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Tesi di Laurea Magistrale in
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Validation of Models to describe Local Transport Phenomena in Bubble Columns.

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Abstract

Multiphase reactors are widely used in chemical and biochemical industry. Among these, bubble columns have several advantages, for example low energy input due to the absence of mechanical parts and low-end construction. Bubble columns are employed in many plants for use in Fischer-Tropsch synthesis and in large scale fermentators. They are also applied to different systems, not only in a two phase system, e.g. air-water, but also in three phase systems, e.g. gas-liquid-catalyst or gas-liquid-enzymes, and for various conditions such as pressure, temperature or viscosity. However, the hydrodynamic is still not well understood and this leads to problems in scale-up and prediction of main parameters.

Gas hold-up and mass transfer coefficient are two very important parameters. To describe their behavior many correlations have been developed. Different kinds of equations and methods were used to obtain accurate results from the experimental data. These include empirical equations, as well as semi-theoretical correlations implemented in the last decade. Nevertheless, the wide range of possible conditions and the narrow and undefined range of validity of the correlations, limit the applicability of one specific correlation.

The purpose of this master thesis is to analyze existing models of gas hold-up and volumetric mass transfer. After extensive literature research, the models are quantitatively and qualitatively compared, underlining whether important aspects are considered or not, for instance the use of distilled water instead of tap water. Experiments will finally test the same important parameters. In the focus of interest are the height to diameter ratio, the gas distributor design and the presence of tap water salts. For this purpose the gas hold-up has to be measured while varying the superficial gas velocity.

Riassunto

Questa tesi vuole analizzare nel dettaglio lo stato attuale dei modelli per la previsione del grado di riempimento e del coefficiente volumetrico di scambio di materia nelle colonne a bolle. Per l’analisi dei modelli è stato creato un database attraverso il quale è possibile visualizzare istantaneamente le caratteristiche di un modello, trovare il valore del grado di riempimento o del coefficiente volumetrico di scambio di materia in base ai parametri desiderati, e.g. dimensione colonna, distributore del gas e densità, confrontare differenti modelli in base a parametri predefiniti e confrontare l’effetto di un parametro nei differenti modelli. Infine sono stati effettuati degli esperimenti in laboratorio per verificare l’efficacia dei modelli esistenti e per testare l’influenza dell’uso di acqua d’acquedotto, invece che di acqua distillata, per lo sviluppo di modelli empirici.

Nella prima parte della tesi viene approfondita la parte teorica, viene analizzata la colonna a bolle come sistema fisico e vengono descritti i parametri che ne influenzano il comportamento. In particolare, è importante considerare la caratterizzazione fluidodinamica di una colonna a bolle, ovvero il regime di flusso omogeneo o eterogeneo e l’influenza del distributore del gas. In tutti i modelli analizzati infatti, le correlazioni differiscono in base al regime fluidodinamico. Inoltre, il distributore del gas risulta avere un’influenza molto marcata in quanto la sua scelta influenza l’intera fluidodinamica del sistema, dal profilo al valore massimo del grado di riempimento per esempio.

Nella seconda parte vengono analizzati, prima in modo fondamentale e poi attraverso i modelli presi in considerazione, il grado di riempimento e il coefficiente di scambio di materia. Per quanto riguarda l’analisi dei modelli, l’attenzione è incentrata sul sistema sperimentale usato, i fluidi utilizzati e le ipotesi fatte per lo sviluppo del modello. Molti autori cercano di creare condizioni possibili per le quali le variabili di interesse, ovvero il grado di riempimento e il coefficiente di scambio di materia, sono indipendenti da alcuni parametri, ad esempio, il diametro della colonna e la dimensione del distributore del gas. Per confrontare diverse correlazioni, le condizioni di indipendenza vanno verificate, ma in alcuni casi gli autori non specificano informazioni necessarie come per esempio se l’acqua utilizzata negli esperimenti è distillata o meno. Infatti, la presenza di ioni nell’acqua influisce sullo stato idrodinamico del sistema ostacolando la coalescenza delle bolle. Per questo motivo il rapporto minimo tra altezza di liquido e diametro della colonna deve essere maggiore affinché il grado di riempimento sia indipendente dal rapporto altezza di liquido - diametro della colonna. Se quindi si vogliono confrontare correlazioni diverse su esempi specifici, risulta difficile trovare modelli compatibili.

Queste considerazioni sono state dedotte da esempi pratici ricavati dal database e riportate nella tesi. Tramite altri esempi sono stati effettuati studi sulla sensibilità delle correlazioni ai diversi parametri, e.g. viscosità, evidenziando come alcuni parametri possono avere una grande influenza nelle variabili considerate.

Nell'ultima parte della tesi vengono descritti gli esperimenti e i risultati ottenuti con il sistema aria-acqua. Vengono condotte più serie di esperimenti, variando il rapporto altezza di liquido - diametro colonna, a diverse velocità del gas e variando la concentrazione di sali nell'acqua. Esperimenti con acqua distillata e con aggiunta di sali sono stati effettuati alternativamente, tuttavia residui di sali sul distributore del gas hanno influenzato gli esperimenti successivi con acqua distillata. Nonostante il parziale inquinamento degli esperimenti è stato possibile fare ulteriore considerazioni, i.e. sull'effetto di quantità residue di sali nell'acqua. Per esempio, anche una minima presenza di sale nell'acqua come potrebbe essere quella dell'acqua del rubinetto, è sufficiente a modificare il sistema idrodinamico rendendo necessaria una maggiore altezza di liquido affinché il grado di vuoto sia indipendente dal rapporto altezza di liquido - diametro della colonna. Il confronto tra gli esperimenti con acqua distillata e acqua del rubinetto sono stati di particolare interesse in quanto l'argomento non era ancora stato trattato in letteratura. E' stato inoltre evidenziato come, nonostante le molte correlazioni presenti, sia difficile rappresentare i dati ottenuti dai nostri esperimenti, in particolare a causa dell'utilizzo di distributori di liquido diversi. Altre ipotesi sono state invece confermate, come per esempio il fatto che il grado di vuoto, nel caso di distributori di liquido a più orifizi, sia massimo a bassi valori del rapporto altezza di liquido – diametro della colonna.

In conclusione, in questa tesi vengono evidenziati i limiti che ancora caratterizzano i modelli per la stima del grado di vuoto e del coefficiente di scambio di materia per le colonne a bolle. Sono inoltre evidenziate anche le strade che sono considerate più promettenti per lo sviluppo futuro.

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Introduction

The behaviour of bubble columns has been analysed, starting from the knowledge of the physical parameters, then analysing the available correlations in literature regarding gas holdup and volumetric mass transfer. All the correlations have been digitalised in a database, in order to use and compare them. Finally experiments have been performed, to verify the validity of the correlations and to investigate critical issues.

The physical knowledge of a system, e.g. the bubble column, is important to develop correlations that are going to be used in different systems from where they have been deduced. In the first chapter a physical background of the bubble columns is given. A bubble column is complex system itself, moreover there are many configurations that lead to different behaviours. In particular is analyzed the role of the gas distributor and the fluid dynamic behaviour. Moving inside the column, some parameters have been identified as more representative of fluid dynamic and analysed in details. All these things have to be taken in account for developing a correlations to predict the behaviour of a bubble column.

In the second chapter have been used the correlations regarding gas holdup and volumetric mass transfer available in the literature. Each correlation has been first filed in a database as function of its parameters and all the possible combinations of values of its parameters have been performed in the range of validity of the correlation. First the gas holdup and the volumetric mass transfer are investigated in relation to the parameters that most influence them, accordingly also to the assumptions made by the different authors in their correlations. Then thanks to the database the correlations are compared, testing different cases are underlined the weaknesses and the potentialities of the correlations and of the database created. Moreover is showed how it is possible, through the database, to perform sensitivity analysis of a single parameter in different correlations.

The third chapter collects the experimental data done in the labs of the TUHH’s University. For these experiments have been used two columns of the same dimensions but with different spargers and in one column have been also performed experiments with salts. The sparger used are a single orifice nozzle and a multi orifice membrane, the effect of the sparger has been studied at different gas velocities and different height to diameter ratios. Another set of experiments has been done to study the effect of tap water instead of distilled water, comparing distilled water and different simulated tap waters. The experiments have all been compared with literature data.

The study of the physic of a bubble column, of the correlations available in the literature, of the database and of the comparison of the correlations, of the experiments with distilled and tap water show how the comprehension of a bubble column is still far from even a sufficient knowledge. This paper especially underline which are the issues of the different correlations and of the methods used to develop such correlations.

Chapter 1

Theoretical Background

The knowledge about bubble columns is still limited, the macroscopic effects are strongly influenced by molecular phenomena, especially regarding coalescence of single bubbles, amplified by the complex structure of bubbles and their interactions in the whole column. For this reason, even if the complete behavior is not clear, a strong physical background is important to try to understand how the bubble column interacts in the different conditions.

1.1 Bubble columns

In bubble columns gas phase is brought into contact with a liquid through bubbles. The simplest operation is just to mix the liquid phase. Moreover, complex operations are possible, bubble columns are employed in stripping and adsorption, transferring chemical species from one phase to another, even at the same time. Chemical or biological reactions can also take place, usually in the liquid phase. For specific applications is needed also to intensify the mass transfer or to modify the residence time distribution.

The liquid can contain also a third phase such as inert, catalyst or reactive particles. Typical reactions are Oxidation, hydrogenation, chlorination, phosgenation and alkylation, these processes and many others have been long developed. Industrial bubble column reactors have volumes of 100-300 m^3. Reactors that perform fermentations for protein production from methanol have capacities of approximately 3,000 m^3. The biggest units are employed for waste-water treatment with a volume of 20,000 m^3 (Zehner and Kraume, 2005).

Before the 1970s few publications regarded bubble columns, after a growing interest brought towards many empirical correlations and theoretical models to simulate the behaviour of a bubble column. Since the 1990s the development of CFD models entered also the study of bubble columns, leading to an improvement in the comprehension of the flow structures without and with reactions. Nevertheless up to date, the computational power limits the simulation to few. For an entire bubble column, especially for the heterogeneous regime, is difficult to simulate the fluid dynamics which describes momentum, mass transfer and reaction rate at the same time.

1.1.1 Different Designs

The simplest design is the bubble column (Fig. 1.1 A), where the gas passes from the bottom, where is fed, to the upper surface and the liquid is not recycled. This solution is also called semi-batch (batch respect to the liquid and continuous respect to the gas). In case that the gas still contains valuable reactants at the outlet, it can be recycled. The liquid can also be led in a co-currently or counter-currently operation mode with negligible differences in the residence time if compared to the gas phase residence time. Therefore the gas is always from the bottom to top.

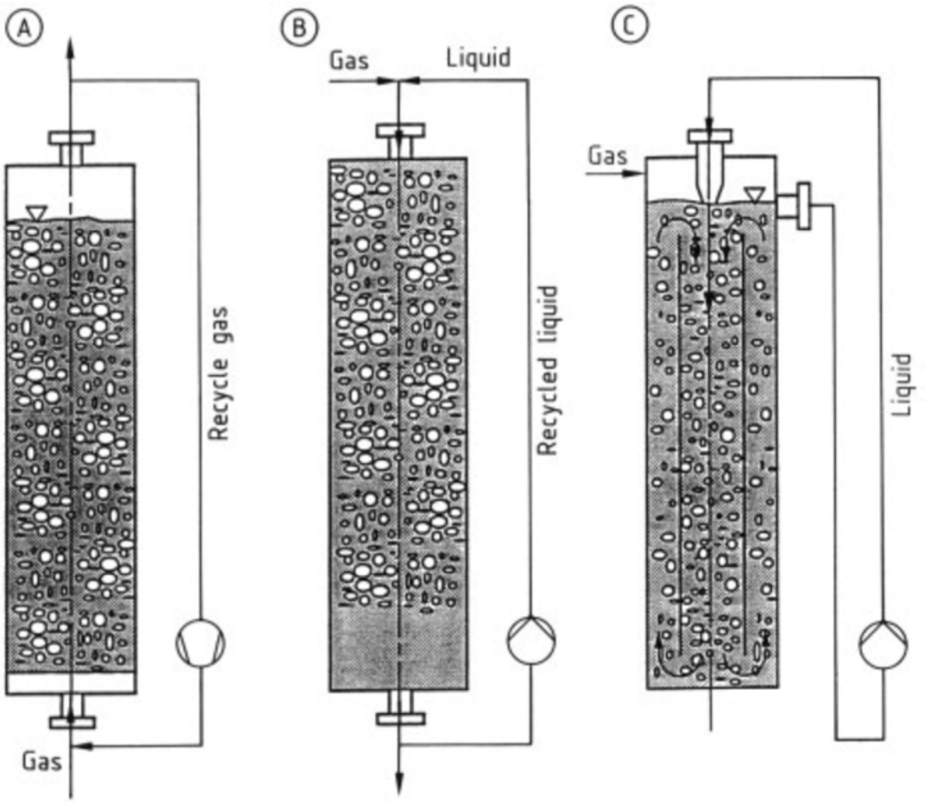


Fig. 1.1: *Simple Bubble columns configurations*
A) Bubble column; B) Down-flow bubble column; C) Jet loop reactor

If a longer gas-phase residence time wants to be achieved, a down-flow bubble column (Fig. 1.1 B) can be employed. The liquid is pumped down through the column at a velocity of more than 20 cm/s, so that gas let in at the top is entrained in the flow and can even be held in a suspension-like state until it has reacted completely. Usually the gas is collected with the liquid and is then separated. Usually this solution is utilized when large streams of liquid are to be contacted with small gas streams in a small liquid residence time. The necessary liquid residence time cannot always be obtained within a single passage. Thus, like the gas in an ordinary bubble column, the liquid in the down-flow bubble column can be recycled. A typical application of these bubble columns is the ozonation of drinking water and the treatment of water in swimming pools.

In both types of column energy must be supplied continuously to the two-phase system to keep the liquid and gas mixed. Only in this way the separation of the phases can be counteracted or reversed. In the first case, the simple bubble column, this energy is supplied by the gas. In the down-flow bubble column the energy is supplied by the down-flowing liquid.

The jet loop reactor (Fig. 1.1 C) utilises another mechanism, an internal circulation is produced instead of a net flow of gas or liquid. One way to achieve this is with a propeller, but other approaches exist. In the most commonly used type of loop reactor, the jet loop reactor, the flows driven by a high-velocity liquid jet. As in the down-flow bubble column, gas is let in at the top and dispersed by the jet energy. Bubbles can be distributed throughout the reactor volume only if the downward liquid flow velocity in the internal tube is greater than the slip velocity of the bubbles. Accordingly, a minimum power input is required.

These simple forms of bubble columns are rarely used in modern complex chemical and biotechnical engineering, instead a combination of them led to many different devices.

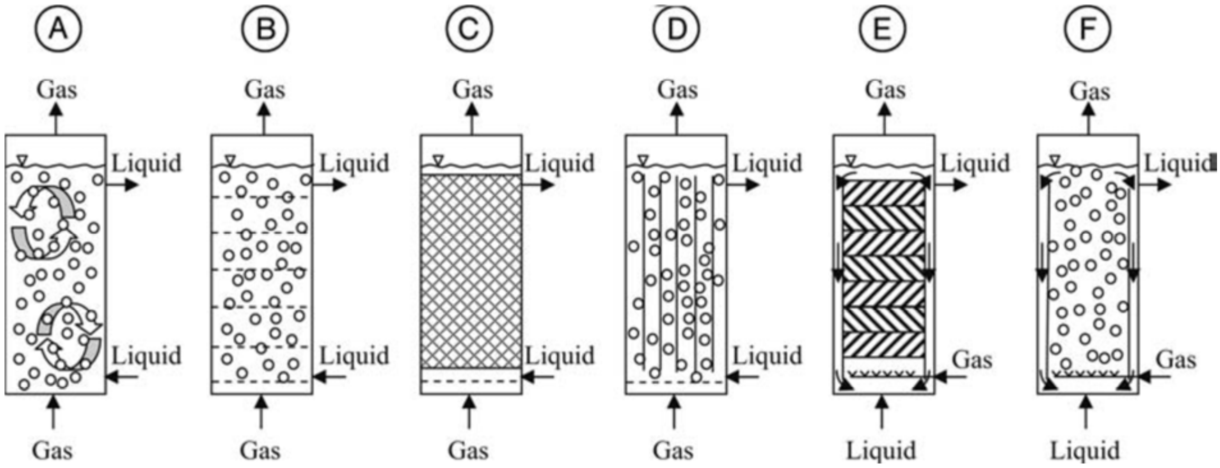


Fig. 1.2: *Types of bubble column reactors.*
A) Simple bubble column; B) Cascade bubble column with sieve trays; C) Packed bubble column; D) Multishaft bubble column; E) Bubble column with static mixers;
F) Airlift loop reactor.

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 reduced by the installation of trays (Fig. 1.2 B), packings (Fig. 1.2 C), or shafts (Fig. 1.2 D). All these devices can operate either in co-currently or counter-currently operation mode. To set up the most homogeneous possible bubble flow, static mixer elements can also be placed in the ascending flow section (Fig. 1.2 E). One can use the action of gravity to generate a global circulation as it is done in airlift loop reactors (Fig. 1.2 F).

1.1.2 Gas Distribution

The gas is dispersed by creating small bubbles, distributed homogeneously throughout the column, in order to increase the mass transfer.

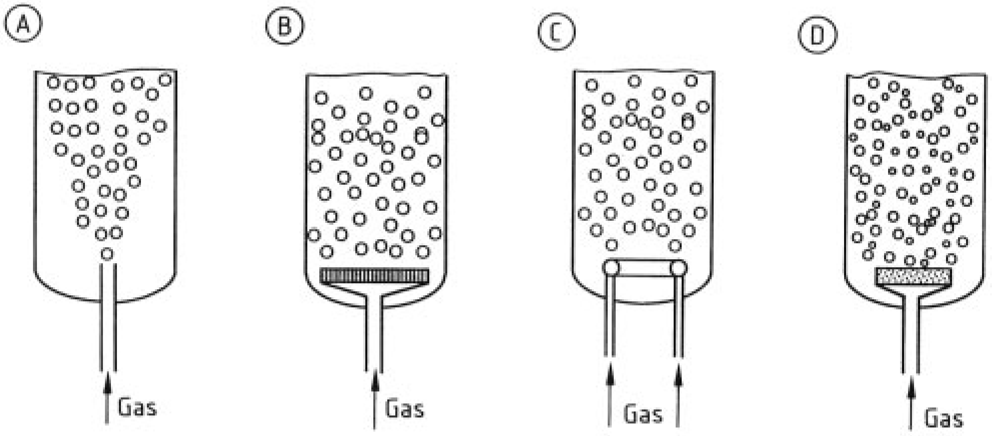


Fig. 1.3: *Static gas spargers.*
A) Dip tube; B) Perforated plate; C) Perforated ring sparger; D) Porous plate.

Figure 5 shows typical forms of “static” gas spargers, in which bubble formation occurs without any additional energy supplied from outside. The simplest of these devices, the dip tube (Fig. 1.3 A), only gives an acceptably uniform gas distribution over the cross section at some distance above the sparger. Perforated plates (Fig. 1.3 B) and perforated ring spargers (Fig. 1.3 C) are more effective. Both of these require a certain minimum gas flow rate to achieve uniform distribution and prevent the liquid from getting into the sparger. Very fine bubbles can be generated by the use of porous plates (Fig. 1.3 D), but their pores are susceptible to fouling, and this type of sparger is seldom used in full-scale equipment.

Dynamic spargers offer an alternative to the static types. They use the power of a liquid jet to disperse gas in a zone of high energy dissipation rate.

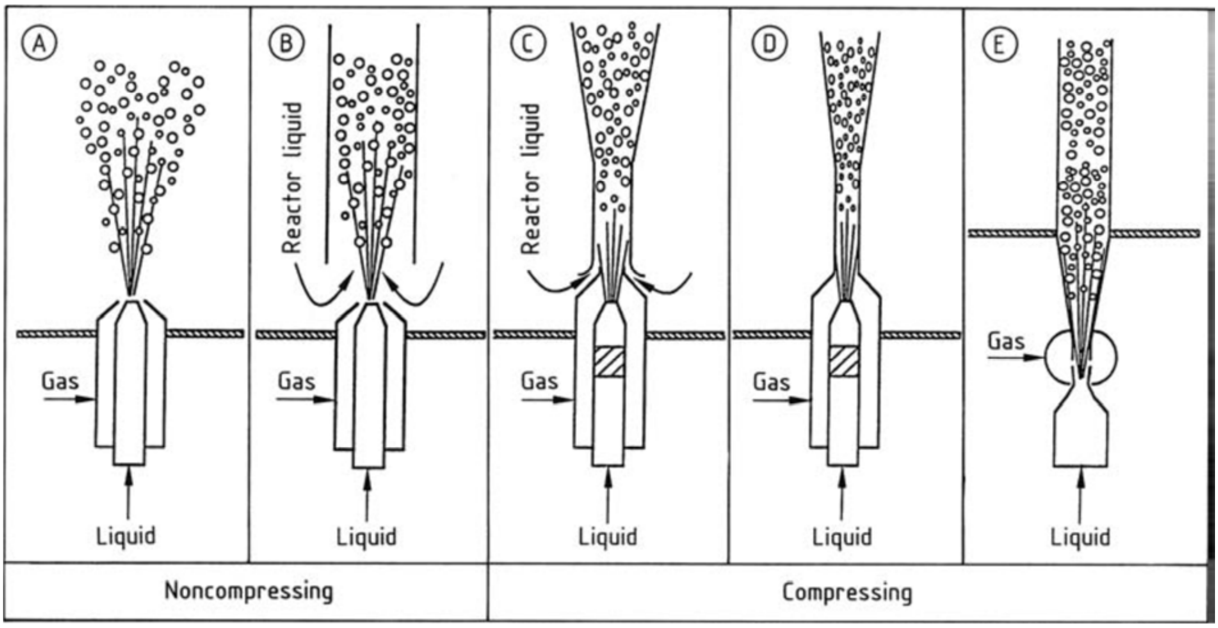


Fig. 1.4: *Dynamic gas distributors.*
A) Two-phase jet nozzle; B) Two-phase jet nozzle with momentum-transfer tube; C) Ejector jet nozzle; D) Ejector; E) Venturi nozzle

Figure 1.4 illustrates several frequently used dynamic gas spargers. The simple two-phase jet nozzle alone (Fig. 1.4 A) or with momentum-transfer tube (Fig. 1.4 B) is not able to simultaneously disperse gas and suck in the gas stream. This can be achieved, however, with the ejector jet nozzle (Fig. 1.4 C), the ejector (Fig. 1.4 D), and the Venturi tube (Fig. 1.4 E). In nozzle selection the ratio of the gas – liquid volumetric flow rates must always be considered. Common values lie between 0.5 and 2.

1.1.3 Flow Regimes

Three main regimes characterize the gas flow in a bubble column. The main factor that affects the transit from one regime to another is the superficial gas velocity.

The homogeneous flow regime is marked by a narrow bubble-size distribution, and bubbles are distributed relatively uniformly over the cross section of the apparatus. This regime extends to superficial gas velocities of 0.03 – 0.08 m/s, depending on the gas – liquid system and column design as the bubble diameter. The uniform distribution of gas bubbles vanishes at higher gas rates, and a highly turbulent flow structure appears.

In this heterogeneous or churn-turbulent flow regime, large bubbles or agglomerates of bubbles form and travel upward at high velocity, mainly in the axis of the column. The circulating flow that results may be so vigorous that bubbles of a size corresponding to that in the homogeneous regime are actually transported downward in the zone near the column wall.

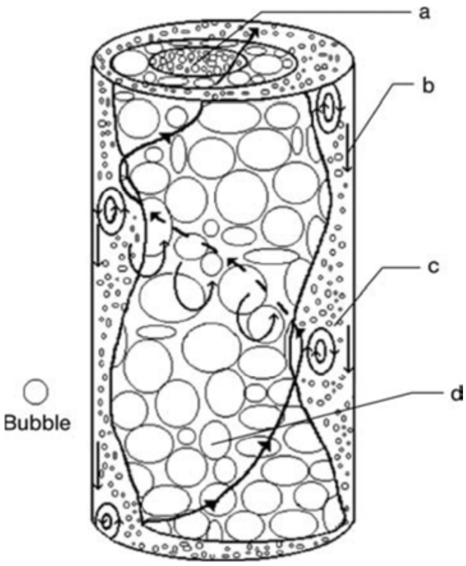


Fig 1.5: *3D flow structure in bubble columns proposed by Chen (Chen et al. 1994) in the heterogeneous flow regime.*
a) Central plum region; b) Descending flow region; c) Vortical-spiral flow region;
d) Fast bubble flow region

In the small-diameter columns often used as laboratory equipment, slug flow occurs at high gas flow rates. Large bubbles are stabilized by the column wall and take on the characteristic slug shape.

The relationship between superficial gas velocity and reactor diameter is illustrated by the flow map of Figure 1.6 (Shah et al. 1982). With small diameter the wall-effect influences the hydrodynamic behaviour. The bubbles near the wall are slowed down by the wall friction and over a certain gas velocity coalescence of the bubbles starts, and if the diameter of the column is comparable to the large bubbles diameter slug flow occurs. At low gas velocities independently from the superficial gas velocity, homogeneous flow regime predominates. The transition velocity, especially at small column diameters, e.g. for water air 0.15m, is function of the diameter itself. For different systems these dependences can totally change.

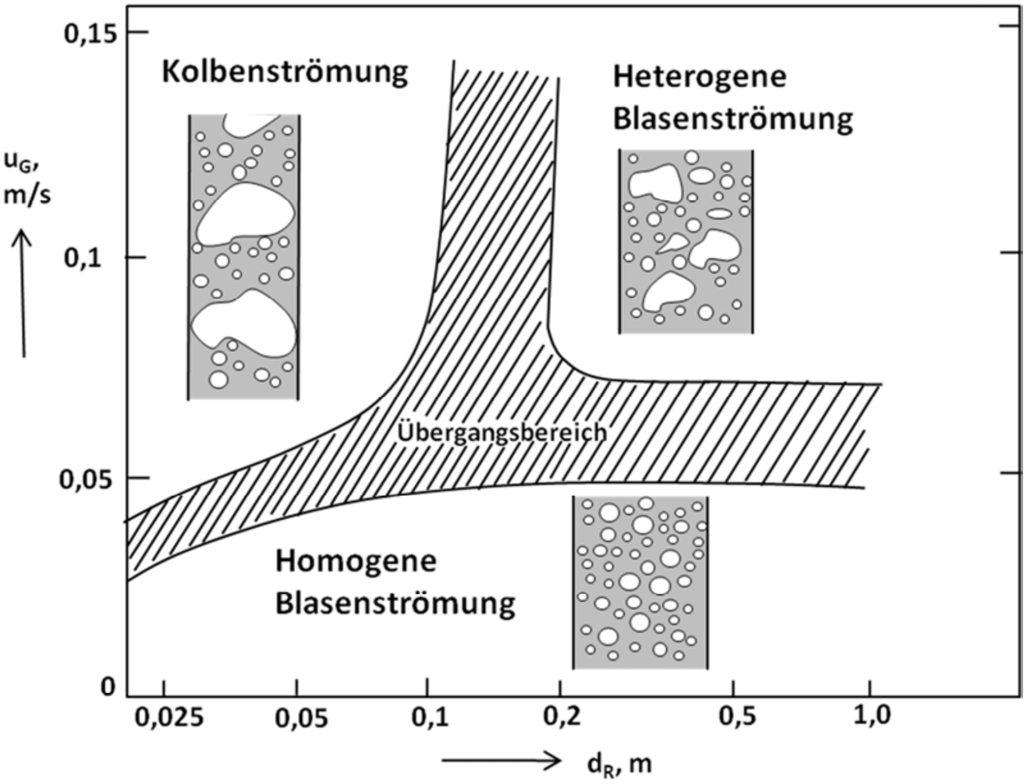


Fig. 1.6: *Flow regimes in a bubble column for the water-air system.*

The broad transition regions are due to the effects of the gas distributor, the gas–liquid system, and the liquid rate. Knowledge of the flow regime is particularly important because it strongly affects the productivity of bubble-column reactors.

1.1.4 Fluid dynamics

The liquid is moving upward in the wakes of the bubbles, with a velocity that is much greater than the net flow rate. Therefore, because of the continuity, there are regions of the column where the liquid is moving downward (Joshi and Shah, 1981). Several models describe this behaviour, both in homogeneous and in heterogeneous flow regime, even if the homogeneous models are just useful theoretically and not for applications. For example, Miyauchi used a force balance over an annular, axially symmetrical volume element to obtain the velocity profile shown in Figure 1.7, (Ueyama and Miyauchi, 1979). Calculation of the velocities, however, requires knowledge of the gas holdup as a function of radial position. Models of circulation velocity based on energy balances, in contrast, assume a cell structure in the bubble column similar to that shown in Figure 1.8 (Joshi and Sharma, 1979).

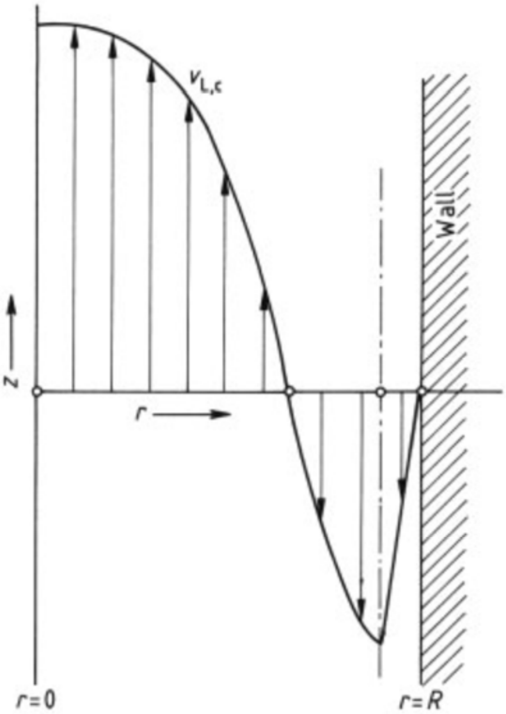


Figure 1.7: Radial distribution of liquid velocity in a bubble column

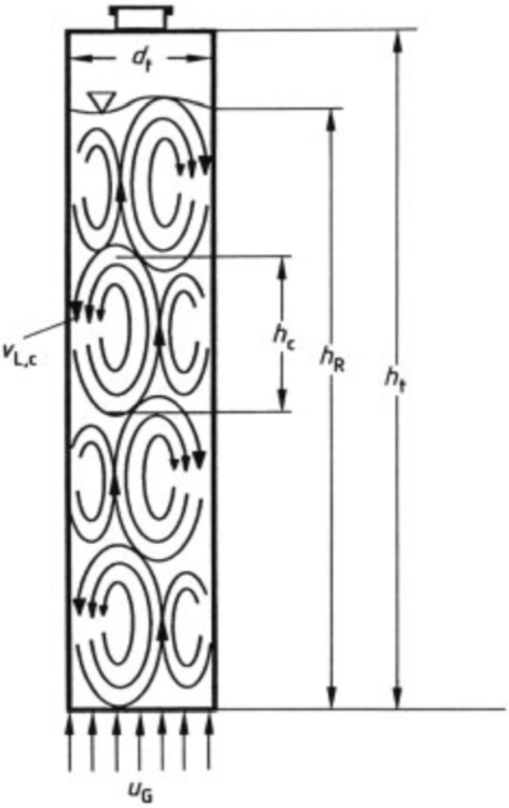


Figure1.8: Cell structure in a bubble column.

Joshi and Sharma take into account the energy input due to gas compression and energy losses by dissipation in the wakes of the rising bubbles, as well as liquid transport across the liquid surface (hydraulic pump), thus obtaining a velocity profile over the cross section.

The velocity profiles derived from the models and, in particular, the mean velocities enable calculation of the essential fluid-dynamic parameters in bubble columns.

1.2 Important Parameters

To describe and to predict the fluid dynamic behaviour, many parameters can be measured and calculated. In this paragraph a simple introduction of the most important parameters is given and in the next chapter, a deeper analysis will tell more about the more industrially relevant ones.

1.2.1 Bubble size

The evaluation of bubble size and bubble size distribution has to be distinguished within the bubble column, according to radial and axial position. Two main zones are to be considered: right after bubble formation at the sparger and further away from the distributor. Because of breakup and coalescence of the rising bubbles, the two distributions can differ significantly. Since the efficiency of bubble columns depends mainly on bubbles far from the gas distributor, the following discussion only concerns these. The analytical methods (photography and probe techniques) to measure the bubble size however, lead to realistic results only if the column is operating in homogeneous regime, i.e. bubbles with a narrow bubble size distribution.

If bubbles are generated in a region of high turbulence, e.g. with dynamic gas spargers, - the following formula (Calderbank, 1976) can be used to describe the Sauter diameter d_{bS} (mean bubble diameter, calculated from the volume to surface ratio) (Nagel et al, 1978).

$$d_{bS} = \frac{2}{e_M^{0.4}}\left(\frac{\sigma}{\rho_L}\right)^{0.6} e_G^{0.5}\left(\frac{\eta_G}{\eta_L}\right)^{0.25} \tag{1.1}$$

This formula is based on Kolmogorov’s theory of isotropic turbulence.

When static gas spargers are used, the bubble diameter is only weakly dependent on gas velocity. Descriptive correlations (Akita and Yoshida, 1974; Koide et al., 1979; Miyahara et al., 1983) are applicable only to the systems and sparger geometries for which they were obtained; a generally valid description of bubble size does not yet exist. The maximum bubble diameter d_b, max can be used for purposes of estimation (Mersman et al., 1989). For low viscosity liquids, the maximum bubble diameter is given by:

$$d_{b,max} = \sqrt[3]{\frac{\sigma}{g\rho_L}} \tag{1.2}$$

where σ is the surface tension. For the water–air system, d_b, max = 8 mm. Larger bubbles have a high probability of being unstable and thus breaking up. The Sauter diameter for real distributions is between 40 and 60 % of the largest stable bubble diameter. However this estimation is not applicable to the heterogeneous flow regime due to the binodal bubble-size distribution in this regime.

1.2.2 Bubble rise velocity

In the homogeneous flow regime, bubbles of almost uniform size and shape rise in the form of a swarm distributed uniformly over the column cross section. When the regime changes, larger bubbles or agglomerates of bubbles form, in addition to the bubbles that already exist (Wezorke, 1986). These aggregates rise at a markedly higher velocity than the small bubbles. Figure 1.9 shows measured velocities for large and small bubbles. Large bubbles first appear at a superficial gas velocity of ca. 0.03 m/s. The formation of large bubbles, however, depends strongly on the type of sparger used. With sintered plates, for example, larger bubbles do not appear at gas rates lower than ca. 0.1 m/s. As shown in Figure 1.9, large bubbles have a rise velocity that is four or more times larger than small ones. Thus, a bigger volume of the gas is transported in the heterogeneous flow regime thanks to large bubbles. In this regime, the quantity of gas transported by small bubbles remains constant, whereas the quantity transported by large bubbles increases linearly with gas velocity. This relationship applies to coalescing and coalescence-hindered gas – liquid systems.

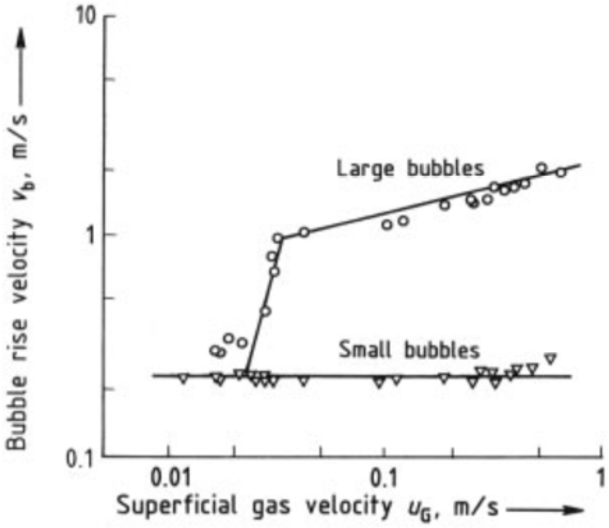


Fig. 1.9: *Rising bubble velocities in the water-air system.*
Reactor: D = 0.44 m, ht = 5m; Gas distributor: perforated plate (dH = 3 mm).

1.2.3 Dispersion of the liquid phase

Because of the large-scale circulation flows, back-mixing occurs in both phases. The resulting dispersion flow J_D is usually governed by an equation analogous to Fick’s first law for molecular diffusion. For the one-dimensional case of axial dispersion, which is generally sufficient for a description, follows

$$J_D = -D_L \frac{d_c}{d_z} \tag{1.3}$$

The dispersion coefficient D_L is essentially a function of the superficial gas velocity and the column diameter (Shah et al., 1978) Flow direction or liquid velocity does not show any effect, provided the superficial liquid velocity remains within the range common in industry (u_L <0.03 m/s). The dispersion coefficient can be estimated fairly accurately on the basis of fluid-dynamic models (Joshi and Sharma, 1979).

1.2.4 Dispersion of the gas phase

Whereas the gas phase in a bubble column with a smaller diameter flows with virtually no back-mixing, large units behave more like stirred tanks. The gas-phase dispersion coefficient depends more strongly on gas velocity and column diameter than the one of the liquid phase. For this reason, the degree of axial gas mixing is especially relevant for scale-up when the gas phase is expected to show strong concentration variations.

1.2.5. Gas Holdup

The Gas holdup is one of the most important parameters because it defines the gas-liquid volumetric ratio, moreover it affects the gas-phase residence time and the mass transfer. A short definition is given here and a deeper analysis in chapter number 3.

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

$$\varepsilon_G = \frac{V_G}{V_G + V_L} \tag{1.4}$$

The relationship between gas holdup and gas velocity is generally described by the proportionality

$$\varepsilon_G \sim u_G^n \tag{1.5}$$

In the homogeneous flow regime, n is close to unity. When large bubbles are present, the exponent decreases, i.e., the gas holdup increases less than proportionally to the gas flow rate (Fig. 1.10). The higher the contribution of large bubbles to the total gas holdup, the smaller is the exponent n. In the fully developed heterogeneous flow regime, n finally takes on values between 0.4 and 0.7, depending on the gas – liquid system.

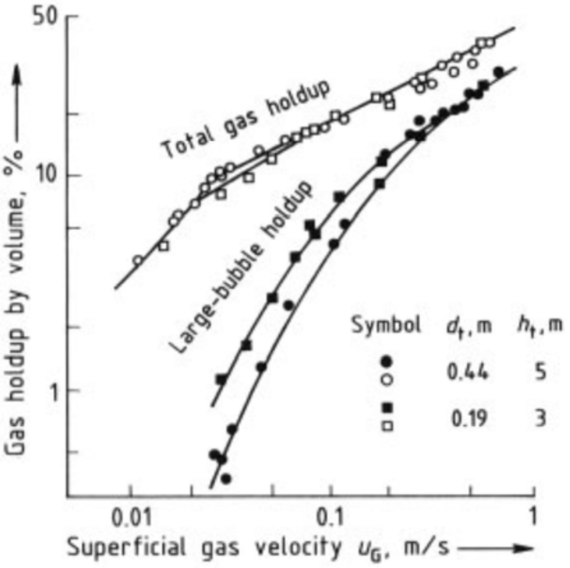


Fig. 1.10: *Gas holdup and fraction of large bubbles in a water-air system , gas distributor: perforated plate* d_h*=3mm.*

1.2.6 Specific interfacial area

The gas-liquid interface area is another very important parameters, especially at higher reaction rates (e.g. absorber bubble column) the interfacial area becomes a crucial factor in equipment sizing.

Similarly to gas holdup, interfacial area depends on the geometry, operating conditions, and gas–liquid system. Gas holdup and interfacial area per unit volume are related as

$$a = \frac{A}{V_R} = \frac{6\epsilon_G}{d_{bS}} \tag{1.6}$$

where V_R is the volume of the reaction mixture and d_{bS} is the mean bubble diameter. As Figure 1.11 shows, the interfacial area increases with increasing gas flow rate. An exception occurs when a porous plate sparger is used; like gas holdup, interfacial area decreases on transition to the heterogeneous flow regime and then approaches the same values observed with perforated plates. The growth in interfacial area with increasing gas velocity is always greater in the homogeneous than in the heterogeneous flow regime. The reason lies in the formation of large bubbles in the heterogeneous regime: the interfacial area of large bubbles per unit volume is markedly lower than that of smaller ones.

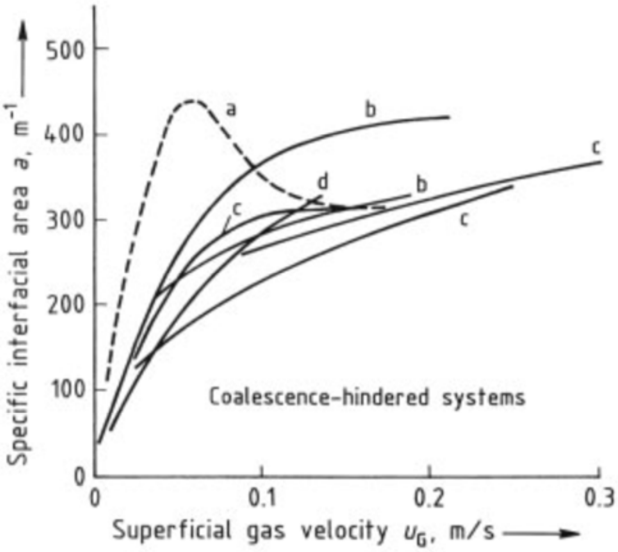


Fig. 1.11: *Specific interfacial area as a function of superficial gas velocity.*
a) d_t= 0.102 m; b) d_t= 0.29 m; c) d_t= 0.14 m; d) d_t= 0.1 m;
– – Porous plate; — Perforated plate

The specific interfacial areas attainable in various gas – liquid reactors can be compared on the basis of power input P_W per unit volume (Nagel et al. 1978). Experimental values can be described by the relation

$$a = k\left(\frac{P_W}{V_R}\right)^m \epsilon_G^n \qquad (1.7)$$

The exponent m is between 0.4 and 1. The plot in Figure 1.12 enables a direct comparison to be made between reactors with respect to the energy required to produce a given interfacial area.

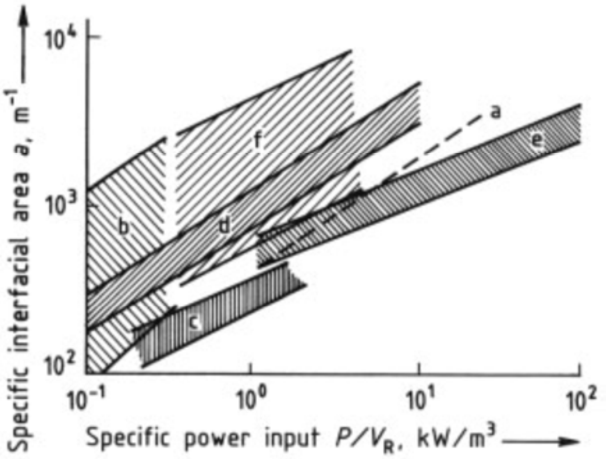


Figure 1.12: *Specific interfacial area as a function of specific power input*
a) Stirred tank; b) Bubble column with porous plate; c) Bubble column; d) Bubble column with two-phase jet nozzle (jet loop reactor); e) Packed column; f) Bubble column with injector nozzle

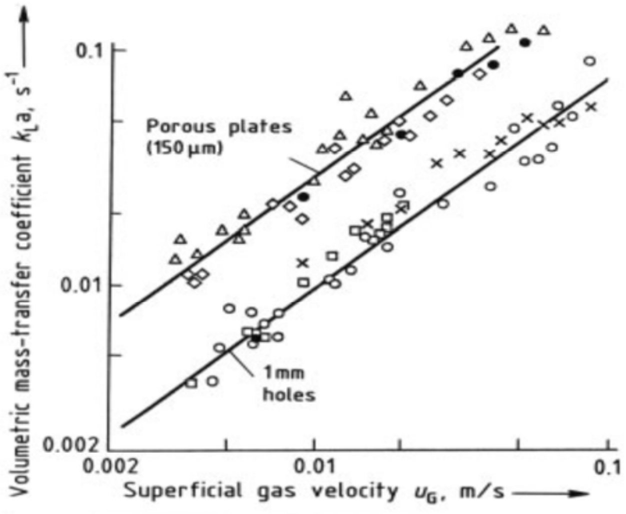
1.2.7 Volumetric mass-transfer coefficient

The overall mass-transfer between the liquid and the gas takes in account the resistance in both phases, however in most of the cases, the resistance is the gas phase is negligible. The mass transfer in the liquid phase k_L is then multiplied by the specific interfacial area to obtain a volume specific mass-transfer coefficient.

To determine the mass-transfer rate, however, the driving concentration difference must be known which in turn requires knowledge of mixing behaviour in the gas and the liquid phase. In industrial units, estimates can be based on the assumption of complete mixing in both liquid and gas phases. Like gas holdup and interfacial area, $k_L\ a$ also depends on the gas flow rate, type of sparger, and gas–liquid system. The mass-transfer coefficient and the gas rate are again proportional to one another:

$$k_L a \sim u_G^n \tag{1.8}$$

where *n* can be between 0.7 and 0.92 (Deckwer et al., 1974). Mass-transfer coefficients two- to threefold higher can be achieved in the homogeneous flow regime if a porous plate is used as sparger instead of a perforated plate (Fig. 1.13). In the heterogeneous regime, however, the effect of the sparger is negligible.



Gas distributor	d_t, m	h_t, m	Flow direction	Symbol
Cross sparger	0.20	0.250	↑↑	×
		0.723	↑↑	○
		0.723	↑↓	□
Porous plate	0.10	0.250	↑↑	●
	0.15	0.440	↑↑	△
	0.15	0.440	↑↓	◇

Fig. 1.13: *Mass transfer coefficients in bubble columns.*

Further analyses on the volumetric mass transfer are done in chapter number 2.2.

Chapter 2

Modelling

In the following chapter the literature research of the models to predict Gas Hold-up and Volumetric Mass Transfer is presented. After this literature analysis, a database of over 390Mb, with the most important correlations and their possible outcomes, has been realized. Therefore, due to the impossibility to show the whole tables only a fragments will be shown and the results of the comparisons between models and the sensitivity analysis.

2.1 Gas Holdup

A deep study of the gas holdup will enables to understand and to be more critical regarding all the amount of information concerning this very important parameter. First, a “classical” background is given and then, what is not rigorous among the hypothesis and the results of the gas holdup correlations is investigated.

After the theoretical part, it is going to be tested in practice, thanks to the correlations’ database created, the real possibility to utilize such correlations.

2.1.1 State of art

The gas holdup, as already introduced in eq. 1.4, is defined as the volume fraction of gas in the gas-liquid dispersion. It is governed by the design parameters and the operating parameters. The value of ε_G increases with increasing superficial gas velocity (see eq. 1.5). The superficial gas velocity is defined as:

$$u_G = \frac{\dot{V}}{\pi D^2/4} \tag{2.1}$$

The ε_G- u_G relationship depends upon the regime of operation.

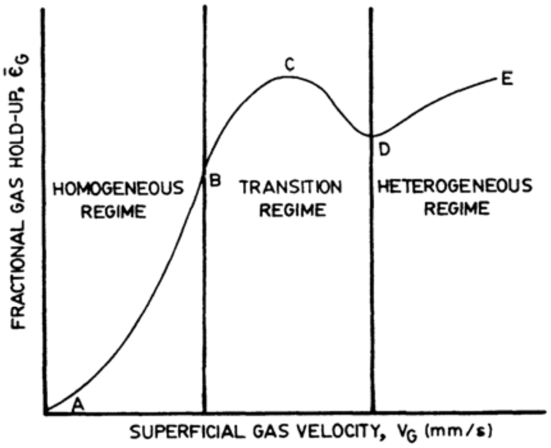


Fig. 2.1: *Schematic of various regimes in bubble column reactor.*

To identify the flow regime a first visual observation is possible, the heterogeneous (or churn turbulent) regime is characterised by intense liquid circulation, whereas more orderly flow prevails in the homogeneous regime. The flow regime can be also identified from the plot gas holdup vs. superficial gas velocity as described in chapter 1.2.5.

Homogeneous regime is characterized by almost uniformly sized bubbles. All the bubbles formed at the sparger rise virtually vertically if the bubble size is less than 1-2mm. However, ellipsoidal bubbles tend to follow a zigzag or spiralling path or rise with transverse and axial oscillations. For all the sized of bubbles there is practically no coalescence or dispersion in the homogeneous regime.

Increasing the gas velocity, from the heterogeneous regime, recirculating turbulent two-phase flow is observed. The radial variation of gas holdup provides the driving force for the recirculation opposing turbulent viscous drag (Miyauchi and Shyu, 1970). Properties of two-phase flow are closely related to the radial distribution of gas holdup, since the buoyant force of the bubble swarm is the driving force of the recirculation flow in bubble columns. Three types of gas holdup distribution can be observed: relatively flat distribution, saddle-shaped distribution and central gathering distribution. Flat distribution is observed in the region of bubble flow without liquid feed, where a swarm of bubbles rises uniformly at a low superficial gas velocity (usually less than 2 to 4cm/sec). Saddle-shaped distribution is observed in the bubble flow regime with upward liquid flow. Central gathering distribution is observed in the turbulent flow regime, either without continuous liquid flow or with upward liquid flow.

Since wide settings for the design of a bubble column are possible, many authors tried to find which conditions could be sufficient to be independent of these geometric variables. To accomplish this, the dependence of the gas holdup from column diameter, liquid height and type of sparger has been studied.

The effect of column diameter on hydrodynamics is widely investigated in literature. Shah et al. (Shah et al., 1982) reported that in bubble columns, the effect of column size on gas holdup is negligible when the column diameter is larger than 10–15 cm. Possible wall effects can appear by using small diameter columns (<10 cm) were also pointed out (Deckwer et al., 1980). It was reported that the gas holdup was not highly dependent on column diameter when the column diameter was larger than 10 cm, as long as mixing was well maintained. It was observed that the holdup in small diameter column was slightly higher than that in larger diameter columns. According to the two-phase model developed by Krishna et al. (Krishna et al., 1996) the effect of column diameter on gas holdup should be separately analyzed for small and large bubble gas holdups. It was found out that the small bubble gas holdup is independent of column diameter, while the large bubble gas holdup decreased with increasing column diameter, at the same gas velocity. As a result the overall holdup is reported to decrease with increasing column diameter due to large bubble holdup.

As far as the height of the column is concerned, in general, three regions of different gas holdup are recognized. At the top of the column, there is often a kind of foam structure with a relatively high gas holdup, while the gas holdup near the sparger is sometimes measured to be higher (for porous plate spargers) and sometimes lower (for single-nozzle spargers) than in the main central part of the column. Obviously the extent to which the gas holdup in the sparger region and in the foam region contributes to the overall average gas holdup depends on the column height. In other words, if the bubble column is very high, then gas holdup near the sparger and in the foam region at the top of the column has little influence on the overall gas holdup, while the influence can be significant for low bubble columns. Furthermore, the column height can influence the value of the gas holdup due to the fact that liquid circulation patterns (that tend to decrease the gas holdup) are not fully developed in short bubble columns (H/D<3). The above-mentioned factors tend to cause a decrease in gas holdup with increasing column height. Most authors who studied this influence of column height on gas holdup, however, also claimed that this influence is negligible for column heights greater than 1-3 m and with height to diameter ratios above 5 (Kastanek et al., 1980).

Gas sparger type is an important parameter that can alter bubble characteristics which in turn affects gas holdup values and thus many other parameters characterizing bubble columns. The sparger used definitely determines the bubble sizes observed in the column. Small orifice diameter plates enable the formation of smaller sized bubbles. Some common gas sparger types that are used in literature studies are perforated plate, porous plate, membrane, ring type distributors and arm spargers. Bouaifi et al. (Bouaifi et al., 2001) stated that, the smaller the bubbles, the greater the gas holdup values. Thus, they concluded that with small orifice gas distributors their gas holdup values were higher. In another study by Luo et al. (Luo et al., 1999), gas holdup was found to be strongly affected by the type of gas distributor. The effect was more pronounced especially for gas velocities below 6 cm/s. Schumpe and Grund (Schumpe and Grund, 1986) worked with perforated plate and ring type gas spargers. They concluded that with ring type distributor, the total holdup was smaller. They also added that the small bubble holdup showed a gradual increase with increasing superficial velocity with ring type sparger. Another conclusion about the type of spargers was that the contributions of both small and large bubbles to gas velocity were lower with ring sparger as compared to the perforated plate.

In order to find a relation of independence from the sparger, Wilkinson (Wilkinson, 1990) has shown that the influence of the sparger design on gas holdup is negligible (for various liquids and at various pressures) provided the sparger hole diameters are larger than approximately 1-2 mm (and care is taken to prevent maldistribution of gas at the sparger). Spargers with small hole diameters (less than 1 mm), however, lead to the formation of smaller bubbles and thus to a higher gas holdup and a higher interfacial area, and appear to be used most frequently for academic research on bubble columns. In spite of the advantageous characteristics of these spargers, in industry usually less effective spargers are used with larger hole diameters that are less sensitive to fouling. In high bubble columns, the influence of the sparger usually diminishes due to the ongoing process of bubble coalescence. Consequently, the relatively high gas holdup that can occur in small bubble columns as a result of the use of small sparger holes will not occur in general as noticeably in a high (industrial) bubble column. It has been argued that the gas holdup is virtually independent of column dimensions and sparger layout (for low as well as high pressures) provided the following three criteria are fulfilled:

1. The column diameter has to be larger than 0.15 m.
2. The column height to diameter ratio has to be in excess of 5
3. The hole diameter of the sparger has to be larger than 1-2mm.

Once the design configuration is fixed to the operating conditions can be analyzed. Changing liquid and gas properties influence the gas holdup, the regime transitions and the hydrodynamic in general.

The liquid phase property has an impact on bubble formation and/or coalescing tendencies and hence is an important factor affecting gas holdup. An increase in liquid viscosity results in large bubbles and thus higher bubble rising velocities and lower gas holdup. It is also reported that adding a small amount of a surface acting material (surfactant) to water, results in significantly higher gas holdup values. Moreover, the presence of electrolyte or impurities also increases gas holdup. Öztürk et al. (Öztürk et al., 1987) investigated the gas holdups in various organic liquids and they reported that in several mixed and adjusted mixtures, the gas holdups were higher as compared to pure liquids with the same properties (surface tension, density, viscosity). They also concluded that the gas holdups were higher with high density gases. Veera et al. (Veera et al., 2004) investigated gas holdup in the presence of foaming liquids and concluded that the effect of foaming agent concentration on holdup profiles depended upon the sparger design, column aspect ratio and superficial gas velocity. The authors also claimed that the gas holdup profiles were flatter at higher foaming agent concentrations.

The liquid velocity in a bubble column is usually relatively low, and consequently its influence on gas holdup is often claimed to be negligible (for example, Akita and Yoshida, 1973, with U,<0.04 m/s) or small (Kelkar et al., 1983). In principle, however, liquid flowing cocurrently upward will lower gas holdup, while a countercurrent liquid flow will increase gas holdup (Otake et al., 1977).

When bubble columns are used for chemical reactions suspended catalyst particles are present. Numerous examples have been listed by Shah et al. (Shah et al., 1982) and Mashelkar (Mashelkar, 1984) including biochemical reactions, hydrogenation of liquid petroleum fractions, and coal liquefaction, while a number of books and review articles have been published (Pandit and Joshi, 1983; Fan, 1989; Beenackers and van Swaaij, 1986) that deal with the estimation of parameters necessary for the design of slurry bubble columns (and other three-phase reactors). From these publications it has become clear that the addition of solids to a bubble column will in general lead to a small decrease in gas holdup (Reilly et al., 1986) and the formation of larger bubbles; an exception occurs for very small particles (0-100 pm**)** at low weight fractions (usually below 4% by weight). For such conditions, Khare and Joshi (Khare and Joshi, 1990) have given numerous examples that can be explained only by assuming that coalescence of bubbles is hindered by small particles and that this leads to smaller bubbles and higher gas holdup values.

The effect of operating pressure and temperature on gas holdup of bubble columns were also investigated in many studies. It is commonly accepted that elevated pressures lead to higher gas holdups. Empirical correlations have been proposed for gas holdup in bubble columns operated at high pressure and temperature (Reilley et al., 1986; Wilkinson et al., 1992). Luo et al. (Luo et al., 1999) carried out experiments at about 5.6 MPa, to investigate the effect of pressure on the hydrodynamics of a slurry bubble column and found that gas holdup increases with pressure and the pressure effect is more pronounced in higher concentration slurries. In the study of Deckwer et al. (Deckwer et al., 1980) typical high pressure conditions of the Fischer– Tropsch process were investigated, i.e. 400–1,100 kPa. However, they concluded that pressure had no significant effect on holdup. The operating temperature is another important factor to be discussed. Although most studies conclude that the temperature effect is not so significant, some disagree with this argument. For instance, Deckwer et al. (Deckwer et al., 1980) reported a decrease in the gas holdup with increasing temperature up to a certain temperature value and the gas holdup had reached a constant value with further increase of temperature. An interesting point in this study was that these results were obtained in a small diameter column, suggesting that in larger diameter columns, such a temperature effect would not be observed. Thus, the authors attributed this trend to possible ‘‘wall effects’’ in the small diameter column. Saxena et al. (Saxena et al., 1990) investigated two and three-phase bubble columns within a 297–343 K temperature range and they found out such a temperature dependence of gas holdup only in the two-phase system.

Another important aspect is the way the overall-gas holdup is used. If the interest regards scale-up purpose, Shakih and Dahnan (Shakih and Dahnan, 2010), noticed that the mean value of the gas hold-up is not sufficient. Maintaining similar overall gas holdup alone can lead to different recirculation and mixing intensity, if gas holdup radial profiles were not considered. The similarity of global parameter alone does not necessarily ensure the similar hydrodynamic performance. The similarity of gas holdup and its cross-sectional distribution is pertinent to obtain similar recirculation and mixing intensity and hence similar hydrodynamic performance in two systems.

The remarks done so far are valid in precise conditions, with their experimental settings, even if general assumption are done, many authors did not consider other important factors, especially in the development of empirical correlations. Beginning with the column diameter, many authors developed correlations for small columns (D<0.1m), this enable to use that correlation only for that specific diameter and make it almost useless for scale up purposes. The choice of the sparger is also very complicated, many different spargers are available and each one has its specific influence on the hydrodynamic, therefore is difficult to compare data with different spargers. The liquid height or better the height to diameter ratio (H_d/D) has to be taken in account carefully, first has to be distinguished between clear liquid and dispersed liquid. In the operating condition is the dispersed liquid that makes the difference in the hydrodynamic behavior, but if the superficial gas velocity changes, also the dispersed liquid change, therefore a starting clear liquid height, high enough to obtain homogeneous values have to be utilized if different gas velocities want to be performed. However also for water-air systems, that seem to be easy to analyze, small details can produce big deviations. For example the use of tap-water: the presence of surface active substances changes the coalescence behavior. Joshi et al. (Joshi et al.1998) found that the minimum H_d/D increases with the increasing of the coalescence hinder behavior of electrolytes and the minimum H_d/D is believed to be bigger than 7. This brings doubts also on the minimum diameter, not to be 0.15m anymore. Moreover, in the tap water are present many other substances, different in any city and as Tang and Heindel (Tang and Heindel, 2004) reported a time-dependency to coalescence inhibition caused by the existence of volatile substances present in tap water. In addition to the studies done with water-air systems there are also all the experiments done with water solutions, often obtained from tap water. The studies done with distilled water are so far, not sufficient, also for the wide range of design setting used and because of some of the problems just discusses.

2.1.2 Comparisons

After the literature research, the focus of the thesis was to create a tool that enables us to a rapid comparison of the equations proposed by the different authors. A list of the main correlations has been done, 20 correlations were analyzed for a total amount of 283Mb.

Table 2.1: Correlations for gas holdup

Reference	Correlation
Hughmark et al. (1967)	$\varepsilon_G = \frac{1}{2+\left(\frac{0,35}{u_G}\right)\left[\frac{\rho_L\sigma_L}{72}\right]^{1/3}}$
Akita und Yoshida (1973)	$\frac{\varepsilon_G}{(1-\varepsilon_G)^4} = C\left(\frac{g{d_R}^2\rho_L}{\sigma_L}\right)^{1/8}\left(\frac{g{d_R}^3}{\nu_L^2}\right)^{1/12}\left(\frac{u_G}{\sqrt{gd_R}}\right)$ C = 0,2 for pure liquids and non-electrolytes C = 0,25 for electrolytes
Hikita and Kikukawa (1974)	$\varepsilon_G = 0,505u_G^{0,47}\left(\frac{0,072}{\sigma_L}\right)^{2/3}\left(\frac{0,001}{\eta_L}\right)^{0,05}$
Hikita et al. (1980)	$\varepsilon_G = 0,672f\left(\frac{u_G\eta_L}{\sigma_L}\right)^{0,578}\left(\frac{{\eta_L}^4 g}{\rho_L\sigma_L^3}\right)^{-0,131}\left(\frac{\rho_G}{\rho_L}\right)^{0,062}\left(\frac{\eta_G}{\eta_L}\right)^{0,107}$ f= 1,0 for non electrolyte f = 10^0,0414I for electrolyte with Ionic strength I<1 kg Ion/m^3 f = 1,1 For electrolyte with Ionic strength I>1 kg Ion/m^3
Hammer et al. (1984)	$\varepsilon_G = 0,2\left(\frac{u_G}{\sqrt{d_R g}}\right)^{0,46}\left(\frac{g{d_R}^3{\rho_L}^2}{{\eta_L}^2}\right)^{0,08}\left(\frac{d_N}{d_R}\right)^{-0,17}$
Joshi et al. (1998)	$\varepsilon_G = 0,62u_G^{0,56}\left(\frac{0,07275}{\sigma_L}\right)^{0,15}\left(\frac{1}{1000\eta_L}\right)^{0,15}\left(\frac{\rho_G}{1,3}\right)^{0,15}\left(\frac{1000}{\rho_L}\right)^{0,15}$

Sotelo et al. (1994)	$\varepsilon_G = 129\left(\frac{u_G\eta_L}{\sigma_L}\right)^{0,99}\left(\frac{{\eta_L}^4 g}{\rho_L{\sigma_L}^3}\right)^{-0,123}\left(\frac{\rho_G}{\rho_L}\right)^{0,187}\left(\frac{\eta_G}{\eta_L}\right)^{0,343}\left(\frac{d_N}{d_R}\right)^{-0,089}$
Kojima et al. (1997)	$\varepsilon_G = 1{,}18{u_G}^{0,679}\left(\frac{\sigma_L}{\sigma_{L,0}}\right)^{-0,546}\exp\left\{1{,}27\times 10^{-4}\left(\frac{\rho_L Q^2}{{d_0}^3\sigma_L}\right)\left(\frac{P}{P_0}\right)\right\}$
Reilly et al. (1994)	$\varepsilon_G = 296u_G^{0,44}\rho_L^{-0,98}\rho_G^{0,19}\sigma_L^{-0,16} + 0{,}009$
Mouza et al. (2005)	$\varepsilon_G = 0{,}001\left[\left(\frac{u_G}{Dg}\right)^{0,5}\left(\frac{D^3{\rho_L}^2 g}{{\eta_L}^2}\right)^{0,1}\left(\frac{D^2\rho_L g}{\sigma_L}\right)^{2,2}\left(\frac{d_S}{D}\right)\right]^{2/3}$
Kazakis et al. (2007)	$\varepsilon_G = 0{,}2\left[\left(\frac{u_G^2}{d_R g}\right)^{0,8}\left(\frac{{d_R}^3 g}{{\nu_L}^2}\right)^{0,2}\left(\frac{{d_R}^2 g\rho_L}{\sigma_L}\right)^{1,6}\left(\frac{d_S}{d_R}\right)^{0,9}\left(\frac{d_N}{d_S}\right)^{0,03}\right]^{2/5}$
Krishna and Ellenberger (1996)	$u_G < u_{trans};\ \varepsilon_G = \varepsilon_{trans}$ $u_G > u_{trans};\ \varepsilon_G = \varepsilon_b + \varepsilon_{trans}(1-\varepsilon_b)$ $\varepsilon_b = 0{,}268\left[\frac{(u_G - u_{trans})^{0,58}}{{d_R}^{0,18}}\right]$ $u_{trans} = V_{small}\varepsilon_{trans}(1-\varepsilon_{trans})$ $V_{small} = \frac{\sigma_L^{0,12}}{2{,}84\rho_G^{0,04}}$
Serrafi et al. (1999)	$\frac{u_G}{\varepsilon_G} - \frac{u_L}{1-\varepsilon_G} = u_B F(\varepsilon_G)$ Homogeneous regime $F(\varepsilon_G) = 0{,}71 - 9\varepsilon_G + 7{,}0\left(\frac{u_G}{u_B}\right)^{3/4}$ Heterogeneous regime $F(\varepsilon_G) = 0{,}045 - 7{,}5\varepsilon_G + 5{,}5\left(\frac{u_G}{u_B}\right)^{1/2}$
Zou et al. (1988)	$\varepsilon_G = 0{,}17283\left(\frac{{\eta_L}^4 g}{\rho_L\sigma_L^3}\right)^{-0,1544}\left(\frac{P+P_S}{P}\right)^{1,6105}\left(\frac{u_G\eta_L}{\sigma_L}\right)^{0,5897}$
Idogawa et al. (1987)	$\frac{\varepsilon_G}{(1-\varepsilon_G)} = 0{,}059(100u_G)^{0,8}\rho_G^{0,17}\left(\frac{1000\sigma_L}{72}\right)^{-0,22\exp(-P/10^6)}$
Nedeltchev and Schumpe (2008)	$\varepsilon_G = f_c\frac{d_S f_B S_B}{6Au_B}$ $S_B = \pi\frac{l^2}{2}\left[1 + \left(\frac{h}{l}\right)^2\frac{1}{2e}\ln\frac{(1+e)}{(1-e)}\right]; e = \sqrt{1-\left(\frac{h}{l}\right)^2}$ For 2<Ta<6: $l = \frac{d_e}{1{,}14Ta^{-0,176}};\ h = 1{,}13d_e Ta^{-0,352}$ For 6<Ta<16,5: $l = \frac{d_e}{1{,}36Ta^{-0,28}};\ h = 1{,}85d_e Ta^{-0,56}$ $Ta = Re_B Mo^{0,23}; Re_B = \frac{d_e u_B\rho_L}{\eta_L};\ Mo = \frac{{\eta_L}^4 g}{\rho_L\sigma_L^3}$ $f_c = 0{,}78\left(\frac{(\rho_L-\rho_G){d_e}^2}{\sigma_L}\right)^{-0,22}\left(\frac{\rho_G}{1{,}2}\right)^{0,07}$
Wilkinson et al. (1994)	$u_G < u_{trans};\qquad \varepsilon_G = \frac{u_G}{u_{s,b}}$

	$u_G > u_{trans};\quad \varepsilon_G = \left(\frac{u_G}{u_{s,b}}\right) + \left[\frac{(u_G - u_{trans})}{u_{1,b}}\right]$ $\frac{u_{trans}}{u_{s,b}} = 0,5 * exp\left(-193{\rho_G}^{-0,61}\right)\eta_L^{0,5}\sigma_L^{0,11}$ $\frac{\eta_L u_{s,b}}{\sigma_L} = 2,25\left(\frac{\sigma_L^3\rho_L}{g\eta_L^4}\right)^{-0,273}\left(\frac{\rho_L}{\rho_G}\right)^{0,077}$ $\frac{\eta_L u_{1,b}}{\sigma_L} = \frac{\eta_L u_{s,b}}{\sigma_L} + 2,4\left[\frac{\mu_L(u_G - u_{trans})}{\sigma_L}\right]^{0,757}\left(\frac{\sigma_L^3\rho_L}{g\mu_L^4}\right)^{-0,077}\left(\frac{\rho_L}{\rho_G}\right)^{0,077}$
Bach and Pilhofer (1978)	$\frac{\varepsilon_G}{(1-\varepsilon_G)} = 0,115\left(\frac{u_G^3\rho_L}{\upsilon_L g(\rho_L - \rho_G)}\right)^{0,23}$
Haque et al. (1986)	$\varepsilon_G = 0,171u_G^{0,6}{\eta_{eff}}^{-0,22}D^{-0,15}$
Schumpe and Deckwer (1987)	$\varepsilon_G = 0,2\left(\frac{g\rho_L D^2}{\sigma_L}\right)^{-0,13}\left(\frac{g\rho_L^2 D^3}{{\eta_{eff}}^2}\right)^{-0,17}\left(\frac{u_G}{(gD)^{0,5}}\right)^{0,54}$
Luo et al. (1999)	$\frac{\varepsilon_G}{1-\varepsilon_G} = \frac{2,9\left(\frac{u_G^4\rho_G}{\sigma_L g}\right)^{\alpha}\left(\frac{\rho_G}{\rho_L}\right)^{\beta}}{\left(cosh\left(Mo_L^{0,054}\right)\right)^{0,41}}$ $\alpha = 0,21Mo_L^{0,0079};\ \beta = 0,096Mo_L^{-0,011};\ Mo_L = \frac{g\eta_L^4}{\rho_L{\sigma_L}^3}$
Urseanu et al. (2003)	$\varepsilon_G = 0,21u_G^{0,58}{\eta_L}^{-0,12}{d_R}^{-0,18}{\rho_G}^{(0,3\exp(-9\eta_L))}$
Behkish (2006)	$\varepsilon_G = 4,94\times10^{-3}\left(\frac{\rho_L^{0,415}\rho_G^{0,177}}{\eta_L^{0,174}\sigma_L^{0,27}}\right){u_G}^{0,533}\left(\frac{P}{P-P_S}\right)^{0,203}\left(\frac{D}{D+1}\right)^{-0,117} \times \Gamma^{0,0253} \times \exp[-2,231C_V - 0,157(\rho_P d_P) - 0,242X_W];$ Γ represent the sparger effect, $\Gamma = (K_d N_O d_O^{\alpha})$
Vatai and Tekic (1987)	$\varepsilon_G = 0,950\left(\frac{u_G\eta_L}{\sigma_L}\right)^{0,769}\left(\frac{{\eta_L}^4 g}{\rho_L\sigma_L^3}\right)^{-0,17}\left(\frac{\rho_G}{\rho_L}\right)^{0,062}\left(\frac{\eta_G}{\eta_L}\right)^{0,107}$
Jordan and Schumpe (2001)	$\frac{\varepsilon_G}{1-\varepsilon_G} = b_1\left(\frac{g\rho_L d_b^2}{\sigma_L}\right)^{0,16}\left(\frac{g\rho_L^2 d_b^3}{\eta_L^2}\right)^{0,04}\left(\frac{u_G}{(gd_b)^{0,5}}\right)^{0,7} * \left[1 + 27\left(\frac{u_G}{\sqrt{gd_b}}\right)^{0,52}\left(\frac{\rho_G}{\rho_L}\right)^{0,58}\right]$
Gandhi and Joshi (2010)	Correlation developed using hybrid genetic algorithm-support vector regressio technique

A sample of the database with all the correlations is presented in table 2.2.

To give an idea of how to deal with the correlations can be confusing, the example of the water-air system is considered. In Fig. 2.2 it can be noticed how many different values can be obtained. This is due to the fact that, the differences are not only quantitative but also qualitative. Since the system (water-air) is defined, the differences should be just in the design variables, i.e. gas distributor, diameter of the column, height to diameter ratio. Nevertheless also the operating variables can differ, such as the quality of the water. The use of tap water instead of distilled water, because of the difference salt composition of the tap water, induces non-homogeneous results.

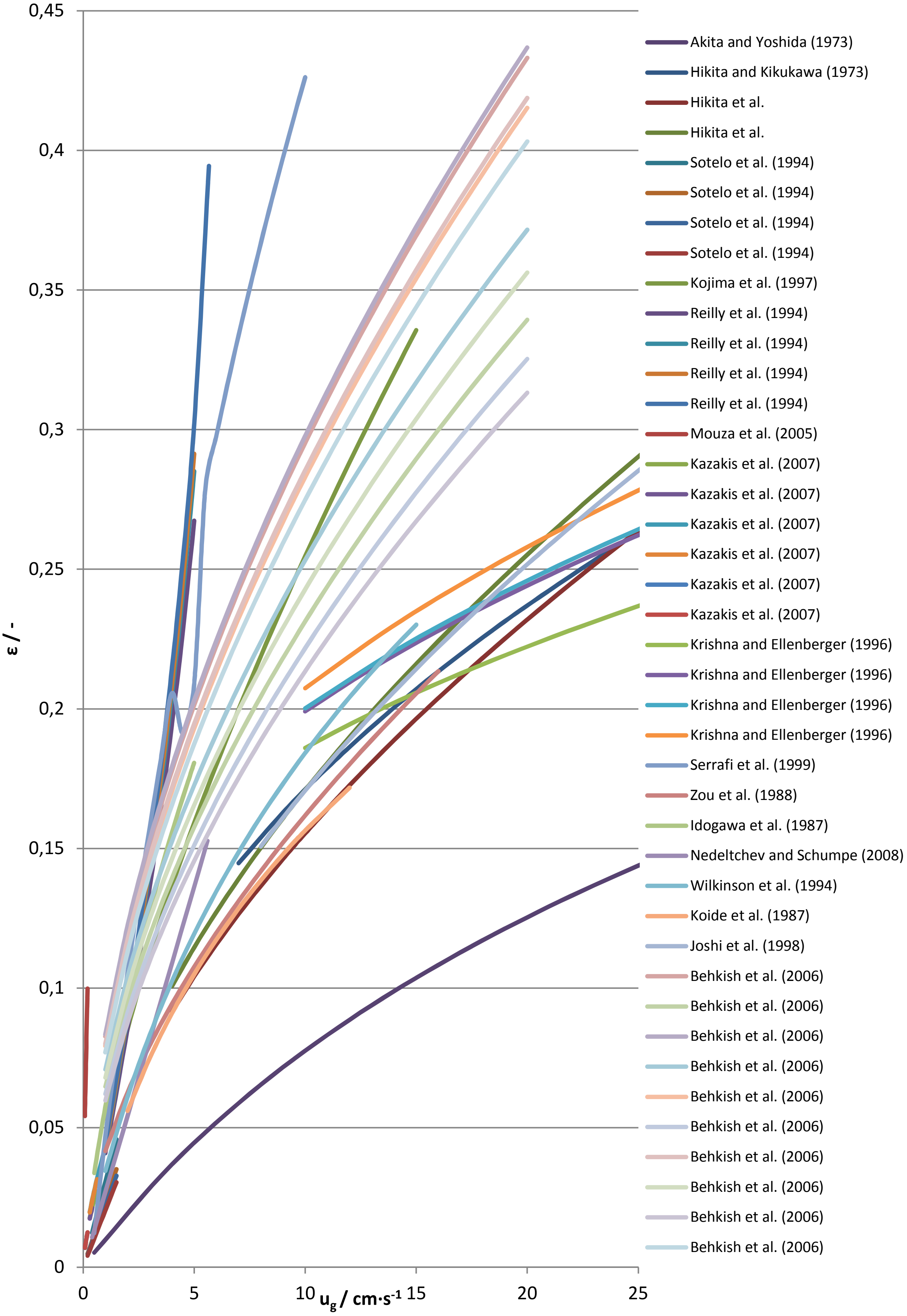


Fig. 2.2: *Superficial gas velocity – gas holdup plot in the water-air system.*

Table 2.2: Example of the database for gas holdup

reference	Research Group	Component System gas1/gas2/..-liquid1/liquid2/..-solid1/solid2/..	deionized water (1=yes, 0=not specified/not) ionized water=2	Type of column (1=cylindrical, 2=square)	D [m]	H/D [-]	Sparger (1=single orifice, 2=porous/sintered plate 3=X-type, 4=sieve plate, 5=perforated plate triangular pitch, 6=sieve plate circular pitch, 7=sieve plate squar pitch, 8=Sieve plate, covered with cloth, 9=ring sparger, 10=perforated plate square pitch)	sparger Diameter [mm]	pitch distance [mm]	N°holes	D holes [mm]	μ_L [Pa*s] (k for non newtonian)	n [-] (for non newtonian)	μ_G[Pa*s]
21	Koide et al. (1987)	Air-Ethylen glycol aqueous solution-glass spheres	1	1	0,3	7	5		50	31	2,5	0,00525		
21	Koide et al. (1987)	Air-Ethylen glycol aqueous solution-glass spheres	1	1	0,3	7	5		50	31	2,5	0,00525		
21	Koide et al. (1987)	Air-Ethylen glycol aqueous solution-glass spheres	1	1	0,3	7	5		50	31	2,5	0,00525		
21	Koide et al. (1987)	Air-Ethylen glycol aqueous solution-glass spheres	1	1	0,3	7	5		50	31	2,5	0,00525		

21	Koide et al. (1987)	Air-Ethylen glycol aqueous solution-glass spheres	1	1	0,3	7	5		50	31	2,5	0,00525		
21	Koide et al. (1987)	Air-Ethylen glycol aqueous solution-glass spheres	1	1	0,3	7	5		50	31	2,5	0,00525		
21	Koide et al. (1987)	Air-Ethylen glycol aqueous solution-glass spheres	1	1	0,3	7	5		50	31	2,5	0,00525		
21	Koide et al. (1987)	Air-Ethylen glycol aqueous solution-glass spheres	1	1	0,3	7	5		50	31	2,5	0,00525		
21	Koide et al. (1987)	Air-Ethylen glycol aqueous solution-glass spheres	1	1	0,3	7	5		50	31	2,5	0,00525		
21	Koide et al. (1987)	Air-Ethylen glycol aqueous solution-glass spheres	1	1	0,3	7	5		50	31	2,5	0,00525		
21	Koide	Air-BaCl2	2	1	0,3	7	5		50	31	2,5	0,000919		

	et al. (1987)	aqueous solutions-glass spheres												
21	Koide et al. (1987)	Air-BaCl2 aqueous solutions-glass spheres	2	1	0,3	7	5		50	31	2,5	0,000919		
21	Koide et al. (1987)	Air-BaCl2 aqueous solutions-glass spheres	2	1	0,3	7	5		50	31	2,5	0,000919		

	ρ_G [Kg/m^3]	σ_L [N/m]	T [K]	P [Mpa]	P^{sat} [Mpa]	u_L [m/s] <0 concorrent	u_G [cm/s]	ε_G	regime (1=only homogeneus, 2=only ehtherogeneus, 3=both, 4=slug flow)	representatio: 1=experimental, 0=random	Volumetric solid concentration in the slurry Cv [v/v]	Density of the particles ρp [Kg/m^3]	Diameter of the particles dp [m]	Weight fraction of the primary liquid in the mixture Xv (0.5<Xv<1) [w/w]
1088		0,0515	298,2				2	0,097521	2	1	0,7	2500	0,000079	1088
1088		0,0515	298,2				3	0,122061	2	1	0,7	2500	0,000079	1088
1088		0,0515	298,2				4	0,141573	2	1	0,7	2500	0,000079	1088
1088		0,0515	298,2				5	0,157828	2	1	0,7	2500	0,000079	1088
1088		0,0515	298,2				6	0,171781	2	1	0,7	2500	0,000079	1088
1088		0,0515	298,2				7	0,184014	2	1	0,7	2500	0,000079	1088
1088		0,0515	298,2				8	0,194909	2	1	0,7	2500	0,000079	1088
1088		0,0515	298,2				9	0,204731	2	1	0,7	2500	0,000079	1088
1088		0,0515	298,2				10	0,213673	2	1	0,7	2500	0,000079	1088
1088		0,0515	298,2				12	0,229464	2	1	0,7	2500	0,000079	1088
1016		0,0724	298,2				2	0,116471	2	1	0,7	2500	0,000079	1016
1016		0,0724	298,2				3	0,14391	2	1	0,7	2500	0,000079	1016
1016		0,0724	298,2				4	0,16535	2	1	0,7	2500	0,000079	1016

This huge amount of data seems to satisfy any need but, if data regarding a specific column want to be found, for example operating with distilled water, diameter bigger than 0.2m and with porous sparger, the result is the sequent in figure 2.3.

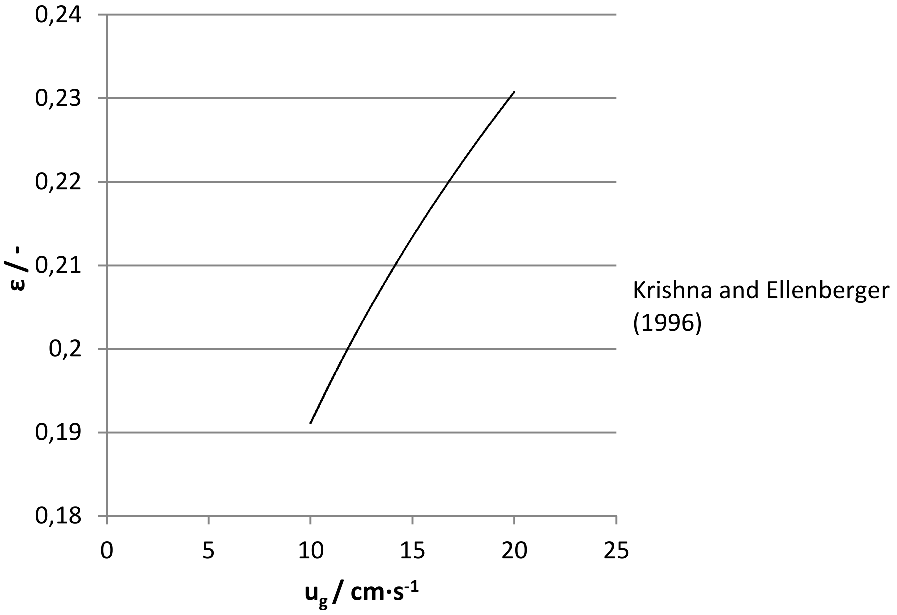


Fig. 2.3: *Correlation for water-air system with distilled water, D>0.2m and porous sparger.*

Only one correlation satisfy our requirements, and only for high gas velocities.

To perform a more accurate analysis all the possible system are going to be taken into account. This is possible since the table has been realized with all the possible result (in a discrete interval) of the gas holdup equations. With the intention to be more precise as possible, the results represent the experiments done for the fitting of the equations. Where this was not possible, because of the lack of information in the author's paper, all the possible combinations of the parameters were performed with a Matlab® routine (appendix A). This procedure generated the large amount of date in the tables. Thanks to a filter function, from a dispersive quantity of information, is possible to arrive at a narrow selection of gas holdup values. The selection can be performed selecting among: Research group, component system, type of water (deionized or not), type of column, diameter, height to diameter ratio, type of sparger, diameter of the sparger, pitch distance, number of holes, diameter of holes, viscosity of the liquid, viscosity of the gas, density of the liquid, density of the gas, surface tension of the liquid, temperature, pressure, saturation pressure of the liquid, gas velocity, gas holdup, operating regime, type of representation (from experimental values or from a random set), as can be seen from table 2.2.

Using the filter function some examples are given.

Example #1

Homogeneous regime, D>0.15 m, H/D>5, ρ_L =1,800 Kg/m^3, 6 Kg/m^3 < ρ_G < 9 Kg/m^3, σ = 0.02 N/m, μ_L= 0.055 Pa*s

The following correlations are left: Reilly et al. (1994) and Wilkinson et al. (1994)

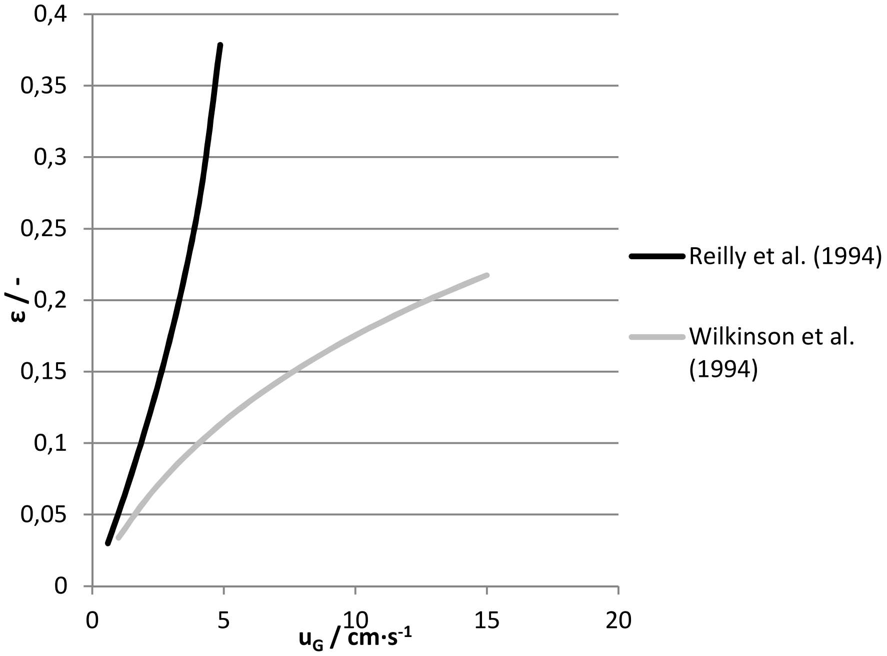


Fig.2.4: *gas holdup vs. superficial gas velocity, example #1*

The problem of this comparison even if it seems very specific, is that in Wilkinson´s data less information are provided, for example none sparger is specified and moreover the data come from a random evaluation, not as representation of experimental data, the correlation is considered to be general in its field of applicability but as can been seen at a gas velocity of 5 cm/s there is a deviation of 0.25 in gas holdup. In the next example correlations with same sparger and type of representation are going to be compared.

Example #2

Homogeneous regime, Experimental representation, $\rho_G = 1.2$ Kg/m^{3,} X-type sparger, X-Type sparger or Perforated plate (otherwise only one correlation was possible), 0.23 N/m < σ < 0.25 N/m

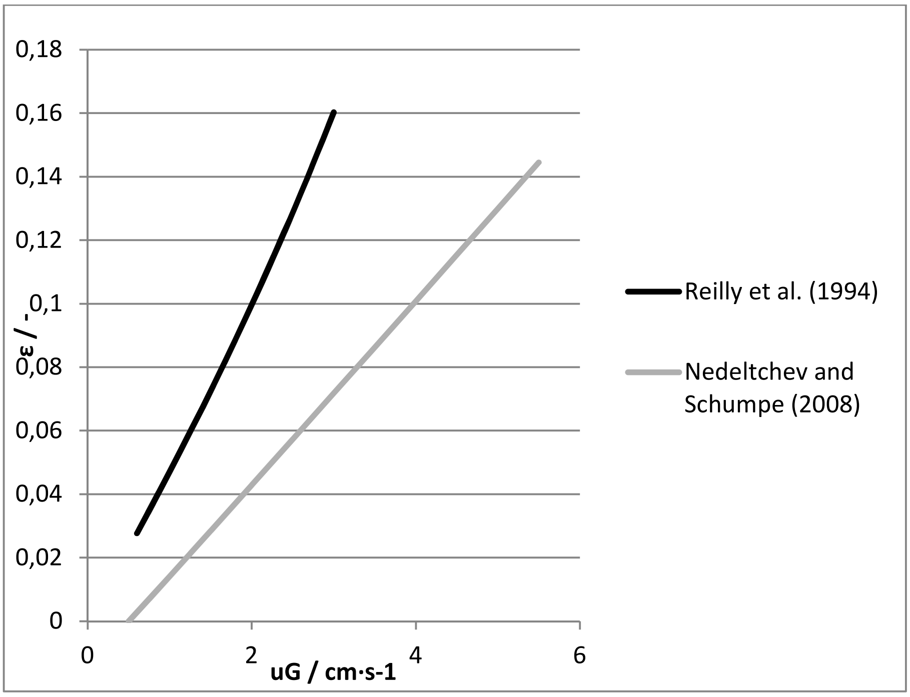


Fig. 2.5: *gas holdup vs. superficial gas velocity, example #2*

Even if many physical variables are similar, the comparison is between two different liquids, one is Isopar-G (Reilly et al.) and the other is Butanol (Nedeltchev and Schumpe). This lead to a difference in gas holdup of 0.6 at a superficial gas velocity of 2cm/s and with increasing gas velocity this value increases. This means that the exponent related to the superficial gas velocity is higher for Reilly. The correlation by Nedeltchev and Schumpe however is not explicit in the gas velocity, as can be seen from table 2.1, therefore a graphical representation is useful also to analyze the single correlations.

Example #3

Heterogeneous regime, Sparger not specified, air-water

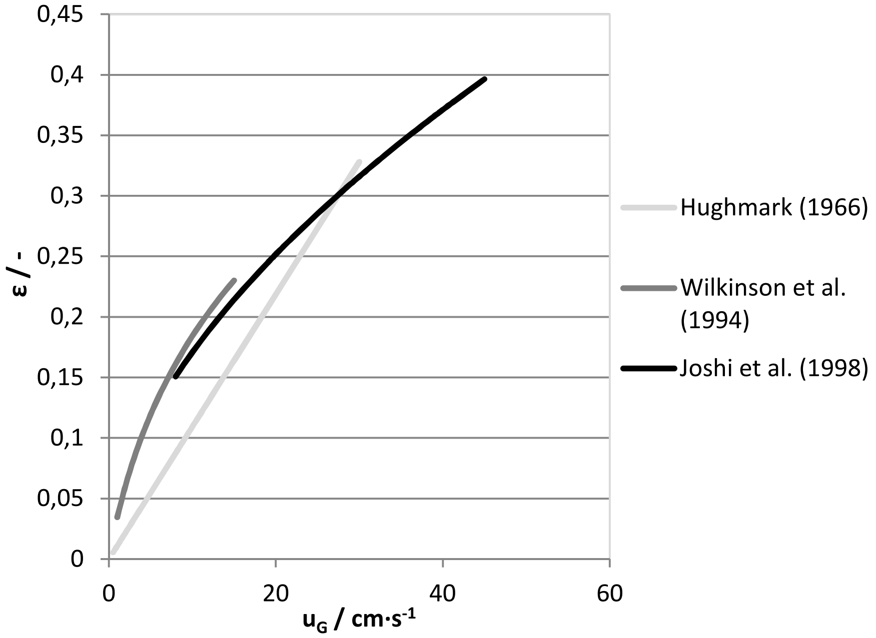


Fig. 2.6*: gas holdup Vs. superficial gas velocity, example #3*

In this example can be noticed how the curves are closer, even if the Hughmark´s correlation does not seem to be very trustable since the exponent for the superficial gas velocity is one, and not smaller than one as it is supposed to be for the heterogeneous regime.

Example #4

Heterogeneous regime, 0.3 < Slurry concentration < 0.4, 0.0001 Pa*s< μ_L< 0.001 Pa*s, 900 kg/m^3 < ρ_L < 1300 kg/m^{3,} 0.2 kg/m^3 < ρ_G < 1.2 kg/m^{3,} σ = 0.75 N/m, ρ_P= 2300 Kg/m^{3,} D>0.15m

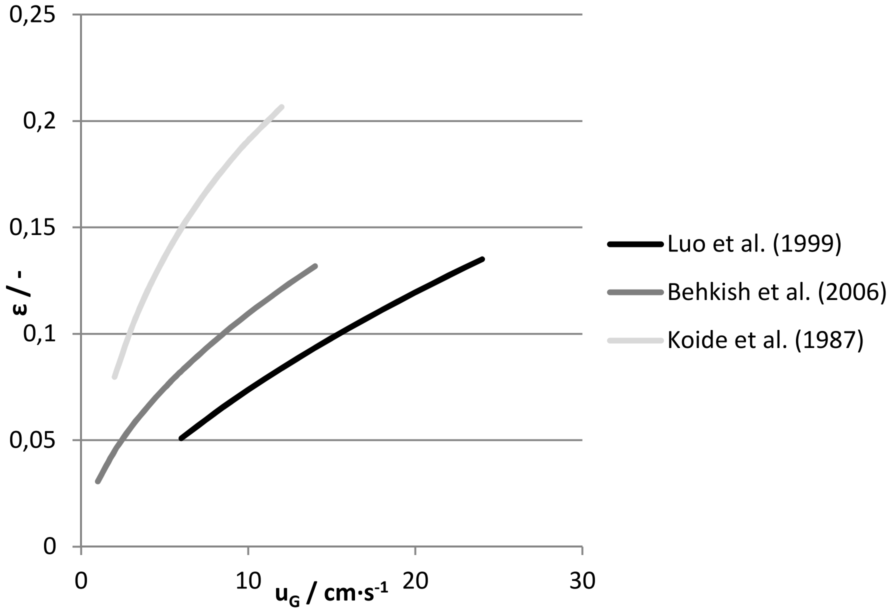


Fig. 3.2: *gas holdup Vs. superficial gas velocity, example #4*

Also in this case the problem has been to select homogeneous data, since the random evaluation of a correlation has limits in covering similar range of the variables. For example, if in a correlation the viscosity is in the range [0.0001;0.001] and in another one [0.0001; 0.01] and if for each one, 4 different values are wanted, the result is the following: for the first range [0.0001; 0.00033; 0.00066; 0.001] and for the second [0.0001; 0.0033; 0.0066; 0.01]. Only the first value of each set is the same, but if even the extremes of the sets are different is even more difficult. The solution should be to increase the number of elements for each set, however if a correlation has 8 parameters, and with the slurry bubble-columns can be even more, and for each parameters a set of 4 values is created, the total number of possible configurations is 4^8=65,000, with 6, the maximum number of rows in excel is exeeded.

Example #5

The work presented by Ghandi and Joshi (Ghandi and Joshi, 2010) seems to redefine the whole apparatus of empirical correlations. They used the genetic algorithm to analyze 3300 experimental point to create a tool for the calculation of gas holdup. The tool is available online as excel paper. With this tool is it possible to change 15 parameters, between physical and design variables.

The system analyzed is water-air, the only variable changed is the sparger design. To identify the gas distributor, 3 parameters are available: sparger distributor coefficient, number of holes and diameter of holes. Multi-orifice spargers, in the configuration of porous/sintered plate and perforated plate and single hole sparger have been tested.

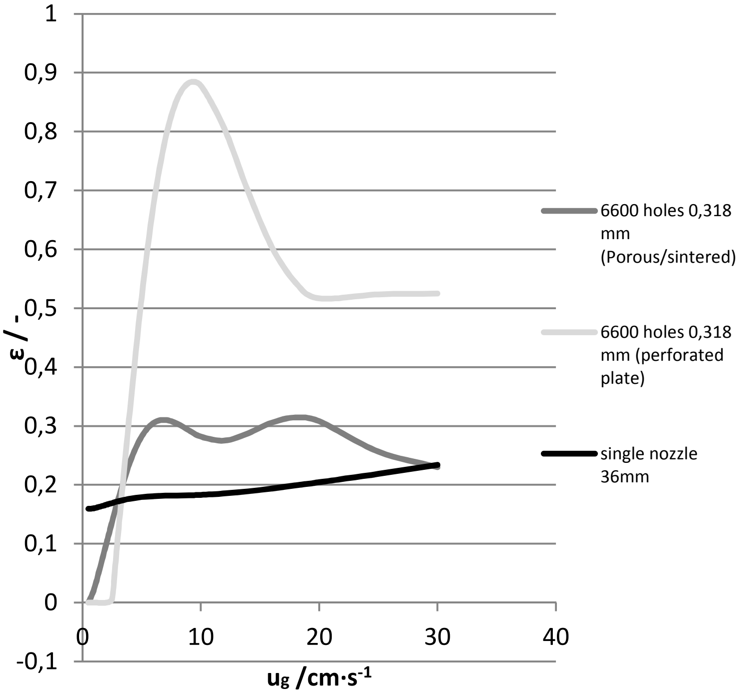


Fig. 2.8: *holdup Vs. superficial gas velocity, example #5*

The trend of the 3 curves is totally different form the “conventional” behavior. Oscillation for the blue curve, maximum for the red one and gas holdup different from zero at no gas velocity for the green one are present. These behaviors do not represent possible situation, therefore this correlation still has to be refined to be usable.

2.1.3 Sensitivity analysis

In this section, the effects of variables different from superficial gas velocity are tested.

Beginning with the surface tension, is interesting to see in which range and with what kind of sensibility the surface tension affects the gas holdup, to create homogeneous conditions the other parameters are kept constant and with similar values. During the selection of the data, in this case is more difficult when the data represent the experimental results since the other parameters are not constant, creating not comparable results, for this reason, this data are kept only if the correlation is not influenced by these parameters.

Example #6

The conditions filtered are: u_G=15cm/s, ρ_L=1500 kg/m^3, μ_L=0.01 Pa*s, ρ_G=1.2 kg/m^3

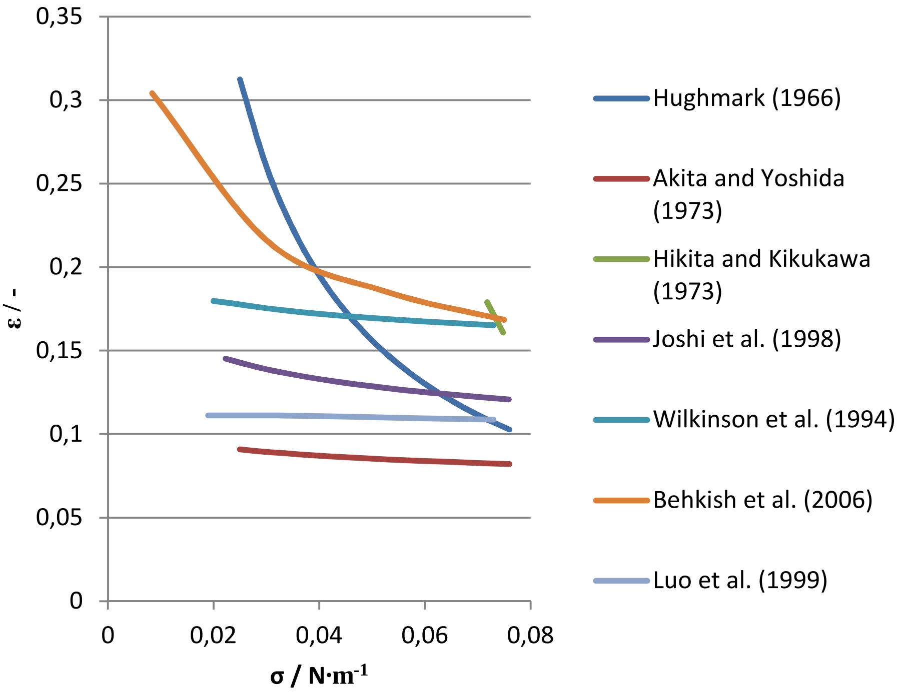


Fig. 2.9: *gas holdup vs. surface tension, example #6*

The differences in the gas holdup in this case are not relevant, since different spargers and slightly different operating conditions are present in the different correlations, however, excepting the older correlations, similar behaviors are represented.

Example #7

The diameter of the column is present in 10 correlations among our selection, even if it is said that it has little influence. Moreover in some correlations the diameter was not studied with its direct influence but for example, through its ratio with the bubble diameter or the sparger diameter. In these cases therefore is not possible to compare that data since the diameter results constant.

The conditions filtered are: diameter dependence and u_G=15cm/s, the other condition were dictated by the single correlation.

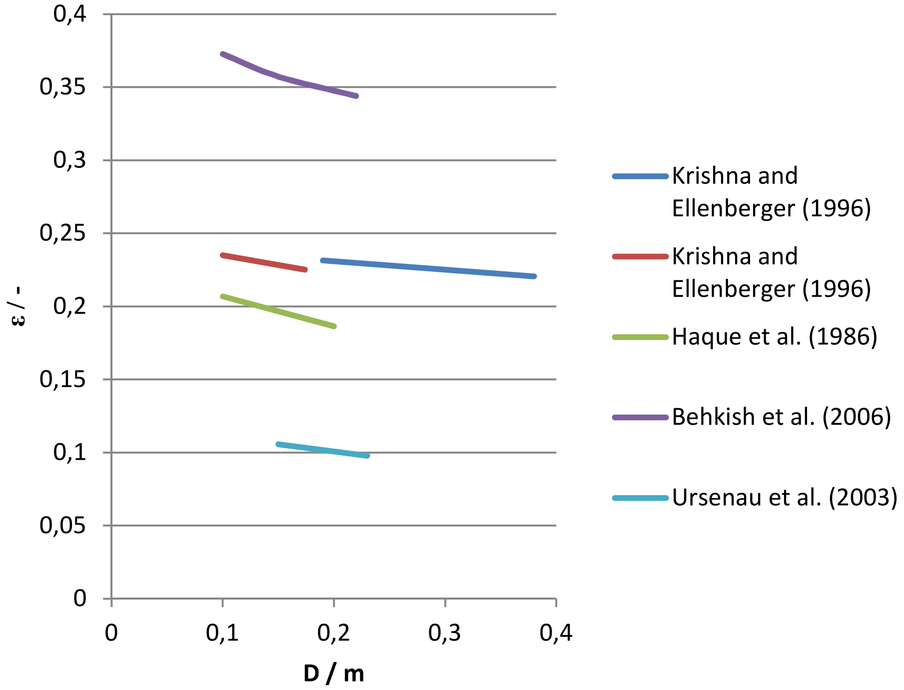


Fig. 2.10: *gas holdup vs. column diameter, example #7*

In all the correlation analyzed, as expected, the gas holdup decreases with increasing column diameter and the behavior is similar in all the correlations.

Example #8

Studies at high pressure are limited since expensive equipment are required, especially if diameters larger than 0.15 want to be utilized. Therefore most of the data collected for this example do not come from the representation of the experiments, but from a general correlation. Some correlations did not specify the pressure but rather than the density of the gas, for this reason this last one was used.

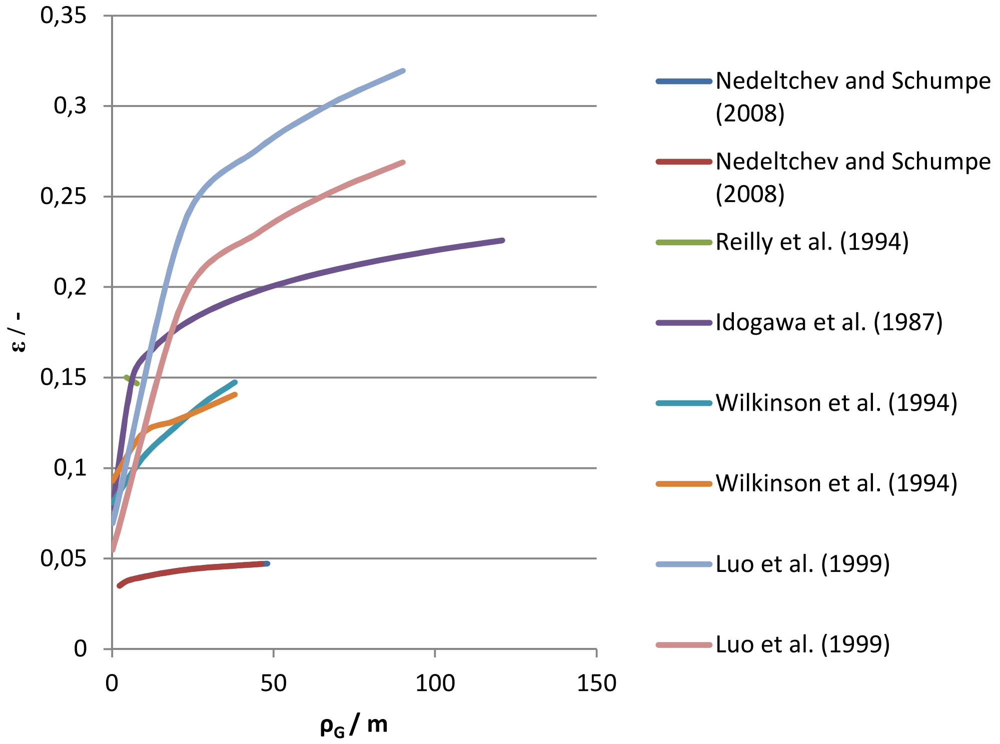


Fig. 2.11: *gas holdup Vs. gas density, example #8*

The data represented by the correlation of Nedeltchev and Schumpe, in this case, are the only ones that represent experimental data and most important thing, they are in the homogeneous regime. For the heterogeneous regime, similar behaviors are represented, with the exception of Reilly et al. that is only one with opposite behavior.

2.2 Volumetric Mass Transfer Coefficient

Also for the mass transfer a deep research has been done, however the complications already encountered in the understanding of the gas holdup are increased. For this reason fewer correlations are available and for limited reaction conditions, especially slurry bubble columns. All the systems analyzed consider the mass transfer between gas and liquid phase without reaction.

2.2.1 State of art

The fundamental transport relations (mass balances and diffusion flux relations) and the transport properties (diffusivities) allow the calculation of the rate of mass transfer within a single phase. However this is possible for well-defined geometries and flow situations or sufficient simplicity. For the bubble columns is not the case, for this reason the mass transport across the interfaces is described by using mass transfer coefficients instead of diffusivities. These coefficients play a role similar to diffusivities in that they describe the transport rate of mass that occurs because of molecular motion. Once this coefficient has been determined experimentally, and correlated by dimensionless groups, the coefficients for analogous situations can be estimated and used for process design.

Mass transfer occurs because of an imbalance of concentrations, a departure from equilibrium. This imbalance provides a driving force for mass transfer. Uniformity of composition is the equilibrium state in a single phase; if mole fractions are not uniform, then a non-equilibrium condition exists and diffusion occurs until uniformity is reached. Two-phase thermodynamic equilibrium is the equilibrium state across an interface; to the extent that the two phases on opposite sides of an interface are not in equilibrium, mass transfer tends to occur in such a way as to move the system toward equilibrium. The degree of departure from equilibrium directly affects the rate of mass transfer. In a single phase, the degree of departure from equilibrium is represented by the mole fraction (or mass fraction) gradient, and Fick’s first law of diffusion (the most commonly factor defines the diffusivity). For mass transfer across interfaces, an analogous relationship is normally used to define mass-transfer coefficients. The mass-transfer flux of a species at an interface is modeled as proportional to the driving force (concentration difference) which exists for that transfer, through a thin film next to the interface. This situation is depicted in Figure 2.12. At the interface the two phases are normally assumed to be in thermodynamic equilibrium. Away from the interface, however, the bulk concentrations of the two phases are not necessarily at equilibrium with each other, and possible concentration or mole fraction profiles are shown as a function of distance from the interface. The majority of the concentration change is modeled to occur over a laminar film region near the interface.

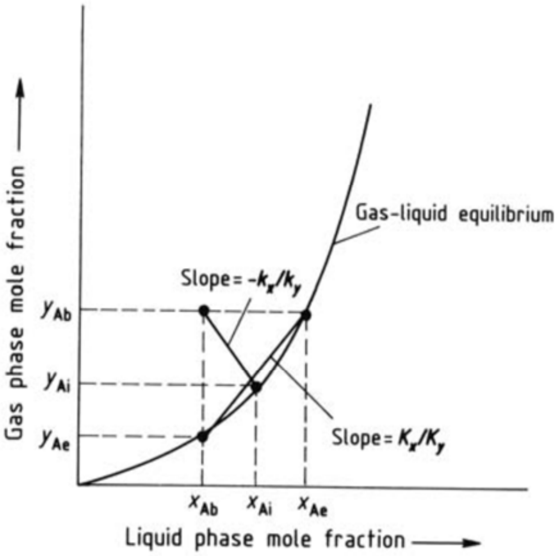


Fig. 2.12: *Concentration profiles across the gas – liquid interface region with the transfer of A from the gas to the liquid* y_{Ab} *= mole fraction of A in bulk gas phase;* y_{Ai} *= gas-phase mole fraction of A at interface;* x_{Ai} *= liquid-phase mole fraction of A at interface;* x_{Ab} *= mole fraction of A in bulk liquid phase.*

The actual concentrations and film depths are not known, however, which makes the definitions quite empirical and dependent on parameters such as fluid flow and turbulence. In Figure 2.12, concentration profiles are shown in both phases and, for simplicity, one phase is called a gas phase and the other a liquid phase, although this is not a limitation or constraint on the situation. The discussion could just as well be for two liquid phases or for a fluid and a solid phase. The model also normally assumes that concentrations at the interface are at steady state; flux to the interface through one phase equals that away from the interface through the other. Mass-transfer coefficients, then, are defined for each of the two phases. The definition of a liquid-phase mass-transfer coefficient (based on a liquid-phase mole fraction driving force) is

$$\text{Flux of A} = k_x (x_{Ai} - x_{Ab}) \qquad (2.2)$$

Likewise, the defining relation for the gas-phase mass-transfer coefficient for species based on the gas-phase mole fractions is

$$\text{Flux of A} = k_y (x_{Ab} - x_{Ai}) \qquad (2.3)$$

In each of these equations, a departure from equilibrium exists that represents the extent to which the interface mole fraction (x_{Ai} or y_{Ai}) differs from that in the bulk fluid (x_{Ab} or y_{Ab}) of the same phase. Whereas the above relations define mass transfer coefficients for a driving force within a single phase at an interface, interphase mass transfer coefficients are also defined according to concentration or mole fraction differences that exist across the two phases, where the average or bulk concentrations are used for each phase. In this case the mass-transfer coefficients K_x and K_y are defined according to the relations

$$\text{Flux of A} = K_x (x_{Ae} - x_{Ab}) \qquad (2.4)$$

Flux of A = K_y ($x_{Ab} - x_{Ae}$) (2.5)

and are called overall mass-transfer coefficients. They describe the flux in terms of mole fractions in the bulk phases.

Here, instead of defining a driving force that exists within one phase or the other, a driving force that spans the two phases is defined. The mole fractions and driving forces are shown relative to a typical interfacial equilibrium curve in Figure 3.12. For a mass-transfer coefficient based on liquid-phase mole fractions, the driving force that is used is the difference between the actual mole fraction of A in the bulk liquid phase (x_{Ab}) and the mole fraction of A that would exist (x_{Ae}) if the liquid phase were in equilibrium with the mole fraction of A in the bulk gas phase. Likewise, in terms of gas-phase concentrations, mass transfer of A occurs to the extent that the bulk gas-phase mole fraction (y_{Ab}) differs from the value that would exist (y_{Ae}) if the gas phase were in equilibrium with the actual bulk liquid-phase mole fraction. The slopes of lines that represent the ratios of mass-transfer coefficients are also shown in Figure 2.11. If species A does not accumulate at the interface, the liquid- and gas-phase relationships for flux in terms of mass-transfer coefficients must be equal. Accordingly,

$$k_x (x_{Ai} - x_{Ab}) = k_y (x_{Ab} - x_{Ai}) \tag{2.6}$$

which gives

$$-\frac{k_x}{k_y} = \frac{x_{Ai} - x_{Ab}}{y_{Ab} - Y_{Ai}} \tag{2.7}$$

and the ratio of the interphase mass-transfer coefficients is the slope of a tie line connecting the point with composition coordinates equal to the liquid- and gas-phase bulk concentrations to a point with coordinates equal to the equilibrium interface liquid- and gas-phase concentrations.

Similarly, a ratio can be obtained for the overall transfer coefficients:

$$-\frac{K_x}{K_y} = \frac{x_{Ai} - x_{Ab}}{y_{Ab} - Y_{Ai}} \tag{2.8}$$

In the limit of small driving forces or for a linear isotherm this ratio is the slope m of a tangent to the equilibrium curve in the concentration region of interest.

From the definition of the mass-transfer coefficients and for a locally linear isotherm (slope = m),

$$\frac{1}{K_x} = \frac{1}{k_x} + \frac{1}{m\, k_y} \tag{2.9}$$

and

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{m}{k_x} \tag{2.10}$$

Hence, the overall or combined resistance to mass transfer through the two phases ($1/K_x$ or $1/K_y$) is equal to the sum of the resistances through each of the phases individually. Before summing, however, one of the individual phase coefficients must be scaled by using the (local) slope of the equilibrium curve in order to be consistent with the resistance offered by the other mass-transfer coefficient. Note that if $k_x/m >> k_y$, then the gas phase mass transfer is limiting and $K_y \approx k_y$.

Because the flux of A is the number of moles of A per time per (cross-sectional) area, the mass transfer coefficients as defined by these relations must also have the dimensions of number of moles per time per area. Other definitions using different driving force concentration units are employed, however, and the dimensions of the mass-transfer coefficient vary accordingly. For example, number of moles per volume is frequently used for liquid-phase concentrations and partial pressure for gas-phase concentration. In these situations, mass-transfer coefficients may be defined according to

$$\text{Flux of A} = k_c\,(c_{Ai} - c_{Ab}) \tag{2.11}$$

$$\text{Flux of A} = k_G\,(p_{Ab} - p_{Ai}) \tag{2.12}$$

$$\text{Flux of A} = K_c\,(c_{Ae} - c_{Ab}) \tag{2.13}$$

$$\text{Flux of A} = K_G\,(p_{Ab} - p_{Ae}) \tag{2.14}$$

Here, k_c and K_c have the dimensions of volume per time per area (length per time), and k_G and K_G have the dimension of number of moles per time per area per unit pressure.

The mass transfer between the gas and liquid phase in a bubble column can be generally described by the volumetric mass-transfer coefficient k_La, which is the liquid-phase mass transfer coefficient k_L multiplied by the specific interfacial area. Gas-phase resistance can usually be neglected, so k_La gives an adequate description. To determine the mass-transfer rate, however, the driving concentration difference must be known which in turn requires knowledge of mixing behavior in the gas and liquid phase. In industrial units (D_t > 1 m), estimates can be based on the assumption of complete mixing in both liquid and gas phases.

Like gas holdup and interfacial area, k_La also depends on the gas flow rate, type of sparger, and gas–liquid system. The mass-transfer coefficient and the gas rate are proportional to one another:

$$K_{La} \sim u_G^{\,n} \tag{2.15}$$

where n can be between 0.7 and 0.92 (Akita and Yoshida, 1974; Deckwer et al., 1974). Mass-transfer coefficients of two- to threefold higher can be achieved in the homogeneous flow regime if a porous plate is used as a sparger instead of a perforated plate.

Interested in the effects of the design parameters, the effects of column dimension, gas sparger and operating conditions are investigated.

Vandu and Krishna (Vandu and Krishna, 2004) observed that k_La/ε showed a slight increase with column diameter. Krishna and Van Baten (Krishna and Van Baten, 2003) carried out CFD simulations and showed that k_La decrease with column diameter. Verma and Rai (Verma and Rai, 2003) reported that the mass transfer coefficient was independent of initial bed height. Higher values were obtained with the spargers for whom the gas holdup values were also higher, i.e. higher values of mass transfer coefficient were obtained with perforated plate distributor.

As far as the liquid properties are concerned, experiments performed with viscous media showed that the volumetric mass transfer coefficient, k_La, decrease with increasing liquid viscosity (Fukuma et al., 1987). It was pointed out that higher viscosity led to increase of the volume fraction of the large bubbles, leading to much lower gas–liquid interfacial areas. Öztürk et al. (Öztürk et al., 1987) investigated mass transfer coefficient in various organic liquids and observed that k_La values increased with increasing gas density. Interestingly, the authors reported that k_La values in mixed liquids were close to those in pure liquids of similar properties. Muller and Davidson (Muller and Davidson, 1992) performed experiments with viscous media and pointed out the effect of surface active agents on the mass transfer. They reported that k_la values increase in the presence of surfactants. The authors attributed this increase to the creation of small bubbles and reduced bubble coalescence due to surfactants. Vandu and Krishna (Vandu and Krishna 2004) reported experimental work on estimation of volumetric mass transfer coefficient in a bubble column. While most of the published work is restricted to low gas velocities, low slurry concentrations and small column diameters, the study of Vandu and Krishna dealt with high slurry concentrations and high superficial gas velocities. They reported that k_La values closely followed the trend in gas holdup and that k_La/ε was found to depend on the liquid-phase Schmidt number.

Vafopulos et al. (Vafopulos et al, 1975) investigated the mass transfer in an air–water bubble column at pressures from 0.1 to 1 MPa. They reported that pressure has no significant effect on gas holdup and volumetric liquid-phase mass transfer coefficient. However, many studies report a significant effect of pressure on mass transfer rates. For instance, Wilkinson and Haringa (Wilkinson and Haringa, 1994) worked in the pressure range of 0.1–0.4 MPa and reported that both the interfacial area and volumetric mass transfer coefficient increase with pressure. Similarly, experiments in the pressure ranges 0.1–0.8 MPa showed that k_la values increased with increasing pressure (Behkish et al. 1984). This was attributed to the corresponding increase of the gas–liquid interfacial area. Still higher pressures (up to 5 MPa) were examined in the study of Maalej et al. (Maalej et al., 2003) and it was reported that both interfacial area and the volumetric mass transfer coefficient (k_La) were affected by pressure, whereas the mass transfer coefficient (k_L) was independent of pressure. It was concluded that for a fixed gas mass flow rate, the interfacial area and the volumetric mass transfer coefficient decrease with increasing operating pressure. However, for a fixed pressure, they increase with increasing gas mass flow rates.

2.2.2 Comparisons

The work regarding the volumetric mass-transfer has been done, like for the gas holdup, collecting first the correlations in a table with the possible results and then analyzing the results. For the volumetric mass-transfer fewer correlations were taken into account since the industrial interest of this parameter is more limited than for the gas holdup. Most of the correlations do not even concern the water-air system. The bubble columns usually employed in this case are slurry bubble columns. The presence of this third phase increases also the number of parameters taken into account and therefore the number of possible combination of the variables, 109Mb is the amount of data to represent thirteen correlations. The correlations are listed in table 3.3.

Table 2.3: Correlations for volumetric mass-transfer.

Reference	Correlations
Akita und Yoshida (1973)	$\frac{k_L a d_R^2}{D_L} = 0{,}6\left(\frac{\nu_L}{D_L}\right)^{0,5}\left(\frac{g d_R^2 \rho_L}{\sigma_L}\right)^{0,62}\left(\frac{g d_R^3}{\nu_L^2}\right)^{0,31}\varepsilon_G^{1,1}$
Deckwer et al. (1981)	$k_L a = 0{,}00315 {u_G}^{0,59} {\eta_{eff}}^{-0,84}$
Nakanoh and Yoshida (1980)	$\frac{k_L a d_R^2}{D_L} = 0{,}09\left(\frac{\rho_L g {d_R}^2}{\sigma_L}\right)^{0,75}\left(\frac{g d_R^3}{\nu_L^2}\right)^{0,39}\left(\frac{\nu_L}{D_L}\right)^{0,5}\left(\frac{u_G}{\sqrt{g d_R}}\right)$
Hikita et al. (1981)	$k_L a = \frac{14{,}9 g f}{u_G}\left(\frac{u_G \eta_L}{\sigma_L}\right)^{1,76}\left(\frac{{\eta_L}^4 g}{\rho_L {\sigma_L}^3}\right)^{-0,248}\left(\frac{\eta_G}{\eta_L}\right)^{0,243}\left(\frac{\eta_L}{\rho_L D_L}\right)^{-0,604}$ f= 1,0 for non electrolyte f = 10^0,0414I for electrolyte with Ionic strength I<1 kg Ion/m³ f = 1,1 For electrolyte with Ionic strength I>1 kg Ion/m³
Öztürk et al. (1987)	$\frac{k_L a d_b^2}{D_L} = 0{,}62\left(\frac{\eta_L}{\rho_L D_L}\right)^{0,5}\left(\frac{g d_b^2 \rho_L}{\sigma_L}\right)^{0,33}\left(\frac{g {\rho_L}^2 d_b^3}{{\eta_L}^2}\right)\left(\frac{u_G}{\sqrt{g d_b}}\right)^{0,68}\left(\frac{\rho_G}{\rho_L}\right)^{0,04}$

Kawase and Moo-Young (1987)	$\frac{k_L a d_R^2}{D_L} = 0{,}452\left(\frac{\eta_L}{D_L}\right)^{0{,}5}\left(\frac{d_R u_G}{\eta_L}\right)^{3/4}\left(\frac{u_G}{g d_R}\right)^{7/60}\left(\frac{\rho_L g d_R^2}{\sigma_L}\right)^{3/5}$
Deckwer et al. (1974)	$k_L a = 0{,}00208{u_G}^{0{,}59}{\eta_{eff}}^{-0{,}84}$
Godbole et al. (1984)	$k_L a = 8{,}35 \cdot 10^{-4}{u_G}^{0{,}44}{\eta_{eff}}^{-1{,}01}$
Alvarez et al.(2000)	$k_L a = k_1{u_G}^{2/3}{\sigma_L}^{3/4}{\eta_L}^{4}{\rho_L}^{3/2}$ k1 depends on the sparger, k1*10^9=[1.924;1.969;2.079]
Lau et al. (2004)	$k_L a = 1{,}77{\sigma_L}^{-0{,}22}\exp(0{,}0165u_L - 65{,}3\eta_L){\varepsilon_G}^{1{,}2}$
Terasaka and Tsuge (1991)	$\frac{k_L a d_R^2}{D_L} = 6{,}34\left(\frac{\eta_L}{\rho_L D_L}\right)^{0{,}5}\left(\frac{\rho_L g {d_R}^2}{\sigma_L}\right)^{0{,}56}\left(\frac{g d_R^3}{\nu_L^2}\right)^{0{,}261}\left(\frac{u_G}{g d_R}\right)^{0{,}526}{N_0}^{0{,}313}$
Sotelo et al. (1994)	$\frac{k_L a u_G}{g} = 16{,}9\left(\frac{u_G}{\eta_L \sigma_L}\right)^{2{,}14}\left(\frac{{\eta_L}^4 g}{\rho_L {\sigma_L}^3}\right)^{-0{,}518}\left(\frac{\eta_G}{\eta_L}\right)^{0{,}074}\left(\frac{\eta_L}{\rho_L D_L}\right)^{-0{,}038}\left(\frac{d_P}{D}\right)^{0{,}908}$
Popovic and Robinson (1989)	$k_L a = 0{,}005{u_G}^{0{,}52}{D_L}^{0{,}5}{\rho_L}^{1{,}03}{\eta_{eff}}^{-0{,}89}{\sigma_L}^{-0{,}75}$

The mass transfer correlations present a narrow variety of types of correlations, while for the gas holdup the empirical correlations present very different structures, not only a product of variables and exponential fitting and dimensional numbers. The differences are just in how the variables are arranged but the structure is always similar with the exception of Lau et al., the most recent approach here presented.

The behavior of the liquid in these systems is often non-Newtonian, therefore the viscosity depends on the velocity and an effective viscosity η_{eff} is introduced. The different correlations use also different formulations of the effective viscosity; a common agreement of this variable´s definition has not yet been found.

Regarding the water-air system, it is taken into account by only three correlations, the results are presented in figure 3.13, further example are going to be presented.

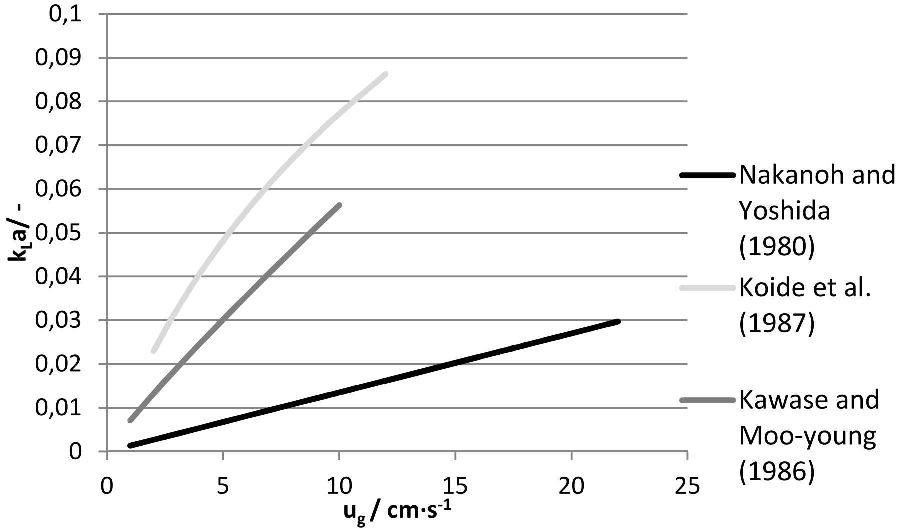


Fig. 2.13: *Volumetric mass transfer vs. superficial gas velocity in oxygen-water system*

In this case the differences between the different curves are, first of all, due to the different design configurations, however also different behaviors are remarkable. This bring again the focus first on the importance of the different design also for the calculation of the volumetric mass transfer, and second on the effect of the operating variables.

Example #9

Higher densities and viscosities are taken into account for the volumetric mass transfer in compared to the gas holdup experiments. Therefore our example will focus on the possibility to analyze this kind of settings.

The variables filtered are: Newtonian behavior, no slurry phase, 0.01 Pa*s< μ_L< 0.02 Pa*s, 1170 kg/m^3 < ρ_L < 1250 kg/m^3, 0.1 m<D<0.15 m, D_L≈10^{-10} m^2/s, 0.6 N/m< σ < 0.75 N/m, ρ_G≈1 kg/m^3

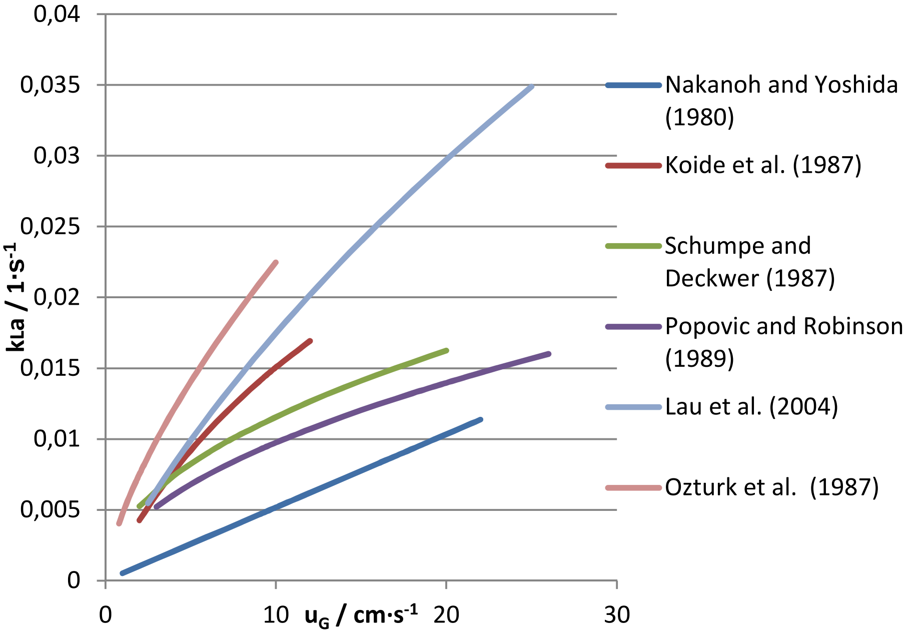


Fig. 2.14: *Volumetric mass transfer vs. superficial gas velocity, example #9.*

For the volumetric mass transfer coefficient seems that more correlations are available, however this due to the fact that half of them are not derived directly from experimental data. Despite of this, the correlations are similar quantitatively, except for the oldest correlations (Nakanoh and Yoshida, Öztürk et al.) and also qualitatively the behavior is similar. It is has to be noticed that the type of sparger is not specified for Lau et al., since his correlation is considered general, and the only apparatus with similar sparger are Nakanoh and Yoshida and Öztürk. However this two correlation have total opposite values (almost 0.015 1/s of difference at u_G=5 cm/s), one important design parameter that differs between the two is the diameter of the column, smaller for Öztürk et al., and also the ratio between the liquid diffusivities of the two systems is almost 10.

Example #10

Since some correlations consider also the case of non-Newtonian liquid, an example of this category is going to be analyzed. The variable that characterize the non-Newtonian behavior is the index n, when n=1 the fluid has a Newtonian behavior.

The conditions filtered are: 0.5 < flow behavior index n < 0.6, ρ_L≈1000 kg/m^3, 1 Pa*s< μ_L< 4 Pa*s.

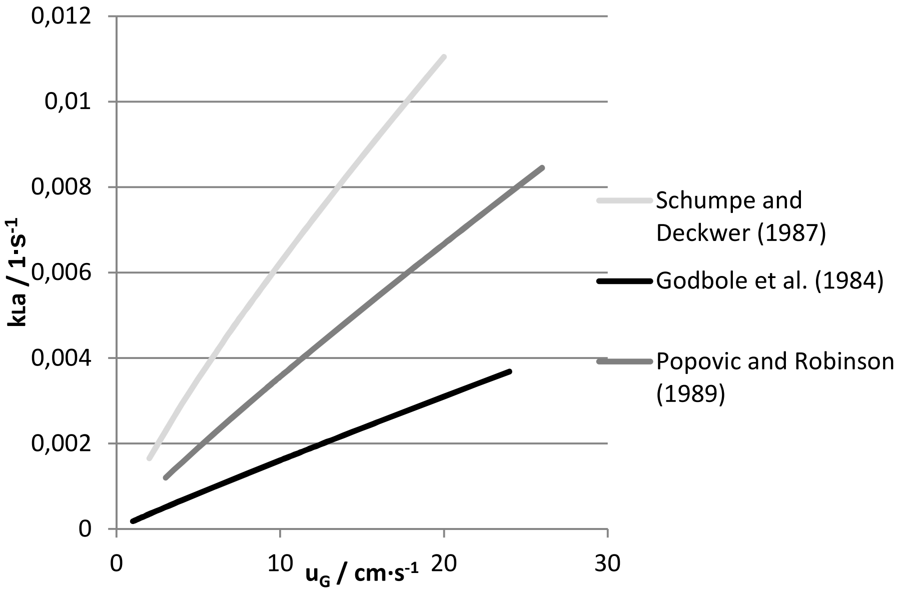


Fig. 2.15: *Volumetric mass transfer vs. superficial gas velocity, example #10.*

Only three correlations fulfill these extreme conditions and the results are based on direct experimental data, therefore there are no general correlations so far, able to predict the non-Newtonian behavior. The differences are correlated more to the difference settings considered for the experiment, different spargers and slightly different liquids are employed.

2.2.3 Sensitivity analysis

A similar approach to the gas holdup is presented, in this part the important variables in the calculation of the volumetric mass transfer are analyzed.

Example #11

For the volumetric mass transfer, differently from the gas holdup, is important to consider the diffusivity in the liquid of the component analyzed. In this example the direct influence of the liquid diffusivity on the volumetric mass transfer is considered.

The conditions filtered are: ε_G=0.15 (since correlations as Akita and Yoshida are based on the gas holdup and not on the gas velocity) or u_G=10 cm/s, 700 kg/m^3 < ρ_L < 800 kg/m^3, 0.00033 Pa*s< μ_L< 0.00058 Pa*s, D=0.15m.

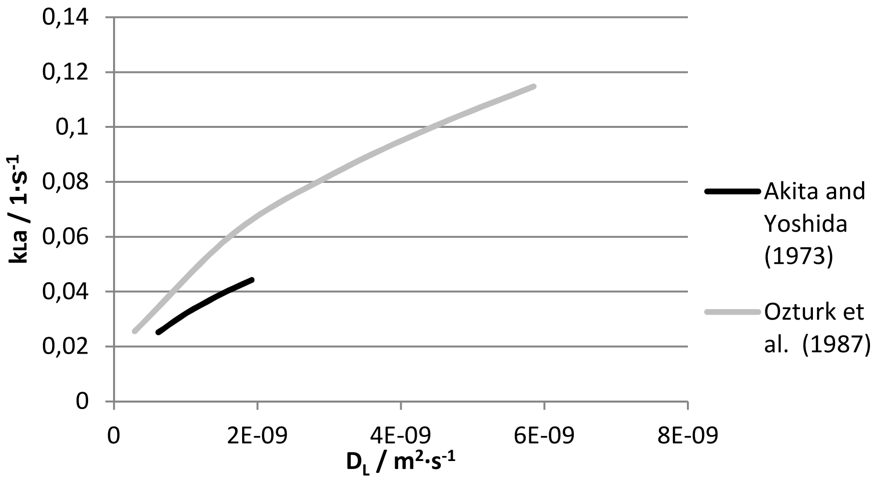


Fig. 2.16: *Volumetric mass transfer vs. liquid diffusivity, example #11.*

To perform this comparison homogeneous data are needed, i.e. all the design and operation variables are constant, this is possible for each curve itself and only with the correlations that are not representative of the experimental data. However, to analyze the influence of one parameter would be enough to see its exponent on the correlation, on the other hand in this way can be also noticed the range of utilization of the target parameter. From the graph is evident how the correlation of Öztürk et al. considers a wider range of liquid diffusivities, the differences of the volumetric mass transfer coefficient are due to the non homogeneity of the data, i.e. different design and operating variables.

Example #12

Since is more efficient to show the range of the important parameters, the range of the liquid density is investigated, in this case however, only the correlations representative of experimental data are going to be selected and even if the viscosities and surface tensions of the liquids used in each correlations are different, the density is considered representative of the entire liquid with its characteristics. Only the design variables are considered for the selection.

The conditions filtered are: or u_G=10 cm/s and Newtonian behavior.

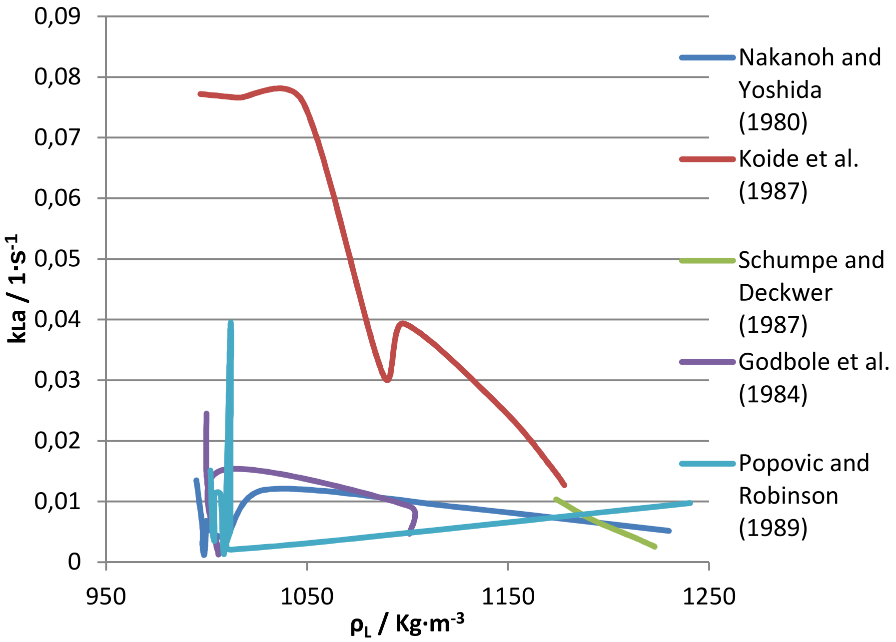


Fig. 2.17: *Volumetric mass transfer vs. liquid density, example #12.*

From the diagram some interesting things can be noticed, for example the density of the liquid employed for the mass transfer coefficient experiments is in the range [975;1250] Kg/m3, a smaller range than for the gas holdup. Changing liquid, but maintaining the same experimental setup, is it possible to obtain a ratio, between the biggest and the smallest value of volumetric mass transport, of 18, in this case for the correlations of Popovic and Robinson and Godbole et al.. The steep variations of the curves highlight also how the volumetric mass transfer is influenced from the other parameters of the liquid phase and therefore, how with a fluid similar in density different values of the mass transfer can be obtained.

Chapter 3

Validation

The information elaborated in the theoretical part suggested some experiments, in order to test the doubts encountered. Despite the large amount of data gathered in the tables, the fewer amount of correlations available in the literature for a specific system has already been noticed. In particular, the possibility to study the air-water system in the laboratories of the university has been verified. Furthermore the consistency of the literature and the experimental data has been investigated.

3.1 Experimental apparatus

Set of experiments have been done in the following way.

Distilled water-air system, with multi-orifice sparger, varying the height to diameter ratio (H_d/D)

Distilled water-air system, with single-orifice sparger, varying H_d/D

Water-air system, varying salt concentrations

The diameter of the column is 0.288 m, the columns height is 2m. The gas distributors are a membrane, designed to create small bubbles, and a single hole of 5 mm sparger. The geometric characteristics of the membrane are very difficult to characterize since there are no real holes, while linear 0.4 mm fissures that open when the gas passes through them.

Fig. 3.1*: Experimental bubble column with multi-orifice sparger.*

The intention of this set of experiments varying the height of the dispersed liquid was to verify the behaviors suggested in the literature. The most important purpose however, was to investigate the minimum height to diameter ratio, in order to achieve a constant value of the gas holdup at a given superficial gas velocity.

To run the experiments at the bottom of the column there are two separated holes through which the liquid and the gas flow. The inlet for the gas is in the middle of the section. Above the bottom is set the membrane, as can be seen in figure 3.2.

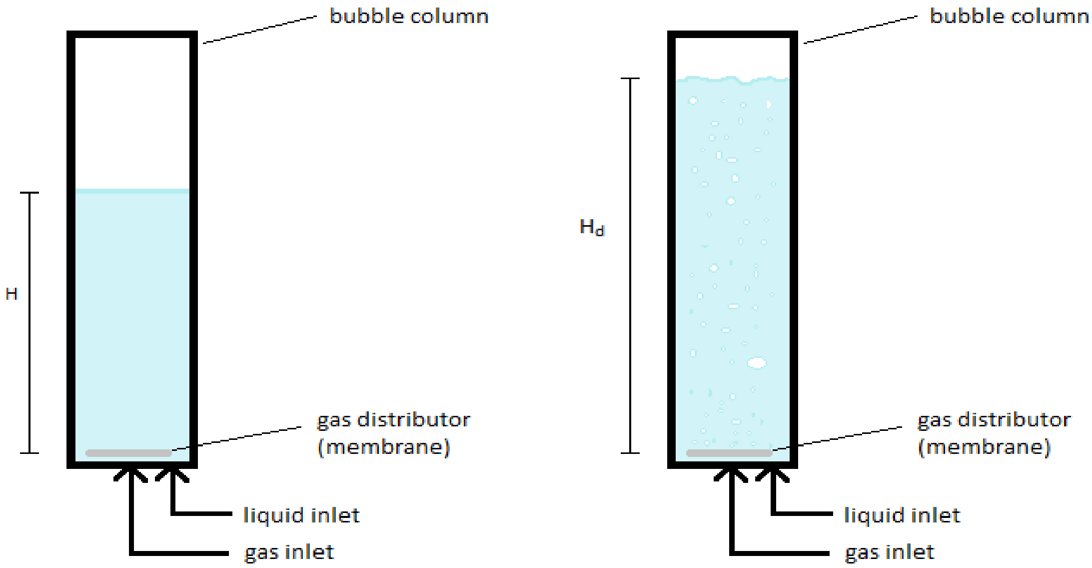


Fig. 3.2*: Experimental set-up sketch.*

The liquid is handled with a simple valve, since all the operations are in batch operation mode, there is no need to control the flow. For the gas flow, a flow-meter and a manometer are available to measure the superficial gas velocity.

The liquid supply for the distilled water was directly connected to the column, through a rubber pipe, the gas supply too. The temperature of the distilled water is 23.5°C, the ambient temperature during the experiments was 22.5°C.

To carry on the investigation in distilled water, different height to diameter ratios have been chosen, depending on the sparger type. While during the experiments with salts, the clear liquid was fixed and the dispersed liquid varied.

The dispersed height is the liquid height in the operation mode, and is this one that is correlated to the hydrodynamic properties. The choice of these values has been dictated by measurement feasibility, e.g. 3.5, and limitations, i.e. 6.5. The liquid height was identified with adhesive tape, as it is shown in figure 3.3, and in all the experiments or the dispersed height or the clear liquid height was constant and the other one was measured to calculate the gas holdup, how it has been represented in figure 3.2.

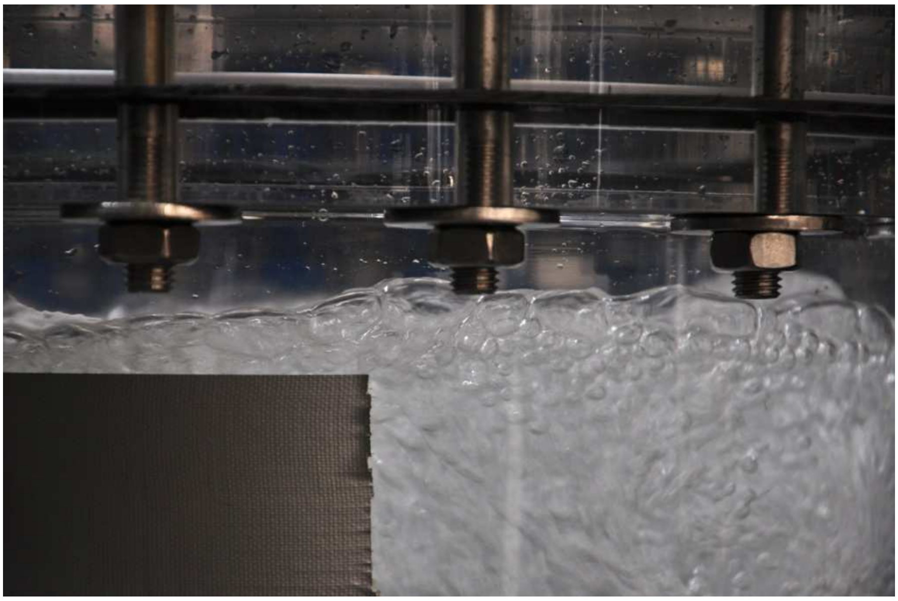


Fig. 3.3: *Dispersed liquid height setting. Water-air, $H_d/D=6.5$, $u_G=0.8$ cm/s.*

The photo from figure 3.3 has been taken with the maximum value of liquid height and the minimum value of superficial gas velocity. It can be noticed that the liquid level is not homogenous in the space, moreover it is not homogeneous in the time either. This was a problem for precise measuring. However also in the literature, most of the data were gathered with this measurement technique.

Decreasing the height to diameter ratio and increasing the superficial gas velocity, the space and time fluctuations increase, as can be noticed in figure 3.4. For high superficial gas velocities, e.g. 4.5 cm/s, the fluctuations were in the order of 5 cm, at H_d/D=6.5.

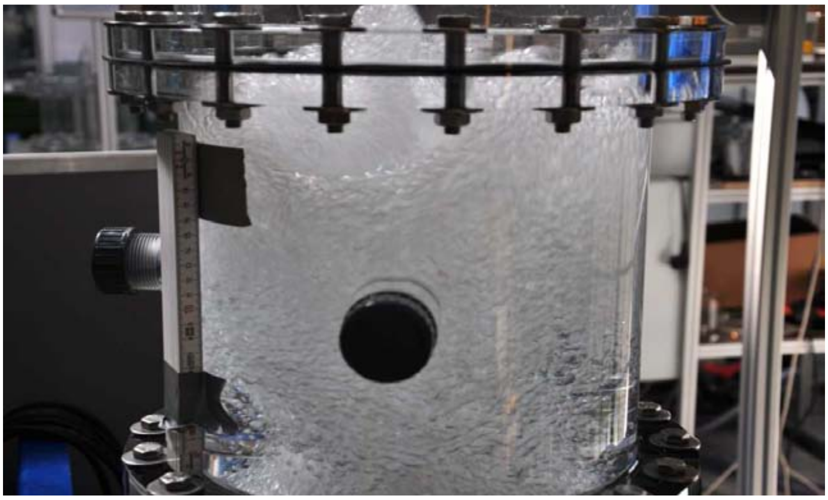


Fig. 3.4: *Dispersed liquid height at maximum superficial gas velocity (u_G=4.5 cm/s) and minimum height to diameter ratio (H_d/D=1)*

During the experiments with distilled water, being in interested also in the influence of the height to diameter ratio, the dispersed height was kept constant, in order to achieve similar hydrodynamic condition. For each dispersed liquid height, also the superficial gas velocity was changed. The lower speed limit was due to the flow-meter lower limit, and the maximum limit was due to the membrane resistance. For every gas velocity, the clear liquid height had to be adjusted, this was done during the operation mode, making align the dispersed liquid height with the tape sign, and after, without gas flow, the clear liquid height was measured.

The gas holdup in the experiments with salts, for practicality, was calculated maintaining a fixed clear liquid height and therefore, measuring the dispersed liquid height, using the maximum height to diameter ratio available. In this way the hydrodynamic conditions should be constant.

To recap, a variable among clear liquid height or dispersed liquid height is fixed and the other is calculated according to the following formula:

$$\varepsilon = \frac{H_D - H_0}{H_D} \tag{3.1}$$

To obtain the superficial gas velocity the flowing relation was used.

$$P_1 \dot{V}_1 = P_2 \dot{V}_2 \tag{3.2}$$

The flow-meter was the reference since a set of values has been chosen in advance.

$$\dot{V}_1 = [2, 2.5, 3, 3.5, 4, 4.5, 5, 6]\ m^3/h$$

For each volume flow rate, the gas pressure changed, therefore, P_1 was red from the manometer. P_2 is the normalized pressure and

$$P_2=P_0=1 \text{ atm} \tag{3.3}$$

Finally the gas volume flow rate was calculated and from that one, through the column diameter, the superficial gas velocity was obtained. Because of the fact that the pressure from the manometer was sometimes slightly different, sometime the superficial gas velocities for the same gas volumetric flow rate are different.

3.2. Distilled water-air system, with multi-orifice sparger, varying *Hd/D*

According to Joshi et al. (Joshi et al., 1998), with multi-orifice spargers, the gas holdup is maximum at $H_d/D=1$ and then decreases. This issue has been investigated varying also the superficial gas velocity for every height to diameter ratio.

3.2.1 Experimental Setup

The set of height to diameter ratios chosen is: $Hd/D=1$, 3.5, 5, 6.5. For every experiment, to reach the height to diameter ratio selected, the liquid content was adjusted. Because, to change superficial gas velocity and maintaining the dispersed height constant, also the liquid in the column has to change. For example, with a certain superficial gas velocity, a certain height to diameter ratio is reached, if the gas velocity increases, the dispersed liquid height increases too (in the homogeneous and heterogeneous regime), and to come back to the liquid height prearranged, liquid has to be removed from the column.

Therefore the reference parameter for the calculation of the gas holdup is now the dispersed height.

The volume flow rates selected, in order to avoid damages to the sparger were: 2, 2.5, 3, 3.5, 4, 4.5, 5 m^3/h.

3.2.2 Results and discussion

The experiments have been repeated three times, however the first set was different from the others because after that, the experiments with salts were done and the impossibility to clean perfectly the column affected the composition of the new batch. Nevertheless important evaluation can still be done since the first set is available, just less accurate values are available.

The second and the third set of experiments can show us important things regarding the accuracy of the measurements.

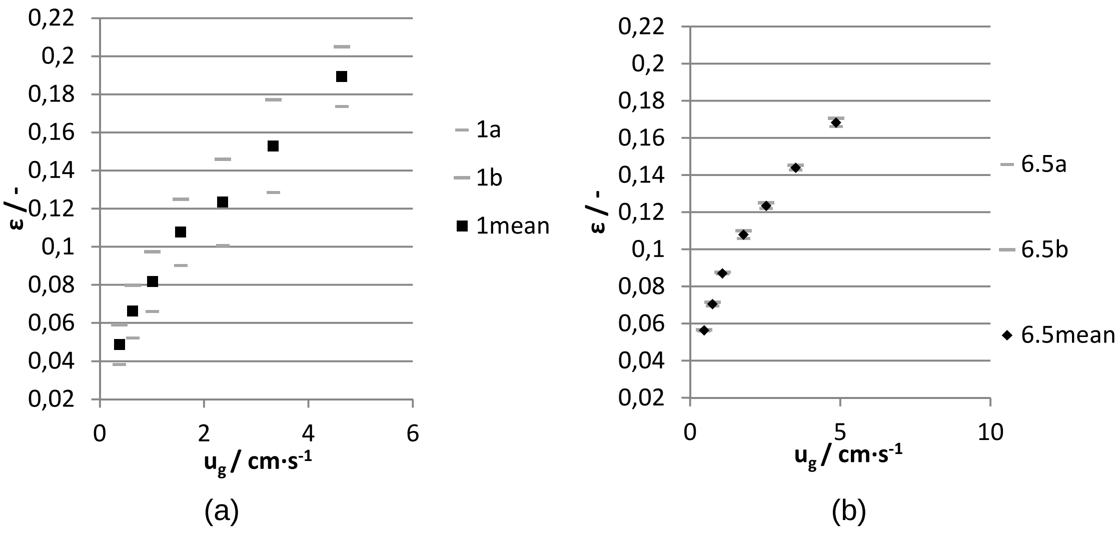


Fig. 3.5: *gas holdup vs. superficial gas velocity, mean values of experiment 2 and 3. (a): $H_d/D=1$; (b): $H_d/D=6.5$*

The higher space and time fluctuation make the measurement more difficult and more imprecise, especially at low height to diameter ratio (figure 3.5), the increasing of the gas velocity seems to have less effect on the precision.

The gas holdup versus superficial gas velocity leads us to the understanding of the flow regime. In figure 3.6 the gas holdup is shown at different height to diameter ratios, the values are the mean values of experiments 2 and 3.

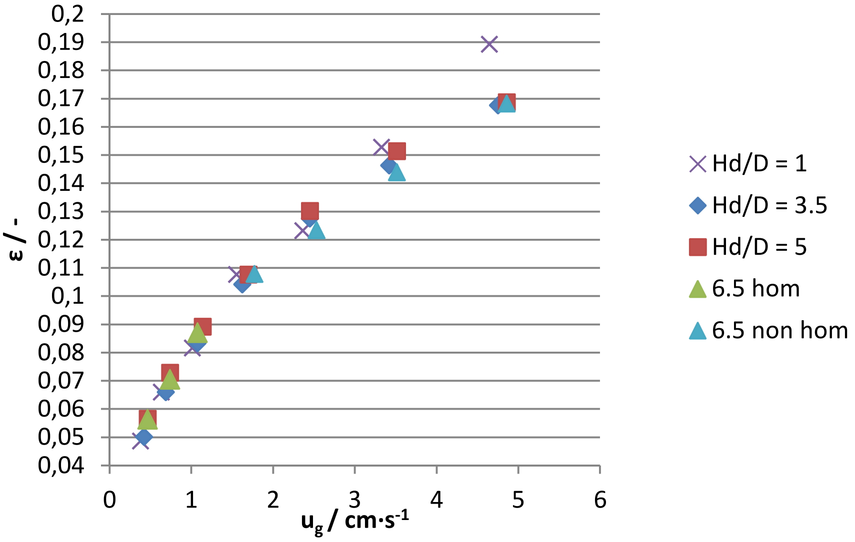


Fig. 3.6: *gas holdup vs. superficial gas velocity at different H_d/D.*

This diagram is difficult to interpret regarding the effect of the height to diameter ratio, however can be analyzed the hydrodynamic flow regime. After fitting the data, has been noticed that the exponential law fits all the data except the first 3 points at *Hd/D*=6, for this reason in the figure 4.6, the set of points “6.5” has been divided in hom (homogeneous flow regime) and non hom (heterogeneous regime). If the flow map in figure 1.6 is taken into account, this low value would have not been expected. The transition velocity in our system is around 1.5 cm/s and only for the highest height to diameter ratio. The flow map is therefore imprecise outside some conditions that are not even specified.

To understand better the effect of different height to diameter ratios another diagram has been employed, as it is shown in figure 3.7.

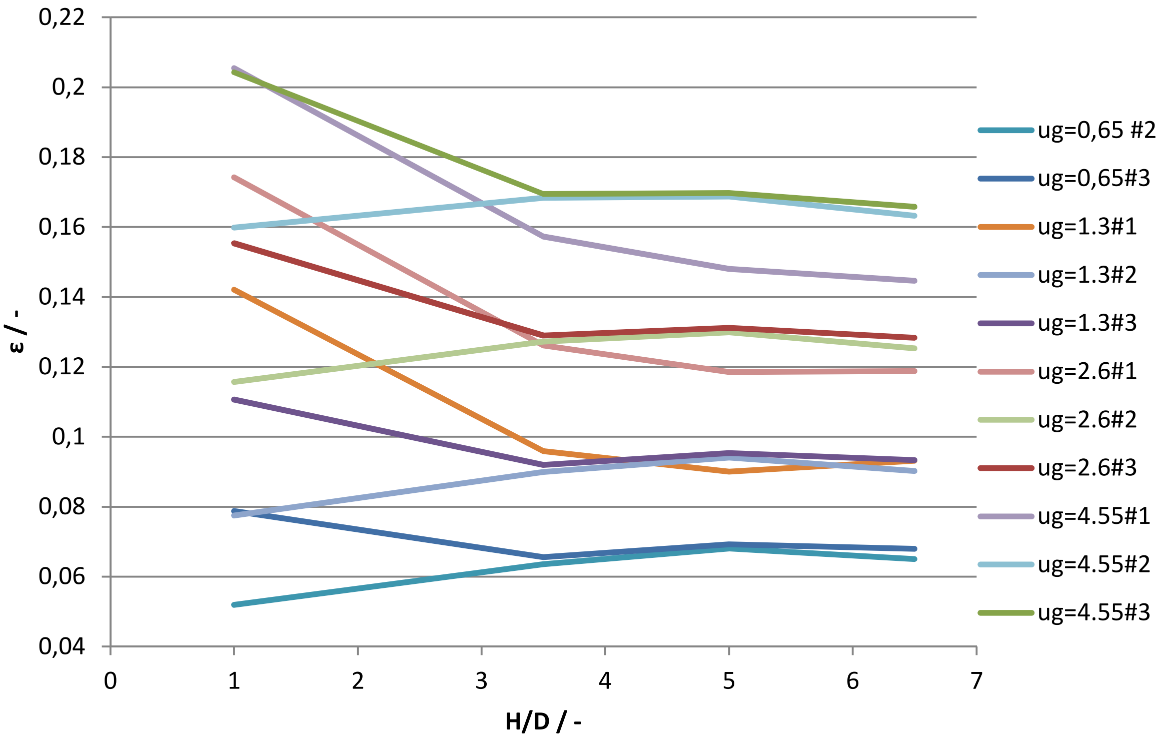


Figure 3.7: *Gas holdup vs. height to diameter ratio at constant superficial gas velocity (e.g.* u_g*= 2.6 cm/s) for the all 3 the set of experiments (#1, #2, #3)*

This diagram contains important information to explain the influence of the height to diameter ratio and its sensibility. The data in the diagram however are not the experimental ones, since as it can be seen for the figure before, there are slightly differences in the gas velocities. The data have been fit with the exponential law and common values were taken. Except at the lowest gas velocity since, in the first (out of 3) set of the experiment that values were not taken.

Analyzing the figure can be noticed that the first set of experiments differ from the others, as explained before. The points at *Hd/D*=1 are more unpredictable and but still for two points over three the gas holdup at the lowest height to diameter ratio is the highest, as suggested for multi-orifice spargers. Increasing the height to diameter ratio, the gas holdup seems to stabilize soon, at least after the value of 5. However, not enough data are available to allow a precise evaluation regarding this.

Now the experimental data are compared with the correlations available in the literature. From the database have been selected correlations for heterogeneous flow regime, porous sparger and both distilled and tap water. For distilled water only the correlation from Krishna and Ellenberger (Krishna and Ellenberger, 1996) is available, but the range were this correlation is defined is out of our experimental range, therefore an extrapolation of our data has been done, as can be shown in figure 3.8.

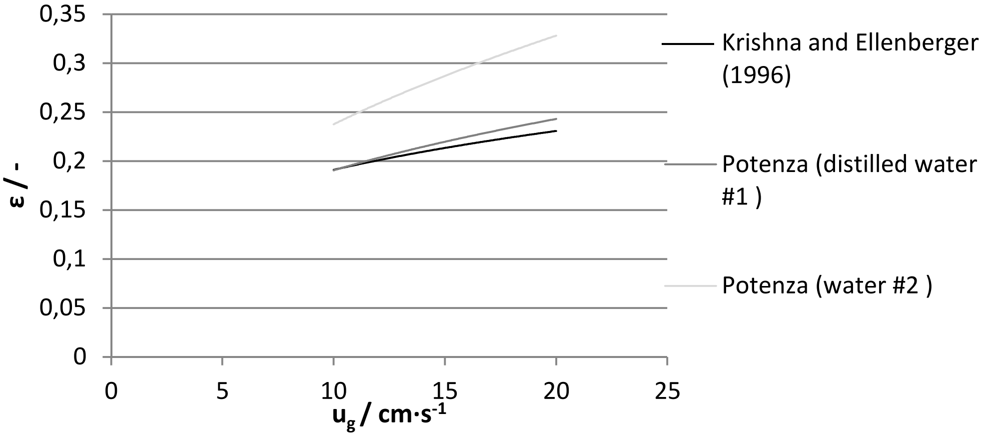


Fig. 3.8: *gas holdup vs. superficial gas velocity, comparison with literature correlation. Water-air system heterogeneous flow regime, porous sparger, distilled water*

The experimental extrapolation of interest is the blue line, the red one was used just for additional comparison. As it can be seen, the correlation represent in a good way the experimental results even if the fact that the data were extrapolated do not allow us to make strong considerations.

On the other hand, it is possible to compare directly the results for tap water, with even two correlations: Sotelo et al. (Sotelo et al., 1994; Behkish et al., 2006). Figure 3.9 shows the comparison. For tap water have been considered the experiments 2 and 3 since the very low concentration of salts still in the column was enough not to consider the water distilled anymore.

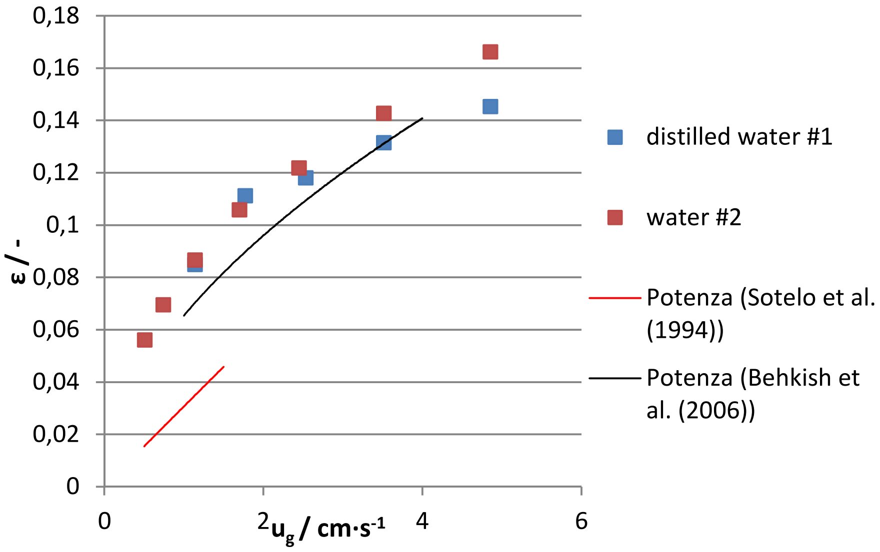


Fig. 3.9: *gas holdup vs. superficial gas velocity, comparison with literature correlation.*

In this case even if the more correlations are available, they do not fit the experimental results, Behkish's one is closer and the trend is similar to our results.

3.3 Distilled water-air system, with single-orifice sparger, varying *Hd/D*

Differently from the multi-orifice sparger, with the single orifice the gas holdup starts from lower values and then it always increases. (Joshi et al., 1998)

This behavior has been verified, changing the superficial gas velocity too, as it has been done in chapter 3.2.

3.3.1 Experimental setup

The single orifice sparger is a 5mm hole sparger. Compared to the membrane, the single hole produces bigger bubbles, and the turbulent motion is increased. A large area nearby the sparger is predominated by clear liquid.

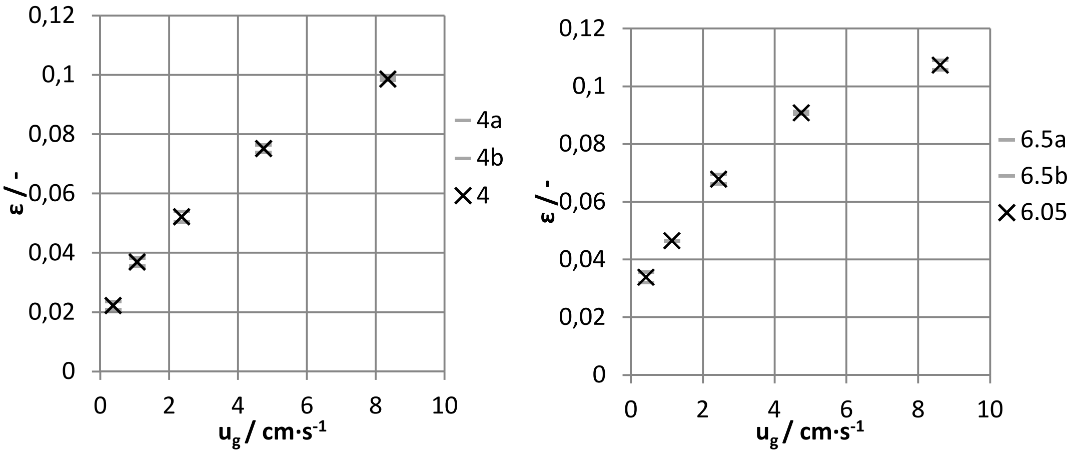
The experiments performed in this apparatus are similar to the others in the multi-orifice sparger column. However the turbulence produced increases also the difficulty to identify the dispersed liquid height. For this reason, the set of values for *Hd/D* starts from a higher value.

$$Hd/D=4,\ 5,\ 6.5 \qquad (3.4)$$

Moreover the gas velocity is no more limited by the flow-meter, but by the manometer, the maximum volume flow rate achievable is 6 m^3/h. Regarding the flow rate, there is also to notice that small intervals of 0.5 m^3/h were difficult to distinguish, therefore a gap of 1 m^3/h has been chosen, and the final set of volume flow rates is 2,3,4,5,6 m^3/h.

3.3.2 Results and discussion

The set of experiments performed with the single hole sparger were not affected by the salts since no experiments with salts were done in that column. However the turbulences created by the single hole sparger were bigger. The set with height to diameter ratios of 4 and 6.5 are reported in figure 3.10.



(a) (b)

Fig. 3.10: *gas holdup vs. superficial gas velocity, mean values of experiment. (a): $H_d/D=4$; (b): $H_d/D=6.5$*

In both cases (a and b) there is not a big difference in terms of deviation from the mean value, a good reproducibility is therefore obtained. The mean values for all the height to diameter ratios are taken and plot together, as it shown in figure 3.11.

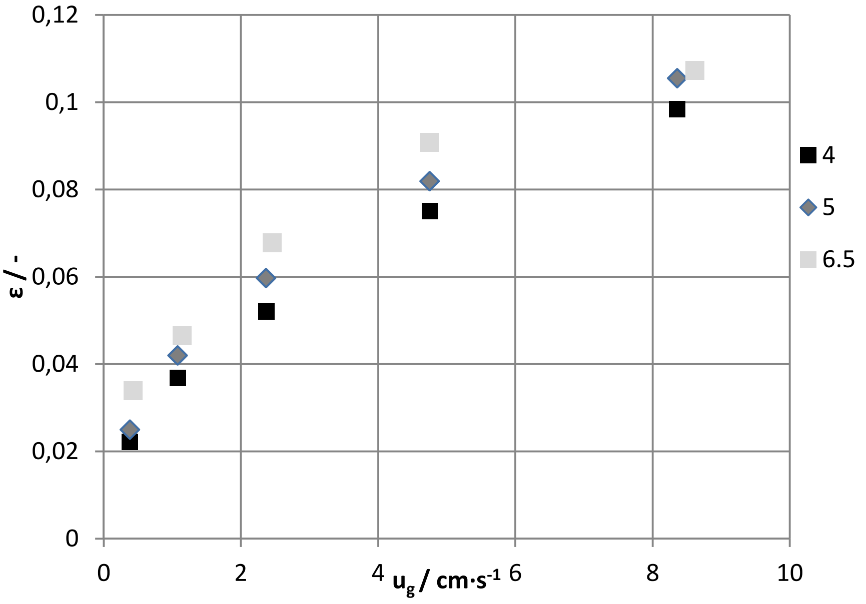


Figure 3.11: gas holdup vs. superficial gas velocity at different *Hd/D*.

In this diagram is more clear the effect of the height to diameter ratio is more clear, increasing it also the gas holdup increases, and as for the multi-orifice sparger, at high gas velocity, the effect is less pronounced. Regarding the flow regime, homogeneous flow regime is detected, through the error found with the fitting of the data, in the first 3 points of the set with *Hd/D*=6.5.

As it has been done for the multi-orifice sparger, the data are evaluated through the point of view given by figure 3.12

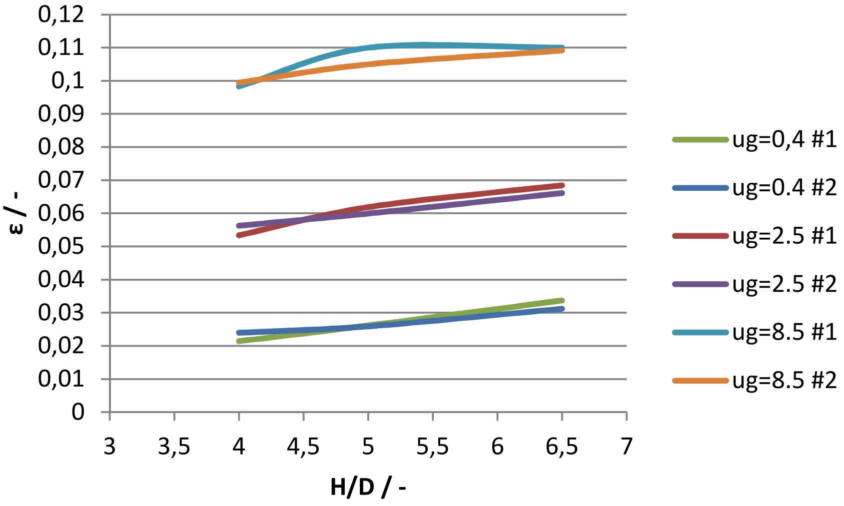


Fig. 3.12*: Gas holdup vs. height to diameter ratio at constant superficial gas velocity (e.g.* u_g*= 2.5 cm/s) for the all 2 the set of experiments (#1, #2)*

For all the gas velocities, the gas holdup increases and is not clear when the value stabilizes. Another thing that can be noticed is that the gas holdup reaches a lower value if compared to the multi-orifice sparger, even if with the single hole higher gas-velocities are reached. This is due to in particular to a dead zone near the sparger that is most composed of pure liquid.

Regarding the correlations available in the literature, three are available with the characteristics comparable to our experimental setup and the result are plotted in figure 3.13

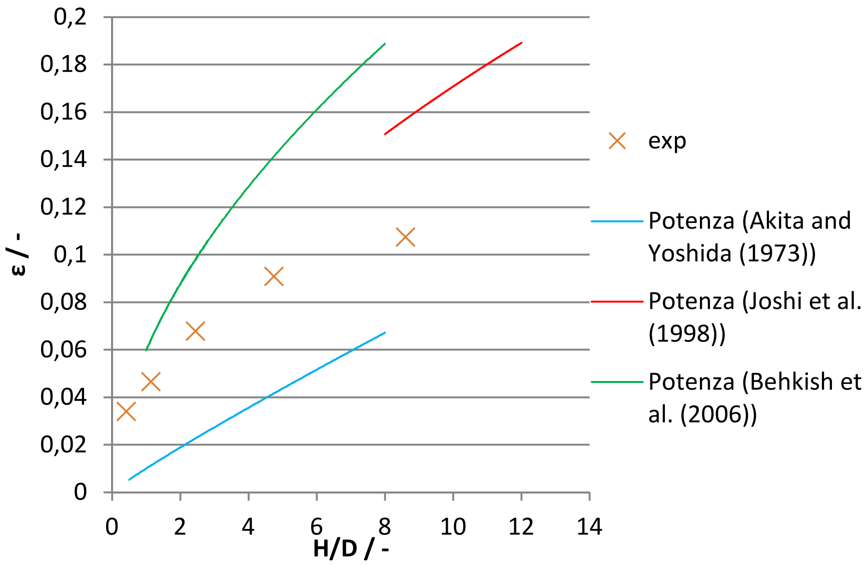


***Fig. 3.13**: gas holdup vs. superficial gas velocity, comparison with literature correlations.*

Even in this case, the experimental results are not comparable with the literature data. The literature correlations were chosen also with the condition that the experiments were done with distilled water, therefore the difference stands in the design parameter.

3.4 Water-air system, varying salt concentration

The third set of experiments was done trying to reproduce tap waters of different places and to compare the results of gas holdup measurements done with distilled water. Furthermore, it has been investigated how different correlations proposed in the past with tap water, can differ by varying the concentrations of salts in the water.

3.4.1 Experimental setup

The analysis of the correlations in the literature showed that many of them were produced with tap water. The problem is that tap water is not the same everywhere. And most important thing is that tap water is very different from distilled water. In tap water are dissolved salts, metals, polluting elements, microorganisms and many other things that make it a very unpredictable fluid and the concentration of these elements changes in every place.

Trying to reproduce the tap water, only the salt concentrations were taken in account. Salt is probable the most affective component of tap water to gas holdup since very small concentrations of salts decrease the surface tension. In addition to the synthetic tap water, tap water from the university has been used. The use of tap water has been suggested from the first experiments with the synthetic water, in order to allow

For the salt concentrations, tap water from United States and Italian database of drinking water were analyzed (http://www.ncbi.nlm.nih.gov/pmc/articles/PMC1495189/table/tbl2/ http://www.cheacquabeviamo.it/lombardia.htm), as it is shown in table 3.1.

Table 3.1: Salt concentrations of the water tested in the plant.

	Ca++	Mg++	Na+	K+
Boston	4	1	7	0
New York	21	4	18	0
Los Angeles	21	5	37	0
Milan	71	13	37	1
Gonzaga	98	53	50	2
Hamburg	34	3	8	1

The salt concentrations refer to the concentration of ions. Therefore to reproduce these concentrations the relating salts have to be used. For the Calcium it has been used Calcium carbonate. For Magnesium: Magnesium carbonate. For Sodium: Sodium Chloride. For Potassium finally: Potassium Chloride. To investigate the effect of the salts, conductivity test were also done.

In the literature some papers describe the effect of salts (Akida an Yoshida, 1973; Yoshi et al., 1998) but not in particular the effect of tap water salts. Another recent paper (Tang and Heindel, 2004) investigate the tap water properties but in terms of volatile substances. It is common to accept that increasing the salt concentration increases also the gas holdup but it is still not in depth analyzed and shallow evaluations are often done.

3.4.2 Results and discussion

The first experiments performed were done with the artificial tap water, i.e. just considering the salt concentrations. It has been possible to use one batch for all of them since the salt concentrations were always increasing. The results of the first two sets of experiments are shown in figure 3.14.

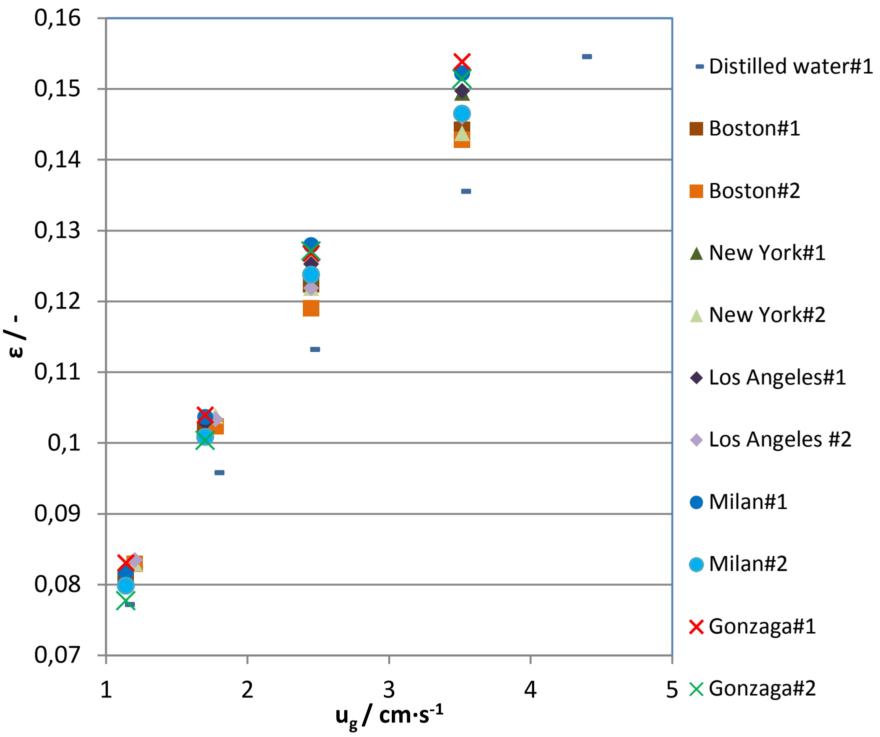


Figure 3.14: *Gas holdup vs. superficial gas velocity varying the salt concentrations.*

It is easy to notice how the distilled water is clearly the smallest value of gas holdup, even if very small amounts of salt were added. Moreover, only with distilled water was possible to reach over 4cm/s of superficial gas velocity because in the other cases, the liquid height would have exceeded the maximum value.

The fact that, it was only possible to overpass the velocity of 4cm/s with distilled water made clear that, even if the column was cleaned several times, the following experiments were corrupted by the presence of residue salts. It is still not clear where the salts were stuck in, since the column has been cleaned in several different ways. The only thing that is not done was do dismount the column, since it would have stopped also other experiments for a too long time. This kind of problem has also been noticed by Sandra et. Al. (Sandra et al., 2009), using perforated plate as gas distributor and water solutions of pure Sodium Chloride the problem was the crystallization of the salt on the orifices, because of the high purity. This problem was not encountered with normal kitchen salt. In our case the salt was also high purity and the orifices are even smaller. The crystallization of the salt changes also the flow behaviour of the membrane since some orifices can be closed.

Even if some salts were left in the column, the difference with the distilled water was still very clear. To simplify the previous plot, only the smallest and the biggest salt concentration are going to be plot in the following diagram. According to figure 3.15 it is very clear the effect of salt concentration in tap water on the first experiment.

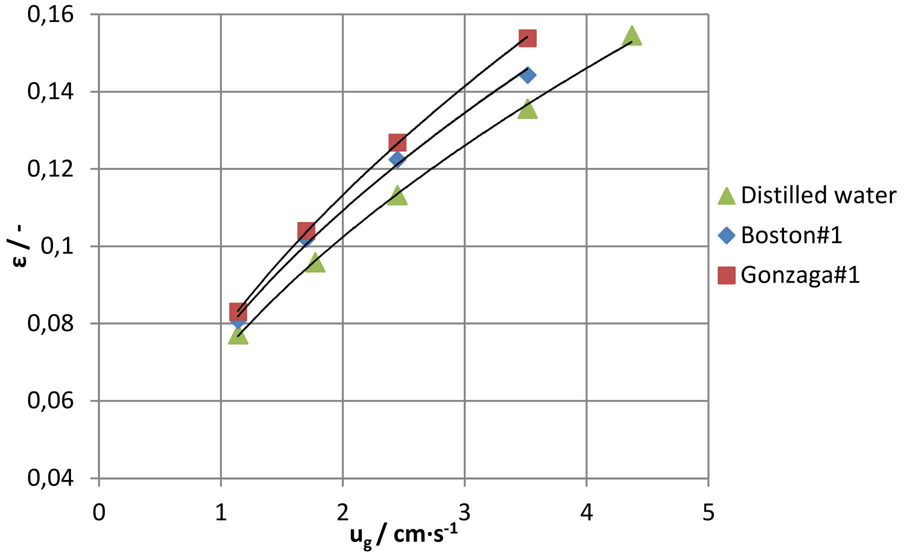


Fig. 3.15: *Gas holdup vs. superficial gas velocity at different salt concentrations.*

Once having performed experiment with "artificial" tap water, our interest came up real tap water. According to the data gathered in table 3.1, Hamburg tap water has a mid salt concentration of salts compared to the other waters, but the result was surprising, as can be seen in figure 3.16.

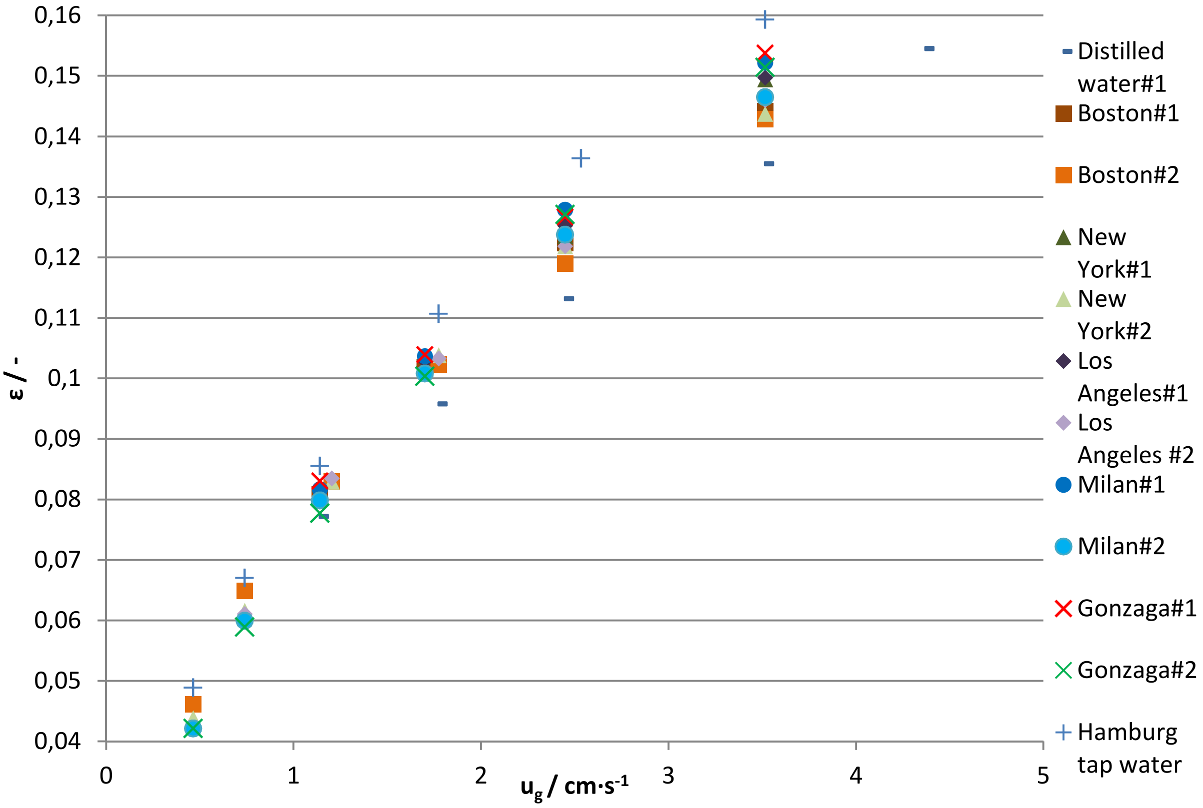


Figure 3.16: *gas holdup vs. superficial gas velocity at different salt concentrations.*

Hamburg tap water has the highest gas holdup to all the other water. The explanation could stand on the fact that in the artificial tap water the salts are not completely solubilised while in the tap water there are so many other components that change the thermodynamic equilibrium of the solution. And probably all this additional compound have an additional influence of the gas holdup. Therefore conductivity test were done, and the results are presented in table 3.2.

Table 3.2: Conductivity tests of the water employed in experiment 1 and 2 with "artificial" tap water and of the Hamburg tap water experiment.

	Conductivity [μS/cm]
Distilled	7,8
Boston#1	60,7
Boston#2	71,4
New York #1	184,1
New York #2	196
Los Angeles#1	289
Los Angeles#2	301
Milan#1	322
Milan#2	338
Gonzaga#1	559
Gonzaga#2	582
Hamburg Tap	250
Artificial Hamburg	94.3

The test was performed at the ambient temperature of 23.5°C, and the results show also the differences between the two set of experiments in the column and make it clear that some residue salts were still in the column since the salts added were the same. It also worth noticing the difference between the "artificial" tap water and the "real" tap water, this shows the difference of solubility. While comparing the results in figure 3.16, seems that even if the tap water of Hamburg has a lower conductivity than the other salt solution, the gas holdup is higher. For this reason, comparing real tap water just on the conductivity may be wrong, especially if compared to salt solution.

The presence of different salts influence in different ways the conductivity, tests on the single salts were done. Figure 3.17 shows the differences on the salts employed to create the "artificial" tap water.

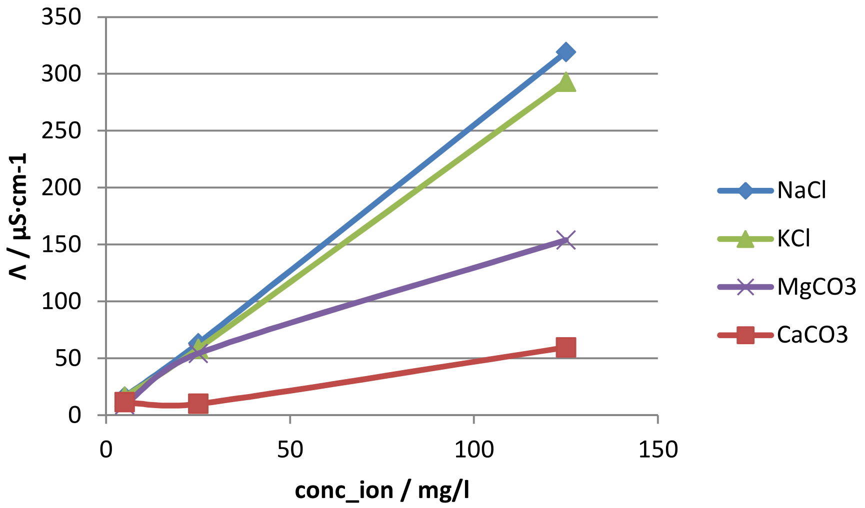


Fig. 3.17: *Conductivity vs. concentration of the ion in water solutions.*

Here can be seen how the different salts behave in different ways, and if the solutions are mixed, the resulting conductivity stands between the maximum and the minimum values of the mixed solutions.

The problem of using different salts, especially in bubble columns, is underlined also by the comparison with the literature correlations. Hikita el al. (Hikita et al., 1980) just used a correlation factor, according to the ionic strength, to characterize water-salt solutions. The factor is the following

$$f(\varepsilon_G) = 10 \cdot \exp(0.0414\, I) \tag{3.5}$$

Where I is the ionic strength.

Using this factor to our experimental data the result is shown in figure 3.18.

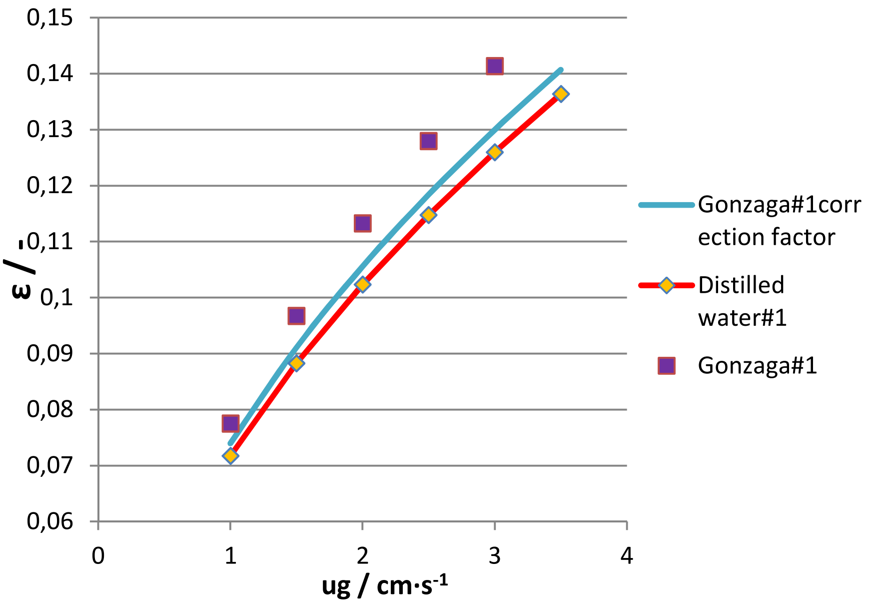


Fig. 3.18: *Gas holdup vs. superficial gas velocity, using the correction factor.*

From the experimental data gathered (distilled water#1, yellow points), an exponential fitting has been done (red line), the exponential law equation of the red line has been multiplied by the correlation factor, obtaining the blue line. However the blue line should fit the purple values (Gonzaga#1), since the correction factor has been calculated on its base.

The use of this correction factor underestimates our experimental data. This is probably do to the different design conditions of the bubble column employed for the estimation of this factor or for the different salts and especially the different mixture of salts used.

3.5 Conclusions

The analysis of the correlations for gas holdup and volumetric mass transfer, but also the way the authors proposed them in their articles, show that the comprehension is still limited. There are not rigorous methods and common structures of comparison. The design of a bubble column (diameter, sparger and height to diameter ratio) is the basement for any experiments but its influence is not defined yet. Moreover are not clear the precise conditions and, if a correlation can be really independent from the design variables, as it has been seen with the height to diameter ratio in water-electrolyte solutions. The authors sometimes are not even fully aware of these problems, for example using tap water instead of distilled water. Sometimes, they do not precise the set of validity of the correlation, to give on one hand more generality to their correlation but on the other hand a lower scientific meaning, since the results are usable only in their specific case.

Since the experiments are not well defined in the primary settings, it also difficult to comprehend the influence of the operating conditions. The different systems studied by the different authors improve the possibility to find a rough prediction of the gas holdup or of the volumetric mass transfer, but the physic behind is still far from being understood. For this reason, also the correlations still present too many different forms. The use of a specific structure instead of another one is often not explained, this is another way to hide the effective validity of a correlation. Even if a correlation is rigorous, in many cases happens that it has been carried out in very small columns, e.g. high pressure conditions, therefore the aim of the study should be specified. The authors instead, tend to give general validity of their correlations without warming of the limited application. Using these correlations for industrial applications is still inaccurate.

Performing the validation made us aware of the doubtfulness of the results and if the data collected can be really compared. For example, calculating the gas holdup for different gas velocities, many authors do not specify if the clear liquid or the dispersed liquid height is constant, if it is the clear liquid, the independence of the gas holdup from the height of dispersed liquid should be proved. For the distilled water-air system with single nozzle, it was still not clear if a constant value of gas holdup was achieved at Hd/D=6.5 with D=0.288, in a region of conditions where most of the authors consider gas holdup independent from design variables. Moreover the utilization of average gas holdup does not assure a comparable behavior of different operation modes.

Correlations derived from very different conditions can lead to errors, even if used within their range of application because, different design and operation settings are at the end unified in the same correlation. For example experiments with one type of column, sparger and liquid-gas system, and experiments with another column, sparger and liquid-gas system, are at the end unified to enlarge the range of application, but leading in this way to an error that increases considerably if also other parameters do not agree with the experimental settings used to produce the correlation.

A relevant example of all these problems is the use of tap water instead of the distilled one. Some authors precise is tap water, some other do not even mention which one they use. The use of tap water can lead to different hydrodynamic behaviors since the composition can be very different from country to country and also from city to city. The gas holdup increases and even very small concentration of salts, e.g. the residual salt after cleaning the column, can lead to evident differences.

Chapter 4

Summary and Forecasts

An extensive literature research has been performed, the knowledge regarding gas holdup and volumetric mass transfer, and the variables that affect them, has been studied.

Both gas holdup and volumetric mass transfer are function of the design parameters; column diameter, height of liquid and gas distributor affect the hydrodynamic behavior, leading to relevant differences between different configurations. Also the gas-liquid system affects the hydrodynamic by modifying the coalescence behavior of the bubbles. The research of common settings, in order to achieve constant values for some variables, led to important evaluations, regarding in particular the minimum diameter, minimum height to diameter ratio and minimum diameter of the sparger’s holes. Other variables, however, influence these relations, like the presence of electrolytes in the solution, hindering the coalescence behavior, the hydrodynamic is modified.

From the correlations collected in the literature research, a database with a discrete set of all the possible exits has been produced. This database made possible to compare the different correlations, noticing where the results agree and especially how they differ. This tool enables also to visualize the range of applicability of a correlation and to compare it with the others, in order to choose which correlation can be used for analyzing a specified system. Since the use of a correlation, as suggested by the research, is more precise in its specific conditions; to select the right correlation is important, and filtering the information from the database can lead directly from millions of data to the very specific ones. The use of the database is useful, in addition to analyze a specific system, also for evaluating the range of validity of a correlation and also for analyze the sensitivity of a parameter. On the other hand, comparing the different correlations is not efficient, since the design conditions are always different.

Finally, experiments in a bubble column have been performed by changing superficial gas velocity, gas distributor, height to diameter ratio and salt composition of water. The experiments confirmed some theoretical issues like the different dependence of the height to diameter ratio/superficial gas velocity between multi-orifice sparger and single hole sparger. The practical investigation clarified also the limits of the literature correlations since the influence of the diameter and the height to diameter ratio is very relevant. Adding salts to the distilled water and using tap water underlined the differences between the different systems. The use of tap water in the literature is not limited to the water-air system but also to all the systems that consider water solutions, e.g. water-CMC for the simulation of high viscosity liquids. In many of the papers analyzed, it was not specified whether the water used was distilled or not.

These facts suggested some possible future in-depth analyses. Since the design variables of a bubble column can be the same in the different vapor-liquid settings, their behavior should be deepened, not only in precise cases but in a more general way. A common factor just for the design variables, to add to any correlation should be designed. To achieve this, it should be proved if really this factor is constant in any system. Often the independence of gas holdup or of volumetric mass transfer coefficient from the design variables is assumed. However the correlations are not comparable in most of the cases, this means that also the independence from some variables is limited in specific cases. A factor, able to overcome these problems, capable to compare single holes spargers and membrane should be developed. A first approach has been done by Behkish (Behkish et al., 2006) and then Gandhi and Joshi (Gandhi and Joshi, 2010) in another way. These methods, however, are mainly based on data gathered by other publications, therefore affected by several possible problems, e.g. the use of distilled water. New independent experiments should focus on these methodologies.

To obtain comparable results the methodologies should be standardize, from the measurement of gas holdup and volumetric mass transfer to a more accurate specification of the liquid and gas properties, and of course the type of sparger. Too many different spargers are used, standard measures and characteristics should be employed throughout the several experiments.

The use of a type of correlation instead of another one should be specified, e.g. exponential law. In this way the correlations would be easily compared; to see where and why the correlations differ could lead to an increased accuracy of the authors in the articles. To do this, to be more accurate, a precise aim has to be defined. The development of correlations for extreme conditions, e.g. non-Newtonian behavior, but developed in very small columns is useless for a scale up aim. If a research wants to have industrial purposes, it has first to satisfy scale up rules, rules that still have to be defined precisely. Therefore if the survey has just scientific purposes, the considerations achieved should not be generalized.

The understanding of the homogeneous regime is farther than the heterogeneous regime, semi-theoretical theories are available, the achievements of the first one can support the research in the other one. For example, considering the gas holdup as sum of small bubbles and big bubbles, since in heterogeneous regime the gas holdup due to small bubbles is supposed to be constant and it is correlated to the homogeneous regime. Wilkinson et al. (Wilkinson et al., 1994) and Krishna and Ellenberger (Krishna and Ellenberger, 1996) used this type of approach, while in more recent times, the researchers tend to use a larger amount of data and just fit the data in a correlation. The semi-empirical approach of Nedeltchev and Schumpe (Nedeltchev and Schumpe, 2008) for the homogeneous regime could be unified to the other approaches for the heterogeneous regime, in order to obtain a more precise evaluation of the latter. The empirical correlations can be more accurate as long as also the physical knowledge is understood.

Nomenclature

u_G = Superficial gas velocity [m·s^{-1}]
u = Velocity [m·s^{-1}]
D = Column Diameter [m]
d_R = Reactor Diameter [m]
d_S = Sauter-mean bubble diameter [m]
d = Diameter [m]
H = Clear liquid height [m]
H_D = Dispersed liquid height [m]
g = Gravitational acceleration [m·s^{-2}]
A = Interfacial area [m^{2}]
a = Volume specific interfacial area [m^{-1}]
J = Diffusive flux [mol·m^{-2}·s^{-1}]
D_L = Diffusion coefficient [m^{2}·s^{-1}]
V = Volume [m^{3}]
$\dot{V}$ = Volumetric flux [m^{3}·s^{-1}]
P_W = Power input [W]
P = Pressure [KPa]
p = Vapor pressure [KPa]
k_i = Mass transfer coefficient in phase i [m·s^{-1}]
K = Overall mass transfer coefficient [m·s^{-1}]
x = Mole fraction in the liquid phase [-]
y = Mole fraction in the vapor phase [-]
c = Molar concentration [mol·m^{-3}]

Greek letters
ε = Hold-up [-]
ρ = Density [Kg·m^{-3}]
μ = Viscosity [Pa·s]
μ_{eff} = Effective viscosity [Pa·s]
σ = Surface tension [N·m^{-1}]

Subscripts

A = Component A
x = Liquid phase
y = Gas phase
i = Interface
b = Bulk
e = Equilibrium
G = Gas
L = Liquid
t = Total
b = Bubble
H = Holes of the gas distributor
N = Nozzle
0 = Ambient conditions
$trans$ = Transition from homogeneous to heterogeneous regime
$part$ = Particles

Appendix I

Given n vectors, with n≤10, each vector vi composed of i elements, with i≤20, the program calculates a matrix with n columns and in the rows, all the possible combinations of the elements of the v_i vectors.

```
clear all
close all
clc
in=0;
disp('This program calculate in one matrix all the possible combinations of a set of at most 10 elements, each one composed of choosen values')
disp('')
while in==0
    var=input('Insert now the number of variables, from 1 to 10 ');
    disp('the number choosen is        ')
    disp(var)
    if var>0 && var<=10 && (var-fix(var)==0)
        in=1;
    else
        disp('the insert number is not correct, please check that it is between 1 and 10 and that it is integer')
    end
end
in=0;
A=zeros(var,20);

for i=1:var
    in=0;
    while in==0
        disp('select a linear set of elements in the variable or a custom composition')
        disp('press L for a linear set or C for a custom composition for variable')
```

```
        disp(i)
        disp('')
        set=input('type=   ','s');
        disp('')
        if set(1)=='L' || set(1)=='l'
            disp('insert now the minimum value of the variable')
            disp(i)
            min=input('min=  ');
            disp(' ')
            disp('insert now the maximum value of the variable')
            max=input('max=  ');
            disp(' ')
            disp('insert now the number of values in the variable, max
20 ')
            punti=input('n. of points=  ');
            disp('----------------------------------------------------
-----')
            if min<max && punti<=20  && (punti-fix(punti)==0) &&
min>=0 && max>=0 && punti>0
                mat=linspace(min, max, punti);
                in=1;
            else
                disp('The insert values are not correct, please set
numbers with min<max and number of points integer and smaller than
20')
            end
        elseif set(1)=='C' || set(1)=='c'
            disp('')
            disp('insert the elements of the variable')
            disp(i)
            disp('max 20 elements')
            disp('')
            disp('insert the elements within brackets in a (1,x)
vector es. [273 293]')
            mat1=input('value=  ');
            disp('----------------------------------------------------
-----')
            if size(mat1,1)==1 && size(mat1,1)<=20
```

```
                mat=mat1;
                in=1;
                punti=size(mat,2);
            else
                disp('The insert values are not correct, please insert elements in a one row vector and with less or equal than 20 elements')
            end
        else
            disp('there is something wrong, please enter a letter for determine the configuration of the variables, try again')
        end
    end
    for j=1:punti
        A(i,j)=mat(j);
    end
end

prename=zeros(1,20);
for i=1:var
    count=1;
    ind=0;
    k=0;
    prename(1,1)=A(i,1);
    for j=2:20
        if A(i,j)~= 0
            count=count+1;
            prename(j)= A(i,j);
        else
            ind=ind+1;
            if ind==1
                k=j;
            end
        end
        if count==20
            k=21;
        end
    end
    eval(['var' num2str(i) ' =zeros(1,k-1);'])
```

```
    for kk=1:(k-1)
        eval(['var' num2str(i) '(kk)' '=prename(kk);'])
    end
end

v1=1;
v2=1;
v3=1;
v4=1;
v5=1;
v6=1;
v7=1;
v8=1;
v9=1;
v10=1;

for vv=1:var
eval(['v' num2str(vv) '=size(var' num2str(vv) ',2);'])
end

if var<10
    for zz=(var+1):10
        eval(['var' num2str(zz) '=zeros(1);'])
    end
end

A=zeros(v10*v9*v8*v7*v6*v5*v4*v3*v2*v1,10);

for l=1:v10
    A(1+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),1)=var10(1,l);
    for ll=1:((v1*v2*v3*v4*v5*v6*v7*v8*v9)-1)
        A(1+ll+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),1)=var10(1,l);
    end
    for i=1:v9
        A(1+v1*v2*v3*v4*v5*v6*v7*v8*(i-
1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),2)=var9(1,i);
        for ii=1:((v1*v2*v3*v4*v5*v6*v7*v8)-1)
```

```
            A(1+ii+v1*v2*v3*v4*v5*v6*v7*v8*(i-
1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),2)=var9(1,i);
        end
        for h=1:v8
            A(1+v1*v2*v3*v4*v5*v6*v7*(h-1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-
1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),3)=var8(1,h);
            for hh=1:((v1*v2*v3*v4*v5*v6*v7)-1)
                A(1+hh+v1*v2*v3*v4*v5*v6*v7*(h-
1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-
1),3)=var8(1,h);
            end
            for g=1:v7
                A(1+v1*v2*v3*v4*v5*v6*(g-1)+v1*v2*v3*v4*v5*v6*v7*(h-
1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-
1),4)=var7(1,g);
                for gg=1:((v1*v2*v3*v4*v5*v6)-1)
                    A(1+gg+v1*v2*v3*v4*v5*v6*(g-
1)+v1*v2*v3*v4*v5*v6*v7*(h-1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-
1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),4)=var7(1,g);
                end
                for f =1:v6
                    A(1+v1*v2*v3*v4*v5*(f-1)+v1*v2*v3*v4*v5*v6*(g-
1)+v1*v2*v3*v4*v5*v6*v7*(h-1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-
1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),5)=var6(1,f);
                    for ff=1:((v1*v2*v3*v4*v5)-1)
                        A(1+ff+v1*v2*v3*v4*v5*(f-
1)+v1*v2*v3*v4*v5*v6*(g-1)+v1*v2*v3*v4*v5*v6*v7*(h-
1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-
1),5)=var6(1,f);
                    end
                    for e=1:v5
                        A(1+v1*v2*v3*v4*(e-1)+v1*v2*v3*v4*v5*(f-
1)+v1*v2*v3*v4*v5*v6*(g-1)+v1*v2*v3*v4*v5*v6*v7*(h-
1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-
1),6)=var5(1,e);
                        for ee=1:((v1*v2*v3*v4)-1)
                            A(1+ee+v1*v2*v3*v4*(e-
1)+v1*v2*v3*v4*v5*(f-1)+v1*v2*v3*v4*v5*v6*(g-
```

```
1)+v1*v2*v3*v4*v5*v6*v7*(h-1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-
1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),6)=var5(1,e);
                        end
                        for d =1:v4
                            A(1+v1*v2*v3*(d-1)+v1*v2*v3*v4*(e-
1)+v1*v2*v3*v4*v5*(f-1)+v1*v2*v3*v4*v5*v6*(g-
1)+v1*v2*v3*v4*v5*v6*v7*(h-1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-
1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),7)=var4(1,d);
                            for dd=1:((v1*v2*v3)-1)
                                A(1+dd+v1*v2*v3*(d-1)+v1*v2*v3*v4*(e-
1)+v1*v2*v3*v4*v5*(f-1)+v1*v2*v3*v4*v5*v6*(g-
1)+v1*v2*v3*v4*v5*v6*v7*(h-1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-
1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),7)=var4(1,d);
                            end
                            for c=1:v3
                                A(1+v1*v2*(c-1)+v1*v2*v3*(d-
1)+v1*v2*v3*v4*(e-1)+v1*v2*v3*v4*v5*(f-1)+v1*v2*v3*v4*v5*v6*(g-
1)+v1*v2*v3*v4*v5*v6*v7*(h-1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-
1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),8)=var3(1,c);
                                for cc=1:((v1*v2)-1)
                                    A(1+cc+v1*v2*(c-1)+v1*v2*v3*(d-
1)+v1*v2*v3*v4*(e-1)+v1*v2*v3*v4*v5*(f-1)+v1*v2*v3*v4*v5*v6*(g-
1)+v1*v2*v3*v4*v5*v6*v7*(h-1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-
1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-1),8)=var3(1,c);
                                end
                                for b=1:v2
                                    A(((b-1)*v1+1)+v1*v2*(c-
1)+v1*v2*v3*(d-1)+v1*v2*v3*v4*(e-1)+v1*v2*v3*v4*v5*(f-
1)+v1*v2*v3*v4*v5*v6*(g-1)+v1*v2*v3*v4*v5*v6*v7*(h-
1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-
1),9)=var2(1,b);
                                    for bb=1:(v1-1)
                                        A(1+bb+v1*(b-1)+v1*v2*(c-
1)+v1*v2*v3*(d-1)+v1*v2*v3*v4*(e-1)+v1*v2*v3*v4*v5*(f-
1)+v1*v2*v3*v4*v5*v6*(g-1)+v1*v2*v3*v4*v5*v6*v7*(h-
1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-
1),9)=var2(1,b);
                                    end
```

```
                                    for a=1:v1
                                        A(a+v1*(b-1)+v1*v2*(c-
1)+v1*v2*v3*(d-1)+v1*v2*v3*v4*(e-1)+v1*v2*v3*v4*v5*(f-
1)+v1*v2*v3*v4*v5*v6*(g-1)+v1*v2*v3*v4*v5*v6*v7*(h-
1)+v1*v2*v3*v4*v5*v6*v7*v8*(i-1)+v1*v2*v3*v4*v5*v6*v7*v8*v9*(l-
1),10)=var1(1,a);
                                    end
                                end
                            end
                        end
                    end
                end
            end
        end
    end
end

A1=zeros(size(A,1),10);
for j=1:10
    A1(:,j)=A(:,11-j);
end

A2=zeros(size(A,1),var);
for i=1:var
    A2(:,i)=A1(:,i);
end

filename = input('Enter name of file: ', 's');
xlswrite(filename, A2)
```

References

Alvarez, E., Sanjuro, B., Cancela, A., Navaza, J.M., “Mass Transfer and Influence of Physical Properties of Solutions in a Bubble Column”, *Trans IChemE*, Vol. 78, 889-893, (2000).

Akita, K. & Yoshida, F., “Gas Holdup and Volumetric Mass Transfer Coefficient in Bubble Columns”, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 12, 76-80 (1973).

Akita, K. & Yoshida, F., “Bubble Size, Interfacial Area and Liquid-Phase Mass Transfer Coefficient in Bubble Column”, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 13, 84-91 (1974).

Beenackers, A., Van Swaaij, W.P.M., “Slurry Reactors, Fundamentals and Applications”, *NATO ASI series*, Series E, cat.inist.fr (1986).

Bach, H. F. & Pilhofer, T., “Variation of Gas Holdup in Bubble Columns with Physical Properties of Liquids and Operating Parameters of Columns”, *Ger. Chem. Eng.*, Vol. 1, 270 (1978).

Behkish, A., Lemoine R. R., Oukaci B. and Morsi B. I., “Novel Correlations for Gas Holdup in Large-Scale Slurry Bubble Column Reactors Operating under Elevated Pressures and Temperatures”, *Chem. Eng. J.*, Vol. 115, 157–171 (2006).

Behkish, A.; Lemoine, R., Sehabiague, L., Oukaci, R. & Morsi, B. I., “Gas Holdup and Bubble Size Behavior in a Large-Scale Slurry Bubble Column Reactor Operating with an Organic Liquid Under Elevated Pressures and Temperatures”, *Chem. Eng. J.*, Vol. 128, 69-84 (2007).

Bouaifi M, Hebrard G, Bastoul D, Roustan M., “A Comparative Study of Gas Holdup, Bubble Size, Interfacial Area and Mass Transfer Coefficients in Stirred Gas–Liquid Reactors and Bubble Columns”, *Chem. Eng Process*, Vol. 40, 97–111 (2001).

Calderbank P.H., “Ozone Decomposition Catalysis”, *Chem. Eng.*, 45 CE 209 (1976).

Deckwer, W.,-D., Burckhart, R., Zoll, G., “Mixing and Mass Transfer in Tall Bubble Columns”, *Chem. Eng. Sci.*, Vol. 29, 2177-2188 (1974).

Deckwer, W.-D., “On the Mechanism of Heat Transfer in Bubble Column Reactors”, *Chem. Eng. Sci.*, Vol. 35, 1341-1346 (1980).

Fan, L.S., “Gas–Liquid–Solid Fluidization Engineering”, Boston: Butterworths (1989).

Fukuma, M., Muroyama, K. & Yasunishi, A., “Specific Gas-Liquid Interfacial Area and Liquid-Phase Mass Transfer Coefficient in a Slurry Bubble Column”, *J. Chem. Eng. Japan*, Vol. 20, 321-324 (1987).

Gandhi A. B. and Joshi J. B., “Unified Correlation for Overall Gas Hold-Up in Bubble Column Reactors for Various Gas–Liquid Systems Using Hybrid Genetic Algorithm-Support Vector Regression Technique”, *Can. J. Chem. Eng.*, Vol. 88, 758–776 (2010).

Godbole, S. P., Schumpe, A., Shah, Y. T., Carr, N. L., “Hydrodynamics and Mass Transfer in Non-Newtonian Solutions in a Bubble Column”, *AIChE J.,* Vol. 30 213- 220, (1984).

Hammer, H., Schrag, H., Hektor, K., Schönau, K., Küsters, W., Soemarno, A., Sahabi U., Napp, „New Subfunctions on Hydrodynamics, Heat and Mass Transfer for Gas/Liquid and Gas/Liquid/Solid Chemical and Biochemical Reactors”, *Front. Chem. Reac. Eng.*, 464-474 (1984).

Haque, M., K. Nigam and J. B. Joshi, “Hydrodynamics and Mixing Studies in Highly Viscous Pseudo-Plastic Non-Newtonian Solutions in Bubble Column,” *Chem. Eng. Sci.*, Vol. 41, 2321–2331 (1986).

Hikita, H., Asai, S., Tanigawa, K., Segawa, K., Kitao, M., “Gas Holdup in Bubble Columns, *Chem. Eng. J.,* Vol. 20, 59-67 (1980).

Hikita, H., Asai, S., Tanigawa, K., Segawa, K., Kitao, M., “The Volumetric Liquid-Phase Mass Transfer Coefficient in Bubble Columns”, *Chem. Eng. J.,* Vol. 22, 61 (1981).

Hughmark, G. A., “Holdup and Mass Transfer in Bubble Columns, *Ind. Eng. Chem. Process”, Des. Dev.,* Vol. 6, 218-220 (1967).

Idogawa, K.; Ikeda, K., Fukuda, T., Morooka, S., “Effect of Gas and Liquid Properties on the Behaviour of Bubbles in a Column Under High Pressure”, *Intern. Chem. Eng.,* Vol. 27, 93-99 (1987).

Jordan, U. & Schumpe, A., “The Gas Density Effect on Mass Transfer in Bubble Columns with Organic Liquids”, *Chem. Eng. Sci.,* Vol. 56, 6267-6272, (2001).

Joshi, J. B.; Shah, Y.T., “Gas-Liquid-Solid Reactor Design”, *McGraw-Hill*: New York (1979).

Joshi J.B., Sharma M.M., “A Circulation cell model for bubble columns”, *Trans. Inst. Chem. Eng.,* Vol. 57, 244–251 (1979).

Joshi, J. B., U. P. Veera, C. V. Prasad, D. V. Phanilumar, N. S. Deshphande, S. S. Thakre and B. N. Thorat, “Gas Hold-Up Structures in Bubble Column Reactors”, *PINSA,* Vol. 64(A), 441–567 (1998).

Kastanek, F., M. Zahradnik and R. J. Kratochvil, “Scaling-up of Bubble Column Reactors on Basis of Laboratory Data”, *Chem. Eng. Sci.*, Vol. 35, 456–462 (1980).

Kawase, Y., Halard, B. & Moo-Young, M., “Theoretical Prediction of Volumetric Mass Transfer Coefficients in Bubble Columns for Newtonian and Non-Newtonian Fluids”, *Chem. Eng. Sci.*, Vol. 42, 1609-1617 (1987).

Kazakis, N.A., Mouza, A.A., Paras, S.V., “Bubble size distribution at the entrance of bubble column with pore sparger”, *7th International Congress of Chemical and Process Engineering*, prague, czech republic (2007).

Kelkar, B. G.; Godbole, S. P., Honath, M. F., Shah, Y. T., Carr, N. L. & Deckwer, W.-D., “Effect of Addition of Alcohols on Gas Holdup and Backmixing in Bubble Columns”, *AIChE J.*, Vol. 29, 361-369 (1983).

Khare, A. S. & Joshi, J. B., “Effect of Fine Particles on Gas Holdup in Three-Phase Sparged Reactors”, *Chem. Eng. J.*, Vol. 44, 11 (1990).

Koide K, Morooka S, Ueyama K, Matsuura A., “Behavior of Bubbles in Large Scale Bubble Column”, *J. Chem. Eng. Jpn.*, Vol.12, 98–104 (1979).

Kojima, H., J. Sawai and H. Suzuki, “Effect of Pressure on Volumetric Mass Transfer Coefficient and Gas Holdup in Bubble Column”, *Chem. Eng. Sci.*, Vol. 52, 21–22, 4111–4116 (1997).

Krishna, R. and J. Ellenberger, “Gas Holdup in Bubble Column Reactors Operating in the Churn-Turbulent Flow Regime”, *AIChE J.*, Vol. 42(9), 2627–2634 (1996).

Krishna, R. & van Baten, J. M., “Mass Transfer in Bubble Columns”, *Catalysis Today* 79-80, 67-75 (2003).

Lau, R., Peng, W., Velazquez-Vargas, G., Yang, G.Q., Fan, L.S., “Gas-Liquid Mass Transfer in High-Pressure Bubble Columns”, *Industrial and Engineering Chemistry Research*, Vol. 43, 1302-1311 (2004).

Luo X, Lee D.J., Lau R., Yang G., Fan L., “Maximum Stable Bubble Size and Gas Holdup in High-Pressure Slurry Bubble Columns”, *AIChE J.*, Vol.45, 665–685 (1999).

Maalej S, Benadda B, Otterbein M., “Interfacial Area and Volumetric Mass Transfer Coefficient in a Bubble Reactor at Elevated Pressures”, *Chem. Eng. Sci.*, Vol. 58, 2365–2376 (2003).

Mashelkar, R.A., “Frontier in Chemical Reaction Engineering”, *John Wiley & Sons*, New Delhi, India, Vol. 1, 330-344 (1984).

Miyauchi, T., Shyu, C.N., “Flow of Fluid in Gas Bubble Columns”, Kagaku Kogaku, (1970).

Mouza, A. A., G. K. Dalakoglou and S. V. Paras, “Effect of Liquid Properties on the Performance of Bubble Column Reactors with Fine Porous Spargers”, *Chem. Eng. Sci.*, Vol. 60, 1465–1475 (2005).

Muller, F. L. & Davidson J. F., “On the Contribution of Small Bubbles to Mass Transfer in Bubble Columns Containing Highly Viscous Liquids”, *Chem. Eng. Sci.,* Vol. 47, 3525-3532 (1992).

Nakanoh, M. & Yoshida, F., “Gas Absorption by Newtonian and Non-Newtonian Liquids in a Bubble Column”, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 19, 190-195 (1980).

Nagel, O., Hegner, B., Keurten, H., “Design of Gas/Liquid Reactors: Mass Transfer Area and Input of Energy”, *Chem. Ing. Tech.,* Vol. 50 n.12, 934-944 (1978).

Nedeltchev, S. & Schumpe, A., “A New Approach for the Prediction of Gas Holdup in Bubble Columns Operated Under Various Pressures in the Homogeneous Regime”, *J. Chem. Eng. Japan,* Vol. 41, 744-755 (2008).

Otake, T., Tone, S., Nakao, K. & Mitsuhashi, Y., “Coalescence and Breakup of Bubbles in Liquids”, *Chem. Eng. Sci.*, Vol. 32, 377-383 (1977).

Öztürk, S, Schumpe, A. & Deckwer, W.-D., “Organic Liquids in a Bubble Column: Holdups and Mass Transfer Coefficients”, *AIChE J.*, Vol. 33, 1473-1480 (1987).

Pandit, A. B. and Joshi, J. B., “Mixing in Mechanically Agitated Gas–Liquid Contactors, Bubble Columns, and Modified Bubble Columns”, *Chem. Eng. Sci.*, Vol. 38 n.8, 1189–1215 (1983).

Popovic, M. and C. W. Robinson, “The Specific Interfacial Area in External Circulation Loop Airlifts and a Bubble Column I. Aqueous Sodium Sulphite Solution”, *Chem. Eng. Sci*. 42 n.12, 2811–2824 (1987).

Reilly, I.G., Scott, D.S., de Bruijn, T.J.W., Jain, A., Piskorz, J., “A Correlation for Gas Holdup in Turbulent Coalescing Bubble Columns”, *Can. J. Chem. Eng.,* Vol. 64, 705-717 (1986).

Reilly, I. G., Scott, D. S., De Bruijn, T. J. W. & MacIntyre, D., “The Role of Gas Phase Momentum in Determining Gas Holdup and Hydrodynamic Flow Regimes in Bubble Column Operations”, *Can. J. Chem. Eng.*, Vol. 72, 3-12 (1994).

Saxena, S.C., Rao, N.S., Saxena, A.C., “Heat-Transfer and Gas-Holdup Studies in a Bubble Column: Air–Water–Glass Bead System”, *Chem. Eng. Commun*., Vol. 96, 31–55 (1990).

Schumpe A, Grund G., “The Gas Disengagement Technique for Studying Gas Holdup Structure in Bubble Columns”, *Can. J. Chem. Eng*., Vol. 64, 891–896 (1986).

Schumpe, A., Deckwer, W.D., “Viscous Media in Tower Bioreactors: Hydrodynamic Characteristics and Mass Transfer Properties”, *Bioprocess Eng*., Vol. 2, 79–94 (1987).

Serrafi, A., Jamialahmadi, M., Müller-Steinhagen, H., Smith, J.M., “Gas Holdup in Homogeneous and Heterogeneous Gas-Liquid Bubble Column Reactors *Can. J. Chem. Eng.,* Vol. 77, 11-21 (1999).

Shah, Y.T., “Gas-Liquid-Solid Reactor Design”, *McGraw-Hill*, New York (1978).

Shah, Y. T., Kelkar, B. G. & Deckwer, W.-D., “Design Parameters Estimation for Bubble Column Reactors”, *AIChE J.*, Vol. 28, 353-379 (1982).

Sotelo, J.L., Benitez, F.J., Beltran-Heredia, J., Rodriguez, C. “Gas Holdup and Mass Transfer Coefficient in Bubble Columns. 1. Porous Glass-Plate Diffusers”, *International Chemical Engineering*, Vol. 34, 82-89 (1994).

Tang, C. and Heindel, M. H., “A New Methodology for Hydrodynamic Similairity in Bubble Column Reactors: Time-dependent Gas Holdup Variation in an Air–Water Bubble Column”, *Chem. Eng. Sci.* (2004).

Terasaka, K., Tsuge, H., Matsue, H., “Bubble Formation in Cocurrently Upward Flowing Liquid”, *The Can. J. Chem. Eng*., Wiley Online Library (1999).

Ueyama, K., Morooka, S., Koide, K., Kaji, H. & Miyauchi, T., “Behavior of Gas Bubbles in Bubble Columns”, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 19, 592-599 (1979).

Urseanu, M. I., Guit, R. P. M., Stankiewicz, A., van Kranenburg, G., Lommen, J. H. G. M., “Influence of Operating Pressure on the Gas Hold-up in Bubble Columns for High Viscous Media,” *Chem. Eng. Sci*., Vol. 60, 1465–1475 (2003).

Vafopulos, I., Sztatescny, K., Moser, F., “Der Einflub des Partial-und Gesamtdruckes auf den Stoffaustausch”, *Chem. Eng. Technol*., Vol. 47, 681–786 (1975).

Vandu, C.O., Krishna, R., “Volumetric Mass Transfer Coefficients in Slurry Bubble Columns Operating in the Churn-Turbulent Flow Regime”, *Chemical and Engineering Processing*, Vol. 43, 987-995 (2004).

Vatai, G. Y., and M. N. Tekic, “Gas Hold-up in Bubbles Columns with Non-Newtonian Liquids”, *Chem. Eng. Sci*. 42 n.1, 166-169 (1987).

Veera U.P., Kataria K.L., Joshi J.B., “Effect of superficial gas velocity on gas hold-up profiles in foaming liquids in bubble column reactors”, *Chem. Eng. J.*, Vol. 99, 53–58 (2004).

Verma, A.K., Rai S., “Studies on Surface to Bulk Ionic Mass Transfer in Bubble Column”, *Chem. Eng. J.*, Vol. 94, 67–72 (2003).

Wezorke, H., “Einflüss von Grössblasen in Blasensäulenreaktoren”, P*h.D. Dissertation*, University of Dortmund, Germany (1986).

Wilkinson, P. M. & van Dierendonck, L. L., “Pressure and Gas Density Effects on Bubble Breakup and Gas Holdup in Bubble Columns”, *Chem. Eng. Sci.,* Vol. 45, 2309-2315 (1990).

Wilkinson, P. M., Spek A. P., Van Dierendonck, L. L., “Design Parameters Estimation for Scale-Up of High-Pressure Bubble Columns”, *AIChE J.,* Vol. 38, 544-554, (1992).

Wilkinson, P. M., Haringa, H., Van Dierendonck, L. L., “Mass Transfer and Bubble Size in a Bubble Column under Pressure”, *Chem. Eng. Sci.*, Vol. 49, 1417-1427 (1994).

Zehner, P., Kraume, M. “Bubble Columns”, Wiley,Weinheim, (2005).

Zou, R., Jiang, X., Li, B., Zu, Y., Zhang, L. “Studies on Gas Holdup in a Bubble Column Operated at Elevated Temperature”, *Industrial and Engineering Chemistry Research*, Vol. 27, 1910-1916 (1988).

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