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Application of the MP-PIC Method for Modelling a Novel Plant Design for Biomass Chemical Looping Gasification

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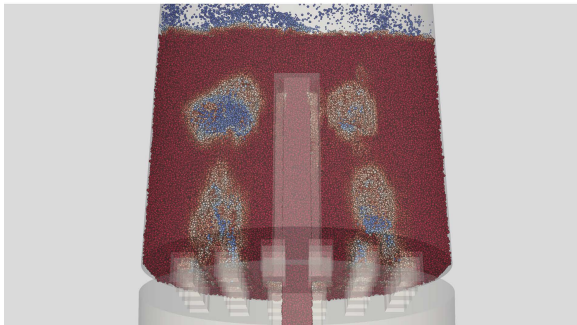
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Introduction

Climate change is one of the most significant and urgent challenges of this century causing global warming, melting polar ice caps and warmer oceans, for instance. One of the reasons for the man-made climate change is the emission of greenhouse gases such as carbon dioxide (CO₂) and methane (CH₄) to the atmosphere (Vijayavenkataraman et al., 2012). The vast majority of the CO₂ emissions (being the primary greenhouse gas) is related to the cement production and the combustion of conventional fossil fuels (Jackson et al., 2018; Nguyen et al., 2021). Due to this, renewable energies became more and more attractive in the recent years. However, promising technologies are necessary for the utilization of renewable energies. The conversion of biomass by fluidized bed gasification is one of the mentioned technologies. As product the so-called *syngas* is obtained, that is mainly composed of hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂) and methane (CH₄). This versatile product can be used for the generation of electricity and heat or the production of hydrogen and synthetic fuels (Gómez-Barea & Leckner, 2010; Kraft et al., 2017; Sikarwar et al., 2016; Sikarwar et al., 2017). Finally, the reliance on fossil fuels can be reduced.

1.1 Fluidized Bed Technology

For a better understanding of the gas-solid processes occurring in fluidized bed gasification of biomass the relevant principles of fluidized bed technology for this work will be summarized in the following.

1.1.1 Fluidization Regimes

When a packed bed of particles is passed by a fluid a "fluid-like" or so-called *fluidized state* can be observed under the prerequisite that the drag forces induced by the fluid is higher than the gravitational and inertia forces of the solid particles. The fluid flow results in a constant movement of the particles leading to a high mixing degree as well as a high heat and mass transfer between both phases. The fluidized bed can be characterized depending on the interactions between the solid and the fluid phase, which are often labeled as *hydrodynamics*, referring to the flow pattern of particles and bubbles as well as their velocity and size for instance. Depending on

the fluid velocity, different flow regimes can be observed with unique flow patterns and mixing behavior of the particles (Grace et al., 2020; Kunii et al., 2013). In Fig. 1.1 the most important flow regimes of fluidized beds are shown.

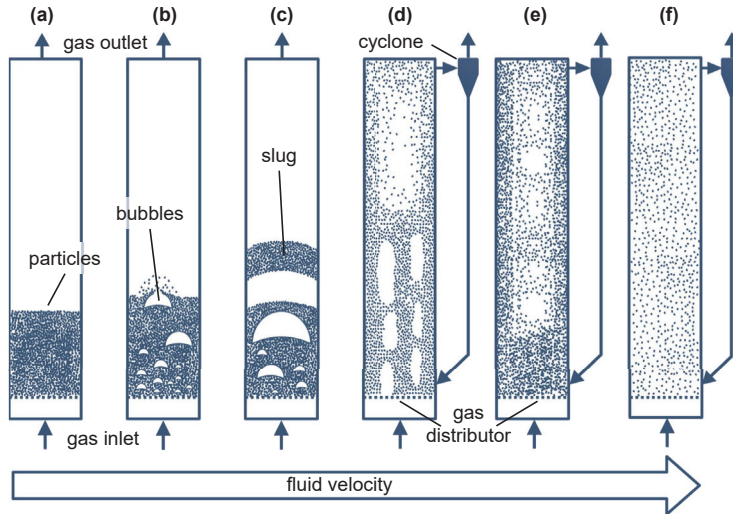


Fig. 1.1.: Flow regimes occurring in fluidized beds with increasing fluid velocity: (a) fixed bed, (b) bubbling, (c) slugging, (d) turbulent, (e) fast fluidization and (f) pneumatic conveying as proposed by Kunii et al. (2013).

In a fixed bed (a) the drag force of the fluid is too low to move the particles. With increasing fluid velocity the drag increases and the particles start to move, which is referred as the state of minimum fluidization at the so-called *minimum fluidization velocity*. With the formation of bubbles (b) an expansion of the bed can be observed due to the increase of the bed porosity. The formation of bubbles also leads to the high mixing between the fluid and solid phase including the already mentioned high heat and mass transfer. With increasing fluid velocity and distance from the gas distributor the bubble size increases due to the coalescence of bubbles. Depending on the bed size and height a slugging bed (c) can be observed resulting from bubbles in the size of the fluidized bed diameter. When the fluid velocity is further increased particles start to get elutriated by the fluid flow at the so-called *elutriation velocity* and the turbulent regime (d) is observed. In contrast to a bubbling fluidized bed a defined bed surface cannot be clearly determined. Particles are moving in the fluidized bed as streams or clusters and falling down near the reactor wall. Due to the particle entrainment a recirculation of solids using a cyclone for instance is necessary for a continuous operation. Finally, the fast fluidization regime (e) and the pneumatic conveying (f) are obtained with fluid velocities beyond the elutriation

velocity leading to significant particle entrainment. A dilute zone is observed for the fast fluidization regime in the bed center, where the particles are carried upwards, and a higher solids concentration is present at the reactor walls, where the particles are descending. This flow structure is referred to as *core-annulus flow* (Basu, 2015; Grace et al., 2020; Kunii et al., 2013). This work focuses on fluidized beds in the bubbling and turbulent regime due to the operation regimes of the investigated reactors, which will be discussed in Sect. 1.2.2.

1.1.2 Lateral Bubble Distribution

In a bubbling fluidized bed the lateral distribution of bubbles is not homogeneous as observed by Werther and Molerus (1973). At the bottom of the fluidized bed (close to the gas distributor) more bubbles are found in the near of the reactor wall compared to the center of the bed. Bubbles tend to coalesce with increasing bed height in the center of the fluidized bed resulting in regions with a lower bubble concentration at the reactor walls. This is mainly due to the limited degree of freedom of the bubbles at the reactor walls, which are forced to move to the center during the rise in the fluidized bed. Furthermore, the aspect ratio of the fluidized bed (i.e. the bed height divided by the bed diameter) influences the flow structure and flow paths as illustrated in Fig. 1.2.

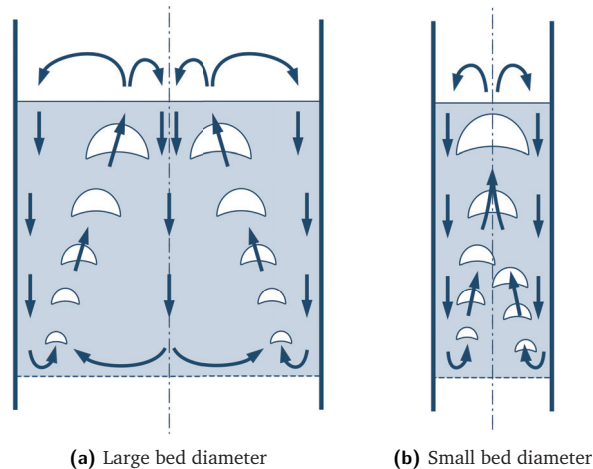


Fig. 1.2.: Bubble distribution and solid flow paths indicated by arrows for fluidized beds with (a) low and (b) high aspect ratios according to Werther and Molerus (1973).

In fluidized beds with a low aspect ratio (a) at least two circulation cells are formed, while for fluidized beds with a high aspect ratio (b) a stream of bubbles can be formed in the center of the bed. The fluid velocity and the coalescence behavior

of the bubbles influence the flow structure as well (Lim et al., 2007; Werther & Molerus, 1973).

1.1.3 Geldart's Particle Classification

The fluidization behavior is significantly influenced by particle properties such as size and density. Therefore, a particle classification based on these two quantities was introduced by Geldart (1973). Molerus (1982) refined this classification by defining the boundaries between the different groups based on force balances. The four different groups (A, B, C and D) are categorized according to their fluidization behavior and can be illustrated in a diagram, where the difference between the particle density ρ_s and the fluid density ρ_f is plotted over the particle diameter d_p , as given in Fig. 1.3.

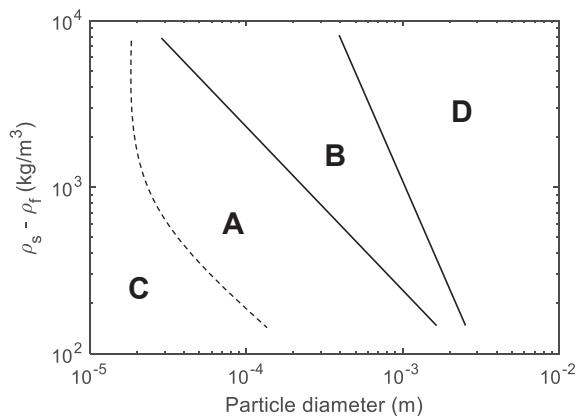


Fig. 1.3.: Particle classification according to Geldart (1973).

- Cohesive and very fine powders with particles diameters of a few μm that are difficult to fluidize are classified to **Geldart's group C**. The fluidization tends to channeling due to the strong inter-particle cohesive forces that also result in the formation of agglomerates.
- Particles of **Geldart's group A** show densities below 1400 kg m^{-3} and a small particle diameter. At the minimum fluidization velocity the bed significantly expands before bubbling fluidization is achieved. The speed of the rising bubble is higher than the superficial gas velocity and the bubble size reaches an equilibrium between bubble growth and break-up with sufficient bed height.

- In comparison to group A, the particles classified to **Geldart's group B** have higher densities and larger diameters. In contrast to group A, a bubbling fluidized state can be observed at minimum fluidization velocity and the bubble size is only limited by the reactor diameter eventually leading to slugging. Furthermore, the bed expansion is lower compared to group A.
- **Geldart's group D** particles have the highest density and diameter compared to the other groups. These particles are preferably fluidized in a spouted bed as they tend to form spoutes. In contrast to group A and B the bubbles rise slower than the fluidizing gas.

The border between group C and A was determined experimentally by Geldart (1973), while the borders between group A and B as well as B and D are given by Eqs. (1.1) and (1.2).

$$(\rho_s - \rho_f) d_p = 225 \quad (1.1)$$

$$(\rho_s - \rho_f) d_p^2 = 10^6 \quad (1.2)$$

1.2 Fundamentals of Biomass Gasification

In 2022, the Federal Government of Germany decided within the so-called *Osterpaket* to increase the share of renewable energies to 80 % by 2030 to reduce the dependency of fossil fuels, and by 2050, electricity has to be produced almost completely with renewable energies (Bundesministerium für Umwelt, Naturschutz, nukleare Sicherheit und Verbraucherschutz, 2016; Webseite der Bundesregierung, 2022). Biomass is one of the most promising renewable energy resources due to its abundant availability and its negative carbon emissions, if the conversion technology is combined with carbon capture and storage processes. Pyrolysis, combustion and gasification are the main thermochemical processes for biomass conversion (Nguyen et al., 2021). This work focuses on the biomass gasification in fluidized beds and the fundamentals will be described in the following.

1.2.1 Gasification of Biomass

The gasification of biomass is a thermochemical conversion process that aims at an efficient conversion of solid biomass to combustible syngas for heat and power generation or for the production of chemicals. The product gas (or syngas) is mainly composed of hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂) and methane (CH₄). However, an unconverted fraction of the solid biomass remains, which is called *char* and mainly composed of carbon and ash. The unconverted fraction depends on the process, the operating conditions and the ash content of the

biomass. The exhaust gas of the reactor can also contain undesired contaminants such as ash, char particles, lighter hydrocarbons such as propane and higher hydrocarbons, so-called *tars*. Furthermore, gases such as chloridic acid (HCl), sulphuric acid (H₂S) and nitrogen (N₂) can be present. As gasifying agent steam, air, oxygen and carbon dioxide can be applied for the gasification in a so-called *gasifier*. In contrast to biochemical conversion the thermochemical conversion shows the advantage of higher energy efficiency, faster conversion times and higher flexibility regarding the biomass feedstock (Loha et al., 2014; Molino et al., 2016; Nguyen et al., 2021; Sikarwar et al., 2016).

The gasification can be separated in three or rather four different steps: Drying, pyrolysis or devolatilization, oxidation or combustion as well as reduction or gasification. Oxidation and reduction are summarized here as one step due to lack of relevance for this work. It has to be noted that these steps do not occur separately but more or less simultaneously depending on the heating rate (Loha et al., 2014; Reschmeier, 2015). A schematic overview of the most relevant species and steps is given in Fig. 1.4 as proposed by Reschmeier (2015).

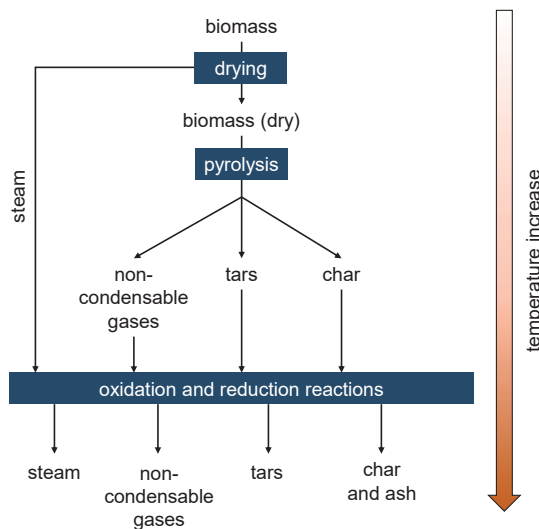


Fig. 1.4.: Schematic illustration of biomass gasification.

- The **drying** of the biomass starts at around 100 °C, where the moisture content of the biomass evaporates. At a biomass temperature of 150 °C the drying can be assumed to be completed. In the later process of the gasification reactions the generated steam can participate in different reactions. Furthermore, the

drying process can delay the heating of the biomass, which is especially noticeable for biomass with high moisture contents (Molino et al., 2016).

- The thermochemical decomposition of the biomass takes place at temperatures between 200 °C to 700 °C, which is called **pyrolysis**. Molecules with higher molecular weight are converted into molecules with lower molecular weight due to cracking of chemical bonds. This decomposition is endothermic and can take place in an inert atmosphere. The obtained fractions can be solid, liquid and gaseous. The solid fraction is called char, which makes up around 5 wt.% to 25 wt.% of the original weight, depending on the process conditions and biomass type. Around 70 wt.% to 90 wt.% of the original biomass are non-condensable gases (or permanent gases) such as hydrogen, carbon dioxide, carbon monoxide and light hydrocarbons, e.g. methane. These are often called *volatiles* due to their volatile nature. The higher hydrocarbons composed of complex organic substances called tars condensate at relatively low temperatures due to their high molecular weight, which is why they are referred as liquid fraction (Molino et al., 2016).
- Subsequent to the pyrolysis the formed products are involved in a complex set of more than a hundred different reactions which are summarized as **oxidation and reduction** reactions. The main reactions that define the resulting syngas composition are the reactions of char with carbon dioxide and steam as well as the water-gas shift reaction and the methanation. Furthermore, a thermal and chemical cracking of the tars takes place. The cracking of tars is vital for the efficiency of the gasification process, because remaining tars have to be removed from the product gas. This is due to the fact that tars can cause operational problems resulting from downstream blockage and lower quality of the resulting syngas (Marx et al., 2021; Molino et al., 2016; Sikarwar et al., 2016).

It has to be noted, that the term *pyrolysis* is often used to name the process of solid fuel conversion without oxygen. Therefore, in this work the term *devolatilization* will be used for this step of the gasification process.

1.2.2 Chemical Looping Gasification

The fluidized bed gasification is a promising technology for biomass conversion, which is mainly due to the high heat and mass transfer, including good mixing properties. Furthermore, the process is suitable for scale-up. The application of the chemical looping principle which will be explained in this section allows a further

reduction of costs as well as emissions compared to similar gasification processes (Condori et al., 2021).

Similar to the *chemical looping combustion* (CLC), an oxygen carrier (OC) is applied in the *biomass chemical looping gasification* (BCLG) process. The OC circulates between two inter-connected reactors, which is illustrated in Fig. 1.5 as proposed by Ge et al. (2016).

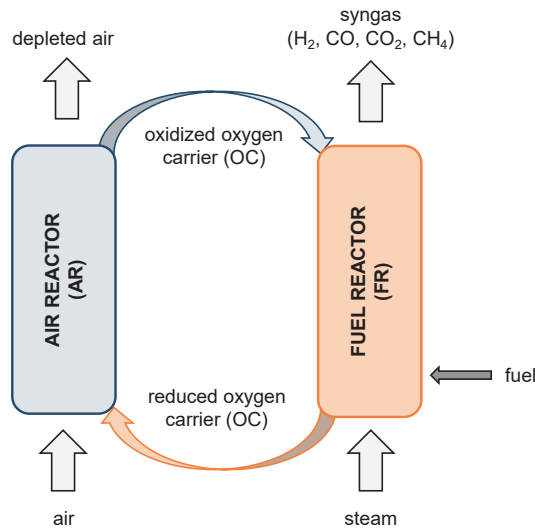


Fig. 1.5.: Schematic illustration of the chemical looping gasification (CLG) process.

In this way, the necessary oxygen for the reactions occurring in the fuel reactor and the required heat for those reactions is transported from the air reactor (AR) to the fuel reactor (FR). The air reactor is used to oxidize the oxygen carrier with oxygen from air, which is used as gasifying agent in this reactor. The air reactor is commonly operated in the turbulent fluidization regime. Due to the exothermic oxidation reaction of the oxygen carrier the necessary heat for the biomass gasification in the fuel reactor can be provided, allowing an autothermal operation of the CLG process. The oxidized oxygen carrier is then transported to the fuel reactor via a loop-seal that allows the transportation of solids, but prevents the syngas from being diluted with the depleted air containing inert nitrogen. Therefore, a higher quality syngas is produced. In the fuel reactor the oxidized oxygen carrier is reduced due to the reactions with the biomass and the reactions with the gaseous species such as hydrogen, carbon monoxide and methane as well as tars. In contrast to the air reactor, the fuel reactor is commonly operated in the bubbling fluidized bed

regime to increase the contact time of the biomass with the bed material. Finally, the reduced oxygen carrier is transported back to the air reactor via a second loop-seal. This separation of the gasification process in two different reactors allows the partial oxidation of the fuel without diluting the product gas with inert nitrogen (Condori et al., 2021; Mendiara et al., 2018; Song et al., 2012; Zhao et al., 2017).

It has to be noted that in contrast to the chemical looping combustion process, where a complete oxidation of all species in the fuel reactor is aspired, in biomass chemical looping gasification the aim is to obtain a high quality syngas with a high heating value (Condori et al., 2021; Marx et al., 2021). Therefore, a mixture of oxygen carrier and inert quartz sand can be used to minimize the oxidation of the desired products hydrogen and carbon monoxide (Ge et al., 2016). However, enough lattice oxygen has to be provided for the oxidation of char and catalytic cracking of tars. It should be mentioned that quartz sand and most oxygen carriers can be classified to Geldart's group B (see Section 1.1.3).

Operating Conditions

The optimization of the operating conditions for the biomass chemical looping gasification process is part of current research. Process parameters such as the operating temperature, the steam-to-biomass ratio, the amount of oxygen carrier and the solid circulation rate have shown to significantly influence the operation and the the syngas composition as well as the syngas yield, which will be explained in the following (Condori et al., 2021; Ge et al., 2016).

It has to be noted that up to this point only lab-scale BCLG plants have been built and the upscaling of this process is a part of ongoing research. Main reason for this is the complexity of the reactor and the lack of a sophisticated model for the process, while a high efficiency is mandatory for the economic operation of an industrial reactor. The syngas yield can be used as parameter to describe the efficiency of the process, which is defined as the ratio of the resulting syngas and the biomass fed to the system. To obtain a high syngas yield it must be ensured that the syngas has a high content of the desired components hydrogen and carbon monoxide. Furthermore, the combustion of char in the air reactor and the elutriation of char has to be prevented. Finally, the tars should be removed by thermal and catalytic cracking as far as possible to prevent costly processing of the product gas (Marx et al., 2021).

Oxygen Carrier

The choice of the oxygen carrier has one of the most significant influences on the syngas yield and composition. Therefore, Adanez et al. (2012) and Marx et al. (2021) gave several criteria for the choice of a suitable oxygen carrier for CLC as well as CLG processes and the most relevant criteria for CLG applications are summarized in the following:

- **Reactivity:** The oxygen carrier has to maintain a high reactivity over a high amount of reduction and oxidation cycles.
- **Stability:** The lower the losses due to breakage and attrition, the longer the lifespan of the oxygen carrier, which reduces the operational expenses.
- **Fluidization:** The formation of bypass streams or the formation of agglomerates should not occur.
- **Cost:** The cost for the oxygen carrier should be as low as possible, which makes naturally minerals more attractive in comparison with synthetic materials.
- **Toxicity:** Non-toxic and environmental friendly oxygen carriers are favored due to the lack for special treatments or technical requirements.
- **Availability:** The oxygen carrier has to be available for the quantity required for application at industrial scale.

Furthermore, it is desired that the oxygen carrier acts as catalyst for the cracking of tars, while the oxidation of hydrogen and carbon monoxide should be as low as possible. For that reason, Sikarwar et al. (2016) investigated different oxygen carriers in terms of a high selectivity towards the reactions with the solid. Unfortunately, synthetic materials are costly, which is why naturally occurring metal oxides are favored despite the oxidation of the desired products hydrogen and carbon monoxide (Condori et al., 2021). However, a significant influence of the catalytic cracking of tars by iron-based oxygen carriers was shown by Ge et al. (2016) and Huang et al. (2013) for instance. Furthermore, Condori et al. (2021) found very low tar contents below 2 g Nm^{-3} with the application of ilmenite as oxygen carrier, which shows the suitability of ilmenite for biomass chemical looping gasification. Additionally, the findings of Condori et al. (2021) showed that the oxygen carrier is operated in a reduced state in contrast to CLC processes.