Thermodynamic analysis of different SE-SMR combined cycle-based plants

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Thermodynamic principles - reforming

Pre-combustion CO₂ capture plants based on conventional reforming technologies:

- SMR / ATR
  \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (\text{SMR}) \quad \Delta H^\circ_r = +205.9 \text{ kJ/mole} \]

- HT-WGS
- LT-WGS

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (\text{WGS}) \quad \Delta H^\circ_r = -41.2 \text{ kJ/mole} \]

- CO₂ absorption
- H₂ oxidation

- 3 reactors for H₂-rich syngas production
- CO₂ removed in a separate process
- Large heat exchanging surface
Thermodynamic principles - reforming

Pre-combustion CO₂ capture plant based on Sorption Enhanced-Steam Methane Reforming (SE-SMR):

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \text{(SMR)} \quad \Delta H^\circ_r = +205.9 \text{ kJ/mole}
\]

\[
\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2 \quad \Delta H^\circ_r = +179.2 \text{ kJ/mole}
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \text{(WGS)} \quad \Delta H^\circ_r = -41.2 \text{ kJ/mole}
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\[
\text{CaO}(s) + \text{CO}_2 \rightarrow \text{CaCO}_3(s) \quad \text{(carb)} \quad \Delta H^\circ_r = -179.2 \text{ kJ/mole}
\]

\[
\text{CH}_4 + 2\text{H}_2\text{O} + \text{CaO}(s) \rightarrow \text{CaCO}_3(s) + 4\text{H}_2 \quad \Delta H^\circ_r = -14.5 \text{ kJ/mole}
\]
Options for power island

- SOFC-based power generation:
  - Low pressure system → high CO₂ capture and H₂ yields
  - Heat for calcination from SOFC waste heat

Technical challenges:
  - Development of high temperature (1100°C) cooled fuel cell
  - Very high temperature SOFC to calciner heat transfer system

- Combined cycle-based power generation:
  - High pressure reformer (H₂ cooling and compression should be avoided)
  - Heat for calcination from oxy-fuel combustion

Technical challenges:
  - Difficult calcination: temperature and/or pressure swing

State of the art gas turbines: 60.75% efficiency achieved at the Irsching (Bavaria) combined cycle power plant
Process modeling calculations performed with the in-house code GS:

- Sophisticated model for the prediction of gas turbines performance
  - Stage-by-stage calculation with pre-design of each turbine row
  - Estimation of the coolant flow rate required by each row
  - Estimation of stage efficiency from geometric parameters and coolant required


- Sophisticated steam turbine model with stage-by-stage calculation
  - Estimation of stage efficiency from non-dimensional parameters (specific speed) and stage size

CC-based plant

- Reformer: 25 bar, 700°C, S/C = 4.5
- Steam dilution in the calciner $\Rightarrow T_{\text{calc}} = 1050^\circ\text{C}$
- Solids preheating between reformer and calciner
- Expander for the steam-rich (~70%H$_2$O) calciner exhaust
• Oxygen produced with O₂ transport membrane @ 850°C
• GT with sequential combustion
# Performance

<table>
<thead>
<tr>
<th></th>
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<th>SE-SMR OTM</th>
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<td>Specific emission, g$_{CO_2}$/kWh</td>
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\[
SPECCA = \frac{\Delta \text{Heat rate}}{\Delta \text{Specific emissions}} = \frac{3600 \cdot (1/\eta - 1/\eta_{ref})}{e_{ref} - e}
\]


Performance

Net efficiency, %LHV

CO2 avoided, %

Ca utilization

- Criogenic ASU
- OTM
Another option for calcination: Cu-Ca process

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- High temperature heat recovered as chemical energy
- lower CH₄ consumption for regeneration: H₂ yield from 2 to 2.5
- lower Cu/Ca ratio required
Cu-Ca process-based CC plant
## Performance

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Conclusions

• SE-SMR in CC-based configurations can assure electric efficiencies in line with competitive technologies for short-mid term power plants and slightly lower CO₂ capture rates.

• Advantages over steam reforming-based plants can arise from a simpler and lower cost hydrogen production island.

• The development of a sorbent with high capacity and able to withstand high calcination temperatures for many cycles is crucial.

• Interesting H₂ yields: higher energy advantages as hydrogen production plants.
Thank you

... and if you need a partner in joint projects for good process integration and simulation...