Abstract

The SER gasification process is an allothermal DFB steam gasification process in which the necessary heat for the endothermic gasification is provided by circulating bed material. Due to the low gasification temperatures of 660 °C and the use of limestone as bed material, in-situ CO₂ capture is possible, leading to a hydrogen-rich, carbon-lean and nitrogen-free syngas. When operating the regeneration reactor in oxy-fuel mode, a high CO₂ concentration of >90 vol-% dry can be produced, what makes the Oxy-SER process a promising CCS technology. In this paper the Oxy-SER process is demonstrated and the effect of the oxy-fuel regeneration on the gasification process shown. The experiments showed, that a stable operation of this process is possible and that the operation mode of the regeneration reactor has only little effect on the gasification reactor. In the experiments a syngas with a high hydrogen concentration of 70 vol-% dry and a suitable stoichiometry for methanation processes was produced.

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Keywords: SER gasification; steam gasification; pre-combustion capture; CO₂ capture; Dual Fluidised Bed; Negative Emissions; Pilot scale demonstration

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Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>a.r.</td>
<td>as received</td>
</tr>
<tr>
<td>AER</td>
<td>absorption enhanced reforming</td>
</tr>
<tr>
<td>ASU</td>
<td>air separation unit</td>
</tr>
<tr>
<td>BFB</td>
<td>bubbling fluidised bed</td>
</tr>
<tr>
<td>CFB</td>
<td>circulating fluidised bed</td>
</tr>
<tr>
<td>daf</td>
<td>dry ash free</td>
</tr>
<tr>
<td>db</td>
<td>dry basis</td>
</tr>
<tr>
<td>DFB</td>
<td>dual fluidised bed</td>
</tr>
<tr>
<td>e.g.</td>
<td>exempli gratia (for example)</td>
</tr>
<tr>
<td>et al.</td>
<td>et alii / et aliae (and others)</td>
</tr>
<tr>
<td>LHV</td>
<td>lower heating value</td>
</tr>
<tr>
<td>Oxy-SER</td>
<td>sorption enhanced reforming with oxy-fuel regeneration</td>
</tr>
<tr>
<td>PLC</td>
<td>programmable logic controller</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PSD</td>
<td>particle size distribution</td>
</tr>
<tr>
<td>S/C</td>
<td>steam to carbon ratio (mol(\text{H}_2\text{O})/mol(\text{C}))</td>
</tr>
<tr>
<td>SER</td>
<td>sorption enhanced reforming</td>
</tr>
<tr>
<td>STP</td>
<td>standard temperature and pressure (273.15 K, 101325 Pa)</td>
</tr>
<tr>
<td>TRL</td>
<td>technical readiness level</td>
</tr>
</tbody>
</table>

1. Introduction

To reach a reliable production of regenerative energy, especially weather independent processes are key technologies. Biomass gasification processes can be such technologies due to the high efficiency and the numerous applications for the produced syngas.

In this work the dual fluidised bed steam gasification process was selected as gasification process. By using steam as gasification agent, a nitrogen-free syngas with a relatively high LHV can be produced. In this dual fluidised bed steam gasification process the necessary heat for the endothermic steam gasification is provided by circulating bed material. The bed material (e.g. silica sand, limestone or olivine) is heated up by the combustion of char in the regeneration reactor. In the last few years several pilot plants were built in Austria, Germany and Sweden with a capacity of 2-20 MW\(\text{th}\) [1–4]. All of these plants use wood chips or wood pellets as fuel. The SER (or also known as AER) process is a modified steam gasification process with lower gasification temperatures and limestone as bed material, which enables in-situ CO\(_2\) capture and simultaneously shifts the syngas composition towards higher H\(_2\) concentrations. Therefore in the SER process the limestone bed material acts as a heat carrier, a CO\(_2\) sorbent and a catalyst for tar reformation [5–7].

In the gasification reactor (Gasifier) the CaO bed material adsorbs the CO\(_2\), formed in the gasification reactions, forming CaCO\(_3\) [8]. This CaCO\(_3\) is transported with the circulating bed material into the regeneration reactor (Regenerator) and decomposes at higher temperatures of >850 °C into CaO and releases the CO\(_2\). The regenerated and heated up bed material is then brought back into the Gasifier. This CO\(_2\) capture and release is characterised by the following equilibrium reaction [9].

\[
\text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 \quad \Delta H_{298K} = -178 \text{kJ/mol}
\]  

Due to the chemical equilibrium of the capture reaction (Figure 1), the gasification temperature is limited to temperatures below 720 °C.
Fig. 1. Equilibrium of the carbonation/calcination reaction [10].

By operating the Regenerator in oxy-fuel combustion mode, a flue gas stream with high CO₂ concentrations of >90 vol-% dry can be achieved, what makes this process a promising CCS technology [11]. When sustainable biomass is used as fuel and the CO₂-rich flue gas stream of the Regenerator purified and permanently stored, this process offers the possibility to achieve negative CO₂ emissions. The schematic of this Oxy-SER steam gasification process is shown in figure 2.

Fig. 2. Schematic of the Oxy-SER steam gasification process

Until now this process was only tested for wood pellets as fuel. The relatively high fuel cost, the local and seasonal availability and the limited sources makes this kind of biomass gasification economically and logistically challenging. Therefore a promising approach would be using other low cost fuels like e.g. sewage sludge, manure, fermentation residues or fossil fuels like lignite coal. Currently there are no publications about the SER gasification of lignite available, but investigations from Saw et al. have shown that by using lignite (Southland, New Zealand) as fuel for the conventional steam gasification process (Gasifier temperature 800°C, silica sand as bed material), the product gas yield is slightly higher compared to wood chips (radiate pine) [12].
2. Description of the Experimental Facility and Experimental Methods

In this work the gasification process is carried out in a 200 kW\textsubscript{th} pilot plant consisting of two fluidised bed reactors. The gasification takes place in a refractory lined bubbling fluidised bed reactor (Gasifier) with an internal diameter of 330 mm and a height of 6 m. The refractory lined circulating fluidised bed combustion reactor (Regenerator) has an internal diameter of 210 mm and a height of 10 m. The circulation rate between the reactors is controlled by the rotational speed of a high-temperature screw conveyor. The plant is not electrical heated and therefore the process can be tested in a representative environment with a TRL of 6 [13].

The Gasifier is fluidised by preheated steam. The fuel is gravimetric dosed and fed via a purged rotary valve and a screw feeder into the Gasifier. There the fuel is partially gasified and the remaining char leaves the reactor together with the bed material via a bottom loop seal into the CFB combustion reactor (Regenerator). Entrained bed material and char particles are recirculated into the Gasifier by an internal circulation. In a second cyclone the dust concentration in the syngas is further reduced. After gas analysis and flow measurement the syngas is combusted in a flare.

In the Regenerator the char is combusted and the combustion energy heats up the bed material and calcines the bed material. Due to the heat losses in this pilot plant, additional fuel is necessary to operate the process. Calculations of Brellochs have shown, that in a commercial plant with low heat losses (compared to this pilot plant) at gasification temperatures of <680 °C no additional fuel is necessary to operate the process [14]. Entrained particles are separated from the gas in two cyclones and a filter house. In the oxy-fuel regeneration mode, a part of the flue gas is recirculated into the combustion reactor to lower the oxygen inlet concentration and therefore control the combustion temperature. The remaining gas leaves the plant via a fan and stack.

In the upper loop seal of the Regenerator the solids are divided into two streams. A part is transported into the Gasifier via a high-temperature screw conveyor and the remaining material returns via an internal circulation into the Regenerator.

In this facility nitrogen is used as fluidization agent for the loop seals and as purge gas for the dosing unit and the pressure transmitters. This leads to a minor dilution of the produced syngas and flue gas.

All operating data like temperatures, pressures, gas concentrations, fuel and steam mass flows are displayed and recorded using a PLC control and data logging software. Pressures and temperatures are measured at several positions along the reactor and the periphery. In the Gasifier the product gas components CO, CO\textsubscript{2}, CH\textsubscript{4}, O\textsubscript{2} and H\textsubscript{2} are measured after condensation, tar removal in isopropanol, gas drying and fine filtration using the online gas analyser ABB AO2020 [15]. Non condensable hydrocarbons (C\textsubscript{2} - C\textsubscript{4}) are measured in a Varian CP-4900 Micro-GC [16]. The water content in the product gas is measured using a Bartec Hygrophil 4220 measurement device [17]. Tar analysis are done according to the CEN/TS tar protocol [18]. The product gas yield is measured by an orifice plate.

In the Combustor the gas components CO, CO\textsubscript{2}, O\textsubscript{2}, NO, NO\textsubscript{2} and SO\textsubscript{2} are measured after condensation and fine filtration in the gas analysers ABB El3020 and EcoPhysics CLD 822 CMhr [19,20].

Figure 3 shows a schematic of the plant.
Limestone is used as bed material (with a composition and mean particle size shown in Table 1) and wood pellets are used as fuel (with a composition shown in Table 2).

Table 1. Composition of the bed materials

<table>
<thead>
<tr>
<th>Element</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>MgO</th>
<th>dp₅₀</th>
<th>μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>88.25</td>
<td>9.55</td>
<td>0.14</td>
<td>0.14</td>
<td>0.16</td>
<td>1.5</td>
<td>670</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Fuel composition of the wood pellets

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>Cl</th>
<th>Ash</th>
<th>H₂O</th>
<th>LHV</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.-%</td>
<td>wt.-%</td>
<td>wt.-%</td>
<td>wt.-%</td>
<td>wt.-%</td>
<td>wt.-%</td>
<td>wt.-%</td>
<td>wt.-%</td>
<td>MJ/kg</td>
</tr>
<tr>
<td>wood pellets</td>
<td>51.4</td>
<td>5.9</td>
<td>42.7</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>0.08</td>
<td>7.72</td>
</tr>
</tbody>
</table>

In advance to the experimental campaign the facility was heated up by the combustion of natural gas until ignition temperature was reached. After about 15 hours wood pellets and limestone were fed into the plant for further heating up and pre-calcining of the bed material. Over a period of several hours in both reactors wood pellets were combusted and bed material was circulated between the reactors to heat up the whole plant. When stable temperatures were reached, the fluidisation of the gasifier was switched from air to steam to start the gasification.

Having reached stable conditions in terms of pressure profiles, temperature profiles, circulation rates, gas compositions and gas yield, the experimental investigations started. For each experiment a stable period of at least one hour was necessary. Since the experiments were done with wood pellets with a low ash content of only 0.1 wt.-%ₐₛₐ, ash accumulation that could influence the process can be neglected. On the other hand the deactivation of the limestone bed material has to be taken into account. Due to the constant calcination and carbonation, the reactivity of the limestone decreases, mostly because of sintering effects, until a minimum activity is reached [21,22]. Therefore a constant addition of limestone is necessary to compensate material loss due to attrition and reactivity loss. Currently there are no detailed economic data for this kind of process available, but studies for the comparable Calcium Looping process by Poboss and Schaupp have shown, that the costs for the limestone is very low compared to the overall operating costs [23,24].
The following figure 4a and b shows the mean pressure and temperature profiles over an experimental period. The hydrodynamics of the facility are described in an earlier work of Bidwe [25].

3. Effect of oxy-fuel regeneration on the Gasifier

When the Regenerator is operated in an oxy-fuel combustion mode, high CO₂ outlet concentrations of > 90 vol-%dry can be reached. After purification this CO₂ gas stream can either be stored (CCS) or used as a raw product for the chemical industry (e.g. Fischer-Tropsch, methanation). In this chapter the effects of oxy-fuel regeneration on the Regenerator itself and the Gasifier are described. Due to the high CO₂ partial pressure in the Regenerator, the calcination behaviour of the sorbent has to be taken into account.

In this campaign a stable DFB steam gasification process was achieved over periods of several hours. The following figure shows the temperature and gas composition in the Gasifier (Figure 5a) and Regenerator (Figure 5b) over a period of 10 h.
Fig. 5. Temperature and gas composition of the Gasifier (a) and Regenerator (b)

It can be seen that the temperatures and the gas compositions were quite stable over this period of time. The increase of CO₂ in the Regenerator after 5 h was caused by the change of the operation mode. At this point the Regenerator was switched from air regeneration to oxy-fuel regeneration. It can be seen that this had no effect on the Gasifier. The gas composition, gas yield and tar concentration were quite similar between the two operation modes. The following graph shows the syngas composition between the two operation modes. The Gasifier temperature was in both modes between 660 and 670°C. This syngas composition corresponds with previous results published from Hawthorne et al. [26].
In contrary to a combustion process not all elements of the fuel (mainly C, H, O) are released during the gasification. Especially a part of the carbon is shifted as char from the Gasifier into the Regenerator where it is combusted to heat-up and to regenerate the bed material. Additionally most of the CO$_2$, formed in the gasification reactions, is captured by the CaO bed material and shifted as CaCO$_3$ into the Regenerator where it is released. To show the carbon balance of the Gasifier the carbon is divided into four fractions: Carbon in the syngas (CO, CO$_2$, CH$_4$, C$_2$-C$_4$), tars (assumed with a carbon content of 90 wt.-% [27]), calcium carbonate and char. Figure 7 shows the distribution of these forms. For comparison, the carbon balance of a conventional steam gasification process (with silica sand as bed material and 800 °C as gasification temperature) is also shown in figure 7 [28]. The organic (mainly char) and inorganic (mainly CaCO$_3$) carbon content in the bed material was analysed according to DIN 19539-E [29].
carbon. The rest of the carbon is transported into the Regenerator as char or calcium carbonate. In the conventional steam gasification process the syngas contains about 70 mol-% of the fuel carbon. Due to the lower carbon content in the syngas this SER process has a suitable composition for methanation processes [30].

Due to the catalytic effect of the limestone bed material, very low gravimetric tar concentrations of about 6 g/m³stp could be achieved. The gravimetric tar concentration didn’t vary between the two operation modes.

4. Effect of oxy-fuel regeneration on the process

In the Regenerator the operation mode has a big influence on the process. The higher CO₂ partial pressure in the oxy-fuel regeneration mode increases the necessary equilibrium temperature for the calcination reaction. Therefore slightly higher temperatures are necessary to achieve similar calcination conditions. The following graph shows the wet CO₂ concentrations in the gasifier and Regenerator for an air regeneration mode and the corresponding oxy-fuel regeneration mode.

![Graph showing CO₂ concentrations in the Gasifier and Regenerator](image)

At temperatures of about 660 °C, the (wet) CO₂ concentration in the Gasifier was about 2.5 vol-% which is close to the chemical equilibrium. Therefore a nearly ideal CO₂ capture was achieved in the Gasifier. But due to the high H₂O concentrations of about 50 vol-%, the dry CO₂ concentration was much higher (about 5 vol-%dry). The good CO₂ capture efficiency can be explained by the good gas-solid contact in the fluidised bed and the high H₂O concentration, which increases the CO₂ capture efficiency [31,32].

In the Regenerator the CO₂ concentration varied significantly between the two operation modes: In the air regeneration mode the (wet) CO₂ concentration was about 41 vol-% at a H₂O concentration of about 14 vol-% (dry CO₂ concentration: 47 vol-%dry). In the oxy-fuel regeneration mode the (wet) CO₂ concentration was 64 vol-% at a H₂O concentration of about 30 vol-% (dry CO₂ concentration: 91 vol-%dry).

This CO₂ partial pressure difference of about 17 kPa has to be taken into account when operating the Regenerator. To achieve the similar calcination conditions, higher temperatures in oxy-fuel mode are necessary.

Additionally to the calcination behaviour, the oxy-fuel operation mode has also an influence on the formation of pollutants in the flue gas of the Regenerator. The most critical flue gas components are CO, NOₓ and SOₓ emissions. There are no detailed emission regulations about DFB steam gasification plants, but based on the German emission limits for conventional power plants with a capacity of <50MWth (TA Luft), the NOₓ emissions have to be below 600 mg/m³STP,6%O₂ [33,34]. Due to limitations in the fuel availability, this kind of biomass gasification plant would have probably in most cases a thermal capacity of between 5 and 50 MWth therefore, in Germany the NOₓ emission
limits would be 600 mg/m³STP, 6% O₂. Generally the limestone bed material increased the production of NOₓ emissions and decreases the N₂O emissions due to the catalytic effect of the bed material [35,36].

![Fig. 9. NOₓ emissions and formation in Air and Oxy Regeneration*](image)

*The experiments in Figure 9 were done with an oxy-fuel combustion in the Regeneration, therefore a calculation of the NOₓ emissions on a basis of 6% oxygen is not possible.

There were no significant SO₂ emissions in the flue gas stream due to the limestone bed material, which acts as a SO₂ sorbent [37]. In the experiments the SO₂ emissions were below 3ppmv.

In the air regeneration experiments the NOₓ emissions were slightly below the emission limits of 600 mg/m³STP at an air ratio of 1.2. Due to the lack of air nitrogen (which “dilutes” the NOₓ concentration in the flue gas) the volumetric NOₓ emissions were much higher in the oxy-fuel regeneration mode. But when calculating the NOₓ formation in mg/MJ (which is proportional to the fuel-N conversion rate), the results show the opposite trend. In the oxy-fuel mode the NOₓ formation rate was slightly lower than in the air combustion mode. This corresponds with the results of Hofbauer et al. [38]. Both experiments were done with an inlet oxygen concentration of 40 vol-%dry.

5. Conclusion and Outlook

The experiments have shown stable oxy-fuel combustion and sorbent regeneration conditions over a period of several hours, achieving CO₂ concentration of >90 vol-%dry. The operation mode (air or oxy-fuel) of the Regenerator has little influence on the Gasifier. Gas yield, gas composition and tar concentration showed a similar trend for the different operation modes. In the Gasifier, hydrogen concentrations up to 70 vol-%dry and CO₂ concentrations of less than 7 vol-%dry where achieved with a stoichiometry suitable composition for methanation processes. As a consequence of the tar cracking effect of the CaO based bed material, the gravimetric tar concentration was below 6 g/m³stp. Due to the nitrogen and sulphur lean fuel the NOₓ formation in the Regenerator wasn’t significantly different in oxy-fuel regeneration mode than in air regeneration mode.

Therefore the Oxy-SER process shows a high potential as a possible CCS process, which should be further investigated. Currently a model for this process is created to calculate the overall process efficiency and to estimate the energetic costs for the oxygen creation in an ASU and the compression and purification of the CO₂ for transport and storage. The results of this study will be published in near future.
Acknowledgements

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