Gasification of biomass with the Oxy-SER process for syngas production with in situ CO₂ capture in a 200 kWₜh pilot plant

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The 6ᵗʰ High Temperature Solid Looping Cycles Network Meeting, September 2ⁿᵈ 2015, Milan
Expertise in Fluidized Bed Processes

Fluidized Bed Processes
- Sorption enhanced reforming (SER)
- Oxy-fuel SER
- Calcium Looping (CaL)
- Chemical Looping (CLC)
- Oxy-fuel CFB

Fuels
- Biomass
- Waste
- Lignite / Coal

Measurement techniques
- Sorbent Characterization (TGA)
- Online gas analysis:
  - CO₂, CO, O₂, H₂, CH₄, SOₓ, Noₓ
- Non-condensable HC: GC
- Tar: wet chemical & online (FID)
- H₂S, HCl, NH₃: wet chemical
Motivation of Biomass Gasification

Biomass: A weather independent renewable energy source

gasification

in situ CO₂-capture

H₂-rich syngas

gas engine, CCGT

fuel cell

fischer-tropsch, methanol synthesis, methanisation

Storage e.g. in the gas grid

Steam gasification is an atmospheric allothermal gasification process where the necessary heat for the endothermic gasification is provided by circulating bed material.

- Bed material (e.g. silica sand) acts as heat carrier.
SER (Sorption Enhanced Reforming) is an atmospheric steam gasification process with in-situ CO₂ capture.

- Limestone shifts the CO₂ from the gasifier to the regenerator.
- Limestone as a bed material leads to a CO₂ lean and H₂ rich product gas.
In Oxy-SER process the regeneration is operated under Oxy-fuel conditions:

- High CO$_2$ output concentrations of $> 90$ vol-\%$_{\text{dry}}$ in the Regenerator can be achieved

→ Possible pre-combustion CCS technology
SER steam gasification

- Due to the chemical equilibrium, the CO$_2$-capture decreases with increasing gasification temperature.
- Limestone bed material acts as:
  - heat carrier
  - CO$_2$ carrier
  - catalyzer for increasing the gas yield
  - catalyzer for tar reforming
**Oxy-SER gasification: Application**

**Diagram:**
- **Oxy-SER**
  - **Gasifier**
    - Temperature: 600-750 °C
  - **Regenerator**
    - Temperature: 850-950 °C

**Inputs:**
- Fuel
- Oxygen
- Limestone (CaCO\(_3\))

**Outputs:**
- Hydrogen
- Fuels
- Chemicals
- CO\(_2\) storage
- Cement production

**Reactions:**
- CaO → CO\(_2\)-rich fluegas → Gas Conditioning → CO\(_2\) storage
- CaCO\(_3\) → Char + CaO
- CaO + CaSO\(_4\) → Purge
- H\(_2\)-rich syngas → Gas Conditioning → Synthesis → Hydrogen

**Notes:**
- Heat is used for conditioning and gasification processes.
Experimental test facility

200 kW\textsubscript{th} DFB pilot plant

- **Gasifier**
  - bubbling bed reactor
  - diameter: 330 mm
  - height: 6 m

- **Regenerator**
  - circulating fluidized bed
  - diameter: 210 mm
  - height: 10 m

- **Gas analyses**
  - **Gasifier**
    - \(\text{H}_2, \text{O}_2, \text{CO}, \text{CO}_2, \text{CH}_4, \text{C}2-\text{C}4, \text{tar}\)
  - **Regenerator**
    - \(\text{CO}, \text{O}_2, \text{CO}_2, \text{SO}_2, \text{NO}_x\)

- no electrical heating
- gravimetric fuel dosing
- wood pellets as fuel
Demonstration of the Oxy-SER process

- After ~5h the Regenerator was switched to Oxy-SER mode
  → Increase in CO₂ concentrations

- Temperature and gas composition in Gasifier are constant
  → Operation mode of Regenerator has only nearly no effect on the Gasifier
Results of the Oxy-SER experiments

- High H$_2$-concentrations in Syngas
- No significant difference in the syngas between the two regeneration modes
- Higher H$_2$O and CO$_2$ concentration in the fluegas due to the gas recirculation
SER Process Modeling

Motivation for modeling

• inter- and extrapolation of experimental data
• access on values that cannot easily be measured
  • gas velocity profiles (with gas yield from gasification)
  • concentration profiles
  • char conversion
  • etc.
• impact of different fuels and loads
• planning of experiments
• improving of reactor design
• scale up
• economical evaluation

→ Model has to be as rigorous as possible to cover all aspects
Gas transport model and reaction kinetics

Based on:

**Gas transport**

- Secondary steam
- Fuel
- Primary steam
- Solid flow
- Gas in/out

**Solid transport**

- Loop seal

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Equation</th>
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<tbody>
<tr>
<td><strong>Drying</strong></td>
<td>$\text{BM}<em>{\text{ar}} \rightarrow \text{BM}</em>{\text{wf}} + \text{H}_2\text{O}$</td>
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<tr>
<td><strong>Primary pyrolysis</strong></td>
<td>$\text{BM}_{\text{wf}} \rightarrow \text{C} + \text{Tar} + \text{Ash} + \text{H}_2\text{O} + \text{CO}_2 + \text{CO} + \text{CH}_4 + \text{H}_2$</td>
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<tr>
<td><strong>Secondary pyrolysis</strong></td>
<td>$\text{Teer} \rightarrow \text{CO}_2 + \text{CO} + \text{CH}_4 + \text{H}_2$</td>
</tr>
<tr>
<td><strong>heterogeneous water-gas</strong></td>
<td>$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$</td>
</tr>
<tr>
<td><strong>Boudouard</strong></td>
<td>$\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$</td>
</tr>
<tr>
<td><strong>heterogeneous methanation</strong></td>
<td>$\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$</td>
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<tr>
<td><strong>Methane reforming</strong></td>
<td>$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$</td>
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<tr>
<td><strong>Water-gas-shift</strong></td>
<td>$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$</td>
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<tr>
<td><strong>Carbonatization</strong></td>
<td>$\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3$</td>
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</table>
SER Modeling: Temperature and Velocity Profiles

![Graph 1: Temperature vs. Reactor Height](image1.png)

- **Simulation**
- **200 kW\text{th} DFB**

![Graph 2: Gas Velocity vs. Reactor Height](image2.png)

- **Gas velocity**
- **Cross sectional area**

Temperature in °C vs. Reactor height in m

Gas velocity in m/s; area in m²
SER Modeling: Syngas composition
Summary and outlook

- Oxy-SER operation process was possible in pilot scale (200 kW\textsubscript{th})
- High H\textsubscript{2} concentrations of > 70 vol-%\textsubscript{dry} in the syngas were achieved
- Changing from SER to Oxy-SER operation mode had no effect on the gasifier
- High CO\textsubscript{2} concentrations of > 90 vol-%\textsubscript{dry} in the Regenerator flue gas were achieved
- Results from fluid dynamic and kinetic modelling of the process are in good agreement with experiments

Future goals
- Use of biogenic residues or waste fuels instead of wood pellets
- Detailed economic and application studies with the SER Model

\rightarrow \textbf{Oxy-SER process is a promising process for the creation of a hydrogen-rich syngas with a pre-combustion CCS}
Thank you for your attention! Questions?

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Fuel and ash composition

- For the experiments wood pellets were used as fuel

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<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>Cl</th>
<th>ash</th>
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<td></td>
<td>wt.-%daf</td>
<td>51.4</td>
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<td>42.7</td>
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<tr>
<td></td>
<td>wt.-%a.r.</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>wood pellets</td>
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<table>
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<tr>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>MgO</th>
<th>Na₂O</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>SiO₂</th>
<th>TiO₂</th>
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</thead>
<tbody>
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<td>wt.-%ash</td>
<td>2.6</td>
<td>50.7</td>
<td>4.0</td>
<td>20.7</td>
<td>6.9</td>
<td>0.3</td>
<td>4.0</td>
<td>5.9</td>
<td>0.3</td>
</tr>
</tbody>
</table>

| wood pellets | 2.6 | 50.7 | 4.0  | 20.7 | 6.9  | 0.3  | 4.0 | 5.9  | 0.3  | 0.3  |