Chapter 1

Introduction

The chemical industry provides a wide range of products that we use in our daily lives. Many of these chemicals are produced with the help of gas-liquid reactions. This type of reaction is used by a spectrum of important processes, including chlorinations, hydrogenations, and oxidations [Loh90]. To achieve an improved use of limited resources by these processes, they have to be optimised in regard to their use of raw materials and energy, while associated waste production and space requirements are to be minimised. Through these steps, harmful environmental impacts are reduced, which is a basic requirement for the transfer to a sustainable, climate-neutral industry of the future.

The presented work is conducted as part of an industrial research project. The aim of the project is the transfer of an agrochemical process, currently implemented in bubble columns, to a new, more efficient and smaller reactor system. Simultaneously, an increase in yield is targeted to achieve better utilisation of the necessary raw materials. These objectives constitute an intensification of the process [Kei18]. This work presents the application of the novel cross-scaling approach, referred to as X-scaling, for the transfer of the process to a two-phase-operated jet loop reactor.

The available process data of the existing implementation of the agrochemical process hint at a mass transfer limitation that needs to be overcome. The jet loop reactor (JLR) is chosen as the tool for intensification, as this type of reactor is able to achieve a high mass transfer performance, while being easily scalable [Ble65, Teb89, Loh90, Wie11]. The X-scaling approach, schematically depicted in Fig. 1.1, is chosen for the scaling scheme of the reactor system to an industrially relevant scale. The basis of this approach is the study of a reactor system through experimental investigations covering different scales, from the laboratory to the pilot scale, using an easily manageable material system. Simultaneously, a twin copy of the

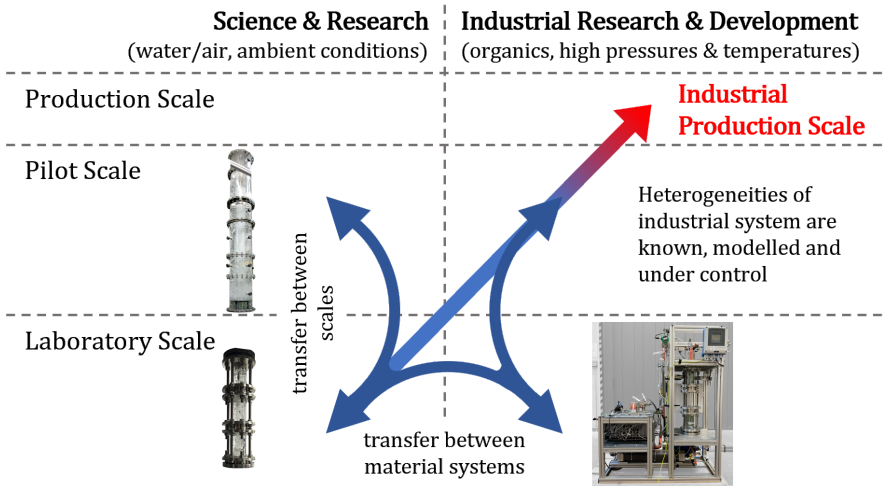

Figure 1.1 Schematic depiction of the applied principle of the X-scaling approach.

reactor in the laboratory scale is used for investigations with the industrially relevant material system. The easily manageable system could be, for example, water and air, which is not wide-spread in the chemical industry, however eases the operation of the respective setup and the conduction of experiments [Beh09]. This enables eased experimental work between scales in order to identify and solve problems relating to the scale-up, such as possibly occurring heterogeneities. Industrial material systems have the potential to be hazardous to environment and life, often requiring stern handling procedures, dedicated facilities, and observation of tight legal regulations. Therefore, their use in research can cause disproportionate efforts and expenses. Experiments with a possibly more demanding and complex industrial material system are reduced to more manageable experiments in the laboratory scale when applying the X-scaling approach, minimising necessary efforts.

Placement of the Presented Work in the Overall Project

The overall project stems from the necessary relocation of a chemical plant, which is home to a decade-old implementation of an agrochemical process. This process is based on a gas-liquid reaction, and is conducted in bubble columns. The relocation offers a possibility for the implementation of improvements for said process, or, if necessary and applicable, even a restructuring of the whole process. Generally, an intensification of the process is desired. The

motivation of the project is, thus, grounded in the investigation of a possible implementation of the process in a JLR, the identification of optimisation potentials, and the provision of data for the scaling of the setup to an industrially relevant scale.

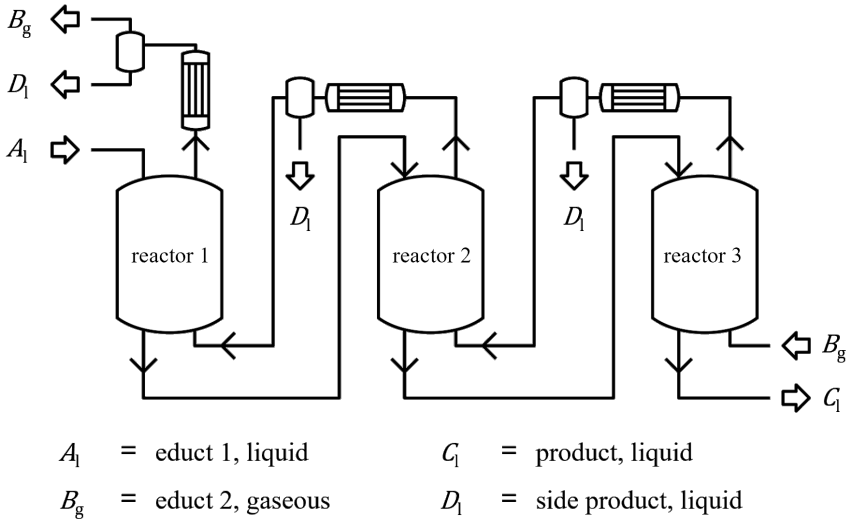

Figure 1.2 Simplified schematic process flow chart of the surveyed implementation of the underlying agrochemical process.

The first step of the project is a survey of the existing process and its decade-old implementation of the gas-liquid reaction. A three-step cascade of bubble columns is used (see Fig. 1.2). It is important to note that the pressures and temperatures in the setup are elevated and lie well above ambient conditions. The liquid and gaseous phases pass the reactor setup in a continuous counter-flow. The process uses the main reaction scheme

$$A_l + B_g \longrightarrow C_l + D_{g,l},$$

in which the liquid reactant A_l and the gaseous reactant B_g form the desired liquid product C_l. At the same time, a side product $D_{g,l}$ is formed, which is soluble in the liquid bulk and can be available both in gaseous and liquid form. The gaseous reactant B_g is a highly caustic reactive gas that is added overstoichiometrically.

The liquid reactant A_l can be rearranged by means of an equilibrium reaction,

$$A_l \rightleftharpoons E_l + D_{g,l},$$

forming a liquid intermediate product E_l that also acts as an reactant, and more side product $D_{g,l}$. The intermediate product can undergo a secondary reaction

$$E_l + B_g \longrightarrow C_l + D_{g,l}$$

with the added gaseous reactant B_g, forming both the desired liquid product C_l and the side product $D_{g,l}$.

The next step within the project is the identification of improvement potentials. Operation data from the existing process indicates a mass transfer limitation. This is apparent in the combination of the overstoichiometric addition of the reactive gaseous reactant B_g and very high residence times τ_l of the liquid phase, while reactive gas can, at the same time, still be found remaining in the effluent gas flow. To overcome said mass transfer limitation, the process is to be intensified by increasing the interfacial area between the phases and, thus, increasing the mass transfer performance. The possibility of a simplification of the setup, by implementation of the process in one single, continuously operated reactor in contrast to a cascade of three reactors, is conceivable.

Based on the previous steps, a new reactor design is required for the intended implementation of the process. A jet loop reactor is chosen due to an easy design and good scalability of the reactor. The desired qualities that are to be provided by this reactor type are an excellent mixing and mass transfer performance.

The current work is based on these preceding steps. Within this work, the scaling of an existing pilot-scale jet loop reactor setup, required for the application of the aforementioned X-scaling approach, and the design of the twin-reactors in laboratory scale are presented. Experiments with the industrial material system are conducted by the project partner. These are required to provide the necessary data for a sufficient basis for a reliable scale-up to the industrial scale, which forms the last step of the project. In this thesis, the necessary experiments in the system water/air, which are conducted in parallel, and the methods and results are presented and discussed.

Chapter 2

State of Knowledge

Chemical conversion processes in technical apparatuses are governed by physicochemical fundamentals, expressed in the form of reaction kinetics and transfer phenomena concerning momentum, mass and heat, which indirectly affect reaction rates, yield and selectivity [Ble65, Teb88, War17, Kex23]. Fast gas-liquid reactions and their selectivity and space-time yield in industrial scale can be critically limited by physical mass transfer restrictions [Nag78, Beh09, Wie10]. In oxidations and chlorinations for example, the absorption of gas in the liquid is the rate-determining process [Zeh75, Mid04]. For a given pressure and thus solubility of gases, an increase of the interfacial area between the phases, which reduces physical mass transfer resistances [Nag70], can be a practical solution to achieve an enhancement of the gas-liquid mass transfer performance [Zeh75, War88, Kei18]. In the field of process engineering, a variety of apparatuses are employed to provide adequately large specific surface areas between the phases. Examples for these apparatuses are gassed tanks, bubble columns, continuous stirred tank reactors (CSTRs), but also different forms of loop reactors [Nag70, Sch80, Loh90, War17]. Within this chapter, relevant phenomena are presented, before taking a closer look at loop reactors and their fluid dynamics.

2.1 Phenomena of Bubbly Flows

This section presents underlying phenomena connected to the gaseous phase, which is mostly present in the form of dispersed bubbles. The basic physical principles are in general also applicable to liquid-liquid systems, when the differing material properties are properly considered.

Knowledge of both the operating and flow characteristics are required when employing all kinds of process engineering apparatuses. These apparatuses often times use bubbly flows, a multiphase application where a gaseous species is dispersed in a continuous liquid phase. In these systems, the behaviour of the gaseous phase is of great importance; Fig. 2.1 depicts exemplary regimes of a bubbly flow in two-phase operated reactors. The operating and flow characteristics are fundamental not only for applicable operational parameters and resulting mass transfer characteristics, but also for operational safety [Loh90]. With all the aforementioned advantages these multiphase apparatuses offer, the processes rely heavily on mixing in the reactor due to the fluid dynamic conditions, the interaction between bubbles, and turbulence induced by bubbles, all of which are challenging to predict.

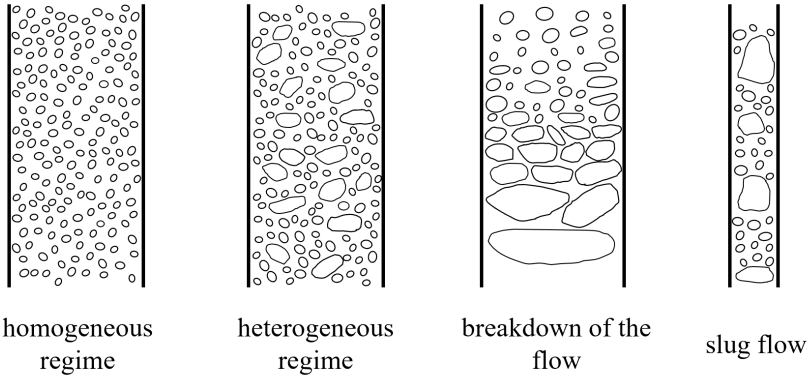

Figure 2.1 Exemplary regimes of two-phase operated reactors; reproduced from [Loh90].

When it comes to bubbly flows, one might exemplarily consider differences in specific interfacial areas between a homogeneous and a heterogeneous regime. In the homogeneous regime, relatively small bubbles exhibit a narrow distribution concerning appearing bubble sizes, which comes along with a rather uniform rise velocity. The heterogeneous flow is marked by a growing share of larger bubbles, which occur due to coalescence effects that stem from higher gassing rates. Coalescence is the process by which gas bubbles collide in a liquid medium and merge into larger bubbles, which they can be subjected to during their path in a reactor [War88, Beh09]. Generally, the lower specific interfacial area of the heterogeneous regime leads to lower conversion rates compared to the homogeneous regime [Loh90]. Large, buoyant gas bubbles that coalesce further can even create a cushion of gas and completely block e.g. the draft tube of a JLR, which can lead to a breakdown of the loop with severe consequences for

the process and, depending on the application, possibly also for operational safety, e.g. when excess heat can not be removed. In JLR setups, the depicted regime of the slug flow in Fig. 2.1, which is exclusively found in laboratory scale [Loh90], is therefore to be avoided.

2.1.1 Bubble Formation

At low gas volume flow rates, the size of bubbles forming in multiphase flows is based on an equilibrium of forces (buoyancy, surface tension, drag and inertia) acting on the bubble surface at the dispersing system, where bubbles are periodically formed, resulting in a primary diameter. A key factor are the hydrodynamic conditions. The bubble size is dominated by coalescence and re-dispersion for systems exhibiting a coalescing behaviour and/or under turbulent conditions. Therefore, the bubble size is dependent on the local energy dissipation. Non-coalescing systems or those with low turbulence exhibit bubble sizes that are almost constant after the initial dispersion. With higher gas flow rates, the resulting size of bubbles is dominated by the fragmentation effect of jet gassing which occurs above the sparger, leading to a smaller, secondary diameter. Here, bubbles detach as single particles and then disintegrate

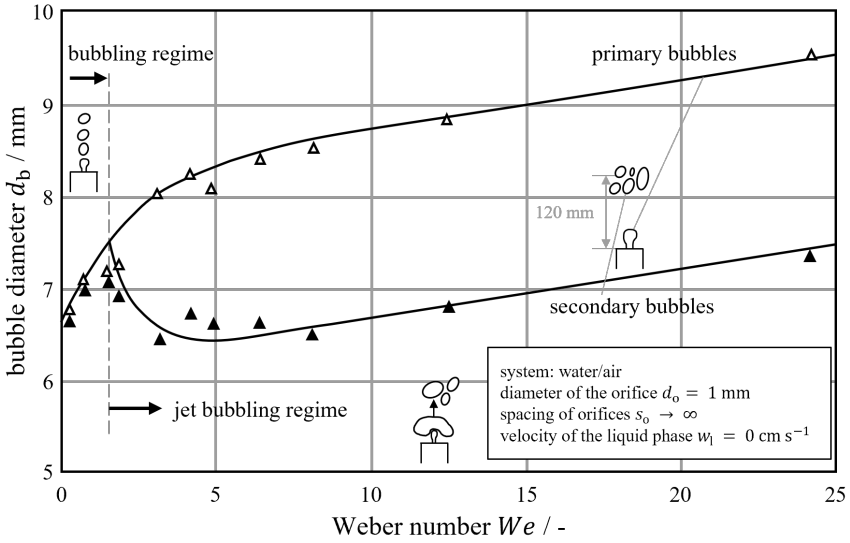

Figure 2.2 Diameters of primary and secondary bubbles at a single orifice according to [Klu83]; reproduced from [Räb10].

into several secondary bubbles due to the dynamic of detachment, where inertia leads to a fragmentation of the primary formed bubbles, forming much smaller bubbles with larger specific interfacial areas, see Fig. 2.2 [Bra71a, Räb10].

As already stated, high gassing rates and small bubble sizes are often desired in industrial applications to achieve the required large specific interfacial areas. These applications therefore tend to use the aforementioned jet gassing or jet bubbling regime.

The dimensionless Weber number

$$We = \frac{\rho_{\mathrm{g}} \cdot w_{\mathrm{n,g}}^2 \cdot d_{\mathrm{n,g}}}{\sigma}, \tag{2.1}$$

with density ρ_{g} and velocity $w_{\mathrm{n,g}}$ of the gas phase at a nozzle with a diameter $d_{\mathrm{n,g}}$, is often used to characterise the range of secondary particle formation, with the dispersing system often designed to obtain a Weber number $We > 2$ and ensure a jet bubbling regime (refer to Fig. 2.2).

2.1.2 Bubble Shapes and Rise Behaviour

A key desire that leads to usage and application of multiphase apparatuses and applications are large interfacial areas. The reactors are therefore usually operated at heightened gassing rates and exhibit large gas hold-ups, which result in high degrees of mixing and mass transfer rates. For these operating parameters, a complex interaction of occurring effects concerning the rise of bubbles takes place; when bubbles rise in swarms, these effects may include wake effects, bubble induced turbulence, and the break-up and coalescence of bubbles. Important factors are the size and shape of bubbles, as these determine the bubble rise velocity and as such directly influence the mass transfer from the gaseous to the liquid phase by determining residence times in the system and the expression of boundary layers around bubbles. Due to the complexity, it often times is easier to investigate the behaviour of single bubbles and then transfer this knowledge to bubbles rising in a swarm, incorporating the additional effects of bubble-bubble interactions.

The fluid dynamic behaviour of bubbles is determined by the interdependent effects of bubble size and shape, interfacial effects due to surface tension or surface active agents, as well as their rise velocities and trajectories. Their behaviour is most famously characterised with the help of three dimensionless numbers, namely the Eötvös number

$$Eo = \frac{(\rho_{\mathrm{l}} - \rho_{\mathrm{g}}) \cdot g \cdot d_{\mathrm{b}}^2}{\sigma}, \tag{2.2}$$

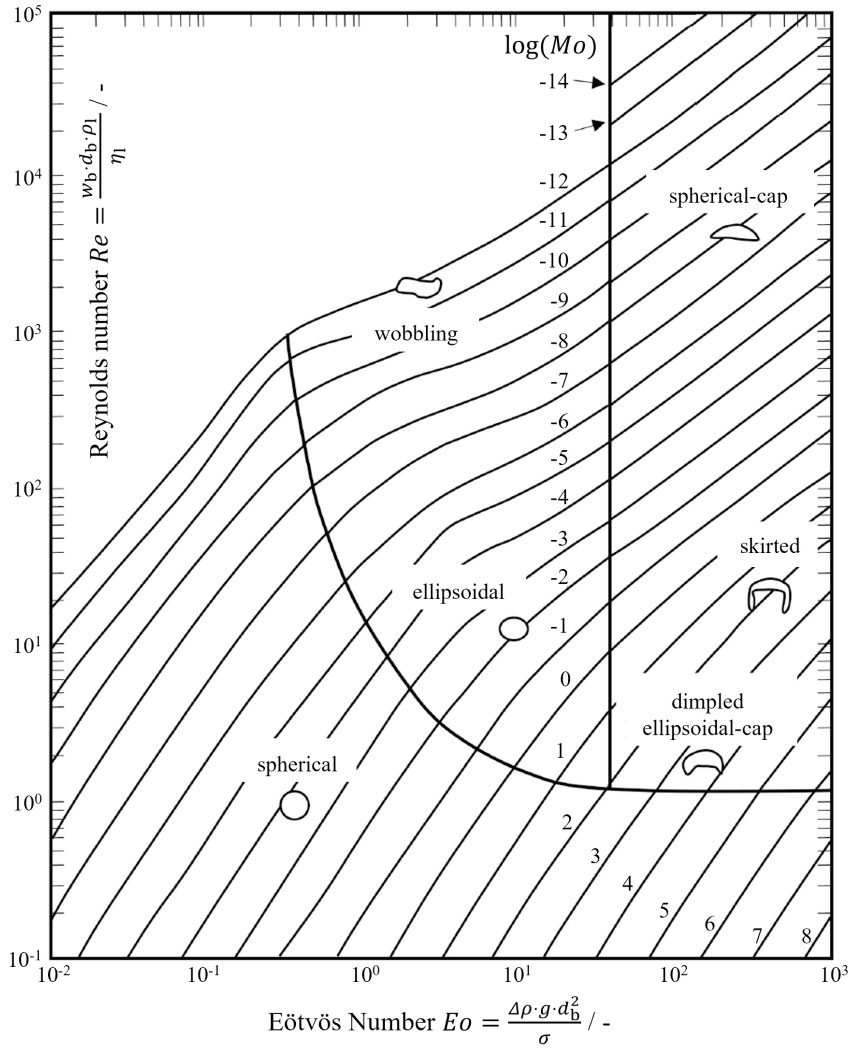

Figure 2.3 Shape regimes for bubbles rising in stagnant liquids; reproduction of [Cli78].

the Morton number

$$Mo = \frac{g \cdot \eta^4 \cdot (\rho_\mathrm{l} - \rho_\mathrm{g})}{\rho_\mathrm{l}^2 \cdot \sigma^3}, \tag{2.3}$$

and the Reynolds number

$$Re = \frac{w_\mathrm{b} \cdot d_\mathrm{b} \cdot \rho_\mathrm{l}}{\eta_\mathrm{l}}, \tag{2.4}$$

with the densities of the liquid and the gas, ρ_l and ρ_g, respectively, the gravity constant g, the bubble diameter d_b, the interfacial tension σ, the dynamic viscosity η of the liquid, and the bubble rise velocity w_b [Cli78]. In place of the bubble diameter d_b, the volume-equivalent diameter

$$d_\mathrm{b,eq.} = \sqrt[3]{\frac{6 \cdot V_\mathrm{b}}{\pi}}, \tag{2.5}$$

which is based on the volume V_b of an individual bubble, is used [Cli78]. The rise velocity

$$w_\mathrm{b} = \sqrt{\frac{4}{3} \frac{|\,\rho_\mathrm{l} - \rho_\mathrm{g}\,|}{\rho_\mathrm{l}} \cdot g \cdot d_\mathrm{b} \cdot \frac{1}{\zeta_\mathrm{D}}} \tag{2.6}$$

in steady state results from the equilibrium of aforementioned buoyancy and drag forces acting on the bubble, with ζ_D denoting the drag coefficient. The Reynolds number, the ratio of inertial to viscous forces, is used to characterize the fluid flow and its condition; here it characterises the flow that is induced by the bubble itself. The Morton number, the ratio of viscous to surface tension forces, depends solely on material properties and gravity. The Eötvös number is the ratio of gravitational forces to surface tension forces. Based on these three dimensionless numbers, a flow map, depicted in Fig. 2.3, was derived by *Clift* et al., which is used in the prediction of bubble shapes [Cli78].

The dependency between the drag coefficient ζ_D and the Reynolds number *Re* is shown in Fig. 2.4. To simplify the description of the drag coefficient and its interplay with viscosities and densities of phases and the mobility of the interface, normally four regimes (A to D in Fig. 2.4) are established in relation to the Reynolds number, each with their own empirical correlations for the calculation of drag coefficients [Bra71a, Räb10]. Fluid particles within regime A behave like solid particles. In regime B, the internal circulation of particles with a moving interface, caused by friction, leads to a decrease in the drag coefficient. In this regime, the mobility of the interface is sensitive to e.g. surface active agents, which may lead to bubbles exhibiting a behaviour similar to drops or solid particles. With increasing Reynolds number, bubbles and droplets in regime C experience a deformation and oscillation of their surface, resulting in a higher drag coefficient in comparison to rigid spheres. Drops in this regime that exceed a critical diameter disintegrate into several fragments, whereas bubbles are able to form irregular shapes with an almost constant drag coefficient in regime D [Räb10]. A variety of empirical and