Calcium looping (CaL) is promising for large-scale CO₂ capture in the power generation and industrial sectors due to the cheap sorbent used and the relatively low energy penalties achieved with this process. Because of the high operating temperatures the heat utilisation is a major advantage of the process, since a significant amount of power can be generated from it. However, this increases its complexity and capital costs. Therefore, not only the energy efficiency performance is important for these cycles, but also the capital costs must be taken into account, i.e. techno-economic analyses are required in order to determine which parameters and configurations are optimal to enhance technology viability in different integration scenarios. In this study the integration scenarios of CaL cycles and natural gas combined cycles (NGCC) are explored. The process models of the NGCC and CaL capture plant are developed to explore the most promising scenarios for NGCC-CaL integration with regards to efficiency penalties. Two scenarios are analysed in detail, and show that the system with heat recovery steam generator (HRSG) before and after the capture plant exhibited better performance of 49.1% efficiency compared with that of 45.7% when only one HRSG is located after the capture plant. However, the techno-economic analyses showed that the more energy efficient case, with two HRSGs, implies relatively higher cost of electricity (COE), 44.1€/MWh, when compared to that of the reference plant system (33.1€/MWh). The predicted cost of CO₂ avoided for the case with two HRSGS is 29.3 €/ton CO₂.

Key words: NGCC, calcium looping, efficiency penalty, techno-economic analysis

1 Introduction

Mitigation of CO₂ emissions is required in order to limit the global concentration of CO₂ to 450 ppm, by 2050 [1]. However, energy demands are expected to grow and the burning of fossil fuels is likely to continue in the medium-term future. Therefore, it is important to find viable routes to achieve CO₂
emission limits before the development and deployment of new, less carbon-intensive sources of energy becomes dominant in our global energy mix. One widely considered approach for reducing CO₂ emissions in the short to mid-term is carbon capture and storage (CCS) [2; 3]. CCS technology is based on avoiding the emission of CO₂ to the atmosphere; instead the carbon dioxide stream is captured and stored in a safe location [4].

Of the carbon capture technologies amine-based scrubbing is the closest to the market and can be deployed in the short term because of its easy retrofit in current power stations [3]. In fact, the first large-scale plant of its kind was commissioned in late 2014 [5; 6]. However, given the high cost of amine scrubbing, alternative technologies are being developed using solids as adsorption material, and among these options, carbonate looping (CaL) [7] seems to be one of the most promising and competitive processes to decarbonise power generation and carbon-intensive industries. The main advantages of CaL are relatively low energy penalties [8] and the widely available and cheap sorbent (typically limestone) [9].

CaL technology comprises two intercommunicated fluidised bed reactors and uses lime (CaO) as a CO₂ carrier regenerable at high temperatures [10]. In the first chamber, the CO₂ present in the flue gas reacts with the sorbent to produce CaCO₃, i.e. saturated sorbent, which is transferred to the second reactor where it is regenerated at high temperature, producing a nearly pure concentrated carbon dioxide stream. After regeneration, the sorbent is transferred again to the first reactor to start the new cycle. The additional advantage of this process is the almost zero waste material produced in some scenarios as spent sorbent can be reused, for example, in the cement industry [11]. Although CaL is estimated to be 60% less costly than amine technology [9] and cheaper than other emerging technologies (chilled ammonia and membrane separation) [12], there are challenges that need further investigation before fully scaling-up the technology. Namely, it is well known that sorbents experiences the reactivity decay with increasing numbers of reaction cycles, mainly due to sintering [13].

Usually in carbon capture technologies, energy is spent in order to remove the carbon dioxide from the flue gas, which results in lower power plant output. However, in calcium looping, the high temperatures in both reactors allow an exceptional opportunity for heat integration in order to increase the power output of the integrated power-capture plant system. The efficiency penalty expected for this carbonate looping is between 7-10% points, but it can be reduced to levels as low as 5% [10; 14-17]. Not only can the heat be recovered from both hot gas and solid streams, but as the carbonation reaction is exothermic, heat generated in carbonator can be used to produce additional steam for a secondary steam cycle [18; 19].

Natural gas combined cycle (NGCC) plants use natural gas as fuel, which is a mixture of gaseous hydrocarbons. The main component is methane, but it usually contains some traces of sulphur, nitrogen and CO₂, among other components including higher hydrocarbons [20]. It is a relatively clean fuel used for electricity generation, which accounts for 21% of electricity generated worldwide [21] Moreover, the efficiency of this kind of plants can achieve values up to 60% [22].

The NGCC consists of two power cycles in series in order to achieve a high overall efficiency of the plant. In this study an detailed analysis of NGCC plants is performed, pointing out the main parameters and key challenges. The aim of this paper is to develop process models of the NGCC plant as well as the CaL plant, integrate them, and to compare the results (thermal efficiency) from different
integration scenarios. In addition a techno economic analysis of two most viable configurations was carried out. The main idea is to evaluate at same time both the thermal efficiencies of the NGCC-CaL systems and the cost of electricity and CO\textsubscript{2} avoided taking into account different complexities considered in the integration scenarios. It should be noted that although in previous studies efficiency penalties, sorbent performance and key process parameters have been analysed, this work also provides insight in the economic aspects of the NGCC-CaL process.

2 Model development

2.1 Natural gas combined cycle (NGCC) power plant

The model of the NGCC was developed using the European Benchmark Taskforce (EBTF) data and the work performed by Manzolini et al. [20]. The configuration of the process comprises two gas turbines plus a single steam cycle. This configuration is used because of the flexibility given by being able to operate with only one gas turbine or both of them, depending on the electricity demand. It provides extra flexibility that cannot be achieved with only one gas turbine [23].

For the modelling of the gas turbine the GasTurb\textsuperscript{®} was used, due to its more accurate calculation options. The gas turbine was modelled in this software in order to satisfy the conditions imposed by the EBTF; blade cooling was also taken into account. The nominal speed of the gas turbine is 1800 rpm, and as the input parameters for the fuel the data for natural gas were extracted from Manzolini et al. [20]. The main air and natural gas inlet conditions are shown in tab. 1, followed by tab. 2 revealing the gas turbine operating parameters.

<table>
<thead>
<tr>
<th>Table 1: Air and natural gas inlet conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air</strong></td>
</tr>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Pressure (bar)</td>
</tr>
<tr>
<td>Mass flow (kg/s)</td>
</tr>
</tbody>
</table>

The rest of the power plant, as well as the capture plant and the compression stage have been modelled using Aspen Plus\textsuperscript{®}. For modelling purposes the combustor was assumed to be a stoichiometric reactor (RStoic), which takes into account the stoichiometry of the oxidation of the fuel in order to calculate the outlet conditions. The HRSG was assumed to have three different pressure turbines and a high number of heat exchangers in order to get a more accurate prediction. The parameters for the HRSG are specified in tab. 3.
### Table 2: Gas turbine main parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbine inlet temperature (°C)</td>
<td>1360</td>
</tr>
<tr>
<td>Pressure ratio in the compressor (-)</td>
<td>18.1</td>
</tr>
<tr>
<td>Compressor efficiency (%)</td>
<td>85</td>
</tr>
<tr>
<td>Turbine efficiency (%)</td>
<td>94.15</td>
</tr>
<tr>
<td>Mechanical efficiency (%)</td>
<td>99.6</td>
</tr>
<tr>
<td>Combustor temperature (°C)</td>
<td>1443</td>
</tr>
<tr>
<td>Combustor pressure (bar)</td>
<td>70</td>
</tr>
<tr>
<td>Mole flow at exit (mol/h)</td>
<td>84251.5</td>
</tr>
<tr>
<td>Temperature at exit (°C)</td>
<td>604</td>
</tr>
<tr>
<td>Vapour fraction (-)</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table 3: Main parameters of the HRSG of the reference plant

#### High pressure turbine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet pressure (bar)</td>
<td>120</td>
</tr>
<tr>
<td>Reheat temperature (°C)</td>
<td>500</td>
</tr>
<tr>
<td>Isentropic efficiency (%)</td>
<td>94</td>
</tr>
</tbody>
</table>

#### Intermediate pressure turbine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet pressure (bar)</td>
<td>28</td>
</tr>
<tr>
<td>Reheat temperature (°C)</td>
<td>291</td>
</tr>
<tr>
<td>Isentropic efficiency (%)</td>
<td>91</td>
</tr>
</tbody>
</table>

#### Low pressure turbine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet pressure (bar)</td>
<td>5</td>
</tr>
<tr>
<td>Isentropic efficiency (%)</td>
<td>90</td>
</tr>
<tr>
<td>Condenser pressure (bar)</td>
<td>0.048</td>
</tr>
</tbody>
</table>
The variables studied in the validation of the model are temperature and pressure at the exit of the turbine and power produced by the gas turbines and the HRSG, as well as the efficiency of the plants. These values can be found in tab. 4 and tab. 5.

**Table 4: Validation of Gas Turbine**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Aspen Plus</th>
<th>EBTF</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas turbine outlet temperature (°C)</td>
<td>604</td>
<td>608</td>
<td>0.65</td>
</tr>
<tr>
<td>Power generated by gas turbine (MW)</td>
<td>277</td>
<td>280</td>
<td>1.07</td>
</tr>
<tr>
<td>Power generated by steam turbine (MW)</td>
<td>265</td>
<td>269.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

**Table 5: Validation parameters of the steam cycle**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Aspen Plus</th>
<th>EBTF</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power generated (MW)</td>
<td>819.9</td>
<td>829.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Net efficiency LHV (%)</td>
<td>57.7</td>
<td>58.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>

**2.2 Capture plant**

The flue gas from the NGCC enters the carbonator, which is assumed to be a stoichiometric reactor for modelling purposes, with three degrees of freedom: sorbent conversion, temperature and pressure. The carbonator temperature is maintained between 580-700°C, which is the optimal capture temperature range due to the trade-off between the equilibrium forces and the reaction kinetics [24; 25]. The calcination occurs at more than 900°C, in a chamber that is modelled as a Gibbs reactor, where extra fuel is burned in an O₂/CO₂ atmosphere to generate heat required for the endothermic calcination reaction [14; 26]. As the sorbent conversion decreases during the carbonation/calcination cycles, the fresh sorbent make-up is considered.

This model uses the semi-empirical correlation for maximum average conversion shown in eq. (1) [27]. The carbonation conversion and the CO₂ capture level are calculated by eq. (2) and eq. (3).

\[
X_{ave} = \left( F_0 + F_R \tau_0 \right) f_{calc} \left[ \frac{a_1 f_1^2}{F_0 + F_R f_{calc} f_{calc} (1 - f_1)} + \frac{a_2 f_2^2}{F_0 + F_R f_{calc} f_{calc} (1 - f_2)} + b \right]
\]  \hspace{1cm} (1)

\[
\Delta X_{calc} = f_{calc} f_{calc} X_{ave}
\]  \hspace{1cm} (2)
This model has been verified elsewhere [28], and the main parameters are shown in tab. 6.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonator temperature (°C)</td>
<td>650</td>
</tr>
<tr>
<td>Calciner temperature (°C)</td>
<td>900</td>
</tr>
<tr>
<td>Carbonated sorbent fraction (-)</td>
<td>0.70</td>
</tr>
<tr>
<td>Calcined sorbent fraction (-)</td>
<td>0.95</td>
</tr>
<tr>
<td>Fluidising fan pressure increase (mbar)</td>
<td>150</td>
</tr>
<tr>
<td>Excess oxygen (% vol)</td>
<td>2.5</td>
</tr>
<tr>
<td>Relative fresh limestone make-up rate¹ (-)</td>
<td>0.05</td>
</tr>
</tbody>
</table>

3 Integration of the NGCC and the CaL plant

The ASU was not implemented in the model, and the energy needed to produce pure oxygen was assumed to be 200 kWh/ton O₂ [29]. Depending on the technology, there are certain ranges of efficiency penalties that are accepted, for calcium looping that is from 8% to around 12% points [14; 30]. In this work efficiency penalties are used as a benchmark to compare configurations [31; 32]. The following cases are studied in more detail. In the Case 1 the capture plant is placed immediately after the gas turbine exit point, and the gas is directly transferred to the carbonator. It should be noted that this configuration is not suitable for the retrofit scenario as the capture plant would be built between the turbine and the HRSG, which is in real plants just one piece of equipment. On the other hand, in Case 2, the capture plant was located after the HRSG to allow retrofitting of existing plants. The HRSG exit gas, which is at 147°C, is preheated to 564°C with the CO₂ stream from calciner. The efficiency penalty results related to two main integration cases considered in this study are presented in tab. 7. These results show that for Case 2 more power is generated compared with both Case 1 and the reference plant, while the net plant efficiency drops in both cases with CaL when compared to the reference plant. The energy penalty for Case 1 is substantially higher than the one for Case 2 due to the higher net plant efficiency in Case 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative fresh limestone make-up rate¹ (-)</td>
<td>0.05</td>
</tr>
</tbody>
</table>

¹ Relative fresh limestone make-up rate is defined as ratio of fresh limestone make-up and sorbent looping rates
Plant with CO\(_2\) capture

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference plant without CO(_2)</th>
<th>CASE 1</th>
<th>CASE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net plant output (MW)</td>
<td>819.9</td>
<td>906.8</td>
<td>1025.4</td>
</tr>
<tr>
<td>Net plant efficiency, LHV (%)</td>
<td>57.7</td>
<td>45.7</td>
<td>49.1</td>
</tr>
<tr>
<td>Efficiency penalty (% points)</td>
<td>n/a</td>
<td>12.0</td>
<td>8.6</td>
</tr>
</tbody>
</table>

4 Techno-economic analysis

The prices used in this techno-economic analysis have been taken from the literature [33-37].

In addition to thermal efficiency, both cost of electricity (€/MWh) and CO\(_2\) avoided (€/tCO\(_2\)) are the main parameters of the process that this study aims to evaluate, and they are the main drivers for the final recommendations of this study. Eq. (4) is used to calculate the cost of electricity, the annuity factor is calculated with eq. (5), and the cost of CO\(_2\) avoided is quantified with eq. (6).

\[
COE = \frac{TFC \times \Psi}{P \times T_{eq}} + \frac{U_{fix}}{P \times T_{eq}} + u_{var}
\]  

(4)

\[
\Psi = \frac{q - 1}{1 - q^{-n}}
\]  

(5)

\[
Cost\ of\ avoided\ tCO_2 = \frac{COE_{capture} - COE_{ref}}{(CO_2_{ref} / \text{MWh})_{capture} - (CO_2_{ref} / \text{MWh})_{ref}}
\]  

(6)

4.1 Operational parameters

No technical or operational issues are considered, so it is assumed that the plant is running at full capacity all the time (8760 h/year).

One of the most sensitive parameter is the fuel price which can fluctuate greatly. According the Energy Information Administration [38], natural gas prices have varied substantially such that they were 8.5 €/GJ in 2005 3.5 €/GJ in 2009 and 2.4 €/GJ in 2011. Currently prices are at 3.5 €/GJ [38] while many studies use a value of 3-9 €/GJ. In this study, the current price will be used followed by a sensitivity analysis in order to evaluate the impact of the fuel price and allow the chance to compare it with other literature data.

Other consumable costs used in this analysis are: fresh water: 6 €/m\(^3\), cooling water: 0.35 €/m\(^3\), fresh limestone: 8 €/t. However, since these prices differ in an open range between studies so an analysis considering these variations is carried out here.

4.2 Cost of electricity and cost of avoided CO\(_2\).

The total costs for the 820 MWel NGCC plant without CO\(_2\) capture are specified in tab. 8.

Table 8: Total costs for the NGCC plant without CO\(_2\) capture
In tab.9 the values for the most important economic values are found for the reference plant and Case 2 as well as the fuel price, the cost of electricity (COE) and cost of CO₂ avoided.

### Table 9: Main economic values COE and cost of avoided CO₂

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference plant</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPC (Dir. + Indir.) (M€)</td>
<td>375.6</td>
<td>715.6</td>
</tr>
<tr>
<td>Owner Costs (5%) (M€)</td>
<td>18.8</td>
<td>35.8</td>
</tr>
<tr>
<td>Contingency (10%) (M€)</td>
<td>37.6</td>
<td>71.6</td>
</tr>
<tr>
<td>TCI (M€)</td>
<td>431.9</td>
<td>822.9</td>
</tr>
<tr>
<td>TCI (specific) (€/kW)</td>
<td>526.8</td>
<td>802.5</td>
</tr>
<tr>
<td>Fuel price (£/GJ)</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Annual fuel cost (M€/a)</td>
<td>157.1</td>
<td>250.5</td>
</tr>
<tr>
<td>Fixed O&amp;M (M€/a)</td>
<td>24.4</td>
<td>45.7</td>
</tr>
<tr>
<td>Variable O&amp;M (M€/a)</td>
<td>1.4</td>
<td>14.6</td>
</tr>
<tr>
<td>Variable O&amp;M (£/MWh)</td>
<td>0.2</td>
<td>1.6</td>
</tr>
<tr>
<td>COE (£/MWh)</td>
<td>33.1</td>
<td>44.1</td>
</tr>
<tr>
<td>Cost of CO₂ avoided (£/tCO₂ avoided)</td>
<td>29.3</td>
<td></td>
</tr>
</tbody>
</table>

5 Discussion

The difference between the costs the reference power plant and the plant with calcium looping can be seen in fig.7.

![Figure 7: Breakdown of the costs for the reference case and the CaL case](image-url)
While the COE increases from 33.1 €/MWh to 44.1 €/MWh, which is a growth of approximately 33%, it can be seen how the capital investment increases when the capture is implemented. Fixed costs are also augmented by 2% points, due to the extra water consumption plus the necessity of a sorbent make-up flow.

Nevertheless, fuel price is in both cases the most critical variable when it comes to the final cost of electricity. Speaking about the CO₂ avoidance cost, while the price of 29.3 €/tCO₂, here it is highlighted that in this case the system does not require any ash or sulphur removal treatments. Also when comparing the results to plants with similar electric output but using other type of capture systems, as amines, the prices becomes substantially lower for the CaL case, with avoided cost for novel amine scrubbing technologies of 38.0 €/tCO₂[39].

In order to obtain more reliable results for different fuel prices scenarios, a sensitivity analysis for the fuel price is carried out and it is shown in fig.8.

![Figure 8: Costs vs fuel price](image)

As can be seen from fig.8, the fact that natural gas is used also for combustions in the calciner makes the COE rise faster in the capture containing system than in the reference plant. It is also shown that the COE\text{cap} and the COE\text{ref} are more affected by the cost of fuel whilst the cost of CO₂ avoided is affected in a less dramatic manner.

6 Conclusions

This work show that putting an additional steam cycle decreases the energy penalty substantially from 12% to 8.6%, due to the high temperatures reached in the carbonator and the calciner. Therefore, this
heat must be utilized in order to achieve a competitive energy penalty comparable to other technologies such as amine scrubbing.

The techno-economic analysis results have shown a potential future for this combination of fuel and technology. While the capital costs of the plant increase considerably, the improved efficiency combined with the capture capacity of the process ensures that the COE remains at a very acceptable range, and is certainly lower than the costs obtained with other technologies, e.g. with novel amine technologies the COE is 78.5 €/MWh [39], in this work these costs are as low as 44.1 €/MWh. It can also be concluded that the fuel costs are the most critical parameter and the idea of using natural gas for the calciner is a viable option, since it avoids future costs for the sorbent regeneration due to sulphur contamination and impurities treatments in the flue gas of the reference plant. Our results have shown costs rapidly increase when the fuel price raises, but gas provisions for the time window where this option is considered appear to be acceptably low.

7 References


**Nomenclature**

\[ a_1 \]  
Model fitting parameter [28]  

\[ a_2 \]  
Model fitting parameter [28]  

\[ b \]  
Model fitting parameter [28]  

\[ F_0 \]  
Fresh-limestone make up rate [kmol/s]  

\[ f_i \]  
Model fitting parameter [28]  

\[ f_2 \]  
Model fitting parameter [28]  

\[ E_{CO2} \]  
CO₂ capture level in the carbonator [\-]  

\[ F_{CO2} \]  
CO₂ flow rate entering the carbonator [kmol/s]  

\[ F_R \]  
CaO looping rate [kmol/s]  

\[ f_{calc} \]  
Calcination reaction extent [\-]  

\[ f_{carb} \]  
Carbonation reaction extent [\-]  

\[ n \]  
Amortization [years]  

\[ P \]  
Power output [MW]  

\[ q \]  
One plus the average discount rate per annum [\-]  

\[ r_0 \]  
Fraction of never calcined limestone in the system [\-]  

\[ T_{eq} \]  
Utilization time at rated power output [h/year]  

\[ U_{fix} \]  
Fixed cost of operation, maintenance and administration [€]
\( U_{var} \) Variable cost of operations, maintenance and administration [\( \text{€} \)]

\( X_{ave} \) Average sorbent conversion [-]

\( X_{calc} \) Sorbent conversion in the calciner [-]

\( X_{carb} \) Sorbent conversion in the carbonator [-]

\( Y_f \) Fuel price [\( \text{€/MJ} \)]

\( \Delta X_{carb} \) Carbonation conversion [-]

\( \Psi \) Annuity factor [-]

\( \bar{\eta} \) Average plant net efficiency [-]

**Abbreviations**

ASU Air Separation Unit

CaL Calcium Looping

CCS Carbon Capture and Storage

COE Cost of Electricity

EBTF European Benchmark Task Force

EPC Engineering, Procurement and Construction

HRSG Heat Recovery Steam Generator

NGCC Natural Gas Combined Cycle

O&M Operation & Maintenance

TCI Total Capital Investment

TPC Total Plant Cost

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Paper revised:

Paper accepted: 15.10.2015.