Backmixing in Gas-Liquid Reactors

This review evaluates the present state of the art on backmixing in gas-liquid and gas-liquid-solid reactors. A brief outline of numerous techniques for measuring residence time distribution (RTD) of various phases in a multiphase reactor is presented. This is followed by a brief description of differential and stagewise models for characterizing backmixing from RTD measurements. Both simple (that is, single-parameter axial dispersion model) and more complex (that is, two-, three-, or four-parameter models) models are evaluated. Backmixing characteristics of various gas-liquid columns such as trickle beds, spray columns, mechanically agitated columns, plate columns, fluidized bed columns, etc., are subsequently evaluated. The performance of a bubble column under various reaction conditions is analyzed. Criteria for the elimination of backmixing in packed-bed reactors are presented, and the effect of backmixing on the multiple steady states in a gas-liquid reactor is briefly reviewed. Finally, the scale-up problems associated with gas-liquid reactors with various degrees of backmixing and the recommendations for the future work in RTD and macromixing models are outlined.

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SCOPE

It is well known that backmixing is detrimental to the performance of a gas-liquid or a gas-liquid-solid reactor. This review outlines various aspects of backmixing in gas-liquid reactors.

The review first outlines the methods for measuring residence time distributions for various phases in a gas-liquid and a gas-liquid-solid reactor. The data for the residence time distributions (RTD) are evaluated by a variety of simple (for example, one-parameter axial dispersion model) and complex (for example, two-, three-, or four-parameter) differential or stagewise macromixing models. These models are briefly evaluated.

From the point of view of backmixing, gas-liquid and gas-liquid-solid reactors can be classified into three broad categories: film reactors where the liquid is the dispersed phase and flows as a film, for example, trickle-bed reactors; gas dispersed as bubbles in a continuous liquid phase, for example, bubble column and slurry reactors; and liquid dispersed as droplets in a continuous gas phase, for example, spray column reactors. Backmixing characteristics of each of these types of reactors are briefly evaluated. The backmixing in these reactors has been largely characterized on the basis of axial dispersion model.

Models for gas-liquid bubble column reactors are briefly reviewed. Slow, fast, and instantaneous gas-liquid reactions are considered. Criteria for eliminating the effect of backmixing on the performance of isothermal and adiabatic trickle-bed reactors are outlined. Unlike a single-phase reactor, an adiabatic gas-liquid reactor can lead to five steady states, and the literature on this unique feature of the gas-liquid reactor is briefly reviewed.

Finally, there is a brief outline of the scale-up problems associated with RTD, and some recommendations for the future work on RTD and macromixing models are presented.

CONCLUSIONS AND SIGNIFICANCE

Over the past two decades, an extensive effort has been directed to the measurement and evaluation of the residence time distributions (RTD) in multiphase systems. For a gas-liquid or a gas-liquid-solid multiphase system, separate RTD measurements are required to evaluate the macromixing characteristics for each phase. The present review indicates that there are numerous methods available to obtain RTDs in complex multiphase systems.

A large number of macromixing models have been proposed to correlate the RTDs in multiphase systems. These models can be simple, single-parameter models, such as the axial dispersion model, or they can be more complex two-, three-, or four-parameter models. More complex models are generally used to correlate the RTDs in complex flow conditions, for example, trickle-bed reactors. These models can be either differential or staged and can usually be related to each other. For some situations, differential models are better than the stagewise models and vice versa; however, these cases are intermediate between differential and stagewise backmixing and are best handled by combining these two types of models. So far, the axial dispersion model has been the most widely examined model; however, it has not been applied sufficiently to systems other than air-water. More complex models are needed to explain more complex flow conditions; however, the parameters of complex models are not evaluated in sufficient details with the help of experimental data to be useful for design or scale-up purposes.

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Experimentally, trickle flow columns and vertically sparged columns have been the most widely examined. Horizontal sparged reactors, mechanically agitated gas-liquid columns, plate columns, and three-phase fluidized-bed columns are also reasonably well examined. In most cases, the experimental data are correlated by empirical relations. Future work should evaluate the RTDs from these columns on a theoretical basis. The backmixing characteristics from all columns except trickle-bed columns have been examined mainly by the axial dispersion model. Very little work on backmixing in spray columns is reported, and the lack of data on backmixing in the pulsating flow regime is evident.

It is well known that backmixing is usually detrimental to the performance of a gas-liquid reactor. The axial dispersion model has been extensively used to model the performance of bubble column and trickle-bed reactors. Future work should include the modeling of gas-liquid or gas-liquid-solid reactors with the use of complex mixing models. The performance of a gas-liquid reactor operating in the pulsating or spray flow regimes is presently not quantitatively evaluated.

An adiabatic gas-liquid reactor can, under some conditions, exhibit five steady states. This unique behavior has been theoretically evaluated by several investigators; however, the presence of five steady states has not been demonstrated experimentally. Future work should include this demonstration.

Finally, there are a number of scale-up problems associated with RTD and macromixing models. This paper outlines some of these problems and makes some recommendations for future study on this subject.

The performance of a chemical reactor with respect to conversion and selectivity depends not only upon the intrinsic kinetics of the various chemical reactions but also on various physical rate processes such as interphase, inter and intra particle heat and mass transfer. The effects of these physical rate processes on the reactor performance have been shown to depend upon the dynamics of the various phases involved. During the past two decades, extensive effort has been devoted to evaluating the effects of nonideal flow on multiphase reactor performance.

The mixing of a fluid within a given phase due to nonideal flow conditions is conventionally divided into two phenomena: micromixing and macromixing. The micromixing phenomenon views the mixing process in terms of the intimacy of mixing of various molecules or entities in a flow system. Micromixing includes all aspects of mixing not defined by the residence time distribution, such as molecular diffusion; its extent is dependent only upon the time of association between various molecules. The two extreme conditions of micromixing are referred to as complete segregation and maximum mixedness. In the first case, mixing of the various entities occurs as late as possible, whereas in the second case, it occurs immediately upon entering the system.

The macromixing component of the overall mixing process, on the other hand, considers the fluid as independent entities and provides information on the residence time experienced by each. This component of mixing occurs solely as a result of convective diffusion. Plug flow and complete mixing are the two extreme cases of macromixing which could possibly exist in a flow system. In the first case, longitudinal mixing is nonexistent; however, owing to complete radial mixing, all fluid elements within the system have identical velocities and hence identical residence times. In a completely mixed system, the residence time distribution (RTD) of the fluid follows an exponential decay, with the exit stream composition being identical to that within the system. In actuality, however, flow reactors deviate considerably from the above extreme cases of macromixing. These deviations may be the result of nonuniform velocity profiles, short circuiting, bypassing and channeling, velocity fluctuations due to molecular and turbulent diffusion, reactor shape and internals, backflow of fluid due to velocity differences between phases, and by recycling due to agitation. As discussed by Mecklenburgh (1974) and Hartland and Mecklenburgh (1968), in these so-called nonideal flow patterns, channeling and recirculation are not random processes as is axial mixing. Backmixing is a specific case of axial mixing in which random movement of fluid is superimposed on and is in the direction of the main flow stream, and where the transverse mixing (that is, mixing in the direction perpendicular to the flow) is complete.

In multistage reactors, the extent of backmixing in each phase is, in general, different and should be considered separately. The most recent review of backmixing in single and multiphase empty-, packed-, and fluidized-bed columns is presented by Wen and Fan (1975). Earlier studies on the mixing characteristics of various types of multiphase reactors are included in the reviews of Ostergaard (1968), Bischoff (1966), Pavlica and Olson (1970), and Mashelkar (1970).

Backmixing in the various phases in a multiphase reactor can have significant effects on the reaction rates and product selectivity. For isothermal systems, backmixing has a detrimental effect on the reaction rate because of the reduction in the effective concentration of the species which affect the rate as well via a reduction in the effective driving force. However, in nonisothermal systems, the backmixing of heat with the fluid may well compensate for the reduction in the reactant concentration due to the effect of temperature on the reaction rate constant.

Gas-liquid reactors can be classified into three broad categories: film reactors, where the liquid is the dispersed phase and flows as a film, for example, trickle-bed reactors; gas dispersed as bubbles in a continuous phase, for example, bubble column and slurry reactors; and liquid dispersed as droplets in a continuous gas phase, for example, spray column reactors. Some examples of industrial and pilot scale systems where backmixing is significant are illustrated in Table 1; others are presented by Ostergaard (1968). When we characterize the backmixing in both the gas and liquid phases, it is essential to properly identify the flow regime, the nature of the gas-liquid flow, and the role of a third phase (for example, solids in the case of three-phase slurry reactors), if any. For example, the liquid-phase backmixing in a wetted wall column reactor is considerably different from

TABLE 1. SYSTEMS WHERE BACKMIXING IS IMPORTANT

System 1	Controlling mechanism 2	Contactor 3	Phase in which backmixing is important 4	Remarks 5	References 6
Removal of lean H_2S from a variety of streams	Gas film	Packed column	G	High degree of removal; outlet H_2S has to be generally less than 5 ppm	Danckwerts and Sharma (1966)
Hydrodesulfurization of heavy petroleum fractions	Liquid film (surface reaction)	Packed bed (trickle bed)	L		Schuit and Gates (1973) Henry and Gilbert (1973)
Hydroformylation of olefins for the manufacture of aldehydes and alcohols (Rh ligands as catalyst)	Liquid film	Bubble column	L and G		Olivier and Booth (1970)
Absorption of SiF_4/HF from air in water	Gas film	Spray column	G	High degree of removal of fluoro compounds	Sherwin (1954)
Removal of lean SO_2 from a variety of streams	Gas film	Packed column	G	High degree of removal of SO_2	Kohl and Resenfield (1974)
Absorption of SO_2 in an aqueous slurry of magnesium oxide and calcium carbonate	Gas film and liquid film	Three phase fluidized bed, slurry reactor	G	High degree of SO_2 absorption	Douglas (1964), Uchida et al. (1975), Sada et al. (1977), Volpicelli and Massimilla (1970)
Oxidation of SO_2 on wetted carbon	Liquid film	Packed bed (trickle bed)	L		Hartman and Coughlin (1972)
Absorption of lean SO_3 in aqueous H_2SO_4 as well as aromatic substances for sulfonation	Gas film	Packed column, agitated contactor	G	High degree of removal of SO_3	Duecker and West (1959), Johnson and Crynes (1974)
Chlorination of variety of organic compounds—paraffins, benzene, toluene, phenols, etc.	Liquid film (very slow, slow or fast reaction)	Bubble column, packed bubble column, agitated contactor	G and L	Almost complete utilization of Cl_2 desired	Hawkins (1965), Ratcliffe (1966), Chua and Ratcliffe (1970), Pangarkar and Sharma (1974)
Liquid phase oxychlorination of ethylene for the production of vinyl chloride; manufacture of vinyl chloride from ethylene (or ethane), Cl_2 (or HCl) and O_2 (or air) by absorption in melts of CuCl/$CuCl_2$	Liquid film	Bubble column			Friend et al (1968), Ramachandran and Sharma (1971)
Removal of phosphine from C_2H_2 by absorption in aq. NaOCl or H_2SO_4	Liquid film (fast reaction)	Packed column	G	Very high degree of PH_3 removal (down to 1 ppm)	Chandrasekaran and Sharma (1977)
Removal of CO_2 by absorption in solutions of alkanolamines	Liquid film (fast reaction)	Packed column	G	In fertilizer plants the outlet concentration of CO_2 has to be reduced below 500 ppm	Danckwerts and Sharma (1966)

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Table 1. (cont'd.)

System 1	Controlling mechanism 2	Contactor 3	Phase in which backmixing is important 4	Remarks 5	References 6
Absorption of CO_2 in ammoniated brine for the manufacture of soda-ash	Liquid film (fast reaction; v. slow reaction in bulk)	Bubble column (sectionalized)	L		Danckwerts and Sharma (1966), Kafarov et al (1976), Todt et al. (1977)
Absorption of CO_2 in aqueous Na_2CO_3 for the manufacture of $NaHCO_3$	Liquid film (slow reversible reaction)	Bubble column (sectionalized)	L		Danckwerts and Sharma (1966)
Simultaneous absorption of NH_3 and CO_2	Liquid film and gas film	Bubble column, packed column	G L		Ramachandran and Sharma (1971)
Coal liquefaction	Liquid film	Three phase slurry and packed bed reactor (solid as reactant as well as catalyst)	L and S		Author's own work
Absorption of CO in CH_3OH for the manufacture of acetic acid	Liquid film or very slow reaction	Bubble column	L		von Kutepow et al. (1965), Hjortkjaer and Jensen (1976)
Methanol production from synthesis gas; methanation and water-gas shift reaction of CO	Liquid film	Three phase fluidized-bed reactor	L and G		Sherwin and Frank (1976), Frank (1977)
Absorption of lean $COCl_2$ in aqueous alkaline solutions	Liquid film, gas film	Packed column	G	High degree removal of $COCl_2$, outlet concentration has to be less than 1 ppm	Ramachandran and Sharma (1971)
Absorption of nitrous gases NO_x in water and aqueous alkaline solutions	Liquid film (slow or fast reaction)	Packed column Plate column	G, L	High degree of NO_x removal required	Kramers et al. (1961), Kameoka and Pigford (1977), Teramoto et al. (1977)
Air oxidation of molten benzoic acid in the presence of cuprous benzoate	Liquid film (fast reaction)	Bubble column	L		van Direndonck et al. (1974, 1975)
Oxidation of acetic acid by copper chromite catalyst, oxidation of formic acid	Liquid film	Packed bed (trickle bed)	L		Goto and Smith (1975), Levec and Smith (1976)
Oxidation of sulphide liquor (black liquor) with air	Liquid film (very slow reaction in the bulk)	Bubble column	L	Na_2S concentration has to be reduced to very low value	Chandrasekaran and Sharma (1974)
Oxidation of *p*-nitrotoluene sulfonic acid	Very slow reaction in the bulk	Bubble column; agitated contactor	L	Yields of the main reaction affected by backmixing	Carleton et al. (1969)
Air oxidation of aldehydes dissolved in corresponding acids	Liquid film (slow or fast reaction)	Bubble column	L	High degree of aldehydes conversion desired	Ladhabhoy and Sharma (1969, 1970)

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Table 1 (cont'd.)

System 1	Controlling mechanism 2	Contactor 3	Phase in which backmixing is important 4	Remarks 5	References 6
Ozonolysis of unsaturated compounds, treatment of waste water containing phenolic and other substances with ozonized air/O_2	Liquid film (slow or fast reaction)	Sieve plate column, bubble column mechanically agitated contactor	L, G	High degree of O_3 removal	Lowndes (1971), Throckmorton and Pryde (1972), Prengle et al. (1975)
Hydrogenation of a-methyl styrene	Liquid film	Trickle bed and slurry reactors	L		Sherwood and Farkas (1966), Germain et al. (1974)
Hydrogenation of benzene	Liquid film	Packed bed (trickle bed)	L		Dufau et al. (1964)
Hydrotreating and hydrocracking of heavy gas oils	Liquid film	Packed bed (trickle bed)	L		Henry and Gilbert (1973)
Hydrogenation of cat cracked furnace oil, lube oil distillates, and aromatics in a naphthenic lube oil distillate	Liquid film	Packed bed (trickle bed)	L		Satterfield (1975)
Absorption of dilute NH_3 in acidic solutions for making fertilizers	Gas film	Spray column	G		Sauchel (1960)
Absorption of ethylene (or propylene) and Cl_2 in water for the manufacture of chlorohydrin	Liquid film (very fast reaction)	Bubble column	L and G		Saeki et al. (1972)
Isomerization of cyclopropane	Liquid film	Packed bed (trickle bed)	L		Satterfield (1975)
Absorption of isobutylene, butenes in aqueous solutions of H_2SO_4	Liquid film (slow or fast reaction)	Bubble column	L and G		Gehlawat and Sharma (1968), Deckwer et al. (1977), Deckwer (1977)
Alkylation of phenols with isobutylene diluted with inert gas	Liquid film (slow or fast reaction)	Bubble column, agitated contactor	L and G		Gehlawat and Sharma (1970)
Reaction between C_3H_6 and peracetic acid to give propylene oxide	Liquid film (slow or fast reaction)	Sectionalized bubble column	L		Yamagishi et al. (1976)

that in a trickle-bed reactor, even though both can be characterized as film reactors. In a mechanically agitated slurry reactor with an L_o/d_t (reactor length to diameter ratio) of 1 and under intense agitation, the gas phase may well move in a plug flow manner, (Juvekar and Sharma, 1973, Niiyama and Smith, 1976) whereas in the absence of solids, the gas phase is found to be backmixed.

The purpose of this review is to evaluate various aspects of backmixing in gas-liquid and gas-liquid-solid reactors which would be useful to the engineer engaged in these types of reactor design. In this review, we first briefly outline the numerous techniques for measuring the residence time distribution (RTD) of the various phases in a multiphase reactor. Models for characterizing the backmixing from the RTD are reviewed next. This is then followed by an analysis of the backmixing characteristics of various gas-liquid columns such as trickle beds, sparged columns, mechanically agitated columns, plate columns, fluidized-bed columns, etc. The performance of a bubble column reactor under various reaction conditions is evaluated. The criteria for the elimination of backmixing in trickle-bed reactors are presented, and the effect of backmixing on the multiple steady states of the gas-liquid reactors is briefly reviewed. Finally, the scale-up problems associated with reactors with various degrees of backmixing are outlined.

RESIDENCE TIME DISTRIBUTION AND BACKMIXING MODELS

Methods for Measuring Residence Time Distribution (RTD)

The backmixing characteristics of various phases in a multiphase reactor are evaluated from the residence time distribution of a tracer injected into the phase of interest. These tracer techniques usually involve the injection of a tracer at one or more locations in the system and detection of its concentration as a function of time at one or more downstream positions. Various types of tracer inputs such as step, pulse, imperfect pulse, sinusoidal, ramp, and parabolic have been employed. The equivalance of the pulse and step residence time measurements in a trickle-bed reactor is shown by Rothfeld and Ralph (1963). Bennett and Goodridge (1970) employed an unusual type of input signal, that is, a step decrease in the concentration of tracer in the liquid entering the bed. The selection of the proper tracer for a given system is extremely important so that the RTD is characteristic of the flowing phase and is not influenced by the tracer. The basic requirements for a satisfactory tracer experiment are:

1. The tracer should be miscible in and have physical properties similar to the fluid phase of interest, and it should not be transferrable to the other phase or phases in the system.
2. The tracer should be accurately detectable in small concentrations so that only a small quantity need be injected into the system, thus minimizing disturbances in the established flow patterns. Also, a concentration range which yields a linear response on the detection equipment is advantageous, since this eliminates the need for prior calibrations.
3. Normally, the tracer should be nonreacting so that the analysis of the RTD is kept simple. However, Parimi and Harris (1975) have developed a technique for identifying residence time models from reacting tracer experiments.
4. The tracer detection device should cause the least amount of disturbances in the flow patterns as possible.
5. For detecting tracers in fast moving phases, good sensitivity and quick response time of the detection and recording equipment are needed.

The nature of the tracer selected usually dictates the detection system. For the liquid phase, quite often the tracers (for example, sodium chloride, sulfuric acid, etc.) are such that the detection probe is inserted directly into the reactor, and continuous monitoring of the tracer concentration at any fixed position is obtained by means of an electrical conductivity cell and a recorder. If the tracer concentration measurement requires an analytical procedure such as titration, etc., sampling of the liquid phase is required. For the solid phase, a magnetic tracer is sometimes used. The concentration of a solid phase tracer can also be measured by a capacitance probe if the tracer material has a different dielectric constant than the solid phase. In general, however, for solid and sometimes gas phases, some suitable radioactive tracer is convenient to use. If the proper safety precautions are enforced, the use of a radioactive tracer has a distinct advantage over other tracers in that the tracer detection devices can be placed externally. In this way, no disturbances in the established flow patterns resulting from the presence of probes or sampling devices are encountered. Also, the use of a radioactive tracer permits the RTD of a fast moving phase to be accurately and conveniently measured, since scintillation detectors can be interfaced with high speed recorders or with multichannel analyzers with data storage capabilities. Some of the tracers for the gas, liquid, and solid phases reported in the literature are summarized in Table 2.

As indicated earlier, the tracer should be normally nonreacting. However, several reactant tracer techniques are worth noting. Denbigh et al. (1962) suggested a "time reaction" technique which produces a dye solution for visualizing the flow pattern. They used potassium iodate and a solution of sodium sulfite with a little starch paste to liberate an iodide starch reaction. Later, Danckwerts and Wilson (1963) modified this method by using sodium persulfate, potassium iodine, sodium thiosulfate, and starch. Goldfish et al. (1965) proposed a flash photolysis method for RTD measurement. This method employs a lightly colored dilute solution which undergoes a chemical reaction. In this method the tracer is in-situ of the reactor, so it avoids the disturbance of flow patterns normally encountered during an injection of the tracer. Finally, Baird et al. (1976) illustrated visual techniques which use the observation of an indicator color change due to chemical reaction. They suggested that, in principle, any instantaneous ionic reaction could be used, but the acid base reactions with phenolphthalein as an indicator give satisfactory results.

Backmixing Models

Once the data for the residence time distribution are obtained, the backmixing characteristics for each phase of a multiphase reactor can be quantitatively evaluated by fitting appropriate models to these data. The models for backmixing can be largely divided into two categories: differential models and stagewise models. The differential models result in differential equations, whereas with steady state conditions, stagewise models result in algebraic equations. The parameters describing the backmixing in these two types of models are usually equivalent. The following sections evaluate the macromixing models for various gas-liquid reactors. The models vary in their complexities, with the simplest being the axial dispersion model and the tanks in series model, both of which use only one parameter to correlate the RTD data. More complex models using two and three parameters are also briefly discussed.

Axial Dispersion Model. The axial dispersion model characterizes the backmixing by a simple, one-dimen-

Table 2. Tracers Commonly Employed in Gas-Liquid-Solid Flow Studies

A. Liquid phase tracers

System	Tracers	Detection apparatus	Reactor	Reference
Air-water	$MgSO_4$ KCl HCl	Titration	Packed bed	Lapidus (1957)
Air-water	HCl	Electrical conductivity	Packed bed	Kunugita et al. (1962)
Air-water	H_2SO_4	Electrical conductivity	Packed bed and bubble column	Stiegel and Shah (1977*a*, *b*)
Air-water	NH_4Cl	Electrical conductivity	Packed bed	Hoogendoorn and Lips (1965)
Air-water	NaCl	Electrical conductivity	Packed bed	Charpentier et al. (1971), Furzer and Michell (1970), Michell and Furzer (1972*a*), Van Swaaij et al. (1969),
Air-water	Methylene blue dye	FEK-M Photoelectric colorimeter	Packed bed	Shestopalov et al. (1964)
Air-water	Methylene blue dye	Spectrophotometer	Packed bed	Anderson et al. (1966)
Air-water	Iodine 131	Baird Atomic Model 812B Scintillation detector	Packed bed	Sater and Levenspiel (1966)
N_2-methanol	KSCN	Electrical conductivity	Packed bed	Hochman and Effron (1969)
Air-water	NaCl	Canalco conductivity meter	Packed bed	Co and Bibaud (1971)
Air-water	Concentrated salt solution	Conductivity meter	Bubble column	Eissa et al. (1971)
Air { water glycerine-water soln tween 20-water soln	Heat, 3N KCl	Copper-constantan Thermocouples Electrical conductivity	Bubble column	Aoyama et al. (1968)
Air { water 8% aq MeOH 15% aq MeOH 53% aq MeOH 35% cane-sugar 50% cane-sugar	KCl	Conductivity	Bubble column	Hikita and Kikukawa (1974)
Air-water	1-1.5N KCl	Electrical conductivity	Bubble column	Kato and Nishiwaki (1972)
Air { water water NaCl soln	NaCl p-sulfobenzeneozo-β naphthol	Electrical conductivity spectrometer	Bubble column	Reith et al. (1968)
Air-water	4N KCl	Electrical conductivity	Bubble column	Ohki and Inoue (1970)
Air-water		Electrical conductivity	Screen packed bubble column	Chen (1972)
Air-water	H_2SO_4	Electrical conductivity	Bubble column	Alexander and Shah (1976)
Water-nitrogen	KCl	Potentiometric titrations	Bubble column	Argo and Cova (1965)
Water-ammonia synthesis gas	NaCl			
Water Acetone CCl_4 Cyclohexanol Ethanol 11% aq ethanol 50% sugar-water } N_2	Heat	Iron-constantan thermocouples	Bubble column	Cova (1974)
Air-water	NaCl	Phillips type PR 9507 conductivity transmitter	Bubble column	Eissa and Schügerl (1975)
Water 0.225 N Na_2SO_4 0.7 N Na_2SO_4 0.17 N NaCl aq molasses soln } Air	Electrolytes, heat, dye		Bubble column	Deckwar et al. (1974)
Air-water	NaCl	Pt electrode	Bubble column	Gondo et al. (1973)

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TABLE 2. (cont'd.)

Tracers	Detection apparatus	System	Reactor	Reference
Air-water	KCl	Electrical conductivity	Slurry reactor	Kato et al. (1972)
Air-water-glass beads	NaCl	Infrared analyzer	Fluidized bed	Schügerl (1967)
Air-water-glass ballotini	Bromine 82	Scintillation detector	Fluidized bed	Ostergaard and Michelsen (1969) Michelsen and Ostergaard (1970*a*)
		B. Gas phase tracers		
Air-H_2O	Helium	Sargent oscillometer (measured strength)	Packed bed	Lapidus (1957)
Air-H_2O	Helium	Thermal conductivity cell	Packed bed	Kunugita et al. (1962)
Air-H_2O	Argon 41	Baird-Atomic Model 812B Scintillation Detector	Packed bed	Sater and Levenspiel (1966)
N_2-methanol	Helium	GowMac Thermal Conductivity Detector	Packed bed	Hochman and Effron (1969)
Air-water	Krypton 85	Anton type 108 CG-M counter	Packed bed	Deckwer et al. (1974)
Air-water-glass beads	CO_2, He	Infrared analyzer	Fluidized bed	Schügerl (1967)
Air-water-glass ballotini	Argon 41	Scintillation detector	Fluidized bed	Ostergaard and Michelsen (1969) Michelsen and Ostergaard (1970*a*)
		C. Solid phase tracers		
Air-water-glass spheres		External sampling	Slurry reactor	Kato et al. (1972)
Glycerine soln } Air water	Glass spheres ion exchange resin $FeSiO_2$ powder, Cu powder	External sampling of solid-liq soln at various points	Slurry reactor	Imafuku et al. (1968)
Air-water-coal	La^{138}	Radioactive tracer detector	Batch three-phase fluidized bed	Our own unpublished work

sional, Fick's law type of diffusion equation. The constant of proportionality in this equation is commonly known as the axial dispersion coefficient. The assumption that all the mixing processes follow Fick's law type of diffusion equation, regardless of the actual mechanism, of course, becomes increasingly dubious with large degrees of backmixing. However, since the model characterizes the backmixing by only a single parameter, its simplicity has made it the most widely used model. The dispersion coefficient is expressed in the dimensionless form as the Peclet number ($Pe = UL_c/E_Z$). In a bubble or spray column, L_c could be either the diameter of the column or the diameter of the bubble. For flow through a fixed bed, L_c is usually the characteristic diameter of the packing. Under this situation, Pe is often denoted as the Bodenstein number. The value of the Peclet (or Bodenstein) number denotes the degree of backmixing. If $Pe = 0$, backmixing is complete, and for $Pe = \infty$, plug flow prevails.

For a multiphase reactor, the backmixing in each phase is considered separately. In a gas-liquid reactor, a considerably different degree of backmixing can exist in each phase. For example, in a bubble column reactor, the backmixing in the fast moving gas phase is considerably smaller than in the slow moving liquid phase. In small scale reactors, the gas phase is usually assumed to move in plug flow.

In a bubble column reactor, significant backmixing in the liquid phase is caused by the gas flow. Furthermore, the backmixing increases with the diameter of the reactor (that is, usually more backmixing occurs in commercial reactors than in pilot scale reactors). The design of a bubble column reactor always requires consideration of the backmixing in the liquid phase. For gas-liquid flow through a packed column, the degree of backmixing in the liquid phase depends strongly upon the flow regime, flow rates of various phases, and the packing characteristics, and is insensitive to the size of the column. Backmixing in most commercial trickle-bed reactors is not important. In a pilot scale trickle-bed, reactor, however, the backmixing could be important because of low liquid flow rates. Some information on the backmixing in the solid and liquid phases in slurry reactors (that is, three-phase fluidized beds) is also available.

Commercial reactors are nonisothermal and often adiabatic. In a nonisothermal gas-liquid reactor, along with the mass dispersions in each phase, the corresponding heat dispersions are also required. Normally, the gas and liquid at any given axial position are assumed to be at the same temperature. Thus, unlike in the case of mass, only a single heat balance equation and the corresponding heat dispersion coefficient are needed. Under turbulent flow conditions such as in the bubble column reactor, the Peclet number for the heat dispersion is often assumed to be approximately equal to the Peclet number for the mass dispersion in a slow moving liquid phase.

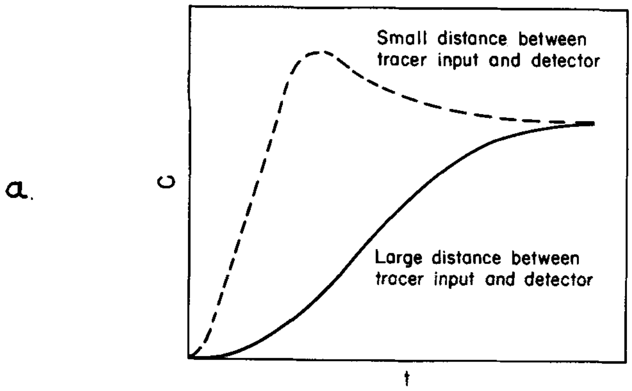

Fig. 1*a*. Residence time distribution for a pulse input of tracer in a batch system or a step input of tracer in a flow system.

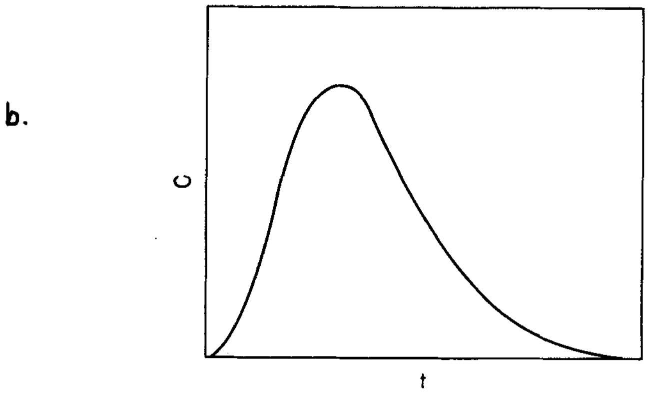

Fig. 1*b*. Residence time distribution for a pulse input of tracer in a flow system.

The standard axial dispersion model is a one-dimensional model which neglects radial dispersion as well as nonuniform velocity distributions. For a single-phase flow, the effects of the parabolic or nonuniform velocity profiles generated from nonuniform cross-sectional tubes have been theoretically examined (Aris, 1956; Bischoff, 1968). The effect of velocity profile on the axial dispersion in packed beds has also been investigated (Converse, 1960). The model is also applied by Kostanyan (1974) to a tube with several mixing zones. Nishiwaki and Kato (1974) and Nishiwaki et al. (1973) have modified the dispersion model by a multistage dispersion model wherein the backmixing is characterized by two parameters, that is, the Peclet number for each stage and the number of stages. The two parameters allow more flexibility in correlating the experimental data. This model is more useful for the reactor with nonuniform mixing characteristics.

Methods for Evaluating the Axial Dispersion Coefficient from RTD Data. As mentioned earlier, the one-parameter axial dispersion model is widely used to correlate the RTD data obtained from tracer techniques. The shape of the RTD depends upon the type of tracer input employed and the nature of the flow characteristics in the system. Two common types of observed RTD curves are shown in Figure 1. In a batch bubble column or a batch three-phase (gas, liquid, and solid) fluidized bed (where only the gas phase is flowing), the RTD curves for the liquid and solid phases will be, in general, of the type shown in Figure 1*a*. As shown by the dotted curve in the same figure, a very small distance between the tracer injection and detection points will give a maximum in the RTD curve. The axial dispersion coefficients for the liquid or solid phases can be obtained by fitting the equation

$$C/C_E = 1 + 2 \sum_{n=1}^{\infty} \left[\left(\cos \frac{n\pi}{L_B} L_Z \right) \exp\left(-n \frac{2\pi^2}{L_B^2} E_Z t \right) \right] \tag{1}$$

to this type of RTD curve (Ohki and Inoue, 1970).

When the phase under consideration is flowing, and its extent of backmixing is intermediate between plug and completely mixed flow, any type of pulse tracer input will yield a Gaussian type of RTD curve similar to that of Figure 1*b*. However, when a step tracer input is used, the RTD curve of the type in Figure 1*a* will be observed for any flowing phase. In a vast majority of experimental studies, the backmixing characteristics of a flowing phase are examined with the use of a pulse tracer input.

If a perfect pulse input is employed for a packed-bed system, the axial dispersion coefficient or the Peclet number can be obtained, as shown by Levenspiel (1972), from the variance of the RTD curve. For example, for a closed system and large extents of dispersion, the variance σ_θ^2 is related to Peclet number as

$$\sigma_\theta^2 = \frac{1}{t_m^2} \int_0^\infty (t - t_m)^2 E(t)\, dt = \frac{2}{Pe} - \frac{2}{Pe^2}(1 - e^{-Pe}) \tag{2}$$

where t_m is given by the normalized first moment of the RTD curve $E(t)$ and $Pe = UL/E_Z$.

Although the above method can give a simple evaluation of the Peclet number for the system, tailing in the RTD curve can cause significant inaccuracies in the evaluation of the Peclet number. Michell and Furzer (1972*a*) suggested that a better estimation of the axial dispersion coefficient is obtained if the observed RTD is correlated statistically to the exact solution of the axial dispersion model equation with appropriate boundary conditions. Their time-domain solution of the axial dispersion model for the RTD is

$$C = \frac{M}{a_c\sqrt{4\pi E_Z t}} \exp\left[\frac{-(L_Z - Ut)^2}{4E_Z t} \right] \tag{3}$$

These authors claim that an accurate estimation of E_Z can be obtained by applying a nonlinear regression analysis to the data using the above equation.

In practice, it is very difficult to introduce a perfect pulse of tracer into the system. In order to eliminate the necessity for a perfect pulse of tracer, the tracer detection measurements are often carried out at two downstream positions. As shown by many investigators (Aris, 1959; Bischoff and Levenspiel, 1962; Levenspiel and Smith, 1957; Sater and Levenspiel, 1966; van der Laan, 1958), the axial dispersion coefficient can be calculated from the first and second moments of the RTD curves at two positions. The first and second moments are given by

$$\mu_i = \left(\frac{U}{L} \right) \frac{\int_0^\infty C_i(t)\, t\, dt}{\int_0^\infty C_i(t)\, dt} \qquad i = 1, 2 \tag{4}$$

and

$$\sigma_{\theta i}^2 = \left(\frac{U}{L} \right)^2 \frac{\int_0^\infty C_i(t)\, t^2 dt}{\int_0^\infty C_i(t)\, dt} - \mu_i^2 \qquad i = 1, 2 \tag{5}$$

Since the first moment of the response curve is essentially the mean of that curve, the average residence time of the tracer can be calculated by taking the difference of the first moments of the response curves

$$t_m = \left(\frac{L}{U}\right)(\mu_2 - \mu_1) \tag{6}$$

The second moment of the response curves indicates the spread of the RTD curve, and the difference of the second moments is a measure of the amount of backmixing occurring between the two measuring points. For the open system, the second moment has been derived analytically by Levenspiel and Smith (1957):

$$\sigma_\theta^2 = 2\left(\frac{E_Z}{UL}\right) + 8\left(\frac{E_Z}{UL}\right)^2 \tag{7}$$

Aris (1959) has shown that for a one-shot injection of tracer, the above equation can be simplified, without introducing any significant error, to

$$\Delta\sigma_\theta^2 = \sigma_{\theta_2}^2 - \sigma_{\theta_1}^2 = 2\left(\frac{E_Z}{UL}\right) \tag{8}$$

Several aspects of the above method of moments are discussed by Butt (1962). In this method also, the tailing in the RTD curves can cause significant errors in the calculation of the Peclet number. An analysis involving the Laplace transform of the axial dispersion model and the evaluation of a linear transfer function is described by Ostergaard and Michelsen (1969) and Michelsen and Ostergaard (1970*a*). These investigators claim that this method produces much more consistent results than the methods of moments, regardless of the severity of the tailing and the location of the cutoff point of the tail. According to this method, the transfer function for a stable, one-dimensional linear system can be calculated from

$$F(s) = \frac{C_2(s)}{C_1(s)} = \frac{\int_0^\infty C_2(t)\exp(-st)\,dt \Big/ \int_0^\infty C_2(t)\,dt}{\int_0^\infty C_1(t)\exp(-st)\,dt \Big/ \int_0^\infty C_1(t)\,dt} \tag{9}$$

where $F(s)$ can be defined from the Laplace transform of the axial dispersion model (Ostergaard and Michelsen, 1969)

$$F(s) = \exp\left\{\frac{Pe}{2}\left[1 - \left(1 + \frac{4st_m}{Pe}\right)^{1/2}\right]\right\} \tag{10}$$

where $Pe = UL/E_Z$. Upon rearranging, one obtains

$$\left[\log\left(\frac{1}{F(s)}\right)\right]^{-1} = t_m s\left[\log\left(\frac{1}{F(s)}\right)\right]^{-2} - \frac{1}{Pe} \tag{11}$$

A plot of $\log\left[\left(\frac{1}{F(s)}\right)\right]^{-1}$ vs. $(s)\log\,[(1/F(s))]^{-2}$ from the above equation should yield a straight line if the axial dispersion model is applicable. The slope and intercept yield the values of the average residence time t_m and Peclet number, Pe. Michelsen and Ostergaard (1970*a*) subsequently proposed three additional methods for calculating the mean residence time and Peclet number based upon numerical evaluation of the transfer function and its derivative for a number of values of the Laplace transform parameter st_m.

Hopkins et al. (1969) showed that the range of s over which this regression is carried out is very important. For small values of s, although the value of the transfer function can be accurately determined, it becomes insensitive to variations in the parameters, and hence small errors in the transfer function are magnified in estimating the parameters. For large values of s, the initial part of the signal, like the tail, has a large relative error and is too heavily weighted, resulting in an inaccurate evaluation of the transfer function. They suggested that the optimum range of s is that for which st_m lies between 2 and 5. Andersen and White (1970) further considered the weighting that this regression technique gives to errors in the time domain. They suggested alternate methods for treating RTD data which considered unequal weighing of the data in the time domain, thereby minimizing the error due to tailing of the RTD curve.

Other methods are also available for the evaluation of the axial dispersion coefficient. Clements (1968) and Michelsen (1972) suggested a least-square method for the evaluation of the axial dispersion coefficient from the RTD obtained with a Dirac-Delta function input. A frequency response method is also suggested by Kramers and Alberda (1953). Johnson et al. (1971) have shown a comparison of the moments, S plane, and frequency response methods for analyzing pulse testing data from flow systems. Gibilaro and Lees (1969) illustrated a method for the reduction of complex transfer function models to simple models using the method of moments. Finally, Vergnes (1976) has outlined a simple method for the determination of the Peclet number when the tracer injection is sharp enough to be considered as a δ impulse, and the system is described as reasonable by the solution of the dispersion model for an open system.

In all of the methods for the determination of the axial dispersion coefficient from the RTD curves described above, one injection and one or two detection points are employed. Midoux and Charpentier (1972) have outlined a method wherein two very similar injections at two different axial positions in the column and one detection point for the tracer are used. They applied this method for the fast moving gas phase in a gas-liquid column.

Finally, it should be noted that although all of the above methods are restricted mainly to impulse, pulse, and imperfect pulse tracer inputs, in general, they can be applied to any arbitrary input. The RTD for an arbitrary input can be obtained from the convolution integral:

$$E(t) = \int_0^t G(\lambda)F(t-\lambda)\,d\lambda \tag{12}$$

The axial dispersion coefficient can also be obtained from the steady state concentration vs. distance profile of the tracer. This method, among others, has been used by Watson and McNeese (1972), Shestopalov et al. (1964), Kato et al. (1972), Imafuku et al. (1968), and Deckwer et al. (1973).

Modified Mixing Cell Model: Deans and Lapidus, 1960a, b; Deans, 1963. This model is an extension of the "perfectly mixed cells in series" model of Deans and Lapidus (1960*a*, *b*). The model assumes that each cell contains stagnant and flowing regions. Owing to backmixing, mass exchange between the flowing and the stagnant regime occurs. When the number of cells is very large, the model can be represented by differential equations (Deans and Lapidus, 1960*a*, *b*; Deans, 1963). If the differential equations are solved for a pulse injection of tracer, the equation representing the tracer RTD is

$$E(t) = \exp(-kt_m)\delta(t - t_i) + \left(\frac{k^2 t_m}{f}\right)$$

$$\exp\left\{ -kt_m\left[2+\left(\frac{\mathrm{t}-t_m}{ft_m}\right)\right] \right\}$$

$$\left\{ I_1\left[2kt_m\left(1+\frac{t-t_m}{ft_m}\right)^{1/2}\right] \Big/ \; kt_m\left(1+\frac{t-t_m}{ft_m}\right)^{1/2} \right\} \tag{13}$$

The model requires two arbitrary parameters, f and k, to describe the extent of liquid backmixing. The relationships between f and k and the characteristics of the experimental residence time distribution curve have been developed by many workers. f can be calculated from

$$f = 1 - (t_i/t_m) \tag{14}$$

Furthermore, the variance of the RTD is given by

$$\sigma_\theta^2 = \frac{2f^2}{kt_m} \tag{15}$$

Thus, k can be calculated by combining Equations (14) and (15). This model has been successfully applied to the liquid phase dispersion in the film reactors (for example, trickle-bed reactors).

Crossflow Model. Conceptually, this model is very similar to the "modified mixing cell model" of Deans. It is, once again, largely applied to the liquid phase backmixing in trickle-bed reactors (Hochman and Effron, 1969; Hoogendoorn and Lips, 1965). The model is based on the assumption that the liquid phase is divided into two regimes: stagnant and plug flow. Possible areas where stagnant liquid might exist in trickle beds are at the top of packing particles, in the interstices between tightly packed particles, and between the packing and the wall of the reactor. The mass can be exchanged between the stagnant and flowing portions of the liquid, and the governing equations are derived from material balances for the two regimes:

$$\phi\frac{\partial C_d}{\partial t} + U_L\frac{\partial C_d}{\partial Z} + k(C_d - C_s) = 0 \tag{16}$$

$$(1-\phi)\,\frac{\partial C_d}{\partial t} - k(C_d - C_s) = 0 \tag{17}$$

Hoogendoorn and Lips (1965) have shown that ϕ can be obtained from the initial breakthrough of tracer

$$\phi = t_i/t_m \tag{18}$$

k can be calculated from

$$k = \frac{2(1-\phi)^2}{\sigma_\theta^2 t_m} \tag{19}$$

As can be seen, the above two parameters ϕ and k are similar to those of the modified mixing cell model. It has been shown (Schwartz and Roberts, 1973) that the parameter ϕ as calculated from the RTD agrees within experimental error with the ratio of the dynamic to the total external liquid holdup. This agreement lends physical support to the cross flow model.

Recently, Hofmann (1977) has extended the crossflow model by the addition of another term for the liquid phase dispersion resulting in a four-parameter model. As he has shown, the axial dispersion coefficients determined from the above two-parameter model possesses a minimum at some definite liquid loading which is indicative of two opposing mechanisms being combined to form a single parameter. This four-parameter model results in an axial dispersion coefficient which is independent of the liquid flow rate and can also be applied to the evaluation of the liquid flow in trickle-bed reactors.

Time Delay Model: Buffham et al., 1970; Buffham, 1971. This model is based on the concept of fluid elements being randomly delayed in time on their passage through the bed. The model is mainly applied to the liquid phase backmixing in a trickle-bed reactor. The model assumes that the liquid would move in plug flow except for the fact that the molecules have a chance of being delayed at many points while traversing the bed. The delayed molecules eventually rejoin the flow stream after a period of time has elapsed and continue with the main stream until delayed again. The developers contend that such a probabilistic model more realistically describes the physical basis for the spread of residence time distribution in trickle-bed reactors than the diffusion based models. The model is, however, in mathematical terms, equivalent to the modified mixing cell or cross flow models, in that they all lead to the same expression for the residence time distribution. Assuming that the delay times are distributed exponentially with a mean delay time t_D, the response to a pulse input of tracer can be shown to be

$$E(t) = \exp\left[\frac{(-t_m - t_i)}{t_D}\right]\delta(t - t_i)$$

$$+ \frac{1}{(t-t_i)}\exp\left[\frac{-t_m - t + 2t_i}{t_D}\right]$$

$$\sum_{\eta_o=1}^{\infty} [(t_m - t_i)(t - t_i)/t_D^2]^{2\eta_o - 1}/\eta_o!(\eta_o - 1)! \tag{20}$$

The delay time t_D can be estimated from the peak height or variance of the RTD. The parameter t_i may be estimated as the initial breakthrough time of the tracer or may be related to the time required to reach a normalized concentration of 0.05. A modified time delay model for flow in packed columns has been developed by Oorts and Hellinckx (1974).

5. Piston Diffusion Exchange, PDE, Model: van Swaaij et al., 1969. This model, which is largely used to correlate trickle-bed RTD data, is based on the same concept as the crossflow or modified mixing cell models, except that axial dispersion is present in the mobile phase. The model, therefore, contains three arbitrary parameters, two of which are the same as those used in the crossflow model, and the third being the axial dispersion coefficient (or the Peclet number in dimensionless form) in the mobile phase. Just as before, all three parameters in this model can be obtained from the experimentally measured RTD curve. For a complete discussion of the model and the relevant material balance equations and their solution, the readers are referred to the article by van Swaaij et al. (1969).

Stagewise Models. Unlike the differential models, the stagewise models basically represent the backmixing in a reactor by a series of tanks with either backflow or interstage circulation between the consecutive tanks. The complete or imperfect mixing in each stage has been considered. The number of tanks or stages along with the amount of backflow or the interstage circulation characterizes the degree of backmixing. In the limiting case of infinite number of tanks in series, plug flow will prevail.

Series of Stirred-Tanks Model or Tanks in Series Model. The series of stirred-tanks model (often referred to as the cell model) is perhaps the simplest type of stagewise model for the backmix reactor. In this model, the reactor is represented by a series of perfectly mixed stages. The degree of backmixing is characterized by the number of stages; the larger the number of stages, the lesser the overall degree of backmixing. Various aspects of this model have been discussed, among others, by Deans and Lapidus (1960*a*, *b*), Nishiwaki and Kato (1974), and Ham and Coe (1918).

A modification of the cell model is considered by Bang and Cholette (1973). They also assumed that a fraction, f_b, of the inlet fluid to each stage bypasses the stage. Furthermore, only a fraction ϕ_a of fluid entering a stage is agitated and the fraction $1 - \phi_a$ is stagnant. The overall backmixing characteristics of the reactor are thus characterized by three parameters, f_b, ϕ_a, and n_s, the number of stages. Bang and Cholette (1973) have shown that this three-parameter model is more versatile than the regular axial dispersion model.

Backflow Model. This generalized stagewise model assumes backflow, superimposed on the net flows through a column, with perfectly mixed stages in cascade. The model describes the backmixing in two-phase countercurrent operation. In this model, the dispersed phase may be treated as a second continuous phase. In the limiting cases of no backflow and the number of stages much larger than unity, this model reduces to the stage model (or perfectly mixed cells in cascade) and the diffusion model (or axial dispersion model for two phases), respectively. The model has been applied successfully to correlate the longitudinal dispersion coefficient for the continuous phase in pulsed sieve plate columns. Various aspects of this model are discussed by Miyauchi and Vermeulen (1963), Sherwood and Jenny (1935), Sleicher (1960), Nishiwaki and Kato (1972, 1974), and Nishiwaki et al. (1973).

A simple extension of the backflow model is considered by Nishiwaki et al. (1973) who assumed each stage to be backmixed but not perfectly mixed. The backmixing in each stage was assumed to be expressed by the dispersion model. This model is thus named the dispersion/backflow model. A comparison of this model with the dispersion model is given by Nishiwaki and Kato (1974).

Interstage Recirculation Model. Conceptually, this model is very similar to the backflow model. The backmix reactor is represented by a series of perfectly mixed stages with recirculation between the two stages. The number of stages and the degree of interstage recirculation characterize the degree of backmixing of the entire reactor. This model is discussed by Mecklenburgh (1974).

Other Models. Besides the differential and stagewise models discussed above, there are several other models (Yagi and Miyauchi, 1955; Schmalzer and Hoelscher, 1971; Michell and Furzer, 1972*b*; Raghuraman and Varma, 1973; Rao and Varma, 1976) reported in the literature. Schmalzer and Hoelscher (1971) reported a stochastic model for the mixing process. The liquid phase mixing in trickle-bed reactors is also evaluated by a single-parameter "by-pass model" of Michell and Furzer (1972*b*) and four-parameter models of Raghuraman and Varma (1973) and Rao and Varma (1976). The macromixing in an agitated reactor can be characterized by the so-called recycle flow with crossmixing model. Various aspects of this model are discussed by Mah (1971), Hochman and McCord (1970), Gibilaro (1971), Gibilaro et al. (1967), Cholette and Cloutier (1954), and Gibilaro and Lees (1969). Various macromixing models for an agitated reactor are also reviewed by Wen and Fan (1975).

The stagewise and differential models can be related to each other. For some problems, differential models are better (for example, trickle-bed reactor) than the stagewise models, and vice versa. There are, however, cases intermediate between differential and stagewise backmixing (for example, tubular reactors partly compart-

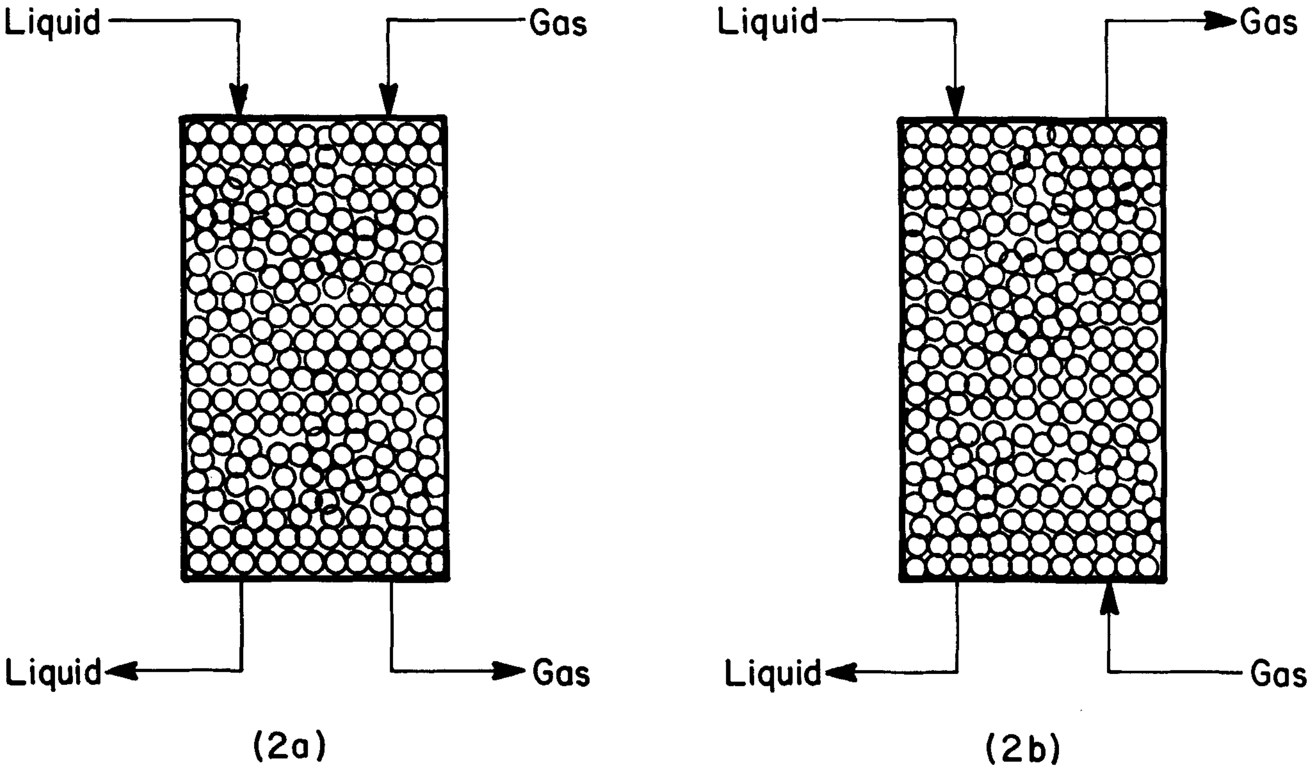

Fig. 2. Schematic diagrams of packed-bed, gas-liquid film reactors: (a) concurrent downflow operation, (b) countercurrent operation.

TABLE 3. SUMMARY OF EXPERIMENTAL BACKMIXING STUDIES IN PACKED-BED FILM REACTORS

Investigator	Packing size, m (× 100)	Reactor diameter, m	Reactor length, m	System and flow conditions
Michell and Furzer (1972*a*)	0.635, Raschig rings 2.54, Lessing rings 5.08, Raschig rings	0.051 0.61 0.61	1.52 1.22, 2.44, 1.22	Air-water countercurrent
Otake and Kunugita (1958)	0.787, 1.55; Raschig rings	0.051, 0.066	0.91, 1.46, 1.65	Air-water countercurrent
Kunugita et al. (1962)	1.02, 1.52, 2.03, 2.54, 2.54; Berl Saddles	0.14	1.01, 1.52	Air-water countercurrent
DeMaria and White (1960)	0.635, 0.953, 1.27; Raschig rings	0.102	1.37	Air-water countercurrent
Sater and Levenspiel (1966)	1.27, Raschig rings 1.27, Berl Saddles	0.102	3.66	Air-water countercurrent
Hochman and Effron (1969)	0.476, glass beads	0.152	1.98	Nitrogen-methanol concurrent
Furzer and Michell (1970)	0.635, Raschig rings	0.051	1.52	Air-water countercurrent flow
Co and Bibaud (1971)	1.27, 2.54; Raschig rings	0.127, 0.279	3.05	Air-water countercurrent
Dunn et al. (1977)	2.54, 5.08; Raschig rings 2.54, Berl Saddles	0.61	0.762, 1.52	Air-water countercurrent
Hoogendoorn and Lips (1965)	1.27, Raschig rings	0.406	1.52, 3.05	Air-water countercurrent
Shestopalov et al. (1964)	1 × 1, 1.5 × 1.5, 2.5 × 2.5, Raschig rings	0.246	1.5	Air-water countercurrent
Woodburn (1974)	2.5, Raschig rings	0.292	0.97	Air-water countercurrent
Charpentier et al. (1971)	0.3 nonporous glass sphere 0.3, porous molybdenum-cobalt alumina spheres	0.1	1.58	Air-water concurrent
Van Swaaij et al. (1969)	0.64, 1.03, 2.2; Raschig rings	0.1, 0.193 square	2.08, 2.1, 2.72	Air-water concurrrent and countercurrent
Anderson et al. (1966)	1.27; Raschig rings	0.305	0.91	Air-water countercurrent
Kramers and Alberda (1953)	1.02; Raschig rings	0.152	0.67	Air-water countercurrent
Polk and Clements (1966)	0.635; Raschig rings 0.635; Berl Saddles	0.121	0.84	Air-water countercurrent
Koen and Nel (1966)	0.635; Raschig rings 0.635; Berl Saddles	0.059, 0.0925	0.1-1.5	Air-water countercurrent
Dill'man et al. (1968)	1.52; Raschig rings	0.152	5.94	Air-water countercurrent
Schiesser and Lapidus (1961)	1.27; glass; spheres 1.27; porous and nonporous alumina 1.27; porous alumina 0.635; molecular sieve	0.102	0.91	Air-water
Mathur and Wellek (1976)	0.635, 0.935, 1.27; Raschig rings	0.102	0.91, 1.52	CO_2-N_2 mixture and water in countercurrent flow

mentalized by coils, segmented bubble column reactor, bubble column reactor with side streams, etc.). These cases are best handled by combining the two types of model discussed above.

CHARACTERIZATION OF BACKMIXING IN VARIOUS TYPES OF GAS-LIQUID REACTORS

Backmixing in Film Reactors

Under certain flow conditions, concurrent (downward) and countercurrent (liquid downward and gas upward) flows of gas and liquid over a fixed solid bed result in the conditions where the gas phase is continuous, and the liquid phase flows through the bed as a film over the solid packing. Similar flow conditions would exist in an open tube when the liquid is trickled down along the walls of the column, that is, wetted wall column reactor. These types of reactors are referred to as film reactors. Figures 2*a* and *b* present schematic diagrams of two methods of operating packed-bed, gas-liquid film reactors, namely, concurrent downflow and countercurrent flow. The film reactor and in particular the trickle-bed reactor, where both the gas and liquid flow downward over a packed bed, is one of the most widely used reactor for commercial hydroprocessing. Some aspects of the gas and liquid flow rates required for trickle flow condition are discussed by Ostergaard (1968), Kawagoe and Kawai (1968), and Sato et al. (1973).

A summary of the experimental backmixing studies for packed-bed film reactors is presented in Table 3. These studies have shown that, unlike for the single gas or liquid phase flow through a packed bed, significant backmixing occurs in both the gas and liquid phases in gas-liquid film reactors. When the RTD data are correlated by the single-parameter axial dispersion model, the axial dispersion coefficient (or Peclet number) for the gas phase is dependent upon the liquid and gas flow rates and the size and nature of the packings. The axial dispersion coefficient for the liquid phase is dependent upon the liquid flow rate and the nature and size of the packings. Schiesser and Lapidus (1961) have shown that the porosity of the packing could also significantly affect the liquid phase axial dispersion coefficient.

Concurrent Downflow Packed-Bed Reactors. The RTD data for this type of reactor are correlated by the axial dispersion model, as well as two-parameter (for example, crossflow, time delay, etc.) and three-parameter (PDE) models. When the RTD data are correlated by the axial dispersion model, the liquid phase Peclet number is correlated to the liquid phase Reynolds number and the Gallileo number. Polk and Clements (1966) presented the relation

$$Pe_L = 5.9\, Re_L{}^{1.35} Ga_L{}^{-0.72} \tag{21}$$

whereas Michell and Furzer correlated their data along with numerous other literature data by the relation

$$Pe_L = 1.00\, Re_L{}^{0.70} Ga_L{}^{-0.32} \tag{22}$$

Here, $Pe_L = U_L d_p / E_{ZL}$; $Re_L = d_p \rho_L U_L / \mu_L$, and $Ga_L = d_p{}^3 g \rho_L{}^2 / \mu_L{}^2$. The dependence of Pe_L and Ga_L outlined above should not be very reliable because all the experimental data were obtained with air-water systems only, and no variations in fluid properties were examined. Hochman and Effron (1969), however, employed a nitrogen-methanol system and correlated their data by

$$Pe_L = 0.042\, Re_L{}^{0.5} \tag{23}$$

where Pe_L is defined in terms of the actual fluid velocity and $Re_L = d_p G_L / \mu_L (1 - \epsilon)$. The above relation is very similar to the one proposed by Co and Bibaud (1971) who reported

$$Pe_L = \exp(-4.105)\,(Re_L)^{0.4313} \tag{24}$$

Here, Pe_L is defined in terms of the interstitial velocity, and $Re_L = d_p G_L / \mu_L$.

A few interesting features of the above correlations are noteworthy. The liquid phase axial dispersion coefficient is essentially independent of the gas flow rate. Except for the correlation of Polk and Clements (1966), all other relations indicate that the liquid phase backmixing coefficient increases with the liquid phase velocity. Finally, for a given value of Re_L, the Peclet numbers obtained from the above correlations are considerably smaller than those obtained for a single phase liquid flow in a packed column.

All the above correlations were obtained by analyzing the RTD curves with the axial dispersion model. Hochman and Effron (1969) employed the *crossflow model* in analyzing their RTD data. The results for the exchange coefficient k and the fractional flowing phase ϕ were correlated as

$$k = 0.01\, Re_L{}^{0.6}; \quad \sigma = \pm 37\% \tag{25}$$

$$\phi = 0.52\, Re_L{}^{0.08} 10^{0.001 Re_G}; \quad \sigma = \pm 8.5\% \tag{26}$$

Unlike the liquid phase Peclet number, the gas phase Peclet number has been found to be dependent upon both the gas as well as the liquid flow rates. Hochman and Effron (1969) presented the following correlation

$$Pe_G = 1.8\, Re_G{}^{-0.7} 10^{0.005 Re_L} \tag{27}$$

where

$$Re_G = \frac{U_G d_p}{E_{ZG}}, \quad Re_G = \frac{G_G d_p}{\mu_G (1 - \epsilon)}, \quad Re_L = \frac{G_L d_p}{\mu_L (1 - \epsilon)}$$

Woodburn (1974) studied the gas phase axial mixing at extremely high irrigation rates in a large packed absorption tower and showed that for $Re_L > 650$, the dispersion in the gas phase becomes essentially independent of liquid flow rate. As in the case of the liquid phase, considerably more axial dispersion has been observed for the gas phase in trickle beds as compared to those observed for single phase flow through a packed bed at the same gas phase Reynolds number.

Countercurrent Flow Packed-Bed Reactors. The literature data indicate that at the same liquid flow rate, countercurrent flow (liquid downward, gas upward) produces more axial dispersion in the liquid phase than concurrent flow. Sater and Levenspiel (1966) presented the following correlation for the liquid phase Peclet number:

$$Pe_L = 19.4 (Re_L)^{0.747} (Ga_L)^{-0.693} (a_s d_p)^{1.968} \tag{28}$$

Because of slight variations in the viscosity and surface area in their experimental measurements, the coefficients -0.693 and 1.968 are not very reliable. Sater and Levenspiel (1966) also presented an alternate, more reliable correlation; that is

$$Pe_L = 7.58 \times 10^{-3} (Re_L)^{0.703} \tag{29}$$

Considerable discrepancies exist in the literature on the gas phase axial dispersion coefficient. Sater and Levenspiel (1966) presented the relation

$$Pe_G = 3.4 (Re_G)^{-0.67} 10^{-0.0076\, Re_L} \tag{30}$$

whereas for the same values of Re_G, DeMaria and White (1960) obtained order of magnitude higher gas phase Peclet numbers. Their data were correlated by the relation

$$Pe_G = 2.4 (Re_G)^{-0.20}\, 10^{-(0.013 - 0.088\, d_p/d_t)} \tag{31}$$

where $(0.013 - 0.088\, d_p/d_t) = 0.002$ for the packing used by Sater and Levenspiel (1966). In the above equations, $Re_L = d_p / G_L / \mu_L$, $Re_G = d_p G_G / \mu_G$, and $Pe_G = U_G d_p / E_{ZG}$.

Very recently, Mathur and Wellek (1976) reported a significant discrepancy in the values of the gas phase Peclet number when the measurements were taken by the steady state procedure which was employed by them and Brittan and Woodburn (1966), as compared to the transient response techniques employed by DeMaria and White (1960) and Sater and Levenspiel (1966). The data of both Mathur and Wellek (1976) and Brittan and Woodburn (1966), illustrating the effect of the liquid phase Reynolds number, agreed qualitatively with those predicted by Equations (30) and (31). The data of Mathur and Wellek showed that the gas phase Peclet number initially decreased with an increase in the gas phase Reynolds number, and after it passed through a minimum, an increase was observed with an increase in the gas phase Reynolds number at constant Re_L, packing size, and bed height. Mathur and Wellek (1976) also showed that the Peclet number increases with packing size and slightly decreases with an increase in packing height.

Recommendations. When employing the above or any other correlations for packed-bed film reactors, extreme caution must be exercised to insure that all terms in the dimensionless groups are used as defined by the original authors. For instance, in the definition of the Reynolds number, some authors employ the superficial velocity, whereas others use the true linear velocity. Also, for the length dimension, usually an average particle diameter is employed (and even this is defined differently at times); however, sometimes an average film thickness, a hydraulic radius, or a ratio of reactor volume to total outside particle area are used.

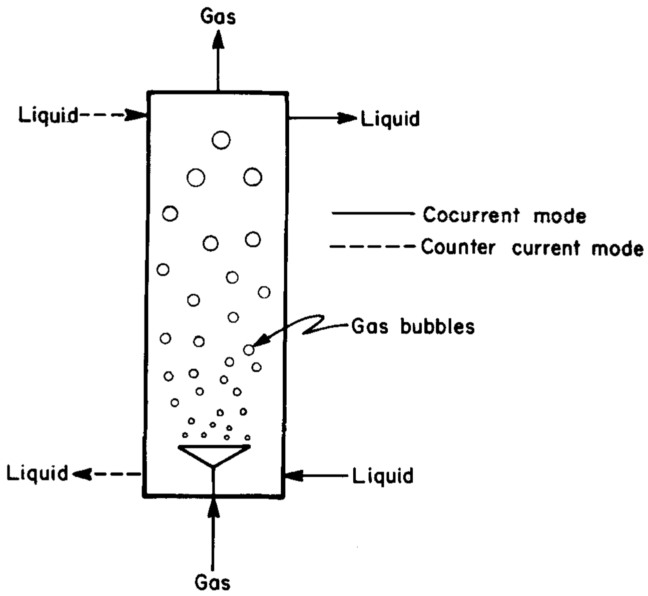

Fig. 3. Schematic diagram of a vertically sparged bubble column.

For designing packed-bed film reactors, it has been suggested (Satterfield, 1975; Schwartz and Roberts, 1973) that the two parameter crossflow model more realistically represents the residence time distributions. This, however, is not to say that the axial dispersion model, if employed, will not yield a workable reactor design. Schwartz and Roberts (1973) showed that for liquid phase Reynolds numbers of 8.3 and 65.8, the ratio of catalyst required using the dispersion model to that for the cross flow model ranged from 1.03 to 1.2 and 1.09 to 1.43 for conversions from 80 to 99%. This suggests that the axial dispersion model usually leads to a conservative design.

Backmixing in Gas-Liquid Reactors Where Gas Is Dispersed as Bubbles in Continuous Liquid Phase

Gas-Liquid Sparged Reactors: Vertical Sparged Reactors. The backmixing characteristics of vertical sparged reactors have been extensively studied in the literature. Some of these are summarized in Table 4. Early reviews on this subject are given by Mashelkar (1970), Bischoff (1966), Pavlica and Olson (1970), and Badura et al. (1974). Figure 3 presents a schematic diagram of a vertically sparged bubble column.

As long as the sparged vessel has a sufficiently large length to diameter ratio, the gas phase is usually assumed to move in plug flow. Earlier studies indicate that the backmixing in the liquid phase depends on the column diameter, gas velocity, and the nature of the gas distributor. Although there are some discrepancies in the literature, it appears that the axial dispersion coefficient in a vertical sparged vessel is essentially independent of liquid velocity and the liquid properties such as viscosity, surface tension, density, etc.

Towel and Ackerman (1972) correlated their data for the backmixing coefficient using the correlation

$$E_{ZL} = 1.23\, d_t^{1.5} U_{oG}^{0.5} \tag{32}$$

Deckwer et al. (1974) reexamined the reported data and suggested

$$E_{ZL} = 0.678\, d_t^{1.4} U_{oG}^{0.3} \tag{33}$$

Cova (1974) found no effect of surface tension and viscosity on the axial dispersion coefficient, but in small diameter columns, an increase in density increased the dispersion coefficient. For a single orifice sparger, he proposed the relation

$$E_{ZL} = 0.344\, U_{oG}^{0.32} \rho_L^{0.07} \tag{34}$$

Hikita and Kikukawa (1974) found the dispersion coefficient to be dependent upon the fluid viscosity and proposed the relation

$$E_{ZL} = (0.114 + 0.523\, U_{oG}^{0.77})\, d_t^{1.25} (1/\mu_L)^{0.12} \tag{35}$$

Recently, Alexander and Shah (1976) reported that the axial dispersion coefficient is independent of the surface tension and viscosity of liquid. Kato and Nishiwaki (1971, 1972) presented the dimensionless relation

$$\frac{U_{oG} d_t}{E_{ZL}} = \frac{13\, Fr_G}{1 + 6.5 (Fr_G)^{0.8}} \tag{36}$$

whereas Reith et al. (1968) claimed that between $0.1 \leqq U_{oG} \leqq 0.45$ m/s, and $d_t = 0.14$ or 0.29m

$$Pe_L = \frac{U_r d_t}{E_{ZL}} = 3.0 \pm 0.3 \tag{37}$$

Ohki and Inoue (1970) presented separate theoretical and experimental studies on the bubble flow (gas velocity between 0-0.07 m/s) and the coalesced bubble slug flow regimes ($U_{oG} > 0.1$ m/s). They presented the correlations

$$E_{ZL} = 75.4\, d_t^2 U_{oG}^{1.2} + 17\,000\, d_h; \quad \text{bubble flow regime} \tag{38}$$

$$E_{ZL} = 0.14\, d_t/(1 - H_G); \quad \text{coalesced bubble slug flow} \tag{39}$$

Most recently, Ueyama and Miyauchi (1977) measured the backmixing in bubble columns with diameters up to 0.6m and superficial gas velocity up to 0.93 m/s.

Kunugita et al. (1970) and Shyu and Miyauchi (1971) studied the dynamic behavior of bubbles, especially the coalescence of bubbles on the dispersion coefficient. Theoretical analyses of the backmixing coefficient in a cylindrical vertical bubble column are given by Ohki and Inoue (1970) and Baird and Rice (1975). With the use of a velocity distribution model, which is a direct extension of Taylor-Aris theory for the dispersion in a single phase flow, Ohki and Inoue (1970) derived Equation (38) for the bubble flow regime. For the slug flow regime, they derived Equation (39) using a so-called expansion model. This model was subsequently evaluated by Gondo et al. (1973) with data taken in both concurrent as well as countercurrent flow bubble columns. A separate approach was taken by Baird and Rice (1975) using the isotropic turbulence model of Hinze (1958). They derived the equation

$$E_{ZL} \alpha\, d_t^{1.33} U_{oG}^{0.33} \tag{40}$$

for a vertical bubble column. The above relationship appears to fit a larger number of reported experimental data compared to the relationship proposed by Ohki and Inoue (1970).

Although most of the literature data for a cylindrical bubble column indicate that the liquid phase axial dispersion coefficient is independent of liquid flow rate, this is not the case for rectangular and coiled bubble columns. Stiegel and Shah (1977*a*) showed that the liquid phase dispersion coefficient in a rectangular bubble column depends on the liquid flow rate. Alexander and Shah (1976) and Stiegel and Shah (1977*a*) also showed that for a given gas velocity, a rectangular bubble column gives considerably larger axial dispersion coefficients than a cylindrical column of the equivalent diameter. The larger axial dispersion coefficient may be due to the effects

TABLE 4. SUMMARY OF MULTIPHASE DISPERSION IN UNPACKED BUBBLE COLUMNS

Reference	System	Flow rate,* m/s	Tracer system	Column characteristics,* m (× 1 000)	Dispersion studied
Ohki and Inoue (1970)	Air-water	L = batch G = 0-0.25	4N aqueous KCl pulse Pt electrical Conductivity cell	d_t = 40, 80, 160 L_c = 200, 250, 300 d_h = 0.4, 0.7, 1, 2, 3 n_h = 2, 5, 7 13, 19, 37, 55, 91	Axial
Kato and Nishiwaki (1972)	Air-water concurrent	L = 0.005-0.015 G = 0-0.3	1-1.5 N KCl pulse Pt electrical Conductivity cell	d_t = 66, 122, 214 L_c = 2 000, 2 010, 4 050 d_h = 1, 1.4, 2, 3 n_h = 7, 19, 31, 37, 97, 336	Axial
Eissa et al. (1971)	Air-water concurrent	L = 0.0075-0.013 G = 0.014-0.078	Salt solution Steady state point source Conductivity meter	d_t = 50 L_c = 420 Multiorifice plate distributor	Axial and radial
Deckwer et al. (1974)	Air-water	L = batch G = 0-0.05	Dye, heat, electrolytes Dirac pulse	d_t = 150, 200 L_c = 4 400, 7 230 Cross of 56, nozzles 1 mm diam, sintered porous plate of 150 μm diam	Axial
Reith et al. (1968)	Air-water cocurrent and counter-current	L = 0-0.02 G = 0.02-0.45	NaCl solution P-sulfobenzeneazo-β-naphthol, conductivity cell and spectrometer	d_t = 50.8, 140, 290 L_c = 152, 200, 353, 380 d_h = one hole of 0.002 m diam 10^4 m^2	Axial
Towell and Ackerman (1972)	Air-water concurrent and counter-current	L = 0.0024-0.014 G = 0-0.152	Methylene blue dye Freon Step and pulse Spectrophotometer Ionization cell (ionization induced by β emission from Tritium source. Ionization current measured by electrometer)	d_t = 406, 1 067 L_c = 2 743, 5 182 d_h = 6.35 n_h = 19, 41	Axial
Aoyama et al. (1968)	Air-water Air-aq glycerine Air-aq tween 20 cocurrent	L = 0.0018-0.011 G = 0.0031-0.078	Heat, 3N KCl Steady state pulse Thermocouples Electrical conductivity Cell	d_t = 50, 100, 200 L_c = 1000, 1 900, 2 020 Porous plate distributors 0.068-0.13 Perforated plate d_h = 0.5, 1 n_h = 19, 31, 33, 85	Axial
Hikita and Kikukawa (1974)	Air-water Air-aq MeOH solutions	L = batch G = 0.043-0.338 m/s	Aq KCl Pulse Pt electrical conductivity cell	d_t = 100, 190 L_c = 1 500, 2 400 d_h = 13.1, 20.6, 36.2 n_h = 1	Axial

(Continued on opposite page)

Table 4. (cont'd.)

Reference	System	Flow rate,* m/s	Tracer system	Column characteristics,* m (× 1 000)	Dispersion studied
Eissa and Schügerl (1975)	Air-water cocurrent	$L = 0.0035\text{-}0.014$ $G = 0.002\text{-}0.06$	NaCl Steady state injection Conductivity meter	$d_t = 159$ $L_c = 3\,900$ $d_h = 2$ $n_h = 200$	Axial
Cova (1974)	N_2-water -acetone -CCl_4 -EtOH -aq EtOH -aq sugar soln -Cyclohexanol -Concurrent	$L = 0.002\text{-}0.0087$ $G = 0.0051\text{-}0.173$	Heat Steady state Thermocouples	$d_t = 19.1, 45.7$ $L_c = 3.8, 4$ ft Sintered, metal disk, single 1.32 mm diam orifice 13 × 0.483 mm diam	Axial
Alexander and Shah (1976)	Air-aq glycerol solutions Air-aq triton DF 12 solutions	L = batch $G = 0\text{-}0.07$	H_2SO_4, pulse Electrical conductivity	$d_t = 60.3, 152.4, 76.2 \times 229$ rectangular $L_c = 1\,240, 3\,080, 1\,120$ 1 × 6.4 mm diam orifice, 13 × 0.79 mm diam porous plate, 10 × 6.35 mm diam porous plate	Axial
Argo and Cova (1965)	N_2-water NH_3-water Countercurrent Concurrent	$L = 0.0038\text{-}0.016$ $G = 0.0041\text{-}0.203$	KCl and NaCl Steady state point source Potentiometric titration Electrical conductivity	$d_t = 45.7, 102, 448$ $L_c = 914, 1\,219, 8\,230$ 18 × 3.18 mm perforated plate	Axial

* L = liquid flow rate.
G = gas flow rate.
d_t = column diameter.
L_c = column height.
d_h = hole diameter.
n_h = number of holes.

of corners (that is, secondary flow effects) on the mixing characteristics within the column.

Rippel et al. (1966) examined the liquid phase backmixing in a coiled bubble column. Their data indicate that unlike in a straight bubble column, the liquid phase backmixing coefficient was a strong function of liquid velocity. At low liquid rates, two-phase flow gave higher liquid phase axial dispersion than single-phase flow; however, at high liquid phase Reynolds numbers (that is, of the order of 400 to 2 000), single liquid phase and two-phase (gas liquid) flow gave the same degree of liquid phase axial mixing.

Davidson (1977) has suggested that E_{ZL} can be correlated with the average liquid circulation velocity U_c. Whalley and Davidson (1975) have considered the various aspects of the liquid circulation in bubble columns. The data on the fractional gas holdup, which is necessary for the calculation of the energy dissipation in the wakes behind the bubbles, are reported in the literature (Mashelkar, 1970). Using the energy balance approach of Whalley and Davidson, the backmixing data in bubble columns may be correlated by the following equation with a standard deviation of 15% (Joshi and Sharma, 1976):

$$E_{ZL} = 0.31\, d_t^{1.5} U_c \tag{41}$$

Here, U_c is dependent upon liquid submergence.

In all of the studies on the axial dispersion coefficient in a bubble column, no length effects were considered. Deckwer et al. (1973) report that in the gas velocity range of 0.005 to 0.006 m/s, zones of different mixing in the liquid phase of concurrent and countercurrent bubble columns exist. The backmixing in the upper region of the column is about twice that in the lower region of the column. For both concurrent as well as countercurrent flow, they proposed

$$E_{ZL} = (1.2 \pm 0.12) d_t^{1.5} U_{oG}^{0.5} \quad \text{in the lower region} \tag{42}$$

$$E_{ZL} = (2.4 \pm 0.18) d_t^{1.5} U_{oG}^{0.5} \quad \text{in the upper region} \tag{43}$$

of the column

Similarly, Schügerl (1967) also noted that the intensity of mixing in both the gas and liquid phases decreases from the top to the bottom of the column. The axial dispersion data were obtained in three sections of the bubble column. Based on the data, he concluded that the bottom section was least mixed, whereas the top section had the highest degree of mixing in both the gas and liquid phases.

The mixing in the dispersed gas phase in a bubble column has been studied by Diboun and Schügerl (1967). They proposed a relation

$$Pe_G = \frac{U_r d_t}{E_{ZG}} = 0.2 \tag{44}$$

Horizontal Sparged Reactors. A schematic drawing of a horizontally sparged reactor is presented in Figure 4.

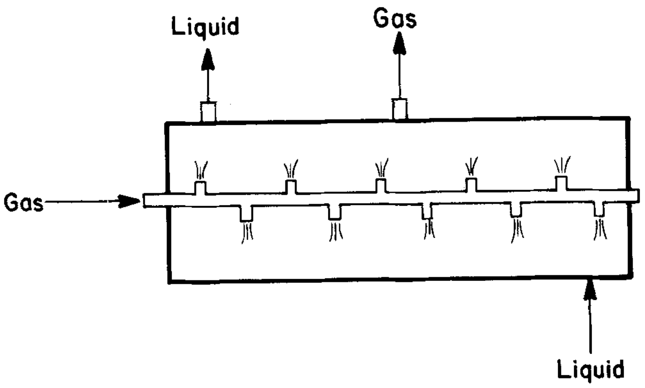

Fig. 4. Schematic diagram of a horizontally sparged reactor.

Zuiderweg and Bruinzeel (1968) reported some data from 0.3, 0.6, and 1.0m ID horizontal sparged contactors, in the range of nozzle gas velocity U_n from 40 to 150 m/s, and suggested the following semiempirical correlation between the dispersion coefficient and the pertinent design variables of the horizontal sparged contactor:

$$E_{ZL} = 1.8 \frac{L_n d_n U_n}{d_t} \sqrt{\frac{\rho_G}{\rho_L}} \tag{45}$$

This correlation suffers from the following drawbacks:

1. It does not take into account the effect of liquid submergence on the dispersion coefficient.
2. It leads to the erroneous conclusion that the decrease in the number of nozzles in the given horizontal sparged contactor (that is, an increase in nozzle spacing L_n) increases the dispersion coefficient.

Joshi and Sharma (1976) analyzed the problem of liquid circulation in horizontal sparged contactors using the energy balance method proposed by Whalley and Davidson (1975). Joshi and Sharma (in press) derived

$$E_{ZL} = 0.07\, U_c^{1.7} \tag{46}$$

In the ranges of $40 < U_n < 180$ m/s, $5 \times 10^{-4} < U_{oL} < 10^{-2}$, $3.18 \times 10^{-3} < d_n < 1.27 \times 10^{-2}$m, they showed that

$$E_{ZL} \alpha U_n^{0.7}$$
$$E_{ZL} \alpha d_n \tag{47}$$
$$E_{ZL} \alpha U_{oL}$$

These authors have also shown that this one parameter, that is, the liquid circulation velocity U_c, can correlate dispersion data for horizontal contactors over a wide range of operating conditions. It is interesting to note also that just as in the case of a vertical bubble column, the backmixing coefficient in a horizontal sparged contactor is independent of the liquid velocity.

Recommendations. For a vertical gas-liquid sparged reactors, use of either Equation (33) or (41) is recommended. For a horizontal sparged reactor, Equation (47) would be useful.

Packed Bubble Column Reactors. Under certain conditions, when the gas phase flows upward and liquid phase flows either upward or downward in a packed bed at low to moderate flow rates, the bubble flow regime prevails. There have been a number of studies (Hoogendoorn and Lips, 1965; Stiegel and Shah, 1970*a* and *b*; Carleton et al., 1967) on the backmixing in packed-bed columns. A summary of some of the important studies is presented in Table 5. Schematic drawings of this type of system are shown in Figures 5 and 2*b*.

Although, as shown in Table 5, there are some discrepancies in the literature on the effects of gas and liquid velocities on the Peclet number, it is generally believed that an increase in gas velocity and a decrease in liquid velocity decrease the Peclet number. The packed bubble column generally gives lower backmixing in both the liquid and gas phases than an unpacked bubble column under equivalent flow conditions. Unlike in an unpacked bubble column, the backmixing coefficient in a packed column depends significantly on the liquid velocity.

The backmixing coefficient in the liquid phase was correlated in dimensionless form by Stiegel and Shah

Table 5. Summary of Backmixing Studies in Packed Bubble Columns

Reference	Column diameter m (× 100)	Packing size m (× 100)	Gas velocity m/s (× 100)	Liquid velocity m/s (× 100)	Pe	Effect on Pe for increase in Gas velocity	Effect on Pe for increase in Liquid velocity
Heilmann and Hofmann (1971)	19, 30	0.1-0.16	0-4	.5-1.45	3-25	Decreases	Increases
Hofmann (1961)	5	0.6	0.1-1.3	0.03-0.37	9-25	Decreases	Increases
Kunugita et al. (1962)	10	1.0-2.0	0-2.8	0.1-3.0		None	$\alpha U_L^{7/9}$
Carleton et al. (1967)	3.4-15.3	0.6-1.9	2.6-8.4	0.09-0.32	2-33.3	None	Increases
Hoogendoorn and Lips (1965)	41	1.3	1.5-13	0.12-0.70	9-25	Reaches maximum	Increases
Stiegel and Shah (1977*b*)	5	0.375-.437	13-75	0.25-3	30-220	Decreases	Increases

(1976*b*) as

$$
\begin{aligned}
&Pe_L = \alpha Re_L^{\beta} Re_G^{\gamma} (a_s d_p)^{\eta} \\
&\alpha = 0.128 \quad \sigma = 0.07 \\
&\beta = 0.245 \quad \sigma = 0.0438 \\
&\gamma = -0.16 \quad \sigma = 0.0356 \\
&\eta = 0.53 \quad \sigma = 0.29
\end{aligned}
\tag{48}
$$

where $Pe_L = U_L d_p / E_{ZL}$, $Re_L = d_p G_L / \mu_L$, $Re_G = d_p G_G / \mu_G$. The value of η is not very reliable because only a small variation in the particle diameter was examined. Heilmann and Hofmann (1971) have presented an alternate dimensional relation for the liquid phase Peclet number. This relationship was also examined by Stiegel and Shah (1977*b*).

All work reported in Table 5 has been carried out in cylindrical columns. Stiegel and Shah (1977*a*) recently studied the backmixing in a rectangular packed column. Quite interestingly, they found that under equivalent flow conditions, a packed rectangular bubble column produced much higher backmixing in the liquid phase than a packed cylindrical column with an equivalent diameter.

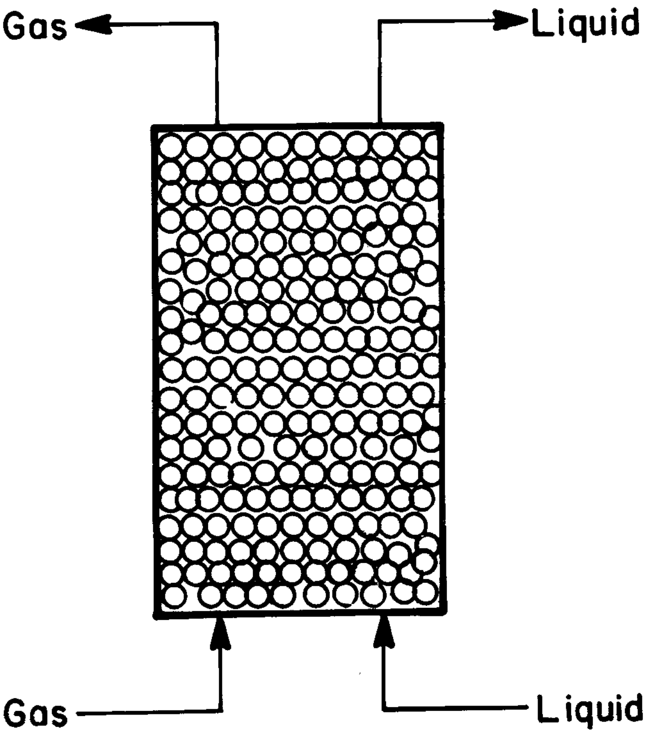

Fig. 5. Schematic diagram of a concurrent upflow packed bubble column.

Chen and co-workers (1971, 1972, 1975, 1976) recently studied the liquid phase backmixing in a column packed with screen cylinders under countercurrent bubble flow conditions. In all of these studies, it was shown that the presence of screen cylinders significantly reduces the axial mixing in the bubble columns. Most studies reported thus far have indicated that the axial dispersion coefficient in an unpacked bubble column is independent of liquid velocity. Chen (1972), however, reported that this observation is due to the fact that in all studies, the interstitial liquid velocity has been less than 10% of the rising velocity of the bubbles U_b. At $U_L > 0.1U_b$, Chen (1972) presented the dependency of the dispersion coefficient on the liquid velocity as

$$E_{ZL} \alpha U_L^{0.234} \tag{49}$$

In a subsequent study, Chen (1976) showed that at high liquid flow rates the dispersion coefficient was proportional to $U_L^{0.24}$.

Very recently, Shah et al. (in press) studied the backmixing of a segmented bubble column, wherein the extrudates were packed in screened tubes which were vertically hung in the bubble column. They also examined the backmixing characteristics of a bubble column with vertically suspended rods. The experiments were carried out in a batch system (that is, no liquid flow). The results show that at low gas flow rates the presence of suspended rods and tubes increased the liquid phase backmixing. At high gas flow rates (that is, velocity >0.1 m/s), however, the tubes or rods had very little effect on the liquid phase backmixing.

Recommendations. For the liquid phase axial dispersion coefficient in a packed bubble column, the use of Equation (48) is recommended. As yet, no information on the effect of fluid properties on the liquid phase axial dispersion coefficient and no data for the gas phase Peclet number in a packed bubble column are available.

Backmixing in Gas-Liquid-Solid Fluidized Bed and Slurry Reactors. In many practical systems such as coal liquefaction, solids are suspended in gas-liquid reactors. Here, the solids may be a reactant or a catalyst. Furthermore, the system can be either batch (that is, no liquid flow) or continuous flow. A schematic of this type of system is shown in Figure 6.

The theoretical aspects of three-phase slurry reactors are analyzed by Govindarao (1975). Massimilla et al. (1971) discussed the gas dispersion in three-phase fluidized beds, whereas Ostergaard and Michelsen (1969) showed a method for evaluating the tailing problem with the RTD in a three-phase reactor. Cova (1966) measured the steady state concentration distribution of solids in a three-phase reactor. Farkas and Leblond (1969) used such data to calculate the backmixing coefficient of solids.

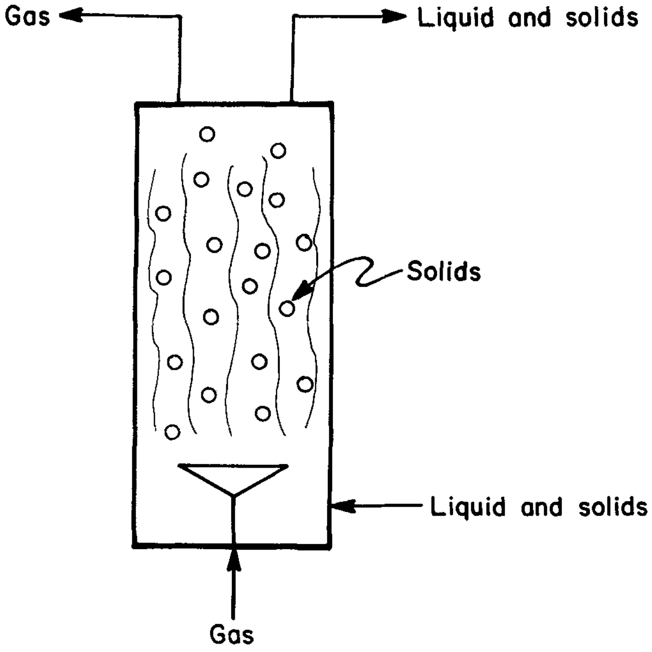

Fig. 6. Schematic diagram of a gas-liquid-solid fluidized bed or slurry reactor.

The values of the backmixing coefficient were, however, not correlated to gas and liquid velocities.

The gas phase RTD in a three-phase fluidized bed have been measured by Schügerl (1967), Michelsen and Ostergaard (1970*b*), and Ostergaard and Michelsen (1969). The quantitative data on the gas phase backmixing coefficient have been, however, presented only by Schügerl (1967). He reported that just as in a bubble column, the intensity of mixing in both the gas and liquid phases in a three-phase fluidized bed decreases from the top to the bottom of the column. At low liquid velocities, the gas phase Peclet number (or Bodenstein number) increases with the gas rate, but at high liquid velocities, the Peclet number shows a maximum with respect to gas rate. From Schügerl's data, the effect of liquid velocity on the gas phase Peclet number is unclear, although at low liquid velocities, the gas phase Peclet number appears to decrease with an increase in liquid velocity.

The effects of suspended solid particles on the liquid phase backmixing have been studied by Schügerl (1967), Vail et al. (1968), Ostergaard and Michelsen (1969), Michelsen and Ostergaard (1970*b*), and Kato et al. (1972). The data of Schügerl (1967), Vail et al. (1968), and Michelsen and Ostergaard (1970*b*) showed that in a three-phase column, the liquid phase backmixing still increases with gas rate. Unlike in a gas-liquid bubble column, the liquid phase backmixing coefficient in a three-phase column is dependent upon the liquid velocity. Vail et al. (1968) showed that the effect of liquid velocity on the axial mixing diminishes with increasing liquid flow rates. The nature of the effect is also dependent upon the gas rate and solids particle size. Vail et al. (1968) showed that the presence of solids reduces the liquid phase backmixing. Similarly, the nature of the effect of solid size on the liquid phase backmixing depends on the gas and liquid flow rates.

Kim et al. (1972) correlated their data for the liquid phase backmixing in a three-phase rectangular column by a dimensionless correlation:

$$(HMU/H_o) - (HMU/H_o)_{U_{OG}=0} = 0.068(Fr_L{}^2\rho_S/\rho_L)^{0.128} (Fr_G{}^2\rho_S/\rho_G)^{0.168}(Re_L Re_G)^{0.120} \quad (50)$$

where

$$HMU = 2H_e/Pe, \quad Fr_L = U_{OL}/\sqrt{d_p g}, \quad Fr_G = U_{OG}/\sqrt{d_p g}$$

$$Re_L = d_p U_{OL}\rho_L/\mu_L \quad Re_G = d_p U_{OG}\rho_G/\mu_G$$

$$Pe = U_{OL}H_e/E_{ZL}$$

$(HMU/H_o)_{U_{OG}=0}$ and H_e can be estimated from the relations

$$(HMU/H_o)_{U_{OG}=0} = 5.05(Fr_L{}^2\rho_S/\rho_L)^{0.842}(Re_L)^{-0.450} \quad (51)$$

$$(H_e/H_o) - (H_e/H_o)_{U_{OG}=0} = 0.0026(Fr_L{}^2\rho_S/\rho_L)^{0.178} (Fr_G{}^2\rho_S/\rho_G)^{0.345}(Re_L Re_G)^{0.252} \quad (52)$$

$$(H_e/H_o)_{U_{OG}=0} = 1.8(Fr_L{}^2\rho_S/\rho_L)^{0.202}(Re_L)^{-0.012} \quad (53)$$

It should be noted that although the above relation correlates the backmixing coefficient to the fluid properties, no experimental data on systems other than air or nitrogen and water have been reported in the literature.

Kato et al. (1972) correlated the longitudinal dispersion coefficient for the liquid in a slurry by

$$Pe_L = U_{OG}d_t/E_{ZL} = 13\,Fr_G/(1 + 8\,Fr_G{}^{0.85}) \quad (54)$$

where

$$Fr_G = U_{OG}/\sqrt{gd_t}$$

Note that Froude number is defined here in terms of column diameter.

The behavior of suspended solid particles and their backmixing have been extensively studied by Kato et al. (1972) and Imafuku et al. (1968). Both batch (that is, no liquid flow) and flow systems were examined. Various types of solid particles such as glass sphere, copper powder, ion exchange resin, etc., with sizes ranging from 5.3×10^{-5} to 2.5×10^{-4}m and particle densities from 1 000 to 9 000 Kg/m^3 were examined. The column diameter ranged from 0.05 to 0.22m, and solids concentrations up to 20% were considered. The most important conclusion of these studies was that for small particle sizes in small diameter columns, the longitudinal dispersion coefficient for the solids in a three-phase fluidized bed is the same as that of the liquid and can be given by Equation (54), if E_{ZL} is replaced by E_{ZS}, the backmixing coefficient for the solid particles. For large diameter particles and large columns, Equation (54) was corrected by Kato et al. (1972) to

$$Pe_S = \frac{U_{OG}d_t}{E_{ZS}} = 13\,Fr_G(1 + 0.009\,Re_p Fr_G{}^{-0.8})/ (1 + 8\,Fr_G{}^{0.85}) \quad (55)$$

where $Re_p = d_p U_{to}\rho_L/\mu_L$.

Recommendations. The correlations of Kim et al. (1972) do not take into account the effect of column diameter on the liquid phase backmixing. For large columns, Equation (50) predicts E_{ZL} about two orders of magnitude smaller than predicted from Equation (54) under similar conditions. The use of Equations (54) and (55) are recommended for the estimations of E_{ZL} and E_{ZS} in three-phase fluidized-bed columns. A correlation for the estimation of gas phase backmixing' coefficient in a three-phase fluidized bed is needed.

Backmixing in an Agitated Reactor: Single Stage. Extensive reviews of this subject are presented by Bates et al. (1966), Calderbank (1967), and Sideman et al. (1966).

Multistage. Backmixing in mechanically agitated multistage contactors, shown schematically in Figure 7, has

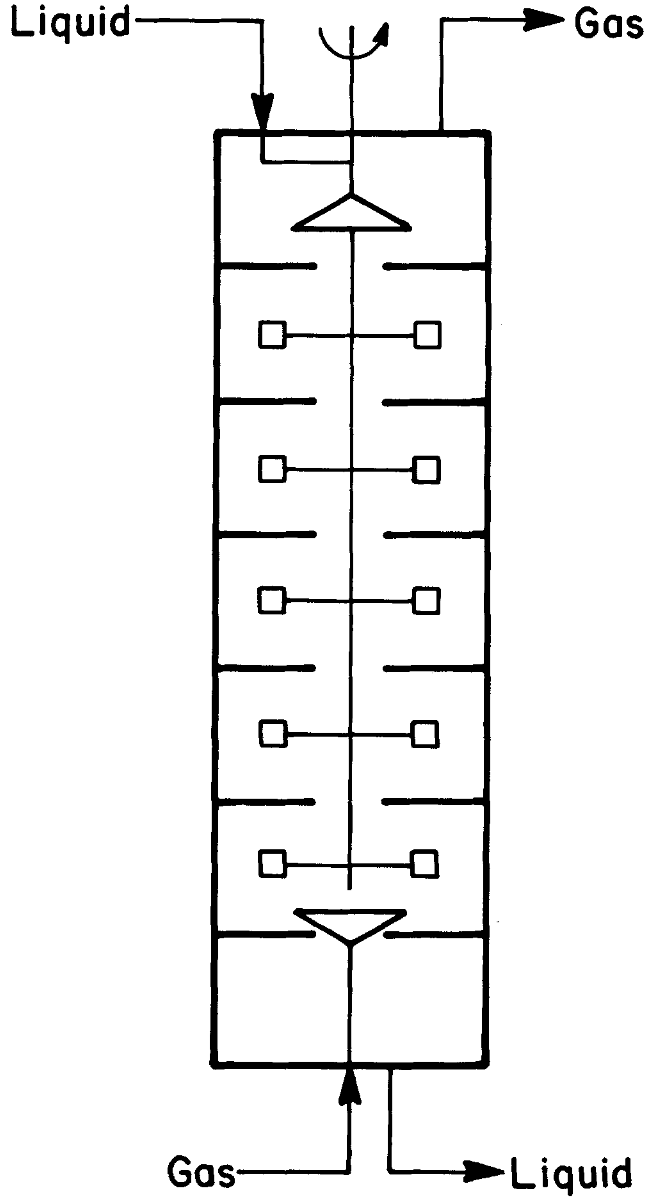

Fig. 7. Schematic diagram of a mechanically agitated multistage contactor.

been studied by Sullivan and Treybal (1970) and Haug (1971). The latter author showed the backmix ratio to be a function of the ratio of impeller tip speed to the superficial flow velocity and of the column configuration and impeller design. Haug (1971) suggested the expression

$$K = 0.0098 \left[\Psi \frac{N d_i}{U_{OL}} \left(\frac{d_i^2 a_b}{d_t L_h a_c} \right)^{1/2} \right]^{1.24} \tag{56}$$

The impeller correction factor Ψ takes into account the differences between impeller types, and for six-blade turbines of the Rushton-Oldshue type, Ψ is unity. For other configurations, Ψ is taken as the ratio of the Power number of the impeller used to that of the six-blade impeller. The Power number is approximately proportional to the square root of the number of blades.

For countercurrent flow of air and water in a mechanically agitated tower, Sullivan and Treybal (1970) gave the following correlation for the liquid phase backmixing coefficient:

$$\frac{E_{ZL}}{U_{OL} L_h} \left(\frac{U_{OL}}{d_i N} \right) = 227.2 \left(\frac{d_i^2 N \rho_L \phi_c^2}{\mu_L} \right)^{-0.928} \tag{57}$$

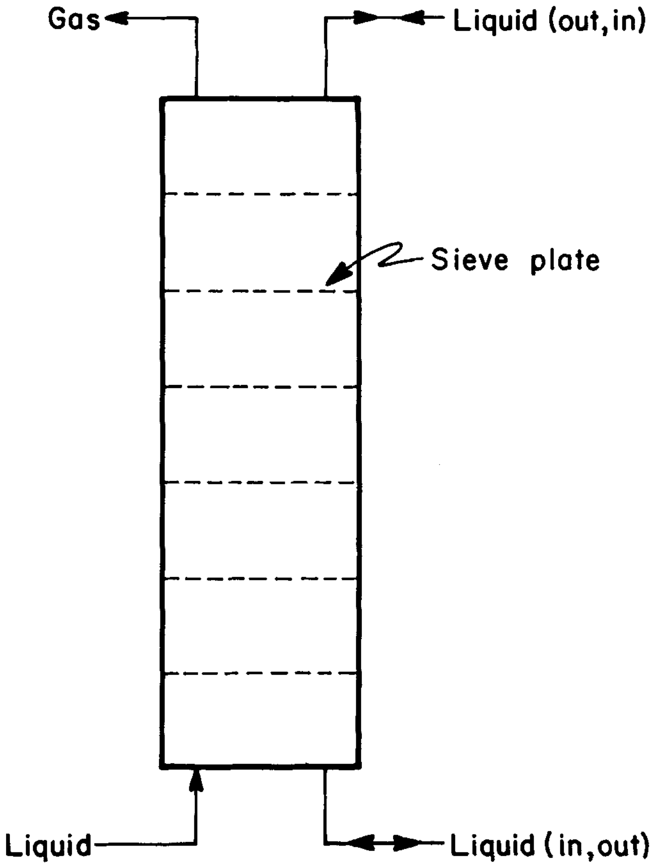

Fig. 8. Schematic diagram of a multistage, sieve plate bubble column.

It should be noted that the dependence of E_{ZL} on d_i, L_h, ρ_L, and ϕ_c given by the above relation may not be very reliable because these parameters were not varied in the experiments.

Recommendations. For backmixing in a single-stage agitated gas-liquid reactor, follow the review by Calderbank (1967). For multistage agitated reactors, Equation (57) should give good estimates for E_{ZL}.

Backmixing in a Multistage Bubble Column. Often bubble columns are divided into various sections by sieve trays or other types of perforated plates. This type of system is shown schematically in Figure 8. Sekizawa and Kubota (1975) and Nishiwaki and Kato (1972) reported that the longitudinal liquid mixing in a multistage bubble column is well described by a flow model which is a series combination of the dispersion in each stage and the backflow through a partition plate. Based on this so-called dispersion-backflow model, Sekizawa and Kubota (1975) derived the relation for the liquid phase overall dispersion coefficient in terms of the dispersion coefficient for each stage:

$$Pe_L = \sum_{i=1}^{n_s} Pe_i + \left[\frac{1}{\dfrac{n_s}{2(n_s - 1)^2} + \dfrac{K}{n_s}} \right] \tag{58}$$

where $Pe_L = \mathrm{Vol}\, L_o/E_{ZL}$.

The above relation holds even in the case where the column is composed of stages of various sizes. An alternate theoretical analysis of this subject is also given by Kats and Genin (1967).

Experimental studies on this subject are given by Kats and Genin (1967), Sekizawa and Kubota (1975), Kafarov et al. (1972), and Bischoff and Phillips (1966). Kafarov et al. (1972) studied the backmixing on a

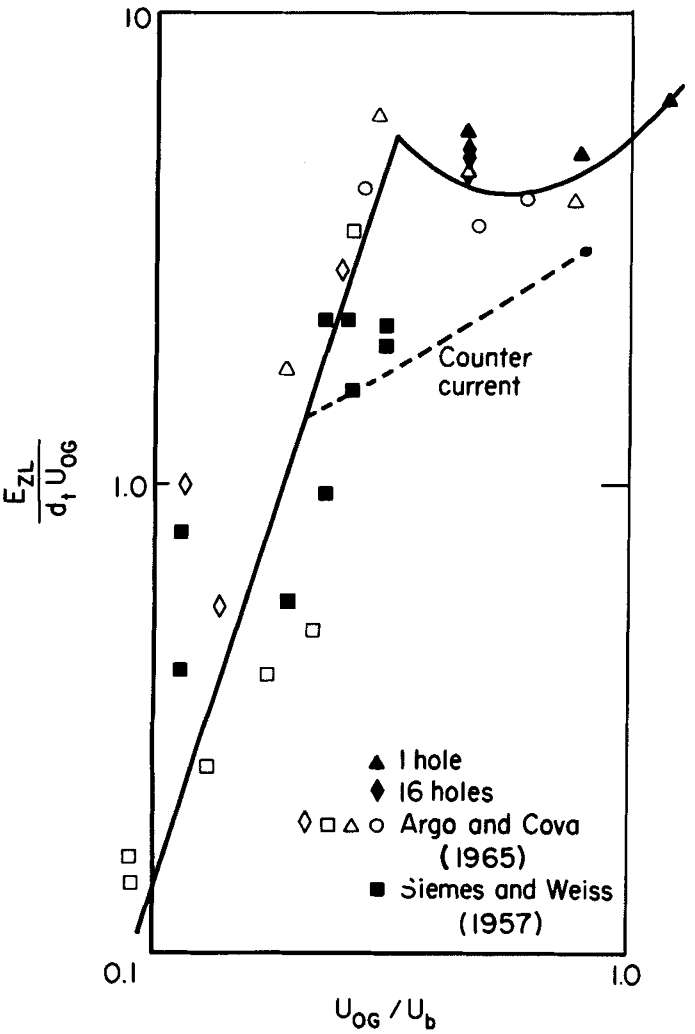

Fig. 9. Axial dispersion in an orifice plate column.

sieve tray equipped with a coil. They showed that on this type of tray, the Peclet number would vary over the width of the tray. The average dispersion coefficient over such a tray was correlated by

$$\frac{2E_{ZLav}}{U_L{}^3 h_L} = 6.34 \times 10^{-3} \left[\frac{h_L}{h_f} U_L \right]^{-2.83} \quad (59)$$

Kafarov et al. (1972) showed that a coil on a sieve tray reduces backmixing.

Kats and Genin (1967) reported the empirical relationships for the mixing coefficient in various zones of a bubble column sectionalized with sieve trays of the dual flow type and bubble cap trays. The mixing coefficients were correlated to the liquid velocity, open fraction of the trays, thickness of the trays, and the diameter of the holes. No correlation for the overall backmixing coefficient was presented.

Bischoff and Phillips (1966) examined the longitudinal mixing in orifice plate gas-liquid reactors. Different plate designs and lengths were considered. The RTD data were correlated by the axial dispersion model. They concluded that the gas-liquid flow gives considerably larger backmixing than those obtained in a single phase flow. Bischoff and Phillips (1966) presented a graphical correlation for the axial dispersion coefficient which is shown in Figure 9. The data of Siemes and Weiss (1957), for no liquid flow, and Argo and Cova (1965) are also included in Figure 9. In this figure, U_b is the rise velocity of the gas bubbles.

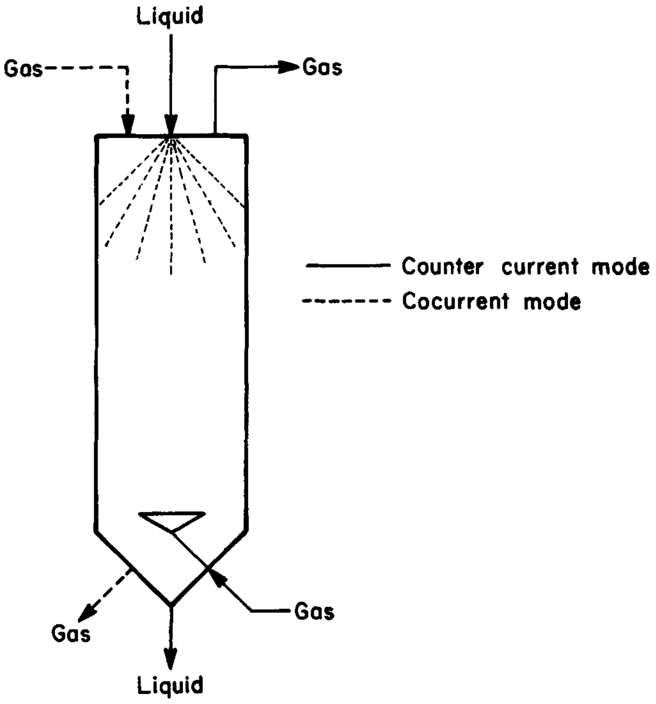

Fig. 10. Schematic diagram of a gas-liquid spray reactor.

Sekizawa and Kubota (1974) studied the backmixing in a concurrent multistage bubble column partitioned by perforated plates. The experimental data were used to obtain correlations for the backflow ratio of each plate and the dispersion coefficient in each stage. The backflow ratio was related to the superficial gas velocity U_{OG}, the free area fraction of the perforated plate a_r, the net value of superficial liquid velocity U_{OL}, the viscosity of the liquid μ_L, the hole diameter of the plate d_h, and the plate thickness L_p by

$$K = \frac{U'_{OL}}{U_{OL}} = \frac{18\, U_{oG}{}^{0.2} a_r}{1 + U_{OG}/a_r} \left(\frac{1}{U_{OL}} - \frac{0.011}{U_{OL}{}^{0.85} a_r{}^{0.2}} \right) \times 1.48/\exp[(0.015/d_h)(3.16\, \mu_L{}^{0.5} + 2.51 \times 10^{-6}\, L_p{}^{0.2}/d_h{}^2)] \quad (60)$$

The longitudinal dispersion coefficient of the liquid E^*_{ZL} obtained in a stage of such a column was smaller than the dispersion coefficient obtained in a column without partition. The ratio E^*_{ZL}/E_{ZL} was related to the gas velocity, column diameter d_t, and plate spacing ΔL by

$$\frac{E^*_{ZL}}{E_{ZL}} = 1.58\, U_{OG}{}^{0.1}/[1 + 0.5(d_t/\Delta L)^{0.2}] \quad (61)$$

Kubota and Sekizawa (1976) studied the dispersion of solid particles in a multistage three-phase fluidized bed. They noted that when the superficial liquid velocity is zero or very small, the presence of partition plates gives the stepwise profile and large solid holdup compared to the column without partition plate. When the superficial liquid velocity is large, the partition plates contribute to the uniform solid distribution and give small solids holdup; the effect of the plate depends upon the magnitude of backflow ratio K. The effect of partition plates becomes smaller with increasing K.

An important practical example for the sectionalized bubble column with solid particles is the Solvay tower used in soda production. In this tower, a definite temperature profile has to be maintained for process reasons, and backmixing in the liquid phase has to be severely restricted both from the point of view of increasing the effective rate of absorption of carbon dioxide and also to provide a favorable driving force (the equilibrium partial pressure of carbon dioxide over the solution is relatively very high in the lower sections of the column). Some modeling work has been done in the recent past; however, there is dearth of data on RTD in such contactors which gets further complicated because of the presence of horizontal heat exchanger tubes in the lower sections of the tower (Kafarov et al., 1976). Towers up to 10 ft in diameter are used in practice.

Recommendations. The studies of Sekizawa and Kubota (1974) and Kubota and Sekizawa (1976) can be used to estimate the liquid phase backmixing coefficient in a bubble column partitioned by perforated plates. When the partition plates are orifice plates, the backmixing in the liquid phase can be evaluated using the study of Bischoff and Phillips (1966).

Backmixing in Gas-Liquid Spray Reactors

Gas-liquid reactors having the liquid phase dispersed as droplets are commonly referred to as spray reactors. Figure 10 represents a schematic drawing of this system. In a spray reactor, the liquid can be either dispersed from the top of a vertical column into a gas stream flowing either concurrently or countercurrently or sprayed concurrently with the gas into a horizontal reactor.

Spray absorbers are sometimes employed in practice when dust laden gases have to be treated and/or where the product consists of solid particles and the pressure drop in the gas phase should be relatively very low. For instance, the absorption of SiF_4/HF from phosphatic fertilizer plants falls in this category. Further, there is an increasing interest in operating sieve plate absorbers in the spray regime so that not only the gas phase pressure drop is low but also the backmixing in the gas phase is severely reduced as compared to a single-stage spray absorber. Spray reactors have also attracted attention for the manufacture of $Na_2CO_3(CO_2 + NaOH)$ and fertilizers.

For countercurrent spray reactors, Treybal (1968) states that unless the column diameter to length ratio is very small, the gas phase will be thoroughly mixed by the liquid spray. This ratio in many cases cannot be made very small because the spray would then quickly reach the reactor walls and become ineffective as a spray.

Keey and Pham (1977) recently studied the gas phase residence time distribution in a spray column 0.4 m in diameter and 2 m long with an 0.55 m long conical bottom. Primary air flow velocities were varied from 0.055 to 2.2 m/s and liquid atomizing air flow rates from 0 to 1.27×10^{-3} m³/s. No liquid was atomized in any run, as it was believed that the presence of the liquid would not appreciably alter the experimental results since the momentum of the liquid is negligible in comparison with that of the atomizing gas. Their results indicated that the lower half of the column was in plug flow while the upper half of the column was well mixed and equivalent to about two equal size tanks in series with a small amount of recycling and bypassing. The atomizing air jet in the primary air stream which is characterized by the Craya-Curtet number

$$Ct = \left[\frac{2d_n^2(U_{nG} - U_{OG}) + U_{OG}^2 d_t^2}{32\, V_G^2/(\pi d_t)^2} - \frac{1}{2} \right]^{-1/2} \tag{62}$$

was found to have a significant effect on the gas backmixing, causing it to pass through a minimum with increasing Ct. This minimum was found to occur at $Ct = 0.25$. Previously, Moeller and Dealy (1970) found that for $Ct < 0.75$, the jet had significant influence on the gas flow pattern, and it caused recirculation.

Recommendation. The literature on this subject is sparse. More work, particularly on the gas phase backmixing in sieve plate absorbers operating in the spray flow regime, is needed.

ROLE OF BACKMIXING ON THE PERFORMANCES OF GAS-LIQUID REACTORS

Bubble Column Reactor

As mentioned earlier, backmixing in the liquid phase is unavoidable, and it usually hurts reactor performance. Pavlica and Olson (1970) outlined a generalized axial dispersion model for the isothermal bubble column reactor in which a pseudo first-order reaction in both the gas and liquid phase occurs. The model considered the axial mixing in both the gas and liquid phases. Todt et al. (1977) evaluated the role of axial dispersion on the extent of microbial growth in various types of continuous flow bubble column reactor.

Here, we review a simple model for the reactor in which a generalized $(m, n)^{th}$-order reaction between a gaseous species A and a liquid species B is carried out in the liquid phase. There are a number of oxidation, ozonolysis, carbonation, carbonylation, alkylation, hydrogenation, etc., reactions which can be approximately modeled by this type of reaction mechanism. No reaction is assumed to occur in the gas phase.

The formulation of the mathematical equations depends upon the reaction regime. If the reaction is slow, most of it would occur in the bulk liquid phase. This reaction regime is characterized by the value of the parameter

$$\sqrt{M} = \frac{\sqrt{\left(\frac{2}{m+1}\right) K_{mn} D_A a_L^{*m-1} b_L^{*n}}}{k_L} \tag{63}$$

much less than unity. When $\sqrt{M} >> 1$ and $\sqrt{M} << q_A$, the reaction is considered to be fast. The parameter

$$q_A = \frac{b_L}{z a_L^*} \tag{64}$$

where b_L is bulk liquid phase concentration of the liquid species B and z, the stoichiometric coefficient for the reaction

$$A(G) + zB(L) \xrightarrow{K_{mn}} \text{Products} \tag{65}$$

In this regime, the reaction is complete in the diffusion film. When $\sqrt{M}$ is substantially greater than q_A, the reaction is instantaneous; that is, it occurs at a plane within the liquid, and species A and B cannot coexist in the liquid phase.

Slow Reaction. For an isothermal concurrent flow of gas and liquid at steady state, the governing differential equations for species A and B in dimensionless form are

$$\frac{1}{Pe_L}\frac{d^2A_o}{dx^2} - \frac{dA_o}{dx} + R_L(A^* - A\ ) - P\ {}_o^m B_o^n = 0 \tag{66}$$

$$\frac{1}{Pe_L}\frac{d^2B_o}{dx^2} - \frac{dB_o}{dx} - PQA_o^m B_o^n = 0 \tag{67}$$

where

$$Pe_L = \frac{U_L L_o}{E_{ZL}} \quad A_o = \frac{a_L}{a_{Li}}, \quad B_o = \frac{b_L}{b_{Li}}, \quad A^* = \frac{a_L^*}{a_{Li}}$$

$$x = \frac{Z}{L_o}, \quad R_L = \frac{k_L \overline{a}(1 - H_G) L_o}{U_L},$$

$$P = \frac{K_{mn} a_{Li}^{m-1} b_{Li}^{n} L_o}{U_L} \qquad Q = \frac{z a_{Li}}{b_{Li}} \tag{68}$$

The above equations are subjected to the boundary conditions

$$\text{at} \quad x = 0 \quad 1 = A_o - \frac{1}{Pe}\frac{dA_o}{dx} \quad 1 = B_o - \frac{1}{Pe}\frac{dB_o}{dx} \tag{69}$$

$$\text{at} \quad x = 1 \quad \frac{dA_o}{dx} = 0 \quad \frac{dB_o}{dx} = 0 \tag{70}$$

The above equations assume that the liquid phase reactant B, the product of the reaction, and the solvent are nonvolatile. The effective interfacial area for mass transfer $\bar{a}$ and the fractional gas holdup H_G are independent of the position of the column. The Peclet number takes into account any variations of concentration and velocity in the radial direction. We assume that Peclet numbers for both species A and B in the liquid phase are equal. For constant A^*, Equation (66) assumes that the gas phase concentration of species A remains essentially constant throughout the reactor. This assumption is reasonable in many instances. If the gas phase concentration does vary, a mass balance for species A in the gas phase is needed.

A very simple approximate solution to the above equations can also be obtained by a linearization technique suggested by Hlavácek and Hofmann (1970).

A rigorous analytical solution to the above set of equations is not possible. If the liquid reactant B is in excess, the reaction depends only on the concentration of A. In this situation Pavlica and Olson (1970) have considered the case of $m = 1$. For $m \neq 1$, a perturbation solution, such as one outlined by Burghardt and Zaleski (1968), or a Galerkin solution, such as the one outlined by Szeri et al. (1976), would be useful. When the species B is not in excess (that is, completely general case), the above equations can be approximately solved by the Galerkin or perturbation methods outlined by Szeri et al. (1976) or the collocation method outlined by Shah and Paraskos (1975).

A practical example for slow reaction is the oxidation of cumene. This reaction is carried out nonisothermally. A mathematical model for a nonisothermal bubble column reactor which carries out this reaction was recently outlined by Hagberg and Krupa (1976). The equations were solved by a numerical method.

Fast Reaction. When the reaction is completed in the diffusion film of the liquid phase, the enhancement factor in the absorption rate equals $\sqrt{M}$. Thus, the absorption rate and the reaction rate in the diffusion film are comparable. The relevant equations and a numerical solution for them are given by Mhaskar (1974). The approximate Galerkin and perturbation solutions for the equations are given by Szeri et al. (1976).

Instantaneous Reaction. The mathematical equations for this case are very similar to those for the case of a fast reaction. The perturbation and the Galerkin solutions to the relevant equations for the concurrent flow case were recently given by Szeri et al. (1976).

Model for Nonisobaric Column with Variable Gas Velocity. The model described above assumes constant gas velocity and pressure in the reactor. Recently, Deckwer (1976) outlined a dispersion model which took into account the opposite effects of gas shrinkage and expansion caused by absorption and reduced hydrostatic head. A first-order reaction in the liquid phase was assumed. Both slow and fast reaction regimes were considered. The governing nonlinear differential equations were solved on the computer.

The analysis of Deckwer (1976) showed that a sophisticated design of an industrial scale bubble column should account for the axial variations in pressure and the gas flow rate. Even under isobaric conditions, the gas flow decreases owing to absorption which in turn leads to increased gas residence time; thus, higher conversions are obtained. Based on his analysis, Deckwer (1976) concluded that simple isobaric, constant gas velocity models can be applied without serious errors if the column operates at elevated pressures, say 20 atm, and if the gas shrinkage by absorption is small. He also pointed out that in large diameter bubble columns (diameter > 50 cm), gas phase dispersion may be important and it may exert a strong influence on the conversion. In a subsequent study, Deckwer (1977) applied his model to the case of absorption and reaction of isobutene in sulfuric acid.

Fixed-Bed Reactors (Trickle-Bed Reactors)

In a bubble column reactor, the axial dispersion in the liquid phase is unavoidable. Even in a packed bed bubble column, the backmixing has been shown to affect the reactor performance (Montagna and Shah, 1975*a*). In a trickle-bed reactor. the backmixing can play an important role in the performance of a small scale reactor (Mears, 1974; Mears, 1971; Paraskos et al., 1975; Montagna and Shah, 1975*b*). Unlike in a bubble column, however, in a trickle-bed reactor the backmixing can be eliminated by properly adjusting the liquid velocity, packing size, and the length of the packed bed. The backmixing is not important in commercial trickle-bed reactors. Since backmixing is usually harmful to the reactor performance, criteria have been developed for designing a reactor where its effect is minimal.

Isothermal Reactors. In many trickle bed or other types of fixed-bed operation, the mass transfer resistance for the gaseous reactant species is considered to be negligible, and the reaction is considered to be psuedo n^{th} order with respect to the liquid reactant. For this situation, Mears (1971, 1974) presents the following criterion for the minimum L_o/d_p ratio required to hold the reactor length within 5% of that needed for plug flow.

$$\frac{L_o}{d_p} > \frac{20n}{Pe_L} \ln \frac{C_{\text{in}}}{C_{\text{out}}} \tag{71}$$

where $Pe_L = U_{oL} d_p / E_{ZL}$. For a first-order reaction, Mears' criterion is more conservative than that of Petersen (1965), who indicated that plug flow would prevail if

$$\frac{L_o}{d_p} > \frac{1}{Pe_L} \ln \frac{C_{\text{in}}}{C_{\text{out}}} \tag{72}$$

In principle, the above criteria are applied to any flow situation as long as a proper relation for Pe_L is used. Hochman and Effron (1969) have shown that Pe_L for the trickle-bed is considerably smaller (by an order of magnitude) than obtained in corresponding single-phase flow situations. The backmixing effect could, therefore, be more important in two-phase flow through packed beds than in single-phase flow through packed beds.

A criterion similar to Equation (66) for the case where the axial dispersion in both phases is important and where there is a fast reaction between gaseous and liquid species was derived recently by Szeri et al. (1976). Similar criteria in the case of slow reaction can be obtained from the solutions of the equations outlined in the earlier section.

Adiabatic Reactors. Large scale hydroprocessing trickle-bed reactors are normally considered to operate under adiabatic conditions because energy losses from the reactor are usually negligible compared to the energy generated by the reaction. Some examples of such operations are residue hydrosulfurization, petroleum hydrogenation of FCC feedstocks, hydrodealkylation, hydrocracking, and lube oil hydrotreating. The pilot scale simulations of such reactors require a knowledge of the axial dispersion effects on the reactor performance. An axial dispersion model for such reactors was recently outlined by Shah and Paraskos (1975). They showed that the critical Peclet number for elimination of the axial dispersion effect is a function of the heat parameter δ', as well as rate constant R_n'. Some typical results are shown in Figures 11*a* and *b*. The parameters δ' and R_n' in these figures are defined as

$$\delta' = \frac{E}{R_g T_i} \frac{\Delta H C_i}{T_i \rho_L C_{pL} \alpha} \tag{73}$$

$$R_n' = k_f (1 - \epsilon) \tau C_i^{n-1} \exp\left(-\frac{E}{R_g T_i}\right) \tag{74}$$

$$\alpha = 1 + \frac{U_G \rho_G C_{pG}}{U_L \rho_L C_{pL}} \tag{75}$$

The results shown in Figures 11*a* and *b* indicate that for low values of R_n', larger Peclet numbers are required to eliminate axial dispersion in adiabatic reactors than in isothermal reactors. The converse is true for larger values of R_n'.

Shah and Paraskos (1975) applied their analysis to evaluate the importance of axial dispersion on pilot scale reactor performance for residue hydrodesulfurization, gas oil hydrocracking, and to shale oil denitrogenation. The calculations indicate that the axial dispersion effect is less important in the third case than in the first two. Under certain pilot scale operations, axial dispersion effects could be significant in the first two cases.

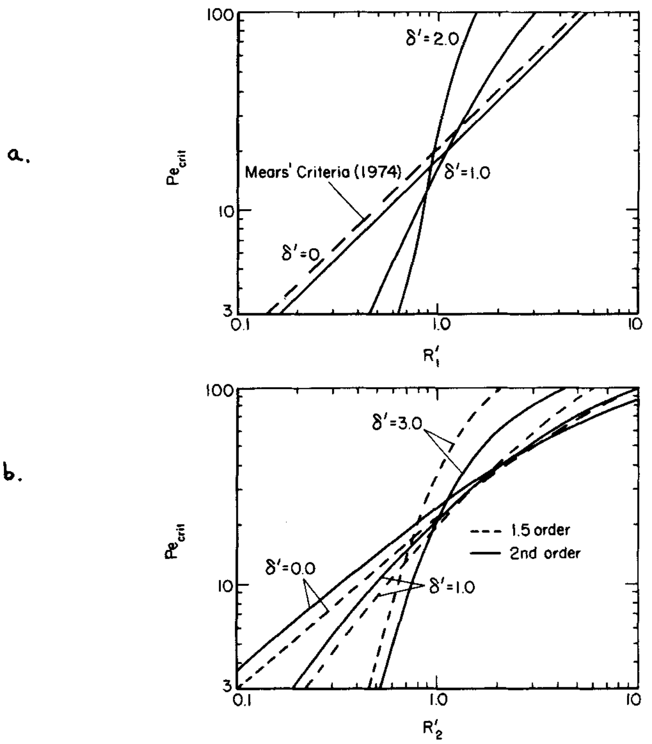

Fig. 11. Critical Peclet number as a function of rate and heat parameters for an adiabatic reactor: (a) first-order reaction, (b) second-order reaction (true second order and effective 1.5 order).

Table 6. Order of Magnitudes of Relevant Kinetic and Transport Parameters for Many Gas-Liquid Systems

Frequency factor for a pseudo just-order reaction $\approx 10^{10}$ s^{-1}

E	= activation energy	≈ 8	to 15 kcal/g mole
ΔH_S	= heat of solution	≈ 2	to 5 kcal/g mole
ΔH	= heat of reaction	≈ 5	to 30 kcal/g mole

Henry's law constant $\approx 1 \times 10^{-6} \dfrac{\text{g mole}}{\text{cm}^3 \text{ atm}}$

MULTIPLE STEADY STATES AND BACKMIXING

Isothermal backmixed gas-liquid reactors are usually stable. The steady state obtained in such reactors is unique. Many gas-liquid reactions, such as chlorination, sulfonation, alkylation, hydrogenation, nitration, coal liquefaction, etc., generate large amounts of heat. On the commercial scale, these reactions are often carried out in adiabatic reactors, which can lead to multiple steady states.

Early studies on stability aspects of two-phase reaction are those by Schmitz and Amundson (1963*a*, *b*, *c*, *d*) and Luss and Amundson (1967).

Hoffman et al. (1975) modeled a gas-liquid CSTR taking into consideration the interactions between the various physical and chemical processes and showed the possible existence of up to five steady states for the single-reaction case. In a subsequent study, Sharma et al. (1976) showed the possible existence of up to seven steady states in the case of two consecutive reactions. The authors claimed that steady state multiplicity is an important discriminatory tool in the estimation of kinetic parameters.

For a pseudo first-order reaction, the analytical criteria for multiplicity of steady states were derived more recently by Raghuram and Shah (1977). The following conclusions were drawn by the authors:

1. Five steady states occur only when the reaction originates in the slow regime and the liquid flow rate is small enough to allow for the accumulation of the gaseous reactant in the liquid phase.
2. In all other instances, only three steady states are possible, except in the case of reaction that originates in the instantaneous regime when steady state multiplicity should not be observed.

From the studies carried out so far, it is believed that the conditions most conducive to multiplicity in steady states are high heats of reaction and solution, high activation energy, and the low value of liquid phase mass transfer coefficient. For many gas-liquid reactions, the values of the observed kinetic and transport parameters are listed in Table 6. The analysis of Raghuram and Shah (1977) indicates that for these values of the parameters, multiple steady states are not likely to occur. It appears that high values of activation energy and the frequency factors are vitally important before the multiple steady states are observed in gas-liquid reaction systems.

As yet, five steady states have not been obtained experimentally. Two relevant studies are those by Ding et al. (1974), who showed multiple steady states during chlorination of *n*-decane, and Hancock and Kenney (1972), who showed unusual dynamic phenomena, such as sustained periodic oscillation, during the formation of CH_3Cl by reaction between CH_3OH and hydrochloric acid in the presence of $ZnCl_2$ catalyst in a bubble column reactor.

RTD AND SCALE-UP PROBLEMS

The RTD and mixing characteristics can be subjected to a host of problems in the proper scale-up of a gas-solid reactor. Van Goolen (1976) and DeRooij et al. (1977) have examined the important scale-up problems associated with the DSM phosphate caprolactam process which uses a three-phase sparged reactor for reduction of NH_4NO_3 with hydrogen in the presence of noble metal on carbon as catalyst. Some of the important scale-up problems can be listed as follows:

1. RTD data from small scale apparatus cannot be used for larger scale units. Ross (1965) has shown this for hydrodesulfurization in a trickle-bed reactor. The prevailing flow regimes in small and large scale reactors may be different.

2. Flow maldistribution of the phases can render the evaluation of RTD data very difficult. In some cases, maldistribution may exist in small units, but it may not exist in large scale units (for example, trickle-bed reactors). In some other cases, such as three-phase fluidized-bed reactors, nonuniform gas distribution in large scale units may cause undesirable recirculation and dead zones. Uniform gas distribution can usually be achieved in the small scale fluidized-bed reactor.

3. In small scale apparatus, no backmixing may be observed, but larger scale units might show substantial backmixing. For instance, in small size packed bubble columns, the gas phase moves in plug flow, but for larger size units, there may be substantial backmixing in the gas phase.

4. In sectionalized bubble columns, we may optimize the height-to-diameter ratio of each section to 0.8 to 1.2 and prevent backmixing of liquid between sections. However, in larger units, this height-to-diameter ratio may be completely unsatisfactory for preventing mixing between sections.

5. In large size mechanically agitated multistage contactors, the speed of the agitator is kept at a relatively low level, and horizontal baffles are provided. Here, RTD in the gas and liquid phases may show different behavior compared to a small scale unit.

RECOMMENDATIONS FOR FUTURE STUDY

From the reactor design and modeling point of view, the RTD analysis has to be combined with the intrinsic kinetics and other mass and heat transfer effects prevailing in the reactor. Unless some simplifying assumptions are made, the mathematical equations describing the performance of a simple gas-liquid reactor can be very complex, even when the RTD is described by the simple axial dispersion model. From this point of view, the macromixing models which include more than two parameters will find very limited use for reactor design and modeling purposes. Further work on macromixing models involving a large number of parameters should therefore be avoided.

Several important practical aspects of the RTD are still unavailable from the reported literature. Future research should include the following studies.

1. Experimental RTD data from real commercial reactors are needed. This type of data would be very useful in examining the applicability of macromixing models discussed here to large scale systems. Furthermore, with the help of such data, one could evaluate the usefulness of various models for scale-up purposes and their applicability to systems other than air and water.

2. The applicability of the proposed macromixing models has been generally restricted to the bubble and trickle flow conditions. Their usefulness in correlating RTD in pulsating and spray flow regimes needs to be investigated.

3. In most of the macromixing models, radial mixing in the bulk fluid phases is assumed to be complete. However, in some flow regimes (for example, pulsating flow regime), this may not be a good assumption. While the assumption of complete radial mixing may be reasonable in some small scale reactors, it may be questionable in some large scale reactors. Some criteria for the reactor conditions where one may assume complete radial mixing (both mass and heat) need to be developed. The criteria, of course, should consider all phases and all possible flow regimes in the reactor.

4. The axial dispersion of heat in large scale reactors should be measured. This information would be useful in modeling large scale nonisothermal reactors.

5. Since gas causes most of the mixing in three-phase reactors, its distribution is, of course, very important. For small diameter columns, the nature of a gas distributor is known to have a significant effect on RTD. Similar information on large diameter columns is presently unavailable. For reactor scale-up purposes, such information is desirable. Studies should consider various reactor configurations and flow regimes.

6. Maldistribution of liquid may be a problem in large columns and/or under low liquid flow conditions. Proper study of liquid distribution (both in small as well as large columns) and its effect on the RTD is needed. The study should include wide ranges of gas and liquid flow rates and a variety of reactor configurations. From this type of study, the design criteria for minimizing the maldistribution of liquid should be developed. Studies should include the role of liquid distributor design.

7. So far only the axial dispersion model has been used for scale-up purposes. Very little knowledge on the effects of reactor configuration and flow conditions on the parameters of more complex macromixing models (for example, two-parameter model, etc.) is available. Since these complex models are more realistic, more information on the relation between their parameters and the system conditions such as packing size, fluid properties, and flow rates needs to be obtained. At present, complex models are not very useful for scale-up purposes.

8. There is a real dearth of RTD data in gas-liquid reactors where non-Newtonian fluids are involved. Future study should obtain these data.

NOTATION

A = gas phase component being absorbed
$\bar{a}$ = interfacial area
a_b = free area in baffles between compartments
a_c = cross-sectional area of the column
a_L = concentration of species A in the liquid phase at distance Z from the bottom of the column
a_{Li} = inlet concentration of A in the liquid phase
a_L^* = solubility of species a in the liquid phase
a_r = free area fraction of a perforated plate
a_s = surface area of packing per unit volume of packed bed
B = liquid phase component
b_L = concentration of species B in the liquid phase at a distance Z from the bottom of the column
b_{Li} = inlet concentration of species B in the liquid phase
b_L^* = gas-liquid interface concentration of species B
C = tracer concentration
C_d = tracer concentration in the mobile phase

C_E = equilibrium tracer concentration
C_i = reactor inlet concentration of reactant
$C_{\text{in}}, C_{\text{out}}$ = inlet and outlet concentrations of reactant
C_p = heat capacity
C_s = tracer concentration in the stagnant phase
$C(s)$ = Laplace transformed distribution of tracer
Ct = Craya-Curtet number defined by Equation (62)
$C(t)$ = tracer concentration at time t
d = characteristic dimension required for dimensionless numbers
D_A = diffusivity of species A in the liquid phase
d_h = diameter of distributor plate holes
d_i = impeller diameter
d_n = nozzle diameter
d_p = characteristic packing dimension
d_t = reactor or column diameter
E = activation energy
$E(t)$ = distribution of tracer
E_Z = axial dispersion coefficient
E_Z^* = axial dispersion coefficient for a stage in a staged column
E_{Zav} = average dispersion coefficient over a tray
f = fraction of stagnant liquid
f_b = fraction of inlet fluid to a stage which bypasses that stage
Fr = Froude number, $U_o/\sqrt{gd_t}$
$F(s)$ = Laplace transfer function
$F(t)$ = arbitrary tracer input signal
g = acceleration of gravity
Ga = Gallileo number, $(d_p^3 g\rho^2)/\mu_L^2$
G_G, G_L = superficial gas and liquid mass velocities
$G(\lambda)$ = response function of a system
H = fluid holdup
H_e = expanded bed height
h_f = height of the foam column
h_L = height of the static liquid column
HMU = height of the liquid phase axial mixing unit, $2H_e/Pe$
H_o = unfluidized bed height
I = first-order Bessel function of first kind
K = backflow ratio
k = mass transfer or exchange coefficient between flowing and stagnant liquid
k_f = reaction frequency factor
k_L = liquid film mass transfer coefficient
K_{mn} = reaction rate constant between species A and B
L = distance between tracer detection points
L_B = bubbling height
L_c = characteristic length
L_h = compartment height
L_n = nozzle spacing
L_o = reactor length
L_p = plate thickness
L_Z = longitudinal distance between the tracer injection and detection points
m = reaction order with respect to species A
M = mass of tracer
$\sqrt{M}$ = system characterization parameter defined by Equation (63)
n = reaction order with respect to species B
N = agitator speed
n_h = number of distributor plate holes
n_s = number of stages
Pe = Peclet number, UL_c/E_Z
Pe_i = Peclet number for a stage, $U_{0L}L_o/E_{ZL}^*$
q_A = parameter defined by Equation (64)
Re = Reynolds number, d_pG/μ
R_g = universal gas constant
R_n' = rate constant defined by Equation (74)
s = Laplace transform parameter
t = time
t_i = time at which tracer first appears in the effluent
T_i = reactor inlet temperature
t_m = mean residence time of the fluid
t_o = average delay time
U = real mean or interstitial fluid velocity
U_b = rising velocity of a gas bubble
U_c = circulation velocity
U_n = nozzle velocity
U_o = superficial fluid velocity
U_o' = superficial velocity of the liquid that backflows at each plate
U_r = relative velocity between the gas and liquid phase
U_{to} = terminal velocity of a single particle
V = volumetric flow rate
z = stoichiometric factor in the reaction between species A and B
Z = axial coordinate

Greek Letters

α = parameter defined by Equation (75)
ΔH = heat of reaction
ΔH_s = heat of solution
ΔL = plate spacing
δ = impulse input of tracer
δ' = heat parameter defined by Equation (73)
ϵ = void fraction
η_o = total number of delays
λ = dummy variable
μ = fluid viscosity
μ_i = first moment of response curve
ϕ = fraction of flowing liquid
ϕ_a = fraction of agitated fluid entering a stage
ϕ_c = volume fraction of the contact zone occupied by a phase
Ψ = impeller correction factor (ratio of the impeller Power number to that of a six-blade impeller)
ρ = fluid density
σ = standard deviation
σ_θ^2 = dimensionless second moment of response curve
τ = space time

Subscripts

G = gas phase
L = liquid phase
S = solid phase
i = position of detection equipment in relation to tracer injection position

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A Constitutive Equation for a Viscoelastic Interface

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A constitutive equation has been developed to relate surface stresses to the deformational history of an interface. This equation is designed to provide a unified description of complex interfacial rheological phenomena. New and as yet unreported behavior such as surface normal stresses and viscoelastic contributions to the dynamic surface tension are predicted.

A monolayer of poly(vinyl alcohol) adsorbed at an air/water interface has been studied using a deep channel surface rheometer and the observed viscoelastic behavior shown to be fitted by the model.

SCOPE

Surface active molecules preferentially adsorb at an interface, often forming a dense, packed monolayer even though the concentrations in the adjacent bulk phases are quite small. The presence of small quantities of surfactants may not measurably change the bulk rheological properties, but mechanical properties may be altered dramatically in the interfacial region. For example, it is possible for the surface viscosity to exhibit shear-rate dependence even though the bulk phases may be Newtonian. Also, viscoelastic behavior in which the surface tends to snap back upon relaxation of stress has been observed. It is the purpose of this paper to unify such phenomena.

The mechanical behavior of bulk phases has, in general, been described through the use of constitutive equations, or rheological equations of state, which contain parameters whose values depend on the nature of the fluid. A parallel approach is taken here. A constitutive equation which applies to the interfacial region is presented. This equation allows for both non-Newtonian steady shear and viscoelastic behavior and therefore provides a unified description of complex interfacial rheological phenomena. Since the constitutive equation contains a number of parameters, it is reasonable to inquire as to whether or not these parameters are experimentally accessible, and, if they are, does the equation represent a real fluid interface. To demonstrate that at least some real surfaces can be represented by the proposed equation, the interfacial behavior of an aqueous solution of poly(vinyl alcohol) has been studied. To evaluate the parameters, a new experimental technique which employs a small amplitude sinusoidal surface deformation has been used in conjunction with surface viscometry. The data are closely approximated by the constitutive equation.

Viscoelastic interfaces have previously been represented using simple rate-type constitutive equations, which contain one or more partial derivatives with respect to time but not more complicated frame indifferent (Astarita and Marrucci, 1974) time derivatives. The Maxwell model (Joly, 1972; Mannheimer and Schechter, 1970) is one example.

Shear-rate dependent surface viscosities (one type of non-Newtonian steady shear behavior) have been treated using generalized Newtonian constitutive equations (Astarita and Marrucci, 1974), where the stress may be a nonlinear function of strain rate but not of the deformational history. The Powell-Eyring model has, for example, been used (Pintar, Israel, and Wasan, 1971). Both the

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