1 Introduction

The constantly changing raw material conditions in the course of global problems such as climate change or resource scarcity require solutions ideally adapted to the specific processes or problems, especially in process engineering. Due to the technological progress of Additive Manufacturing (AM), new reactor concepts and particularly geometries can be conceived, which could not be realized with the common manufacturing methods so far. The methods and possibilities of 3D printing are now so advanced that there are a large number of processes, some of which can produce components from various polymers up to 100 times faster than the common AM methods [Bee19, Par18]. While the construction space, printing costs, production times and possibilities were particularly of great interest for prototyping, AM is also becoming increasingly important in industry. Large corporations such as Siemens, BASF or Evonik Industries have established large departments for these areas in order to use the new degrees of design freedom, for example in conjunction with AI-supported topology optimization, to improve their products [Gar19, BAS22, Evo20]. This development allows new degrees of freedom, especially in the design of structures and internals of e.g. gas-liquid reactors. Due to the complexity of multiphase systems, the industry always relies on highly simplified models and heuristics for determining and estimating the parameters relevant to operation. These are for example gas holdup, bubble size distribution, or the specific interfacial area required for mass transfer between the phases, since it is difficult to measure these parameters in steel apparatuses of industrial size. By means of structuring and internals, these parameters can be realized much more favorably for mass transfer performance [Höl05, Dre01, Roy04, Cav99, Car67]. However, the question arises as to whether it is not possible to specifically influence and adjust the parameters relevant for mass transfer with the aid of a customized design of structured packings, such as Additively Manufactured Lattice Structures (AMLS) or, the simplest form of these, Periodic Open-Cell Structures (POCS) (s. Figure 1).

This thesis deals with the design, characterization and optimization of 3D printed structures as internals for gas-liquid reactors and the identification of potentials by using them for future multiphase applications.

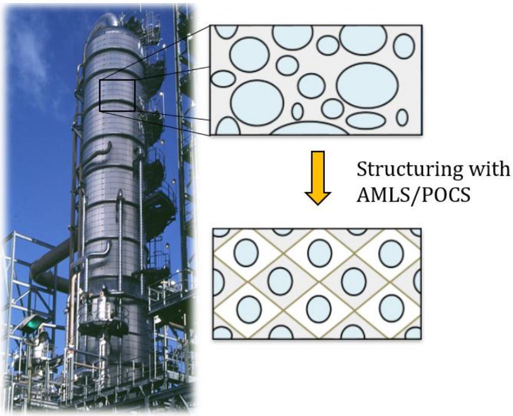

Figure 1: Abstract representation of a tailor made Additively Manufactured Lattice Structures (AMLS) or Periodic Open-Cell Structures (POCS) approach to adjust the parameters relevant for mass transfer ($k_L a$) and control e.g. the gas holdup (ε_G) and/or bubble size distribution (d_B).

In Hamburg, efforts have been underway since 2017 to investigate new reactor concepts and designs for chemical and biochemical synthesis processes in an interdisciplinary network within the Hamburg metropolitan region as part of the state research funding [Büs20, Spi20b, Spi20a, Hu20b, Eix20, Spi21, Hu20c]. On the biochemical side, e.g., for the model reaction of the enzyme-catalyzed conversion of ferulic acid (decarboxylation of ferulic acid to 2-methoxy-4-vinylphenol (MVP)) it was shown that by using a rapid prototyping approach for the implementation of design-optimized 3D printed structures, POCS can be used to[Büs20]:

I. Serve as an enzyme support structure for the immobilized enzymes and thus to form an essential step for continuous process operation in biochemistry.
II. Selectively adjust the specific droplet size of the product-extracting agent used to minimize product inhibition, resulting in a homogenous distribution across the reactor cross-section and the smallest possible defined droplets with a high specific interfacial area for mass transfer.
III. Enhance the mass transfer performance at all.

On the chemical side, the heterogeneously catalyzed epoxidation of propylene to propylene oxide using titanium silicate-1 (TS-1) in the so-called HPPO process [Kah11, Rus13], i.e. using hydrogen peroxide (H_2O_2) at industrially relevant conditions (30 bar and 40 °C), is focused on. One problem with this reaction is that alternative processes, such as the chlorohydrin process in large-scale industrial production, produce large amounts of waste product (100 kg of propylene oxide produces 200 kg of calcium chloride). For this reason, the reaction is carried out with hydrogen peroxide (H_2O_2), since only water remains as a "waste product". The reaction with H_2O_2 also offers the advantage that, depending on the pressure and temperature, it can be run in the liquid or gas phase. Here, a 3D printed structure coated with TS-1 is compared to the conventional fixed bed catalyst. The advantages of a design-optimized structure compared to the catalyst bed are also due to an increased heat transport (dissipation) of the reaction heat in the course of the metal structure and thus the avoidance of hot spots, as well as the avoidance of possible channeling, i.e. unwanted channel formation within the bed.

In the course of fruitful cooperation, a follow-up project in the context of the growth strategy of the Hamburg University of Technology (TUHH) has emerged from this project, the I^3-Lab: "Smart Reactors". In this project, efforts are being intensified with the aim of establishing a Collaborative Research Centre for process engineering at the TUHH. The scientific goal of this I^3-Lab is a knowledge-based design of "smart reactors", which enable significantly higher yields in chemical and biochemical reactions through an optimal reaction environment. This is realized by geometrically enforced adaptation of transport and reaction processes on all scales.

Within these two projects, i.e. the state research funding for the investigation of "New Reactor Technologies for Chemical and Biochemical Synthesis Processes" [Fre17], as well as the follow-up project I^3-Lab: “Smart Reactors" [Ham20] all the research results documented and partially published in this thesis have been achieved. In chapter 2, the theoretical background of this work is explained, regarding bubble column reactors and their structuring, as well as the latest research in the field of Additively Manufactured Lattice Structures. In addition, the mass transport in gas-liquid systems and how Additively Manufactured Lattice Structures are influencing it regarding the boundary layer dynamics, the role of specific interfacial area and the residence time for mass transport are highlighted. In chapter 3, in addition to the structure design and the overview of the structures used, the two main experimental setups are explained. The first setup comprises a 30x30 mm² square flow channel with a length of L = 600 mm operated in co-current flow, which had the advantage of printing the structures much more efficiently. Simplified optical images of the bubble images resulting from the structures are generated, and the pressure drop (two-phasic) and the mass transfer performance (stationary method) from air/O_2 to water are measured. However, since this setup can only capture bubble images above the structures, a second setup, a DN 110 pipe with height H = 1000 mm, is realized with an Electrical Capacitance Volume Tomography (ECVT) for the non-invasive capture of the fluid dynamics inside the structures. Furthermore, a fiber optical needle probe is used to measure the bubble sizes, bubble size distribution and phase velocities, correspondingly to validate the ECVT data. In chapter 4, the results will be presented and discussed. The focus is on the explanation of the influence of the structures used on the phases and bubble size distribution, on the bubble velocities and residence times of the bubbles, the influence on the two-phase pressure drop and thus a first proof of the decoupling of the gas-liquid dynamics from each other. Last but not least, the influence on the transport properties is shown and discussed as well. In chapter 5, new innovative approaches for the development of smart reactors by the use of so-called "smart structures" are shown, which autonomously change their shape and size in response to changing properties such as temperature or the pH value of the medium surrounding the structure and thus influencing and controlling the process itself. Finally, the findings are summarized and an outlook for future research in this field is given.

2 State of knowledge

The aim of the work is to explore the new design possibilities and degrees of freedom gained through Additive Manufacturing (AM) in the development of structured packings in order to specifically influence the fluid and transport properties in gas-liquid contact apparatuses and multiphase reactors. In particular, potentials for possible applications in chemical and biochemical gas-liquid synthesis processes are to be identified, and the extent to which the targeted and knowledge-based design of additively manufactured structures can have a positive influence on, e.g., the phase and bubble size distribution, the heat and mass transport, the residence and contact times or also the pressure loss and thus the energetic evaluation.

Many research work has been done before in the field of process intensification with structured packings. In this chapter an overview will be given about the state of knowledge regarding bubble column reactors, the operating modes, common structuring forms (trays, packed beds, structured packings), and the possibilities of process enhancement. The new possibilities and methods of AM are explained. Furthermore, the process of rapid prototyping will be introduced as a fast and efficient tool to get information and knowledge from complex (multiphase) systems to achieve a fast and cost effective improvement of the structural geometry design. This is followed by a state of the art on the structural designs used in this work, called Additively Manufactured Lattice Structures (AMLS), as well as the simplest form of these, called Periodic Open-Cell Structures (POCS). The state of research of all relevant working groups in this field is explained. Since a significant positive effect of the investigated structures results from the significantly increased gas-liquid mass transport, the mass transport in gas-liquid systems is explained in general, and the model on which the mass transport investigations are based. Finally, the influence of three parameters essential for mass transport, namely the boundary layer thickness, the specific interfacial area, and the residence time of the disperse phase, are discussed, since their understanding is essential for the evaluation of the results.

2.1 Bubble column reactors

Bubble columns or bubble column reactors are mass transfer and reaction apparatuses in which one or more gases can be brought into contact with or react with a liquid phase. A characteristic feature of these apparatuses is that the gas flow is dispersed in the liquid phase. Furthermore, no mechanically moved internals, such as agitators, are present in the system. For chemical reactions, reactive and catalytically active particles can additionally be suspended or adapted in alternative designs of modified bubble column reactors in the form of reactive packings or internals. The actual chemical reaction is based on upstream and downstream mass transport processes which, under certain conditions, define the rate-determining step of the overall process. Consequently, for mass transfer limited reactions the generation of high mass transfer rates is of particular importance. This essentially means increasing the mass transfer area and thus the specific interfacial area, as well as increasing and selectively inducing turbulence e.g. to reduce the boundary layer thickness. [Dec85]

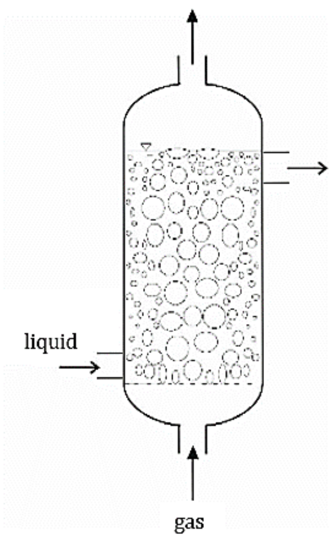

Figure 2: Example of a bubble column operated in co-current flow.

A bubble column can be operated in a co-current flow (Figure 2). The gas is fed into the liquid-filled column from below via various forms of gas distributors or dispersers. The liquid is either fed in portions (batch operation) or supplied and discharged in co-current or countercurrent (continuous operation). The ratio of height H to diameter D of the column is also referred to as the aspect ratio and is usually between 3 and 6 on an industrial scale, but can also be above 10. The volume of large plants in chemical reaction technology ranges from 100 to 200 m^3. In biochemical or biotechnological applications, the plants are significantly larger due to the comparatively slow processes and can have volumes of up to 20,000 m^3, for example in the field of biological wastewater treatment. [Dec85]

The relatively simple design and the absence of mechanically moving components allow to use aggressive gases, high temperatures and pressures, since, for example, sealing of a possible stirrer shaft is not necessary. Due to the low energy demand (only for gas dispersion), bubble columns are energetically efficient devices. They are also characterized by strong mixing and high heat transfer rates, in the course of the induced turbulence, but also by the drag effect of the rising gas bubbles. A disadvantage is the short residence time of the gases, which, without special internals, is primarily determined by the rise velocity of the gas. Despite or due to this simple design and the lack of mechanical components, the hydrodynamic conditions in bubble columns are extremely complex. As a result, hydrodynamic parameters such as gas holdup ε_G and mass transfer parameters, like the mass transfer coefficient $k_L a$, are extremely sensitive to material properties, and even the use of heuristic correlations can be subject to considerable uncertainties. [Dec85]

An overview of the classification of multiphase reactors in general is given according to Coulson et al. (Figure 3) [Cou07]. Thus, multiphase reactors can be divided into the so-called suspended bed reactors, which can be distinguished into bubble columns, agitated tank reactors and three phase fluidized bed reactors, and the fixed bed reactors, which can be classified as co-current down- or upflow or countercurrent flow reactors. In this work, the focus is on the bubble columns, as well as the gas-liquid contact apparatus packed by the adapted and developed structures and operated in co-current upflow.

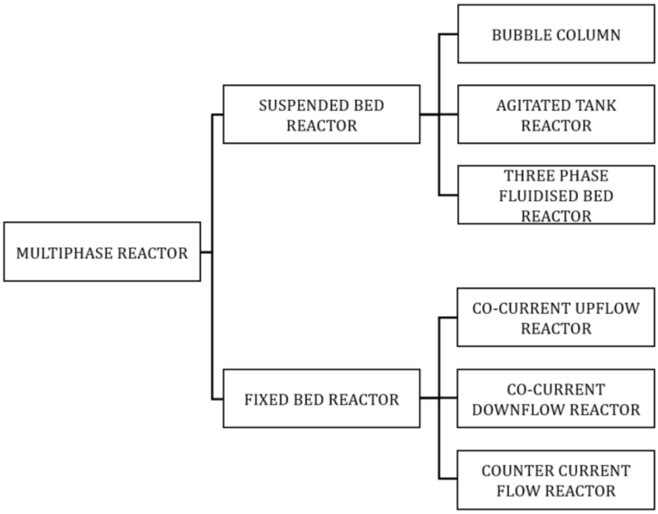

Figure 3: Classification of multiphase reactors after Coulson et al. 2003 [Cou07].

2.1.1 Operating modes

Bubble columns are usually operated at low liquid flow rates due to the high liquid holdup compared to the gas phase. The main operating parameter is the gas velocity u_G, or the so-called superficial gas velocity $u_{G,0}$ in relation to the mean cross-sectional area of the reactor. Depending on the coalescence properties (surface tension, possible presence of surface-active substances or salts, etc.), this influences the formation of the interfacial area relevant for mass transfer [Dec85]. The rising gas bubbles draw adhering liquid upwards in the wake. For reasons of continuity, this causes downstream effects near the wall and increased reverse flows within the column. The effect is intensified by the formation of large bubbles, which increasingly rise in the reactor center, and leads to the formation of a radial phase and velocity profile despite supposedly uniform gassing. This is also the reason for high radial cross-mixing and practically undetectable concentration gradients in the liquid phase [Dec85].

Three different flow regimes can be distinguished in bubble columns (Figure 4).

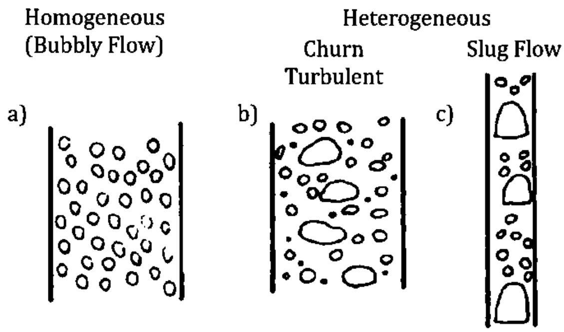

Figure 4: Flow regimes in bubble columns by Shah et al. [Sha82].

In the homogeneous regime, low gas loads result in an increased number of small bubbles with a comparatively narrow bubble size distribution. If the gas load is increased, turbulence and coalescence effects are more pronounced, resulting in a broader bubble size distribution with more large bubbles, and this is referred to as the heterogeneous flow regime. The larger bubbles usually reveal higher mass transfer coefficients k_L, but show strongly under-proportional increasing interfacial areas with the gas flow rate. Consequently, the conversions achievable in the heterogeneous regime are almost always lower than those achievable with homogeneous bubbly flow. However, the heterogeneous regime can be selectively suppressed or the negative effect on the conversion and the space-time yield can be compensated for by the use of various equipment measures and installations, such as perforated trays, the use of certain gas distributors, or special bubble column designs. [Dec85]

In the third regime (Figure 4, c), a slug flow can be observed due to comparatively small diameters of the bubble column, as is the case e.g. in laboratory scale, and occurring wall effects with large bubbles. In this case, the large bubbles form stabilized and plug-like pistons with the wall. These gas plugs (slugs) fill the entire reactor cross-section and collect smaller bubbles. In the course of the low transferability to larger scales and only low turnovers and reactor capacities, the slug flow should be strictly avoided. [Dec85]

Figure 5 shows the ratio of gas velocity to reactor diameter for an air-water system according to Shah et al. [Sha12]:

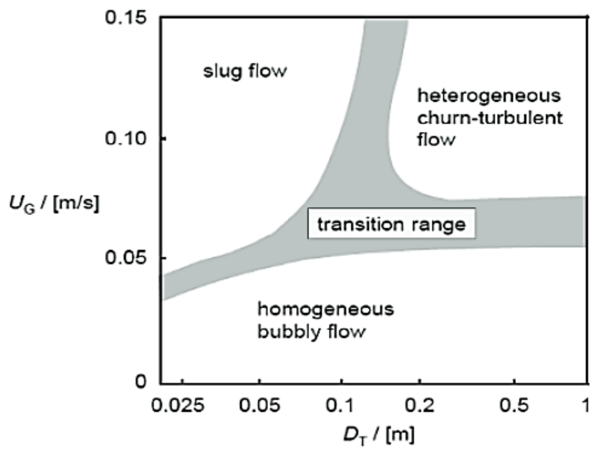

Figure 5: Approximate flow regime map for an air-water system in bubble columns by Shah et al. [Sha12].

One can see that the transition range is quite big (gray area), so that a distinct regime classification in that area is not always clear. Figure 6 shows various designs and installations of modified bubble column reactors which have been adapted to the special requirements of practice.

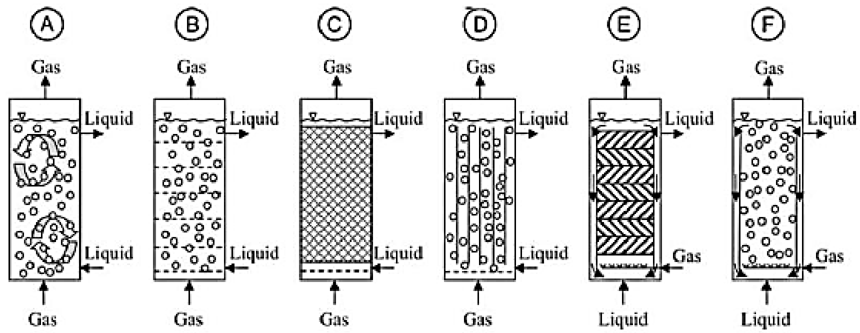

Figure 6: Modified bubble column reactors: A) Simple bubble column B) Cascade bubble column with sieve trays C) Packed bubble column D) Multishaft bubble column E) Bubble column with static mixers F) Airlift loop reactor after Deen et al. [Dee10].

In addition to the general design, the choice of the sparger is decisive for the performance of the bubble column. Figure 7 shows different static gas sparger, each of which has a large