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Multiphase reactors – revisited

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Abstract

Multiphase reactors are found in diverse applications such as in manufacture of petroleum-based fuels and products, in production of commodity and specialty chemicals, pharmaceuticals, herbicides and pesticides, in refining of ores, in production of polymers and other materials, and in pollution abatement. In all such applications, the knowledge of fluid dynamic and transport parameters is necessary for development of appropriate reactor models and scale-up rules. The state of the art of our understanding of the phenomena occurring in three-phase reactors such as packed beds with two-phase flow, slurry bubble columns and ebullated beds is summarized in this review.

Keywords: Trickle bed; Ebullated bed; Bubble column; Fluid dynamics

1. Introduction

Processes based upon multiphase reactions occur in a broad range of application areas and form the basis for manufacture of a large variety of intermediate and consumer end-products. Some examples of multiphase reactor technology uses include: (1) the upgrading and conversion of petroleum feed stocks and intermediates; (2) the conversion of coal-derived chemicals or synthesis gas into fuels, hydrocarbons, and oxygenates; (3) the manufacture of bulk commodity chemicals that serve as monomers and other basic building blocks for higher chemicals and polymers; (4) the manufacture of pharmaceuticals or chemicals that are used in fine and specialty chemical markets as drugs or pharmaceuticals; and (5) the conversion of undesired chemical or petroleum processing by-products into environmentally acceptable or recyclable products. An overview of the chemistry and process technology of these various application areas is provided in the monograph of Weissermel and Arpe (1993). The importance and contribution of the products generated by the mutliphase reactor technology to the national economy of the United States is illustrated by the pie chart of Fig. 1. Due to lack of space, we are unable to discuss here the various emerging chemistries that demand multiphase reactor technology and will present such a discussion elsewhere. Instead, we focus here on three-phase multiphase reactors and attempt to describe our current understanding of them. This is becoming increasingly important for rapid commercialization of new technologies.

The new paradigm of simultaneous catalyst and reactor development for new processes is becoming prevalent in modern chemical engineering (Villermaux, 1993; Lerou and Ng, 1996). To use this parallel approach, in addition to the firm grasp of chemistry and catalysis, one needs to have a good knowledge of what various reactor types can and cannot do. Krishna and Sie (1994) advocated a simple but effective approach to multiphase reactor selection which examines the particle scale phenomena, phase contacting pattern and flow, and the mixing pattern expected in a particular reactor from the point of view of their effect on the chemical pathways and energy requirements of the process under consideration. Such analysis can then guide the development of the catalyst with desirable properties and of the right size and shape to fit into the best reactor type. However, if

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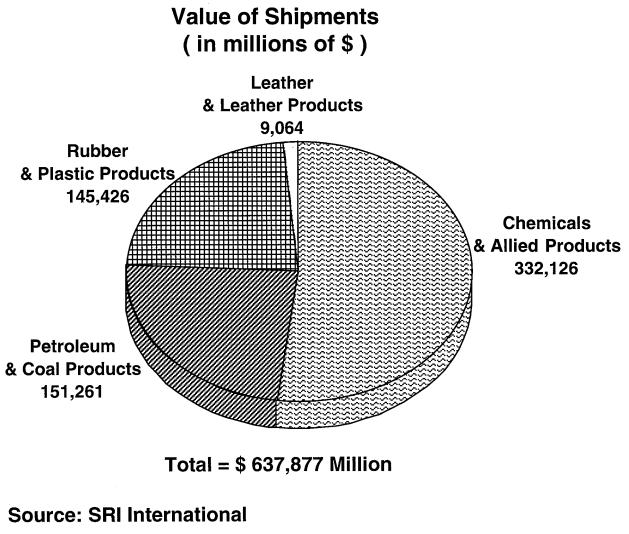

Fig. 1. Value generated by multiphase reactor technology.

one is to attempt scale-up from laboratory scale to industrial scale, as the current economic climate increasingly demands, then one must assure either that the scale-up will be forgiving or one must have a profound and detailed understanding of the multiphase reactor that is being considered for scale-up. Hence, improved understanding of the fluid dynamics and transport processes in frequently used multiphase reactors is more important than ever for accomplishing large scale-up factors with confidence. Lack of thorough understanding of the phenomena occurring in multiphase reactors can lead to disasters in scale-up or design. The price paid for such failures can ultimately be quite costly as the plant has to be used as a pilot or lab in seeking a way to improved performance.

The need to quantify the performance of multiphase reactors leads to their modeling. A typical model of a multiphase reactor rests on the solution of the generic conservation equation (1) applied to species mass and energy of the system:

$$\begin{pmatrix}\text{rate of}\\ \text{output}\\ \text{by phase } i\end{pmatrix}-\begin{pmatrix}\text{rate of}\\ \text{input}\\ \text{by phase } i\end{pmatrix}-\begin{pmatrix}\text{net rate of}\\ \text{interphase transport}\\ \text{into phase } i\end{pmatrix}=\begin{pmatrix}\text{rate of}\\ \text{generation}\\ \text{in phase } i\end{pmatrix}-\begin{pmatrix}\text{rate of}\\ \text{accumulation}\\ \text{in phase } i\end{pmatrix}. \quad (1)$$

The sophistication of our reactor model depends at which level we treat the molecular, single eddy or catalyst particle, and reactor scale, as indicated in Table 1. Naturally, the more sophisticated the model the more expensive it is to develop and run. With that in mind, one simple rule should be followed. The level of sophistication used in modeling the reactor flow pattern and mixing should be commensurate with the level of modeling used to understand the kinetics, i.e. species generation rate. Whenever that is not the case, the modeling effort yields less than maximum benefits.

In addition to computation of molecular level events, which have become increasingly popular, the recent rapid advances in available software for computational fluid dynamics (e.g. CFDLIB, FLUENT, PHOENICS, FLOW 3D, FIDAP, etc.) make it possible to simulate the gross flow patterns in large reactors. However, for multiphase flows experimental verification, at least via cold flow models, is still needed due to the uncertainty of the closure forms used in the description of phase interaction terms. A review of the role of CFD in chemical reaction engineering appeared recently (Kuipers and Van Swaaij, 1997). It is clear from this review that two types of efforts are encountered: (a) global system models, which typically provide the overall features of flow in large reactors and are sometimes tied with various degrees of empiricism to transport and kinetics to describe reactor performance, and (b) detailed models that describe the phenomena on various scales from first principles. This second type of model cannot yet be implemented on multiphase reactor systems. In absence of detailed models for most multiphase reactor types and chemistries conducted in them, lower level models provide valuable tools in process development but still need experimental verification.

This brings us to the perennial problem in multiphase reactors which is that of scale-up, i.e., how to achieve the desired results in a large scale reactor based on observations made on the laboratory unit. All reaction engineers know that success of scale-up rests on our ability to understand and quantify the transport-kinetic interactions on a particle scale (or single eddy scale), interphase transport on particle and reactor scales, flow pattern of each phase and phase contacting pattern and their changes with the changes in reactor scale and operating conditions. It is with the goal of providing such improved understanding of multiphase reactors that research on fluid dynamics and transport in multiphase systems continues to be performed at an increased rate. We now consider how much progress has been made in the understanding of three-phase reactors.

The importance of this topic is evident in the fact that three international conferences were held on

Table 1
Levels of multiphase reactor modeling

Modern reaction engineering requires handling phenomena over a multitude of scales:			
Molecular scale (kinetics)			
Eddy or particle scale (local transport phenomena)			
Reactor scale (flow patterns, contacting and flow regime)			
Possible level of description			
Molecular scale (*rate forms*)			
Strictly empirical	Mechanism based	Fundamental elementary	
Eddy or particle scale transport			
Empirical	Micromixing models	DNS CFD	
Empirical part of rate equation	Thiele modulus	Rigorous	
Reactor scale			
Ideal reactors	Empirical models	Phenomenological models	CFD models
PFR, CSTR	Axial dispersion		

Gas-Liquid-Solid Reactor Engineering; the first one in October of 1992 in Columbus, OH (Chem. Engng Sci. 47 (13/14) 1992), the second in Cambridge, England, in March, 1995 (Trans. IChemE. 73, 1995) and the third one in Osaka, Japan, in December, 1997 (Chem. Engng. Sci. 52, (21/22) 1997). There were also two highly interdisciplinary international symposia on Catalysis in Multiphase Reactors (I, Lyon, France, 7–9 December, 1994; II, Toulouse, France, 16–18 March, 1998) the proceedings of which appeared in the Journal of Applied Catalysis. Therefore, for additional information, and regarding multiphase reaction engineering topics that we do not manage to cover here, the reader is referred to the proceedings of ISCRE 13 and 14 published in Chemical Engng Sci. 49 (24A/B) and Vol 51(1/11), respectively, to ISCRE 15 and to the publications that resulted from the above-cited conferences.

2. Fixed beds with two-phase flow

Packed-bed reactors processing gas and liquid reactants can operate in downward cocurrent two-phase flow (trickle-bed reactors – TBR), in upward cocurrent flow (packed-bubble columns – PBC) and in countercurrent flow. The three modes of operation are illustrated in Figure 2 and the processes recently investigated in these reactor types are listed in Table 2. The importance of packed beds with two-phase flow to the petroleum, petrochemical, chemical and other industries attracted numerous review papers. Among the more recent ones are the contributions by Zhukova et al. (1990), Gianetto and Specchia (1992), Martinez et al. (1994), Saroha and Nigam (1996) and Al-Dahhan et al. (1997). Here we mention only the newest results and findings that have been implemented in practice.

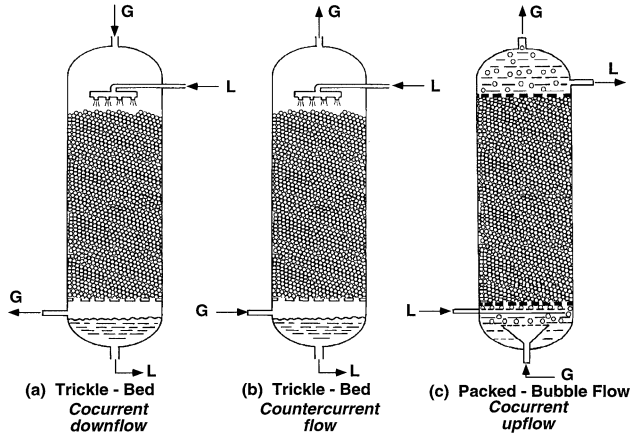

Fig. 2. Packed bed reactors for gas-liquid-solid catalyzed systems (from Mills and Chaudhari, 1997). (a) Trickle-bed with cocurrent downflow. (b) Trickle-bed with countercurrent flow. (c) Packed bed bubble flow reactor with cocurrent upflow.

2.1. Fluid dynamics

An extensive review of hydrodynamic and transport parameters for two-phase flow systems in packed beds appeared recently (Al-Dahhan et al., 1997) and there is no point in repeating here the numerous tables and references that were provided in that review. We attempt here to summarize the key findings that ought to be of importance to the research and plant engineer.

2.1.1. Flow regimes

It is well known that trickle beds can and do operate in the variety of flow regimes ranging from spray flow (liquid drops and continuous gas flow), trickle flow (continuous gas phase and one directional liquid rivulets and some discontinuous liquid films), pulse flow (intermittent passage of gas- and liquid-rich zones through the reactor) and downward bubble flow (continuous liquid and dispersed gas flow). Similarly, cocurrent upflow packed bubble columns can experience the so-called homogeneous and heterogeneous bubble flow, while the onset of flooding is of great importance in countercurrent flow operation. While the existence of the various flow regimes has been proven and many criteria have been proposed to delineate the regime boundaries (see Al-Dahhan et al., 1997) none of them is yet entirely successful in accomplishing such a task (Wild et al. (1991). Attempts have been made by Larachi et al. (1993) for high-pressure operations and Burghardt and Bartelmus

Table 2
Some recent applications of three-phase reactions carried out in TBR/PBC

Residuum and vacuum residuum desulfurization for the production of low-sulfur fuel oils (Meyers, 1996)
Hydrodesulfurization of atmospheric gas oil (Chen and Tsai, 1997)
Catalytic dewaxing of lubestock cuts to produce fuel or lube products for extremely cold conditions (Meyers, 1996)
Sweetening of diesel, kerosene, jet fuels, heating oils (Meyers, 1996)
Hydrodemetallization of residues (Trambouze, 1993; Euzen et al., 1993; Chen and Hsu, 1997)
Hydrocracking for production of high-quality middle-distillate fuels (Meyers, 1996; Landau et al., 1998)
Hydrodenitrification (Meyers, 1996)
Isocracking for the production of isoparaffin-rich naphtha (Meyers, 1996)
Production of lubricating oils (Meyers, 1996)
Selective synthesis of wax from syngas (Fan et al., 1997)
Selective hydrogenation of 1,5,9-cyclododecatriene (Stüber et al., 1996), hydrogenation of C_4-olefins (Vergel et al., 1995), naphthalene (Huang and Kang, 1995), 3-hydroxypropanal (Valerius et al., 1996), acetophenone (Bergault et al., 1997), maleic anhydride (Herrmann and Emig, 1997), α-nitromethyl-2-furanmethanol (Khadilkar et al., 1998c), 2,4-dinitrotoluene (Rajashekharam et al., 1998), Dicyclopentadiene (Chou et al., 1997), glucose (Tukac, 1997), nitrotoluene (Westerterp et al., 1997), α-methylstyrene (McManus et al., 1993; Lange et al., 1994; Castellari and Haure, 1995; Frank, 1996)
Synthesis of butynediol from acetylene and aqueous formaldehyde (Gianetto and Specchia, 1992)
VOC bio-scrubbers (Dicks and Ottengraf, 1991; Alonso et al., 1997; Rihn, et al., 1997; Laurenzis et al., 1998; Wübker et al., 1998; Stoffels et al., 1998), VOC chemical abatement in air pollution control (Cheng and Chuang, 1992)
Hydration of propene (Westerterp and Wammes, 1992), 2-methyl-2-butene (Goto et al., 1993)
Wet air oxidation of waste water and model pollutant effluents: phenol (Fortuny et al., 1995; Pintar et al., 1997; Alejandre et al., 1998), substituted phenols (Tukac and Hanika, 1997, 1998), n-propanol (Mazzarino et al., 1994)
Oxidation of SO_2 (Haure et al., 1990b; Kiared and Zoulalian, 1992; Ravindra et al., 1997); Oxidation of glucose (Tahraoui et al., 1992), poly(α-olefin) lubricant (Koh and Butt, 1995).

(1996) and Burghardt et al. (1996) for organic systems. A priori prediction of foaming also remains elusive.

A number of useful observations were summarized by Al-Dahhan et al. (1997): the trickle-to-pulsing transition is a function of gas density so that high pressure operation with light gases like hydrogen can be simulated via heavier gases like nitrogen at a much lower pressure; higher gas density broadens the trickle flow regime while higher liquid denisty makes it narrower; hydrophobic packing broadens the trickle flow regime (Horowitz et al., 1997), while non-Newtonian fluids cause the transition to pulsing at lower velocities (Iliuta and Thyrion, 1997).

Novel experimental techniques are allowing us to collect more precise flow regime data in trickle beds. Noteworthy are the micro electrode sensors used to detect wall shear and to elucidate the local flow regime (Rode et al., 1994, 1995; Latifi et al., 1992a, b). Smooth signals were characteristic of trickle flow, whereas high-frequency, high-amplitude fluctuations were observed in dispersed bubble flow and in liquid slugs during pulse flow. Based on these measurements the conclusion is reached that pulsing flow represents a hybrid of trickle flow and dispersed bubble flow.

2.1.2. Pressure drop and liquid holdup

Recent correlations and semi-theoretical models for prediction of two-phase pressure drop and liquid holdup at high-pressure operation have also been recently summarized by Al-Dahhan et al. (1997). No method emerges as clearly superior to others but those based on semi-theoretical and phenomenological models seem more reliable than strictly empirical correlations. The effect of elevated pressure mainly manifests itself via increased gas density. Hence, high-pressure operation can be successfully simulated with gases of higher molecular weight at lower pressures. The following qualitative observations emerge. At a given density, the two-phase pressure drop increases with gas and liquid mass fluxes, superficial velocities and liquid viscosity. Liquid holdup increases with liquid mass flux and superficial velocity, and liquid viscosity, but decreases with increasingly gas mass flux or superficial velocity. Hydrodynamic hysteresis may occur at high pressure when the liquid is contaminated with impurities, e.g. an antifoam agent. However, for common single-component liquids or liquid mixtures consisting of similar components, hysteresis is not detected at high pressure. For very low gas velocities ($U_G < 1$–2 cm/s) liquid holdup is pressure insensitive and equals the value determined at atmospheric pressure. At given superficial velocities as gas density is increased, pressure drop increases and liquid holdup decreases. When the pressures of gases of different molecular weights are set to have equal densities, identical pressure drops occur for the same fluid throughputs (see Fig. 5c in Al-Dahhan et al.,1997). Liquid holdup in PBC in bubble flow is greater than in TBR in trickle flow, whereas in pulse flow, they tend to be quite close in values. For design purposes, PBC and TBR can be treated as hydrodynamically similar in the pulse flow regime (Yang et al., 1992a).

Recently, more detailed information about liquid holdup and the nature of liquid flow in trickle beds has become available due to the increased use of non-invasive

sophisticated measurement techniques. For example, Reinecke and Mewes (1996, 1997), Reinecke et al. (1998) and Schmitz et al. (1997) used capacitance tomography imaging to capture the transient pattern of liquid flow in a trickle bed. Toye et al. (1994, 1996, 1997) utilized X-ray transmission tomography to capture two-phase flow distribution in trickle beds. It is expected that in the near future additional studies of this type will provide sufficient information on two-phase flow structure in trickle beds to allow for verification of more detailed models of flow. Non-invasive measurement techniques that can be utilized in multiphase flows have recently been summarized both in a book edited by Chaouki et al. (1997a) and in an extensive review article (Chaouki et al., 1997b).

2.1.3. Gas–liquid interfacial areas and interphase mass transfer coefficients

Correlations and models for predicting gas–liquid interfacial areas and volumetric gas–liquid and liquid–solid mass transfer coefficients in PBC/TBR were also summarized by Al-Dahhan et al. (1997). The scarcity of gas-side volumetric mass transfer coefficients is noteworthy; and to the best of our knowledge no experimental data on $k_G a$ are available for high-pressure operation. Gas–liquid and liquid–solid mass transfer involving non-Newtonian liquids is also sparcely addressed in the literature (Iliuta et al., 1997a; Iliuta and Thyrion, 1997b). Considering the large number of biochemical processes that utilize PBCs and TBRs, this gap in knowledge needs to be filled. The overwhelming majority of gas–liquid mass transfer parameters in TBR/PBC are derived based on the so-called chemical methods. A significant step forward was achieved when these methods were adapted to measure mass transfer in pressurized vessels (Oyevaar et al., 1990). Soda or potash carbonation, sulfite oxidation and amine carbonation are known to be coalescence inhibiting systems which may cause problems in assessing mass transfer parameters in the high interaction regimes. There is a need to implement new gas–liquid chemical methods using coalescing systems, such as hydrazine oxidation (Lara-Marquez et al., 1994) to study gas-liquid mass transfer in TBRs and PBCs. From the experimentally determined gas–liquid interfacial areas and liquid-side volumetric mass transfer coefficients at elevated pressure (Lara-Marquez et al., 1992; Wild et al., 1992; Stüber et al., 1996; Molga and Westerterp, 1997a,b; Larachi et al., 1997a; Larachi et al., 1998a), the following qualitative observations can be made: at a given gas density, gas–liquid interfacial areas and volumetric liquid-side mass transfer coefficients increase as liquid and gas mass fluxes or superficial velocities increase; both mass transfer parameters improve in TBR/PBC as gas density increases for given gas and liquid superficial velocities.

2.1.4. Catalyst wetting

During the past couple of decades it has been established that incomplete catalyst utilization may occur, especially in the trickle flow regime, and that it has two main causes. One is reactor scale liquid maldistribution that may leave certain portions of the bed poorly irrigated. Proper design of liquid distributors, operation with packing that assures needed minimal pressure drop, and redistribution of the liquid in quench boxes and other devices can take care of this problem. Large-scale CFD computations are helpful in establishing the effect of the bed voidage variation and of the presence of internals on gross liquid distribution. The other cause of incomplete catalyst utilization is particle scale incomplete external wetting. This results from the fact that at sufficiently low liquid mass velocity the liquid flow available is insufficient to cover all the catalyst particles with a continuous liquid film at all times. In a time-averaged sense the external surface of the particle is then only partially covered by the flowing liquid. Correlations and models developed for liquid–solid contacting efficiency (defined as the fraction of the external catalyst area covered by the flowing liquid film) have been summarized and discussed by Al-Dahhan et al. (1997). The ability of the Al-Dahhan and Dudukovic's (1995) correlation, which is the extension of the work done by El-Hisnawi (1981) to high pressure, to properly predict catalyst wetting and, hence, catalyst effectiveness and reactor performance has been documented by a number of studies performed by different investigators (Beaudry et al., 1987; Wu et al., 1996a; Khadilkar et al., 1996; Llano et al., 1997). At fixed liquid mass flux, and at high gas velocities, contacting efficiency improves noticeably with the increase in pressure. Increased pressure drop and liquid mass velocity lead to increased contacting efficiency also. Hence, both liquid and gas velocity increase the contacting efficiency at high pressures.

In scale-up and scale-down of TBRs it is highly desirable to run laboratory reactors at the well defined state of catalyst wetting (often complete wetting) while matching the LHSV of the large units. Close to complete external catalyst wetting can be achieved in upflow reactors, at the expense of much larger liquid holdup than in the commercial scale TBR. This may be undesirable if side reactions occur in the liquid phase or if gas–liquid mass transfer rate is impaired by larger liquid film resistance in the small unit. An alternative is to run a laboratory trickle bed where the voids among catalyst particles are filled with fines. If proper packing procedure is used (Al-Dahhan et al., 1995; Al-Dahhan and Dudukovic, 1996) a bed packed with the mixture of catalyst and fines decouples the apparent kinetics from hydrodynamics, which is desired. Packed beds containing fines perform then identically in upflow and downflow at the same set of mass velocities (Al-Dahhan and Dudukovic, 1996).

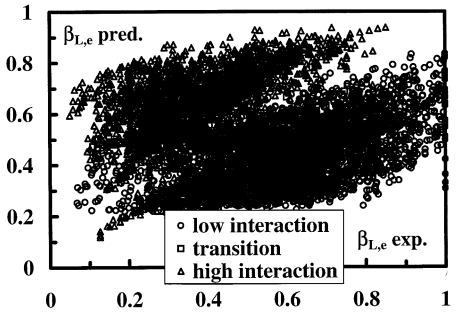

Fig. 3. Prediction of external liquid holdup in low and high interaction regime.

In summary, we can say that in spite of considerable research, the fluid dynamic parameters in packed beds with two-phase flow cannot be predicted with desired accuracy. An engineer attempting to evaluate the hydrodynamic parameters needed for design or scale-up, such as external liquid holdup, flow regime and pressure drop, has to select a suitable correlation. By "suitable" one usually means a correlation that in its data base contains operating conditions and physical system properties that are the closest to the system of interest. Can one not do better now at the turn of the millenium and recommend the best universal correlation? The answer unfortunately is negative. The ability (or lack of it) of the currently available methods to predict the key fluid dynamic parameters is illustrated in Fig. 3, which is a parity plot of the 8000 external liquid holdup data, collected from various sources in both low and high gas-liquid interaction regimes, against the predictions of the appropriate form of the empirical Ellman (1988) and Ellman et al. (1990) correlation. The lack of success is self-evident. We chose Ellman's correlation as an illustration not because we believe it is inferior to others, but on the contrary, because it covers the broadest data base at elevated pressure and, hence, is expected to be among the better choices. Clearly, Fig. 3 indicates the need for a renewed effort to reach more predictability in evaluation of two-phase flow packed beds hydrodynamic parameters. One approach is to increase our reliance on fundamental approaches and utilize improved computational power to solve the resulting more complex flow models. The other (perhaps parallel approach pursued by one of the authors (F.L.)) is to utilize the advances in computers and neural networks to train a neural net model based on a huge set of available data (F.L. has accumulated over 30,000 data for the fluid dynamic parameters discussed above) and make predictions based on such a model. Two recent papers by Bensetiti et al. (1997) and Larachi et al. (1998b) illustrate the possibilities of such an approach (see also André, 1997). These authors show that if one selects randomly about 60% of the available data, a neural net can be trained to achieve a remarkable fit of the training set. The advantage arises that when the neural net predictions are tested against the remaining 40% of the data very good agreement is found. This is illustrated in Fig. 4 for mass transfer coefficient. Needless to say the classical correlations without neural nets provided the quality of fit observed for holdup in Fig. 3.

2.2. *Comparison of upflow packed bubble columns* (*PBC*) *and downflow trickle bed reactors* (*TBR*)

When a fixed bed is chosen to process gas and liquid reactants the question whether to use upflow or downflow

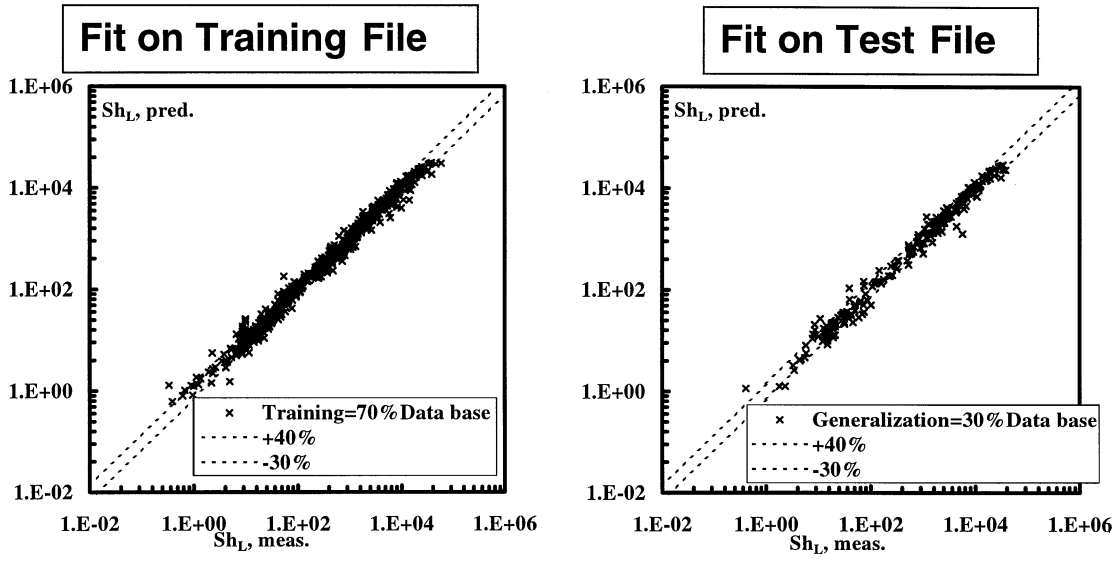

Fig. 4. Neural network based predictions of mass transfer coefficients (a) Training set. (b) Comparison with other data.

operation is frequently asked. Liquid holdup is higher and liquid is typically the continuous phase in the former, while gas is the continuous phase in TBR and liquid holdup is lower.

Goto and Mabuchi (1984) demonstrated that for the atmospheric pressure oxidation of ethanol in presence of carbonate, downflow is superior at low gas and liquid velocities but upflow should be chosen at high gas and liquid velocities. Beaudry et al. (1987) studied atmospheric pressure hydrogenation of α-methylstyrene in liquid solvents at high liquid reactant concentration in the feed and observed that downflow performance is better than upflow except at very high liquid reactant conversion. Mazzarino et al. (1989) observed higher rates in upflow than in downflow for ethanol oxidation and attributed the observed phenomenon to better effective wetting in upflow. Liquid holdup measurements at elevated pressure using water/glycol as liquid with H_2, N_2, CO_2 as the gas phase by Larachi et al. (1991) indicate that liquid saturation is much greater in upflow than in downward flow at all pressures (up to 5.1 MPa). Lara-Marquez et al. (1992) studied the effect of pressure on upflow and downflow using chemical absorption, and concluded that the interfacial area and the liquid side mass transfer coefficient increase with pressure in both cases. Goto et al. (1993) observed that downflow is better than upflow at atmospheric pressure (for hydration of olefins) and noted that the observed rates in downflow were independent of gas velocity while those in upflow were slightly dependent on it.

In order to provide general guidance to practicing engineers as to which reactor type to choose, Khadilkar et al. (1996) examined all the previously reported studies. They concluded that most reaction systems can be classified as being liquid reactant or gas reactant limited. The value of parameter γ, wh ich represents the ratio of the liquid reactant flux to the catalyst particle to the gas reactant flux to the particle, scaled by the ratio of stoichiometric coefficients, delineates these two categories. For $\gamma \gg 1$ the reaction can be considered gas reactant rate limited, while for $\gamma < 1$ it is the liquid reactant that is rate limiting. For liquid-limited reactions upflow reactor should be preferred as it provides for complete catalyst wetting and for the fastest transport of the liquid reactant to the catalyst. For gas limited reactions, downflow reactor, especially at partially wetted conditions, is to be preferred as it facilitates the transport of the gaseous reactant to the catalyst. Applying this criterion to the previously reported studies in the literature, the conclusions regarding the preferred mode of operation can be reached and are tabulated in the last column of Table 3. This agreed with all experimental observations except the one by Mazzarino et al. (1989) at low pressure and high liquid reactant concentration. This observation is suspect because the comparison between "upflow and downflow" performance was not executed with the same catalyst bed. To further illustrate the usefulness of the proposed criterion, Khadilkar et al. (1996) and Wu et al. (1996a) conducted an experimental study of hydrogenation of α-methylstyrene on the same catalyst bed using upflow and downflow mode of operation. By changing hydrogen pressure and feed α-methylstyrene concentration they were able to run the reaction as gas reactant limited ($\gamma = 8.8$ at high feed liquid reactant concentration and at atmospheric hydrogen pressure) and as liquid reactant limited ($\gamma = 0.87$ at high hydrogen pressure and low feed α-methylstyrene concentration). The experimental results confirmed the predictions based on the value of γ which indicate that downflow is preferred for the gas limited reaction and upflow for the liquid limited

Table 3
Identification of the limiting reactant for literature data

Authors	Reaction system	Operating conditions[a]	Gamma (γ)	Limiting reactant	Preferred mode
Goto and Mabuchi (1984)	Oxidation of ethanol in presence of carbonate	Low concentration and atmospheric pressure	314	Gas	Downflow
Mills et al. (1987)	Hydrogenation of alpha-methylstyrene	High concentration low pressure	92	Gas	Downflow
Mazzarino et al. (1989)	I. Ethanol oxidation	Low concentration and atmospheric pressure	0.51	Liquid	Upflow
	II. Ethanol oxidation	High concentration and low atmospheric pressure	17	Gas	Downflow
Goto et al. (1993)	Oxidation of ethanol in presence of carbonate	Atmospheric pressure	10300	Gas	Downflow
Khadilkar et al. (1996); Wu et al. (1996a)	I. Hydrogenation of alpha-methylstyrene	High concentration low pressure	8.8	Gas	Downflow
	II. Hydrogenation of alpha-methylstyrene	Low concentration high pressure	0.87	Liquid	Upflow

[a]Concentration refers to liquid reactant feed concentration.

one. Moreover, it was shown that when the bed is packed with fines the differences between upflow and downflow disappear completely as transport effects in both modes of operation become identical (Wu et al., 1996b).

2.3. Unsteady-state operation of trickle-bed reactors

The concept of using unsteady state operation to enhance performance is not new to the field of chemical engineering. In case of trickle-bed reactors, however, unsteady-state operation has been considered only in the past decade or so and several strategies such as modulation of flow, composition, and activity have been suggested (Silveston, 1990). Modulation of flow of gas or liquid is done to achieve the desired ratio of liquid and gaseous reactants on the catalyst as well as to allow a controlled exotherm (Gupta, 1985; Haure et al., 1990a; Lee et al., 1995). Modulation of composition can improve selectivity or control phase change by addition of inerts or products (Lange et al., 1994) or by injecting cold shots of gas (Yan, 1980). Modulation of activity is usually accomplished by an extra component, which can help catalyst regeneration and prevent build up of poisons or inhibitors in the catalyst (Chanchlani et al., 1994; Haure et al., 1990a).

The experimental studies of unsteady-state operation in trickle-bed reactors are summarized in Table 4 and only key observations are briefly discussed here. The terminology used is that the total time of one cycle is referred to as cycle time (or period, denoted as τ) and the part of the cycle when modulation is active is referred to as the ON part (denoted by $s\tau$, where s is the fraction of total time corresponding to the ON part) and the rest of the cycle is the OFF part (corresponding to $(1-s)\tau$). Haure et al. (1990b) and Lee et al. (1995) studied periodic flow modulation of water in SO_2 oxidation to obtain concentrated sulfuric acid from dilute SO_2 gaseous streams. They observed an enhancement in supply of SO_2 and O_2 to the catalyst during the OFF part of the cycle, resulting in higher performance and temperature rise of 10–15°C. They also observed that the reaction results in formation of SO_3 which is adsorbed on the catalyst until it is washed by the pulse of water during the ON part of the cycle, which results in concentrated sulfuric acid formation as well as restoration of the catalytic activity. Lange et al. (1994) experimentally investigated the hydrogenation of cyclohexene, and the hydrogenation of α-methylstyrene on Pd catalysts by manipulation of liquid feed concentration and feed rate, respectively. They used non-isothermal composition modulation of cyclohexene to control conversion and keep the reaction system from switching from a three-phase system to a two-phase one, and, designed their total cycle time based on this criterion. For the case of hydrogenation of α-methylstyrene under isothermal conditions, the authors observed maximum improvement at a cycle period of 8 min at cycle split of 0.5. The observed improvement (between 2 and 15%) was attributed to better wetting due to the liquid pulse which caused the removal of stagnant liquid. Castellari and Haure (1995) investigated the performance enhancement due to the large temperature rise during the OFF part of the cycle. They observed gas-phase reaction at semi-runaway conditions and a large enhancement resulting from the high gas-phase reaction rates.

Most of the studies reported in the open literature are for gas-limited conditions. They indicate that periodic operation under gas-limited conditions can ensure completely internally wetted catalyst pellets, provide direct access of gaseous reactant to the catalyst sites, replenishment of catalyst with liquid reactant, periodic removal of products by fresh liquid, and quenching of a predetermined rise in temperature. Under liquid-limited conditions, catalyst external wetting and liquid supply to the particles is crucial, and periodic operation can reduce and eliminate liquid maldistribution, ensure a completely irrigated bed, and, quench developing hotspots. Several industrial reactors are operated under liquid-limited

Table 4
Literature studies on unsteady state operation of trickle beds

Author(s)	System studied	Modulation strategy	L and G flow rates	Cycle period (τ) and split (σ)	% Enhancement
Haure et al. (1990a)	SO_2oxidation	Flow (non isothermal)	$V_L = 0.03$–1.75 mm/s $V_G = 1$–2 cm/s	$\tau = 10$–80 min ($\sigma = 0.1$, 0–0.5)	30–50%
Lange et al. (1994)	Cyclohexene hydrogenation	Composition (non isothermal)	$Q_L = 80$–250 ml/h Conc = 5–100%	τ = up to 30 min. ($\sigma = 0.2$–0.5)	2–15% (temp rise = 30°C)
	α-MS hydrogenation	Liquid flow (isothermal)	$Q_L = 0$–300 ml/h, $Q_G = 20$ l/h	$\tau = 1$–10 min ($\sigma = 0.25$–0.5)	
Stegasov et al. (1994)	SO_2 oxidation	Model	$V_L = 0.1$–0.5 cm/s, $V_G = 1.7$–2.5 cm/s	$\tau = 10$–30 min. ($\sigma = 0.1$–0.5)	Max = 80%
Lee et al. (1995)	SO_2 oxidation	Adiabatic flow modulation	$V_L = 0.085$–0.212 cm/s, $SV_G = 1000\ h^{-1}$	τ = up to 60 min ($\sigma = 0.02$–0.1)	
Castellari and Haure (1995)	α-MS hydrogenation	Non isothermal	$Q_L = 2.27$ ml/s $Q_G = 900$ ml/s	$\tau = 5$ to 45 min ($\sigma = 0.3$–0.5)	400% (temp. rise = 35°C)

conditions at high pressure and suffer from maldistribution of the liquid reactants, which can cause externally dry or even internally dry catalyst pellets. At high liquid and gas mass velocities, in the pulsing flow regime, a significant improvement in catalyst wetting and effective removal of hot spots has been reported (Blok and Drinkenburg, 1982). However, achieving this regime is not always practical in industrial reactors due to large pressure drop and little control over the slugging process. Periodic flow modulation, with a low base flow and a periodic slug of very high liquid flow, can improve catalyst utilization even at low mean liquid flows (lower pressure drop) and still achieve temperature and flow control due to artificially induced pulses (or slugs). No study has been reported in the open literature on liquid-limited reactions or on unsteady-state performance data of large reactors. At ISCRE 15, Khadilkar et al. (1998a) presented the first experimental data for the effect of flow modulation on performance of a trickle-bed reactor for a liquid-limited reaction. The effect of the natural pulsing flow regime as opposed to the trickle flow regime on selectivity has also been investigated recently by Wu (1997). Some industrial processes do employ periodic localized quenching of hot spots by injection of cold fluids at selected axial locations along the reactor (Yan, 1980).

2.4. Modeling TBR performance

Most of the trickle-bed reactor models reported in the literature considered isothermal operation and used either a pseudo-homogeneous approach (Collins et al., 1984; Kheshgi et al., 1992) or a heterogeneous model with plug flow for gas and liquid phase (El-Hisnawi et al., 1981; Mills and Dudukovic, 1984; Hekmat and Vortmeyer, 1994; Rajashekharam et al., 1998). Some models accounted for liquid flow non-uniformity and maldistribution by using an axial dispersion model (Chu and Ng, 1986). Most investigations dealt with hydrogenation or oxidation in pure or moderately concentrated organic or aqueous solutions (large excess of liquid reactant), and, hence, considered zero-order rate with respect to the liquid reactant concentration and first order with respect to dissolved gaseous reactant concentration. Liquid reactants/solvents were assumed to be non-volatile and gas phase assumed to be pure at constant partial pressure of the reacting gas. Thus, the primary model variables of interest have been the dissolved liquid-phase concentrations of the gaseous reactant and the conversion of the liquid-phase reactants. The key effect that was incorporated in most recent models was that of partial wetting and transport of gaseous reactant to dry external areas of the catalyst resulting in higher rates observed in most of the experimental data (El-Hisnawi et al., 1981; Berruti et al., 1984; Ruzicka and Hanika, 1994). Some models considered non-isothermal effects and used a pseudo-homogeneous energy balance to solve for the temperature at any axial location (Yang and Li, 1992; Harold and Watson, 1993; Rajashekaram et al., 1998). Others considered evaporation effects by adding vapor-liquid equilibrium calculations and flash units to simplified pseudo-homogeneous or equilibrium model mass balance equations on the reactor scale (LaVopa and Sattefield, 1988; Collins et al., 1984). Other approaches include a cell model (Sims et al., 1994), a cross-flow model (Tsamatsoulis and Papayannakos, 1995) and some other models based on liquid flow maldistribution (Funk et al., 1990) or stagnant liquid zones in the reactor (Rajashekharam et al., 1998). Table 5 summarizes the application of TBR/PBC models in interpretation of mainly laboratory-scale reactor performance.

Pellet-scale reaction and diffusion have been studied by taking reactant limitation in account in simpler versions (Beaudry et al., 1987), and in the general case by considering partial internal wetting of pellets, resulting in gas and liquid-phase reaction zones, and solving for the gas–liquid interface by considering liquid inbibition, pore filing and capillary condensation (Harold and Watson, 1993). Approximate solutions of the gas–solid catalyst level equations have also been verified by numerical solution for non-linear kinetics (Lemcoff et al., 1988).

The earliest unsteady-state modeling used a plug-flow equilibrium model for predicting the hot spot formation and movement during start-up of a trickle bed and investigated the effect of a gas/liquid quench stream axial position on the developing hot spot (Yan, 1980). Pseudo-transient behavior was also modeled by considering similar equations (Warna and Salmi, 1996; Sundmacher and Hoffmann, 1994). Mass transfer terms are considered in extension of these models to predict periodic variation of temperature and concentration (Haure et al., 1990a; Stegasov et al., 1994). Spatial terms were dropped in some subcases of this model to study time variation of mass transfer coefficients and enhancement in rates and selectivity for the model reaction system (Wu et al., 1995). Catalyst wetting effects during periodic operation (Gabarain et al., 1997a, b) were also studied with elimination of spatial terms in the model equations. This was done primarily to reduce computational complexity. Activity modulation was incorporated in recent transient models for optimizing the performance on the basis of catalyst activity (Yamada and Goto, 1997).

The level of complexity and features available in the models in the literature are sufficient for evaluation of steady-state experiments in comparison of trickle beds and packed bubble columns as outlined previously. These models are still far from mimicking reality in industrial hydrocracking and hydrotreating applications due to three main shortcomings. They do not consider multicomponent transport and multiple reactions properly, do not account for change of phase (evaporation and condensation) and for its effect on holdup and velocities. An improved model for unsteady-state

Table 5
Application of TBR/PBC models to laboratory studies

Reaction	Rate analysis	Model assumptions	Source/reactor
H_2O_2 decomposition	Linear kinetics	Isothermal, partial wetting, 2-region cell reactor	Sims et al.(1994)/TBR
Hydrogenation of C_4-olefins	L-H kinetics	Isothermal, plug flow	Vergel et al. (1995)/PBC
Hydrogenation of 3-hydroxy-propanal	L-H kinetics	Isothermal, plug flow, partial wetting, heat balance	Valerius et al. (1996)/TBR
Hydrotreating of vaccum gas oil	L-H kinetics	Isotherm., plug flow, partial wetting	Korsten, Hofmann (1996)/TBR
H_2O_2 decomposition	Linear kinetics	Isotherm., plug flow, partial wetting	Wu et al. (1996a)/TBR
Hydrogenation of α-Me-styrene	L-H kinetics	Isothermal, plug flow, partial wetting, high pressure	Khadilkar et al. (1996)/TBR, PBC
Selective hydrogenation of 1,5,9-cyclododecatriene	Linear kinetics	Isothermal, axial dispersion, high pressure/temperature	Stüber et al. (1996)/ PBC
SO_2 oxidation	Linear kinetics	Isothermal, full wetting	Ravindra et al. (1997)/TBR
Phenol oxidation	L-H kinetics	Isothermal, full wetting, plug flow, high pressure/temperature	Pintar et al. (1997)/TBR
SO_2 oxidation	L-H kinetics	Isothermal, partial wetting, axial dispersion, static-dynamic	Iliuta and Iliuta (1997)/TBR, PBC
Phenol biodegradation	Haldane kinetics	Isotherm., plug flow, static-dynamic	Iliuta (1997)/TBR, PBC
Toluene bioscrubbing	Monod kinetics	–	Alonso et al. (1997)/TBR
Hydrogenation of α-Me-styrene	Linear kinetics	Isothermal, plug flow, partial wetting	Castellari et al. (1997)/TBR
Hydrogenation of acetophenone	L-H kinetics	Non-isothermal, plug flow, full wetting, high press./temp.	Bergault et al. (1997)/TBR
Hydrogenation of unsaturated ketones in supercritical CO_2	Power law kinetics	Non-isothermal, plug flow, full wetting	Devetta et al. (1997)/TBR
Hydrogenation of 3-hydroxypropanal	L-H kinetics	Non-isothermal, deactivation, partial wetting, plug flow	Zhu and Hofmann (1997)/TBR
Hydrogenation of 2,4-dinitrotoluene	L-H kinetics	Non-isothermal, plug flow, partial wetting, stagnant liquid	Rajashekharam et al. (1998)/TBR
Hydrogenation of α-nitromethyl-2-furanmethanol	L-H kinetics	Isothermal, plug flow, partial wetting	Khadilkar et al. (1998c)/TBR Jiang et al. (1998)/TBR
Oxidation of substituted phenols	Linear kinetics	Isothermal, partial wetting	Tukac and Hanika (1998)/TBR
Hydrodesulfurization of atmospheric residue	Power law kinetics	Non-isothermal, plug flow, deactivation, complete wetting	Lababidi et al. (1998)/TBR
Hydrogenation maleic anhydride	L-H kinetics	Isotherm., axial dispersion, full wetting	Herrmann, Emig (1998)/PBC

operation that removes many of the above deficiencies has been developed and is presented at ISCRE 15 (Khadilkar et al., 1998b).

2.5. Packed beds with countercurrent flow

Conventional gas–liquid absorbers have traditionally operated in this mode in order to maximize the driving force for gas–liquid mass transfer. In multiphase reactors of this type precise estimates of liquid holdup, pressure drop and mass transfer coefficients are difficult to make because the extensive data banks, utilized by the correlations for these parameters, do not include data for the small porous catalyst packing used in packed bed reactors with two phase flow. Qualitatively, of course, one knows that pressure drop and holdup are intimately related and that an increase in one leads to the increase in the other. Flooding by and large follows the Sherwood type of correlation but detailed and accurate predictions of holdup, pressure drop and flooding conditions may be elusive on most catalyst packing of interest. In order to lower the pressure drop, high voidage packing or packing with special characteristics is preferred. The possibility that countercurrent flow packed beds will be implemented in refinery operations provides a strong motivation for investigating new types of structural packing with low-pressure drops and good gas–liquid and liquid–solid contacting. Structural packing for countercurrent flow containing three porosity levels was recently reported by Van Hasselt et al. (1997), while Sie and Lebens (1998) illustrated the application of monoliths. Both reactors featured low-pressure drop compared to randomly packed beds. Flow transients, pressure drop overshoots and pressure drop hysteresis in countercurrent packed beds was recently studied by Stanek and Jiriczny (1997), Jiriczny and Stanek (1996) and Wang et al. (1997), respectively. Iliuta et al. (1997b) compared hydrodynamic parameters in cocurrent and countercurrent flow.

The introduction of countercurrent flow fixed-bed reactors in a number of refining operations is likely, either via re-design of existing reactors or by introduction of

new process technology. The goal is not improvement in reactant (hydrogen) mass transfer, which is not rate limiting, but enhanced removal of inhibitory by-products or in situ product separation. Dassori et al. (1998) have illustrated the advantage in hydrodesulfurization. ABB Lummus is marketing such a technology and other studies involving this concept have been reported.

2.6. Concluding remarks

During the last decade or so our understanding of catalytic packed beds with two-phase flow has improved considerably. These are now recognized as reactors of choice when large catalyst to liquid volume ratio is desired, and when plug flow of both phases is to be preferred, when reaction rates are not overly high and catalyst deactivation is very slow or negligible. It has also been accepted that in trickle flow both reactor scale maldistribution can occur as well as incomplete external wetting of particles. To combat the former phenomenon, liquid redistribution is needed or induced pulsing flow. The phenomenon of incomplete external catalyst wetting is detrimental to liquid-limited reactors only. It is now also understood that for liquid limited reactions scale-up at constant LHSV is forgiving since it results in improved wetting efficiency, and better catalyst utilization. For gas limited reactions such scale-up at constant LHSV can lead to very poor performance (Dudukovic, 1998) as the catalyst effectiveness factor drops with increased contacting efficiency due to a reduction in the gas reactant supply. Hence, for gas-limited reactions constant LHSV and constant reactor height are required in order to maintain the same performance upon scale-up. This leads sometimes to undesirable pan-cake reactor geometry which can be a problem in achieving uniform liquid distribution and hence model based scale-up ought to be used. By addition of fines to the laboratory catalyst beds fluid dynamics can be separated from kinetics and transfer of laboratory data to industrial practice becomes possible. For well-established liquid-reactant-limited processes scale-up and scale-down between laboratory reactors and large industrial units can be accomplished. The choice of upflow vs. downflow reactors can be based on rational considerations as to what is the limiting reactant at the operating conditions of interest. As already mentioned countercurrent flow will become more prominent in the future in processes that suffer from by-product catalyst inhibition.

The available correlations for important hydrodynamic parameters leave a lot to be desired. As the use of novel structural packing becomes more widespread it will become increasingly necessary to re-establish engineering type of correlations for such packing. It is hoped that fundamental approaches involving CFD and proper description of multiphase mass transfer will also be increasingly used.

3. Reactors with moving catalyst

3.1. Bubble columns and slurry bubble columns

Bubble columns and slurry bubble columns are used extensively in a variety of processes for hydrogenation, oxidation, chlorination, hydroformylation, cell growth, bioremediation, etc. Recently they have been identified as reactors of choice for gas conversion (e.g. liquid phase methanol synthesis, Fischer–Tropsch synthesis, etc.) due to their excellent heat transfer characteristics. Fig. 5 schematically represents a typical bubble column reactor (minus the internals needed for heat transfer). Gas is sparged at the bottom of the column and the resulting buoyancy driven flow creates strong liquid recirculation. Thus, as long as the liquid superficial velocity is an order of magnitude smaller than that of the gas, it is the gas superficial velocity that is the dominant variable which drives the fluid dynamics of the whole system, and whether the liquid is processed batch-wise or flows cocurrently or countercurrently to the flow of the gas is immaterial from the fluid dynamics point of view. Slurry particles, as long as they are small (typically less than 60 μm) follow liquid motion except perhaps at very high slurry loadings exceeding 20–30%. While in some applications bubbly flow is practiced (typically gas superficial velocities smaller than 2–3 cm/s) of current industrial interest is the churn-turbulent flow (with gas superficial

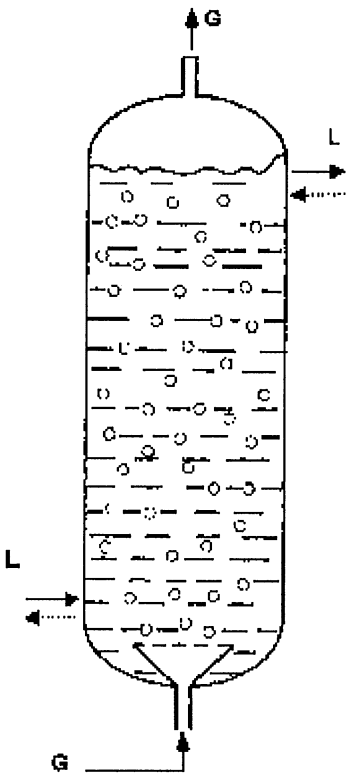

Fig. 5. Schematic of a bubble column.

velocities in excess of 10 cm/s up to the 30–50 cm/s range).

3.1.1. Fluid dynamics

Recent advances in bubble column fluid dynamics have resulted from novel measurements and computational modeling efforts. Hot-wire anemometry (HWA) was used by Menzel et al. (1990) successfully to map the velocity as well as the turbulent stress field in three dimensional (3D) bubble columns up to reasonable gas velocities of 8 cm/s. Yang et al. (1990) also measured the time-averaged gas and liquid velocity distributions in 3D columns. L.S. Fan introduced the use of particle image velocimetry (PIV) to 2D and 3D bubble columns in bubbly flow (Tzeng et al., 1993; Reese et al., 1993, 1996; Reese and Fan, 1994, 1997a; Mudde et al., 1997). They mapped the instantaneous velocity and holdup fields, as well as the turbulent stresses, in 2D columns and showed good comparison with the volume-of-fluid computational predictions. The same group also developed a flow visualization experiment at high pressure and generated an extensive correlation for bubble rise velocity and size as a function of operating conditions. The group at Delft (Gröen et al., 1995, 1996) implemented a novel fiber optic probe for bubble columns for examination of bubble size and rise velocity and mapped via LDA (Laser Doppler Anemometry) the Reynolds stresses in a 3D column close to the wall. At the Chemical Reaction Engineering Laboratory (CREL) at Washington University (Devanathan et al., 1990, 1995; Devanathan, 1991; Moslemian et al., 1992; Yang et al., 1992b, 1993; Kumar et al., 1994, 1995a, b, 1997; Dudukovic et al., 1997) computer-automated radioactive particle tracking (CARPT) and computed tomography (CT) were implemented for complete mapping of the velocity and holdup field in bubble columns. CARPT allows us to map the Lagrangian tracer particle trajectories throughout the column, and from these trajectories determine instantaneous velocities, time averaged flow patterns, turbulent stresses and turbulent kinetic energy due to measured fluctuating velocities. From CARPT data mixing parameters such as the eddy diffusivity tensor are also readily calculated. The principles of CARPT (also called radioactive particle tracking, RPT) have been reviewed in detail by Larachi et al. (1997b) and this will not be repeated here. The interested reader is directed to the above-cited chapter and to the many references within it or to the above papers related to CARPT. Very briefly, in CARPT the position of the single radioactive particle is continuously monitored by a series of pre-calibrated scintillation detectors. The particle is made of the same size and mass as the particles in the system, if motion of solids is monitored in slurries or fluidized beds, or it is neutrally buoyant when tracing the liquid motion. It can be shown that motion up to frequencies of 20–30 Hz can be followed. The gamma ray tomography setup in CREL allows one to obtain time-averaged holdup-profiles in column cross sections at desired elevations. The CARPT-CT combined setup provides unique capabilities for mapping the flow field in the whole enclosure (column) for opaque systems when other techniques fail.

The CARPT-CT data have provided a unique view of the time-averaged flow field and gas holdup distribution in bubble columns. While in bubbly flow at low gas superficial velocities the radial gas holdup profile is almost flat (with somewhat more gas in the center), in churn turbulent flow the gas holdup profile is almost parabolic. The non-uniform gas holdup profile drives liquid circulation and throughout most of the column, except in the distributor region and in the disengagement zone, the liquid rises in the center and falls by the walls. The instantaneous flow patterns are complex and involve toroidal, swirling vortex structures. CARPT provides information on the turbulence intensity, the anisotropy of turbulence and axial and radial diffusivities (Devanathan et al., 1990; Degaleesan, 1997; Yang et al., 1992b, 1993).

The CARPT-CT have been used to relate the axial dispersion coefficient to the measured liquid recirculation and eddy diffusivities (Degaleesan, 1997; Degaleesan and Dudukovic, 1998). Based on the hydrodynamic behavior that the data reveal, a recycle with cross-flow with dispersion model was developed and used successfully for interpretation of tracer data (Degaleesan et al., 1996). The ensemble averaged liquid velocities and eddy diffusivities determined by CARPT and time-averaged holdup profiles obtained by CT were used in the convection-diffusion model to predict the residence time distribution of a liquid tracer (Degaleesan et al., 1997).

3.1.2. CFD models

The simplest one-dimensional model relates the gas holdup profile to the radial profile of the axial velocity in the fully developed flow region. Kumar et al. (1995a) have shown that existing correlations for turbulent viscosity and mixing length yield inaccurate velocity predictions, given the gas holdup profile. Degaleesan et al. (1997) provided an improved approach to such predictions.

Two-dimensional models for gas–liquid flow in bubble columns have also been studied extensively. A recent review by Jakobsen et al. (1997) covers the pertinent literature well. Two approaches are basically used: the Euler–Euler formulation, based on the interpenetrating two-fluid model, and the Lagrange–Euler approach. In the former Navier–Stokes equations are ensemble averaged using the approach of Drew (1983). Expressions for all interphase interaction terms are then required, and these mainly consist of the models for the drag, lift and added mass force. Also a turbulence model is required for the liquid phase (and perhaps gas phase at higher pressures). The Lagrange–Euler method solves the original Navier–Stokes equations for the continuous phase, (the

density and viscosity of which are often modified to account for the presence of the low volume fraction of the dispersed phase) and then solves for the motion of each bubble by applying Newton's second law to it where all the forces on the bubbles are calculated based on the local velocity patterns in the continuous phase. This approach, while it appears at first glance "more fundamental", hides in the different realizations that appeared in the literature some additional tuning parameters (e.g. effective diffusivity for the dispersed phase, effective viscosity of the continuous phase, etc.). Both approaches have their ardent advocates, and each approach has its advantages and disadvantages. The Lagrange–Euler approach seems quite appealing for bubbly flow, but even at those situations it has not been documented that it can handle coalescence-redispersion at increased volume fraction of the dispersed phase. It is rather dubious that the Lagrange–Euler approach can be used in churn-turbulent flow where at very high gas holdup of 25–50% no individual bubbles preserve their identity for long and where liquid and gas essentially battle for the available space. The Euler–Euler interpenetrating two-fluid model seems much more attractive under those conditions; unfortunately it is not clear yet what are the appropriate forms to use for the drag, lift and virtual mass under such conditions. Appropriate models for multiphase turbulence also remain elusive.

In the chemical reaction engineering literature it was Professor Svenden's group at Trondheim (Torvik and Svendsen, 1990; Jakobsen et al., 1997; Jakobsen, 1993) that were the first to develop steady-state Euler–Euler fluid dynamic 2D models for bubble columns. Such models show reasonable agreement with data for time-averaged axial velocity profiles and somewhat less favorable agreement with radial holdup profiles obtained in presumably axisymmetric 3D columns. They even tied the computed flow field to predictions of reactor performance. Lapin and Lübbert (1994) introduced the Lagrange–Euler description to the simulation of bubbly flows in 3D columns and presented impressive transient velocity and holdup profiles, which qualitatively compared well with observations, and also showed semi-quantitative agreement with measured mean values. Sokolichin and Eigenberger (1994) used the direct solution of Navier–Stokes equations for the liquid and gas and presented reasonable agreement with selected experimental studies. Recently, Delnoij et al. (1997a–c) developed a more detailed model for dispersed gas–liquid two-phase flow based on Euler–Lagrangian approach. All relevant forces (drag, virtual mass, lift and gravity) acting on the bubble are accounted for. Direct bubble–bubble interactions are also accounted for via an interaction model that resembles the collision approach followed in fluidized bed modeling. With this model Delnoij et al. (1997c) were able to simulate reasonably well the experimental observations of Becker et al. (1994), who monitored a gas plume created by a few clustered orifices at the bottom of a 2D column.

In addition to the above-described methods, Tomiyama et al. (1993) used the volume of fluid method (which allows tracking of the gas-liquid interface) to analyze the shape and motion of a single rising bubble in liquid. Recently, Lin et al. (1996) applied the VOF to study the time dependent bubbly flows at low gas holdup and compared their computational results with experimental data obtained with Particle Image Velocimetry. Several bubbles emanating from a small number of orifices were tracked by VOF and satisfactory agreement with experiments were reported.

It should be mentioned, however, that most of the comparisons between CFD model predictions and data were qualitative or semi-quantitative in nature. Successful quantitative comparison of the time-averaged velocity profiles based on 2D axisymmetric Euler–Euler model (CFDLIB of Los Alamos was used for computations) and 3D data obtained by CARPT was reached (Kumar et al., 1995b) but the model was not truly predictive as the assumed bubble size for drag computations and turbulent viscosity could be adjusted. Moreover, no amount of adjustments could reconcile the experimentally measured gas holdup profiles via CT, which showed the customary maximum in the center, and the computed ones which indicate a peak in between the center and the wall but closer to the wall. Some were inclined to blame the 2D nature of the model for the inability to capture the spiraling gas plumes, and hence the correct gas holdup profiles, others doubted the adequacy of the models used for drag, lift, virtual mass and turbulence. This issue remains unresolved.

3.1.3. Bubble size

The treatment of bubble column fluid dynamics would not be complete without discussing the bubble size distribution. Based on the dynamic gas disengagement technique in 3D columns and visual observations in 2D columns, Krishna and his co-workers have advocated a bimodal bubble size distribution in churn-turbulent flow (Krishna et al., 1993; Ellenberger and Krishna, 1994; Krishna and Ellenberger, 1996). However, it is suspected that dynamic disengagement does not capture the true distribution of bubble sizes, because of the fact that neither liquid circulation nor bubble coalescence and redispersion die out as the gas flow is cut off. Hence, no simple relationships exist between the rate of drop of the free surface of the gas–liquid dispersion and bubble sizes that are disengaging. Moreover, visual experiments at high pressure shed some doubts as to whether two classes of bubbles indeed exist at high pressure. This issue is important as it affects how the bubble column reactors are modeled and should be resolved.

In summary, while advanced 2D and 3D models of bubble column two-phase flows have been developed,

experimental verification is still needed. This is especially true of churn turbulent flows. No fundamental model for mass transfer has yet been coupled successfully to the flow models and reliable reactor performance predictions based on these models are not imminent. However, improved knowledge of the hydrodynamics is helping the practicing engineer develop improved phenomenological models for assessment of reactor performance.

As far as experimental verification is concerned, PIV, LDA, HWA are fine tools for dilute dispersed flow systems but in churn turbulent bubble columns one needs to rely on CARPT, gamma ray CT, X-ray tomography and possibly in the future on impedance tomography.

3.2. Three-phase fluidized-bed reactors

Gas–liquid–solid fluidized-bed reactors are receiving considerable attention in research and process development. They are an off-shoot of slurry bubble columns except that the particles are now sufficiently large that they behave as a distinct third phase. Besides their traditional applications in hydrotreating, Fischer–Tropsch synthesis, coal combustion, etc., three-phase fluidized beds or ebullated beds are also considered as viable options in the fields of aerobic and anaerobic waste water treatment, as well as in the production of valuable substances by means of bacteria, fungi, animal and plant cells (Godia and Sola, 1995; Wright and Raper, 1996; Schügerl, 1997).

3.2.1. Fluid dynamics

With the advent of three-dimensional particle image velocimetry (3-DPIV) and radioactive particle tracking techniques (CARPT, RPT) in gas–liquid–solid flows, it has become possible to map the 2D and 3D full-field of the instantaneous and time-averaged phase holdup and velocity distributions, and to capture more quantitatively the phenomena, such as emulsion vortices and hindered swirling large bubbles, that occur deep in the reactor remote from its walls, etc. The first adaptation of PIV to three-phase fluidized beds was reported by Fan and co-workers (Chen and Fan, 1992), which was followed, after further improvements of the technique (Chen et al., 1994; Reese et al., 1995; Reese and Fan, 1997b), by refined qualitative and quantitative descriptions of the freeboard region in terms of three-phase velocity fields, bubble-size, gas and liquid holdup distributions, and slip velocities. A radioactive particle tracing technique, more convenient for probing dense emulsions, was employed by Chaouki and co-workers, Dudukovic and co-workers and Larachi (Larachi et al., 1995a,b, 1996; Limtrakul, 1996) to measure the 3-D Lagrangian movement of the solids in dense three-phase fluidized beds without draft tubes. CARPT measurements were utilized to quantify the mechanisms of the solids motion, to evaluate and model the solids mixing and circulation times and to map the time-averaged Eulerian full flow velocity vectors and turbulence fields. A draft tube clearly intensifies the magnitude of the axial average solids velocities due to the extinction of the turbulent radial transport at the radius of the draft tube, but also because of the additional outward spill-over of the solids towards the annulus right above the draft tube. In the standard fluidized bed, the solids mean flow evolves clockwise in a 3D toroidal recirculation cell; whereas the draft tube brings about a two-stage vertical clockwise rotational flow pattern of the solids, fast in the bottom stage and slow in the upper stage.

Identification of the hydrodynamic regimes has been attempted based on visual observation, wall pressure fluctuations, and bubble sizes (Wild and Poncin, 1996; Fan, 1989) and time-series conductivity probe signals (Briens et al., 1996). However, predicting the flow regime in three-phase fluidization is hampered by the complex dependence of flow regimes upon column diameter, distributor type, settled bed height, particle density, geometry, and wettability, coalescence inhibition of the liquid, etc. (Bigot, 1990; Nacef, 1991; Nore, 1992; Nore et al., 1992). Bejar et al. (1992) derived a flow chart suitable for fermentation media in three-phase fluidization to distinguish the dispersed bubble flow from the coalesced bubble flow regimes with Ca-alginate or carrageenan immobilizing particles. Zhang et al. (1997), by using a two-element conductivity probe, provided a refined discrimination of flow patterns in three-phase fluidized beds and arrived at seven flow regimes: dispersed-, discrete-, coalesced-bubble flow, slug flow, bridging flow, churn flow, and annular flow. They also proposed a set of correlations to predict changeover between these different regimes.

The following rules of thumb regarding flow regimes in three-phase fluidization emerge (Nacef, 1991; Nore, 1992; Cassanello et al., 1995; Wild and Poncin, 1996). In bed inventories made up of small/dense particles ($\leqslant 1$ mm) and light particles (density $\leqslant 1700\ \mathrm{kg/m^3}$), only the coalesced bubble flow regime is most likely to occur. In those cases, the flow regime can be coerced to the dispersed bubble flow regime by adding large and light bubble breakers (Kim and Kim, 1990). The dispersed bubble flow prevails at low gas velocity and high liquid velocity, in bed inventories of large particles ($\geqslant 3$–4 mm), whereas coalesced bubble flow dominates for low liquid and/or high gas velocities. Slug flow occurs in small-diameter columns (<0.1 m) at high gas velocity (>0.1 m/s). Further complications in flow regimes arise when non-wettable particles are fluidized, Tsutsumi et al. (1991) thus identified aggregative fluidization at moderate velocities, and dispersed fluidization at higher velocities.

3.2.2. Minimum fluidization velocity, porosity, phase holdups

Minimum fluidization velocity and phase holdups can only be estimated based on empirical correlations. Nacef

Table 6
Impact of operating conditions on the phase holdups in three-phase fluidization

Increase in ↓ Effect on →	Bed expansion	Gas holdup	Liquid holdup
Superficial liquid velocity	Increase	No change	Increase
Superficial gas velocity	Increase	Increase	Decrease
Particle diameter	Decrease	N/C	N/C
Particle density	Decrease	Decrease	N/C
Liquid density	Increase	Decrease	N/C
Liquid viscosity	Increase	Decrease	Increase
Pressure	N/A	Increase	Decrease
Coalescence inhibition	Increase	Increase	Decrease
Distribution quality	Increase	Increase	No change

N/C: no clear cut; N/A: not available

(1991) and Zhang et al. (1995) provide correlations for minimum fluidization velocity, while Han et al. (1990) and Nore (1992) present correlations for bed expansion and liquid holdup. The impact of the change in various operating or process variables on phase holdups in three phase fluidization is illustrated in Table 6 (Wild and Poncin, 1996; Luo et al., 1997).

3.2.3. Bed contraction/expansion

Bed contraction, a phenomenon peculiar to three-phase fluidized beds, occurs when sufficient liquid is sucked up in the bubble wakes to starve significantly the liquid flow in the emulsion phase; as a result the bed contracts. The following rules were drawn based on experimental observations of bed contraction/expansion (Han et al., 1990; Nacef, 1991; Wild and Poncin, 1996; Jiang et al., 1997). With moderately viscous liquids and for particles with size below 2.5 mm, bubble coalescence is promoted and bed contraction is likely to occur; larger particles (>2.5 mm) tend to promote bubble break-up and bed expansion increases with increasing gas velocity. For highly viscous liquids, bed contraction and bubble coalescence occur regardless of particle size. Badly designed distributors promote bed contraction even for large size particles. High pressure/temperature reduces the extent of bed contraction as a result of reduction in bubble size.

3.2.4. Heat and mass transfer

Heat and mass transfer in three-phase fluidization seem to depend on many parameters in a very complex manner (Tang and Fan, 1990; Kim et al., 1990; Kang et al., 1991; Del Pozo et al., 1992; Nore et al., 1992; Kim and Kang, 1997; Luo et al. 1997). Wall to bed, as well as immersed heater-to-bed, heat transfer coefficients are reported. In general, the heat transfer coefficient in three-phase fluidized beds increases with gas/liquid superficial velocities, size and density of particles, column diameter, thermal conductivity and heat capacity of the liquid; whereas it decreases with liquid dynamic viscosity. The gas–liquid volumetric liquid-side mass transfer coefficient increases with fluid throughputs, size and density of particles; it decreases with increasing surface tension and dynamic viscosity of the liquid, and solids holdup for light particles. Bubble breakers improve mass transfer; mismatch to verticality of the column may improve or deteriorate the gas–liquid mass transfer. There are no data available on heat transfer at high temperature, on the impact of coalescence inhibitors, quality of gas–liquid initial distribution, liquid surface tension and density. Recent correlations and models developed for the prediction of the various heat and mass transfer coefficients for three-phase fluidized beds are discussed thoroughly in Kim and Kang (1997).

3.2.5. High-pressure operation

Despite the fact that high-pressure and high-temperature operations are most often encountered in industrial three-phase fluidization practice, the paucity of studies relevant to these conditions is notorious. Only some papers on high-pressure/temperature three-phase fluidized beds (up to 15.6 MPa and 94°C) have been published by Fan and co-workers (Jiang et al., 1992, 1997; Luo et al., 1997). The consequences of increased pressure and temperature on hydrodynamic and heat transfer parameters of three-phase fluidized beds can be summarized as follows: The transition between the dispersed bubble flow and the coalesced bubble flow regimes is moved with increased pressure towards higher gas superficial velocities. As pressure increases up to 6 MPa, the transition velocity and gas holdup is increased; beyond this value, the transition velocity nearly levels off. Gas velocity at the inception of the coalesced bubble flow regime increases with liquid superficial velocity and particle diameter.

3.3. Concluding remarks

It is fair to say that the knowledge base for reactors with moving catalyst is even less complete than for fixed-bed

reactors. The scale-up procedures are prone to more uncertainty and it is not possible in general to relate via simple scale-up rules the performance of laboratory size units to large-scale reactors. Careful investigation of kinetics in another reactor type coupled with cold flow and CFD models of the large units such as risers, ebullated beds, bubble columns is usually the preferred route in process development. In these reactor types both improved scale-up procedures and utilization of CFD have an important role to play. Clearly, much more work based on fundamental approaches remains to be done.

4. Final remarks

Our intent was to provide a more systematic review that includes two-phase systems such as packed beds, fluidized beds and risers as well as other frequently used reactor types such as stirred tanks for gas–liquid and liquid–solid operation. In addition, it is important to access the state-of-the-art of unconventional reactors, such as monoliths for two-phase processing, and reactors that combine separation and reaction, such as chromatographic reactors, catalytic distillation columns or rotating packed beds. While all of this has been prepared, due to space limitations it could not be included in this review. We will attempt to publish the whole comprehensive chapter elsewhere.

This review as presented, attempted to summarize as to what is known about the flow patterns, fluid dynamic parameters and transport phenomena in some commonly used three-phase reactors. This information is needed in reactor modeling or scale-up for any particular process. Four important areas were not discussed in detail. First, although we have indicated that the improved understanding of fluid dynamics in multiphase reactors can only be reached by non-invasive experimental means, and that such data are essential for verification of computational models, we have not reviewed the available experimental techniques. This was omitted since two of the authors (M.P.D. and F. L.) have recently co-authored with Professor Chaouki an extensive review dedicated to this very topic (Chaouki et al., 1997b). In addition, a book has been edited on the subject that summarizes all the available techniques (Chaouki et al., 1997a). Second, while the importance of computational fluid dynamic models for multiphase reactors is stressed throughout this review, no attempt was made to systematically summarize this vast field in view of the recent comprehensive review by Kuipers and van Swaaij (1997). Third, we have not had the space to discuss process chemistries and kinetic modeling. In order to limit the size of this review, we had to focus on description of flow patterns and transport. One of the authors (P.L.M.) has recently discussed the process chemistries and kinetic modeling effects of some processes of the pharmaceutical (Mills and Chaudhari, 1997) and specialty industries (Mills et al., 1992). This brings us to the final, and arguably most important, area that was not covered in our review. That is the art and science of experimental multiphase reactors. From the process development point of view it is most important to have microreactors that are well instrumented in which mixing and contacting patterns are well characterized. Rapid evaluation of various catalysts is then followed by direct scale-up to large units with the help of CFD and cold flow models. In our opinion, it is this area of currently available and current developments in the laboratory multiphase reactors that merits the attention of a review dedicated to that topic alone. Finally, the area of reactor safety, runaway prevention and control is essential to proper and safe usage of multiphase reactors and needs to be reviewed in the future. This is often more effectively done in the context of a specific process type rather than in a generic sense. We hope that the present review will provide the reader with the overall view of where do we currently stand with respect to our knowledge of various multiphase reactor types and as to what needs to be done to improve the state-of-the-art.

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