A HT-PEM fuel cell system model for the electric power supply on ships
motivation
reduction of emissions

state of the art
- diesel electric ships

challenge
- reduction of emissions

dieselgenerator
(500 kW)

fuel cell system
(2 x 5 kW)

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

HT-PEM fuel cell system

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
- ???

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
**fuel cell system module**
- anode gas: synthesis gas (H2 + CO2 + H2O)
- Methanol steam reforming in processing unit called: reformer
- stack waste heat recovery: fuel mix evaporation

**reformer**
- catalytic burner: burns anode off gas
- reactor: CH3OH + H2O → 3 H2 + CO2
- evaporator uses waste heat from: stack, fluegas & synthesis gas
physical model reformer

first principle of thermodynamics
\[
\frac{dE}{dt} = \sum Q = \dot{\vartheta}_{CV} \cdot m_{CV} \cdot c_{p, CV}
\]

Process unit

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

**Measurements**
- fluegas reactor in
- fluegas reactor out
- fluegas reformer out
- oil tank
- oil evaporator in
- oil evaporator out

**Simulation**
- syngas reactor in
- syngas reactor out
- syngas reformer out

**Feed Flow**
- time in seconds

**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
\[ \frac{dE}{dt} = \sum Q = \dot{g}_{CV} \cdot m_{CV} \cdot c_{p, CV} \]

bipolar plate \( \sim 3 \text{ mm} \) \( \rightarrow \)

thermal model

not modelled: membrane

boundary condition
\[ \vartheta_{left} = \vartheta_{right} \]

air oil synthesisgas

bipolar plate
- 1 plate represents the stack \( \rightarrow \) massflows are scaled
- simple geometry: identical geometric data in every section (total 5)
- not validated with measurements
- geometry known, physical properties from literature
**HT-PEM model**

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

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**reformer control**
- $\lambda_{H2}$-stack changes in order to supply heat for a constant reactor temperature
  - $\lambda_{H2}$-stack current
- $\lambda_{O2}$-reactor follows the measurements
  - $\lambda_{O2}$-reactor current

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**stack control**
- electric power is a control objective
  - $\lambda_{H2}$-stack current
- $\lambda_{O2}$-stack is constant
  - $\lambda_{O2}$-stack current
- oil mass flow is controlled to keep stack temperature constant
  - oil mass flow

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**Meyer-Werft measurements**

- Polarization curves
- Power curve
simulation results  
FCSM characteristics

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


cooling water wh

exhaust gas wh

H2O overproduction

\[
\frac{3}{2} \text{H}_2\text{O} + \text{CH}_3\text{OH} \rightarrow 3\text{H}_2 + \text{CO}_2 + \frac{1}{2} \text{H}_2\text{O}
\]

combustion

steam reforming

\[
3\text{H}_2 + \text{CO}_2 + \frac{1}{2} \text{H}_2\text{O} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + \frac{7}{2} \text{H}_2\text{O}
\]
FCSM results

- **efficiency** (> 40 %)
- **air demand** (similar DG)

**simulation results:**

- Fuel supply
  - Methanol bunker
  - Water: recycle/evaporate

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

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

**System Simulation**

- Consumer
  - power timeseries
- w
  - setpoint (SOC)
- net-load
- rate-limiter
- transient-load
- base-load
- Control
  - PI(s)
  - state of charge
- storage
- fuel cell system
- storage-load

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**Data:**

- Date: 25.10.2017
**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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**general consumer**

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**fuel cell system**

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**state of charge (battery)**

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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

## Measured 12 Day Scenario: ~ 1,5 MW

<table>
<thead>
<tr>
<th></th>
<th>High Speed Diesel Generator</th>
<th>Fuel Cell System</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Specific Mass</strong></td>
<td>9 kg/kW</td>
<td>19 kg/kW (incl. battery)</td>
</tr>
<tr>
<td><strong>Specific Volume</strong></td>
<td>14 ... 20 l/kW</td>
<td>20 l/kW</td>
</tr>
<tr>
<td><strong>CO2</strong></td>
<td>100 %</td>
<td>83 %</td>
</tr>
</tbody>
</table>

## Conclusion

- FCS reduce air pollutants (humid air + CO2, low noise, no vibrations)
- Energy storage necessary
- Comparable size and volume to medium speed diesel generator
- Expensive
thank you for your attention!

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Simulation results
FCSM characteristics

- From simulation extracted data for steady states
- S1/S2 different operating modes
- S1/S3 new ↔ degraded polarization curve
  → OK efficiency match
energy simulation

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 critical load cases)
- FCS can operate highly decoupled from load (Alternative II)
## fuel cell systems vs diesel generators (10.2017)

<table>
<thead>
<tr>
<th></th>
<th>MSL</th>
<th>SL</th>
<th>PEM (H2)</th>
<th>HT-PEM (CH3OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass / power</td>
<td>17 kg/kW_{el,AC}</td>
<td>9 kg/kW_{el,AC}</td>
<td>10 kg/kW_{el,DC}</td>
<td>12 ... 15 kg/kW_{el,DC}</td>
</tr>
<tr>
<td>volume / power</td>
<td>27 ... 37 l/kW_{el,AC}</td>
<td>14 ... 20 l/kW_{el,AC}</td>
<td>14 l/kW_{el,DC}</td>
<td>17 l/kW_{el,DC}</td>
</tr>
<tr>
<td>fuel consumption</td>
<td>205 g/kWh</td>
<td>225 g/kWh</td>
<td>72 g/kWh</td>
<td>440 g/kW_{el,DC}</td>
</tr>
<tr>
<td>price</td>
<td>280 ... 400 €/kW_{el,AC}</td>
<td>5000 €/kW_{el,DC}</td>
<td>5000 €/kW_{el,DC}</td>
<td>5000 €/kW_{el,DC}</td>
</tr>
<tr>
<td>electric energy price</td>
<td>0,06 €/kWh_{AC}</td>
<td>0,10 €/kWh_{AC}</td>
<td>0,68 €/kWh_{DC}</td>
<td>0,15 €/kWh_{DC}</td>
</tr>
</tbody>
</table>

HFO = 294 €/t; MGO = 428 €/t; H2 = 9500 €/t; CH3OH = 330€/t
Methodology
Measurements + Simulation

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 ($\theta$-controlled)
- catalytic burner (controlled MFCs H2 & air)
- synthesis gas composition using gas chromatography
simulation results
new vs degraded
steady state measurements

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: \( (X_i) \)

<table>
<thead>
<tr>
<th>( m_{\text{Feed}} )</th>
<th>( X_{\text{CH}_3\text{OH}} )</th>
<th>( X_{\text{H}_2\text{O}} )</th>
<th>( X_{\text{CH}_3\text{OH}}^{\text{Measure}} )</th>
<th>( X_{\text{CH}_3\text{OH}}^{\text{Calc}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.59 kg/h</td>
<td>1.000</td>
<td>0.645</td>
<td>0.1 Vol.-%</td>
<td>0.0 Vol.-%</td>
</tr>
<tr>
<td>1.34 kg/h</td>
<td>0.997</td>
<td>0.645</td>
<td>0.3 Vol.-%</td>
<td>0.6 Vol.-%</td>
</tr>
<tr>
<td>2.12 kg/h</td>
<td>0.980</td>
<td>0.640</td>
<td>2.7 Vol.-%</td>
<td>3.6 Vol.-%</td>
</tr>
<tr>
<td>3.85 kg/h</td>
<td>0.900</td>
<td>0.593</td>
<td>14.2 Vol.-%</td>
<td>14.1 Vol.-%</td>
</tr>
<tr>
<td>4.90 kg/h</td>
<td>0.890</td>
<td>0.587</td>
<td>13.9 Vol.-%</td>
<td>15.1 Vol.-%</td>
</tr>
</tbody>
</table>
Theoretical considerations
Steam to carbon ratio

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.

\[
\frac{S}{C} = \frac{n_{H_2O}}{n_{CH_3OH}}
\]

\[
n_{Mix} = n_{H_2O} + n_{CH_3OH}
\]

\[
x_{CH_3OH} = \frac{n_{CH_3OH}}{n_{H_2O} + n_{CH_3OH}}
\]

<table>
<thead>
<tr>
<th>Masse MeOH</th>
<th>Stoffmengenanteil MeOH</th>
<th>Volumen MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>2.87</td>
<td>6.22</td>
</tr>
<tr>
<td>10</td>
<td>5.88</td>
<td>12.29</td>
</tr>
<tr>
<td>15</td>
<td>9.03</td>
<td>18.21</td>
</tr>
<tr>
<td>20</td>
<td>12.32</td>
<td>23.97</td>
</tr>
<tr>
<td>25</td>
<td>15.78</td>
<td>29.60</td>
</tr>
<tr>
<td>30</td>
<td>19.42</td>
<td>35.09</td>
</tr>
<tr>
<td>35</td>
<td>23.24</td>
<td>40.44</td>
</tr>
<tr>
<td>40</td>
<td>27.26</td>
<td>45.68</td>
</tr>
<tr>
<td>45</td>
<td>31.51</td>
<td>50.78</td>
</tr>
<tr>
<td>50</td>
<td>35.99</td>
<td>55.78</td>
</tr>
<tr>
<td>55</td>
<td>40.73</td>
<td>60.65</td>
</tr>
<tr>
<td>60</td>
<td>45.75</td>
<td>65.42</td>
</tr>
<tr>
<td>65</td>
<td>51.08</td>
<td>70.08</td>
</tr>
<tr>
<td>70</td>
<td>56.75</td>
<td>74.64</td>
</tr>
<tr>
<td>75</td>
<td>62.78</td>
<td>79.10</td>
</tr>
<tr>
<td>80</td>
<td>69.22</td>
<td>83.46</td>
</tr>
<tr>
<td>85</td>
<td>76.11</td>
<td>87.73</td>
</tr>
<tr>
<td>90</td>
<td>83.50</td>
<td>91.90</td>
</tr>
<tr>
<td>95</td>
<td>91.44</td>
<td>95.99</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Methanex 2006
Theoretical considerations
Steam to carbon ratio

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

\[ x_i = \frac{n_i}{\sum n_i} \]

<table>
<thead>
<tr>
<th>objective</th>
<th>S/C</th>
<th>temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2 ↑</td>
<td>~ 1</td>
<td>150 °C</td>
</tr>
<tr>
<td>CO ↓</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>CH3OH ↓</td>
<td>high</td>
<td>High</td>
</tr>
<tr>
<td>η ↑</td>
<td>High</td>
<td>small</td>
</tr>
</tbody>
</table>
Theoretical considerations
Steam to carbon ratio

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

\[ S/C = 1.5 \ (60\% \ CH_3OH) \]

OK!

\[ \vartheta = 150 \ C \ldots 250 \ C \]

\[ \eta_{\text{Prozess}} = \frac{\dot{m}_{H_2} \cdot H_{i,H_2}}{\dot{m}_{Ss} \cdot H_{i,Ss} + \sum \Delta H + \sum H_{T \rightarrow g} + \sum \Delta_r H} \]

\[ \dot{m}_{Ss} \cdot H_{i,Ss} = \dot{m}_{CH_3OH} \cdot H_{i,CH_3OH} + \dot{m}_{H_2O} \cdot \Delta_v h_{H_2O} \]
Measurements
Sankey Diagram (Load = 100 %)

ΔRH
synthesis gas (X_i)
standard state

cooling & condensation

combustion

exhaust

heat loss

\[
\frac{\dot{H}_{\text{Out}}}{\dot{Q}_{\text{In}}} = \frac{2.71}{3.35 + 1.25} = 59 \%
\]

\[
\frac{\dot{Q}_{\text{Loss}}}{\dot{Q}_{\text{In}}} = \frac{0.14}{3.35 + 1.25} = 3 \%
\]

\[
\frac{\dot{Q}_{\text{WH}}}{\dot{Q}_{\text{In}}} = \frac{0.75}{3.35 + 1.25} = 16 \%
\]

\[
\frac{\dot{Q}_{\text{Cond}}}{\dot{H}_{\text{Eva}}} = \frac{0.54}{2.26 + 0.28} = 21 \%
\]
Measurements
Dynamic behaviour

No hydrogen discontinuities are detected for changing feed flow!

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

Vorangegangene Forschungsprojekte

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

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- & Festkörpertextemperaturen

\[ \text{Reformer} \quad \lambda_{O_2} \quad \lambda_{H_2} \quad \text{Anode} \quad \text{Kathode} \]

\[ \begin{align*}
\text{Abgas} & \rightarrow \text{Luft} \\
[O_2] & \rightarrow [H_2O] \\
[N_2] & \rightarrow [H_2O] \\
[CO_2] & \rightarrow [H_2O] \\
\end{align*} \]

\[ \text{Brenner} \quad [\text{CO}_2] \quad [\text{H}_2] \quad [\text{H}_2O] \quad *) \]

\[ \text{Abgas} \rightarrow \text{Abgas} \]

\[ \text{[*]) zusätzlich Spuren von [CH}_3\text{OH}] \quad \text{und [CO]} \]

**Diagramm:**
- H₂ reduziertes Synthesegas
- O₂ reduzierte Luft / H₂O
- Katalysatorschicht
- Bipolarplatte mit Öl- und Gaskanälen (innen)
- Synthesegas
- Luft

\[ \theta = 160 \degree \text{C} - 180 \degree \text{C} \]

\[ \text{Anode: } H_2 \rightarrow 2H^+ + 2e^- \]
\[ \text{Kathode: } 2H^+ + 1/2 \text{O}_2 + 2e^- \rightarrow H_2O \]
\[ \text{Gesamt: } H_2(g) + 1/2 \text{O}_2(g) \rightarrow H_2O(g) \]

**Polarisationskurve:**
- Zellspannung in V
- Strom in A

Messung 1
Messung 2
Messung 3
Modell
Metrological investigation
Steady State Measurements

fluegas

synthesis gas

oil

feed in kg/h

feed in kg/h

feed in kg/h

The diagrams show the temperature $\theta_{Kg}$ in °C as a function of the feed rate in kg/h for fluegas, synthesis gas, and oil. The graphs indicate the temperature changes at different feed rates for various conditions labeled (E), (F), (G), (B), (C), (D), (K), (H), and (J).
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