Chemical Engineering Science, Vol. 48, No. 5, pp. 889–911, 1993.
Printed in Great Britain.

0009–2509/93 $6.00 + 0.00
Pergamon Press Ltd

IMPROVED TOOLS FOR BUBBLE COLUMN REACTOR DESIGN AND SCALE-UP

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ABSTRACT

The past two decades have seen a steadily increasing number of papers on bubble columns and related reactors. In spite of the many publications, the design and scale-up of bubble column reactors is still an often difficult task and subjected to errors, as the multiphase flow in bubble columns is complex in structure. The uncertainties can be partly due to the use of models being too much simplified. However, more important seems the accessibility of those parameters which largely depend on scale, reactor operation conditions and physico-chemical properties. The present status of estimating gas hold-ups, mass transfer and mixing coefficients is reviewed. Emphasis is given on proven correlations and recent improvements. Specific recommendations are given for their application.

KEYWORDS

Bubble column, scale-up, parameter estimation, gas hold-up, mass transfer and mixing coefficients.

INTRODUCTION

Bubble column reactors (BCR) are multiphase reaction devices in which a discontinuous gas phase moves in form of bubbles relative to a continuous liquid phase. Eventually, a reactive solid or catalyst is fluidized in the liquid phase. In its most simple form the BCR is a vertical cylinder where the gas enters at the bottom through a gas sparger which may vary in design. The liquid (slurry) phase can be batchwise or continuously fed to the reactor. Continuous BCR can be operated cocurrently and countercurrently. However, as a result of considerable mixing and the low liquid flow rate usually being applied, counterflow offers no significant advantages. Temperature control is achieved by wall heat transfer or internal heat exchangers.

Compared with other multiphase contactors (stirred vessels, packed towers, trickle bed reactors etc.) the BCR offers some advantages such as

- little maintenance due to simple construction and no problems with sealing due to the absence of moving parts
- high liquid (slurry) phase content for the reaction to take place

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Presented at the First International Conference on Gas–Liquid and Gas–Liquid–Solid Reactor Engineering, Columbus, OH, 13–16 September 1992. The main proceedings of that conference have been published in *Chemical Engineering Science*, Vol. 47, No. 13/14.

- excellent heat transfer properties and, hence, easy temperature control
- reasonable interphase mass transfer rates at low energy input
- solids can be handled without serious erosion or plugging problems
- little floor space required
- BCRs are relatively cheap.

Disadvantages are, however, considerable backmixing in both the continuous liquid (slurry) phase and the dispersed gas phase, high pressure drop (if operated at atmospheric conditions) and bubble coalescence. To suit the specific requirement of special reaction systems, BCRs can be modified in various ways. In sectionalized apparatuses like multistaged and multichannel reactors or BCRs with static mixers, mixing can be suppressed and interphase mass transfer rates improved.

Loop reactors with directional liquid circulation flow are preferentially applied in biotechnological applications. Examples are air-lift reactors with internal or external circulation, the ICI pressure cycle reactor and its deep shaft version. Another variant of BCRs is downflow operation which is recommended when complete gas phase conversion and, hence, a long bubble residence time is required. On the other hand, in some air oxiditions gas phase conversion is not important, then horizontally sparged reactors can be used which offer low pressure drop. In today's industry the vertically sparged, single staged BCR is the most widely used and in what follows emphasis is given to this type of reactor. Reviews on BCRs and its numerous variants are given by Deckwer (1985, 1992), Fan (1989) and Chisti (1989).

REACTIONS TYPICALLY CARRIED OUT IN BCR

Gas-liquid reactions can roughly be classified to belong either to the slow or fast reaction-absorption regime (Astarita, 1967; Dankwerts, 1970). In the fast reaction-absorption regime the space-time-yield is mainly governed by the available interfacial area and, hence, high gas hold-up and small bubbles are desired. In contrast, the slow reaction-absorption regime requires a high liquid hold-up for the reaction to take place. However, the mass transfer rate must also be sufficiently high as both liquid hold-up and mass transfer are inversely affected by gas velocity and the proper gas flow rate has to be found to give optimum space-time-yield.

As the BCRs provide for both large relative liquid hold-up and sufficient mass transfer rates, they are particularly well-suited for gas-liquid reactions taking place in the slow reaction-absorption regime. Indeed, the majority of oxidations, hydrogenations, chlorinations etc. carried out by industry belongs to the slow reaction-absorption regime. Examples are reported in the monographs by Deckwer (1985, 1992) and Fan (1989). In particular, absorption enhancement, typical for the fast reaction-absorption regime, does obviously not occur in biotechnological processes such as aerobic microbial cultivations and in catalytic slurry reactions. Strictly speaking, enhancement and, hence, transition into the fast reaction-absorption regime can only be expected if the diameters of the particle fines (catalyst or microbial cell) are considerably smaller than the liquid film thickness at the gas-liquid interface. This is hardly possible in view of the liquid-side mass transfer coefficients reported in BCRs. In some cases, however, there may be other reasons (as, for instance, heat removal) which recommend the use of BCRs also in the fast reaction-absorption regime.

SCALE-UP METHODS

Though BCRs are simple in their construction and operation their design and scale-up can be a difficult task. In general, reactor performance is governed by reaction specific quantities and reactor specific phenomena. While the reaction specific data such as physical properties, stoichiometry, thermodynamics, kinetics etc. are approximately independent of reactor type and design, the reactor specific phenomena are largely dependent on operating conditions, physical properties, reactor type, and its geometrical dimensions as is shown schematically in Fig. 1. It is the scale-dependency of the fluid dynamic phenomena and the heat and mass transfer properties which cause the so-called scale-up problem. The scale-up methods used in biotechnology and chemical industry range from empirical know-how (guidelines, scale-up rules, dimensional analysis) to know-why based approaches. In case of BCRs, know-why based scale-up should favorably start with regime analysis, i.e., an estimation of the various rates and recognition of the limiting steps ("bottle necks") of the entire process. Regime analysis is followed by setting-up appropriate models which may be simplified with regard to the complex hydrodynamic structure or be more sophisticated and fundamental and based on first principles. However, fundamental and often even simplified models suffer on the accessibility of the many parameters involved, their numerical values are often difficult to be estimated reliably. In this regard, sensitivity analysis may help to recognize most influential scale-dependent phenomena and eventually lead to the application of more simplified models. In these days, there is no doubt that the know-how based scale-up methods still often practicized in many industries should be replaced by know-why based models.

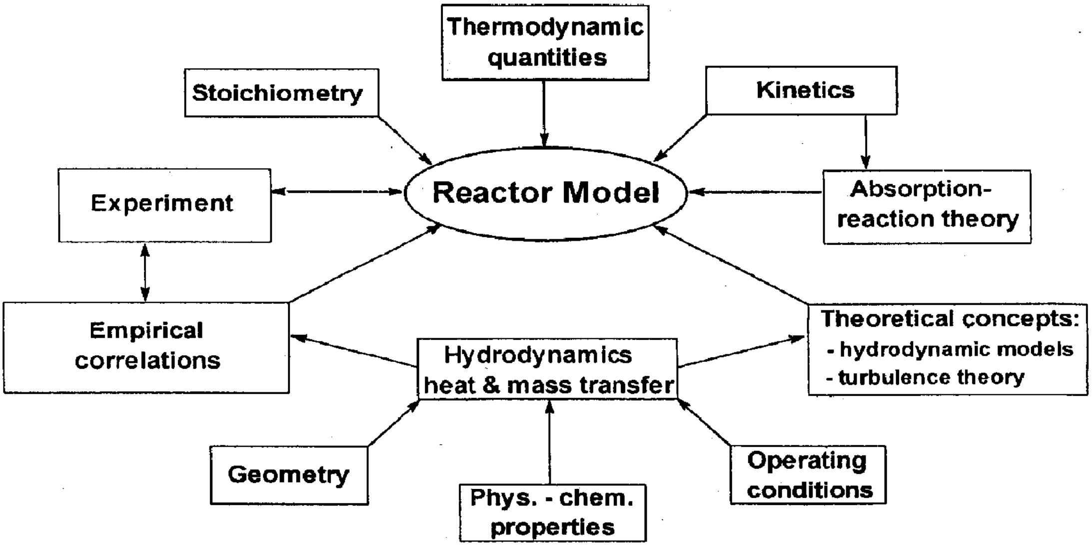

Fig. 1: Phenomena involved in Modeling BCRs

Models for BCRs can be set up with consideration of various phenomena. The mathematical structure is mainly dependent on the reaction kinetics, the number of reactive species and phases, the absorption-reaction regime (mass transfer terms) and the fluid dynamics of the phases. In the classical models it is anticipated that the fluid dynamics can be sufficiently characterized by the liquid and gas phase RTDs measured by various methods inside the reactor or at the outlet. The RTDs can be interpreted to be either completely mixed (STR), partially mixed or unmixed (PFR). Of course, partial mixing is the case most often encountered and this can conveniently be described by tank-in-series models (with or without backflow between neighboring cells) or by the one-dimensional axial dispersion model (ADM). In the ADM all the individual mixing phenomena taking place in each phase are all lumped to an axial dispersion coefficient. It is well known that this lumping presents a coarse simplification of the reality. Indeed, a lot of newer experimental studies have clearly shown that the liquid phase fluid dynamics is better characterized by circulation flows which either occur sectionwise (circulation cell model) or extend over the entire reactor height. Improved hydrodynamic models have been proposed which account for the more realistic circulation flow pattern. It is understood that circulation flows contradict the ADM which basically assumes plug flow with superposed dispersive flow.

The fluid dynamics of the gas phase is seemingly even more complex and different flow regimes are observed. Bubbly flow or quiescent bubbling with almost uniformly sized bubbles having similar rise velocities prevails at low gas flow and is referred to as the homogeneous flow regime. At higher gas velocities, homogeneous flow can not be maintained and transition to heterogeneous or churn-turbulent flow is observed which is characterized through the appearance of larger bubbles rising with higher velocities through the bed of the small bubbles. As an approximation it is often anticipated, that when increasing the gas flow, the fraction of small bubbles is constant and corresponds with the highest gas hold-up of the homogeneous flow regime while the fraction of large bubbles steadily increases (Grund *et al.*, 1992). Again, the ADM seems not appropriate the account for bubble dynamics in the heterogeneous flow regime and two-bubble-class models have been proposed (Joseph and Shah, 1984; Shah *et al.*, 1985). In spite of the serious drawbacks of the ADM to describe realistically the fluid dynamic behavior of the gas and liquid phase it has proven as and still is an effective tool to model BCRs. Therefore, when discussing parameter estimations also the dispersion coefficients will be dealt with briefly.

PARAMETER ESTIMATIONS

In the set of model equations, various parameters are involved which are partly model specific, at least. As schematically indicated in Fig. 1, the parameters characterizing fluid dynamics and transport phenomena are influenced by various factors and the intrinsic dependencies are often difficult to discern. Therefore, parameter estimations are based on correlations which are frequently only empirical or derived by dimensional analysis. However, increasing tendencies can be observed to interpret such correlations by theoretical reasoning and physical laws. In this regard the more fundamental and realistic fluid dynamic models are very stimulating and helpful.

Correlations for parameter estimations are often developed from "cold flow" measurements and non-reactive conditions. It is therefore understood that the use of empirical correlations is of limited value and their predictions may lead to errors. This is particularly valid for those quantities which affect interfacial properties like mass transfer coefficients, interfacial areas and phase hold-ups. It appears obvious that properties like density, viscosity and surface tension are not always sufficient to describe fluid dynamics and interfacial phenomena. As a general rule of thumb, caution and reserve is recommended when applying empirical correlations to new processes. They may predict reliable data in many cases while in others they fail. The various empirical and semi-theoretical correlations for estimating design parameters of BCR have been reviewed and critically evaluated by Shah *et al.* (1982), Shah and Deckwer (1986) Fan (1989) and Deckwer (1985, 1992). Therefore, emphasis will be given to new developments and only those of the many correlations reported earlier will be presented briefly which have proven as significant and of broader applicability.

Gas hold-up

The relative gas hold-up is of utmost importance. It is not a constant quantity but varies locally in axial and radial direction. As already pointed out the internal structure of the gas distributed in BCRs largely depends on the flow regime. One discriminates among homogeneous (bubbly) and heterogeneous (churn-turbulent) flow. In addition, slug flow (Taylor bubbles) may occur at high gas velocities in small diameter BCRs, especially for highly viscous liquids. In industry, the majority of BCRs is operated with heterogeneous flow where two-bubble-classes with significantly differing sizes and rise velocities can be observed (Grund *et al.*, 1992). However, the homogeneous flow regime is encountered as well, particularly in pressurized BCRs (Wilkinson and van Dierendonck, 1990).

The integral hold-up (averaged over the entire volume of the gas-in-liquid dispersion) can easily be measured at atmospheric conditions and plenty of data are available. The dimensionless correlation of Akita and Yoshida (1973) is given by

$$\frac{\varepsilon_G}{(1-\varepsilon_G)^4} = \alpha \left(\frac{d_R^2\, \rho_L\, g}{\sigma}\right)^{1/8} \left(\frac{g\, d_R^3\, \rho_L^2}{\mu_L^2}\right)^{1/12} \frac{u_G}{\sqrt{g\, d_R}} \tag{1}$$

where $\alpha = 0.2$ for pure liquids and non-electrolyte solutions and $\alpha = 0.25$ for salt solutions. Usually, the Akita-Yoshida correlation provides for a reliable conservative estimate. Hikita *et al.* (1980) reported on gas hold-up measurements in a 10-cm diameter BCR using various gases and liquids. These authors proposed the following relation

$$\varepsilon_G = 0.672\, f \left(\frac{u_G\, \mu_L}{\sigma}\right)^{0.578} \left(\frac{\mu_L^4\, g}{\rho_L\, \sigma^3}\right)^{-0.131} \left(\frac{\rho_G}{\rho_L}\right)^{0.062} \left(\frac{\mu_G}{\mu_L}\right)^{0.107} \tag{2}$$

where f = 1 for non-electrolyte and for salt solutions f is a function of ionic strength. Hikita *et al.* (1980) were the first who considered physical properties of the gas. As the exponents show, they appear of little relevance, but if omitted the deviation of the data fit may rise to 15 % as opposed to 4.2 % as a result of their inclusion.

Öztürk *et al.* (1987) studied gas hold-up in 50 different gas-liquid systems (gases: H_2, He, N_2, Air, CO_2 at atmospheric pressure) and applied correlations reported in the literature to fit the data. Among the applicable correlations those of Akita and Yoshida, eq. (1), and Hikita *et al.*, eq. (2), gave the best fit with a mean error of only 11 %. Therefore, Öztürk *et al.* felt no need to propose modified correlations and recommended eq. (1) and (2) as suitable for design purposes. However, these authors pointed out that the fit with Akita and Yoshida's correlation could be improved by considering the density ratio of the phases.

Also other authors reported on careful experimental studies in which a significant effect of gas density either due to increasing gas molecular mass or operating pressure was observed (Reilly *et al.*, 1986; Idogawa *et al.*, 1986, 1987; de Bruijn *et al.*, 1988; Zou *et al.*, 1988; Oyevaar, 1989). All the previous work on the effect of gas density and elevated pressure on gas hold-up in BCRs has been critically reviewed and analyzed by Wilkinson and van Dierendonck (1990) and Wilkinson (1991). These authors conclude that the gas hold-up increases with gas density due to a reduction in bubble size.

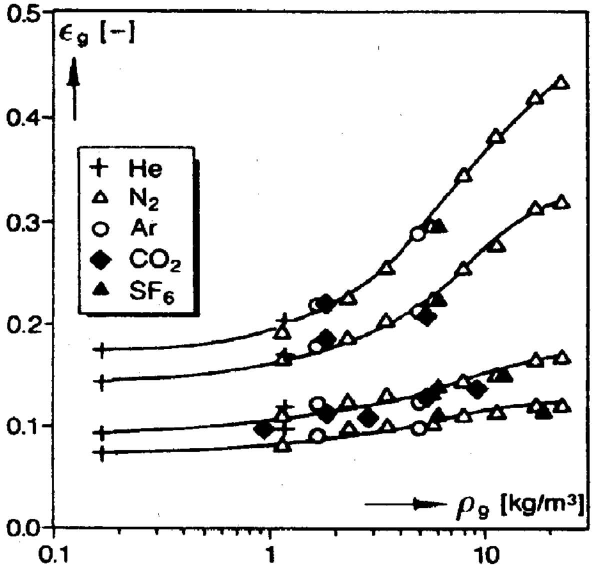

Fig. 2: Gas hold-up in water vs ϱ_G for 4 different gas velocities. From top to bottom: u_G = 12, 8, 4 and 3 cm/s (taken from Wilkinson and van Dierendonck, 1990)

Increase of gas density either by molecular weight or by elevated pressure has the same effect. However, as pointed out by Wilkinson and van Dierendonck (1990), the physical explanation for the decrease in bubble size and the increase of gas hold-up is not clear. Some authors attribute the gas density effect to influence bubble formation at the sparger while others speculate on reduced coalescence of bubbles. Experiments of Wilkinson and van Dierendonck (1990) on gas hold-up in pressurized columns with gases of different molecular weight confirmed the above conclusions and, in addition, an effect of gas density on bubble formation in BCRs could be ruled out. Typical findings are given in Fig. 2. These authors also studied bubble dynamics in a well defined turbulent pipe flow and observed a drastic reduction of the number of large bubbles having high rise velocities (churn-turbulent flow regime). This is shown in Fig. 3 where the bubble swarm velocity is plotted vs. the superficial gas velocity for various pressures. At high pressure no large bubbles are present and the bubble swarm velocity approaches the terminal rise velocities of single bubbles (22 - 25 cm/s) up to relatively high velocities, while at low pressure the number of larger bubble is maximal and so is the bubble swarm velocity.

The large bubbles observed are highly irregular and considerably deformed and their break-up is due to loss of fragments at the rim of the bubbles, the growth of disturbances on the roof of the bubbles (Rayleigh-Taylor instabilities) and large deformations. Kelvin-Helmholz stability analysis is applied to explain qualitatively the observed bubble break-up rates. The experimental results shown in Fig. 2 indicate that gas density has little effect on break-up at low density but is especially significant at higher gas densities. Such behavior is predicted by the theoretical considerations. In summary, the investigations of Wilkinson and van Dierendonck (1990) clearly demonstrate that the influence of pressure and gas molecular mass on bubble size and gas hold-up is due to a decrease in bubble stability with increasing gas density. It is important to point out that the results and interpretations given by Wilkinson and van Dierendonck also explain the high gas hold-up observed in coal liquefaction processes (Tarmy *et al.*, 1984) and Fischer-Tropsch synthesis in slurry phase (Deckwer *et al.*, 1980, 1981). It is understood that the gas density effect as analyzed by Wilkinson and van Dierendonck (1990) is not only of significance for BCRs but also for all other gas-liquid contactors. Indeed, when studying a loop-venturi-reactor, Cramers *et al.* (1992) did not only confirm the gas density effect on the hold-up in the main reactor but also observed an increased gas entrainment by the liquid jet with increasing gas density. Again these finding can reasonably be explained by referring to Kelvin-Helmholz stability analysis.

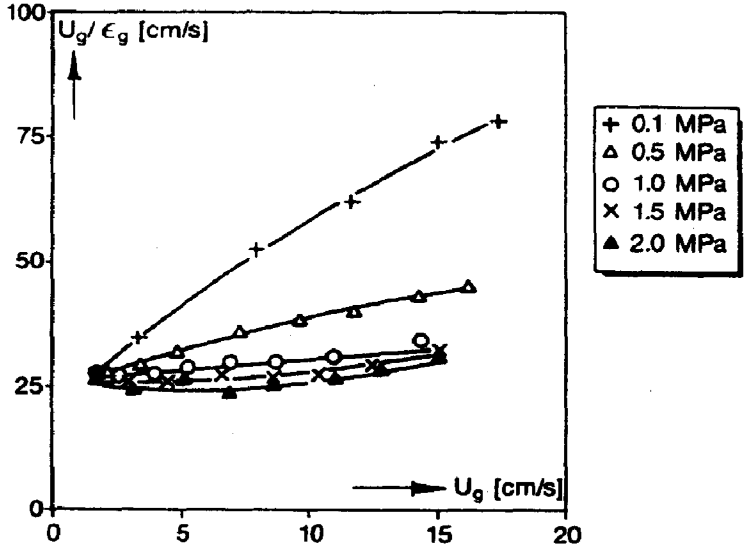

Fig. 3: Bubble swarm velocity vs superficial gas velocity for the system N_2/H_2O as function of pressure (taken from Wilkinson and van Dierendonck, 1990)

On the basis of the results of Wilkinson and van Dierendonck (1991) and additional measurements with the dynamic gas disengagement technique of Vermeer and Krishna (1981), Krishna *et al.* (1991) proposed a model for the gas hold-up in BCRs which incorporates the influence of gas density on flow regime transitions. The major features of the model are

- ε_G depends linearly on gas velocity in the homogenous flow regime

$$\varepsilon_{Ghom} = C\ u_G \tag{3}$$

  The constant C is essentially the reciprocal of the rise velocity of the (small) bubbles in the swarm ($C = 1/u_{sb}$) which has a value of about 0.25 m/s, hence eq. (3) can be written as $\varepsilon_{Ghom} = 4\ u_G$.

- At heterogeneous flow Krishna *et al.* (1991) assume that the small bubble hold-up is constant and corresponds with the end of the homogeneous flow regime (ε_{Gtrans}).

- Increasing the gas velocity beyond the transition velocity (u_{trans}) from homogeneous to heterogeneous flow increases only the large bubble hold-up and the following relation is assumed to apply

$$\varepsilon_{Glb} = A\ (u_G - u_{trans})^n \qquad u_G \geq u_{trans} \tag{4}$$

Hence, the total hold-up at heterogeneous flow follows from

$$\varepsilon_{Ghet} = \varepsilon_{Gtrans} + A\ (u_G - u_{trans})^n \tag{5}$$

with $\varepsilon_{Gtrans} = 4\ u_{trans}$ as limiting case from eq. (3).

With A = 1, n = 0.8 and u_{trans} taken from experiment, Krishna *et al.* (1991) could describe gas hold-up data up to 0.5 with striking agreement.

The proposal of Wilkinson (1991) to predict the gas hold-up basically uses the same assumptions as Krishna *et al.* (1991), i.e.,

$$\varepsilon_G = u_G/u_{sb} \qquad u_G \leq u_{trans} \tag{6}$$

and

$$\varepsilon_G = \frac{u_{trans}}{u_{sb}} + \frac{u_G - u_{trans}}{u_{lb}} \qquad u_G > u_{trans} \tag{7}$$

To estimate the rise velocities of the small and large bubbles in the gas-in-liquid dispersion, Wilkinson (1991) recommends the following relations

$$\frac{u_{sb}\ \mu_L}{\sigma} = 2.25 \left(\frac{\sigma^3\ \rho_L}{g\ \mu_L^4}\right)^{-0.273} \left(\frac{\rho_L}{\rho_G}\right)^{0.03} \tag{8}$$

$$\frac{u_{lb}\ \mu_L}{\sigma} = \frac{u_{sb}\ \mu_L}{\sigma} + 2.4 \left[\frac{\mu_L\ (u_G - u_{trans})}{\sigma}\right]^{0.757} \left(\frac{\sigma^3\ \rho_L}{g\ \mu_L^4}\right)^{-0.077} \left(\frac{\rho_L}{\rho_G}\right)^{0.077} \tag{9}$$

and suggests the following empirical correlation for u_{trans} (in SI units)

$$\frac{u_{trans}}{u_{sb}} = \varepsilon_{Gtrans} = 0.5 \exp\left(-193\ \rho_G^{-0.61}\ \mu_l^{0.5}\ \sigma^{0.11}\right) \tag{10}$$

Eqs. (6) to (10) give an excellent description of the experimental data for gas-liquid systems the physical properties of which cover the subsequent ranges: σ =

0.02 - 0.073 N m^{-1}, μ_L = 0.0004 - 0.055 Pa s, ϱ_L = 683 - 2960 kg m^{-3} and ϱ_G = 0.09 to 38 kg m^{-3}. The average error is only 10 % and experimental gas hold-up data up to 0.5 are successfully described by the correlations.

Of course, the approach of Krishna *et al.* appears reasonable but reality is more complex and indicates that one of the major assumptions of Krishna *et al.* can only be a limiting case. As an example, Fig. 4 shows hold-up data of small and large bubbles as function of the gas velocity for 4 different gas/liquid systems at atmospheric pressure (Grund, 1988). The small bubble hold-up is only approximately constant for the air/methanol system but not for the other systems studied by Grund, in particular, ε_{Gsb} increases considerably for the air/ligroin system. Therefore, the assumption of a constant small bubble hold-up in the heterogenous flow regime cannot be generalized. Obviously, also at heterogeneous flow the small bubble hold-up increases significantly with gas velocity.

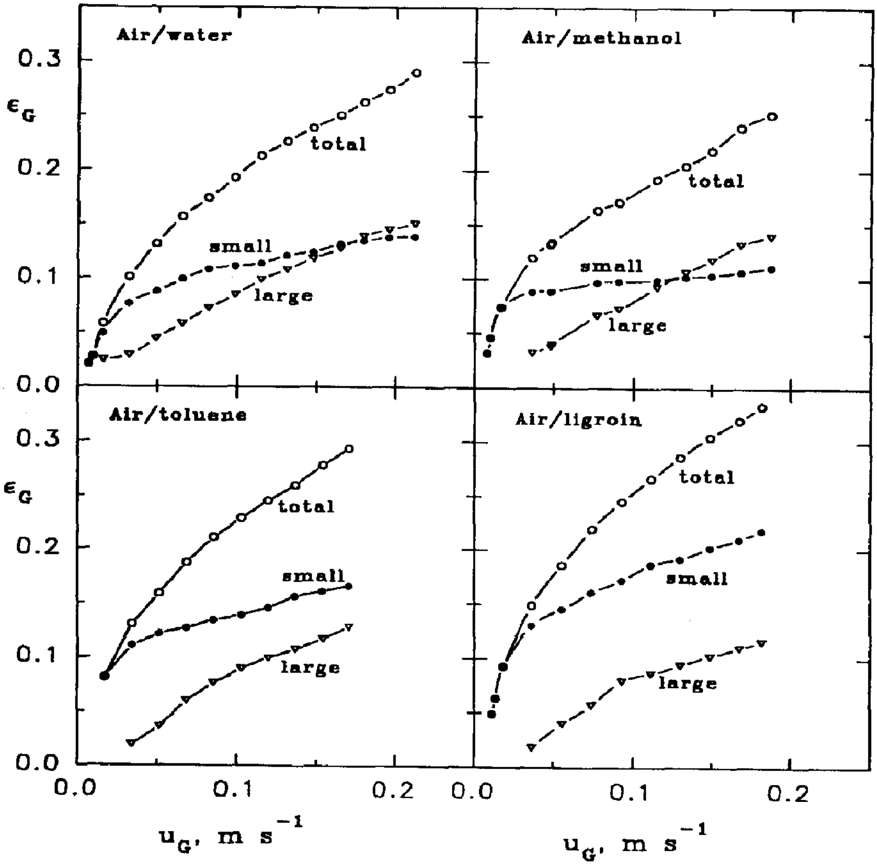

Fig. 4: Hold-up of small and large bubbles and total gas vs. superficial gas velocity for 4 aerated liquids (data taken from Grund, 1988)

In viscous liquids (Newtonian and non-Newtonian) homogeneous (bubbly) flow produced by spargers with small openings is limited to very low gas velocities. The critical value of u_G for the transition to heterogeneous flow decreases with increasing viscosity. As coalescence proceeds, gas slugs (Taylor bubbles) are formed and for BCRs with smaller diameters ($d_R \leq 0.3$ m) slug flow prevails at higher gas velocities and viscosities. Flow charts to order the regimes observed are reported by Schumpe and Patwari (1985) and Haque *et al.* (1986).

Correlations for the gas hold-up in BCRs with highly viscous media were reported by Godbole *et al.* (1982), Schumpe and Deckwer (1982), Haque *et al.* (1986) and Kawase and Moo-Young (1987). On the basis of 200 data points for heterogeneous flow (own and taken from literature) Schumpe and Deckwer (1987) proposed a correlation which uses to same dimensionless groups as suggested by Akita and Yoshida (1973). However, instead of the group $\varepsilon_G/(1-\varepsilon_G)^4$ the gas hold-up itself was correlated directly for simplicity and better data fit.

$$\varepsilon_G = 0.20 \left(\frac{g\ d_R^2\ \rho_L}{\sigma}\right)^{-0.13} \left(\frac{g\ d_R^3\ \rho_L^2}{\mu_{eff}^2}\right)^{0.11} \left(\frac{u_G}{(g\ \ d_R)^{0.5}}\right)^{0.54} \qquad (11)$$

The groups vary in the following ranges

$$1.4 \times 10^3 \leq Bo \leq 1.4 \times 10^5$$
$$1.2 \times 10^7 \leq Ga \leq 6.5 \times 10^{10}$$
$$3.0 \times 10^{-3} \leq Fr \leq 2.2 \times 10^{-1}$$

The effective viscosity μ_{eff} which appears in the Galilei number was calculated from the Ostwald-de Waele relation ("power law") using

$$\dot{\gamma}_{eff} = 2800\ u_G \qquad (12)$$

to estimate the effective shear rate for non-Newtonian liquids in BCRs. Eq. (11) describes the experimental data of the heterogeneous flow regime with an average error of 8.1 %. Suh (1992) measured ε_G in saccharose and xanthan solutions in a 0.15 m diameter bubble column (3 m height). Among the suggested ε_G correlations eq. (11) gave the best fit of Suh's data.

The gas hold-ups of viscous media in the slug flow regime can be estimated by the empirical correlation suggested by Godbole *et al.* (1982)

$$\varepsilon_G = 0.239\ u_G^{0.634}\ d_R^{-0.5} \qquad (13)$$

However, a more fundamental approach outlined by Schumpe and Deckwer (1987) gives an even better description. Combining Dumitrescu's relation for the rise velocity of individual gas slugs $u_B = 0.35\ (g\ d_R)^{0.5}$ with the findings of Nicklin (1962) one obtains

$$u_B = C\ (u_G + u_L) + 0.35\ (g\ d_R)^{0.5} \qquad (14)$$

The gas hold-up is related to u_B by $\varepsilon_G = u_G/u_B$, hence

$$\varepsilon_G = \left(C\ \frac{u_G + u_L}{u_G} + \frac{0.35}{Fr}\right)^{-1} \qquad (15)$$

For viscous media laminar flow prevails and for power law liquids C is given by

$$C = \frac{3\ n + 1}{n + 1} \qquad (16)$$

The theoretically expected value of C applies only at high ratios of h/d_R where h denotes the height the gas hold-up is representative for. Data analysis indicated that in many studies the column height was too low for full development of slug flow. Then bubbles are accelerated in the wake of preceding bubbles and coalesce with them to form larger slugs. With increasing distance from the sparger, u_B decreases and ε_G increases as coalescence proceeds. The account for the effect of slug formation Schumpe and Deckwer (1987) proposed the following empirical correlation which may be useful for scale-up purposes

$$C = \frac{3\,n + 1}{n + 1} + 3.4 \exp\left(-\,0.20\ h/d_R\right) \tag{17}$$

Eqs. (15) and (17) give an excellent description of ε_G in the slug flow regime (mean error 6.2 %). Eq. (12) was also found useful to interpret hold-up data in a bubble column and an airlift (Philip et al., 1990).

In summary, one can conclude that the integral value of the relative gas hold-up in BCRs can be estimated with an average error of about 10 to 20 % for a large variety of gas-liquid systems. In BCRs of sufficient size and height, ε_G is mainly governed by gas velocity and the physical properties of both the liquid and the gas irrespective of the sparger used. Of special significance are the flow regimes. Eq. (10) of Wilkinson (1991) giving the transition gas velocity from homogeneous to heterogeneous flow is very helpful in this regard but probably needs further experimental evidence. In addition, further studies are needed which focus on the internal structure of the gas hold-up (fractions of the bimodal bubble size distributions and their rise velocities). This will enable the design of flow regime charts which present ε_G as function of gas velocity, gas density (pressure) and liquid viscosity to name only the most important influences.

Mass Transfer

As BCRs are predominantly used in the slow reaction-absorption regime and gas side resistances to interphase mass transfer are often negligible, the (liquid side) volumetric mass transfer coefficient k_La is sufficient to describe the gas-liquid mass transfer rates. Owing to the greater difficulty of reliable k_La determinations there are only a few correlations which have been proven to be of broader applicability. Based on their experimental data with various gas-liquid systems (air, O_2, CO_2, He/water, glycol, methanol and mixtures) Akita and Yoshida (1973) proposed the following dimensionless correlation

$$\frac{k_La\ d_R^2}{D_L} = 0.6\left(\frac{\mu_L}{\rho_L\ D_L}\right)^{0.5}\left(\frac{g\ d_R^2\ \rho_L}{\sigma}\right)^{0.62}\left(\frac{g\ d_R^3\ \rho_L^2}{\mu_L}\right)^{0.31}\ \varepsilon_G^{1.1} \tag{18 a}$$

or

$$Sh = 0.6\ Sc^{0.5}\ Bo^{0.62}\ Ga^{0.31}\ \varepsilon_G^{1.1} \tag{18 b}$$

By considering the Akita-Yoshida correlation for ε_G (eq. (1)) and neglecting the dependency on physical properties eq. (15) reduces to

$$k_La \propto d_R^{0.17}\ u_G^{0.7} \tag{19}$$

The dependency of k_La on d_R exists, if at all, only for small diameter reactors, and for $d_R \geq 0.6$ m it is recommended to use $d_R = 0.6$ m. Thus, k_La data for the air-CO_2/water system in large scale bubble columns (1 and 5.5 m diameter) could be successfully described with eq. (18). The k_La dependency on u_G as given by eq. (18) has been observed by many authors (Deckwer, 1985, 1992). Another dimensionless correlation which incorporates gas viscosity (air, O_2, H_2, CO_2, CH_4) has been proposed by Hikita *et al.* (1981)

$$\frac{k_L a\, u_G}{g} = 14.9\, f \left(\frac{u_G\, \mu_L}{\sigma}\right)^{1.76} \left(\frac{\mu_L^4\, g}{\rho_L\, \sigma^3}\right)^{-0.248} \left(\frac{\mu_G}{\mu_L}\right)^{0.243} \left(\frac{\mu_L}{\rho_L\, D}\right)^{-0.604} \qquad (20)$$

in which f = 1 for non-electrolytes (water, butanol, methanol and sugar solutions) and a function of ionic strength in case of electrolyte solutions. The measurements in columns with 0.1 and 0.19 m diameter did not reveal a significant effect of d_R.

Comprehensive $k_L a$ data were determined by Öztürk *et al.* (1987) in organic liquids applying also different gases (CO_2, air, N_2, He, H_2). On the whole, over 400 $k_L a$ values were measured for 50 gas-liquid systems in a 0.095 m diameter column. Eqs. (8) and (20) of Akita and Yoshida and Hikita *et al.*, respectively, described the experimental data with errors of 25 to 37 %. Even if modified by an optimized factor the error exceeded 20 %. This was thought to be unsatisfactory in view of a data reproducibility within 5 %. In addition, the data show a remarkable dependency on gas properties which is shown in Fig. 5 for xylene as liquid phase. The differences in $k_L a$ can not be explained by the viscosity ratio of the phases as suggested by Hikita *et al.* (1981). Therefore, Öztürk *et al.* (1987) developed a new correlation on the basis of a modification of the Akita-Yoshida correlation suggested by Nakanoh and Yoshida (1980). In addition, the surface-to-volume mean bubble diameter d_B rather than the column diameter was used as the characteristic length as the column diameter has little influence on $k_L a$ (Schumpe

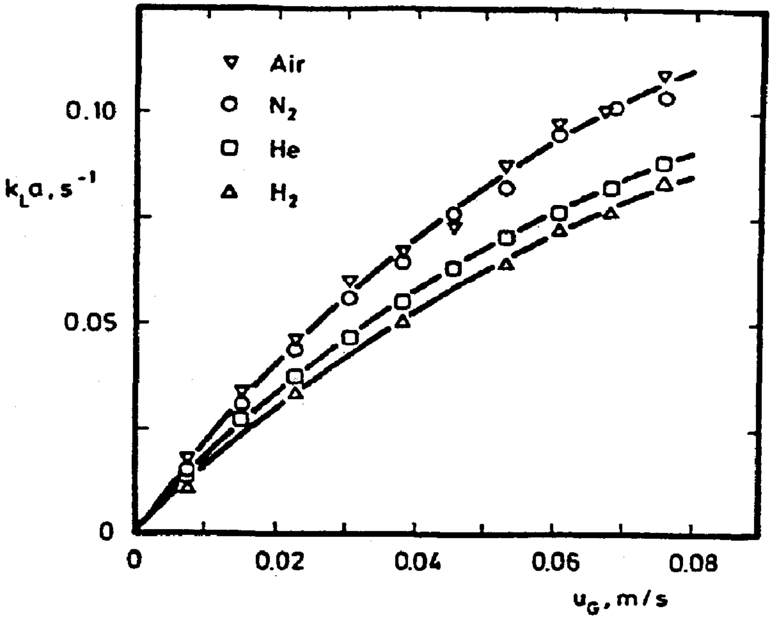

Fig. 5: Influence of gas properties on $k_L a$ for O_2 transfer in xylene (taken from Öztürk *et al.*, 1987).
▽ absorption, ○ □ △ desorption

and Deckwer, 1987). The value of d_B was assumed to be approximately constant (d_B = 0.003 m) as recommended by several investigators (Gestrich and Rähse, 1975; Quicker and Deckwer, 1981). The correlation of Öztürk *et al.* (1987) obtained from non-linear regression is as follows

$$\left(\frac{k_L a\, d_B^2}{D_L}\right) = 0.62 \left(\frac{\mu_L}{\rho_L D_L}\right)^{0.5} \left(\frac{g\, \rho_L\, d_B^2}{\sigma}\right)^{0.33} \left(\frac{g\, \rho_L^2\, d_B^3}{\mu_L^2}\right)^{0.29} \left(\frac{u_G}{\sqrt{g\, d_B}}\right)^{0.68} \left(\frac{\rho_G}{\rho_L}\right)^{0.04} \qquad (21)$$

which involves the following dependencies

$$k_L a \propto D_L^{0.5}\, \rho_L^{0.37}\, \mu_L^{0.08}\, \sigma^{-0.33}\, \rho_G^{0.04}\, u_G^{0.68} \qquad (22)$$

Due to the many gas liquid systems studied, the physical properties were varied considerably. Eq. (21) describes the measured $k_L a$ values with an average error of 13.3 %.

Viscous media of Newtonian and non-Newtonian character are frequently encountered in polymer processing and biotechnology. Considerable efforts have been undertaken to understand the mass transfer properties of such solutions. In this regard, the estimation of effective shear rates and viscosities for power law fluids in BCRs is of particular concern (Nishikawa *et al.*, 1977; Henzler and Kauling, 1985; Schumpe and Deckwer, 1987; Allen and Robinson, 1989). Empirical dimensionless correlations for the volumetric mass transfer coefficient have been proposed by Nakanoh and Yoshida (1980), Schumpe and Deckwer (1987) and Suh *et al.* (1991). A semi-theoretical approach based on Higbie's penetration theory and Kolmogoroff's theory of isotropic turbulence has been developed by Kawase *et al.* (1987). All the previous work has been reviewed by Suh *et al.* (1991). On the basis of their own comprehensive measurements (with sucrose, xanthan and viscoelastic PAA solutions) and numerous literature data Suh *et al.* (1991) suggested the following correlation

$$Sh' = 0.018\, Sc^{0.50}\, Bo^{0.20}\, Ga^{0.62}\, Fr^{0.51}\, (1 + 0.12\, Wi)^{-1} \qquad (23)$$

In eq. (23) Sh′ is formed with the volumetric mass transfer coefficient referred to liquid volume ($k_L a'$). The dimensionless numbers cover the following ranges

$$\begin{array}{rcccl}
6.25 \times 10^{3} & \leq & Sh' & \leq & 2.31 \times 10^{6} \\
1.73 \times 10^{3} & \leq & Sc & \leq & 2.27 \times 10^{5} \\
4.91 \times 10^{2} & \leq & Bo & \leq & 1.40 \times 10^{4} \\
2.05 \times 10^{5} & \leq & Ga & \leq & 1.07 \times 10^{10} \\
0.14 & \leq & Fr & \leq & 0.4 \\
0 & \leq & Wi & \leq & 41.4
\end{array}$$

In the development of eq. (23) the effective viscosities were calculated by the power law (Ostwald-de Waele relation) using a modified form of the proposal of Nishikawa *et al.* (1977) to estimate the effective shear rate in the BCR, i.e., $\dot{\gamma}_{eff} = 2800\, u_G$. The viscoelastic properties were accounted for by introducing the Weissenberg number Wi instead of the Deborah number (Nakanoh and Yoshida, 1980), the latter being difficult to determine reliably. The Weissenberg number is defined as the ratio of the first normal stress difference to the shear stress at a given shear rate: $Wi = N_1/\tau$. The effect of the elastic properties as expressed by Wi on the mass transfer properties is demonstrated in Fig. 6. Here, the ratios of the experimental Sherwood number to the ones calculated from eq. (23) when neglecting the elasticity effect are plotted vs. the Weissenberg number. Surprisingly the effect of Wi is most pronounced at low Wi and then levels off. This sensitivity to even slight elasticity possibly explains the discrepancies observed in previous studies in which fluid elasticity was not considered.

Eq. (23) is restricted to the churn-turbulent and slug flow regimes and describes the experimental data with an average error of 16 %. It involves the subsequent dependencies for inelastic fluids

$$k_L a' \propto D_L^{0.5}\ d_R^{0.005}\ \rho_L^{0.94}\ \sigma^{-0.20}\ \mu_{eff}^{-0.74}\ u_G^{0.51} \tag{24}$$

Hence, $k_L a'$ is almost independent of column diameter. There is also little discrepancy between the exponents of μ_{eff} and u_G in eq. (24) and previous correlations (Deckwer *et al.*, 1982; Schumpe and Deckwer, 1982, 1987).

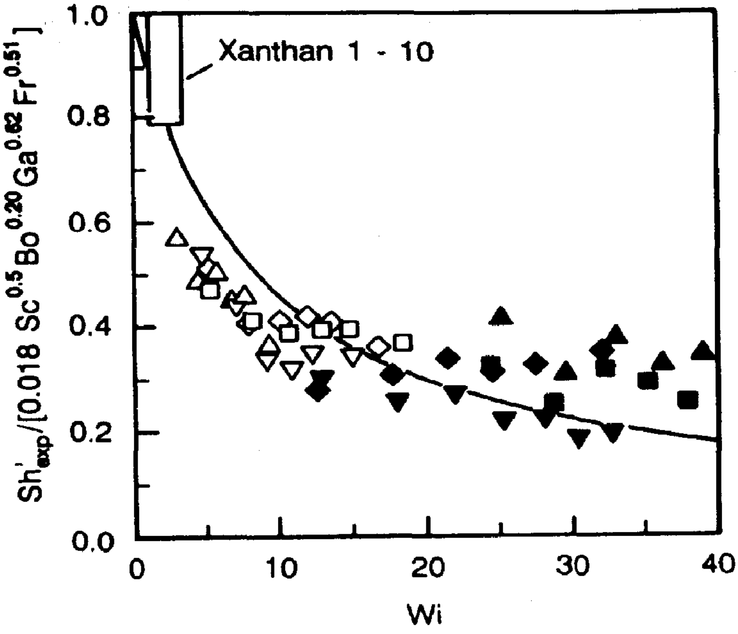

Fig. 6: Influence of Weissenberg number on the volumetric mass transfer coefficient in viscoelastic liquids. Open symbols: mixed solutions of xanthan and PAA, closed symbols: solutions of PAA, ——— eq. (23) (taken from Suh *et al.*, 1991)

In summary, the Akita-Yoshida correlation has been proven to be applicable for scale-up (only shown for air/CO_2/water system). However, this correlation usually provides for a conservative (low) estimate which may lead to considerable overdesign. The correlation of Öztürk *et al.* is based on a large number of gas-liquid system and its use is recommended though the column diameter was small (0.095 m). This correlation also considers the gas density effect but only molecular weight was varied at atmospheric pressure. Further work is needed to investigate the gas density effect on $k_L a$ at elevated pressures. Wilkinson (1991) recommend to account for the gas density by using the following relation

$$\frac{(k_L a)_{P_{G2}}}{(k_L a)_{P_{G1}}} = \left(\frac{(\varepsilon_G)_{P_{G2}}}{(\varepsilon_G)_{P_{G1}}}\right)^n \tag{25}$$

This would allow to calculate $k_L a$ in pressurized BCRs from atmospheric $k_L a$ data and the corresponding gas hold-ups. However, due to the complex hold-up structure n may be dependent on physical properties and flow regime. Therefore, the approach suggested by Wilkinson will be of limited applicability (Grund *et al.*, 1992). k_La data in highly viscous media (Newtonian, non-Newtonian with and without elastic properties) can be estimated from the correlation suggested by Suh *et al.* (1991).

Liquid Mixing

Mixing of the liquid phase in BCRs has attracted many researchers in the past 35 years and apparently continues to be a subject under study (Myers *et al.*, 1987; Clark *et al.*, 1987; Rice and Littlefield, 1987; Anderson and Rice, 1989; Lübbert and Larson, 1990; Rice and Geary, 1990; Rice *et al.*, 1990; Devanathan *et al.*, 1990; Joshi, 1992; Dudukovic *et al.*, 1992; Geary and Rice, 1992; Yang *et al.*, 1992; Schmidt *et al.*, 1992; Ranade, 1992). In spite of the many new hydrodynamic models proposed, it is still common to make use of the axial dispersion model (ADM) to describe liquid phase mixing in BCRs. As an alternative to the ADM, backflow cell models (BFCM) can be applied which deliver an equivalent description provided the proper relations are used to convert backflow ratios into actual dispersion coefficients. Instead of using the axial dispersion coefficient E_L some authors characterize the mixing behavior in bubble columns by mixing times which always have to be referred to a given degree of homogeneity and then can be converted into dispersion coefficients.

The majority of the experimental findings on E_L can be consistently interpreted by a theoretical relation derived by Baird and Rice (1975) on the basis of dimensional analysis and Kolmogoroff's theory of isotropic turbulence

$$E_L = K\, l^{4/3}\, \varepsilon^{1/3} \tag{26}$$

In eq. (26) K is a constant and the specific energy dissipation in a BCR can be written as $\varepsilon = g\, u_G$. l is the approximate diameter of the large vortices. Baird and Rice (1975) assumed that the primary vortices are responsible for liquid mixing and their sizes are considerably larger than the bubble diameter. Then the reactor diameter presents an upper limit of l. Thus, it follows from eq. (26)

$$E_L = K\, d_R^{4/3}\, (g\, u_G)^{1/3} \tag{27}$$

The dependency of E_L on d_R and u_G as expressed by eq. (27) has been confirmed by many studies (Kato and Nishiwaki, 1972; Deckwer *et al.*, 1974). Eq. (27) can be rendered dimensionless

$$\frac{E_L}{d_R\, u_G} = K \left(\frac{g\, d_R}{u_G^2} \right)^{1/3} \tag{28}$$

or

$$Pe = (1/K)\, (Fr^2)^{1/3} \tag{29}$$

with K = 0.35, eq. (29) describes experimental data of various authors and is in close agreement with predictions of empirical correlations (Kato and Nishiwaki, 1972). The influence of the physico-chemical properties of the liquid on the dispersion coefficient has been investigated by several authors, but little effect has been observed.

Mixing of the liquid phase in the BCR has to be attributed to various phenomena such as turbulent vortices, liquid entrainment in the wakes of rising bubbles, liquid circulation, radial exchange flows etc. All these phenomena are obviously interrelated and are primarily dependent on the gas hold-up structure, i.e., local hold-up variations, bubble size and rise velocity distributions. It is understood that lumping of the various phenomena, which differently contribute to mixing into a dispersion coefficient (E_L) is a rough simplification of the reality and hydrodynamic models which account for radial liquid velocity and hold-up profiles are more appropriate. However, at least some of the hydrodynamic models proposed can be reduced to the dispersion model and relations for E_L are derived which are in striking agreement with eq. (27), i.e., $E_L \propto d_R^{4/3} u_G^{1/3}$ (Joshi and Sharma, 1979; Joshi, 1980; Riquarts, 1981; Zehner, 1986).

In contrast to the many investigations carried out on liquid phase mixing, its effect on BCR performance is only minor and seemingly often overestimated. In many practical applications (air oxidations, hydrogenations) and reaction engineering estimates, the assumption of a backmixed liquid phase is justified. Indeed, when using bubble columns as absorbers and reactors, the available space-time-yields are little affected by variation of liquid phase dispersion or circulation. Also, when evaluating mass transfer coefficients, k_La for measured steady state liquid phase concentration profiles, k_La shows little sensitivity to considerable variations of E_L (Deckwer *et al.*, 1983). In the fast reaction absorption regime reactor performance is not influenced at all by liquid mixing as the reaction takes place only at the gas-liquid interface. In the slow reaction-absorption regime assuming a gas phase component (A) reacting in the liquid phase with a liquid reactant B complete backmixing can usually be assumed for component B. This assumption is justified as the reaction time is usually much higher than the effective mixing time. However, whether or not a backmixed liquid phase can be assumed for the dissolved gaseous reactant A depends on various factors. In this case, the dimensionless group

$$\Phi = \frac{\text{mixing time}}{\text{mass transfer time}} = f\,\frac{L^2/\varepsilon_L E_L}{1/K_L a} \qquad (30)$$

has a significant effect on the profile of A in the liquid phase. Setting f = 1, Φ is the product of the Bodenstein ($u_L L/\varepsilon_L E_L$) and Stanton ($k_L aL/u_L$) numbers and can be interpreted as the ratio of the characteristic times for mixing ($\tau_M = L^2/\varepsilon_L E_L$) and mass transfer ($\tau_{MT} = 1/K_L a$). As both refer to different final states (τ_M corresponds with 99.9 % mixing while τ_{MT} with 63 % liquid phase saturation) it is recommended to introduce the factor f in eq. (30) which can be estimated to be about 0.2. Values of Φ for reactions typically carried out in BCRs are given in Table 1 for two reactor sizes (Deckwer, 1986). For the majority of reactions $\Phi \gg 1$, hence, mass transfer is fast compared with mixing and pronounced A profiles are established in the liquid phase. Hence, the ADM or equivalent models must be applied. In tall reactors with high mass transfer rates it may be justified to assume a unmixed liquid phase (giving maximum gradients). On the other hand, unusually high gas and liquid side mass transfer resistances have been observed in the chlorination of aromatic compounds (Lohse *et al.*, 1983). Hence, mass transfer times are high giving low values of Φ which justify a backmixed liquid phase for the A reactant, even in tall BCRs. However, it has to be pointed out that the effect of liquid phase mixing on the A profile is not only governed by the Φ criterion, eq. (30). In addition, the profile of A in the gas phase and, hence, conversion largely effects the liquid phase profile of A. Clarity and conclusive results can be obtained by simulations on basis of the ADM applied to both phases. Summaries on the effective application of the ADM for various gas-liquid and gas-liquid-solid systems have been given by Deckwer (1985, 1986, 1992).

Table 1: Typical values of Φ (ratio of mixing to mass transfer time)

Reaction	d_R / L of BCR in m	
	0.2/2	1/10
Isobutene hydration form C_4 cuts	3.6	9.4
Fischer-Tropsch synthesis in slurry phase	10.6	28.2
Chlorination of toluene	0.04	0.1

Gas mixing

BCRs are often modeled with neglect of gas phase mixing. This is only permitted for tall bench-scale reactors where the Bodenstein numbers ($Bo_G = u_G L/\varepsilon_G E_G$) with E_G calculated from the available correlations are high, say $Bo_G \geq 10$. For large diameter columns the plug flow assumption is no more justified. Mixing of the gas phase of BCRs is considerable and has to be attributed to different bubble rise velocities, bubble coalescence and break up and circulation of bubbles. Again, all the various phenomena are lumped into the gas phase axial dispersion coefficient E_G and the ADM is used to describe globally gas phase mixing. In contrast to the liquid phase, gas phase dispersion largely effects BCR performance. In case of the fast reaction-absorption regime (and the diffusional regime) the influence of gas phase dispersion on conversion corresponds with single phase reactors (Levenspiel, 1972). In spite of its importance, comparatively little work has been reported on gas phase dispersion. One reason may be that gas phase dispersion coefficients are relatively difficult to determine.

Shah *et al.* (1982) recommended the correlation suggested by Mangartz and Pilhofer (1980, 1981) to estimate the gas phase dispersion coefficient

$$E_G = 50\ d_R^{3/2}\ (u_G/\varepsilon_G)^3 \tag{31}$$

Field and Davidson (1980) studied gas phase dispersion in a 3.2 m diameter bubble column. These authors proposed an empirical correlation similar to eq. (31) and, thus, apparently confirmed the concept of using the bubble swarm velocity (u_G/ε_G) as a correlating factor. However, as $\varepsilon_G \propto u_G^n$ and n often being in the range of 0.5 to 0.75, eq. (31) can be reduced to ($n = 2/3$)

$$E_G \propto d_R^{3/2}\ u_G \tag{32}$$

Such a relation has been derived theoretically by Wachi and Nojima (1990) on the basis of the recirculation theory of Ueyama and Miyauchi (1979) and Miyauchi *et al.* (1981). From own measurement in 0.2 and 0.5 m diameter bubble columns with the air/water system and literature data, Wachi and Nojima proposed

$$E_G = 20\ d_R^{3/2}\ u_G \tag{33}$$

A plot of the experimental data according to eq. (33) is shown in Fig. 7 and clearly demonstrates the general dilemma encountered with gas phase dispersion data. Not only the data of different authors vary by nearly one order of magnitude, but even data of the same authors using the same measuring technique are subjected to large scatter (more than factor 5). Also Grund (1988) measured E_G data in a 15 cm diameter column with organic liquids and found large scatter. The range of data reported by Grund are indicated in Fig. 5 by the vertical line.

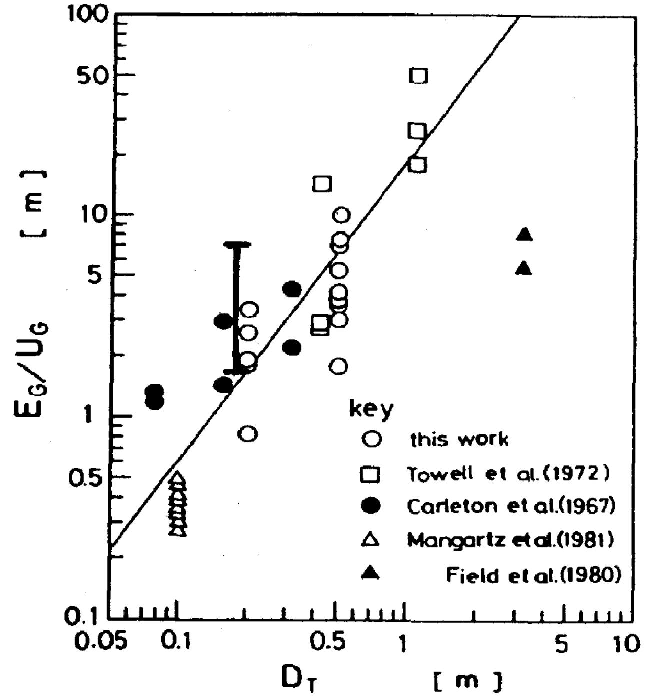

Fig. 7: E_G/u_G vs column diameter (taken from Wachi and Nojima, 1990). Solid line shows eq. (33), vertical solid line presents data field reported by Grund (1988) for aerated organic liquids.

In view of the results shown in Fig 6 it is understood that the present status of E_G data description is not satisfactory. Obviously, correlations such as eq. (31) and (33) are too simple and do not account for additional major influences. This is certainly a consequence of applying the ADM which might be applicable at homogeneous bubbly flow but is insufficient in the heterogeneous flow regime. Consideration of an averaged bubble swarm velocity (eq. (31)) does not resemble reality as in the heterogeneous flow two distinct bubble classes are observed (Fig. 4). Hence, two-bubble-class models (Joseph and Shah, 1984; Shah *et al.*, 1985) are recommended. However, such models are expected to be successful only if they additionally implement appropriately the dynamics of bubble coalescence and break up. Few information is available in this area (Shah and Deckwer, 1983). Studies which support the development of structured hydrodynamic models of the gas phase in the BCRs are urgently needed. The recent work of Prince and Blanch (1990) could be a starting point in this regard.

MODELS FOR BCR

In the industries, the BCRs are often scaled up by empirical rules and guidelines ("know-how"). As to models, non-gradient (liquid phase) and maximum gradient (gas phase) approaches are helpful and, in addition, the hydrodynamically lumped ADM can be used. Scale-up on the basis of such simplified model has been reported as feasible and successful in many cases but is unsatisfactory from the scientific view and may lead to uncertainties and failures. The early hydrodynamic models have been reviewed by Shah and Deckwer (1983) and Deckwer (1985, 1992). Fan (1989) particularly emphasizes on the special effects caused by the presence of particles. It is out of the scope of this contribution to review and evaluate such models suggested more recently. Some references are given when dealing with liquid phase mixing as the majority of the hydrodynamic models focuses on radial liquid velocity and hold-up profiles. Only the approach given by Torvik and Svendsen (1990) incorporates mass transfer and chemical reaction among other phenomena. The model suggested by these authors is based on first principles starting with the two-dimensional equations for conservation of mass, momentum and energy in the three phases (gas-liquid-solid). Computer simulations show reasonable agreement with the predictions of the ADM for the slurry phase methanol synthesis (Öztürk *et al.*, 1988). However, significant differences are found for the overall conversion when enlarging column diameter from 1 to 3 m. Torvik and Svendsen (1990) explain this typical scale-up effect by assuming that the liquid phase mixing has been overestimated with the ADM, however, other arguments may apply as well.

Owing to its general and fundamental approach the Torvik-Svendsen model needs to be persued furthermore. In particular, experimental studies under reactive conditions are required. Such investigations should emphasize on measuring the two-dimensional profiles of the reactants in both phases. This will largely contribute to discriminate among the applicability of seemingly rival models. For solving the scale-up problems encountered in today's industry the hydrodynamic models are helpful but to predict reactor performance on their basis is yet too sophisticated and time consuming. In addition, one should keep in mind that BCR conversions and productivities are usually more sensitive to uncertainties of the scale independent parameter (such as solubilities, kinetic data etc.) than to variations of hydrodynamic parameters.

NOTATION

a	specific interfacial area (referred to volume of gas-liquid dispersion)
a'	specific interfacial area (referred to liquid volume)
Bo	Bond number, $g\, d_R\, \varrho_L / \sigma$
d_B	bubble diameter
d_R	reactor diameter
D	diffusivity
E	axial dispersion coefficient
Fr	Froude number, $u_G/(g\, d_R)^{0.5}$
g	gravitational constant
Ga	Galilei number, $g\, d_R^2\, \rho_L^2 / \mu_{eff}^2$
h	height
k_La, $k_L'a$	volumetric (liquid side) mass transfer coefficient
K_La	overall volumetric mass transfer coefficient
Sc	Schmidt number, $\mu/(\varrho D)$
Sh (Sh')	Sherwood number $k_La\ (k_La')\ d_R^2/D_L$
u	superficial velocity
u_B	rise velocity of bubble slugs
$\dot{\gamma}_{eff}$	effective shear rate
ε_G	relative gas hold-up
μ	dynamic viscosity
ϱ	density
σ	surface tension

Indices

eff	effective
G	gas phase
het	heterogeneous flow regime
hom	homogeneous flow regime
lb	large bubbles
L	Liquid phase
sb	small bubbles
trans	transition (from homogeneous to heterogeneous flow)

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