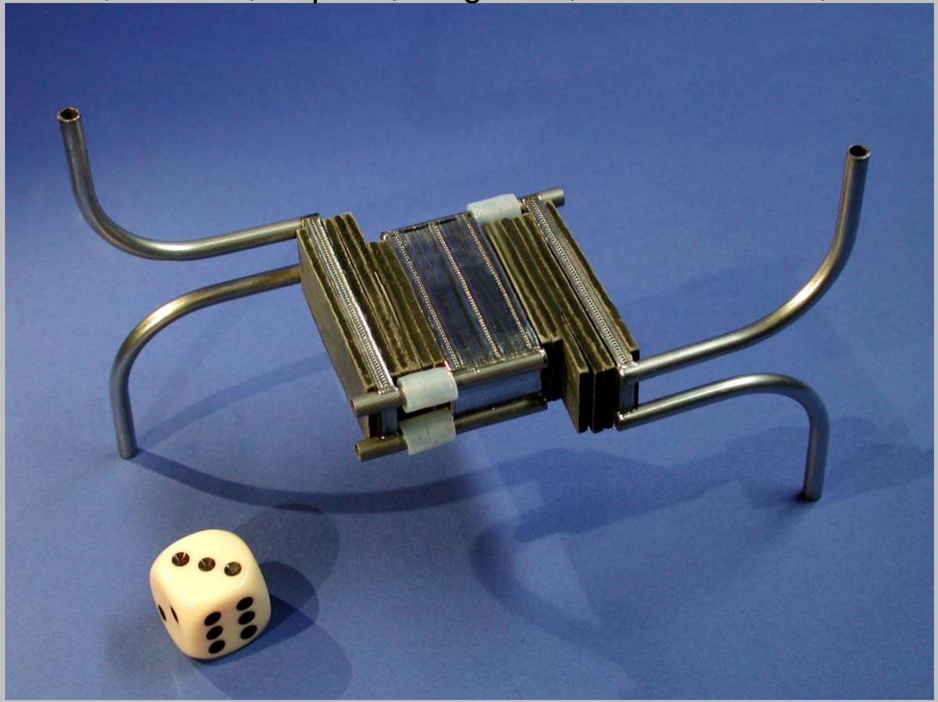
(demonstrated in the

kW size range):



Second Generation Prototype

Cominos V., Hessel V., Hofmann C., Kolb G., Zapf R., Ziogas A., Delsman E.R., Schouten J.C., Catal. Today 110 (2005) 140



SELOX reactor sealed by laser-welding

Dimensions: **17x64x55 mm³**

Volume: **60 cm³**

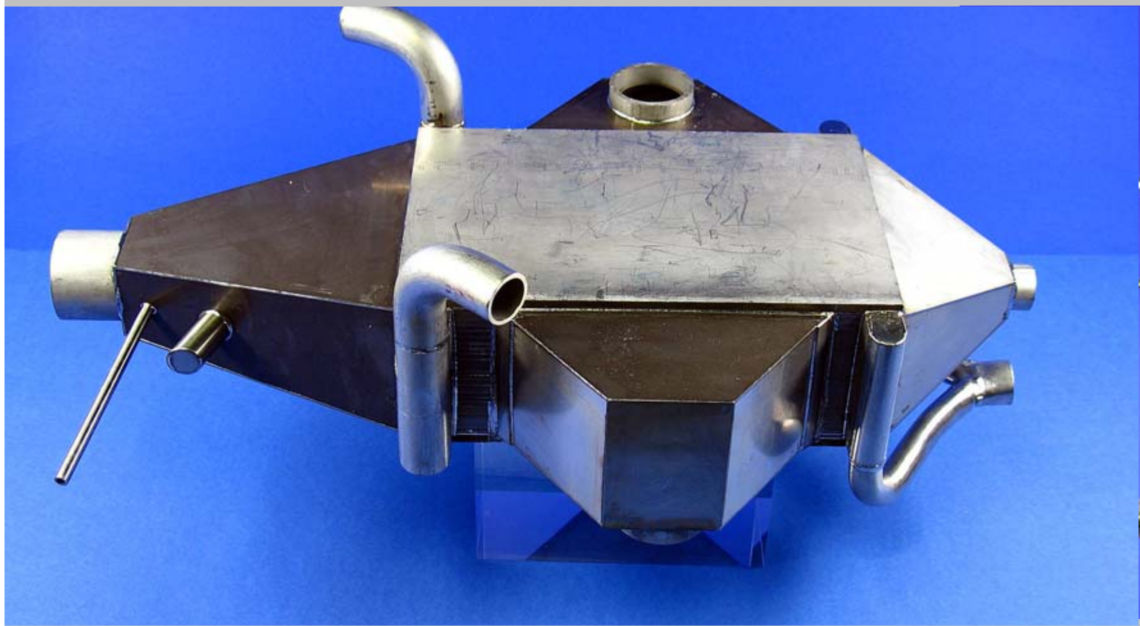
Weight: **150 g**

1 cm Klingersil insulation between single components

Parameter	Heat exchangers		PrOx reactor	
	Ref[a]	Cool	Ref	Cool
Plate dimensions ($w \times l$) (mm)	17 × 50		17 × 40	
Number of plates	2	4	22	11
Channels per plate	29	29	13	10
Channel width (μm)	400	400	1000	500
Channel height (μm)	300	300	200	250
Channel length (mm)	40	40	30	30

[a] Ref : reformate side, Cool : coolant side.

Coupled Dynamic Operation of Water-gas shift and Preferential Oxidation – 5 $kW_{el,\ net}$ size



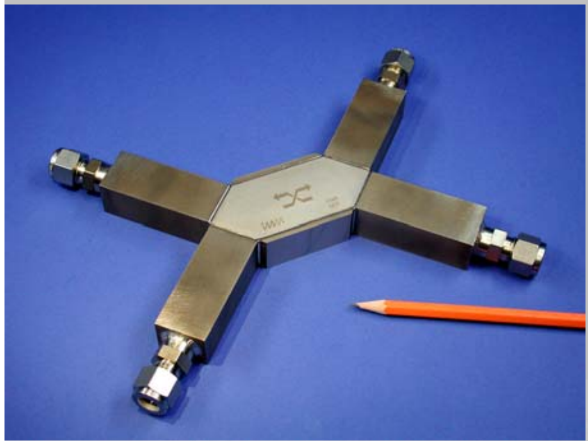
Balance-of-Plant:

Heat-exchangers, Evaporators

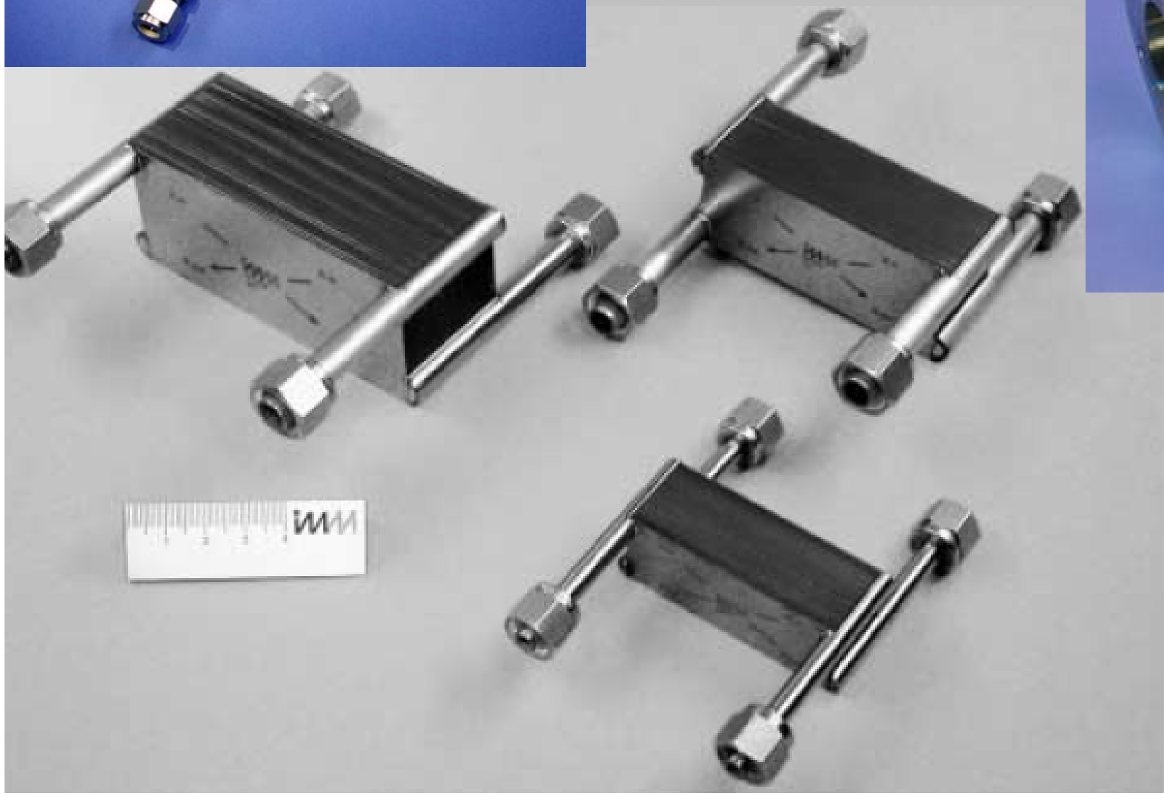
(for Fuel Processors and Fuel Cells)

Counter-flow Heat-exchangers

2 kW; 800°C

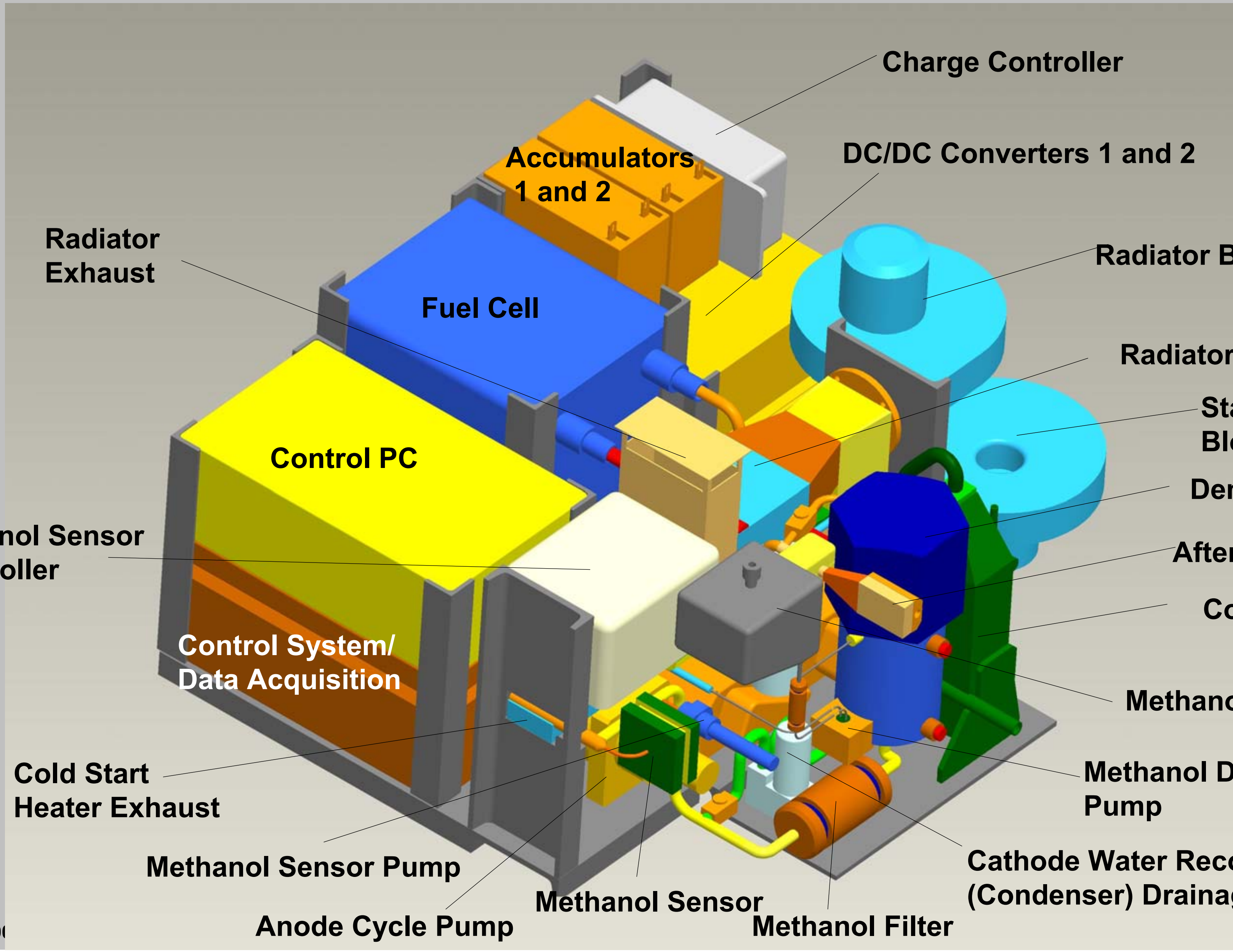


< 2kW; 500°C



10 kW; 600°C

Virtual System – 500 W DMFC



Components for 500 W DMFC (BoP)

Cold-Start Heater

Demister

1 kW Radiator

Condenser

Production Issues

Future Fuel Processors for:

Yachts / Caravans (< 1 kW):	1,000 – 10,000 / y
Automotive APU‘s (< 10 kW):	10,000 – 100,000 /y
Lap-tops (≤ 100 W):	> 100,000 / y

→ Mass production required.

Reactors are one-way products (already)

And need to be:
1) Cheap
2) Cheap
3) Cheap

Fabrication Techniques Available	Sealing Techniques Available

- Conventional Machining (IMM)
- Micromilling (IMM)
- Wire- and Bulk EDM (IMM)
- Laser-Cutting (Gaskets, IMM)

- Etching (External)
- Laser-Micromachining (Ablation, IMM)

- Embossing (External)
- Punching (External)

- Gaskets – Graphite / Metallic

- Laser-Welding (IMM + External)

- Brazing (External)
- Laser/ Electron Beam Welding (External)

Prototypes

Small Series (< 1000);

Big Devices for Chemicals Production

Mass Production (> 100 000)

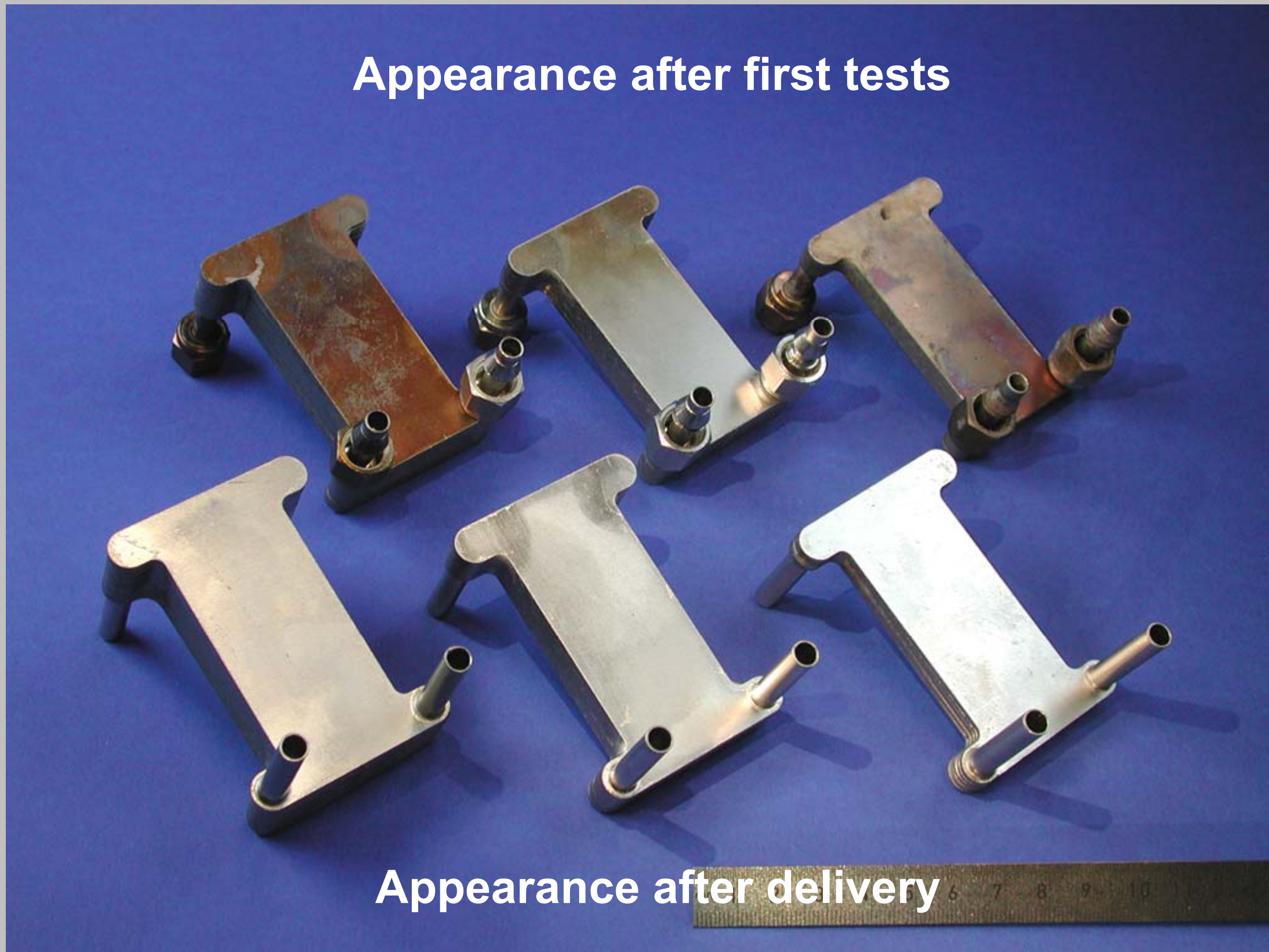
Fabrication of the Reactors

Fabrication steps (prototypes):

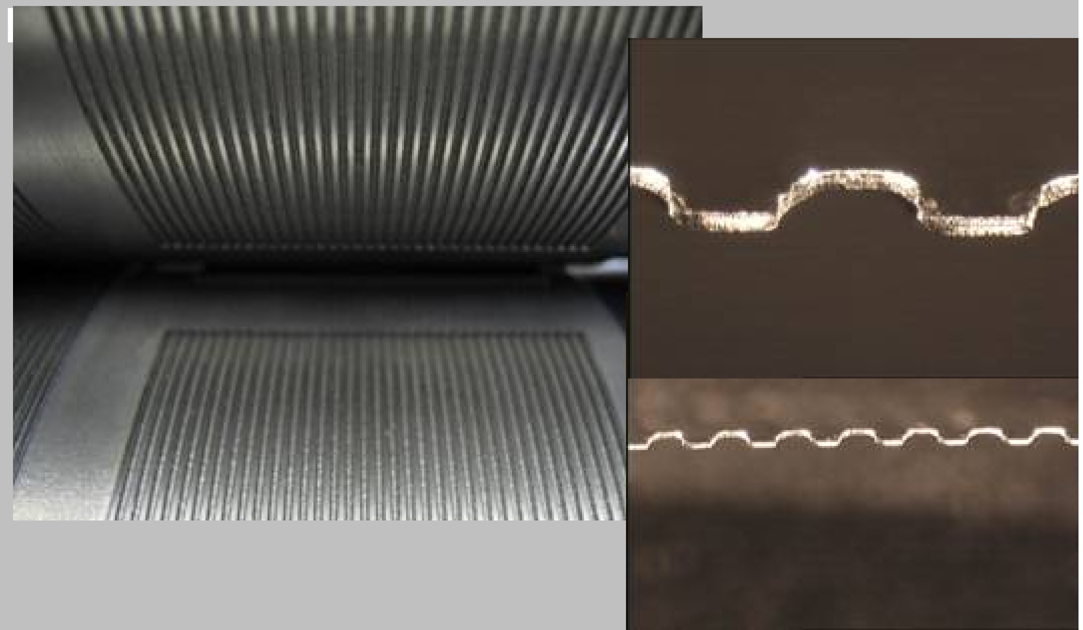
- **Wet chemical etching of the microchannels into the steel foils**
- **Catalyst coating**
- **Laser welding of the foil stack**
- **Laser welding with additional welding filler for the inlet and outlet ports**

Joining techniques: Brazing

View of small series of HX assembled



Development of Microstructuring Techniques- Rolling



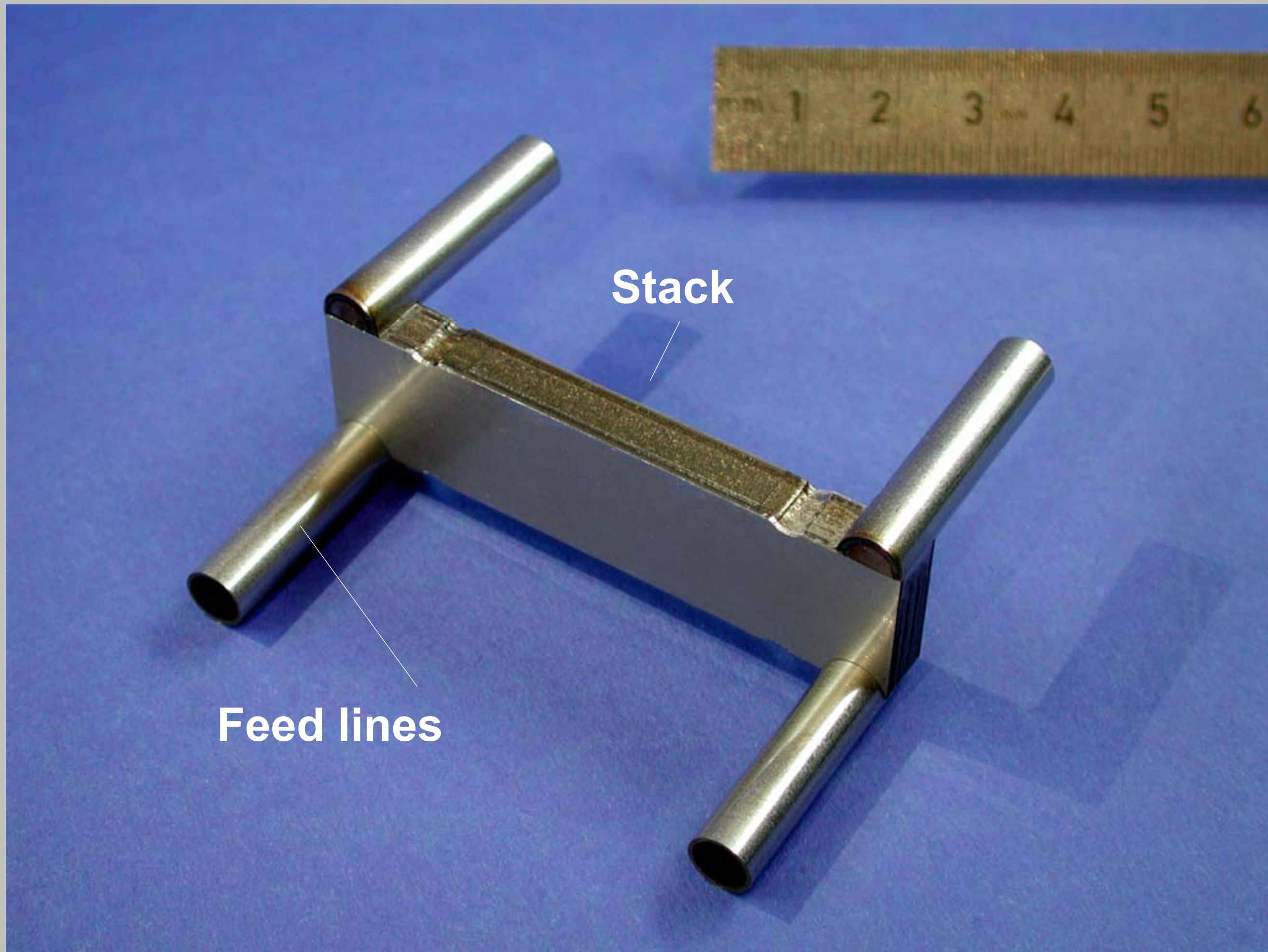
Rolling is well suited for structuring thin metal sheets

With one pair of rollers lots of channel sizes can be realized (depending on sheet thickness and gap between rollers

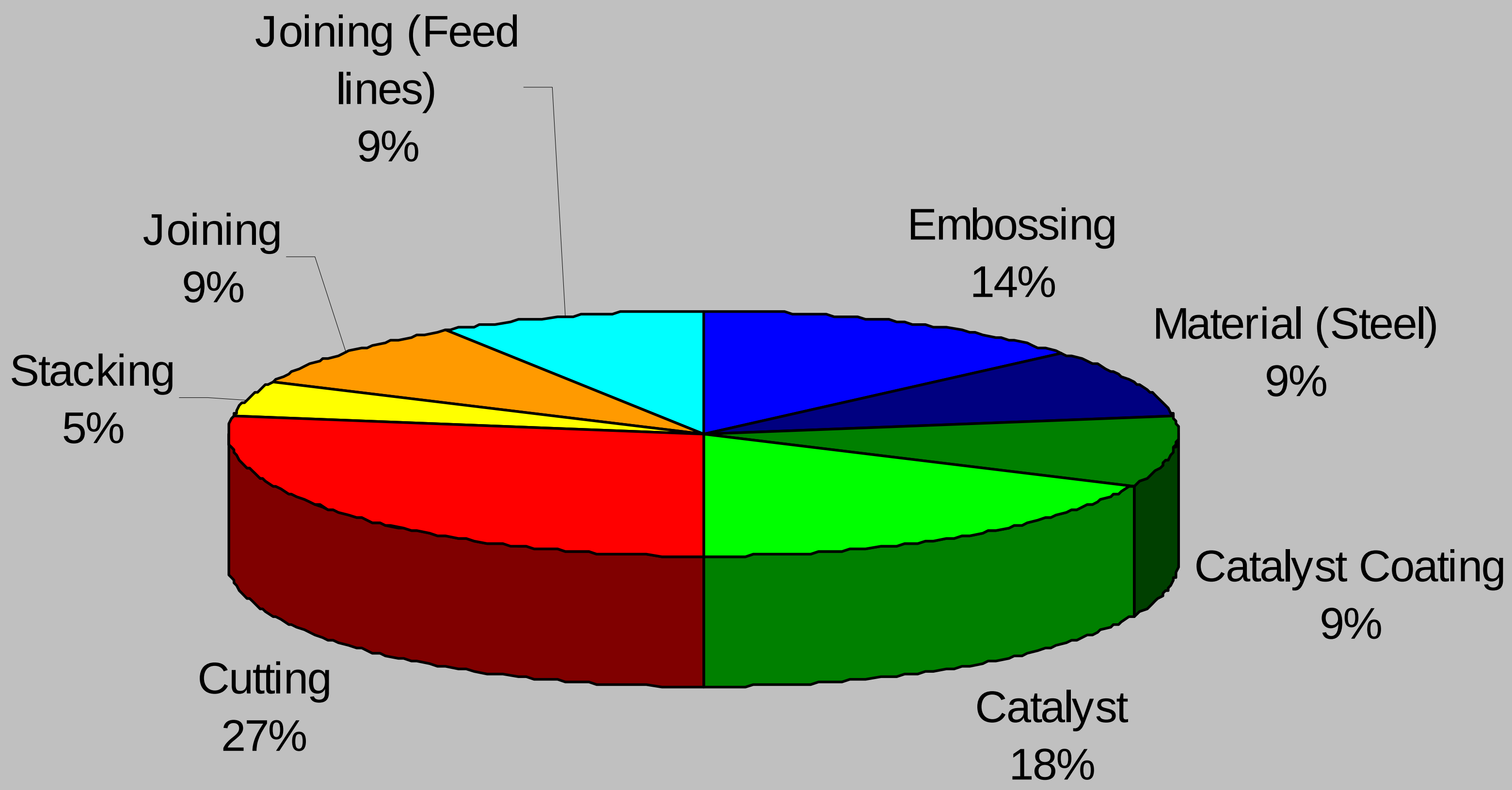
Mass Production: In case fourfold structured rolls are used, around 2,000 plates (structured surface 150 x 50 mm) can be fabricated per hour

Embossing

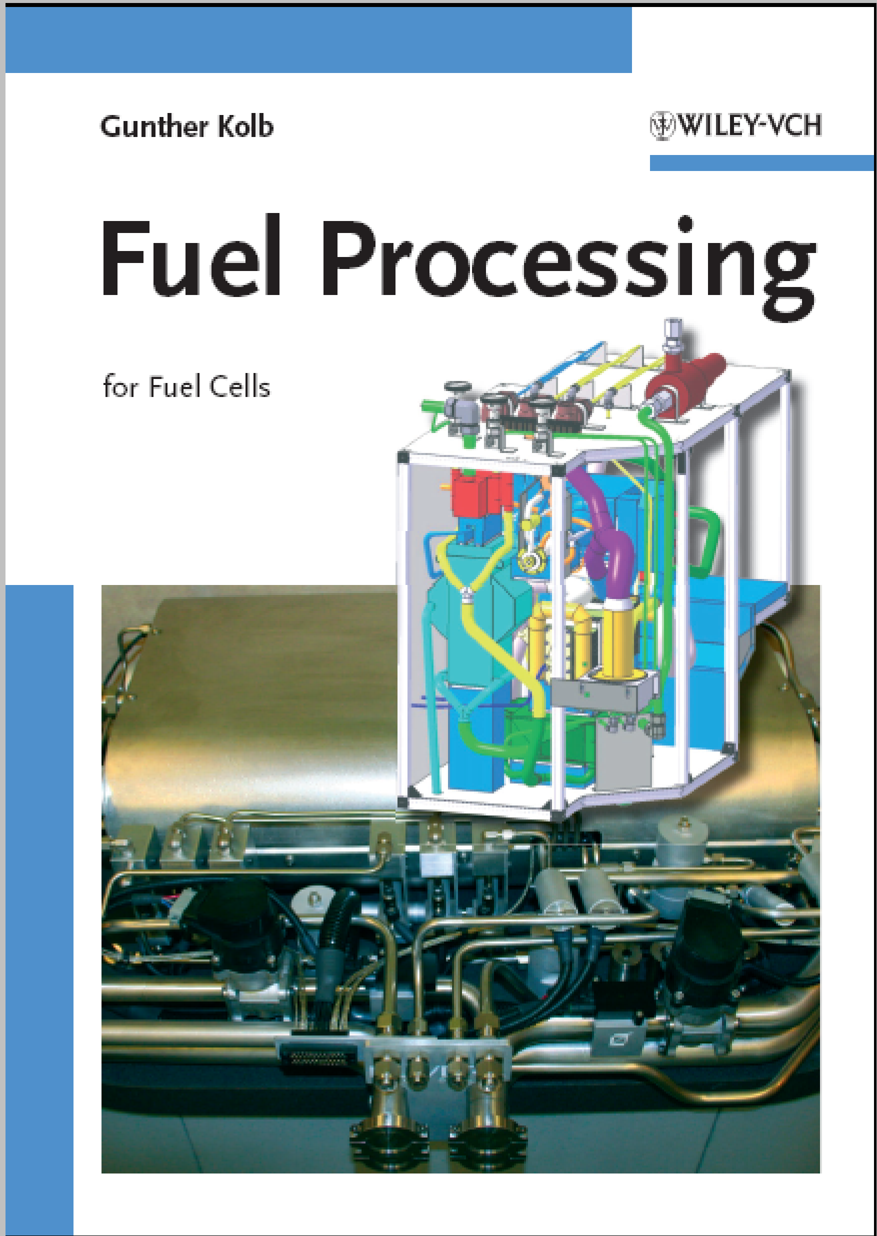
Embossed and laser welded microstructured heat exchanger



Cost Distribution for a Microstructured Heat-Exchanger/Reactor



Basis: 100,000 Reactors/y



ca. 400 pages

about 650 references

more than 280 figures and tables

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