

Abstract

Reactive bubbly flows are widely used in industrial processes to perform fast gas-liquid reactions, although the investigations are already intensified in the 1970s, a reliable prediction of yield and selectivity for fast parallel/consecutive reactions is still not possible. In this work different benchmark setups are developed to investigate the influence of mixing on mass transfer and chemical reaction. These setups will allow the investigation of a parallel/consecutive reaction in the same manner in the future.

For a reliable prediction of the yield and selectivity, the accurate determination of the intrinsic kinetics without mass transfer limitation is required. An experimental setup based on the SuperFocus-Mixer (SFM) is developed and successfully used to determine the kinetics of the oxidation of sodium sulfite in combination with numerical simulations.

The knowledge of the intrinsic kinetics allows the investigation of the reactive mass transfer in bubbly flows in more detail. As a first step, todays techniques are applied to a known problem, the rectilinear bubble rise (bubble diameter d_b below 1 mm), to gain data as a reference for numerical simulations. Planar laser induced fluorescence (p-LIF) is applied to determine local concentration fields, which enables the evaluation of the mass transfer coefficient through mass balancing. The results of rise velocity and mass transfer coefficient testify a surfactant behavior of the fluorophore, which is so far not considered within the literature.

In a second step, with a higher degree of complexity, the physical and reactive mass transfer in case of bubble-bubble interactions is investigated. By the use of background illumination recording, the mass transfer coefficient in dependency of the bouncing frequency is quantified and key effects for mass transfer enhancement are identified by analysis of local concentration fields. Based on the findings, a semi-empirical model for the description of the determined dependency is developed.

For the development of parallel/consecutive reaction systems for gas/liquid flows, that are applicable under academic conditions, a setup with small volume is required, which allows detailed investigations at different mixing conditions already in a small volume.

The system of choice is the Taylor bubble experiment that has been developed within the DFG SPP 1740 with a few adaptations for oxygen exclusion. With different substance and reaction systems it is proven that the results are transferable and reliable.

Because the wake structure of free rising bubbles above $d_b < 1$ mm typically not show a rotational symmetry, within this work the time resolved scanning laser induced fluorescence (TRS-LIF) technique is used to investigate the three-dimensional concentration field. Additionally, separation points are easily identified by this technique, so that significant data for numerical validations are supplied.

This thesis contributes within the SPP 1740 "Reactive Bubbly Flows" to a better understanding of gas-liquid reactions in bubbly flows. Within this framework, several cooperations are used to develop

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an approach for the detailed investigation of parallel/consecutive reactions. Additionally, new insights in mass transfer processes at rectilinear rising bubbles, bubble-bubble interactions and wake structures are obtained. Furthermore, a model for the description of bubble bouncing is developed, which can be included in numerical simulations of bubble columns.

Zusammenfassung

Obwohl reaktive Blasenströmungen bereits vielfach in der chemischen Industrie zur Durchführung von gas-flüssig Reaktionen verwendet werden und die Untersuchung derselben bereits mit dem Beginn der 1970er Jahre intensiviert wurden, ist die Vorhersage von Ausbeute und Selektivität schneller, paralleler oder konsekutiver Reaktionen bisher noch nicht möglich.

Um eine belastbare Vorhersage von Ausbeute und Selektivität chemischer Reaktionen zu erreichen, ist eine genaue Bestimmung der intrinsischen Kinetik ohne Stofftransport Limitierung erforderlich. In dieser Arbeit wurde daher ein Versuchsaufbau basierend auf dem SuperFocus Mischer (SFM) entwickelt und erfolgreich eingesetzt, um die Kinetik der Sulfitoxidation zu bestimmen.

Die Kenntnis der intrinsischen Kinetik erlaubt den reaktiven Stofftransport in Blasenströmungen detailliert zu untersuchen. Dazu wird in einem ersten Schritt ein bereits bekanntes Problem, der geradlinige Blasenaufstieg (Blasendurchmesser d_b unter 1 mm), detailliert betrachtet und mit numerischen Ergebnissen validiert. Zu diesem Zweck werden unter Verwendung der planaren Laser Induzieren Fluoreszenz (p-LIF) lokale Konzentrationsfelder aufgezeichnet und der Stofftransportkoeffizient ermittelt. Die Ergebnisse der Blasenaufstiegsgeschwindigkeit und Stofftransportkoeffizienten belegen, dass der verwendete Fluoreszenzfarbstoff als oberflächenaktive Substanz fungiert, was in der aktuellen Literatur bisher jedoch nicht berücksichtigt wird. Basierend auf diesem Ergebnis werden von der Arbeitsgruppe Bothe an der TU Darmstadt numerische Simulationen durchgeführt, welche die experimentellen Ergebnisse ebenfalls bestätigen.

In einem zweiten Schritt, mit einer erhöhten Komplexität, wird die Auswirkung von Blase-Blase-Interaktionen auf den physikalischen und reaktiven Stofftransport untersucht. Mithilfe von Gegenlichtaufnahmen wird zunächst der Stofftransportkoeffizient in Abhängigkeit der Stoßfrequenz ermittelt und anschließend basierend auf diesen Ergebnissen ein semiempirisches Modell zur Beschreibung dieser Abhängigkeit entwickelt. Um Schlüsselschritte zu identifizieren, erfolgt eine Bestimmung lokaler Konzentrationsfelder mittels p-LIF. Die beobachteten Phänomene werden anschließend in einer modellhaften Beschreibung zusammengefasst.

Zur Entwicklung eines parallelen bzw. konsekutiven Reaktionssystems in gas/flüssig Strömungen bei akademischen Bedingungen, muss ein Versuchsaufbau gefunden werden, der eine detaillierte Untersuchung bei unterschiedlichen Mischungszuständen und gleichzeitig kleinem Probenvolumen erlaubt. Das Taylor Blase Experiment, welches innerhalb des DFG SPP 1506 entwickelt wurde, erscheint mit kleineren Änderungen, wie beispielsweise dem Ausschluss von Sauerstoff, als geeignet. Durch Versuche mit unterschiedlichen Reaktions- und Stoffsystmen wird gezeigt, dass die Ergebnisse dieses Versuchsaufbaus belastbar und eine Übertragung auf allgemeine Blasenströmungen möglich ist.

Ellipsoide und formdynamische Blasen, wie sie in realen Blasenströmungen auftreten, zeigen jedoch keine so gut einstellbare Nachlaufstruktur wie Taylor Blasen oder eine Symmetrie wie kleine

Blasen ($d_b < 1$ mm). Daher muss eine Technik gefunden werden, die es erlaubt auch diese komplexen Nachlaufgebiete zu visualisieren. Im Rahmen der vorliegenden Arbeit wird dazu die Time Resolved Scanning Laser Induzierte Fluoreszenz (TRS-LIF) weiterentwickelt und eingesetzt, um dreidimensionale Konzentrationsfelder zu untersuchen. Zusätzlich erlaubt diese Technik auch das Aufzeigen von Separationspunkten und liefert daher wichtige Daten für eine numerische Validierung.

Die vorliegende Arbeit wird im Rahmen des SPP 1740 „Einfluss lokaler Transportprozesse auf chemische Reaktionen in Blasenströmungen“ mit dem Ziel eines besseren Verständnisses von gasflüssig-Reaktionen in Blasenströmungen durchgeführt. Innerhalb dieses Netzwerks werden zahlreiche Kooperationen erfolgreich initiiert um einen experimentellen Ansatz zur detaillierten Untersuchung von parallelen und konsekutiven Reaktionen zu entwickeln. Zusätzlich werden neue Einblicke in die Stofftransportvorgänge bei geradlinigem Blasenaufstieg, bei Blase-Blase-Interaktionen und freiem Blasenaufstieg formdynamischer Blasen erreicht. Darüber hinaus wird ein Modell zur Beschreibung von Blasenkollisionen entwickelt, welches sich zur Verbesserung der numerischen Simulation von Blasensäulen eignet.

Chapter 1

Introduction

Bubbly flows are widely used within chemical process engineering to perform fast gas-liquid reactions, like for example oxidations, hydrogenations, chlorinations or alkylations. Typically the bubbles are irregularly in shape and are inducing complex flow structures within the bulk phase during the buoyancy driven rise. Until today, these complex flow structures are evading from an encompassing understanding and the influence on mixing, mass transfer and chemical reactions is as well unknown. Especially the mass transfer from the bubble into the boundary layer is tough to grasp, but has to be understood for a description of the influence on yield and selectivity of chemical reactions. The selectivity within this work is defined as

$$S_p = \frac{Y_p}{X_i} \quad (1.1)$$

Where X_i is the conversion and describes the ratio of the reacted amount of substance n_i to the total amount of reactant $n_{i,0}$

$$X_i = \frac{n_{i,0} - n_i}{n_{i,0}} \quad (1.2)$$

and Y_p is the yield which is defined as the ratio of the amount of substance of a specified product n_p and a reference amount of substance $n_{ref,0}$ under consideration of the stoichiometry (v_{ref} , v_p) [Bae87]

$$Y_p = \frac{n_p - n_{p,0}}{n_{ref,0}} \frac{|v_{ref}|}{v_p} \quad (1.3)$$

The clarification of this process is vital, since the timescales of mixing are dominating yield and selectivity through boundary layer deformations, interactions between bubbles and turbulences induced by the surrounding bubble swarm. To enable an effective utilization of the gaseous phase with a minimum energy consumption, optimal contact times and high mass transfer rates for process intensification and optimization are required and therefore a reliable and exact design of multiphase reactors have to be performed. So far empirical and semi-empirical correlations from literature or ascertained by lab/pilot plant experiments are mostly based on integral data. These correlations, like equation 1.6, usually consider the bubble diameter d_b , rise velocity w_b represented by the Reynolds number Re

$$Re = \frac{w_b d_b \rho}{\eta_l} \quad (1.4)$$

and substance system represented by viscosity η , diffusion coefficient D represented by the Schmidt number Sc

$$Sc = \frac{\nu}{\rho D} . \quad (1.5)$$

The transport resistance is dedicated as an influence of the fluid phase and the local hydrodynamic due to bubble swarms, like the mixing in chaotic wake structures, are considered within these correlations in the form of constants C_1 or exponent's a, b according to

$$Sh = 2 + C_1 \cdot Re^a \cdot Sc^b . \quad (1.6)$$

In addition to these classical descriptions, gas bubbles are considered since a few years more as a local mixing element, which allows a new control of reactive processes.

Within the priority program SPP 1740 "Reactive Bubbly Flows" of the German Research Foundation (DFG), a close interaction between engineering, chemistry and mathematics on the field of gas/liquid mass transfer with superimposed reaction is realized. This thesis contributes within the priority program to a better understanding of gas-liquid reactions.

Chapter 2

State-of-the-art

The design of gas-liquid reactors is a laborious task due to its interdisciplinary conjunction of chemical (reaction kinetics) and physical (fluid mechanics, molecular diffusion, etc.) processes. Figure 2.1 shows schematically the stages of a design process for gas-liquid reactors [Alp83].

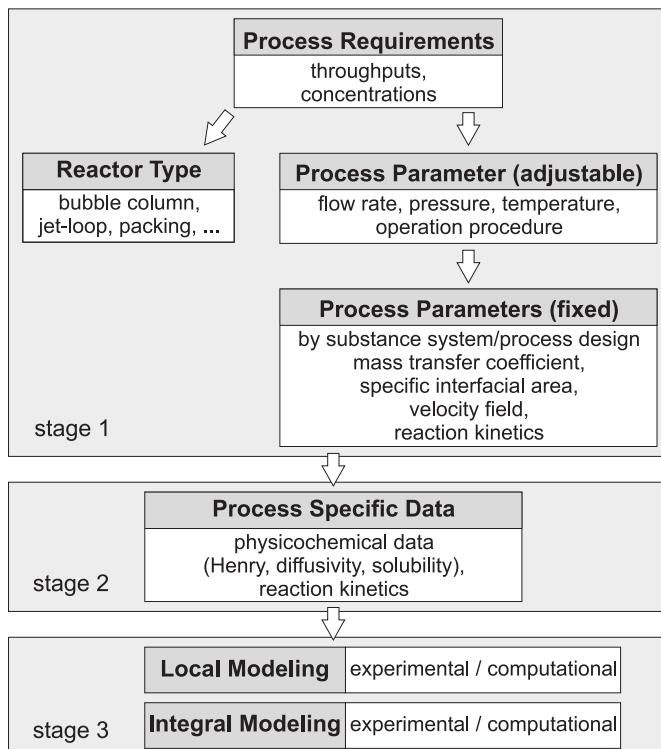


Figure 2.1 Procedure for the design of gas-liquid reactors according to Alper [Alp83].

At first the process requirements like throughput and concentrations have to be specified and lead to a variety of adjustable parameters such as temperature, pressure, flow rates or reactor type. Defining these parameters is not easy to accomplish and is today mostly based on empirical or semi-



empirical correlations combined with numerical simulations. The mass transfer coefficient, the specific interfacial area, the reaction kinetics or the velocity field are typically not easily adjusted in a static geometry and are therefore fixed parameters and have to be determined within the design process.

In a second stage of process design, the fixed parameters and process specific data, like solubilities, diffusivities or reaction kinetics, are determined by experimental investigations on lab or pilot scale. These data depend strongly on the substance system and have to be determined at the operating conditions to gain a similar behavior.

Within the last stage of the design procedure, local and integral scale modeling is performed to compute the expectable performance. Several models allow already a description of flow structure or chemical reaction. Beside these complex and often inaccurate theoretical modeling, also laboratory experiments on local and/or integral scale are used. These experimental investigations often enable to bypass the experiments performed in stage two. Nevertheless, all parameters of stage one are required for a reliable design.

While a detailed procedure for designing gas-liquid reactors already exists, the prediction of yield and selectivity is still insufficient and is typically adjusted within pilot and production scale experiments. However, an improvement of energy consumption and yield is often still possible, so that a more accurate prediction is aimed by actual research and industry through gaining more detailed information about the processes occurring in bubbly flows and their influence on mass transfer and following chemical reactions.

2.1 Bubbly Flows

The flow regime within gas-liquid reactors strongly influences the yield and selectivity of chemical reactions due to the different degrees of mixing and back mixing through the interaction of bubbles with each other and the occurring turbulence [Kaš93]. Figure 2.2 a) shows the possible flow regimes within bubble column reactors in dependency of column diameter and superficial gas velocity in a watery system [Sha82]. Additionally, the flow regime is influenced by the type of gas distributor, column internals, liquid flow rate and the substance system, which in combination is the reason for a very broad transition band.

Three major flow regimes are distinguished: homogeneous, heterogeneous and slug flow. The homogeneous bubbly flow is characterized by a narrow bubble size distribution with a nearly similar bubble rise velocity and a uniform distribution across the column diameter at a low superficial gas velocity (up to $w_g^0 = 0.03 \text{ m}\cdot\text{s}^{-1}$). At very low superficial gas velocities, a small bubble size, a unidirectional rise and small velocities similar to the free rise of single bubble results. As a consequence the bubbles do not move significantly in horizontal direction and only small mixing through bubble interactions and macro turbulence occurs, so that a uniform distribution of gas holdup in radial and axial direction is observed [Kaš93].

With rising superficial gas velocity above $w_g^0 = 0.05 \text{ m}\cdot\text{s}^{-1}$ the gas hold up is increasing and a turbulent flow structure with irregular distribution results.

At column diameters above approximately 0.15 m a heterogeneous bubbly flow is observed. Due to the rising gas hold up, a frequent interaction between bubble-bubble and bubble-wake occurs, so that higher shear and pressure stresses influence the bubbles and lead to break up and coalescence.

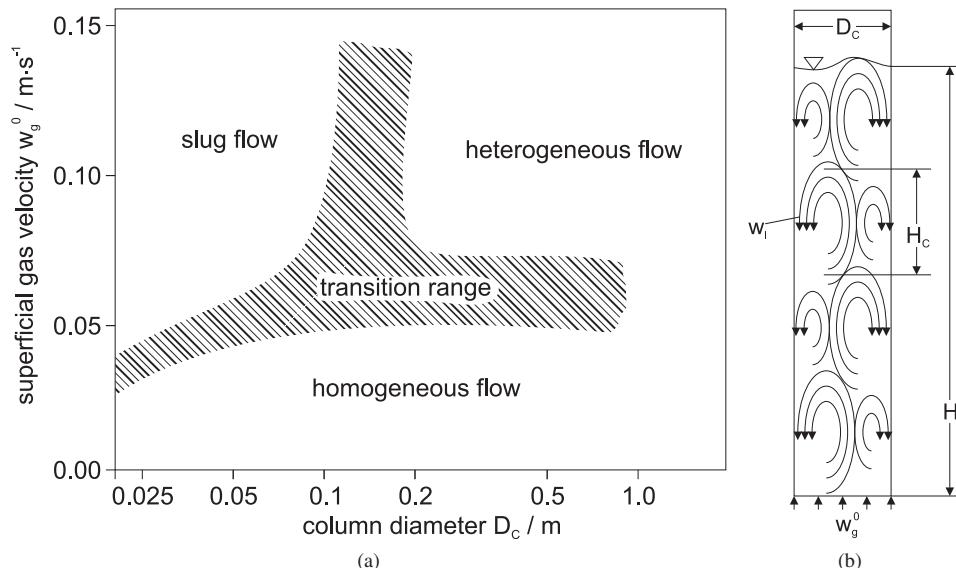


Figure 2.2 (a) Approximated dependency of flow regimes in bubble column reactors on gas velocity and column diameter in a watery system according to Shah [Sha82]. (b) Scheme of mixing zones in a bubble column reactor [Kra12].

Therefore a broad bubble size distribution with slow to fast rising bubbles is found. While the largest bubbles rise preferred in the column center with a velocity up to $1 \text{ m} \cdot \text{s}^{-1}$, the smallest bubbles are trapped in back mixing zones close to the wall [Kaš93]. Therefore, a density distribution across the column causes a downward flow close to the wall and an upwards flow in the column center, so that back mixing zones like shown in figure 2.2 b) results. The intensity of these zones depends on the superficial gas velocity, column diameter, bubble size distribution and other parameters [Kra12]. Large bubbles represent the major part of the overall gas throughput, but have a small surface to volume ratio with a small residence time, so that the contribution to mass transfer is low, but dominates the flow structure and back mixing. Nonetheless, or actually because of these observations, it is assumed that small bubbles are mainly contribute to the mass transfer performance [Kaš93].

At small column diameters below 0.15 m , which are typically used within lab scale experiments, slug flow at high gas flow rates is observed. The column diameter is here in the range of the bubble diameter, so that wall-effects are affecting the rise by stabilizing the bubble shape and lowering of the rise velocity and a characteristic slug is formed [Kra12].

2.1.1 Bubble Shape and Rise Velocity of Bubbles

The rise velocity w_b of gas bubbles within a bubble column determines several crucial parameters that affect the mass transfer performance. As already described above, the gas hold up is mainly influenced by the bubble size distribution which also determines the bubble rise velocity. Additionally, the residence time and therefore the contact time between gas and liquid phase, respectively the boundary layer thickness, are significantly influenced.



Due to the size and shape distribution additionally to the flow regime in bubble columns, a broad velocity distribution results and is typically taken into account within the design process as an averaged velocity (\bar{w}_b)

$$\bar{w}_b = \frac{\sum_{i=1}^{i=n} w_{b,i}}{i} \quad (2.1)$$

where n is the number of velocities. Many workers (e.g. [Nic62, Zub65, Bra71a, Uey79, Zeh85]) developed empirical correlations to describe the relative bubble velocity within a bubble swarm ($\bar{w}_{b,rel} = w_b - \bar{w}_l$) based on the rise velocity of a single bubble. In case of a stagnant bulk phase, the relative velocity is equal to the absolute velocity ($\bar{w}_{b,rel} = w_{b,abs} = \bar{w}_l$) [Sch02]. One example is the correlation according to Zehner [Zeh85]

$$\bar{w}_{b,rel} = w_b (1 - \varepsilon_g)^{m(1 + \frac{q\delta}{d_b})^2} \quad (2.2)$$

where δ is the thickness of the velocity boundary layer and d_b the bubble diameter. By fitting this semi-empirical correlation to experimental data, the constants are set to $m = 1.75$ and $q = 3/4$. This correlation is deduced for solid spheres, but it has been shown, that the correlation is also valid for bubble swarms by Zehner [Zeh88], if the bubble velocity and bubble diameter are calculated according to Mersmann [Mer77].

Single Bubble Rise

While the influence of the flow regime on the rise velocity is already revealed, still the behavior of single bubbles is used as a parameter for the design of bubble column reactors. The rise velocity of a single bubble is determined, in the simplest case, by the size and shape through the equilibrium of buoyancy force F_b

$$F_b = d_b^3 \frac{\pi}{6} g (\rho_l - \rho_g) \quad (2.3)$$

and drag force F_d

$$F_d = c_d d_b^2 \frac{\pi}{4} \frac{\rho_l w_b^2}{2} \quad (2.4)$$

in a stagnant liquid. Identifying equation 2.3 with 2.4 and conversion to w_b lead to

$$w_b = \sqrt{\frac{4}{3} \frac{d_b g (\rho_l - \rho_g)}{c_d \rho_l}} \quad (2.5)$$

where g is the gravitational constant, ρ_l the liquid density, ρ_g the gas density and c_d the drag coefficient. However, the rise velocity in bubbly flows is typically not described that easy, due to superimposed liquid flow fields, that influence the rise velocity. The drag coefficient of a rising bubble is in difference to the drag of a solid sphere, which depends mainly on size and shape, additionally influenced by the deformation of the shape. Since a complex combination of compressibility and density gradients additionally to the interdependency between shape, size and flow around the bubble exist, a continuous description of the drag coefficient is not found so far. Figure 2.3 shows a scheme