Chapter 1

Introduction

In the chemical industry, gas-liquid reactions, usually carried out as a bubbly flow, are of great importance as they are providing a vast proportion of the bulk chemicals used in our everyday life e.g., by oxidation, hydrogenation, or chlorination. Therefore, the optimization of these processes regarding their raw material and energy consumption, space requirements and waste production is crucial, especially in times of limited resources and increasing environmental awareness.

The efficiency of large scale industrial processes is usually characterized by the reaction yield

$$Y_{i,k} = \frac{N_i - N_{i,0}}{N_{k,0}} \cdot \frac{|\nu_k|}{\nu_i}, \tag{1.1}$$

which is the amount of substance produced N_i in relation to a consumed reactant $N_{k,0}$ considering the reaction stoichiometry ν_i and ν_k, and the reaction selectivity

$$S_i = \frac{Y_i}{X_k} \tag{1.2}$$

describing the ratio of the product yield Y_i and reaction conversion X_k. The conversion

$$X_k = \frac{N_{k,0} - N_k}{N_{k,0}} \tag{1.3}$$

is defined as the amount of reacted substance n_k to the initial amount available for reaction $n_{k,0}$. In particular, an improvement in selectivity represents a significant lever for process optimization, since an increased selectivity reduces energy consumption for downstream purification processes.

The influence of mixing on the yield and selectivity of single phase reactions is known from literature [Bał99, Bou03, Pau03]. While the relevant mixing effects on a proceeding reaction are well studied for single phases, for example miscible liquid-liquid reactions, the influence of mixing in multiphase systems such as gas-liquid reactions is not yet fully understood. This is mainly due to a lack of detailed understanding of the complex interplay and interdependencies of fluid dynamics, gas-liquid mass transfer, and chemical reaction, which are schematically illustrated in Figure 1.1.

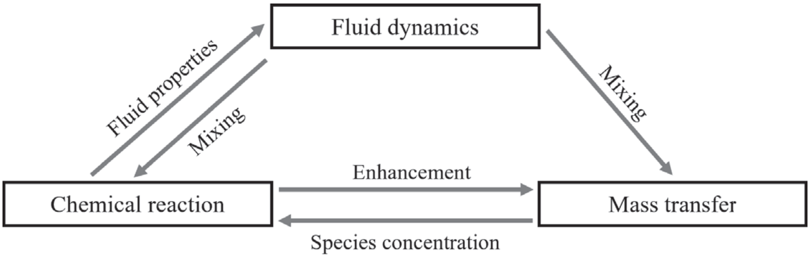

Figure 1.1: Scheme of interdependencies occurring in reactive bubbly flows, influencing the yield Y and selectivity S in large scale processes according to [Sch21]

Obtaining a deeper understanding about those complex interdependencies is highly desired, since tuning the timescales of mixing, mass transfer across the gas-liquid interface and the chemical reactions provide a significant potential for process optimization and thus lowering production and environmental costs. In order to gain the required information, constant and reproducible fluid dynamic conditions, as well as an applicable gas-liquid model reaction, are necessary. The model reaction applied in this thesis, the so-called MNIC-DNIC reaction, is following a consecutive competitive reaction scheme

$$\mathrm{A}_{(\mathrm{g})} + \mathrm{B}_{(\mathrm{l})} \xrightarrow{k_1} \mathrm{P}_{(\mathrm{l})}$$

$$\mathrm{A}_{(\mathrm{g})} + \mathrm{P}_{(\mathrm{l})} \xrightarrow{k_2} \mathrm{S}_{(\mathrm{l})},$$

where the dissolved reactant $\mathrm{B}_{(\mathrm{l})}$ and the intermediate product $\mathrm{P}_{(\mathrm{l})}$ are competing for the available gaseous species $\mathrm{A}_{(\mathrm{g})}$. On the basis of this reaction scheme, the determination of the selectivity S towards the desired intermediate product $\mathrm{P}_{(\mathrm{l})}$ or side product $\mathrm{S}_{(\mathrm{l})}$ is enabled.

A suitable experimental setup, providing the necessary fluid dynamic conditions, is the Taylor bubble setup elaborated by [Kas15], schematically depicted in Figure 1.2. Taylor bubbles are large elongated gas bubbles, rising in a narrow capillary or pipe, with a well-defined and constant rise velocity v_b creating very well-defined wake and mixing structures [Tay61, Whi62, Cam88, Kas17]. The rising behavior is volume independent, and solely dependent on the ratio of buoyancy force and surface tension described by the dimensionless

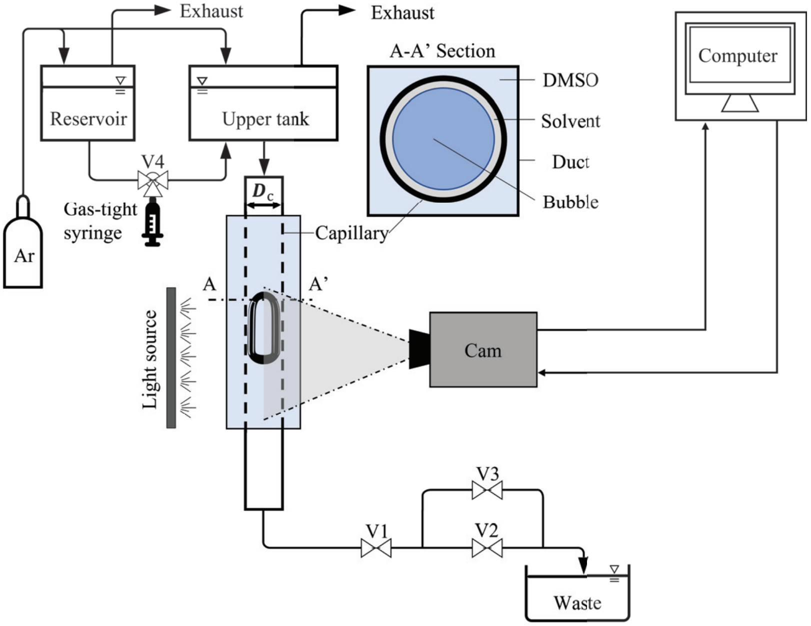

Figure 1.2: Scheme of the basic Taylor bubble setup adapted from [Kas15]

Eötvös number

$$Eo = \frac{\left(\rho_l - \rho_g\right) g D_c^2}{\sigma}, \tag{1.4}$$

where ρ_g and ρ_l are the densities of the liquid and gaseous phase, g the gravitational acceleration, σ the surface tension and D_c the capillary diameter. Taylor bubbles are buoyancy driven, inducing a flow field by themselves, if a critical Eötvös number $Eo_{crit} \approx 4$ is exceeded [Tay61]. This yields a critical capillary diameter D_{crit} for a given system, for example, $D_{crit,H_2O} = 5.4\,\text{mm}$ for aqueous systems [Kas15]. Due to the volume independent rise velocity, Taylor bubbles are easily kept at a fixed position by a counter current flow, enabling a rather long observation time period t_{obs}, compared to freely ascending bubbles. Thus, in this thesis Taylor bubbles are utilized as a tool for gaining the necessary insights.

This thesis aims to acquire the necessary information, in order to understand the complex interplay of fluid dynamics, mass transfer and chemical reactions. For this purpose, three sets of experiments are conducted. Firstly, the global rising behavior of Taylor bubbles in industrial relevant organic solvents is studied. Secondly, the local flow fields in the wake of Taylor bubbles in one of the most common organic solvents, methanol, are studied in detail. Finally, the concentration and selectivity fields behind reactive Taylor bubbles are analyzed with high spatial and temporal resolution. For this purpose, a new measurement technique is developed and established, the high speed imaging UV-VIS spectroscopy, which is based on the fundamentals of UV-VIS spectroscopy and Beer-Lambert's law. All experiments are conducted in small sized capillaries ranging from $4.0\,\mathrm{mm} < D_\mathrm{c} \leq 5.0\,\mathrm{mm}$ and at low Eötvös numbers in the range of $4 < Eo \leq 10$.

This Thesis within the Framework of the DFG SPP1740 Reactive Bubbly Flows

As this thesis has been issued within the framework of the priority program SPP1740 "*Reactive Bubbly Flows*" funded by the German Research Foundation (DFG), a brief overview on the program and the key findings will be shortly recapitulated.

The SPP1740 aimed to gain a deeper understanding of the complex interplay of fluid dynamics, mass transfer and chemical reactions. Therefore, an interdisciplinary approach was chosen, closely connecting engineers, chemists, and mathematicians, as illustrated in Figure

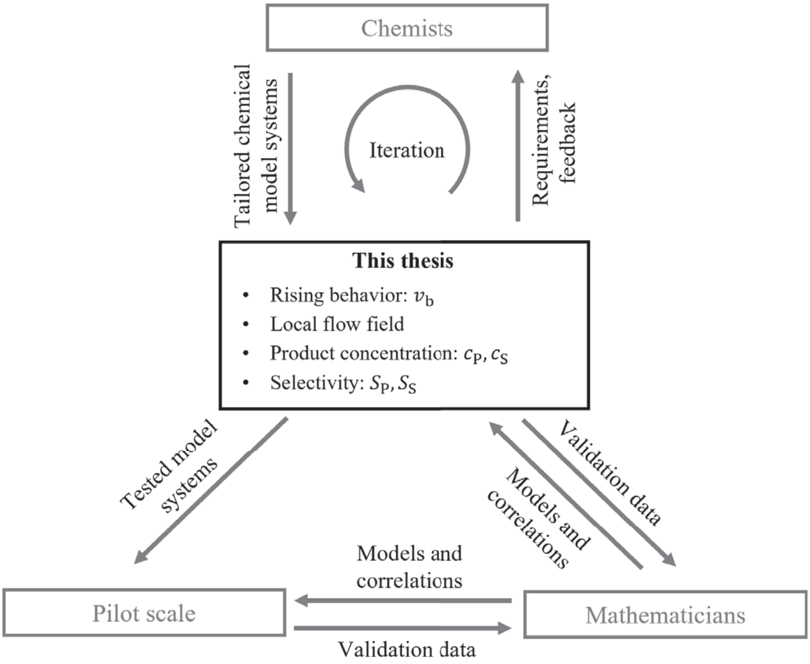

Figure 1.3: Objective of this thesis within the framework of the DFG SPP1740 "*Reactive Bubbly Flows*"

1.3. Within this interdisciplinary approach, the engineering and experimental working groups had to define industrial relevant process conditions and develop experimental approaches, capable of measuring the local concentration and velocity fields and their interplay with model chemical reactions. To unravel the effects of mixing performance onto chemical reactions, the expertise of chemists was needed. The applied model reactions had to be tailored to the experimental realities, such as available measurement techniques, and understood in detail. In this context, known reaction kinetics and measurable product concentrations had been in focus for tailoring, with the reactions ideally following a consecutive competitive scheme. In order to transfer the gained experimental data into reliable models and correlations, mathematics were indispensable, accurately describing the measured transport processes by analytical or numerical approaches.

Within the project period, various results could be achieved on the basis of this interdisciplinary cooperation. Experiments with different complexities, starting from a SuperFocus mixer [Sch16, Mie17] and Taylor bubbles, being the main topic of this thesis, to freely rising single bubbles and bubble swarms, were performed. The experiments in the SuperFocus mixer and on Taylor bubbles were of particular importance, since they were used as guiding measures, which have been used for the development of the chemical model systems and the validation of numerical approaches. In addition, several new measurement techniques like the Time Resolved Scanning - Laser Induced Fluorescence (TRS-LIF) or the high speed imaging UV-VIS spectroscopy have been developed in order to visualize concentration fields in the wake of bubbles. To meet the demands of the experimental working groups, the chemical model systems were constantly developed and adjusted by the chemists. A good example of this continuous adaptation is the chemical system used in this thesis, which will be described in detail in Chapter 5.1. An overview about the other available model systems is given in Chapter 2.4.2. On the numerical side, new modeling techniques have been developed, enabling the modeling of reactive mass transfer at single rising bubbles, while tackling the high Schmidt number problem, by applying subgrid-scale modeling approaches [Wei21]. Furthermore, the data available from the guiding measures have been used in a reverse engineering framework for single and multiphase flows accompanied by chemical reactions, yielding good agreements with the available reference results [Mie21].

In summary, it can be concluded that the interdisciplinary approach of the DFG SPP1740 showed that the fluid dynamic conditions can impact the proceeding of chemical reactions in an industrial context, though it must be stated that the gained insights are limited to the laboratory scale and need to be transferred onto larger systems in the future [Sch21].

Chapter 2

State of Knowledge

In order to outline the framework of this work and to derive some necessary fundamental principles, firstly, a brief overview about bubbly flows, the behavior of freely rising bubbles and the effect of confining walls on the bubble motion are given. Subsequently, the focus is laid on the fundamentals of Taylor bubbles, their fluid dynamic behavior, shape, and wake dynamics. Afterwards, the most relevant mass transfer models are introduced, the occurring mass transfer phenomena at Taylor bubbles are discussed and governing mechanisms of reactive mass transfer are thematized. To conclude this chapter, the influence of mixing on chemical reactions and available information on reactive model systems and suitable measurement techniques are presented and discussed.

2.1 Bubbly Flows

Bubbly flows are multiphase applications, where a gaseous species is dispersed into a continuous liquid phase. Usually, the gaseous species is dissolved into the liquid phase in order to enable a chemical or biological conversion. Commonly used apparatuses in industry are for example bubble columns with and without static mixing devices, slurry reactors containing a third, solid phase, often acting as a catalyst, or monolith reactors. The advantages of these concepts are large effective interfacial areas, a high overall mass transfer performance, a low space demand, an adjustable residence time and intense mixing. However, there are also several disadvantages. In particular the influence on mixing in the reactor due to the fluid dynamic conditions, bubble-bubble interactions and the occurring bubble induced turbulence are challenging to predict. This makes it difficult to accurately estimate the reactor performance in terms of yield and selectivity [Sha82, Kra20]. The fluid dynamic conditions in bubbly flows can be influenced by several parameters, which are the superficial gas velocity $v_{\mathrm{g},0}$, the superficial liquid velocity $v_{\mathrm{l},0}$, the reactor diameter D_r and the gas hold up ε_g. The

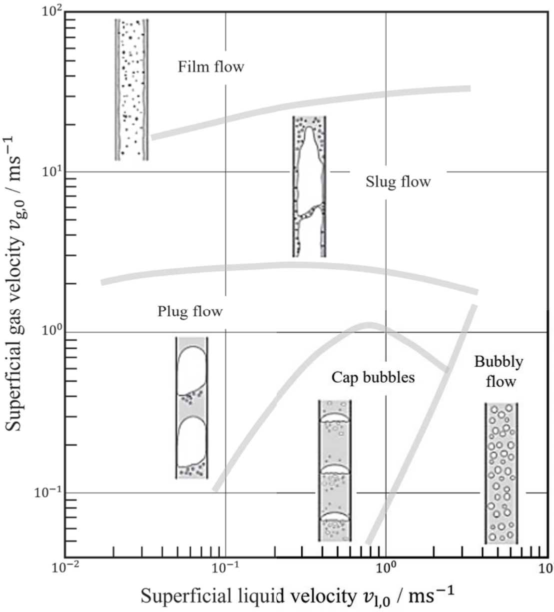

Figure 2.1: Flow regimes in a narrow channel $D_r = 0.1$ m in dependency of the superficial gas velocity $v_{g,0}$ and superficial liquid velocity $v_{l,0}$ according to [May82]

gas hold up is the ratio of the gas volume V_g and the total reactor volume, which is the sum of the liquid volume V_l and the gas volume $V_{tot} = V_g + V_l$, such that $\varepsilon_g = V_g V_{tot}^{-1}$. According to Shah et al., three different flow regimes in bubble columns can be distinguished, depending on the superficial gas velocity and the reactor diameter: homogeneous flow, heterogeneous flow and slug flow [Sha82]. The homogeneous flow regime occurs at low superficial gas velocities and is characterized by a narrow bubble size distribution and a uniform distribution of the gas across the reactor cross-section. At large reactor diameters and with increasing gas load, the heterogeneous flow regime is reached. This leads towards the formation of large bubbles, bubble-bubble interactions as coalescence or bubble break up and therefore a broader bubble size distribution. In addition, large bubbles tend to rise along the center axis at a high rise velocity, causing mixing zones close to the reactor walls, trapping smaller bubbles. The resulting bubble size distribution across the cross-section and accumulation of large bubbles in the center axis causes local density differences, leading to a downward flow close to the reactor walls. If the reactor diameter is rather narrow ($D_r < 0.1$ m) as it often is the case in laboratory setups, an increasing gas load results in a slug flow and the bubble rise is affected by wall effects, which are stabilizing the bubble shape [May82].

As bubbly flows in narrow channels differ from those in wide bubble columns due to arising wall effects, the flow regimes need to be further differentiated. Mayinger et al. provide a flow map for a bubbly flow in a narrow channel with a diameter of $D_\mathrm{r} = 0.1\,\mathrm{m}$. They report different flow regimes in dependency of the superficial gas and liquid velocities, which range from bubbly, film or annular, to plug or slug flow [May82]. The type of phase distribution in the vertical tube depends on the interaction of the shear, inertia and surface forces. The resulting flow map is displayed in Figure 2.1. From the reported flow patterns in tubes, slug flow marks the most important one, due to numerous technical applications such as vapor-liquid absorbers, vapor generators, reboilers, buoyancy-driven fermenters, in monolith reactors and many others [Mor16].

2.1.1 Fluid Dynamics of Freely Rising Bubbles

Technical multiphase applications, as for example bubble columns, are usually operating at a high gas hold up ε_g, causing a large specific interfacial area a, a high degree of mixing and a good mass transfer performance. In nearly all processes, bubbles rise in swarms or plumes, causing complex wake effects, bubble break up or coalescence and bubble induced turbulence. Furthermore, the rise velocity defines the residence time of the bubbles in the system and is influencing the bubble boundary layer, which significantly influences the mass transfer from the gaseous to the liquid phase. Although the fluid dynamic behavior of single rising bubbles differs from the one of bubble swarms, single bubble experiments have been seen as a suitable instrument to reduce complexity, in order to investigate the motion of bubbles, before transferring gained knowledge to more sophisticated bubble swarms with stochastic characteristics. Therefore, the motion of individual gaseous particles or bubbles in a stagnant liquid phase, commonly demineralized water, has been the topic of several comprehensive studies in the past e.g., Peebles and Garber [Pee53], Clift et al. [Cli92], Fan and Tsuchiya [Fan90] or Tomiyama et al. [Tom02].

The fluid dynamic behavior of bubbles is influenced by several effects, which are all interdependent: the bubble size, the bubble shape, interfacial effects due to surface tension or surfactants, the rise velocity and the bubble trajectories. Although, according to literature, bubbles can be parameterized by three dimensionless numbers. Those are the already introduced Eötvös number (cf. Equation 1.4), the bubble Reynolds number

$$Re = \frac{v_\mathrm{b} D_\mathrm{b} \rho_\mathrm{l}}{\eta} \tag{2.1}$$

and the Morton number

$$Mo = \frac{g\eta^4\left(\rho_\mathrm{l}-\rho_\mathrm{g}\right)}{\rho_\mathrm{l}^2\sigma^3}, \tag{2.2}$$

with ρ_l and ρ_g denoting the density of the liquid and gaseous phase, η the dynamic viscosity of the liquid phase, g the gravity, σ the interfacial tension and v_b the velocity of the bubble. The bubble diameter D_b is usually set equal to the volume equivalent bubble diameter D_eq. The Reynolds number, commonly used to characterize the induced flow of a bubble or particle in a fluid as well as the fluid flow conditions itself, depicts the ratio of inertial to viscous forces. The Morton number is specified solely by substance properties and depicts the ratio of viscous forces to surface tension forces. Based on those three dimensionless quantities, Clift et al. derived a flow map, given in Figure 2.2, which has been used for the prediction of the bubble shapes in the past decades with great success [Cli92].

The rise velocity of a single bubble v_b, which is not further accelerated and in steady state, is defined by the expression

$$v_\mathrm{b} = \sqrt{\frac{4}{3}\frac{\left|\rho_\mathrm{l}-\rho_\mathrm{g}\right|}{\rho_\mathrm{l}}gD_\mathrm{b}\frac{1}{\zeta_\mathrm{D}}} \tag{2.3}$$

resulting from the equilibrium of the acting buoyancy and drag forces and with ζ_D representing the drag coefficient.

From Equation 2.3 it becomes evident, that the bubble rise velocity is dependent on the drag force, pointing in the counter direction of the bubble motion. Based on the work of Peebles and Garber [Pee53], the drag coefficient is a function of the Reynolds number, displayed in Figure 2.3, defining four bubble regimes:

(A)	Spherical bubbles with an immobile interface acting as solid particles
(B)	Spherical bubbles with internal circulation and a mobile interface
(C)	Ellipsoidal bubbles with internal circulation and a mobile interface
(D)	Irregular shaped bubbles

For bubbles with small diameters, where the Reynolds number $Re < 1$, the viscous forces dominate and bubbles can be usually seen as rigid spheres. In this case, the drag coefficient of bubbles can be described according to Stoke's law

$$\zeta_\mathrm{D} = \frac{24}{Re}. \tag{2.4}$$