Dual fluidized bed based technologies for carbon dioxide reduction

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Abstract

The dual fluidized bed technology offers a broad range of applications for the utilization of CO_2 neutral energy carriers like biomass. This work provides an overview about dual fluidized bed technologies, which could contribute to a more sustainable future. The conventional biomass steam gasification is an already well-known technology. However, an advanced reactor design enables several further processes. These processes could be appropriate for a general CO_2 reduction in the atmosphere.

Based on this technology the **sorption enhanced reforming process (SER)** was developed and enables the in-situ removal of CO_2 from the product gas. Consequently, the chemical equilibrium of the product gas is shifted and a high H_2 content can be obtained in the product gas. Another variation of the DFB process is the **gasification with CO_2** instead of steam as gasification agent. This enables the utilization of a CO_2 stream and the production of a product gas with high carbon content from biomass. Last but not least, a DFB reactor system can also be used for the so-called **chemical looping combustion** process of biomass **(BioCLC)**, which has enormous potential for capturing CO_2 due to its low energy demand. The principle is based on the use of a metal oxide as bed material and oxygen carrier. This oxygen carrier is used to burn the gas, which is produced by the gasification reactions of the biomass with steam.

1. Introduction:

In the last decades, fossil energy carriers were established as the main energy source in industrialized countries and all over the world. Decreasing fossil resources and climate change lead to a demand of innovative technologies for decreasing the share of fossil energy carriers.

The dual fluidized bed technology offers a broad range of applications for the utilization of CO_2 neutral energy carriers like biomass. This work provides a review about technologies which are suitable to contribute to a CO_2- neutral future.

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Based on this technology the **sorption enhanced reforming process (SER)** was developed and enables the in-situ removal of CO_2 from the product gas. Consequently, the chemical equilibrium of the product gas is shifted and a high H_2 content can be obtained in the product gas. By applying oxyfuel combustion in the combustion reactor (OxySER), an almost pure CO_2 – stream can be obtained [1]. Thus, both gas streams can contribute to a CO_2 reduction in the atmosphere: On the one hand, a H_2 rich product gas is produced, which can be used directly as a reducing agent in steel industry or as basis for synthesis processes like methanation. On the other hand, a pure CO_2 stream is produced, which either can be stored or, again, used for synthesis processes like methanation. A scheme of the process can be found in Figure 1.

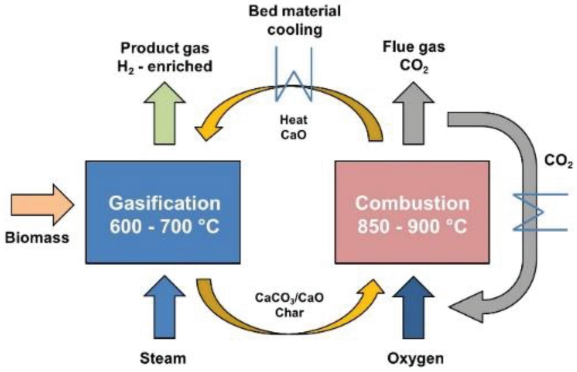

Fig. 1: Sorption enhanced reforming with oxyfuel combustion (OxySER)

Another variation of the DFB process is the **gasification with CO_2** instead of steam (Figure 2). This enables the production of a product gas with a high carbon content from biomass. This seems to be contradictory, since decarbonization is the overall aim of energy intensive industries. Nevertheless, CO_2 is an unavoidable component in many processes and could be used in this way to produce a product gas as basis for synthesis processes with high carbon demand, such as the Dimethyl ether (DME) synthesis.

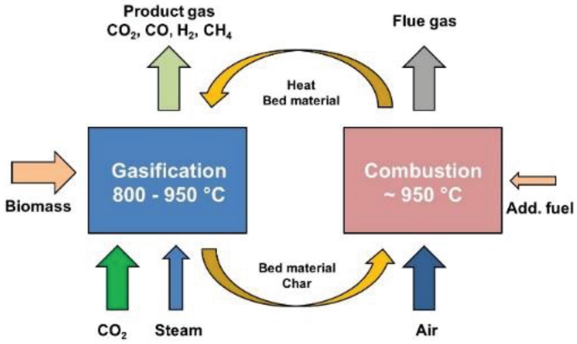

Fig. 2: CO_2/steam gasification within a DFB reactor system

Last but not least, a DFB reactor system can also be used for the so-called **chemical looping combustion of solid biogenic fuels (BioCLC)** process, which has enormous potential for capturing CO_2 due to its low energy demand. The principle of the chemical looping process is shown in Figure 3 and is based on the use of a metal oxide as bed material and oxygen carrier. This oxygen carrier is used to burn the gas, which is produced by the gasification reactions of the biomass with steam. The oxygen carrier itself is oxidized in the air reactor again. This procedure allows for the production of a N_2-free flue gas.

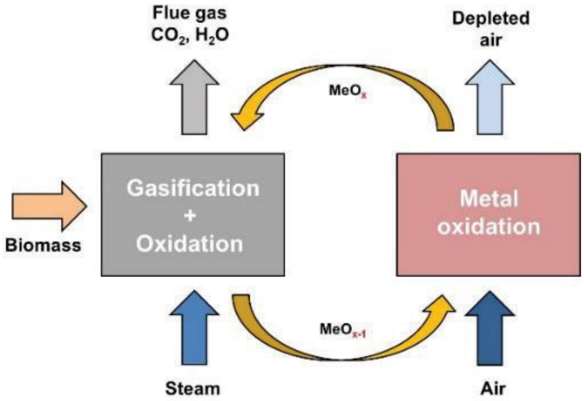

Fig. 3: Chemical looping combustion of solid biogenic fuels within a DFB reactor system

2. Concept and methodology:

Several experimental campaigns have been conducted with the advanced $100\ kW_{th}$ pilot plant at TU Wien to investigate different technologies (OxySER, CO_2 gasification and BioCLC). The pilot plant consists of two reactors (gasification reactor and combustion reactor) with an overall height of about 7 m. More details about the reactor-design can be found in Figure 4 and Figure 5 and were described by Benedikt et al. [2] The pilot plant facility including a fuel supply equipment, a control room and equipment for gas cooling, cleaning and measurement, covers two floors of around 35 m^2.

During a test run, the pilot plant is controlled througha programmable logic controller (PLC). The PLC continuously measures and records data of all relevant flow rates, temperatures, pressures as well as the main gas composition of the product gas (H_2, CO, CO_2, CH_4) with a Rosemount

NGA 2000 measurement device. Additionally, C_2H_4 and other higher hydrocarbons are analyzed every 12 min by a gas chromatograph (Perkin Elmer ARNEL - Clarus 500). For analyzing the tar content in the product gas, a standardized arrangement of sampling equipment is used. Single tar components are measured by gas chromatography coupled with mass spectrometry (GCMS). For tar measurements at the advanced pilot plant, toluene is used as solvent instead of isopropanol, because the solubility for tar in toluene is higher and the water content in the gas can be measured continuously.

The advanced 100 kW_{th} pilot plant, which is in operation since 2014, is equipped with an enhanced gasification reactor system, which increases the product gas quality significantly. Therefore, an upper gasification reactor with geometrical constrictions leads to an increased hold-up of hot bed material particles and increases the contact time between product gas and hot bed material particles.

Fig. 4: Picture of the control room, 2nd floor and 1st floor of the advanced 100 kW$_{th}$ pilot plant

The enhanced gas-solid contact in these turbulent fluidized zones promotes tar cracking and reforming reactions by the use of a catalytic bed material. Thus, the conversion efficiency is increased. Further, the advanced reactor system allows for the usage of different fuels, bed materials and gasification agents.

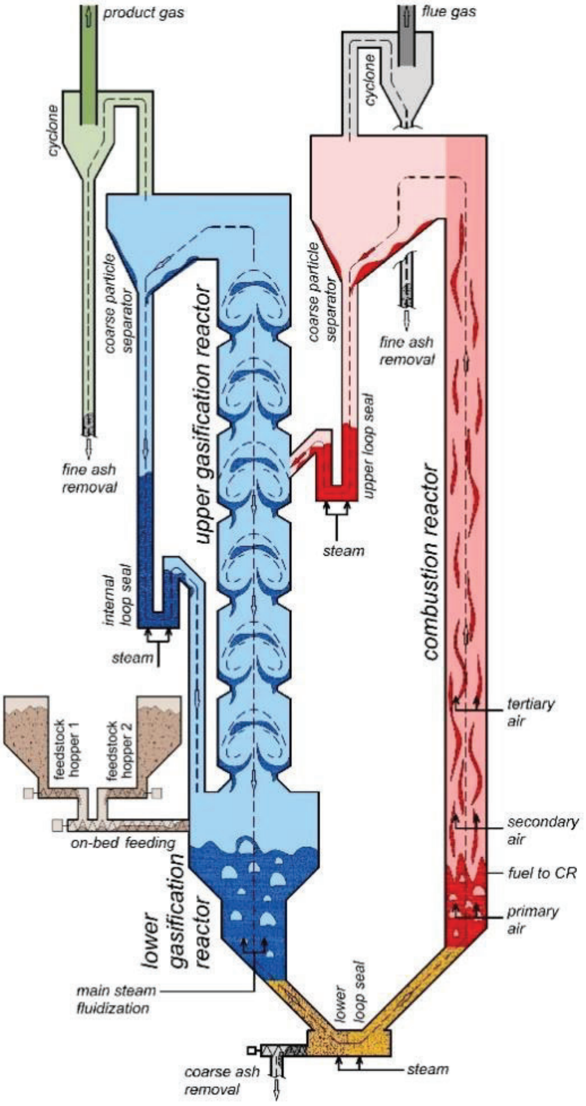

Fig. 5: Scheme of the advanced 100 kW$_{th}$ pilot plant

3. Results and discussion

SER/OxySER

Since hydrogen is regarded as a promising future energy carrier, the SER process aims for the production of a hydrogen rich product gas. On the other hand, carbon is sequestrated in-situ from the gasification process and could be further utilized.

For the SER process the bed material additionally acts as a selective sorbent for CO_2 (Equation 1) when keeping temperatures between 600 and 700 °C in the gasification reactor and temperatures above 830 °C in the combustion reactor (reverse of Equation 1). Typically a calcium based sorbent (limestone, dolomite) is used. Thus, the composition of the product gas is developed towards high H_2 contents and low CO_2 and CO contents. The reason for the strong shift in the product gas composition can be traced back to the water-gas-shift reaction (Equation 2), which is one of the most important reactions in the gasification reactor. A scheme of the principle can be found in Figure 1.

$$CaO + CO_2 \rightarrow CaCO_3 \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (2)$$

Research on the dependency of the product gas composition on gasification temperature showed, that the highest H_2 content can be reached from 600 °C to 700 °C. The course of the product gas composition up to 800 °C can be found in Figure 5 [3]–[7].

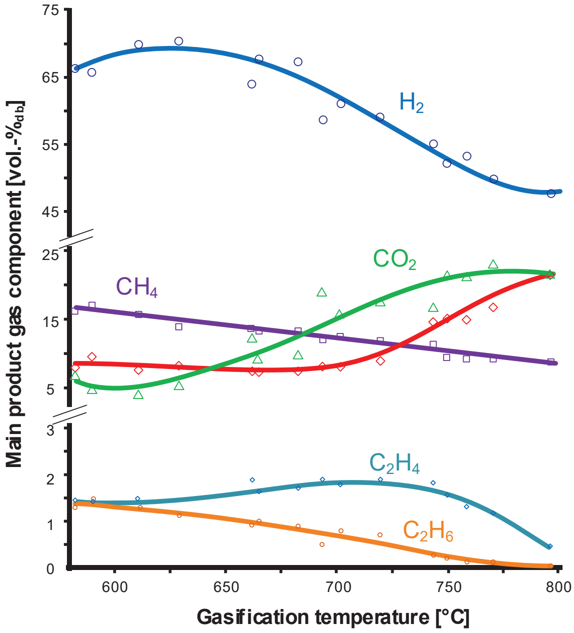

Fig. 5: Dependency of the SER/OxySER process on temperature

Since the gasification temperature influences the CO_2 sorption of the bed material on the one hand, but also the char formation from gasification on the other hand, the carbon balance can be influenced significantly (Figure 6). It can be found, that up to 80% of the total carbon in the fuel can be removed from the gasification reactor and transported to the combustion reactor via char and CO_2 in the bed material ($CaCO_3$). By applying oxyfuel-combustion in the combustion reactor, a pure CO_2 stream could be obtained and used as raw material for the chemical industry.

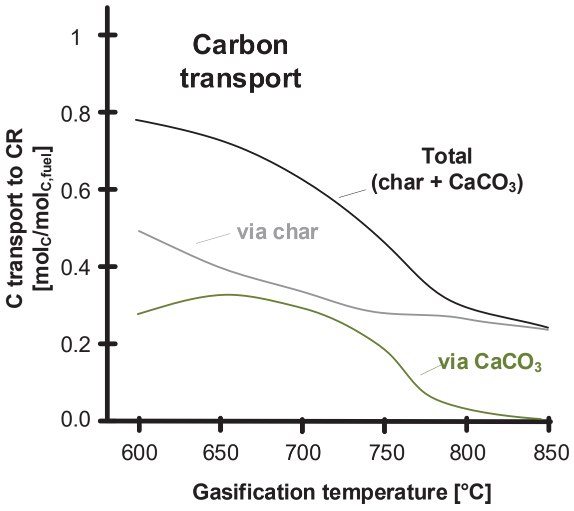

Fig. 6: Dependency of the carbon balance of the SER/OxySER process on temperature

However, the bed material cycle rate in the DFB system was identified as a second influencing factor on the product gas composition [8]. This behavior can be traced back to the change of the residence time of the bed material in the reactors. Recent investigations showed, that the calcination reaction is the limiting factor within the advanced 100 kW_{th} pilot plant.

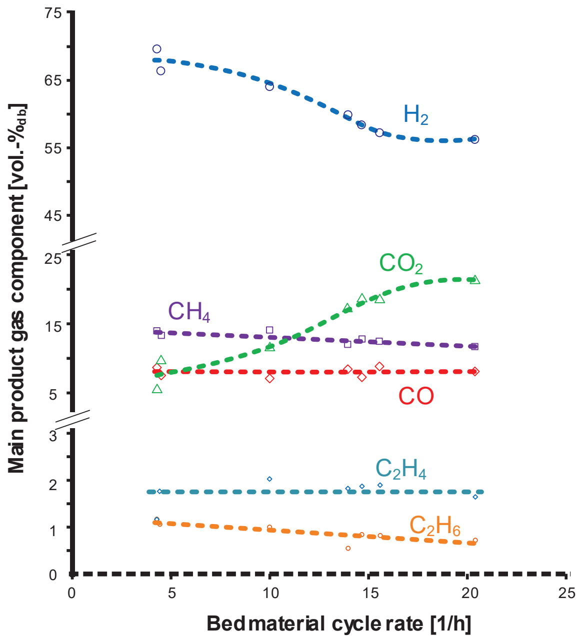

Fig. 7: Dependency of the SER/OxySER process on bed material cycle rate

CO_2 gasification

An option to reduce CO_2 emissions could be the sequestration of CO_2 from different industrial processes and its utilization again for the dual fluidized bed gasification technology. Thus, experimental campaigns [9] regarding CO_2 as gasification agent (together with steam or pure) have been conducted in the advanced 100 kW_{th} pilot plant.

Through the gasification of biomass with CO_2 as gasification agent, a CO-rich product gas could be generated, which could further be processed to valuable synthetic fuels. By increasing the CO_2 content in the gasification agent while decreasing the steam content leads to an increased CO and CO_2 content in the product gas, while the H_2 content is decreasing (Figure 8). This product gas composition was recorded at a gasification temperature around 825 °C.

Further, the process is strongly dependent on gasification temperature (Figure 9). Higher temperatures tend to push the Boudouard reaction (Equation 3) further towards its products CO.

$$C + CO_2 \leftrightarrow 2\,CO \qquad (3)$$

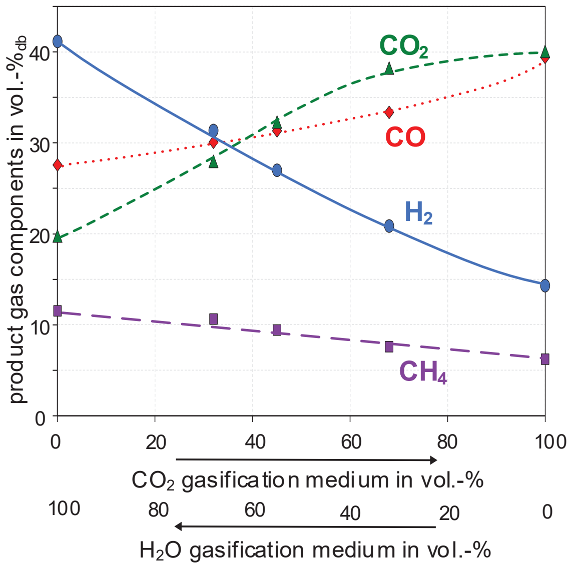

Fig. 8: Dependency of the CO_2 gasification process on gasification agent [9]

Therefore, a higher CO content can be produced with higher gasification temperatures.

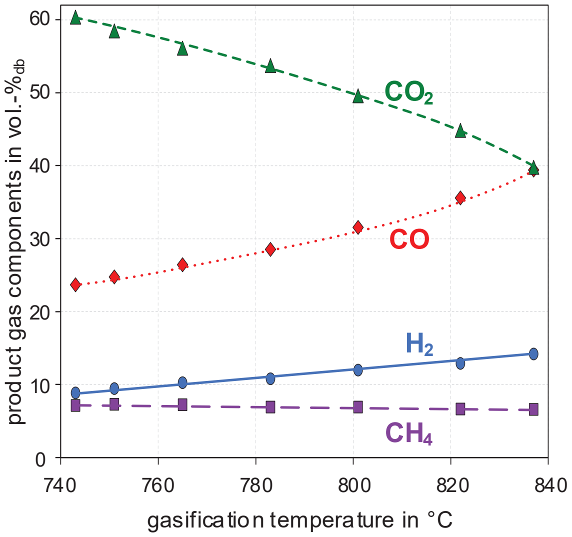

Fig. 9: Dependency of the CO_2 gasification process on temperature

BioCLC

Another process realized using the dual fluidized bed gasification technology is chemical looping combustion of solid biomass [10]. In addition to the steam gasification in the gasification reactor, an in-situ combustion of the produced gas takes place via the bed material, which serves as oxygen carrier (see also principle in Figure 3). Thus, a nearly nitrogen-free flue gas from the gasification reactor (Figure 10) and an oxygen depleted air stream from the combustion reactor are obtained. The bed material (and oxygen carrier) used in such a system could be metal oxides of iron, manganese or copper.

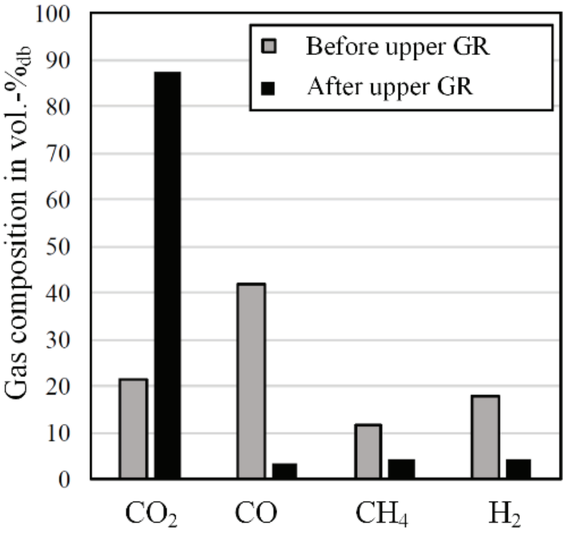

Fig. 10: Flue gas composition of the BioCLC process with ilmenite as oxygen carrier [10]

In contrast to gasification processes, a high CO_2 content in the case of BioCLC means high fuel conversion. Figure 10 shows, that the advanced reactor design leads to a significant improvement of the fuel conversion: The CO_2 content is low before the upper gasification reactor, whereas nearly 90 vol.-%$_{db}$ can be reached after the upper gasification reactor. The improvement of the process can also be seen from the temperature profile in the reactors (Figure 11): The highest temperature can be found in the upper gasification reactor. Thus, heat is released through oxidation of the gas produced from steam gasification via the oxygen carrier (bed material).

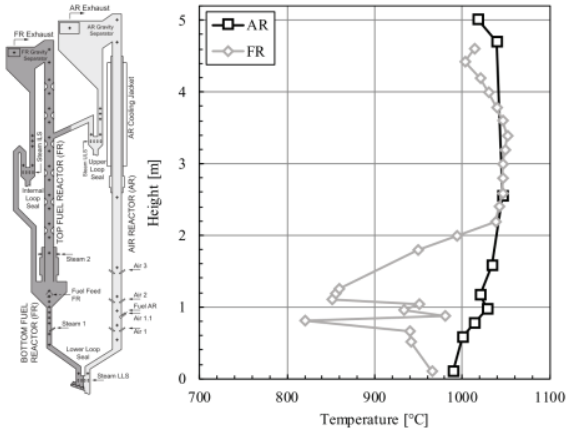

Fig. 11: Temperature profile of the gasification reactor (fuel reactor) and combustion reactor (air reactor) [10]

4. Discussion

Three very different dual fluidized bed technologies are introduced in this work. However, Table 1 provides and overview about different parameters of these processes. Typically, the gasification processes OxySER and CO_2 gasification produce a product gas which contains chemical energy, whereas the CLC process as a typical combustion process provides heat.

Especially the OxySER process offers advantages, but also disadvantages. On the one hand a H_2 rich product gas is produced, on the other hand carbon from renewable sources (biomass) is sequestrated. Since biomass is the only renewable carbon source, the OxySER concept must be implemented wisely. This means the integration in an environment where H_2 on the one hand, but pure CO_2 on the other hand is needed.

Table 1: Comparison of presented processes regarding different parameters

	OxySER	**CO_2 gasification**	**BioCLC**
Product	Chemical Energy + CO_2 + Heat	Chemical Energy + Heat	Heat + CO_2
Technical readiness	Pilot scale / test run on industrial scale for SER [11]	Pilot scale	Pilot scale
Advantages	Product gas with high H_2 content and pure CO_2 for further utilization	Potential of CO_2 utilization as gasification agent	Pure CO_2 for further utilization
Disadvantages	Air separation unit necessary, purity of CO_2	Low CO_2 conversion expected	No chemical energy

5. Conclusion and Outlook

The dual fluidized bed technology, which was originally invented for the steam gasification of biomass, is also suitable for various other processes. Especially the advanced reactor design enables several further processes. These processes could be appropriate for a general CO_2 reduction in the atmosphere, by using biogenic fuels and producing a pure CO_2 stream, which could be further utilized in industry (OxySER and BioCLC) or using a CO_2 stream as gasification agent (CO_2 gasification).

6. References

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