



# 1 Introduction

In bubble column reactors, 30 million tons of intermediate and final products are annually produced. Despite frequent application, the complex flow conditions and the enormous number of coupled parameters which determine the mass transfer between the liquid and gaseous phase are still hardly predictable. Thus bubble column reactors are still designed by using semi-empirical equations. In order to reach a more tailored and improved design, modeling of mass transfer performance has to be enhanced. For this purpose, basic research into large-scale plants must be safely transferred. The fundamental condition for this transfer is the formulation of models independently of dimensions, in other words with consideration of scale overlapping effects.

Models available until now do not only comply this but are mostly not sufficiently validated, particularly under industrial conditions, such as organic solvents under elevated pressure and temperature. This can likely be attributed to the lack of experimental investigations under equivalent conditions. In turn this is due to the fact that measurement techniques must be applicable in organic solvents at elevated pressure and temperature.

Motivated by the fact that a lot of knowledge exists about the test system water/air but in turn less experience with organic solvents under elevated pressure, the aim of this thesis is to investigate the organic substitution system for the hydroformylation reaction, cumene/nitrogen, under industrial conditions. As a first step single bubbles are considered to study the influence of the pressure on shape, size and velocity as well as the verification, if the well-known equations are able to describe the single bubble behavior. In order to be able to predict in a more rigorous way the behavior of BCRs by using local parameters, a measurement method for determining bubble sizes as well as bubble velocities under the above mentioned conditions is developed. The target of the investigations is the specific interfacial area which is the essential parameter for dimensioning BCRs, when dealing with mass transfer limited systems. The specific interfacial area depends on the gas holdup which in turn is determined by the relative velocity of the bubble. Therefore measurements of the liquid and absolute bubble velocity are obtained with the purpose of calculating the relative velocity.

In association with the present thesis, the joint research project “Chemical Processes: Multiscale Modeling of Multiphase Reactors (Multi-Phase)” (Ref.-No. 01RC1102) funded by the Federal Ministry of Education and Research (BMBWF) was initiated in November 2011. Experimental studies, development of



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measurement techniques, modeling, as well as CFD simulation were combined in order to improve the design and to optimize bubble column reactors.

## 2 State-of-the-Art

### 2.1 Design and Operation of Bubble Column Reactors

Bubble column reactors (BCRs), an example of multiphase reactors, have been proven effective for a variety of chemical reactions and thus, are widely used in the chemical and biochemical industries. Typical reactions are oxidation, hydrogenation, chlorination, phosgenation, hydroformylation and alkylation as well as fermentation processes [Zeh00].

The Hock process, an example of an oxidation reaction according to **Figure 2.1** for the synthesis of phenol and acetone, is usually applied in bubble column reactors with an annual production of 1,870 kt of phenol and 1,160 kt of the co-product acetone [INE14]. This large capacity is feasible due to volumes of 100- 300 m<sup>3</sup> in industrial bubble column reactors whereas reactors that perform fermentations, such as for protein production from methanol, have even capacities of approximately 3,000 m<sup>3</sup>. The largest units are employed for waste-water treatment with a volume of 20,000 m<sup>3</sup> [Zeh00]. Beside the fact that no moving parts are employed, BCR are known for good heat removal as well as for the conversion of safety critical gas and liquid systems under elevated pressure and temperature [Dec85]. Depending on the specific application, different designs and operation modes of bubble column reactors as well as gas distributors are used.

#### 2.1.1 Types of Bubble Column Reactors

The simplest design of the BCR can be seen in **Figure 2.2 A**. The gas phase, induced at the bottom into the liquid phase, rises due to buoyancy. A third phase such as inert, catalyst or reactive particles can also be contained in the liquid phase. The simple BCR can be operated in semi-batch mode, where the batch is in respect to the liquid phase, or in a continuous mode. The liquid

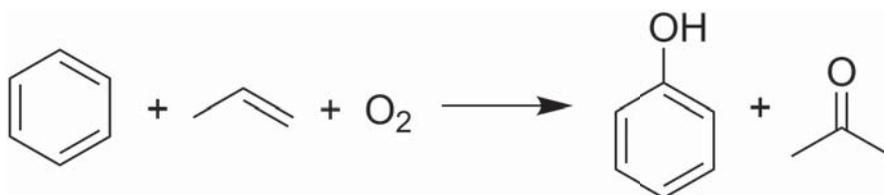


Figure 2.1: Reaction equation of the Hock process.

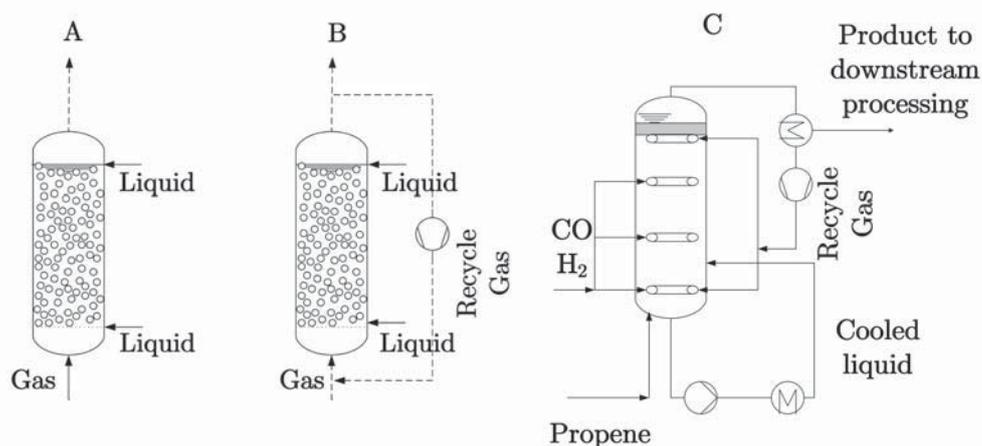


Figure 2.2: Configuration of the simple bubble column (A) and simple bubble column with recycled gas (B). Reactor configuration for the hydroformylation of propene [Zeh00] (C).



Figure 2.3: Reaction equation for the hydroformylation of propene.

phase can also be operated in a co-current or counter-current operation mode. In the case that the gas still contains valuable reactants at the outlet, it can be recycled (**Figure 2.2 B**). One application of the simple bubble column is the homogeneously catalyzed hydroformylation of propene according to **Figure 2.3** with carbon monoxide (CO) and hydrogen (H<sub>2</sub>) as synthesis gas. As can be obtained from **Figure 2.2 C**, non-completely reacted gas is reversed. Two additional levels are used for the gas recycling with the purpose of avoiding the formation of large bubbles which in turn would lead to a limitation of the mass transfer from gaseous into the liquid phase. Due to the high exothermic reaction, heat removal is supported by an external cooling loop. After the reaction zone, separation of the hydroformylation product and gas is done by condensation. [Zeh00]

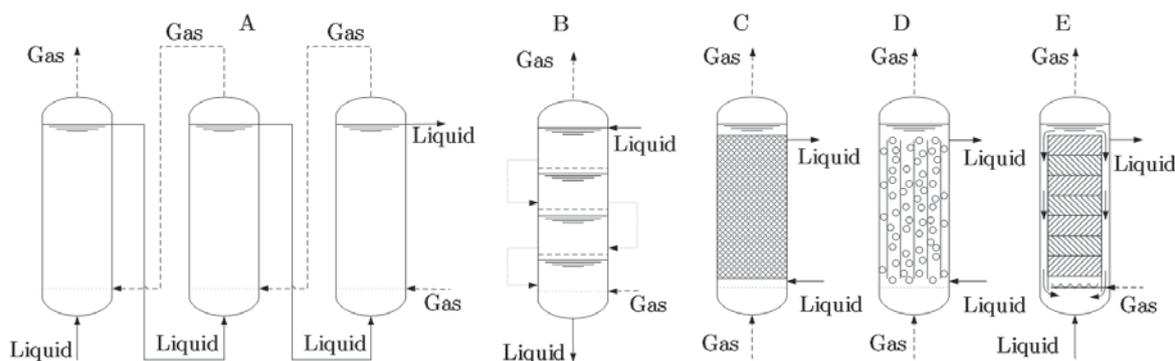


Figure 2.4: Types of bubble column reactors: A) cascade of three bubble columns B) bubble column cascade with sieve plates C) packed bubble column D) multishaft bubble column E) bubble column with static mixers.

Apart from the simple design of a BCR, different implementations according to the particular requirements in modern complex chemical and biochemical engineering are used. Configurations of BCRs can be separated into bubble column reactors *with* and *without* liquid circulation. In **Figure 2.4** typical configurations *without* a hydraulic circuit are shown such as a bubble cascade (**Figure 2.4 A**) by connecting several reactors or using trays (**Figure 2.4 B**). Advantages are a comparable narrower residence time distribution as well as an opportunity for an effective counter-current flow [Ger79]. By using the trays the distribution of gas is rearranged, therefore large bubbles are eliminated and the mass transfer process is intensified [Dec85]. The back-mixing of gas and liquid phases in the simple bubble column and the non-uniform distribution of gas bubbles over the cross-section can be also reduced by the installation of packings (**Figure 2.4 C**) or shafts (**Figure 2.4 D**). In order to set up the most homogeneous possible bubbly flow, static mixer elements can also be placed in the ascending flow section (**Figure 2.4 E**).

BCR *with* a hydraulic circuit are shown in **Figure 2.5**. In the case that a longer residence time of the gas phase is required, a down-flow bubble column (**Figure 2.5 A**) can be employed. In loop reactors, shown in **Figure 2.5 B** and **C**, an internal circulation is produced by the drag effect of the bubbles and the density difference of gas and liquid phases.

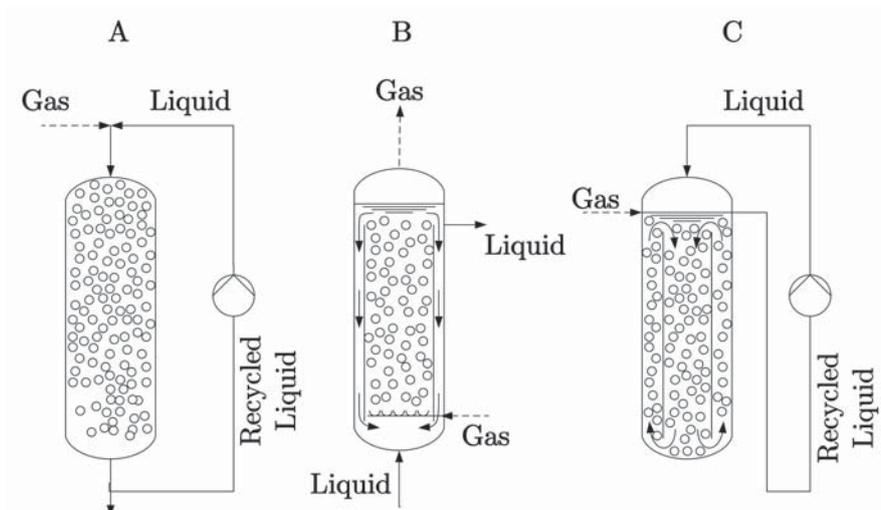


Figure 2.5: Configurations of bubble columns with directional liquid circulation: A) down-flow bubble column; B) jet loop reactor; C) jet loop reactor with external circulation.

### 2.1.2 Gas Distribution

Besides the design and operation mode of the BCR, gas distribution is affected by the important hardware settings. In order to get an optimal mass transfer, the gas is dispersed by creating small bubbles, distributed homogeneously throughout the column.

Gas distributors can be divided into static and dynamic. Some typical designs of “static” gas spargers are shown in **Figure 2.6**. In this case bubble formation is done without any additional energy supplied from outside. The dip tube, as the simplest of these devices (**Figure 2.6 A**), leads to a uniform gas distribution with some distance behind the gas sparger. Whereas a more effective way is the usage of perforated plates (**Figure 2.6 B**), perforated ring spargers (**Figure 2.6 C**) or porous plates (**Figure 2.6 D**). A certain minimum

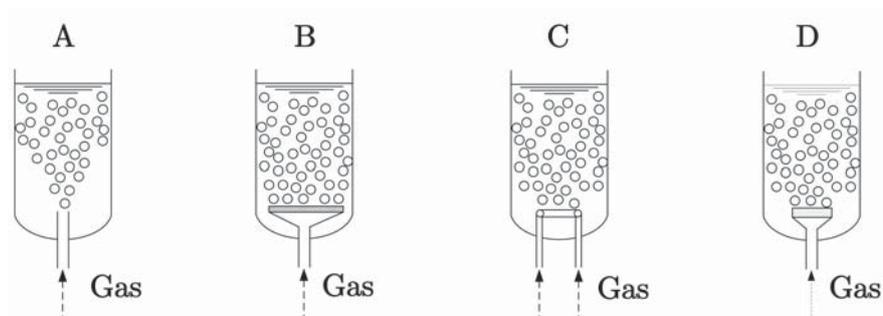


Figure 2.6: Static gas spargers: A) dip tube; B) perforated plate; C) perforated ring sparger; D) porous plate.

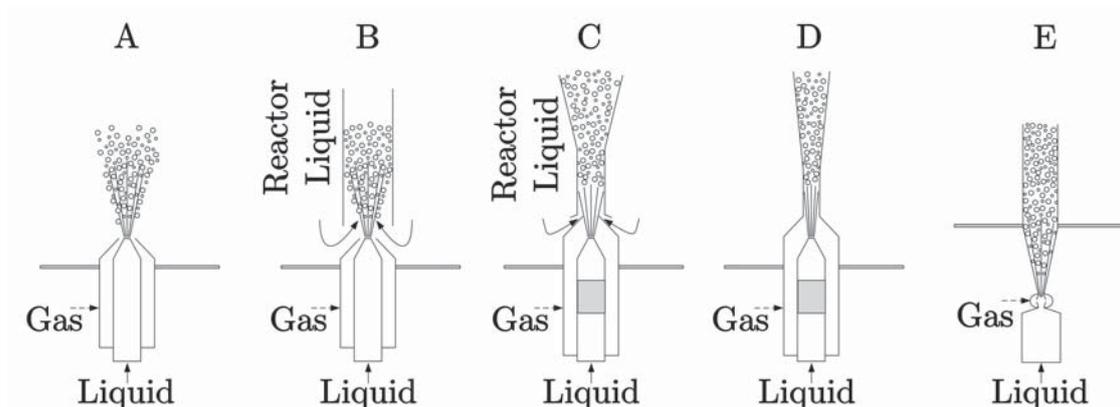


Figure 2.7: Dynamic gas distributors: A) two-phase jet nozzle; B) two-phase jet nozzle with momentum-transfer tube; C) ejector jet nozzle; D) ejector; E) venturi nozzle.

gas flow rate is required to achieve uniform distribution and to prevent the liquid from getting into the sparger. Porous plates are used for generating very fine bubbles. However, there are sometimes problems in industrial application due to fouling.

Dynamic spargers offer an alternative to the static types, particularly if the interfacial area is the essential design parameter, i. e. for mass transfer limited reactions. They use the power of a liquid jet to disperse gas in a region where the energy dissipation rate is high. **Figure 2.7** illustrates several frequently used dynamic gas spargers. The simple two-phase jet nozzles (**Figure 2.7 A**) as well as those with a momentum-transfer tube (**Figure 2.7 B**) are not able to simultaneously disperse and suck the gas stream. This can be achieved, however, with the ejector jet nozzle (**Figure 2.7 C**), the ejector (**Figure 2.7 D**), and the Venturi tube (**Figure 2.7 E**). In nozzle design the ratio of the gas–liquid volumetric flow rates must always be considered as the critical parameter. Common values lie between 0.5 and 2 [Zeh00].

## 2.2 Modeling of Bubble Column Reactors

Before the 1970s only a few publications were available concerning the modeling of bubble column reactors. After interest grew, many empirical correlations and theoretical models to describe the behavior of bubble column reactors were published. In the 1980s and 1990s intensive and successful research was conducted to improve the global description and design of bubble column reactors. Significant studies in this field were accomplished and published in standard text books by Brauer [Bra71], Clift [Cli78], Deckwer [Dec85], Fan and Tschuiya [Fan90] and Kraume [Kra12], among others. Since the 1990s the development of Computational Fluid Dynamics (CFD) simulations



also entered the study of bubble columns, leading to an improvement in the comprehension of the flow structures with and without reactions. Nevertheless, up to date computational power limits the simulation. For an entire bubble column, especially for the heterogeneous regime, it is still difficult to simulate momentum, mass transfer including reaction with sufficient temporal and spatial resolution. Thus, dimensioning of bubble columns still has to be done with the help of semi-empirical equations.

### 2.2.1 Flow Regimes

The knowledge of the flow regime is particularly important because it strongly affects the productivity of BCRs. Three flow regimes characterize the gas flow in a bubble column: *homogenous*, *heterogeneous* and *slug* flow. The main factor that affects the transition from one regime to another one is the superficial gas velocity  $w_g^0$

$$w_g^0 = \frac{\dot{V}_g}{A} \quad (2.1)$$

the gas volume rate  $\dot{V}_g$  divided by the cross-sectional area  $A$ . The interrelation between superficial gas velocity and reactor diameter is illustrated by the well-known flow map in **Figure 2.8** [Sha82]. Depending on the gas distributor, the gas–liquid system and the liquid flow rate this interrelation is shifted. This also explains the broad transition region. The *homogeneous* flow regime is marked by a relatively uniform distribution of the bubbles over the cross-section of the BCR due to low gas flow rates. Without significant motion in the horizontal direction neither bubble coalescence nor fragmentation takes place, and thus bubble size distribution is quite narrow [Dec85]. This regime extends to superficial gas velocities of approximately 3– 8 cm s<sup>-1</sup>, depending on the gas – liquid system and column design. The uniform distribution of gas bubbles vanishes at larger gas flow rates, and a highly turbulent flow structure appears. In this *heterogeneous* or churn-turbulent flow regime, higher shear and pressure forces affect the bubbles. This leads to bubble coalescing as well as break-up and thus the bubble size distribution becomes broader. There is an upward bulk flow at a higher velocity in the axis of the column and a downward flow zone near the column wall. In the bulk zone, mainly larger bubbles are rising fast compared to the smaller bubbles, which are rising near to the wall or are actually transported downward [Ger79]. Chen et al. 1994 [Che94] analyzed the flow structure and identified a helical bubble swarm as shown in **Figure 2.9**. In small-diameter columns, often used as laboratory equipment, *slug* flow at high gas flow rates is observed. In smaller columns the wall-effect dominates the hydrodynamic behavior due to the fact that the bubbles near to the wall are slowed down by the wall friction. Above a certain gas velocity, bubbles start coalescing, and in the case that the diameter of the column is comparable to the diameter of large bubbles, slug flow occurs. Large

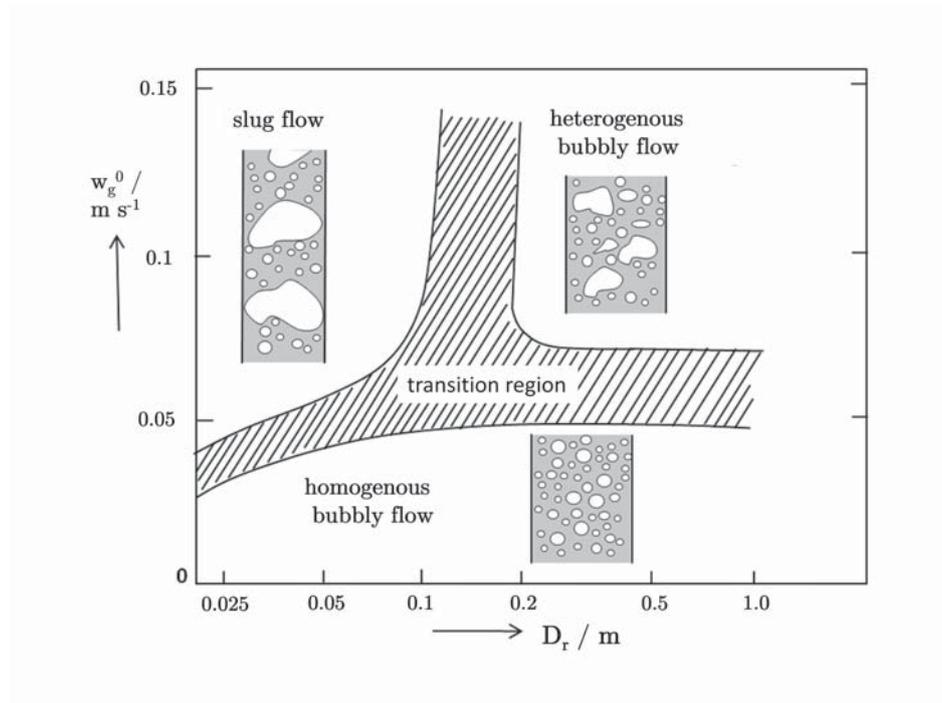


Figure 2.8: Flow regimes in a bubble column with respect to superficial gas velocity and reactor diameter for the water-air system [Sha82].

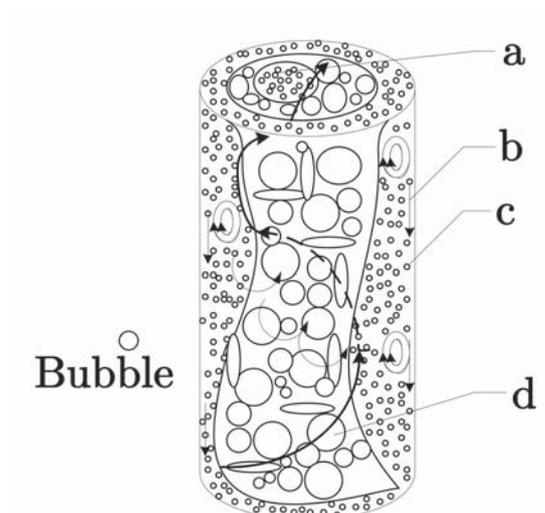


Figure 2.9: 3D flow structure in bubble columns proposed by Chen et al. 1994 [Che94] in the heterogeneous flow regime: a) central plume region; b) descending flow region; c) vortical-spiral flow region; d) fast bubble flow region.



bubbles are stabilized by the column wall and take on the characteristic slug shape. However, at low superficial gas velocities, homogeneous flow regime predominates, independently from the column diameter.

### 2.2.2 Gas Holdup

Gas holdup is defined as the volume of the gas phase divided by the total volume of the dispersion according to

$$\varepsilon_g = \frac{V_g}{V_{tot}} = \frac{V_g}{V_g + V_l} \quad (2.2)$$

for gas-liquid systems. Gas holdup is governed in a complex way by design and operating parameters, dominated by the superficial gas velocity. The relationship between gas holdup and gas velocity is generally described by

$$\varepsilon_g \propto (w_g^0)^n \quad (2.3)$$

as proportional to each other. In the homogenous flow regime,  $n$  is close to unity, whereas in the heterogeneous regime, when larger bubbles arise, the exponent decreases, i. e., the gas holdup increases less than proportionally to the gas flow rate (**Figure 2.10**). The higher the contribution of large bubbles to the total gas holdup, the smaller the exponent  $n$  is. In the fully developed heterogeneous flow regime,  $n$  finally takes a value between 0.4 and 0.7, depending on the gas – liquid system. Much research has been conducted to describe the main influence factors on gas holdup. Mostly the correlations are based on a dimensional analysis and fitted to experimental data. In order to chose the right correlation, sensitive parameters such as geometry, gas distributor, system and operation conditions have to be considered. According to these parameters, different ranges of validity prevail for particular correlations. One very frequently mentioned equation is the one developed by Akita and Yoshida [Aki73]

$$\frac{\varepsilon_g}{(1 - \varepsilon_g)^4} = C \left( \frac{gd_r^2 \rho_l}{\sigma} \right)^{\frac{1}{8}} \left( \frac{gd_r^3}{\nu^2} \right)^{\frac{1}{12}} \left( \frac{w_g^0}{\sqrt{gd_r}} \right) \quad (2.4)$$

with  $C = 0.2$  for pure liquids and non-electrolyte as well as  $C = 0.25$  for electrolyte [Ges75], [Dee00], [Cho88], [Özt87], [Dec85], [Sha82], [God84]. For non-newtonic liquids the correlations given by Joshi [Jos98], Deckwer [Dec85], Schumpe and Deckwer [Sch87] as well as Haque [Haq86] are often used. In **Figure 2.11** correlations developed on a water/air system are shown. This underscores on the one hand that water/air is the frequently used material system. On the other hand it also shows the large deviations depending on which correlation is applied. Consequently gas holdup is a very uncertain