Advanced biomass CCHP based on gasification, SOFC and cooling machines
Solide oxide fuel cell performance with gases from biomass gasification

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Highlights of Bioenergy Research 2020
6. Central European Biomass Conference
Graz, Austria; January 24th, 2020

Institute of Thermal Engineering, Inffeldgasse 25b, 8010 Graz, Austria, www.iwt.tugraz.at
Biomass to power

- **Combustion based**
  + consolidated technology:
    - $\eta_{el} \sim 15-25\%$ (only for tens of MW\(_{th}\))

- **Gasification based**
  → State of the art power generator: **Gas Engine**
  + robust & flexible & mature → cost-effective
  - Carnot limitation + gas cooling → $\eta_{el} < 35\%$

  → Alternative power generator: **SOFC**
  + Hot gas usage + no carnot → $\eta_{el} > 40\%$
  - sensitive to impurities


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CEBC20, January 2019
Agenda

- Project overview
- Methodology and results
- Summary & Outlook
SOFC Combined Cold Heat Power plant

- Net efficiency increase with SOFCs
- Overall efficiency increase with
  - Heat usage
  - Cold generation

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BIO-CCHP: Advanced biomass CCHP based on gasification, solid oxide fuel cells and cooling machines

- ERA-NET Bioenergy project (11th Call)
- Coordinator of project: ITE TU Graz
- Scientific and industrial partners from 3 countries
- April 2018 → March 2021

Goals:
- Novel trigeneration system
- Electric efficiency > 40%
- Enhanced fuel flexibility

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Project goal

BIO-CCHP

**Project overview**

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Solid Oxide Fuel Cell

- **Solid Oxide Fuel Cell**
- 600 – 1000 °C
- H₂ & CO to electricity
- Internal reforming of CH₄

**Degradation**

- Sulfur and chlorine → poisoning of catalyst
- Low Steam to carbon Ratio (SCR) → carbon depositions
- Dependent on celltype
Development challenges SOFC

Cell performance

Cell degradation
• carbon deposition
• catalyst poisoning

Operating point
• product gas feed
• temperature
• electric load

Syngas cleaning level
• tar compounds
• sulfur compounds
• chlorine compounds
• dust
SOFC goal

define

optimal SOFC operating conditions and impurity tolerances
to ensure
stable, economic operation
with
maximum efficiency
high lifetime

- Experimental studies
- CFD simulations
  (Computational Fluid Dynamics)
Agenda

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Literature

Evaluation of relevant
- Product gases
- Impurity amounts
- Cell types
- Substrate
- Structure
  ↓ promising test configuration

Short-term experiments
- H₂, H₂O, CO, CO₂, CH₄ mixtures
  ↓ performance influence

Long-term experiments
- synthetic product gas
  ↓ operation stability

In progress

Short & Long-term experiments
- Real coupling
  ITE gasifier „real“ conditions
  ↓ stability & efficiency

CFD modelling

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Short term testing: Parameter study

- Cell type with high potential coupling with gasifier
- 50 operating points → CO, CO$_2$ and CH$_4$ varied
- Electrochemical characterization

Which ratios of carbonaceous species are advantageous for FDA/FBS gas mixtures?

<table>
<thead>
<tr>
<th>vol% w.b.</th>
<th>Influence CO</th>
<th>Influence CH$_4$</th>
<th>Influence CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>CO</td>
<td>5</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>Reference</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>CO$_2$</td>
<td></td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>N$_2$</td>
<td>25</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

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Short term testing: Parameter study

- $\text{H}_2 \gg \text{CO} = \text{beneficial}$
- $\text{H}_2\text{O} / \text{CH}_4 > 1 = \text{recommended}$
- $\text{CH}_4 \uparrow$ instead of $\text{CO} \uparrow = \text{recommended}$
- $\text{CO}_2 \downarrow = \text{beneficial}$

<table>
<thead>
<tr>
<th>vol% w.b.</th>
<th>Influence CO</th>
<th>Influence CH4</th>
<th>Influence CO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>50 50 50 50</td>
<td>50 50 50 50</td>
<td>50 50 50 50</td>
</tr>
<tr>
<td>CH4</td>
<td>5 10 25</td>
<td>5 10 25</td>
<td>5 5</td>
</tr>
<tr>
<td>CO2</td>
<td>15 15 15 15</td>
<td>15 15 15 15</td>
<td>15 15 15 15</td>
</tr>
<tr>
<td>N2</td>
<td>25 20 15</td>
<td>20 15</td>
<td>10 5 5</td>
</tr>
</tbody>
</table>
Fixed bed Downdraft Air (FDA) vs. Fluidized bed Steam (FBS)

- $P_{\text{max,FBS}} > P_{\text{max,FDA}}$
- FBS stable for 500 h @ 36% $\text{H}_2\text{O}$
- FDA also suitable for SOFC
  - Higher SCR necessary
  - Agent: Air + steam
  - Product gas steam injection

**FBS**: performance potential
**FDA**: suitable with higher SCR

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Performance degradation H$_2$S

Simulation of gas cleaning malfunction at stable operation → H$_2$S in fuel gas

- Initial voltage drop ↑
  - T ↓
  - H$_2$S concentration ↑
  - Less tolerant substrate

- Full regeneration up to 10ppmv
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Summary

- Beneficial cell type for coupling identified
- High potential of FBS gasifier for coupling with SOFC claimed
- No degradation using steam-rich FBS gases
- Also high potential for FDA, improved with steam + O₂ enriched air
Outlook

Real coupling

- Coupling of cell with in-house FBS gasifier using
  1. sulfur- and tar free gas
  2. sulfur free gas
  3. raw product gas

Synthetic gas mixtures

- Addition of cell contaminants: H₂S, Thiophene, HCl, Toluene (as tar content)
- Comparison of different cell types

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Backup
Project goal

BIO-CCHP

Biomass (1000 kW)

Gasifier

Gas cleaning

SOFC

Anode

Cathode

Absorption machine

Recuperator

Flue gas (80°C, 60 kWth)

Heat: 235 kW

Air (20°C, λ=3)

80°C (125 kWth)

800°C (485 kWth)

625°C (485 kWth)

300°C (270 kWth)

550°C (505 kWth)

1050°C (990 kWth)

800°C (125 kWth)

800°C (125 kWth)

800°C (125 kWth)

80°C (125 kWth)

Emission: 75 kW

P_{el, SOFC}: 420 kW

\eta_{SOFC} = 52.5\% (Fuel utilization = 70\%)

\eta_{cold, gasifier} = 80\%

(480 Nm³/h; 6 MJ/m³)

Cold: 170 kW

COP = 0.8 (1-stage)

Off-gas (240 kWchem)

(140 Nm³/h; 1.8 MJ/m³)

Post-combustion

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**Single cell testing**

- Ceramic cell housing
- Commercially available cells with 80cm² active area
- In-situ measurements:
  - IVC, EIS
  - Temperature distribution
- Post-mortem analyses:
  - SEM, EDX

**Methodology**

- Mechanical load
- Drillings for Thermocouples
- Air distribution plate
- Pt contact mesh
- Ceramic frame
- Glass seal
- SOFC single cell
- Ceramic frame
- Ni contact mesh
- Gas distribution plate

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IVC...current-voltage-curve
EIS...electrochemical impedance spectroscopy
SEM...scanning electron microscopy
EDX... energy-dispersive X-ray spectroscope

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Testrig

- Main gas components
- Dry/wet operation
- Gas analysis
- Contaminant dosing
  - gaseous
  - liquid + vaporizer

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Cell type comparison

- **Substrate**: Ni/GDC most degradation tolerant commercially available substrate
- **Cell structure**: Failure due to substrate degradation less severe in ESC than in ASC

ESC-SOFC with Ni/GDC anode fuelled with FBS gasifier-like product gas most promising configuration

Ni/GDC...nickel/gadolinium-doped ceria
ESC...electrolyte supported cell
ASC...anode supported cell
Increasing CO fraction

At $\text{H}_2 / \text{CO} < 5$ stagnating power output as CO oxidizes before reacting via WGS to high reactive $\text{H}_2$

$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$$

$\text{H}_2 >> \text{CO}$ beneficial

$\text{ASR} = \frac{\Delta U_{\text{loss}}}{i} \quad [\Omega \text{cm}^2]$  

...Area specific resistance at $i = 300 \text{ mA/cm}^2$

$\text{OCV}$...open circuit voltage
Increasing CH₄ fraction

At H₂O / CH₄ < 1 disproportionately high ASR increase as H₂O gets “used up” in methane reforming leading to high voltage losses

CH₄ + H₂O ⇌ CO + 3H₂

H₂O / CH₄ > 1 recommended

\[ \text{ASR} = \frac{\Delta U_{\text{loss}}}{i} \quad \text{[Ωcm²]} \]

...Area specific resistance at \( i = 300 \text{ mA/cm}² \)

OCV...open circuit voltage

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Comparing CO with CH₄

\[ P(5\% \text{ CH}_4) = P(25\% \text{ CO}) \]
despite 16% smaller LHV

→ \( \eta_{\text{el}} \) increased

small CH₄ amounts preferable to larger CO amounts

\[ ASR = \frac{\Delta U_{\text{loss}}}{i} [\Omega \text{cm}^2] \]

...Area specific resistance at
\( i = 300 \text{ mA/cm}^2 \)

OCV...open circuit voltage
Addition of CO2

Even small CO₂ amount turns high reactive H₂ into less reactive CO via WGS → performance decrease

CO + H₂O ⇌ CO₂ + H₂

CO₂ ↓ beneficial

\[
ASR = \frac{\Delta U_{loss}}{i} \quad [\Omega \text{cm}^2]
\]

...Area specific resistance at \( i = 300 \text{ mA/cm}^2 \)

OCV...open circuit voltage
FDA vs. FBS product gas

**Product gas** of steam-blown fluidized bed gasifier (FBS) compared to air-blown fixed bed downdraft (FDA) gasifier:

<table>
<thead>
<tr>
<th>vol% w.b.</th>
<th>H₂</th>
<th>H₂O</th>
<th>CO</th>
<th>CO₂</th>
<th>CH₄</th>
<th>N₂</th>
<th>SCR</th>
<th>H₂/CO</th>
<th>LHV [MJ/Nm³ w.b.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FDA</td>
<td>16</td>
<td>15</td>
<td>17</td>
<td>13</td>
<td>3</td>
<td>36</td>
<td>0.8</td>
<td>0.94</td>
<td>4.6</td>
</tr>
<tr>
<td>FBS</td>
<td>24</td>
<td>37</td>
<td>15</td>
<td>13</td>
<td>7</td>
<td>4</td>
<td>1.7</td>
<td>1.6</td>
<td>6.5</td>
</tr>
</tbody>
</table>

+ higher lower heating value (LHV)
+ higher H₂ / CO ratio → less voltage losses expected
+ higher steam-to-carbon ratio (SCR) → less carbon deposition risk

Bridgwater 1995 / 2009, Pfeifer 2011, internal data
Long-term testing: degradation stability

Is it possible to run the cell stable on a steam-rich product gas without nickel re-oxidation for many hours?

Operating point

- Simulated FBS product gas
- 80% of maximum achievable load
- 500 h stability experiment
- Cell measurements every 2 h

No degradation identified

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Degradation analysis

No performance and microscopic substrate degradation detected

FBS gas suitable for Ni/GDC SOFC

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Results: Degradation stability