Assessment of CO₂ Capture by Calcium Looping from Natural Gas Combined Cycle (NGCC) Power Plants

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Developing innovative power generation technologies with low fossil CO₂ emissions is of paramount importance in modern society. Natural gas-based energy applications have the highest conversion efficiency, this fuel being considered the cleanest fossil fuel in terms of specific CO₂ emissions. Carbon Capture, Utilisation and Storage (CCUS) technologies are seen as important future ways to reduce fossil CO₂ emissions from the energy sector (heat and power production) as well as from other energy-intensive industrial applications (e.g. cement, petro-chemical and metallurgy sectors). Among various advanced carbon capture methods, Calcium Looping (CaL) option seems to be very promising in reducing both energy and cost penalty for CO₂ capture. Potential utilisation of natural materials (limestone) and spent sorbent usage in construction sector are other attractive features of this carbon capture process.

The paper evaluates in details the Natural Gas Combined Cycle (NGCC) power plant concept with calcium looping cycle used for post-combustion CO₂ capture. Plant operational aspects, mass and energy integration aspects, scale-up issues from current state of development (laboratory and pilot installations) to industrial scale and estimation of overall techno-economic performances are discussed within the paper. The plant design was modelled and simulated using process flow modelling software, the simulation results (the mass and energy balances) being used to assess the overall techno-economic and environmental indicators. For comparison reason, two benchmark NGCC power plant concepts were considered: a conventional NGCC power plant without carbon capture and a NGCC power plant with post-combustion capture using gas-liquid absorption (MDEA). The integrated techno-economic and environmental assessments show that calcium looping has significant advantages compared to benchmark cases such as higher plant energy efficiency, lower energy and cost penalties for CO₂ capture and improved overall techno-economic and environmental performances.

1. Introduction

Reducing the greenhouse gas emissions (mainly CO₂) together with enhancing and diversifying the primary energy supply sources (fossil fuels but also renewable energy sources) are primarily objectives of the energy sector and other energy-intensive industrial applications. Since the fossil fuels are predicted to remain the backbone of the power generation sector, Carbon Capture, Utilisation and Storage (CCUS) technologies are attractive solutions to simultaneously reduce the CO₂ emissions and continue to use the fossil fuels (Metz et al., 2005). Natural gas-based power generation schemes (e.g. Natural Gas Combined Cycle - NGCC power plants) have the highest energy efficiency (in the range of 50 – 60 %) coupled with the lowest specific CO₂ emissions (about 350 kg/MWh).

Various carbon capture options are under consideration to be integrated in energy sector as well as other energy-intensive industrial applications. Among these, post-combustion methods are one of the obvious options to be considered taking into account the process configuration issues (e.g. integration of carbon capture step into the overall power plant scheme). The main drawback of post-combustion capture using gas-liquid absorption systems (e.g. aqueous alkanolamine solutions) are the high energy and cost penalty for CO₂ capture (e.g. about 10 net electricity percentage points). Calcium Looping (CaL) is a promising post-combustion carbon capture option to reduce both energy and cost penalties (Fan, 2010).
This paper presents in details the NGCC power plant concept with post-combustion capture using calcium looping cycle (NGCC-CaL). The techno-economic evaluation of NGCC-CaL scheme is based on mathematical modelling and simulation to produce the mass and energy balances of the process. Various operational aspects such as mass and energy integration issues (e.g. Pinch Analysis was used to perform plant thermal integration) were presented. The present analysis aims also to address the scale-up issues for CaL technology from current state of development - laboratory and pilot installations in the range up to 10 MW scale (Dieter et al., 2014) to the full industrial size of hundreds of MW scale and the influence on main techno-economic and environmental performances. For comparison reason, two benchmark concepts were considered: a conventional NGCC power plant without carbon capture and a NGCC power plant with post-combustion capture based on gas-liquid absorption using Methyl-DiEthanol-Amine (MDEA). The assessment show that calcium looping cycle integrated into an NGCC power plant has significant improved techno-economic and environmental performances compared to benchmark cases.

2. NGCC power plant with calcium looping concept and main design assumptions

Calcium looping cycle in a NGCC-based post-combustion capture configuration uses the flue gases from the gas turbine. The CaL cycle implies two interconnected circulated fluidised bed reactors, in the first reactor (carbonation reactor), CO₂ from flue gases reacts CaO according to the exothermic reaction:

\[ CO_2(g) + CaO(s) \rightarrow CaCO_3(s) \quad \Delta H = -178.2 \text{kJ/mole} \]  \hspace{1cm} (1)

The gas-solid system resulted from the carbonation reactor is separated in a cyclone. The gas phase is cooled down by generating steam and then vented into atmosphere. The solid phase is sent to the calcination reactor in which the calcium carbonate is decomposed to calcium oxide for sorbent regeneration and then recycled back to the carbonation reactor. The decomposition reaction is:

\[ CaCO_3(s) \rightarrow CO_2(g) + CaO(s) \] \hspace{1cm} (2)

Since the decomposition reaction is highly endothermic, additional natural gas has to be oxy-combusted in the calcination reactor to provide the reaction heat. The captured CO₂ stream resulted from the calcination reactor is cooled down, the condensate is removed, the CO₂ is then dried using tri-ethylene-glycol (TEG) and compressed to 120 bar to be sent to storage / utilisation sites. The conceptual layout of NGCC power plant with post-combustion CO₂ capture based on CaL cycle is presented in Figure 1.

![Figure 1: NGCC power plant with post-combustion capture based on calcium looping](image-url)
As benchmark cases used to compare the performances of NGCC-CaL concept, two NGCC power plants were considered. The first benchmark case is an NGCC power plant without carbon capture. The second benchmark case is also an NGCC with post-combustion capture using MDEA-based gas-liquid absorption (Berstad et al., 2014). For CCS designs, the captured CO₂ has to comply with strict quality specifications (Cormos and Cormos, 2013): >95 % CO₂; <2,000 ppm CO; <500 ppm H₂O; <100 ppm H₂S and <4 % all non-condensable gases (H₂, N₂, Ar etc.). All gas compositions are expressed in % vol.

The following NGCC-based power plant concepts were evaluated in this paper:

Case 1 – NGCC power plant with post-combustion capture using CaL;
Case 2 – NGCC power plant without carbon capture;
Case 3 – NGCC power plant with post-combustion capture using MDEA.

All evaluated NGCC cases have a combined cycle based on M701G2 (Mitsubishi Hitachi Power Systems) gas turbine. The main design assumptions of evaluated plant concepts are presented in Table 1.

Table 1: Main design assumptions

<table>
<thead>
<tr>
<th>Plant unit</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas turbine</td>
<td>Type: M701G2; Net power output: 334 MW; 39.5 % efficiency</td>
</tr>
<tr>
<td>Steam cycle</td>
<td>Steam pressure: 120 bar / 34 bar / 3 bar &amp; MP steam reheat</td>
</tr>
<tr>
<td>Air separation unit (Case 1)</td>
<td>Oxygen purity: 95 % O₂; Power consumption: 225 kWh/t O₂</td>
</tr>
<tr>
<td>Carbon capture unit</td>
<td>Case 1: Calcium looping / Case 3: MDEA (gas-liquid absorption)</td>
</tr>
<tr>
<td>CO₂ drying and compression</td>
<td>Final delivery pressure: 120 bar; Drying solvent: TEG</td>
</tr>
<tr>
<td>Condenser pressure</td>
<td>46 mbar</td>
</tr>
<tr>
<td>Cooling water temperature</td>
<td>15 °C</td>
</tr>
<tr>
<td>Heat exchanger ΔT_{min.}</td>
<td>10 °C</td>
</tr>
<tr>
<td>HX pressure drop (ΔP)</td>
<td>2 - 5 %</td>
</tr>
</tbody>
</table>

3. Results and discussions

All plant concepts were modelled and simulated using ChemCAD. The mathematical models are based on process flow modeling with detailed definition of the unit operations (e.g. power block, calcium looping cycle reactors, gas-liquid CO₂ capture cycle). The models were validated against available data (Varel et al., 2013). No significant differences were reported (Cormos and Simon, 2013).

The case studies were subject of Process Integration analysis using Pinch technique for quantification of energy efficiency as presented by Cormos (2014). As illustrative example, Figure 2 presents hot and cold Composite Curves for Case 1 (NGCC power plant with calcium looping) for the two main plant subsystems [the power block - Figure 2(a) and the calcium looping unit - Figure 2(b)].

Figure 2: (a) Composite Curves for power block unit; (b) Composite Curves for calcium looping

After modelling, simulation and thermal integration, the mass and energy balances of evaluated cases were used to assess the key techno-economic and environmental plant performances. The first evaluated operation scenario was considered only power generation. Table 2 presents the key technical and environmental indicators for evaluated cases.
The following economic indicators were calculated for the evaluated power plant cases:

- Net power efficiency: $\frac{D}{A} \times 100\%$
- Gross power efficiency: $\frac{B}{A} \times 100\%$
- Net power output: $D = B - C$
- Gross power output: $B$
- Steam turbine output
- Gas turbine output
- Natural gas consumption
- Ancillary power consumption
- Net power output
- Carbon capture rate
- CO₂ specific emissions

Table 2: Key plant performance indicators

<table>
<thead>
<tr>
<th>Main plant parameter</th>
<th>Units</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas flowrate</td>
<td>t/h</td>
<td>94.15</td>
<td>65.15</td>
<td>65.15</td>
</tr>
<tr>
<td>Natural gas thermal energy (A)</td>
<td>MWₜ</td>
<td>1,222.23</td>
<td>845.76</td>
<td>845.76</td>
</tr>
<tr>
<td>Gas turbine output (1 x M701G2)</td>
<td>MWₜ</td>
<td>334.00</td>
<td>334.00</td>
<td>334.00</td>
</tr>
<tr>
<td>Steam turbine output</td>
<td>MWₜ</td>
<td>296.30</td>
<td>164.99</td>
<td>124.32</td>
</tr>
<tr>
<td>Gross power output (B)</td>
<td>MWₜ</td>
<td>630.30</td>
<td>498.00</td>
<td>458.32</td>
</tr>
<tr>
<td>Ancillary power consumption (C)</td>
<td>MWₜ</td>
<td>28.60</td>
<td>2.58</td>
<td>12.62</td>
</tr>
<tr>
<td>Net power output (D = B - C)</td>
<td>MWₜ</td>
<td>601.70</td>
<td>495.42</td>
<td>445.70</td>
</tr>
<tr>
<td>Gross power efficiency (B/A * 100)</td>
<td>%</td>
<td>51.56</td>
<td>58.88</td>
<td>54.19</td>
</tr>
<tr>
<td>Net power efficiency (D/A * 100)</td>
<td>%</td>
<td>49.23</td>
<td>58.57</td>
<td>52.69</td>
</tr>
<tr>
<td>Carbon capture rate</td>
<td>kg/MWh</td>
<td>98.85</td>
<td>0.00</td>
<td>90.16</td>
</tr>
<tr>
<td>CO₂ specific emissions</td>
<td>kg/MWh</td>
<td>2.80</td>
<td>350.96</td>
<td>38.35</td>
</tr>
</tbody>
</table>

As can be noticed from Table 2, the evaluated power plants with carbon capture case studies generate about 445 – 600 MW net power with an electrical efficiency in the range of 49.23 – 52.69 % and specific CO₂ emissions in the range of 2.8 – 38.35 kg/MWh. NGCC power plant without CCS has a net electrical efficiency of 58.57 % and specific CO₂ emission of about 350 kg/MWh. The most energy efficient plant concept with CCS is the one based MDEA gas-liquid absorption system (Case 3) with about 2.4 net electricity percentage points higher than calcium looping (Case 1). The main reasons for slightly superior energy efficiency of gas-liquid absorption system compared to the calcium looping case are: (i) the heat duty of the calcination reaction has to be covered by natural gas oxy-combustion (the combined cycle has a superior energy efficiency than the steam cycle), (ii) the usage of an Air Separation Unit (ASU) for CaL concept to provide the oxygen for oxy-combustion and (iii) lower ancillary consumption. Despite the superior efficiency of NGCC-MDEA concept, one can notice that the NGCC-CaL concept has a superior carbon capture rate (98.85 % vs. 90.16 %). As shown in the next section of the paper, this key aspect has an important influence on overall plant economic performances.

The following economic indicators were calculated for the evaluated power plant cases: capital costs, specific capital investments, operational and maintenance (O&M) costs, cost of electricity, CO₂ removal and avoidance costs. The capital costs were calculated by cost correlations as presented by Cormos (2014). The capital costs for the power block and the gas-liquid CO₂ capture unit were estimated using a power law of capacity equation [see Eq.(3)] in which material / energy flows were used as scaling factors.

\[
C_E = C_B \times \left( \frac{Q}{Q_B} \right)^M
\]  
(3)

where:
- $C_E$ – equipment cost with capacity $Q$;
- $C_B$ – known base cost for equipment with capacity $Q_B$;
- $M$ – constant depending on equipment type.

For CaL unit, the following equation was used to estimate the capital cost (Romano et al., 2013):

\[
C_{CaL} = C_B \times \left[ \alpha * \left( \frac{Q_{LHV, calciner}}{Q_0} \right)^{SF,Q} + (1 - \alpha) * \left( \frac{V_{calciner}}{V_0} \right)^{SF,V} + (1 - \alpha) * \left( \frac{V_{carbonator}}{V_0} \right)^{SF,V} \right]
\]  
(4)

where:
- $C_{CaL}$ - capital cost of CaL unit having capacity Qₗₜₜ, $V_{calciner}$ and $V_{carbonator}$;
- $C_B$ - base capital cost of CaL unit having capacity $Q_0$ and $V_0$;
- $\alpha$ - relative weight of heat transfer surfaces on the total cost of a cooled CFB reactor;
- SF,Q - scaling factor for heat input to the calciner (LHV basis);
- SF,V - scaling factor for volume (carbonator and calciner).

From the total capital (investment) cost, the specific capital investment (SCI) per gross or net power generation (€/kW) was calculated using Eq(5).

\[
SCI \ per \ kW(\text{gross/net}) = \frac{\text{Total investment cost}}{\text{Gross/Net power output}}
\]  
(5)
Simulation results, in form of mass and energy balances for each evaluated cases, were then used for calculation of operational and maintenance (O&M) costs. These costs have variable and fixed components depending on the proportionality to the power output. Variable costs, proportional to amount of generated power, cover the following items: fuel, chemicals, calcium sorbent, solvents, waste disposal etc. Fixed operating costs, independent of the amount of generated power, cover: maintenance, plant depreciation, direct labour, administrative costs etc. Table 3 presents the plant capital costs, specific capital investments as well as fixed and variable operating and maintenance (O&M) costs for the investigated cases.

### Table 3: Capital, specific investments and operation & maintenance (O&M) costs

<table>
<thead>
<tr>
<th>Main plant parameter</th>
<th>Units</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total investment cost</td>
<td>MM €</td>
<td>583.15</td>
<td>339.70</td>
<td>552.01</td>
</tr>
<tr>
<td>Specific capital investment per kW gross</td>
<td>€ / kW</td>
<td>925.19</td>
<td>682.12</td>
<td>1,204.42</td>
</tr>
<tr>
<td>Specific capital investment per kW net</td>
<td>€ / kW</td>
<td>969.16</td>
<td>685.67</td>
<td>1,238.52</td>
</tr>
<tr>
<td>Total fixed O&amp;M costs (y)</td>
<td>ME / y</td>
<td>24.63</td>
<td>17.81</td>
<td>22.51</td>
</tr>
<tr>
<td>Total fixed O&amp;M costs (MWh)</td>
<td>€ / MWh</td>
<td>5.46</td>
<td>4.79</td>
<td>6.73</td>
</tr>
<tr>
<td>Total variable O&amp;M costs (y)</td>
<td>ME / y</td>
<td>168.61</td>
<td>108.08</td>
<td>132.07</td>
</tr>
<tr>
<td>Total variable O&amp;M costs (MWh)</td>
<td>€ / MWh</td>
<td>37.36</td>
<td>29.09</td>
<td>39.51</td>
</tr>
<tr>
<td>Total fixed and variable costs (y)</td>
<td>ME / y</td>
<td>193.24</td>
<td>125.89</td>
<td>154.58</td>
</tr>
<tr>
<td>Total fixed and variable costs (MWh)</td>
<td>€ / MWh</td>
<td>42.82</td>
<td>33.88</td>
<td>46.24</td>
</tr>
</tbody>
</table>

As investment cost indicators, the evaluated CCS cases have total investment costs in the range of 552 to 583 MM €. The specific capital investments are in the range of 969.16 to 1,238.52 €/kW net. It can be observed that for calcium looping concept (Case 1), the specific capital investment has the lowest value compared to MDEA-based gas-liquid absorption system (Case 3) with about 27.7 %. The capital cost penalty for carbon capture for CaL concept is 283.49 € / kW net (or expressed in percentages 41.34 %) compared to the case without CCS (Case 2). The O&M costs reported on generated power show also the superiority of CaL case compared to MDEA case: 42.82 € / MWh vs. 46.24 € / MWh. The O&M cost penalty for carbon capture for CaL concept is 8.94 € / MWh (or expressed in percentages 26.38 %) compared to the case without CCS (Case 2).

CO₂ removal and avoidance costs are important parameters when assess carbon capture technologies (lowest values being more favourable). These indicators are using the levelised cost of electricity (LCOE) in a power plant with CCS compared with cost of electricity without CCS as well as specific CO₂ emissions in both cases. These costs are calculated using Eq(6) and Eq(7).

\[
CO_2 \text{ removal cost } t = \frac{LCOE_{with\, CCS} - LCOE_{without\, CCS}}{CO_2 \text{ removed}} \tag{6}
\]

\[
CO_2 \text{ avoided cost } t = \frac{LCOE_{with\, CCS} - LCOE_{without\, CCS}}{CO_2 \text{ emissions}_{without\, CCS} - CO_2 \text{ emissions}_{with\, CCS}} \tag{7}
\]

To calculate the levelised cost of electricity, net present value method was used (Cormos, 2014). Table 4 presents the CO₂ removal and avoidance costs as well as cost of electricity for investigated cases.

### Table 4: Capital, specific investments and operation & maintenance (O&M) costs

<table>
<thead>
<tr>
<th>Main plant parameter</th>
<th>Units</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levelised cost of electricity (LCOE)</td>
<td>€ / MWh</td>
<td>56.91</td>
<td>45.15</td>
<td>66.12</td>
</tr>
<tr>
<td>CO₂ removal cost</td>
<td>€ / t</td>
<td>30.00</td>
<td>-</td>
<td>59.88</td>
</tr>
<tr>
<td>CO₂ avoided cost</td>
<td>€ / t</td>
<td>33.77</td>
<td>-</td>
<td>67.08</td>
</tr>
</tbody>
</table>

The levelised cost of electricity shows a moderate increase of about 26 % for calcium looping design (Case 1) compared to MDEA design (Case 3) which exhibits an increase of about 46 %. The CO₂ removal and avoided costs are almost double for MDEA concept compared to CaL concept. Cumulative cash flow analysis is an important economic parameter to be considered. In the current analysis, 28 years was considered as project life divided as follow: 2 years for plant construction, 25 years for plant operation and 1 year for recovering the working capital. The cumulative cash flow analyses for NGCC power plants with and without carbon capture are presented in Figure 3.
4. Conclusions

This paper focuses on detailed evaluation of techno-economic performances for NGCC power plant with post-combustion capture based on calcium looping concept. Two benchmark cases without carbon capture and with carbon capture based on gas-liquid absorption were considered. The evaluations show that calcium looping concept is a very promising option to reduce both energy and cost penalties for carbon capture having techno-economic significant advantages: an almost total fuel decarbonisation rate (>98%), lower specific capital investment (969.16 vs. 1,238.52 € / kW net), lower O&M costs (42.82 vs. 46.24 € / MWh) and lower electricity cost (56.91 vs. 66.12 € / MWh) compared to gas-liquid applications.

Acknowledgements

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