1. Introduction

Extraordinary weather conditions are felt to happen in an ever-increasing frequency in modern times. In history one can find many exceptional climate situations, but statistically relevant changes in the commonness of those can be noticed. The research community and most parts of the political establishment agree that the emission of anthropogenic greenhouse gases is the main reason for the changing climate conditions. Greenhouse gases can be mainly traced back to the economic activities and development of humankind; these are among others generating heat and electricity by fossil fuels, transportation powered by combustion engines, agricultural activities and fertilizer use as well as land use change. The greenhouse effect describes basically that gases in the atmosphere, mainly carbon dioxide, methane, ozone and water vapor, reflect the heat, which is emitted from earth's surface. On the one hand, this effect raises the overall temperature to livable temperatures, on the other hand, an increased greenhouse effect by higher concentrations of the mentioned gases in the atmosphere can lift the surface temperature to problematic levels and is then called global warming. Today, nearly all countries on this planet, decided that they want to limit global warming to 2°C in the Paris Agreement [1].

To achieve the 2°C target, especially the industrialized countries in the EU, China, India and the US must take strong measures to reduce their emission of climate active gases [2]. Most reliable research points in a direction that the reduction of climate gases is not even enough, and Negative Emission Technologies (NETs) have to be applied on a big scale to keep the temperatures on the planet in reasonable limits [3].

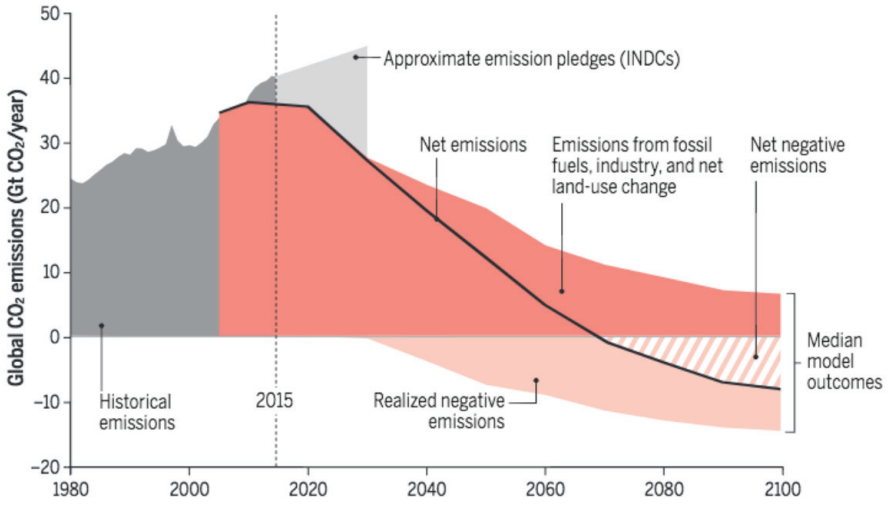

Figure 1: A standard scenario of future CO_2 emissions to keep the 2°C global warming target. [4]

For the energy sector this means that decarbonization of power production must take place. Decarbonization means that fossil fuel power plants are shut down in favor of renewable energies, like wind and solar. Heat can be generated by biomass, which is also considered mostly carbon neutral. Another approach to meet the climate goals are so called carbon

capture and storage technologies (CCS). These technologies are used to capture carbon dioxide after the combustion process with the heat release. The carbon dioxide is then compressed and stored in various possible underground formations. CCS has the main advantage that the current energy system based on big shares of fossil fuel can be modified and does not need to undergo drastic changes. A major disadvantage of CCS technologies is still the elevated cost during electricity generation compared to venting the carbon dioxide into the atmosphere. This could be solved by carbon pricing and carbon trading, in which a reasonable price for carbon dioxide emissions is set by a governmental player and companies profit strongly from reducing them. Another reason why CCS could become important in the future is its ability to allow for negative emissions. When biomass is used in a thermal power station and the exhaust gases stored instead of emitted one can create a negative balance of emissions in the atmosphere, because the biomass absorbed carbon from the atmosphere before. In this case one speaks of Bio-Energy Carbon Capture and Storage (BECCS) [5].

Currently, some encouraging developments take place in the energy sector not only in Germany. Wind power turbines become economically competitive even during low electricity stock prices. Several days a year the complete electricity demand in Germany can be met by renewables. Contrariwise, when wind or sun generation is low, the need for power generation via thermal power plants arise. This is because the capacity of storing electricity is limited not only in Germany. If carbon dioxide emissions are to be avoided, CCS technologies are an option to provide energy in times of low renewable production.

One of the most discussed CCS technologies is the Chemical Looping Combustion (CLC) process. Contrary to the regular air-fired combustion, which takes place in one combustion chamber, the CLC process is carried out in two or more interconnected reactors. Between the reactors oxygen is transported via an oxygen carrying particulate, which is called oxygen carrier (OC) [6]. By separating the air intake to the process and the oxidation of the fuel in two different reactors, a pure stream of carbon dioxide can be achieved without the usage of air separation or flue gas carbon dioxide removal. The carbon dioxide should be relatively easily made available for compression and storage. The CLC process shows some interesting features, which make it a practical object for studies on heterogeneous reaction networks, interconnected fluidized bed reactors and the multiple involved reactive solids.

In the past, besides nuclear power plants, the energy system was based on fossil fuel fired power plants running on lignite and coal, which were erected to supply mid and base load. Peak loads were handled with power plants, which were a bit more flexible in their power supply, often gas turbines, hydro dams and pumped-storage hydroelectricity. Nowadays, the fluctuations inside the energy system are growing due to the intermittent renewables and existing regulating capacities are insufficient, leading to obscure phenomena, like negative or skyrocketing electricity prices. These effects are often attributed to the renewable energy use only, but another problem inside the energy system can be found in the thermal power plants itself. They cannot arrange their power output according to the demand fast enough due restrictions in load change rates, which are due to thermal expansion of the equipment and stress of the refractory lining [7]. Operation is most efficient when the designed power is achieved and, furthermore, personal talks of the author with plant operators and plant

equipment suppliers revealed that there is limited knowledge about the operation of plants outside of the designed conditions, like shutdown and startup.

To bring renewable energies, fossil fuel fired power plants and novel thermal CCS technologies together in the future, the need for a more dynamic operation of the thermal plants arises, so that the intermittency of renewable sources can be accepted. This means that the thermal power plants will be operated often at part-load and changes in fuel load might be needed within minutes or hours. Also, shutdown and startup can be expected to happen more regularly if an energy system is achieved in which most of the electricity is provided by renewables.

For the design and implementation of flexible CCS thermal power plants, novel simulation tools could be beneficial, which can predict their operational behavior at a variety of conditions. One option for this is the widely used engineering tool of flowsheeting. In this approach, the modeling is broken down to all unit operations which constitute the entire process. To this day flowsheeting tools do not allow for dynamic analyses for complex solids processes. In this work a novel flowsheeting software tool called Dyssol is applied on a system of interconnected fluidized bed reactors used for CLC. A pilot scale and a lab scale reactor system are used to gather experimental data and reaction kinetics for an accurate flowsheet modeling of CLC.

This PhD thesis was financed and conducted within the framework of the research priority program of the German Research Foundation (DFG) SPP1679 “Dynamic Simulation of Interconnected Solids Processes”. The goal of the research program is to develop simplistic and dynamic process models for a variety of solids processes. These models shall be integrated into a novel software, which is programmed in concourse of the entire research program.

The aim of this work is the development of process models for fluidized bed reactors and their integration into the simulation software Dyssol. Further, auxiliary equipment needed to model the exemplary process of Chemical Looping Combustion must be integrated into Dyssol. With the help of the dynamic models and the software, dynamic simulations have to be carried out, which will then be compared to experimental results at the pilot plant operated at the Institute. The pilot plant will be operated in a way to make dynamic effects, like start-up, shut-down and load changes visible. As a result, a validated software tool for dynamic simulation of interconnected fluidized bed reactors should be ready, which can later be used for process optimization and control of interconnected fluidized bed reactors.

Another aim of this work is to establish a database of experimental findings of the CLC process. This is done by searching for necessary series of experiments, which deliver the validation data for the simulations.

2. State of the art

According to scientific data based on various approaches, if humankind wants to achieve the 2°C goal put out during the Paris climate conference, strategies for CCS and NETs must be implemented into our energy systems [8]. Several concepts for the capture of climate gas emissions have been proposed. One of the major issues found in applying CCS technology is the nitrogen in the ambient air. Nitrogen has a fraction of around 79 vol.% in air and will be found in similar shares in the flue gases of regular air-fired boilers. For compression and storage of CO_2 this nitrogen creates a big overhead, which increases the costs for CCS to prohibitive levels. Also, CO_2 can be stored in its supercritical state due to the volume reduction, whereas this is not possible for N_2. Therefore, the most prominent technologies, namely Pre-Combustion, Oxyfuel und Post Combustion Capture, rely on an air separation process step, which heavily decreases overall efficiency of the process.

Another option is the Chemical Looping Combustion, where the separation of oxygen and nitrogen from the air takes place via a chemical reaction of a solid material. The research on CLC has reached several milestones in the meantime. The first being the research on suitable materials for the usage as OC in the system. A plethora of natural ores, refined ores, base chemicals and synthetic materials have been investigated for the suitability in CLC systems [9]. The second aspect is the successful operation of more than 15 CLC pilot plant units for solid fuels [9]. With the knowledge about OCs and pilot plant operation, process modeling was used to propose designs for upscaling considerations of the process to industrial scales. Standard terminology and evaluation procedures for the process were proposed in work of the research groups at Chalmers University of Technology in Gothenburg, Sweden and the Instituto de Carbochimica (CSIC-ICB) in Zaragoza, Spain, which resulted in review papers and overview works [10–13]. Song and Shen [14] reviewed most reactor concepts used in CLC.

In the present chapter, a process description is given in concourse with a definition of the main evaluation criteria for CLC. Afterwards, recent developments of the pilot plant operations in the years 2012-2018 are shown and concluded. This is because the two previous PhD theses by Thon [15] and Kramp [16] at Hamburg University of Technology (TUHH) were summarizing the field until 2012. This helps to discuss findings at the own pilot plant operation in Hamburg. Afterwards the status of process simulations for CLC is recapped to lead over to the own simulation work.

2.1. Fundamentals and modeling of fluidized bed reactors

The first CLC pilot operation was carried out in a system of interconnected fluidized bed reactors [6]. Since then most of the installed pilot plants were based on this technology. Two other reactor types have been reported, namely a moving bed reactor [17,18] and a rotating reactor [19], but they play a minor role in CLC research.

A fluidized bed is formed when an upwards directed flow through a particle bed exerts a force on the particles, which lifts them up and starts a movement of the particles. Depending on the shape and density of the particles and the porosity of the bulk as well as properties of the fluid

used to fluidize, a certain velocity of the fluid is needed to enable fluidization, the so-called minimum fluidization velocity u_{mf}. If the reactor superficial velocity u_R is above this velocity, sand-like or aeratable solids will form a fluidized bed. This was categorized early by Geldart, who investigated powders with different particle size distributions and densities for their fluidization behavior [20].

Depending on the operating superficial velocity u_R, different fluidization states of the particle bed can be achieved. Above $u_{mf,}$ particles will be put into motion and a bubbling fluidized bed (BFB will form, meaning that from the gas distributor bubbles will rise to the surface of bed. If the velocity is strongly increased, more and more particles will be entrained with the gas flow and no clear bed surface is visible anymore. At these conditions, a large mass flow of particles is moved out of the fluidized bed to a cyclone, where it is separated and led back to the lower part of the fluidized bed. This operation mode is called circulating fluidized bed (CFB), which shows other fluid mechanic structures than the bubbling bed, for example strands and clusters.

If the velocity is further increased, the exerted force on the particles is so high that they are directly lifted to the exit of the reactor. This setup is then called an entrained flow reactor, which is based on the pneumatic transport of all inserted particles. Distinctive operation states of fluidized beds are shown in Figure 2.

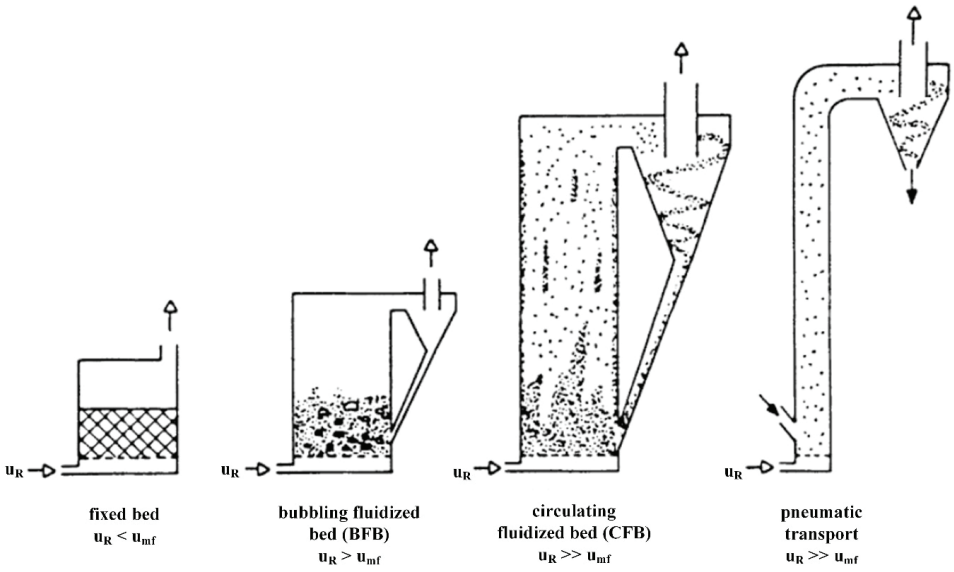

Figure 2: Fluidized bed operation states depending on the reactor superficial velocity; translated from Wirth [21].

The fluidized bed reactor concept was applied to a variety of processes within chemical and energy engineering. Major processes carried out are for example biomass and waste combustion, drying, fluid-catalytic cracking, agglomeration and coating. This is due to several advantages, which the fluidization of particles establishes. Those are for example the easy handling of solids material and the intense mixing of gases and solids. Further, in a fluidized

bed a uniform temperature distribution can be achieved due to the large solid holdup combined with resolute movement of solids. During operation, high heat transfer coefficients between gas and particles as well as bed and internals and walls can be found compared to other reactor concepts. Altogether, this leads to a uniform product quality if the process is carried out properly.

Some disadvantages are usually connected with the usage of fluidized beds. The first one is the possibility for bed agglomeration and a subsequent defluidization of the particle bed. This can be caused for example by ashes during coal combustion, which have a relatively low melting temperature and then can form agglomerates with the bed material. Another aspect to mention is the scale-up from laboratory scale to industrial scale units, because small and local phenomena, like wall effects, can have tremendous effects on fluid mechanics. Further, the fluidization gas elutriates particles, which must be separated by cyclones or filters from the exhaust gases. Especially at high temperatures, the erosion induced by the particle flows can cause problems and the need for continuous maintenance. As a last disadvantage, it can be observed that the used particles have a broad residence time distribution meaning that for example with coal combustion some coal particles can leave the reactor unconverted.

The complex flow structure inside fluidized beds was the object of major research dedicated to describing and predicting the operation of fluidized beds. According to Werther et al. [22], CFBs are simulated on different length and timescales. For example, the Navier-Stokes equations are used in Computational Fluid Dynamics (CFD) code to resolve even the smallest scales of particle-gas suspensions on a 2- or 3-dimensional grid. Until now, CFD calculations of multiphase flows need considerable computational time to calculate only a small timeframe of several tens of seconds of operation.

In contrast to that, mathematical process simulation tools, like flowsheeting, are used to quickly estimate the macroscopic effects taking place in individual units of a complex process. Mathematical modeling can be based on black-box models, which simply solve mass and energy balances according to empirical or semi-empirical model equations or simple reactor models. These black box models can be enhanced with information about fluid dynamics of solids and gases as well as heat and mass transfer considerations to be able to describe the activity inside the process units more accurately. One approach to describe the hydrodynamics in fluidized bed reactors is 1-D modeling, which was used by numerous researchers summarized in Table 1. In this approach, the solids concentration of CFBs and BFBs is determined along the reactor height. Empirical and semi-empirical correlations extracted from a variety of operation conditions and fluidized bed geometries are available in literature. Further, main flow structures like bubbles were investigated and size correlations derived. In this work such empirical and semi-empirical models were used for the characterization of the fluidized behavior.

Modeling of bubbling bed reactors usually is based on a two zones approach, dividing the reactor volume in a dense lower zone and a dilute upper zone. The dense zone is characterized by the presences of a bubble and a suspension phase, which comprises a two-phase model. Sometimes a so-called wake phase with a lower solids concentration around the bubbles is included in the modeling. As explained above the bubbling bed will form a distinguishable

surface, whose height can be determined by an overflow weir or a standpipe. Above that dense phase, a fraction of particles is entrained by the gas flow. Figure 3 shows an idealized bubbling fluidized bed with the bubble and suspension phase as well as the declining number of entrained particles above the dense bed. On the other side of the Figure, typical results of 1-D modeling are shown, which can be seen for example in Abad et al. [23] and Puettmann et al. [24]. This approach can be seen as the state of the art for the mathematical process modeling of bubbling fluidized beds. Differences between various models lie in different correlations, which are for example used for the bubble size development, the bubble rise velocity and the entrainment from the dense bed. These basic concepts can for example be found in the book "Fluidization Engineering" by Kunii and Levenspiel [25] or in the Handbook of Fluidization and Fluid-Particle Systems edited Yang [26].

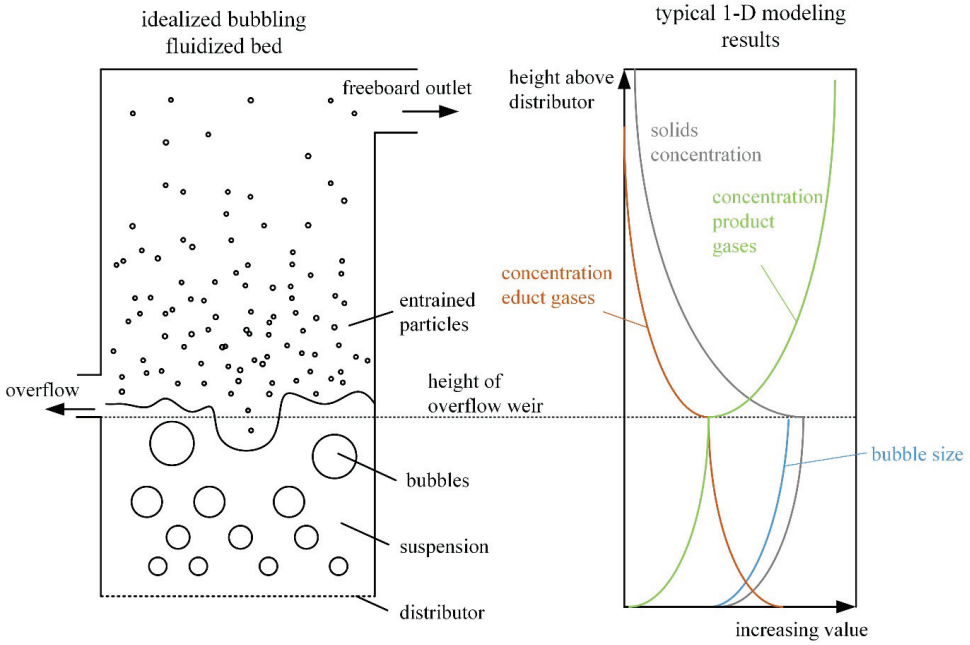

Figure 3: Idealized visualization of a bubbling fluidized bed and typical outcome of 1-D modeling of bubbling fluidized beds.

The flow structure and the physical phenomena in CFB riser reactors differ from what was seen in bubbling beds. Even though several researchers found a dense bed at the bottom of their riser reactor, the solids concentration there is typically only a fraction of the one seen in bubbling beds. This is due to the presence of different meso structures, like strands and clusters, in CFB risers, which are more solid lean. On the other hand, towards the top of the reactor, usually one can find higher solids concentrations than the ones seen in bubbling beds, due to the higher drag force, which is induced on the entrained particles. Furthermore, there is a radial gradient of solids concentration in CFB risers, which is traced back to the presence of a core-annulus flow structure. In the core of the reactor, particles are pneumatically transported upwards at high velocities. In an annulus close to the wall, the upwards velocity becomes much smaller or even negative and, with it, the particles are transported downwards

there. These flow phenomena were investigated broadly by a series of researchers, which investigated the axial 1-D distribution of solids in CFB risers, the size of the core-annulus flow, or even the radial distribution of solids at certain reactor heights. Major findings are summarized in Table 1 and arranged according to their investigation aim.

Table 1: Modeling of CFB riser reactors. Axial 1-D modeling, annulus size determination and radial resolution of solids position in reactors.

researcher	approach/ focus	description/governing equations	ref.
Li and Kwauk (1980)	1-D	Porosity calculated from known porosity of lower bed and at the end of the riser. Knowledge about inflection point needed to plot porosity profile. $\ln\frac{\varepsilon-\epsilon_a}{\varepsilon^*-\varepsilon} = -\frac{1}{z_o}(z - z_i)$ zi = position of inflection point ε* = porosity lower bed ε_a = porosity riser exit Z_0 = characteristic length of fast fluidization	In book: [27]
Kunii and Levenspiel (2014)	1-D dense bottom, dilute upper zone	A dense bottom zone with known solids concentration is used together with the assumption of an exponential decay of solids concentration above the dense phase. knowledge about dense phase porosity needed. Dilute upper zone is calculated via: $\frac{\varepsilon_s-\epsilon_s^*}{\varepsilon_{sd}-\epsilon_s^*} = e^{-az_f}$ The dense bottom is considered constant at ε_{sd}. z_f = height above distributor ε_s = porosity at height z_f ε_s* = saturation porosity riser exit ε_{sd} = porosity bottom riser a = decay constant for exponential elutriation	[25]
Zhang et al. (1981)	1-D dense bottom, dilute upper zone	The riser is modeled first with an increase of solids concentration from a known starting value. From a known height of a dense bed, an exponential decay towards a known outlet concentration is calculated. Dilute upper zone is calculated via: $\varepsilon = \varepsilon_a + \frac{\epsilon^*-\epsilon_a}{2} e^{\frac{-(z-z_i)}{A}}$ The dense dense bottom zone follows: $\varepsilon = \varepsilon^* - \frac{\epsilon^*-\epsilon_a}{2} e^{\frac{(z-z_i)}{A}}$ A = characteristic length ε* = porosity lower bed ε_a = porosity riser exit z = height of dense bed	In book: [28]

Table 1 (continued)

Bai and Kato (1999)	1-D dense bottom, dilute upper zone	17 sets of experimental data investigated about their solids concentration along riser height.
		The proposed model equations distinguish between dense bottom zone and dilute upper region. For both regions 2 sets of correlations were proposed. They separate the flow regimes according to the solids circulation G_s and whether it is above or below a so-called saturation carrying capacity G_s^*.
		Dilute upper zone is calculated via:
		$\frac{\varepsilon^*}{\epsilon_s'} = 4.04\ \epsilon_s'^{0.214}$ for ($G_s < G_s^*$)
		$\frac{\varepsilon^*}{\epsilon_s'} = 1 + 0.208\left(\frac{G_s}{\rho_s U_0}\right)^{-0.5}\left(\frac{\rho_s-\rho_g}{\rho_g}\right)^{-0.082}$ for ($G_s > G_s^*$)
		
		The dense bottom zone is described as:
		$\frac{\varepsilon_{sd}}{\varepsilon_s'} = 1 + 0.00614\left(\frac{G_s}{\rho_s U_0}\right)^{0.23}\left(\frac{\rho_s-\rho_g}{\rho_g}\right)^{1.21}\left(\frac{\sqrt{gD}}{U_0}\right)^{0.383}$
		for ($G_s < G_s^*$)
		$\frac{\varepsilon_{sd}}{\varepsilon_s'} = 1 + 0.103\left(\frac{G_s}{\rho_s U_0}\right)^{-1.13}\left(\frac{\rho_s-\rho_g}{\rho_g}\right)^{-0.013}$
		for ($G_s > G_s^*$)
		An ideal solids volume concentration is assumed at:
		$\varepsilon_s' = \frac{G_s}{\rho_s(U_0-V_t)}$
		ε_{sd} and ε^* = upper and lower limit of solids concentration at bottom and top of reactor, respectively
		G_s^* = saturation carrying capacity of gas
			[29]

Werther and Hartge (2004)	1-D dense bottom, dilute upper zone	A dense bottom zone is modeled with a bubble and a suspension phase. The governing equation is the bubble size change above the distributor. The dilute region above the dense region is characterized by an exponential decay of solids concentration. dilute upper phase: $c_{v,i}(h) = \left(c_{v,d,i} - c_{v,i}^*\right)e^{-(a(h-H_d))} + c_{v,i}^*$ dense bottom zone: c_v = solids concentration h = discretized height, H_d = height of dense zone i = particle size class a = decay constant d_v = bubble size ε_b = bubble volume fraction λ = bubble lifetime	[30]
Werther (2002)	Annulus size	For radial profiles, the annulus thickness needs to be known. The research investigated large scale units for the annulus size and defined the empirical correlation $\left(\frac{\delta}{D_t}\right) = 0.55\ Re_t^{-0.22}\left(\frac{H_t}{D_t}\right)\left(\frac{H_t-z}{H_t}\right)$ δ = diameter between core and annulus D_t = diameter of the reactor H_t = Total height of the reactor z = height above distributor Re = Reyonolds number based on reactor diameter	In book: [31]