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A HT-PEM fuel cell system model for the electric power supply on ships

motivation
reduction of emissions

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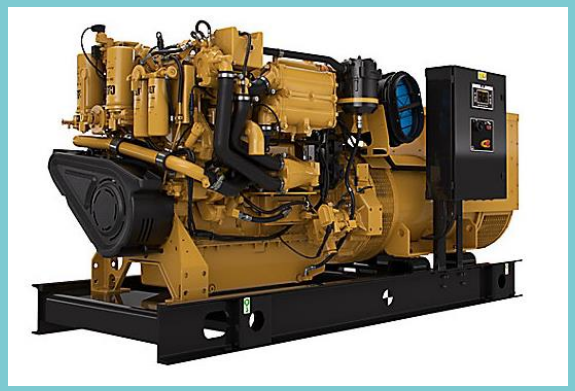

dieselgenerator
(500 kW)

fuel cell system
(2 x 5 kW)

state of the art
- diesel electric ships

challenge
- reduction of emissions

alternative
- unconventional fuels and energy converter
- since 2012 HT-PEM

source picture: Topaz – M. Fischbach; C18 – www.cat.com; H3 5000 Rack – www.serenergy.com

HT-PEM fuel cell system

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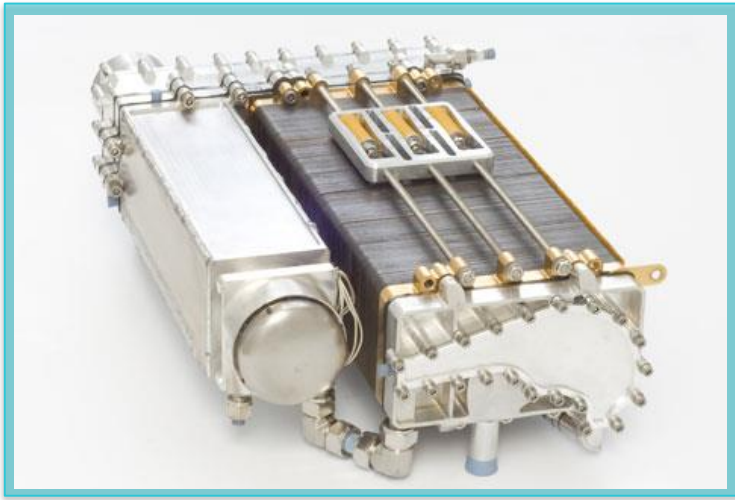
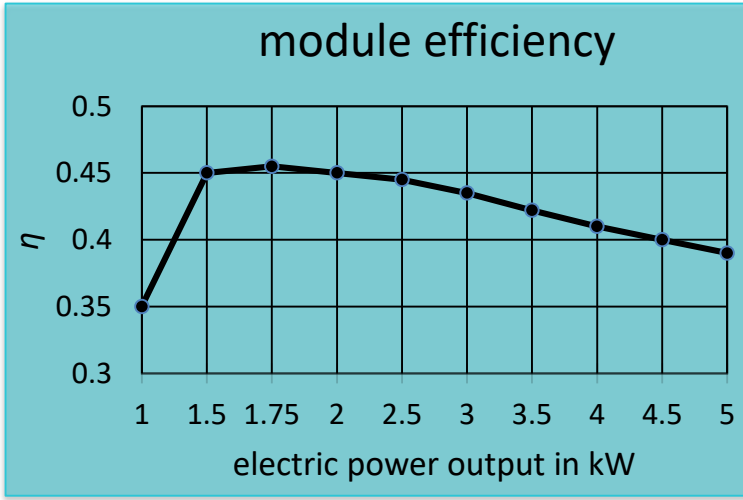


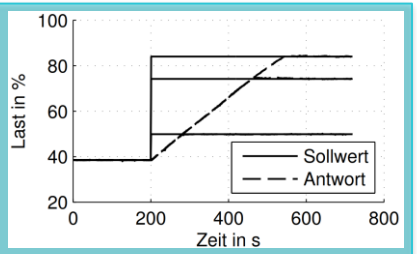
object of investigation

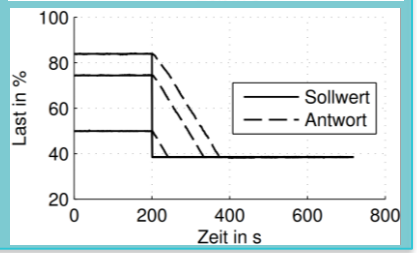
- HT-PEM with water-methanol fuel mix
- developed for TELCO industry
- nominal power output: 5 kW el, DC



known characteristics

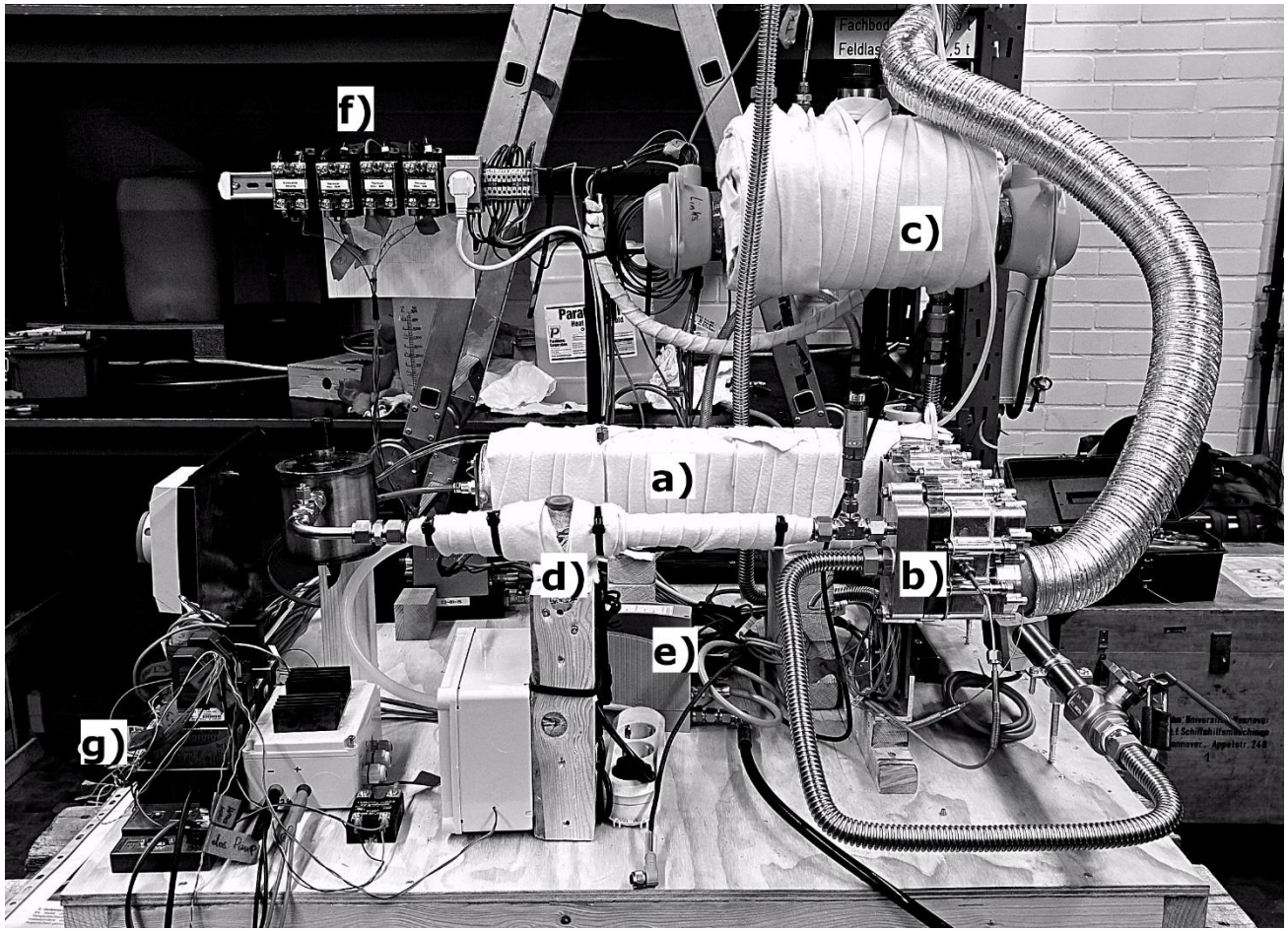
- fuel mix: S/C = 1,5
- system efficiency
- load acceptance
- ???





source picture: H3 5000 – www.serenergy.com, source efficiency: e4ships Brennstoffzellen im maritimen Einsatz 2009 – 2016 (2016)
pilot plant: METHANOL POWERED FUEL CELL SYSTEMS FOR MARINE APPLICATIONS, C. Thiem, C. Gentner & G. Ackermann; SCC 2015

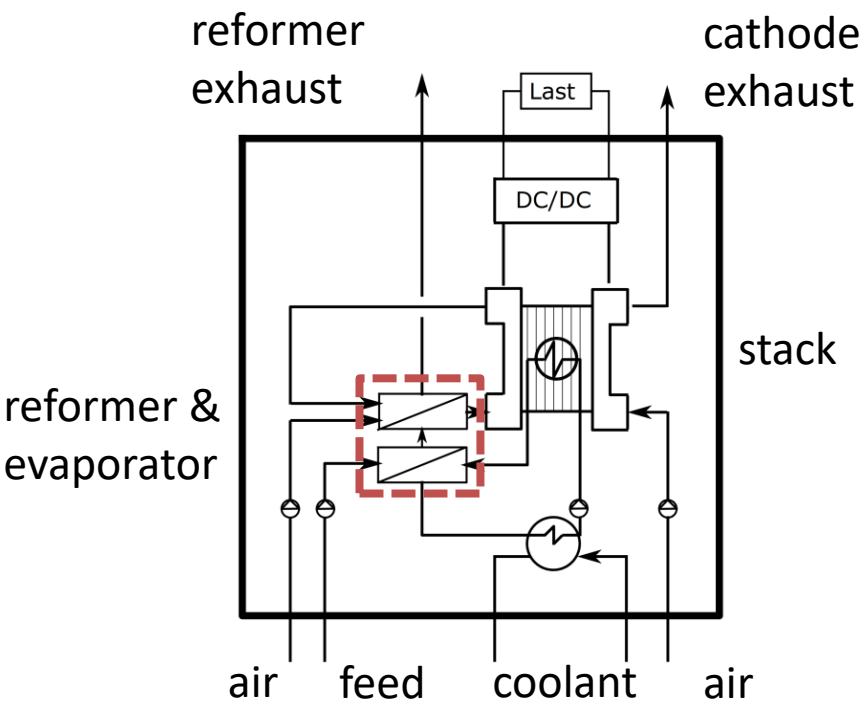
measurements

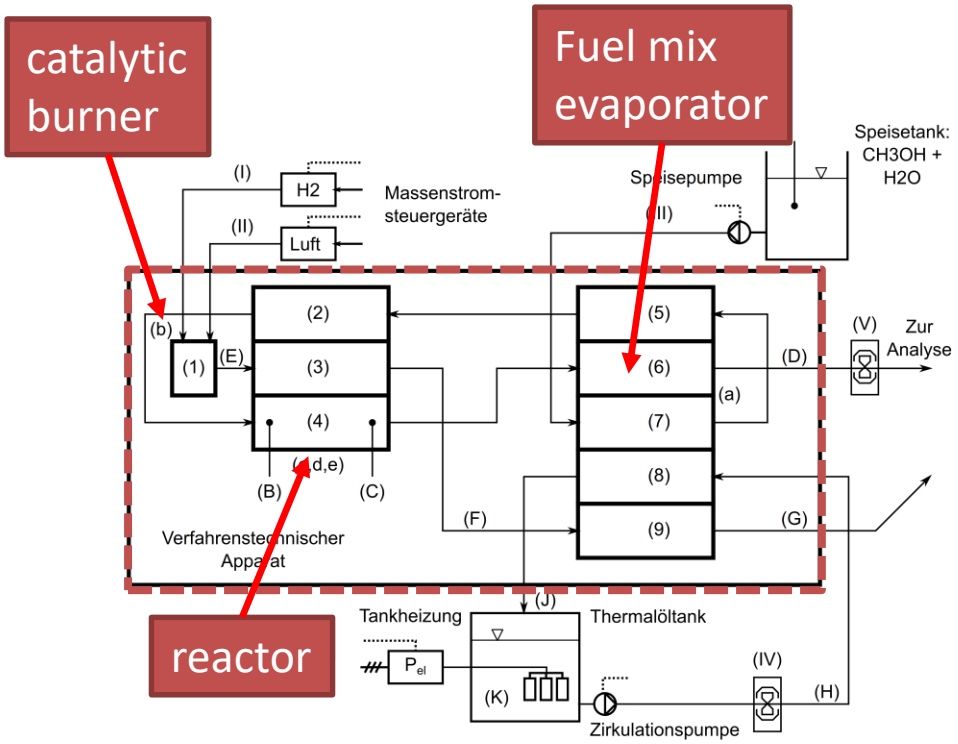


setup

a) reactor with fluegas heat exchanger
b) evaporator with oil inlet and exhaustgas pipe
c) heated oil tank
d) heated measuring pipe
e) MFCs for air and hydrogen
f) solid state relais
g) Labview compact rio

HT-PEM
FCS module and reformer





fuel cell system module

- anode gas: synthesis gas ($H_2 + CO_2 + H_2O$)
- Methanol steam reforming in processing unit called: reformer
- stack waste heat recovery: fuel mix evaporation

reformer

- catalytic burner: burns anode off gas
- reactor: $CH_3OH + H_2O \rightarrow 3\ H_2 + CO_2$
- evaporator uses waste heat from: stack, fluegas & synthesis gas

physical model reformer

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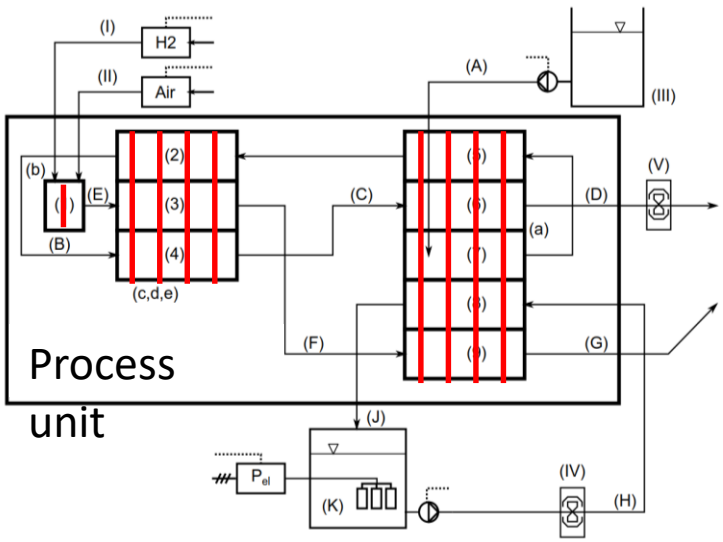
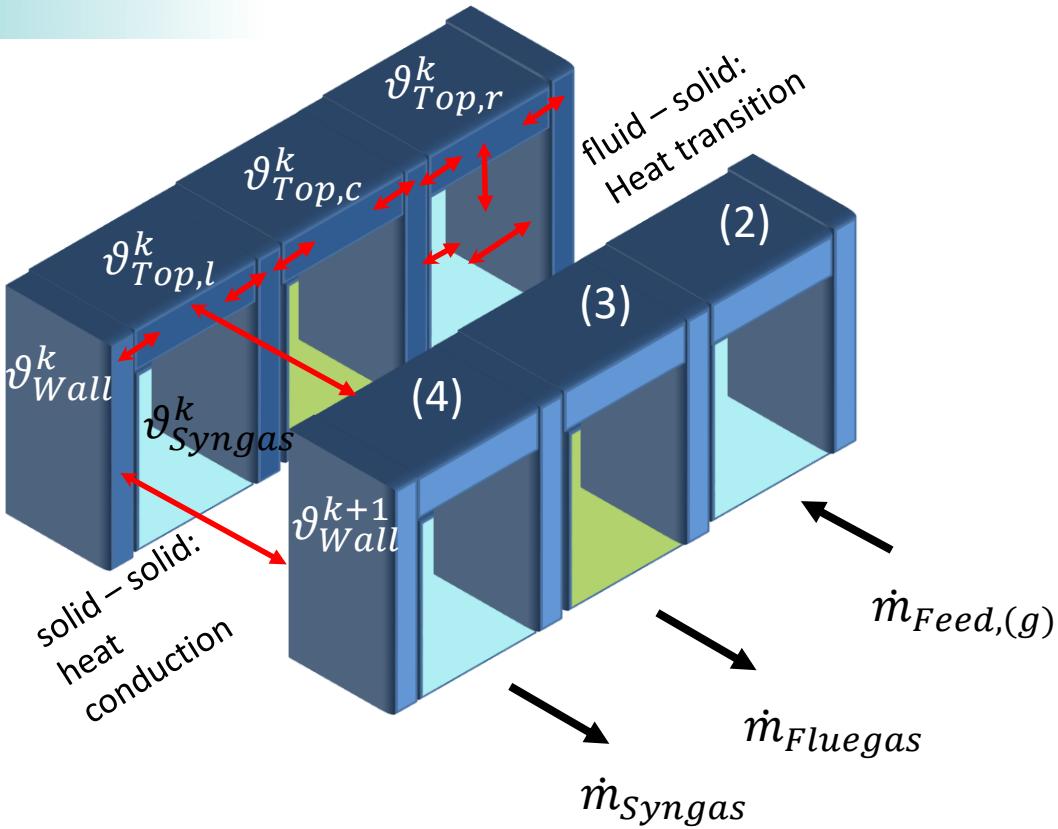
first principle of thermodynamics

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \sum \dot{Q} = \dot{\vartheta}_{CV} \cdot m_{CV} \cdot c_{p,CV}$$





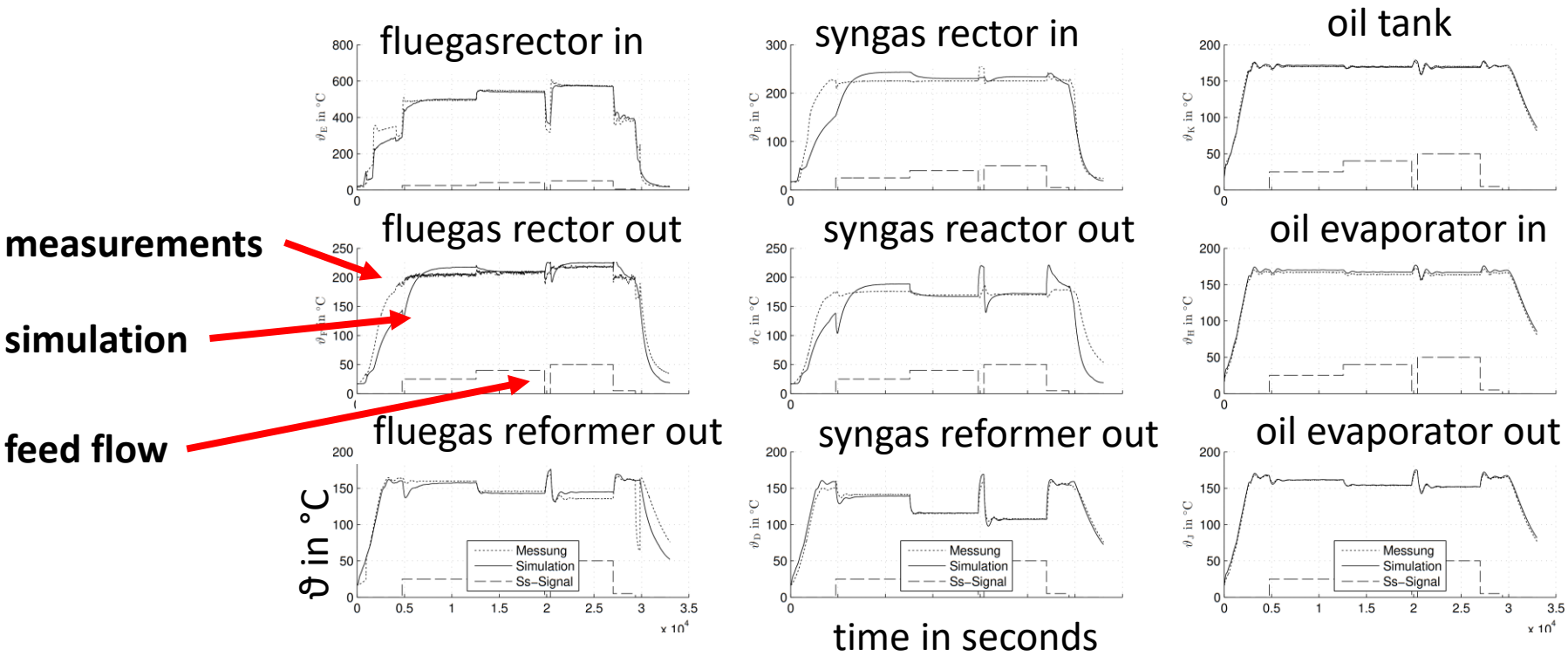
discretization in flow direction

- 2 sections catalytic burner
- 5 sections reformer
- 5 sections evaporator

controlvolumes

- every element has its own mass, connecting areas, conductivity and specific heat. → $\dot{\vartheta}_{CV}$
- elements (fluid & solid) are coupled by heat transition and conduction

model calibration



parameter estimation

- minimisation of the quadratic difference to measurements
- simple geometry: identical geometric data in every section
- time intense iterative procedure: ~ 100 Parameters to guess
- direct feedback to the user: e.g. heat conduction in aluminum housing

physical model bipolar plate

first principle of thermodynamics

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \sum \dot{Q} = \dot{\vartheta}_{CV} \cdot m_{CV} \cdot c_{p,CV}$$

bipolar plate

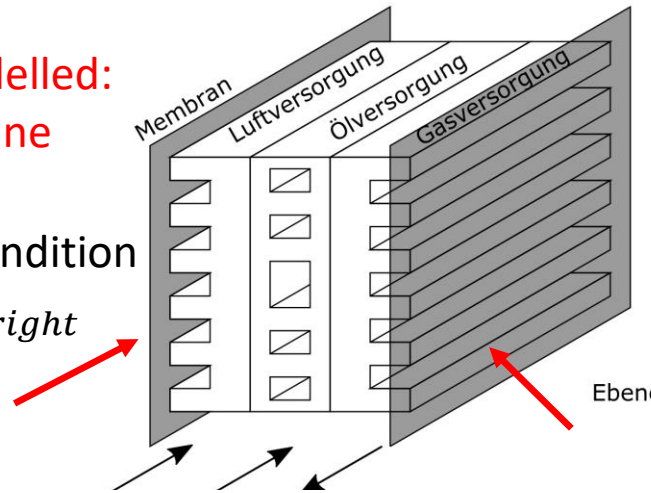
← ~ 3 mm →

thermal model

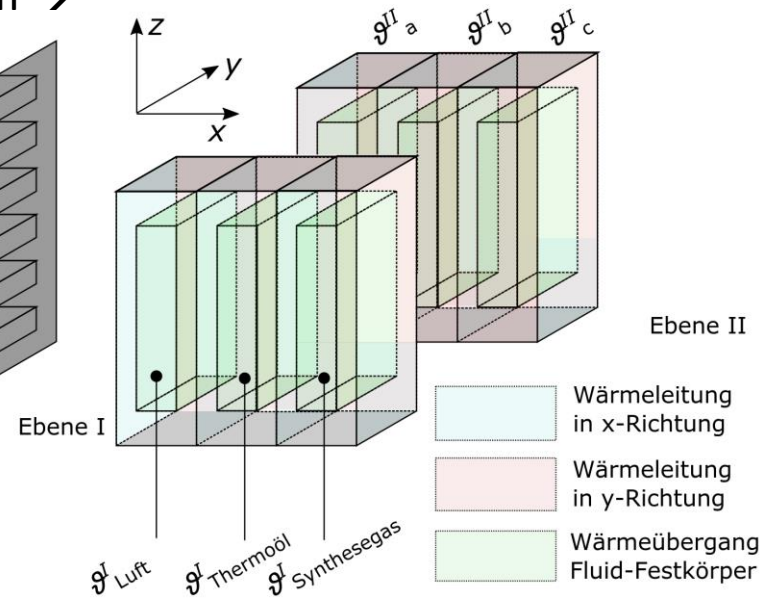
not modelled: membrane

boundary condition

$$\vartheta_{left} = \vartheta_{right}$$



air oil synthesisgas



bipolar plate

- 1 plate represents the stack → massflows are scaled
- simple geometry: identical geometric data in every section (total 5)
- not validated with measurements
- geometry known, pyhsical properties from literature

HT-PEM model

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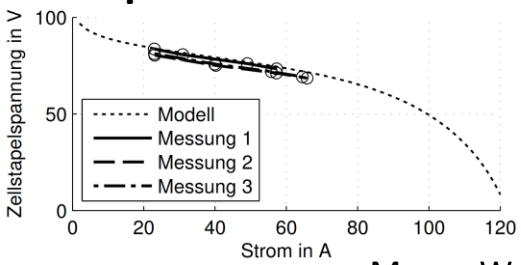
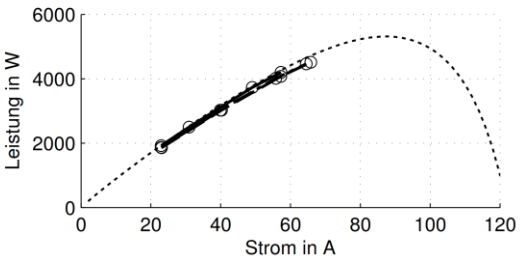
fuel cell system model
- reformer
- stack (5300 W)
- auxiliaries (300 W)
- control

polarization curves



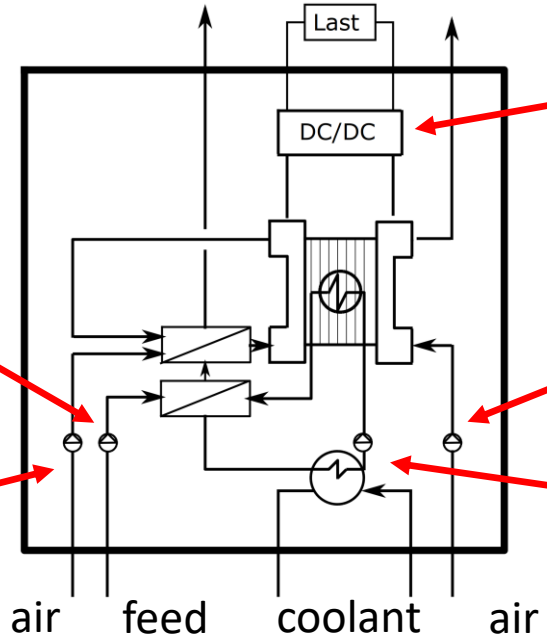
power curve



Meyer-Werft measurements

reformer control
- λ_{H2}-stack changes in order to supply heat for a constant reactor temperature
→ *feedflow*

- λ_{O2}-reactor follows the measurements
→ *airflow*



stack control
- electric power is a control objective
→ *stack current*

- λ_{O2}-stack is constant
→ *cathode airflow*

- oil mass flow is controlled to keep stack temperature constant
→ *oilmassflow*

simulation results
FCSM characteristics

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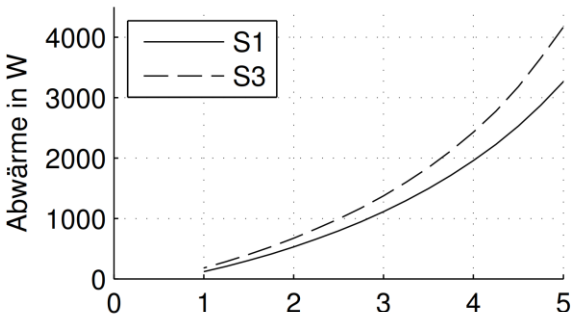
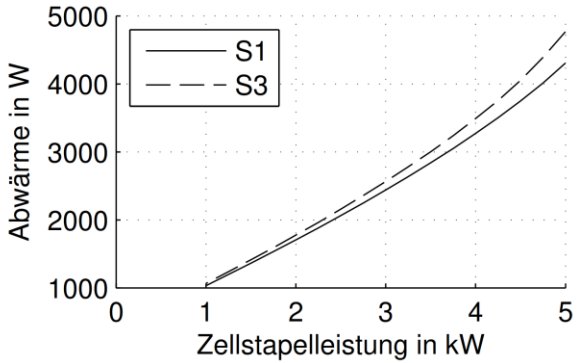
cooling water wh

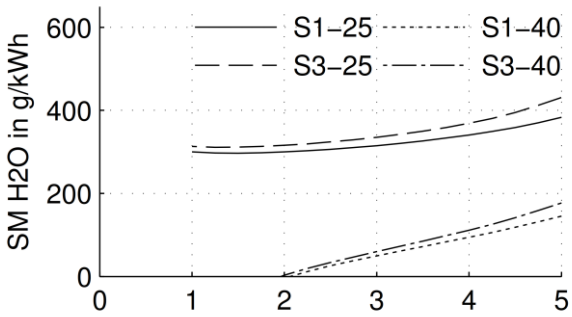


el. power FCSM in kW

exhaust gas wh



H2O overproduction



SM H2O > 0:
self supply possible

$$\boxed{\frac{3}{2}H_2O} + CH_3OH \longrightarrow \boxed{3H_2 + CO_2 + \frac{1}{2}H_2O}$$

steam reforming

combustion

$$\boxed{3H_2 + CO_2 + \frac{1}{2}H_2O} + \frac{3}{2}O_2 \longrightarrow CO_2 + \boxed{\frac{7}{2}H_2O}$$

characteristics

- waste heat in cooling water and exhaustgas
- fuel cell stack produces water
- exhaustgas cooling recovers water (25 °C & 40 °C)

FCSM results

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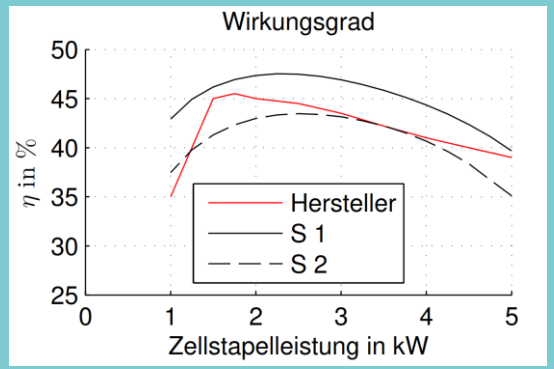
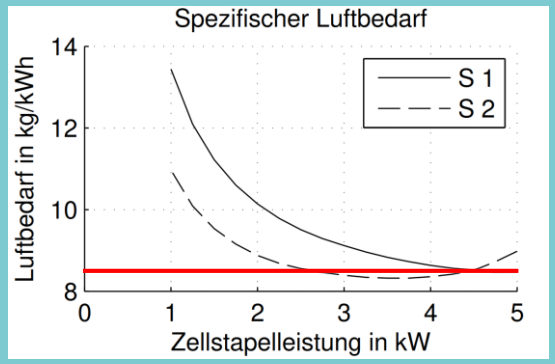
simulation results:

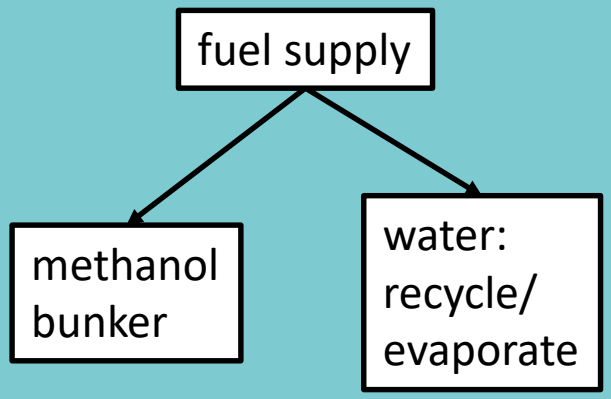
- **efficiency**
  (> 40 %)



- **air demand**
  (similar DG)

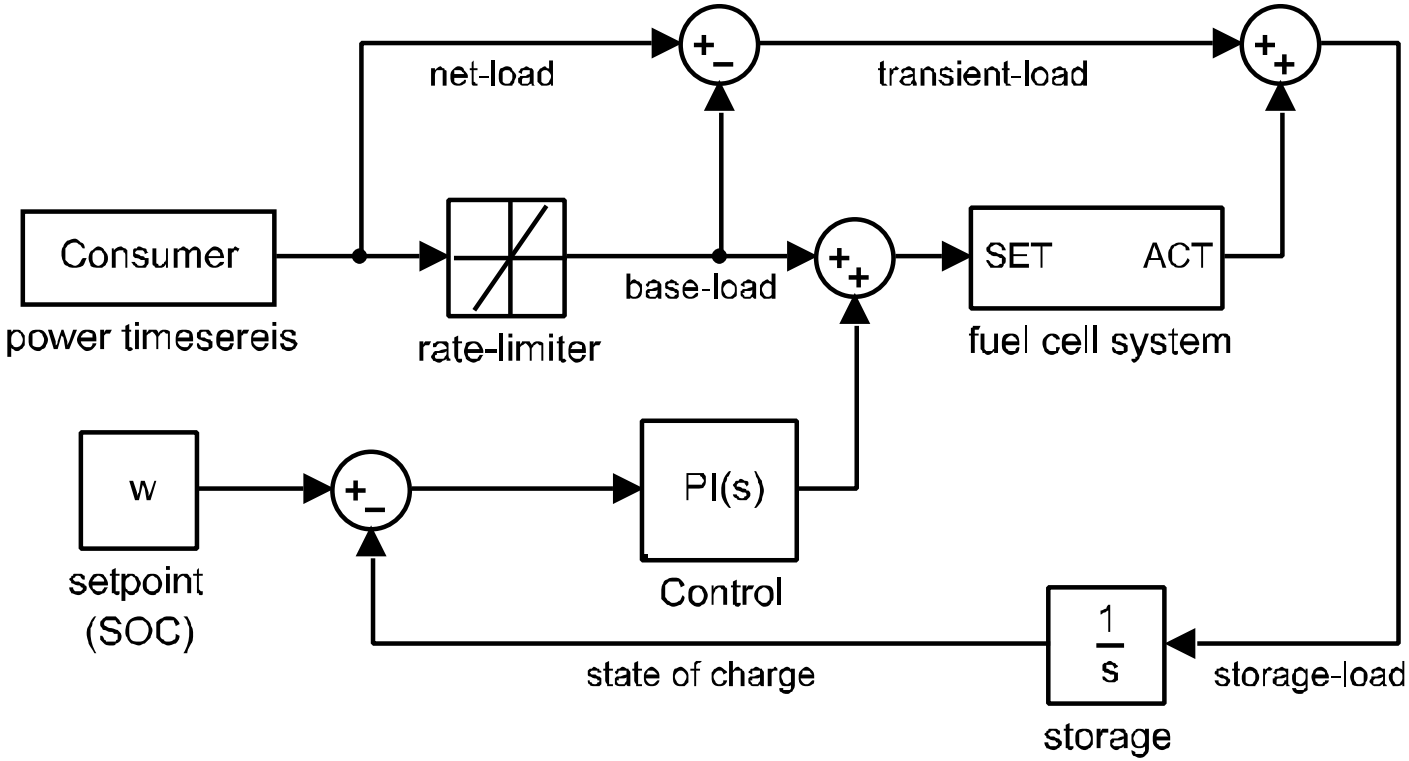


new pol. curve (S 1), degraded (S 2)



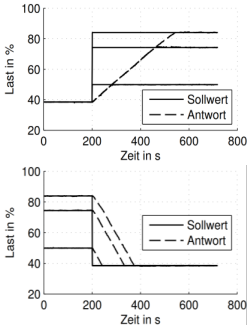
- **exhaustgas composition**
  (humid air and CO2)
- **waste heat use:**
  (for seawater evaporation)

energy simulation



system simulation

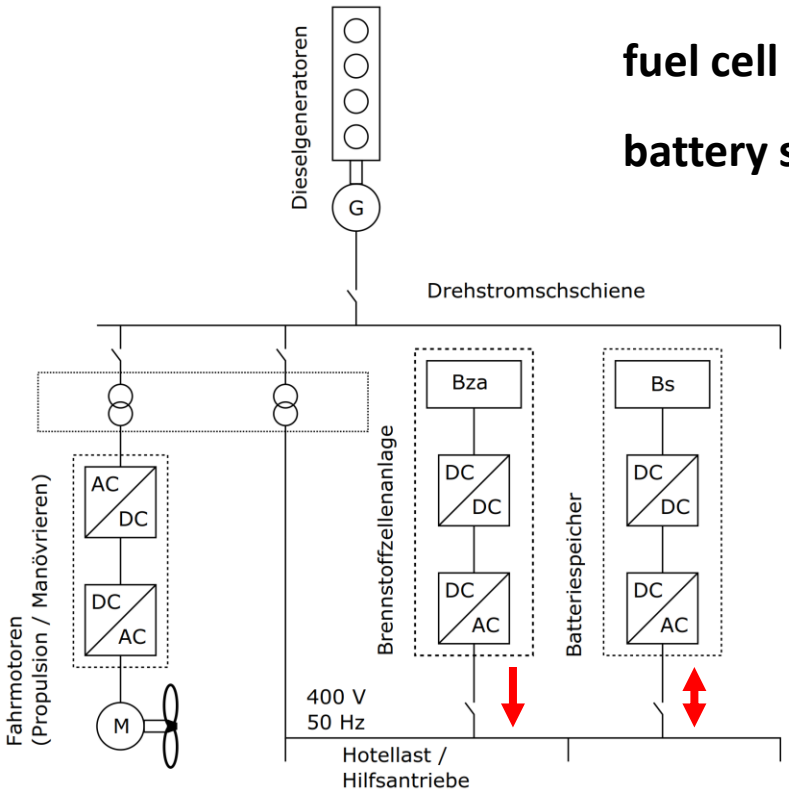
- Input: measurements general consumers
- Fuel cell system model with load dynamics
- Transients loads for battery storage
- Controlled variable: state of charge

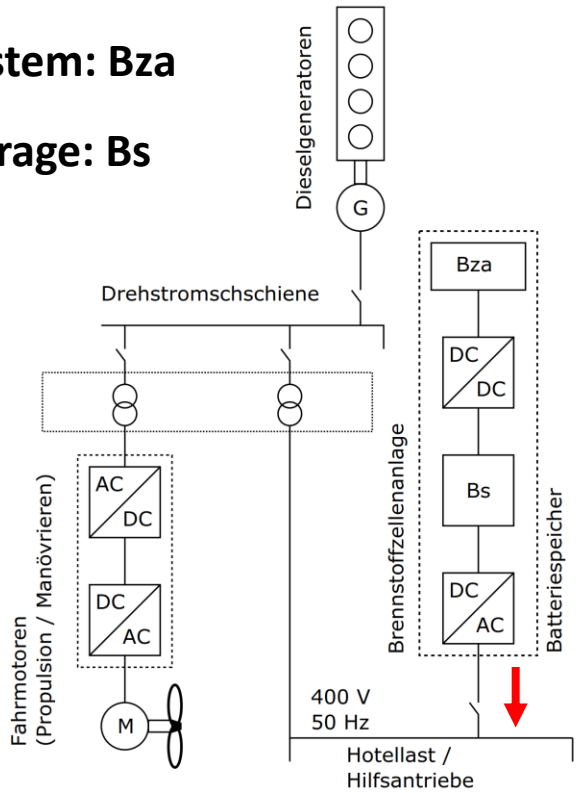


integration

fuel cell system: Bza

battery storage: Bs





single line diagram a

- FCS independent (directional energy flow)
- BS independent (bidirectional energy flow)
- controlled SOC

single line diagram b

- FCS charges the battery storage
- integrated system (unidirectional energy flow)
- Controlled SOC

sizing of a battery storage

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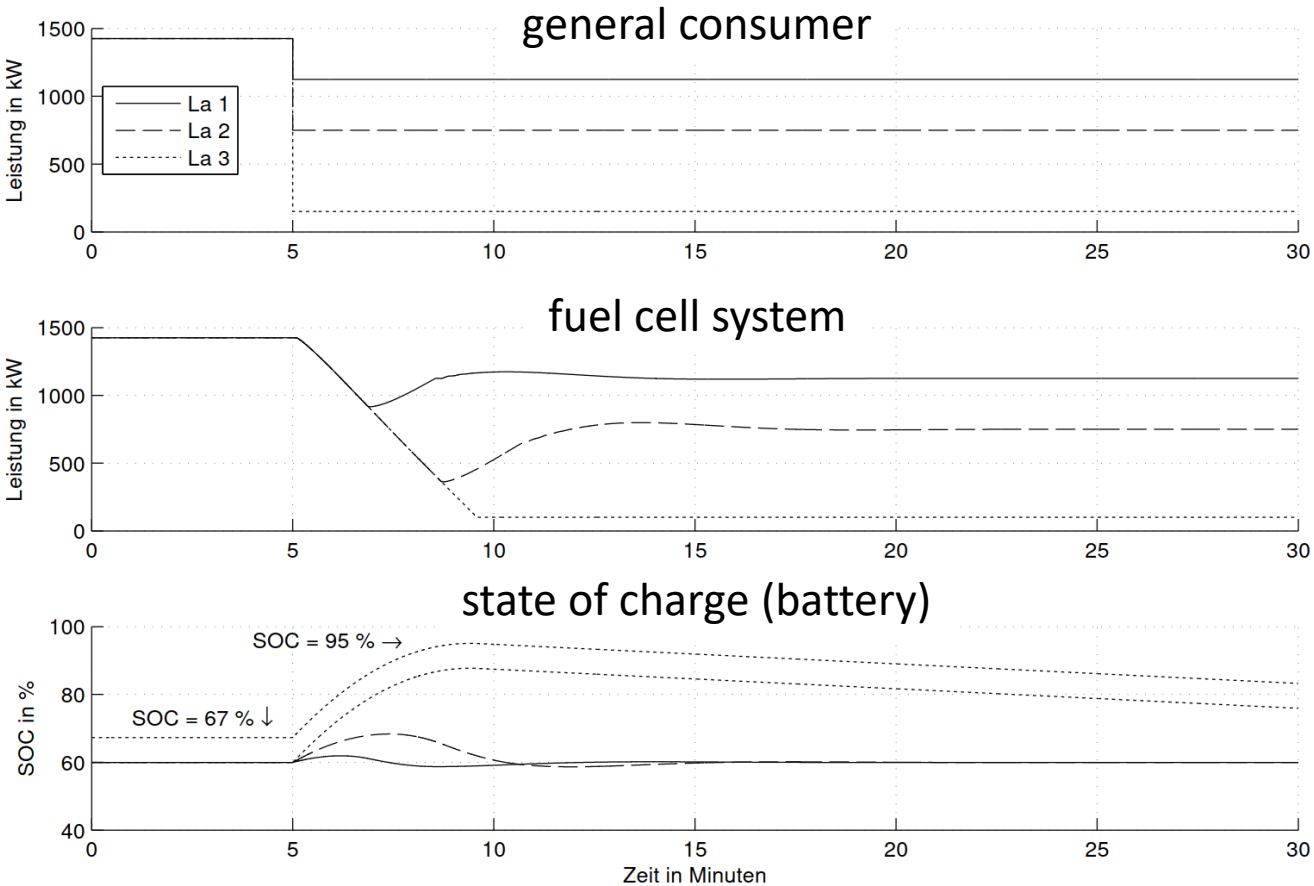

legend

La1: 95 % → 75 %
La2: 95 % → 50 %
La4: 95 % → 10 %

---

battery:

161 kWh
C-Rate < 1

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worst case scenario

- load shedding (La3)
- FCS ramps down
- SOC increases (start: 60 %)

energy simulation results

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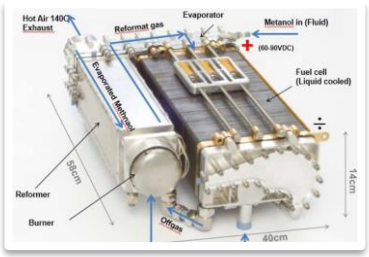

measured 12 day Scenario: ~ 1,5 MW	high speed diesel generator	fuel cell system
specific mass	9 kg/kW	19 kg/kW (incl. battery)
specific volume	14 … 20 l/kW	20 l/kW
CO2	100 %	83 %

conclusion

- FCS reduce air pollutants (humid air + CO2, low noise, no vibrations)
- energy storage necessary
- comparable size and volume to medium speed dieselgenerator
- expensive

thank you for your attention!

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simulation results
FCSM characteristics

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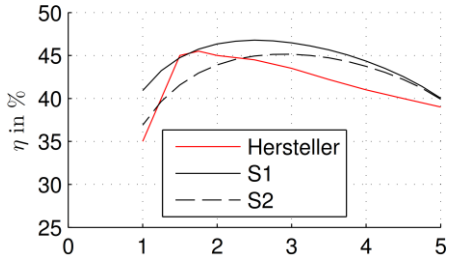
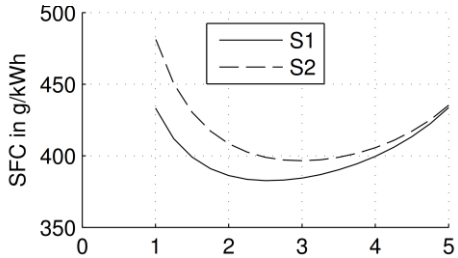
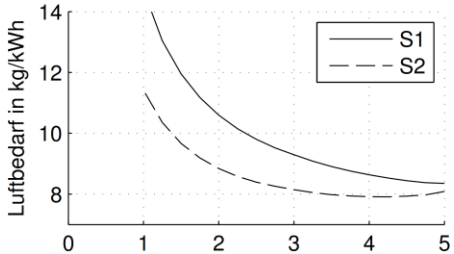
efficiency



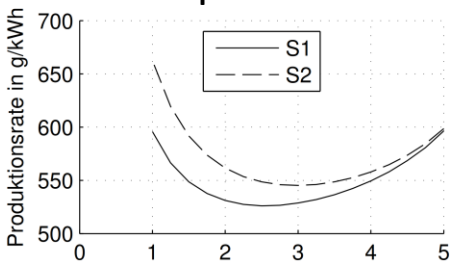
CH3OH consumption



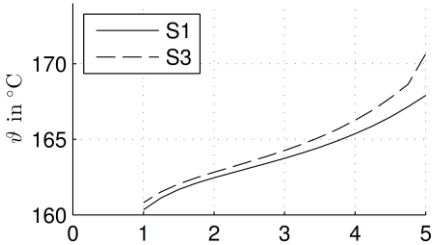
air demand



CO2 production



exhaustgas temperature



el. power FCSM in kW

characteristics

- from simulation extracted data for steady states
- S1/S2 different operating modes
- S1/S3 new ←→ degradated polarization curve

→ OK efficiency match

energy simulation

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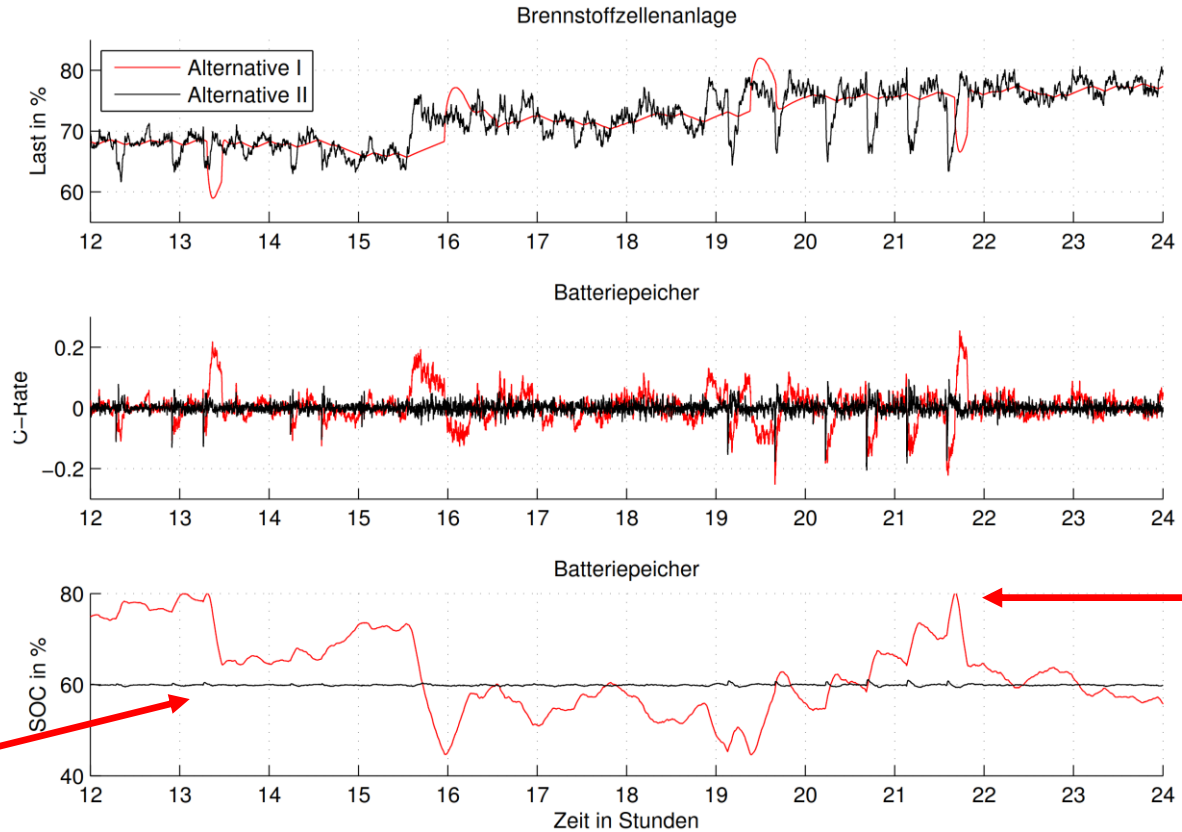

mode for critical operations

mode for uncritical operations

load following mode or SOC boundary

- FCS can follow the load in 80 % of all cases
→ no significant change of SOC (high frequency switching: load - unload)
→ SOC always at setpoint of 60 % (good to survive crtical load cases)
- FCS can operate highly decoupled from load (Alternative II)

fuel cell systems vs dieselgeneratorors (10.2017)

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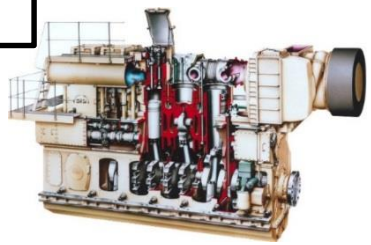
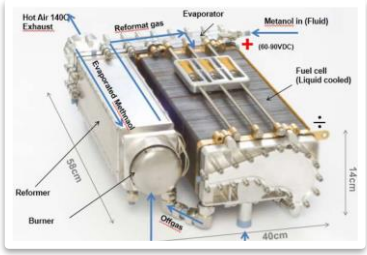
HFO = 294 €/t;
MGO = 428 €/t;
H2 = 9500 €/t
CH3OH = 330€/t





	MSL	SL	PEM (H2)	HT-PEM (CH3OH)
mass / power	$17\ \frac{kg}{kW_{el,AC}}$	$9\ \frac{kg}{kW_{el,AC}}$	$10\ \frac{kg}{kW_{el,DC}}$	$12 \ldots 15\ \frac{kg}{kW_{el,DC}}$
volume / power	$27\ \ldots\ 37\ \frac{l}{kW_{el,AC}}$	$14\ \ldots\ 20\ \frac{l}{kW_{el,AC}}$	$14\ \frac{l}{kW_{el,DC}}$	$17\ \frac{l}{kW_{el,DC}}$
fuel consumption	$205\ \frac{g}{kWh}$	$225\ \frac{g}{kWh}$	$72\ \frac{g}{kWh}$	$440\ \frac{g}{kWh}$
price	$280\ \ldots 400\ \frac{€}{kW_{el,AC}}$		$5000\ \frac{€}{kW_{el,DC}}$	$5000\ \frac{€}{kW_{el,DC}}$
electric energy price	$0{,}06\ \frac{€}{kWh_{AC}}$	$0{,}10\ \frac{€}{kWh_{AC}}$	$0{,}68\ \frac{€}{kWh_{DC}}$	$0{,}15\ \frac{€}{kWh_{DC}}$

Methodology
Measurements + Simulation

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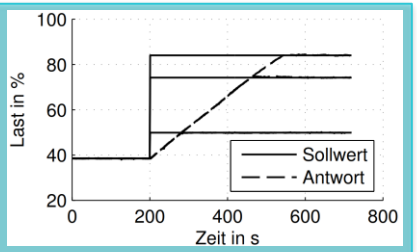
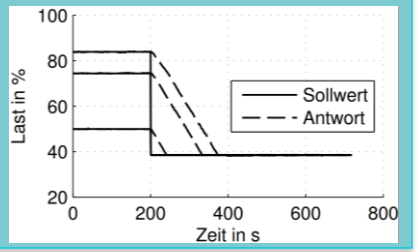
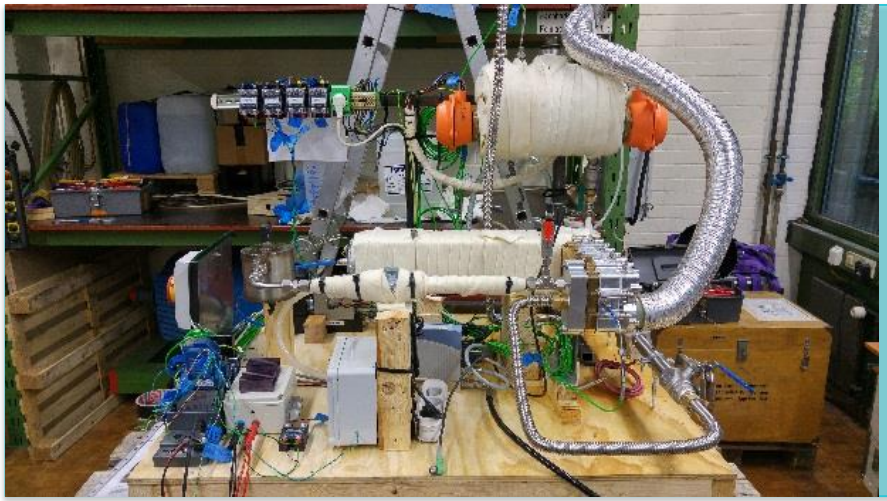
pilot plant (2 x 5 kW)
- AC operation
- exhaustgasanalysis
- waste heat potential

→ limited load change
(8 %/min & 17 %/min)



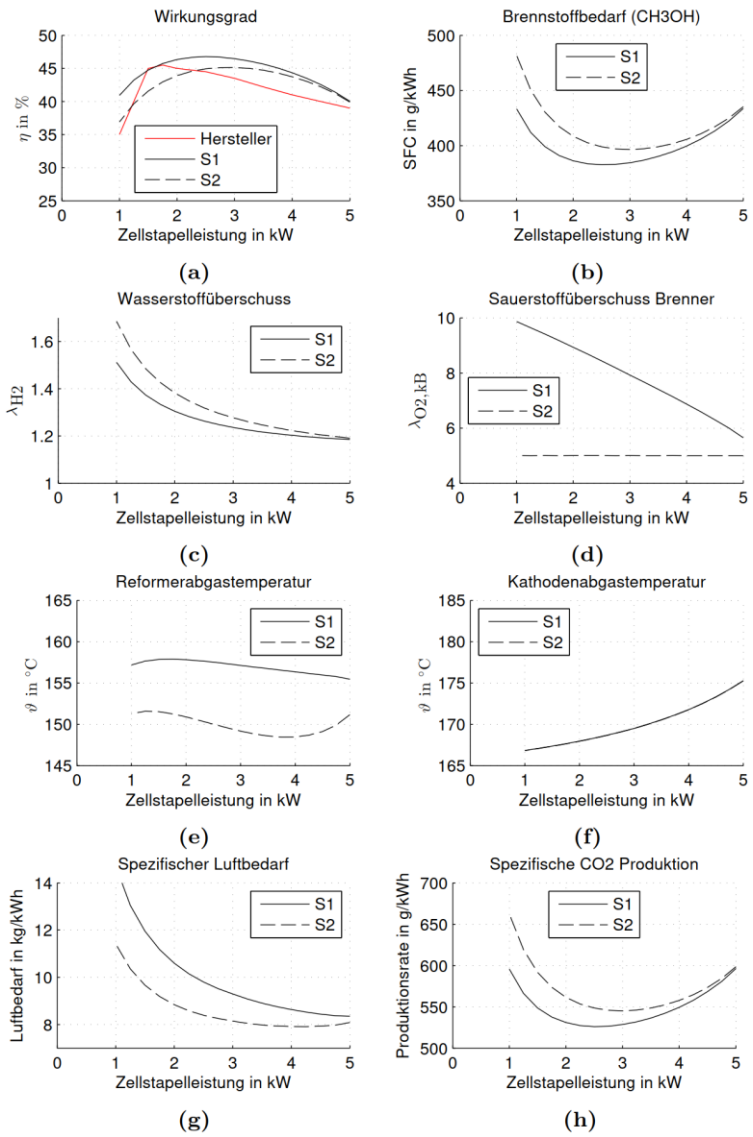


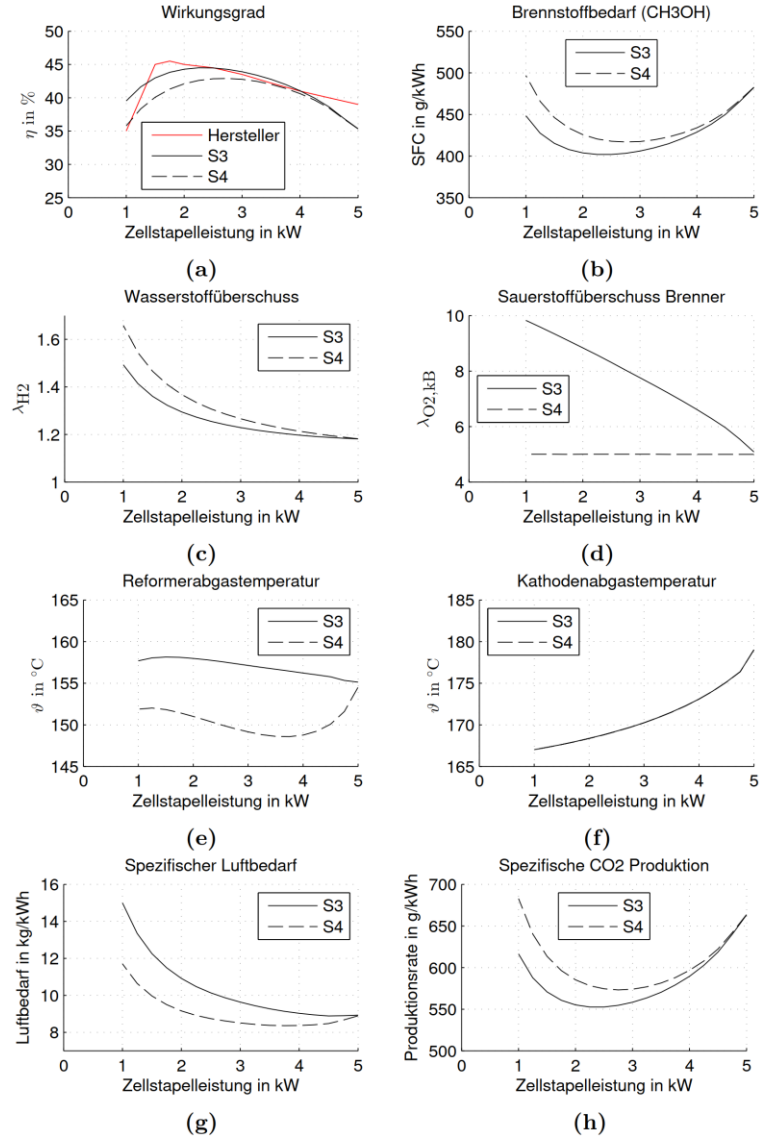


methanol reformer
- dynamics (syngas output: vane anemometer)
- temperatures (fluids & body)
- FC-stack waste heat (ϑ-controlled)
- catalytic burner (controlled MFCs H2 & air)
- synthesis gas composition using gas chromatography

pilot plant: METHANOL POWERED FUEL CELL SYSTEMS FOR MARINE APPLICATIONS, C. Thiem, C. Gentner & G. Ackermann; SCC 2015

simulation results new vs degraded





steady state measurements

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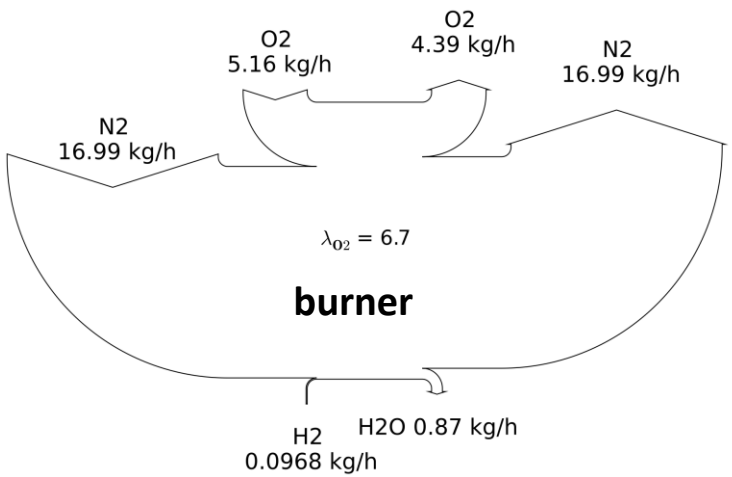
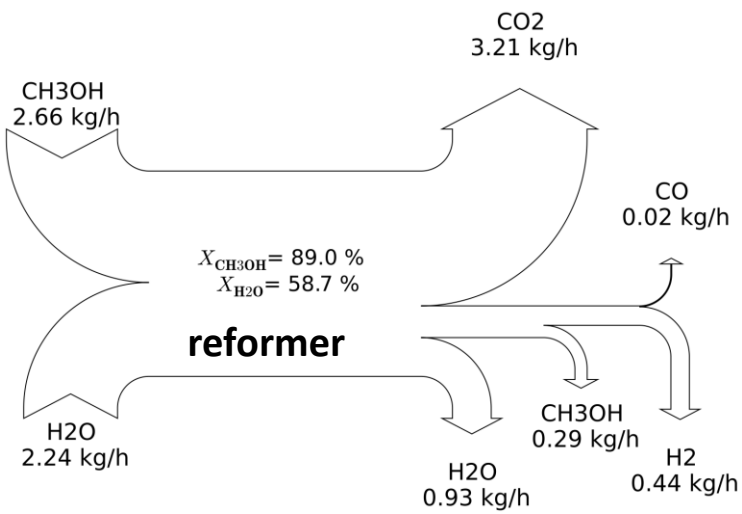
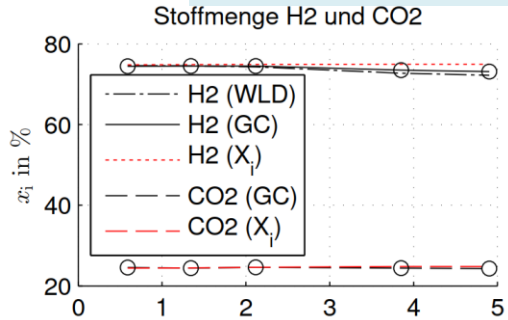
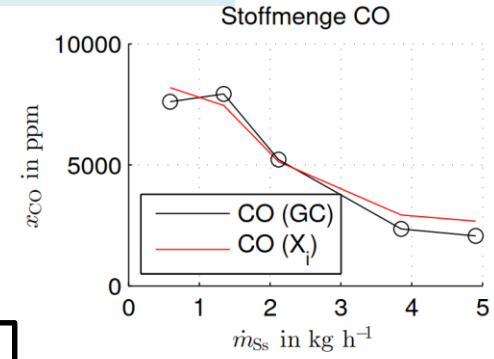




analysis of synthesis gas composition

- H2 using a thermal conductivity sensor (WLD)
- H2 using gas chromatography (GC)
- CO2 … (GC)
- CO … (GC)
- CH3OH: condensate head space analysis (GC)





stoichiometric results: (X_i)

$\dot{m}_{Feed}$	X_{CH_3OH}	X_{H_2O}	$x_{CH3OH}^{Measure}$	x_{CH3OH}^{Calc}
0,59 kg/h	1,000	0,645	0,1 Vol.-%	0,0 Vol.-%
1,34 kg/h	0,997	0,645	0,3 Vol.-%	0,6 Vol.-%
2,12 kg/h	0,980	0,640	2,7 Vol.-%	3,6 Vol.-%
3,85 kg/h	0,900	0,593	14,2 Vol.-%	14,1 Vol.-%
4,90 kg/h	0,890	0,587	13,9 Vol.-%	15,1 Vol.-%

Theoretical considerations
Steam to carbon ratio

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The fuel mix (feed) consists of 60 vol.-% methanol and 40 vol.-% water (S/C = 1,5).
Is it the optimum?

How do the equilibrium states look like?
→ Minimize the Gibbs energy.

$$\frac{S}{C} = \frac{n_{H2O}}{n_{CH3OH}}$$

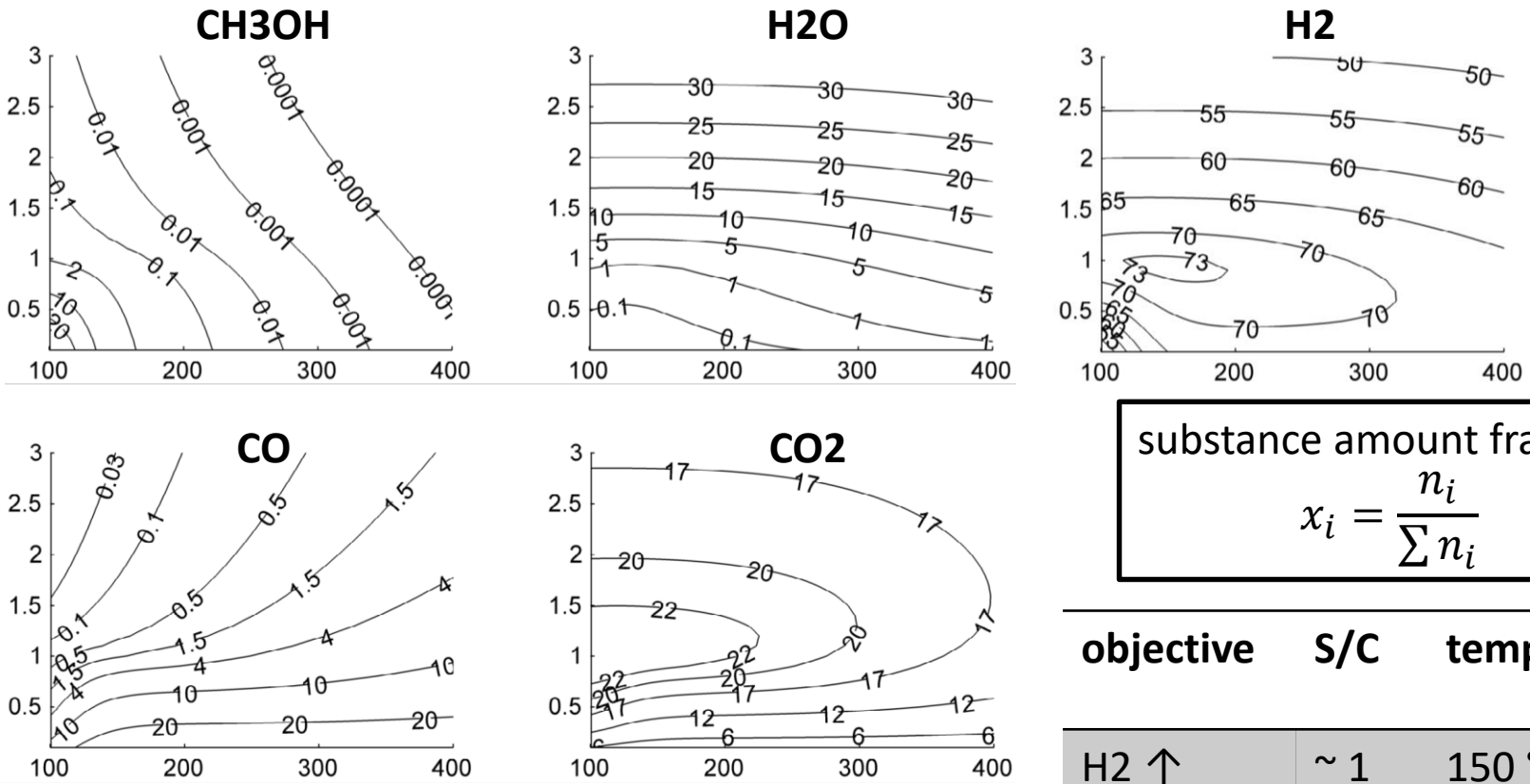
$$n_{Mix} = n_{H2O} + n_{CH3OH}$$

$$x_{CH3OH} = \frac{n_{CH3OH}}{n_{H2O} + n_{CH3OH}}$$

Masse % MeOH	Stoffmengen-anteil % MeOH	Volumen % MeOH
0	0	0
5	2,87	6,22
10	5,88	12,29
15	9,03	18,21
20	12,32	23,97
25	15,78	29,60
30	19,42	35,09
35	23,24	40,44
40	27,26	45,68
45	31,51	50,78
50	35,99	55,78
55	40,73	60,65
60	45,75	65,42
65	51,08	70,08
70	56,75	74,64
75	62,78	79,10
80	69,22	83,46
85	76,11	87,73
90	83,50	91,90
95	91,44	95,99
100	100	100

Methanex 2006

Theoretical considerations
Steam to carbon ratio



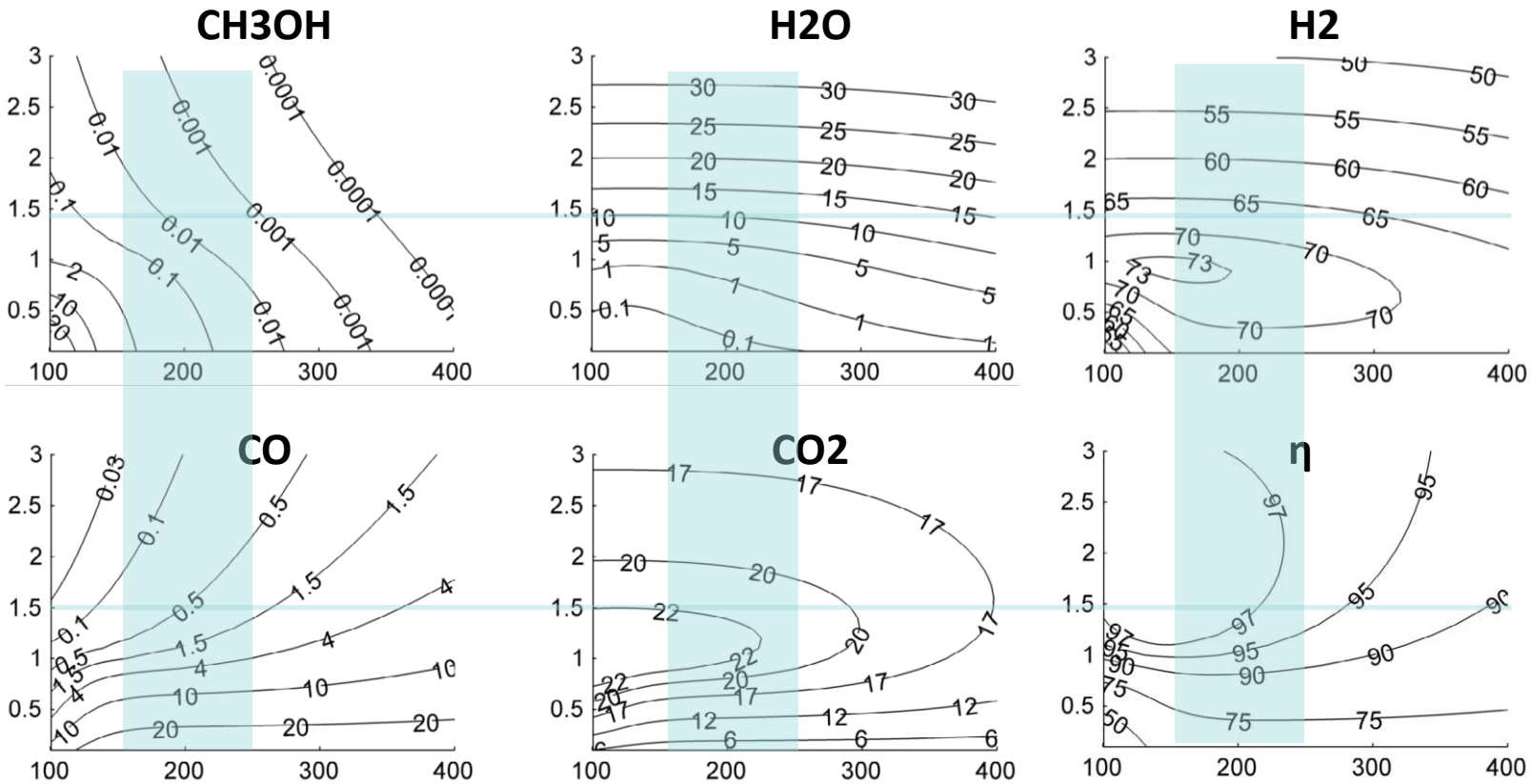
X-axis: temperature in °C
Y-axis: S/C ratio

substance amount fraction

$$x_i = \frac{n_i}{\sum n_i}$$

objective	S/C	temperature
H2 ↑	~ 1	150 °C
CO ↓	high	low
CH3OH ↓	high	High
η ↑	High	small

Theoretical considerations
Steam to carbon ratio



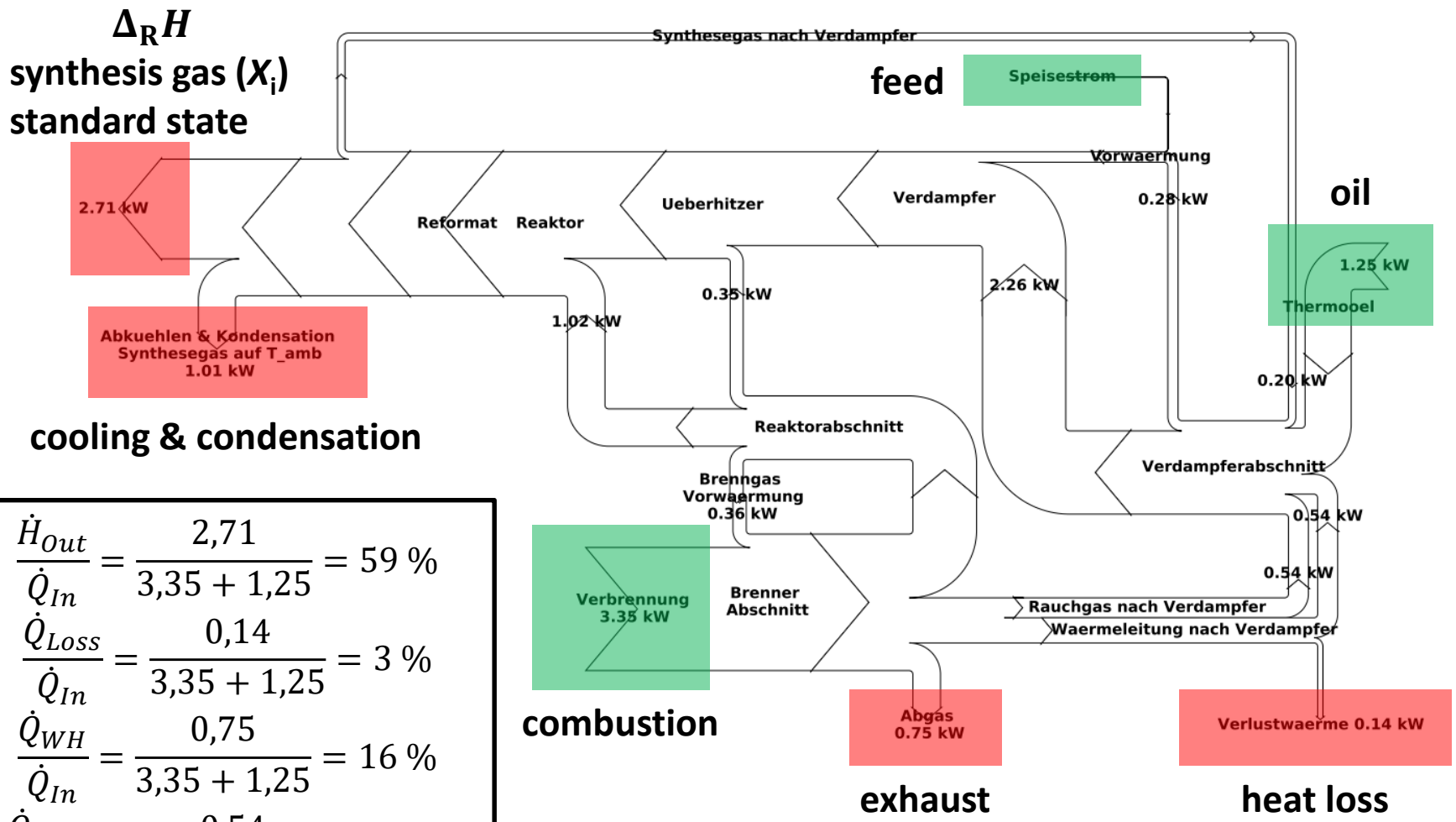
S/C = 1,5 (60 % CH3OH)
OK!
ϑ = 150 °C … 250 °C

X-axis: temperature in °C
Y-axis: S/C ratio

$$\eta_{\text{Prozess}} = \frac{\dot{m}_{\text{H}_2} \cdot H_{\text{i,H}_2}}{\dot{m}_{\text{Ss}} \cdot H_{\text{i,Ss}} + \sum \Delta \dot{H} + \sum \Delta \dot{H}_{\text{f}\rightarrow\text{g}} + \sum \Delta_R \dot{H}}$$

$$\dot{m}_{\text{Ss}} \cdot H_{\text{i,Ss}} = \dot{m}_{\text{CH}_3\text{OH}} \cdot H_{\text{i,CH}_3\text{OH}} + \dot{m}_{\text{H}_2\text{O}} \cdot \Delta_{\text{v}} h_{\text{H}_2\text{O}}$$

Measurements
Sankey Diagram (Load = 100 %)



$$\frac{\dot{H}_{Out}}{\dot{Q}_{In}} = \frac{2{,}71}{3{,}35 + 1{,}25} = 59\ \%$$

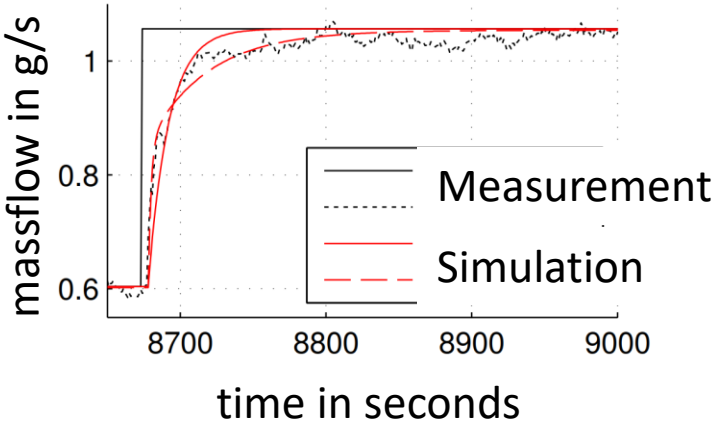
$$\frac{\dot{Q}_{Loss}}{\dot{Q}_{In}} = \frac{0{,}14}{3{,}35 + 1{,}25} = 3\ \%$$

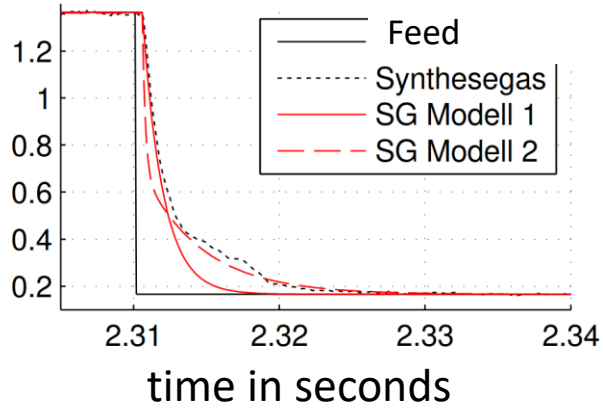
$$\frac{\dot{Q}_{WH}}{\dot{Q}_{In}} = \frac{0{,}75}{3{,}35 + 1{,}25} = 16\ \%$$

$$\frac{\dot{Q}_{Cond}}{\dot{H}_{Eva}} = \frac{0{,}54}{2{,}26 + 0{,}28} = 21\ \%$$

Measurements
Dynamic behaviour

No hydrogen discontinuities are detected for changing feed flow!



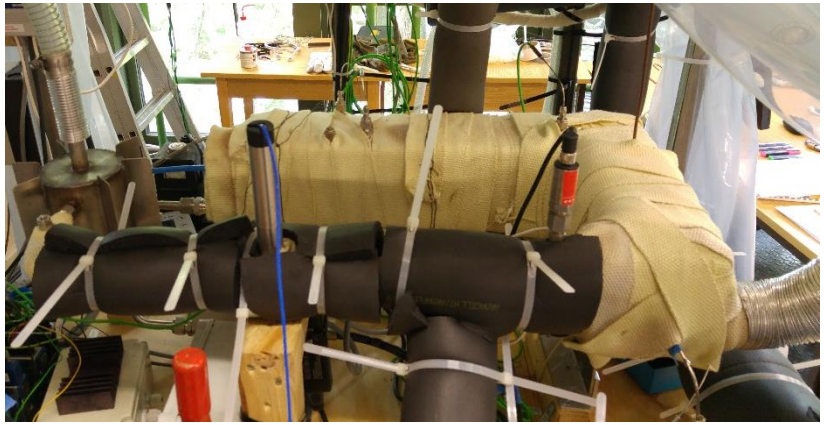


$$G_{\text{Modell 1}}(s) = \frac{0,0713}{s + 0,0713}\, e^{-5\ s}$$

$$G_{\text{Modell 2}}(s) = \frac{0,2865\ s + 0,012}{s^2 + 0,516\ s + 0,012}\, e^{-5\ s}$$

reasons for high order system with dead time

- film flow evaporation causes timedelay
- higher order due to series connection of control volumes:
  1. evaporator
  2. superheater
  3. reactor
  4. heat exchanger



insulated temperature controlled measuring section with vane anemometer

Stand der Wissenschaft
Brennstoffzellen auf Schiffen

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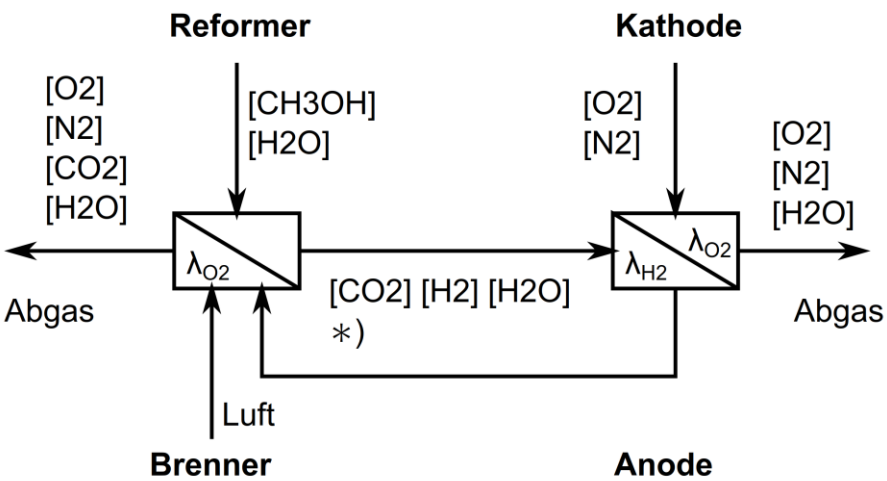
Vorangegangene Forschungsprojekte

Projekt	Schiff	Bz-Technologie	Leistung / kW	Brennstoff
1985 ff. Studie	Vindicator	MCFC	4 x 625	MDO
2003 ff. Demo.	Viking Lady	MCFC	320	LNG
2006 ff. Demo.	Undine	SOFC	20	CH3OH
2006 ff. Demo.	Alsterwasser	PEM	50	H2O

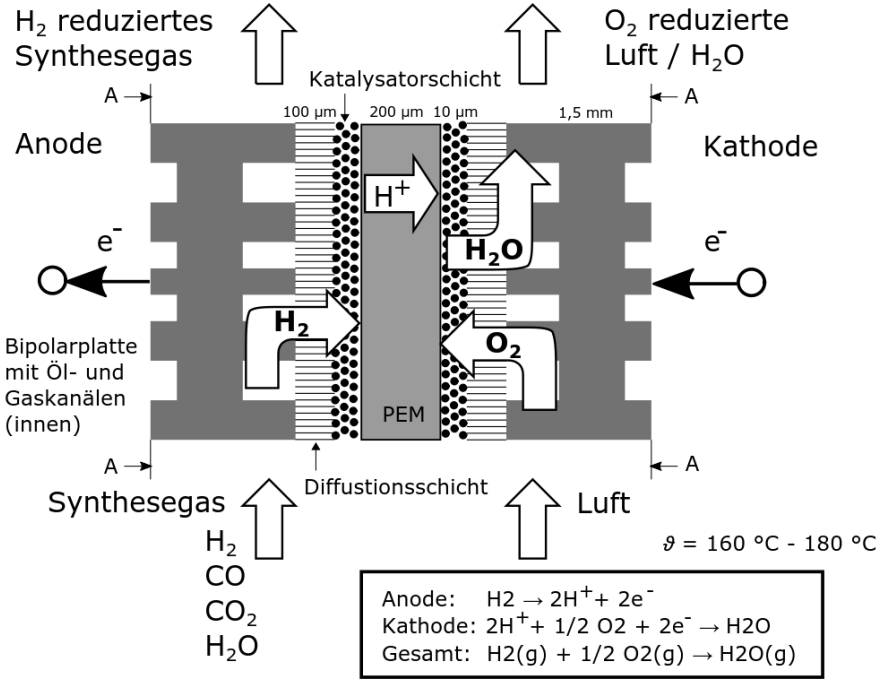
ab 2009 folgen: Rivercell, E4Ships, E4Ships 2 und viele weitere
- Pa-X-ell (HT-PEM mit Methanol + Wasser)
- ShiBZ (SOFC mit Diesel)

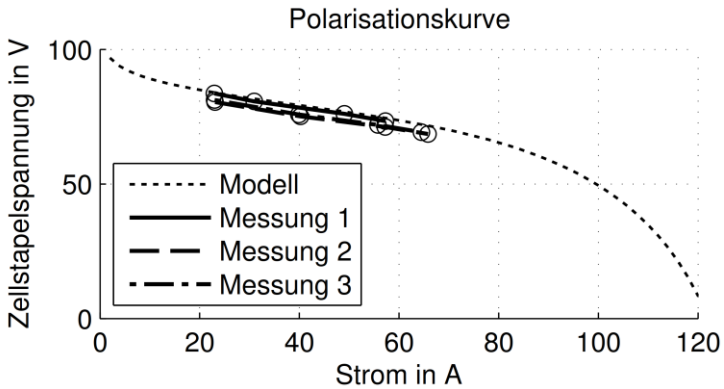
HT-PEM Modellierung

- **Massenbilanz:**
  Reaktorumsatz -> Polarisationskurve
- **Energiebilanz:**
  Fluid- & Festkörpertemperaturen



∗) zusätzlich Spuren von [CH3OH] und [CO]





Metrological investigation
Steady State Measurements

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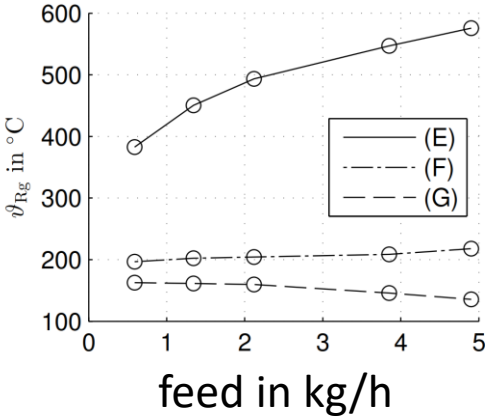
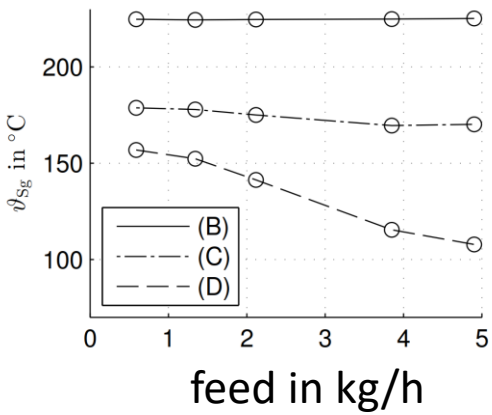
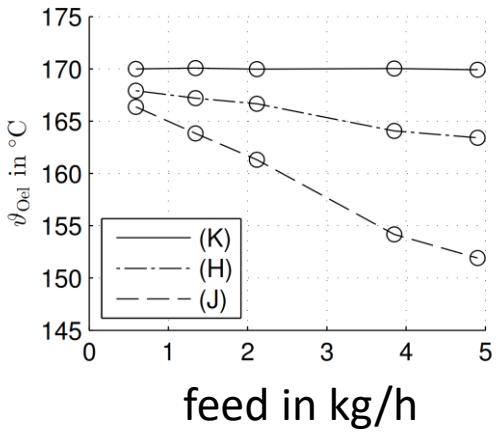
fluegas

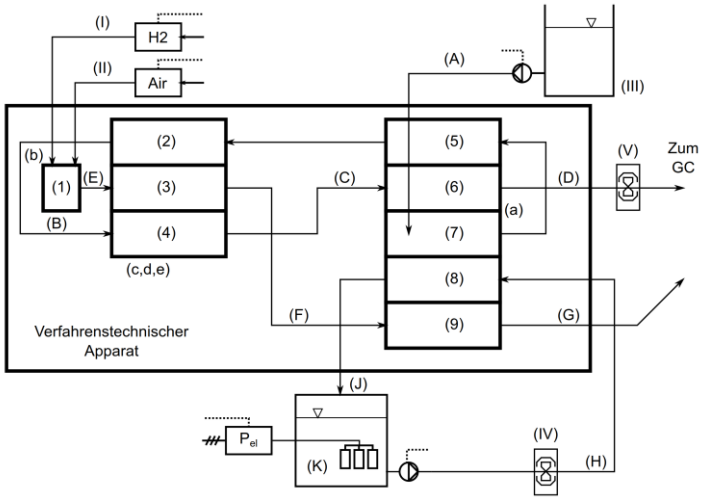


synthesis gas

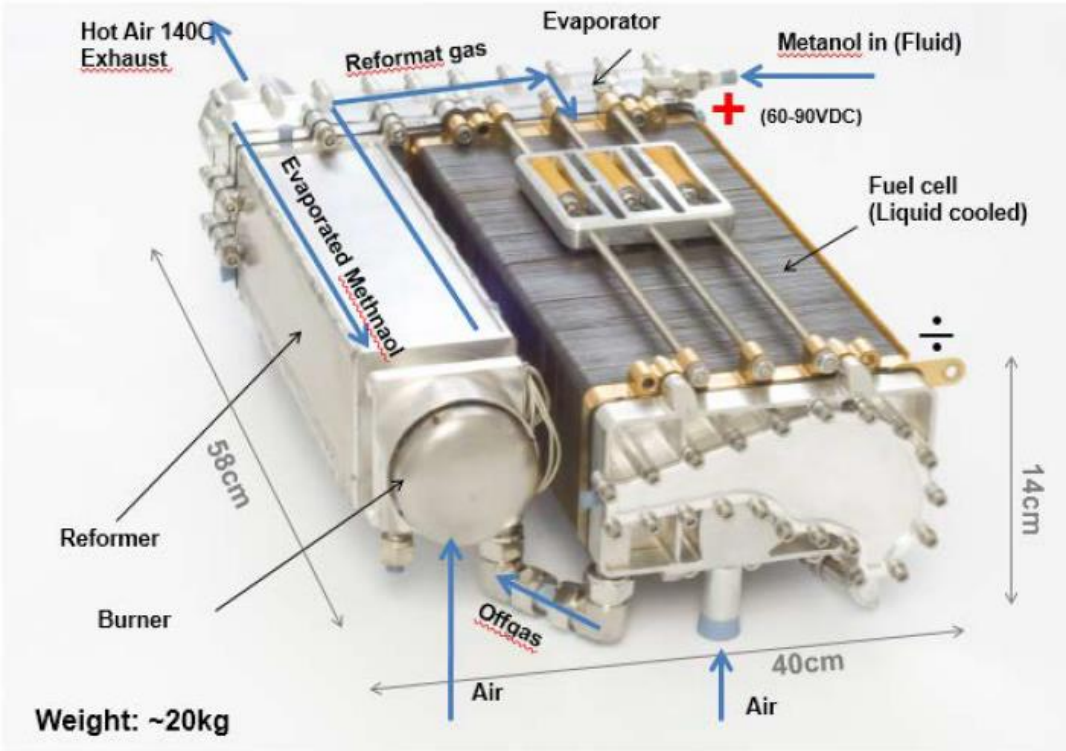


oil





Systembeschreibung H3 5000



- Electric power: 5kW
- Thermal power: 4-5kW
- Total efficiency (LHV): >85%
- Elec. efficiency(LHV): 40-50%
- Weight: 45kg
- Dimensions:
  - Width: 19”/430mm
  - Length: 700mm
  - Height (6U/253mm)
  - Volume: 77L
- DC/DC: integrated – bat charging capability
- Output voltage: 24/48/80 or 400-600 VDC

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