Advanced Exergoenvironmental Analysis of a Near-Zero Emission Power Plant with Chemical Looping Combustion

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ABSTRACT: Carbon capture and storage (CCS) from power plants can be used to mitigate CO2 emissions from the combustion of fossil fuels. However, CCS technologies are energy intensive, decreasing the operating efficiency of a plant and increasing its costs. Recently developed advanced exergy-based analyses can uncover the potential for improvement of complex energy conversion systems, as well as quantify and identify plant component interactions. In this paper, an advanced exergoenvironmental analysis is used for the first time as means to evaluate an oxy-fuel power plant with CO2 capture. The environmental impacts of each component are split into avoidable/unavoidable and endogenous/exogenous parts. In an effort to minimize the environmental impact of the plant operation, we focus on the avoidable part of the impact (which is also split into endogenous and exogenous parts) and seek ways to decrease it. The results of the advanced exergoenvironmental analysis show that the majority of the environmental impact related to the exergy destruction of individual components is unavoidable and endogenous. Thus, the improvement potential is rather limited, and the interactions of the components are of lower importance. The environmental impact of construction of the components is found to be significantly lower than that associated with their operation; therefore, our suggestions for improvement focus on measures concerning the reduction of exergy destruction and pollutant formation.

INTRODUCTION

With conventional exergy-based analyses, the locations, magnitudes, and causes of thermodynamic inefficiencies, costs, and environmental impacts are identified, and strategies for improvement can be found.1−6 However, when component interactions are not considered, optimization strategies can be misguided, especially when complex systems with a large number of mutually affected components are considered. Advanced exergy-based analyses attempt to address this shortcoming.5−11

Advanced exergy-based analyses have been developed at the Institute for Energy Engineering of the Technische Universität Berlin. In past publications, the exergoenvironmental analysis has only been partly presented, while advanced exergetic and exergoeconomic analyses have considered only relatively simple plants.8−11 This paper presents the results of the first application of an advanced exergoenvironmental analysis applied to a power plant incorporating CO2 capture.

The calculations conducted in an advanced exergoenvironmental analysis depend on the results of an advanced exergetic analysis5 and are, to a large extent, analogous, as long as no significant component-related (i.e., construction-related) environmental impacts are found. In an advanced exergoenvironmental analysis, the environmental impacts associated with exergy destruction and pollutant formation are separated into avoidable/unavoidable, endogenous/exogenous, and the respective combined parts (e.g., avoidable endogenous, avoidable exogenous, etc.). In most cases, the component-related environmental impact is of low importance when compared to that of the operation of the plant (impact of exergy destruction) and it is therefore not analyzed in detail.

The plant considered here (Figure 1) is an oxy-fuel combined cycle power plant incorporating chemical looping combustion (CLC).12−17 This plant has already been examined using conventional exergy-based analyses.6 The structure and operating conditions of the plant are based on a reference plant that does not consider CO2 capture.6 Here, the conventional exergoenvironmental analysis is reassessed, while the results of the advanced exergetic and exergoeconomic analyses for the plant can be found in ref 18.

METHODOLOGY: ADVANCED EXERGOENVIRONMENTAL ANALYSIS

In an advanced exergoenvironmental analysis, the environmental impacts associated with exergy destruction and pollutant formation (PF) are split based on their source.5 By considering different operating conditions, we can distinguish whether the environmental impacts of exergy destruction and/or pollutant formation are caused by the component itself (endogenous, $B_{EN}$, $B_{PF,EN}$) or by the operation of the remaining components (exogenous, $B_{EX}$, $B_{PF,EX}$). In more detail, the endogenous environmental impact of a component is associated...
with its operating conditions and the irreversibilities caused by its performance. Exogenous environmental impact, on the other hand, is the part of the impact of a considered component that exists due to the assigned role of the remaining plant components of the structure. Depending on the operation of the remaining components, the environmental impact of the component of interest will either increase or decrease.

The calculation of the endogenous environmental impacts is based on calculations conducted in an advanced exergetic analysis.3,7 To calculate the endogenous exergy destruction of component $k$, the component must operate under real conditions, while all other components of the process must operate without irreversibilities (i.e., theoretically). In all cases, the net power output of the overall plant is kept constant and equal to that of the initial simulation (real case).

$$\dot{B}_{D,k}^{EN} = b_{F,k}^{real} - \dot{B}_{D,k}$$  \hspace{1cm} (1)

$$\dot{B}_{k}^{PF,EN} = \sum \dot{b}_{i}^{PF} (m_{i,\text{out}} - m_{i,\text{in}})^{EN}$$  \hspace{1cm} (2)

$\dot{b}_{i}^{real}$ is the specific environmental impact of fuel of component $k$ in the real case and $\dot{b}_{i}^{EN}$ is its endogenous exergy destruction. The difference $m_{i,\text{out}} - m_{i,\text{in}}$ in the calculation of the environmental impact of pollutant formation refers to the net mass flow of each pollutant $i$ exiting the reactor (and emitted to the environment), and $\dot{b}_{i}^{PF}$ is its specific environmental impact. The mass flows of the pollutants in the endogenous operation of the reactor have been calculated in the simulations used for estimating the endogenous exergy destruction. Although the composition of the flue gases of the reactor remains the same, the different operating conditions result in changes in the mass flows in the overall plant. Thus, the absolute mass flows of the pollutants differ from those of the real case. Here, the life cycle impact assessment method Eco-indicator 99 has been used, and the considered values of $\dot{b}_{i}^{PF}$ are shown in Table 1.19

The exogenous parts of the environmental impacts ($\dot{B}_{D,k}^{EX}$, $\dot{B}_{k}^{PF,EX}$) are calculated by subtracting the endogenous from the real parts, $\dot{B}_{D,k}^{real}$ and $\dot{b}_{k}^{PF,real}$:

$$\dot{B}_{D,k}^{EX} = \dot{B}_{D,k}^{real} - \dot{B}_{D,k}^{EN}$$  \hspace{1cm} (3)

$$\dot{B}_{k}^{PF,EX} = \dot{b}_{k}^{PF,real} - \dot{b}_{k}^{PF,EN}$$  \hspace{1cm} (4)

The exogenous impacts are therefore the impacts imposed on component $k$ through the operation of the remaining $n - 1$ components that constitute the plant. The $\dot{B}_{D,k}^{EX}$ of component $k$ can also be traced to the specific components that cause it, and it is calculated by examining the plant components in pairs ($r+k$). However, the sum of these individual exogenous environmental impacts differs from the exogenous impact of component $k$ (calculated with eq 3). This leads to the definition of the
The unavoidable environmental impact of exergy destruction of a component is calculated based on its unavoidable exergy destruction, $\dot{B}^{\text{EN}}_{D,k}$, and its specific environmental impact of fuel, $b^{\text{real}}_{k,i}$. The assumptions used to calculate the unavoidable exergy destruction include high efficiencies with minimum irreversibilities and are to some extent arbitrary, i.e., they depend on the decision maker. The unavoidable environmental impact of pollutant formation includes the CO$_2$ emissions, because complete combustion is assumed (in eq 7, i: CO$_2$).

\[
\dot{B}^{\text{UN}}_{D,k} = b^{\text{real}}_{k,i} \dot{E}^{\text{D},k}
\]

The unavoidable impact of exergy destruction is obtained with eq 8, while the avoidable pollutant formation includes the NO$_X$ and CH$_4$ emissions that could eventually be avoided by changing the combustion conditions:

\[
\dot{B}^{\text{AV}}_{D,k} = \dot{B}^{\text{real}}_{D,k} - \dot{B}^{\text{UN}}_{D,k}
\]

The avoidable and unavoidable environmental impacts of component k can also be split into endogenous and exogenous parts as:

\[
\dot{B}^{\text{PF,UN,EN}}_{k} = b^{\text{real}}_{F,k} \dot{E}^{\text{D},k}
\]

The avoidable endogenous and exogenous impacts are then calculated by subtracting the corresponding unavoidable part from the total endogenous and exogenous environmental impacts, respectively:

\[
\dot{B}^{\text{AV,EN}}_{D,k} = \dot{B}^{\text{EN}}_{D,k} - \dot{B}^{\text{UN,EN}}_{D,k}
\]

\[
\dot{B}^{\text{PF,AV,EN}}_{k} = \dot{B}^{\text{PF,EN}}_{k} - \dot{B}^{\text{PF,UN,EN}}_{k}
\]

\[
\dot{B}^{\text{AV,EX}}_{D,k} = \dot{B}^{\text{EX}}_{D,k} - \dot{B}^{\text{UN,EX}}_{D,k}
\]

\[
\dot{B}^{\text{PF,AV,EX}}_{k} = \dot{B}^{\text{PF,EX}}_{k} - \dot{B}^{\text{PF,UN,EX}}_{k}
\]

By now we can characterize specific parts of the environmental impacts of each plant component depending on their source and potential for mitigation. However, to identify the real improvement potential of individual plant components, the total avoidable environmental impact including both exergy destruction and pollutant formation must be calculated at the component level:

\[
\dot{B}^{\text{PF,AV}}_{k} = \dot{B}^{\text{PF,AV,EN}}_{k} + \dot{B}^{\text{PF,AV,EX}}_{k}
\]

The oxy-fuel power plant considered in this paper includes chemical looping combustion for easy CO$_2$ capture (CLC plant). In this plant, the conventional combustion chamber is replaced by two reactors, an oxidizing or air reactor (AR), and a fuel reactor (FR). A metal oxide is used as a solid oxygen carrier (OC) between these two reactors; thus, no direct contact between the air and the fuel takes place. The two reactors are simulated here as a black box (CLC reactor). We assume that...
in the FR, 98% of the methane reacts with oxygen transferred from the AR. The remaining unreacted 2% of the fuel is not recycled back to the FR but represents a loss. The air ratio, the ratio between the oxygen included in the air and the oxygen needed for stoichiometric combustion, is set to 2.9, which is required to achieve outlet temperatures of the air and the fuel reactors of 1200 °C and 930 °C, respectively. These temperatures are also the inlet temperatures of the expanders of the plant. It has been suggested that the inlet temperature of the CO2/H2O expander (GT2) should be as low as 900 °C, to increase the conversion of the fuel in the FR and the energy available for the oxidation of the metal in the AR.22 With this lower temperature, a lower cost for the expander is also achieved. When compared with various metals that have been suggested as oxygen carriers, Ni and its corresponding oxides generally show higher oxidation and reduction rates, as well as greater durability after many repeated cycles.26 Thus, here, a Ni-based OC is considered, and the reacted CH4 is fully converted to CO2.

### RESULTS AND DISCUSSION

The CLC plant has been examined with conventional and advanced exergy-based environmental analyses. The conventional exergoenvironmental analysis has been performed using Eco-indicator 99.2,4,19 The data considered here are different from those presented in ref 4, because pollutant formation impacts have now been considered.5 In addition, the environmental impacts associated with exergy destruction and pollutant formation have been split. The component-related environmental impacts have been found to have a relatively negligible influence on the total impact, and thus they have not been split further. Selected results of the advanced exergoenvironmental analysis at the component level are presented in Tables 2–5.

For the majority of the components, most of the environmental impact has been found to be unavoidable. Exceptions are the expander of the main gas turbine system (GT1), the high- and intermediate-pressure steam turbines (HPST and IPST), the CO2 compressors (C1–C4), the additional steam turbine that drives the CO2 compressors (ST4), GT2, and the natural gas preheater (NGPH). The high avoidable environmental impact of exergy destruction of the NGPH is associated with simulation assumptions. In the initial simulation, the preheater is considered together with a control valve, the exergy destruction within which is associated with pressure reduction. This exergy destruction is assumed to be avoidable when the preheater is considered in isolation. Changes to components with high avoidable environmental impact of exergy destruction can affect the overall plant significantly. Nevertheless, interactions among components should be considered in parallel to achieve improvement of the overall process. As shown in Table 2, most of the BUN is found to be endogenous, suggesting that component interactions are of lower significance. Specifically, for the component with the highest impact of exergy destruction, the CLC reactor, the endogenous impact is six times higher than the exogenous impact. Thus, the internal operation of this component has priority when considering improvement measures.

With advanced exergy-based methods, we reveal both positive and negative effects among plant components. A positive exogenous value of component k means that if the overall
We find that the effect of the CLC reactor on the other environmental impact of exergy destruction caused within the plant. We find that the effect of the CLC reactor on the other component considered has small exergy destruction, and thus endogenous values are rare and they are only obvious when the component works more efficiently when it operates in the plant special case, due to component interactions, the considered simultaneous interactions among all plant components. In this explained through the mexogenous impacts that are a result of exergy destruction per exergy of product. This effect can only be avoided endogenous exergy destruction. Negative avoidable (e.g., the IPEC in Table 3) stem from negative values of the avoidable endogenous environmental impacts have the opposite effect on component k, i.e., it would result in an increase in its environmental impact. Additionally, negative values of avoidable endogenous environmental impacts (e.g., the IPEC in Table 3) stem from negative values of the avoidable endogenous exergy destruction. Negative avoidable endogenous values are found when the endogenous is smaller than the unavoidable endogenous part of exergy destruction, which happens when the unavoidable surpasses the endogenous exergy destruction per exergy of product. This effect can only be explained through the mexogenous impacts that are a result of simultaneous interactions among all plant components. In this special case, due to component interactions, the considered component works more efficiently when it operates in the plant and with the conditions required for the calculation of its endogenous exergy destruction than when it operates in isolation and under the conditions required for the calculation of the unavoidable exergy destruction. Nonetheless, negative avoidable endogenous values are rare and they are only obvious when the component considered has small exergy destruction, and thus plays a less significant role in the structure.

Results from splitting the exogenous environmental impacts of exergy destruction for selected components are shown in Table 3. The sum of the columns refers to the total exogenous environmental impact of exergy destruction caused within the considered component k by the remaining components of the plant, while the values in the parentheses show the impact caused by component k to the remaining components of the plant. We find that the effect of the CLC reactor on the other components of the plant is of similar magnitude to the effect the other components exert on the reactor. These calculations are determined by the intense interactions among the three components of the GT system. On the other hand, GT1 is not influenced so much by the other components, but it influences the operation of the other components greatly. This happens because the expander directly influences the operation of the majority of the components in the steam cycle, since its operation determines the thermal energy available through the flue gases. In summary, the highest exogenous impact is caused by the components of the gas turbine system, i.e., the reactors, followed by GT1 and C1. These components influence each other substantially: 41% of the impact of the reactors is caused by C1 and GT1, while a large part of the impact imposed on C1 and GT1 stems from the reactors.

The total avoidable environmental impact of exergy destruction has been calculated based on eq 19, and the results of the most influential components of the plant are shown in Table 4. The CLC reactor presents relatively high avoidable endogenous and exogenous values, when compared to the other components, resulting in a higher overall impact. GT1 is ranked second, C1 third, and ST4 fourth. A large difference between C1 and GT1 is the relatively larger avoidable exogenous value of GT1, because C1 influences the remaining components of the plant less. In general, it has been found that the components with the highest avoidable values are also those with the highest influence on the plant. Thus, improving these components will also improve the operation of other components and lead to a significant reduction in the environmental impact of the overall plant.

In summary, the components of the plant with the highest influence and avoidable impacts are the components constituting the GT system. The CLC reactor is the most important component with the highest environmental impact of exergy destruction, although it also has the highest unavoidable impact. This component has an approximately four times higher total avoidable impact than GT1. Since the total environmental impact of the CLC reactor is mostly exogenous and can, components of the plant is of similar magnitude to the effect the other components exert on the reactor. These calculations are determined by the intense interactions among the three components of the GT system. On the other hand, GT1 is not influenced so much by the other components, but it influences the operation of the other components greatly. This happens because the expander directly influences the operation of the majority of the components in the steam cycle, since its operation determines the thermal energy available through the flue gases. In summary, the highest exogenous impact is caused by the components of the gas turbine system, i.e., the reactors, followed by GT1 and C1. These components influence each other substantially: 41% of the impact of the reactors is caused by C1 and GT1, while a large part of the impact imposed on C1 and GT1 stems from the reactors.

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In summary, the components of the plant with the highest influence and avoidable impacts are the components constituting the GT system. The CLC reactor is the most important component with the highest environmental impact of exergy destruction, although it also has the highest unavoidable impact. This component has an approximately four times higher total avoidable impact than GT1. Since the total environmental impact of the CLC reactor is mainly determined by its exergy destruction, measures to improve the mixing of streams and to minimize temperature differences and pressure losses have to be considered. Additionally, the avoidable impact of pollutant formation of the CLC reactor is mostly endogenous and can,

Table 3. Selected Results from Splitting the Exogenous Environmental Impact of Exergy Destruction (mPts/s)\textsuperscript{a}

<table>
<thead>
<tr>
<th>component, k</th>
<th>$\beta_{PF,EX}^{k}$</th>
<th>component, r</th>
<th>$\beta_{PF,EX}^{r}$</th>
<th>component, k</th>
<th>$\beta_{PF,EX}^{k}$</th>
<th>component, r</th>
<th>$\beta_{PF,EX}^{r}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLC</td>
<td>95.27</td>
<td>C1</td>
<td>10.85</td>
<td>ST4</td>
<td>16.06</td>
<td>C1</td>
<td>0.72</td>
</tr>
<tr>
<td>GT1</td>
<td>28.62</td>
<td></td>
<td></td>
<td>GT1</td>
<td></td>
<td></td>
<td>0.83</td>
</tr>
<tr>
<td>ST4</td>
<td>3.80</td>
<td></td>
<td></td>
<td>SUM</td>
<td>11.23 (5.24)</td>
<td></td>
<td>4.30</td>
</tr>
<tr>
<td>SUM</td>
<td>81.22 (70.89)</td>
<td></td>
<td></td>
<td>MX\textsuperscript{b}</td>
<td>14.05</td>
<td></td>
<td>3.25</td>
</tr>
<tr>
<td>MX\textsuperscript{b}</td>
<td>14.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>32.65</td>
<td>CLC</td>
<td>22.69</td>
<td>GT1</td>
<td>38.62</td>
<td>C1</td>
<td>2.00</td>
</tr>
<tr>
<td>GT1</td>
<td>2.11</td>
<td></td>
<td></td>
<td>ST4</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ST4</td>
<td>0.28</td>
<td></td>
<td></td>
<td>SUM</td>
<td>15.37 (64.16)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SUM</td>
<td>27.98 (22.92)</td>
<td></td>
<td></td>
<td>MX\textsuperscript{b}</td>
<td>23.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MX\textsuperscript{b}</td>
<td>23.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}In parentheses the sum of exergy destruction caused by component k to the remaining components r is shown. \textsuperscript{b}Mexogenous environmental impact, as calculated with eq 5.

Table 4. Avoidable Environmental Impact of Exergy Destruction (mPts/s)

<table>
<thead>
<tr>
<th>component, k</th>
<th>$\sum_{r \neq k}^n \beta_{PF,AV,EX}^{k,r}$</th>
<th>$\beta_{PF,AV,EN}^{k}$</th>
<th>$\beta_{PF,AV,MX}^{k}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLC</td>
<td>20.48 (9.4%)</td>
<td>197.48 (90.6%)</td>
<td>217.96</td>
</tr>
<tr>
<td>GT1</td>
<td>16.93 (30.4%)</td>
<td>38.70 (69.6%)</td>
<td>55.63</td>
</tr>
<tr>
<td>C1</td>
<td>1.31 (5.8%)</td>
<td>21.27 (94.2%)</td>
<td>22.58</td>
</tr>
</tbody>
</table>

Table 5. Splitting the Environmental Impact of Pollutant Formation (mPts/s)

<table>
<thead>
<tr>
<th>Pollutant, k</th>
<th>$\beta_{PF,UN}^{k}$</th>
<th>$\beta_{PF,AV}^{k}$</th>
<th>$\beta_{PF,EX}^{k}$</th>
<th>$\beta_{PF,AVX}^{k}$</th>
<th>$\beta_{PF,UNX}^{k}$</th>
<th>$\beta_{PF,UNX}^{k}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLC</td>
<td>237.89</td>
<td>205.89</td>
<td>32.09</td>
<td>206.46</td>
<td>31.44</td>
<td>32.24</td>
</tr>
</tbody>
</table>
therefore, be decreased through changes in its operating conditions. The results from splitting the environmental impact of pollutant formation within the reactors of the plant are shown in Table 5. Overall, the majority of the environmental impact related to the exergy destruction is unavoidable and endogenous. Thus, the interactions of the components are of secondary importance. Nevertheless, changes to both component interactions and/or avoidable/unavoidable impacts can influence one another and should be considered in parallel when an overall improvement is desired.

CO₂ capture in combined cycle power plants is generally a costly process and only small improvements of the presented CLC process are possible. However, the application of improvement steps suggested by the advanced exergy-based analyses should lead to an improved performance of the overall plant.

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