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Gas-Liquid Mass Transfer in Fixed-Bed Reactors with Cocurrent Downflow Operating in the Pulsing Flow Regime

Liquid-side mass transfer coefficients were measured for cocurrent two-phase downflow in 5 and 10 cm diameter columns packed with 2.5 and 4 mm Raschig rings. Experiments were specifically carried out in the pulsing flow regime. The mass transfer coefficients were determined via absorption of CO₂ into buffer solutions with the advantage of a high absorbing capacity. Thus columns of 1 m length could be used. Relations are proposed based on the hydrodynamic phenomena observed in pulsing flow. From these relations a correlation for k_L is found in terms of flow rates and packing characteristics that satisfies the experimental data.

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SCOPE

Packed columns with cocurrent downflow of gas, trickle-bed reactors, are often used in industry. Different flow regimes can be distinguished, normally operation is in the so-called gas-continuous regime, where hydrodynamic interaction between gas and liquid is low as in a countercurrently operated column. At higher gas and liquid loads liquid-rich waves travel through the column, pulsing flow. In the pulsing flow regime operation

can be very advantageous, since the degree of axial mixing decreases and the rate of mass transfer between gas and liquid increases.

In this contribution relations are given for the rate of mass transfer between gas and liquid in dependence on gas and liquid velocity and holdup in the pulsing flow regime.

CONCLUSIONS AND SIGNIFICANCE

It appears possible to explain experimental mass transfer between gas and liquid in pulsing trickle bed reactors with a model that assumes that in pulsing flow two distinct phases of the liquid can be distinguished: the pulses and the regions in between the pulses. Increasing the liquid flow rate means that more pulses appear in the bed, but the regions in between the pulses remain the same in liquid holdup and mass transfer rate per unit volume. Since the holdup and pulse frequencies are known from earlier investigations, we can work out a relation-

ship for the mass transfer coefficient that covers the experimental findings within 20%:

$$k_L a = 5.9 \cdot 10^{-2} \cdot Sc^{-2.2} u_{Lg}^{0.58}$$

The results support the concept of pulsing flow being a transition zone between the gas-continuous and the dispersed bubble flow regime, where the pulses are moving zones in the bed, already in the dispersed bubble flow regime, interspaced by gas-continuous zones.

INTRODUCTION

Packed columns with cocurrent downflow of gas and liquid are widely used in the chemical and especially the petrochemical in-

dustry. One of the main advantages is the fact that high throughput rates are possible for liquid and gas. The disadvantage that only one theoretical mass transfer stage can be attained is generally overcome by a great absorbing capacity in one of the two phases, be it physically or chemically; often the transferred component is consumed by a chemical reaction either directly in the liquid phase or at the catalytic surface of the packing. The overall rate of the

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process is controlled by the following steps (Satterfield, 1975)

- a) Mass transfer at the gas side of the interface
- b) Mass transfer at the liquid side of the interface
- c) Mass transfer at the liquid side of the catalyst particles
- d) Transport within the catalyst particles
- e) Chemical reaction

One or several of these steps can be rate-determining. Especially the steps a, b and c will be influenced by the column hydrodynamics.

In cocurrently-operated columns several patterns of gas and liquid flow can occur. Commonly the gas-continuous, the pulsing and the dispersed bubble flow regime are distinguished (Charpentier, 1976; Blok and Drinkenburg, 1982).

The gas-continuous regime, encountered at relatively low gas and liquid flow rates, resembles very much the situation in countercurrent flow below the loading point. Mass transfer rates across the gas-liquid interface were studied in this regime by Ufford et al. (1973) and Goto et al. (1975) in a situation with controlling resistance in the liquid phase (step b). Shende and Sharma (1974), and Wen and O'Brien (1963) did the same with controlling resistance in the gas phase (step a). In the work of Goto, for small particles (3–4 mm), no influence of the gas flow rate on the liquid-side mass transfer coefficient was found.

Mass transfer in the pulsing flow regime was studied by Reiss (1967), Gianetto et al. (1970, 1973), Hirose et al. (1974), and Sylvester et al. (1975). In this regime, it was found at higher gas and liquid loads, that the liquid periodically blocks the gas channels in the bed. A liquid plug then develops that is blown away by the gas flow and that travels downward with a relatively high velocity (~ 1 m/s) (Charpentier, 1976; Blok et al., 1982). The phenomenon recurs with a frequency of 1 to 10 Hz depending on the gas and liquid flow rate. The boundary between gas-continuous flow and pulsing flow is sharp. It has been found that the liquid-side mass transfer coefficient strongly increases in the pulsing flow regime with increasing liquid and gas flow rate (Mahajani and Sharma, 1979); this was less pronounced for the gas-side mass transfer coefficients. Gianetto suggested that the high rate of transfer is particularly due to the strong increase of the available gas-liquid contact area in the pulsing flow regime. So did Mahajani and Sharma (1980).

The transition from the pulsing to the dispersed bubble flow regime is not sharp. As the liquid flow is increased, pulse frequency also increases until it is not possible to distinguish between the separate pulses; the bed is then said to be in the dispersed bubble flow regime. The liquid phase is now the continuous phase and the gas flows in the form of small bubbles. Some data from Hirose et al. (1974) are available for this regime.

GENERAL DISCUSSION

This paper will further concentrate on the pulsing flow regime. Reported values for gas-side mass transfer coefficients are at least a factor 10 higher than those for the liquid side. Moreover the solubility of the components to be transferred in the liquid phase is often low; so in most cases mass transfer rates for the gas-liquid interface are completely determined by the liquid-side mass transfer resistance. The experimental work was thus focused on this last parameter.

Mass transfer rates have most often been determined by experiments that employed pure physical transfer operations. Values for the product of transfer coefficient and active specific surface presented in the literature are always calculated on the basis of a plug assumption for the gas and liquid flow thereby using concentrations measured outside the column. These values are so-called "exterior apparent" data. Since assumption of plug flow is reasonably well justified for columns having a length of 1 m and more, the deviation from the real "interior" values will not be serious in these cases. Nevertheless it should be remembered that the data for small packing particles (Gianetto et al., 1973; Hirose et al., 1974) also include values based on experiments in very short columns;

used while the rapid establishment of physical equilibrium between gas and liquid in a cocurrent operated column with high interfacial areas did not permit the use of tall columns.

The value of $k_L a$ in the pulsing flow regime is significantly higher than in the gas-continuous flow regime. Also the value is strongly dependent on the gas flow rate. Some of the proposed correlations (Gianetto, 1973; Reiss, 1967) are founded on the premise of a relationship between the energy dissipation in the column and the value of $k_L a$. As a measure of this dissipation the product of pressure drop per unit length and the superficial liquid velocity ($-(dP/dz)u_L$) is taken. As pointed out by Hirose this is in fact the energy required to drive the liquid into the column per unit column volume, which is not necessarily connected with the energy dissipated at the gas-liquid interface only, the gas flow rate being much higher than the liquid flow rate. Besides this interpretation problem such correlations have the disadvantage that all the relevant hydrodynamic information has to be properly accounted for by single parameter: the energy dissipation. Moreover it also leaves the problem of predicting this energy dissipation (Rao and Drinkenburg, 1983).

Part of this investigation is therefore directed towards correlations for the mass transfer coefficient based on a more detailed description of the hydrodynamical behavior of the column. Expressions are sought in terms of external and thus well-known parameters like fluid flow and packing characteristics. We will thereby make use of our work on the hydrodynamical properties of pulsing flow (Blok and Drinkenburg, 1982).

It was found that pulses occur in the column when a minimum real vertical liquid velocity is exceeded, the real vertical liquid velocity defined as the superficial liquid velocity divided by the relative liquid holdup. Further it was shown that the liquid holdup between pulses is fairly constant and independent of the liquid flow rate. All liquid flow in excess of the flow rate at the transition is in the pulsing flow regime carried through the bed in the form of pulses. Consequently the hydrodynamical situation between pulses is not affected by the liquid flow rate.

This leads to the idea that at constant flow rate the pulses themselves must be responsible for the increase of the rate of mass transfer with an increase of the liquid flow rate (Mahajani and Sharma, 1979). Remains the question of how the action of the pulses must be looked upon. An interpretation in terms of the penetration model in which the pulse itself would act as a surface renewer and the penetration time would be given by the elapsed time between pulses does not seem likely; the residence time of a liquid element on a packing particle is in the order of magnitude of 0.05 second. When the liquid-gas interface is assumed to be refreshed after the passage of one packing particle it would require pulse frequencies of about 20 Hz to contribute sensibly to the process. It is thought that the pulses activate poorly wetted or refreshed parts of the packing (dead zones) and increase the local mass transfer coefficient by high turbulence.

In our view it seems thus likely to conceive the pulses as zones which are already in the dispersed bubble flow regime having a higher value for the mass transfer rate. The pulsing flow regime is then considered to be a transition regime between the gas-continuous and the dispersed bubble flow (liquid-continuous) regime. In this concept the local $k_L a$ values vary with time; between pulses the value is lower than during the passage of a pulse. To verify and develop these considerations it is necessary to have data on the pulse frequencies together with $k_L a$ values for different column diameters and packing particles. Also scale-up problems can be expected in case of different pulse characteristics in different columns (Blok and Drinkenburg, 1982). Therefore $k_L a$ values were measured in columns of 5 and 10 cm diameter, 1 m in length, and filled with either 2.5 or 4 mm Raschig rings. Liquid flow rates ranged from 0.007 to 0.025 m/s and gas flow rates from 0.5 to 1.9 m/s. Details are given in the experimental section.

$k_L a$ DETERMINATION METHOD

In a cocurrent system the determination of the rate of mass transfer poses problems. Physical absorption or desorption can only

be tolerated for measuring heights up to 30–40 cm, physical equilibrium then normally is reached. In case this method is chosen there are two possibilities. One could use a column not larger than say 20–25 cm, or install in a larger column, a differential element of about 20 cm over which the transfer takes place. The first approach has the advantage in that, since pulses are only fully developed about 20 cm from the top of the column, the influence of the pulses on the mass transfer rate is minimal and thus hard to discover. In the second approach the component to be transferred has to be introduced, at a certain height, into the column. This has to be realized in such a way that the time required to reach a constant concentration across the column cross-section is short compared to the time available for mass transfer. Also the determination of the actual entrance concentration may cause severe problems. Both methods suffer from the fact that the measured “exterior apparent” values of $k_L a$ differ more from the real values since it might not in all cases be justified to neglect the effect of axial mixing on the concentration gradient.

The limitations of the above technique arise from the small capacity of the liquid phase compared to the rate of mass transfer. By increasing the absorbing capacity of the liquid phase without affecting the rate of mass transfer a reasonable column length may be employed, and the introduction and detection of the component to be transferred is also relatively simple. Danckwerts and Sharma (1966, 1970) and coworkers have developed several methods for increasing the ratio of absorbing capacity over mass transfer rate by making the liquid phase chemically active towards the transferring component. In his review on mass transfer in packed columns, Charpentier (1967) presented a summary of the methods and results. For the present work it was decided to use the absorption of carbon dioxide into buffer solutions composed of potassium carbonate/bicarbonate in order to determine the $k_L a$ values. As pointed out by Joosten and Danckwerts (1975), differences will exist between $k_L a$ values obtained at different capacity over absorption rate ratios. The lower this ratio (lowest value for pure physical transfer), the sooner parts of the liquid with a low refreshing rate can become saturated and thus inactive. This effect also reduces the meaning of separating $k_L a$ into k_L and a . In most cases the $k_L a$ value and the a value are determined at different absorbing capacity over absorption rate ratios. For design calculations data should be taken for a ratio as close as possible to the practical solution.

EFFECT OF GAS-SIDE RESISTANCE

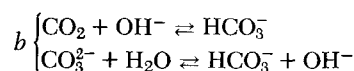
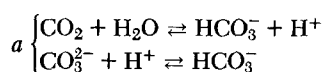
The overall resistance to mass transfer across the gas-liquid phase boundary is basically written as:

$$\frac{1}{k_{oL}} = \frac{1}{mk_g} + \frac{1}{k_L}$$

with k_g and k_L representing the partial mass transfer coefficients for gas and liquid side respectively; m is the distribution coefficient defined as the ratio of the gas- and liquid-phase concentration at physical equilibrium (modified Henry coefficient). According to Gianetto, the expected values for k_g are in the range 0.02–0.06 m/s whereas those for k_L are reported between 10^{-4} and $6 \cdot 10^{-4}$ m/s in the pulsing flow regime. The minimum m value for the solutions used is 2.4 so the resistance to mass transfer may well be considered to be entirely in the liquid phase as long as no appreciable enhancement of the transfer, due to the chemical reaction, takes place.

DETERMINATION OF $k_L a$

For the absorption of CO_2 into $\text{HCO}_3^-/\text{CO}_3^{2-}$ solutions the following reactions must be considered:



In both cases the overall reaction is: $\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^-$. The reaction with water (scheme a) is slow with respect to the reaction with hydroxyl ions. In a separate study this reaction system in a cocurrent gas-liquid flow has been analyzed (Blok, 1981). The relation between $k_L a$ and the system variables was found to be:

$$\frac{1}{k_L a} = \frac{1}{R_a} - \frac{1}{k_r \beta} + C \quad (1)$$

R_a is an “apparent” value of $k_L a$, found from the experimental data when ignoring the presence of a nonzero background concentration of CO_2 in the liquid phase, as well as mass transfer enhancement by chemical reaction. k_r is the pseudofirst-order reaction rate constant; β is the relative liquid holdup; and C is a correction term resulting from the fact that at chemical equilibrium $[\text{CO}_2]$ is not zero. R_a and C can be determined from the experimental data via:

$$R_a = \frac{m \varphi_{vo}}{V} \cdot \frac{P_o}{P_o + \Delta p} \cdot \ln(y_H/y_o) \quad (2)$$

$$C = \frac{-C_e VRT}{p_o \varphi_{vo}(y_H - y_o)} \quad (3)$$

It is rather inaccurate to determine the value of k_r from literature data due to a lack of data in the ionic strength range used. Therefore the absorption rate was explicitly determined in a wetted wall column for the solutions used. In order to calculate values for k_r from these measurements the values of c^*/D were taken from the work of Joosten (1975) who used the same cation and ionic strengths, Table 1.

TABLE 1. DETERMINATION OF k_r

CO_3^{2-} mol/L	HCO_3^- mol/L	I g ion/L	c^*/D mol·m ⁻² ·s ^{-1/2}	k_r s ⁻¹
1.3	0.65	4.6	$5.1 \cdot 10^{-4}$	5.1
1.2	0.8	4.4	$5.6 \cdot 10^{-4}$	4.0
1.0	1.0	4.0	$6.0 \cdot 10^{-4}$	3.0
0.8	1.2	3.6	$6.5 \cdot 10^{-4}$	2.3

The values of k_r are higher than predicted on these basis of literature data. This might be caused by the uncertainties mentioned in the estimates based on literature data, but also by the presence of various metal ions from our partly metal experimental apparatus that could be promoting the reaction of CO_2 with water. From Table 1 the following correlation was developed for use in the calculations:

$$k_r = 14 \cdot I^{-1.1} \cdot [\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (4)$$

The relations are valid over the whole column as long as the reaction rate constant is unchanged; i.e., the ratio of carbonate over bicarbonate concentrations should be constant along the column height. This might be verified by the following calculation.

The amount of CO_2 absorbed per unit liquid volume is given by

$$k_L a \cdot H \cdot \Delta c / u_L$$

H is the column height, Δc the driving force in the liquid phase, and u_L the liquid superficial velocity. Assuming the maximum value for $k_L a$ to be 1.0 s^{-1} and the bulk liquid concentration to be zero so that Δc is equal to the physical equilibrium concentration, c^* , the worst case, can be determined, Table 2.

TABLE 2. MAXIMUM ERROR IN THE REACTION RATE CONSTANT

$[\text{CO}_3^{2-}]_o$ mol/L	$[\text{HCO}_3^-]_o$ mol/L	q_o —	q_H —	I_o g ion/L	I_H g ion/L	$\Delta k_r/k_r$ %
1.3	0.65	2	1.8	4.5	4.5	9
1.0	1.0	1	0.91	4.0	4.0	9
0.8	1.2	0.63	0.61	3.6	3.6	9

TABLE 3. SELECTED BUFFERS

CO ₃ mol/L	HCO ₃ mol/L	I g ion/L	k _r s ⁻¹	η N·s/m ²	ρ kg/m ³
1.3	0.65	4.6	5.1	1.44 · 10 ⁻³	1,150
1.2	0.80	4.4	4.0	1.39 · 10 ⁻³	1,180
1.0	1.0	4.0	3.0	1.36 · 10 ⁻³	1,170
0.80	1.2	3.6	2.3	1.34 · 10 ⁻³	1,170

All values at 25°C.

In practice the error in k_r will be less than 9% since the background concentration will not be equal to zero, thus the mean driving force (Δc) will be lower. Therefore k_r is assumed to be independent of the axial position in the column.

To determine experimentally the value of $k_L a$ the procedure has been followed to perform experiments with liquids having various reaction rate constants. The selected buffer concentrations are reported in Table 3.

A plot of $1/R_a + C$ vs. $1/k_r$ yields a straight line with slope $-1/\beta$ and intercept $1/k_L a$. Since in our situation β is also known from other experiments it is theoretically possible to determine $k_L a$ from only one experiment with a known reaction rate constant. Nevertheless, preference was given to the first-mentioned procedure because less weight is given to systematic errors in k_r and the value of β is not needed at all.

EXPERIMENTAL

The experiments were carried out in the same apparatus as used in our earlier investigations; the liquid could be supplied from one of four vessels (250 L) each containing a buffer solution. The buffer solutions were prepared with the chemicals K₂CO₃ and KHCO₃ of normal "pure" quality (free of water) together with demineralized water.

Carbon dioxide was added to the pretreated air stream. Entrance con-

TABLE 4. PACKING MATERIAL SPECIFICATIONS

RR Glass	Height 10 ⁻³ m	Ext. Diam. 10 ⁻³ m	Int. Diam. 10 ⁻³ m	Porosity m ³ Void/ m ³ Column	Spec. Area m ² /m ³ Column
2.5	2.57	2.51	1.25	0.60	1,720
4	4.14	4.00	2.87	0.73	1,070

centrations of CO₂ were about 5% by volume. The two columns used had diameters of 5 and 10 cm respectively and were 1 m long. Raschig rings, 2.5 and 4 mm, made of glass, were used as the packing material. In Table 3 the specifications of the buffer solutions and in Table 4 those of the packings are listed.

The operating temperature was always 25°C. Because the liquid was recirculated to the storage tank, the ratio $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ was determined every 10 to 20 min (depending on the total mass transfer rate) during the experiment, by means of titration of samples with HCl. When the ratio differed more than 5% from the original setting, a KOH (5N) solution and water were added to readjust this ratio, at the same time keeping the ionic strength constant.

The entry and exit concentrations of carbon dioxide in the gas phase were determined. A small sample gas stream was drawn from the entrance and exit gas streams. The streams were dried over silicagel and fed to the two measuring chambers of an interferometer (Jena LI 3, cells of 1 m in length). In this way direct concentration difference measurements between the top and the bottom of the column were possible. Subsequently the cell, filled with the bottom sample, was blown through with CO₂-free air and the absolute concentration at the column entrance was thus determined. The absolute accuracy of these measurements was better than 0.05 vol. % CO₂, which guaranteed a measurement of the carbon dioxide depletion with an error of less than 5%.

RESULTS AND DISCUSSION

The experimental results are presented in Figures 1 and 2. $k_L a$

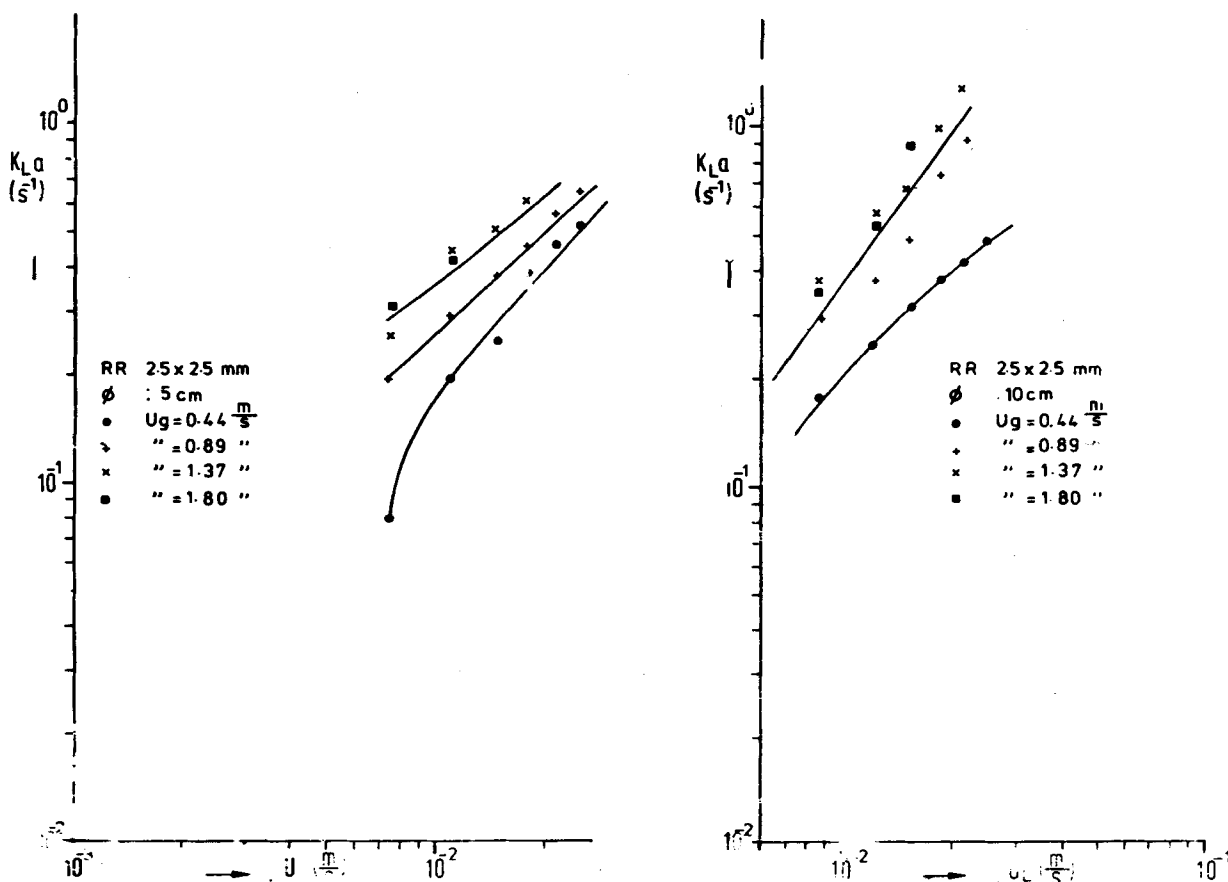


Figure 1. $k_L a$ vs. superficial liquid flow rate at various gas flow rates; column diameter 5 cm and 10 cm; RR 2.5 mm.

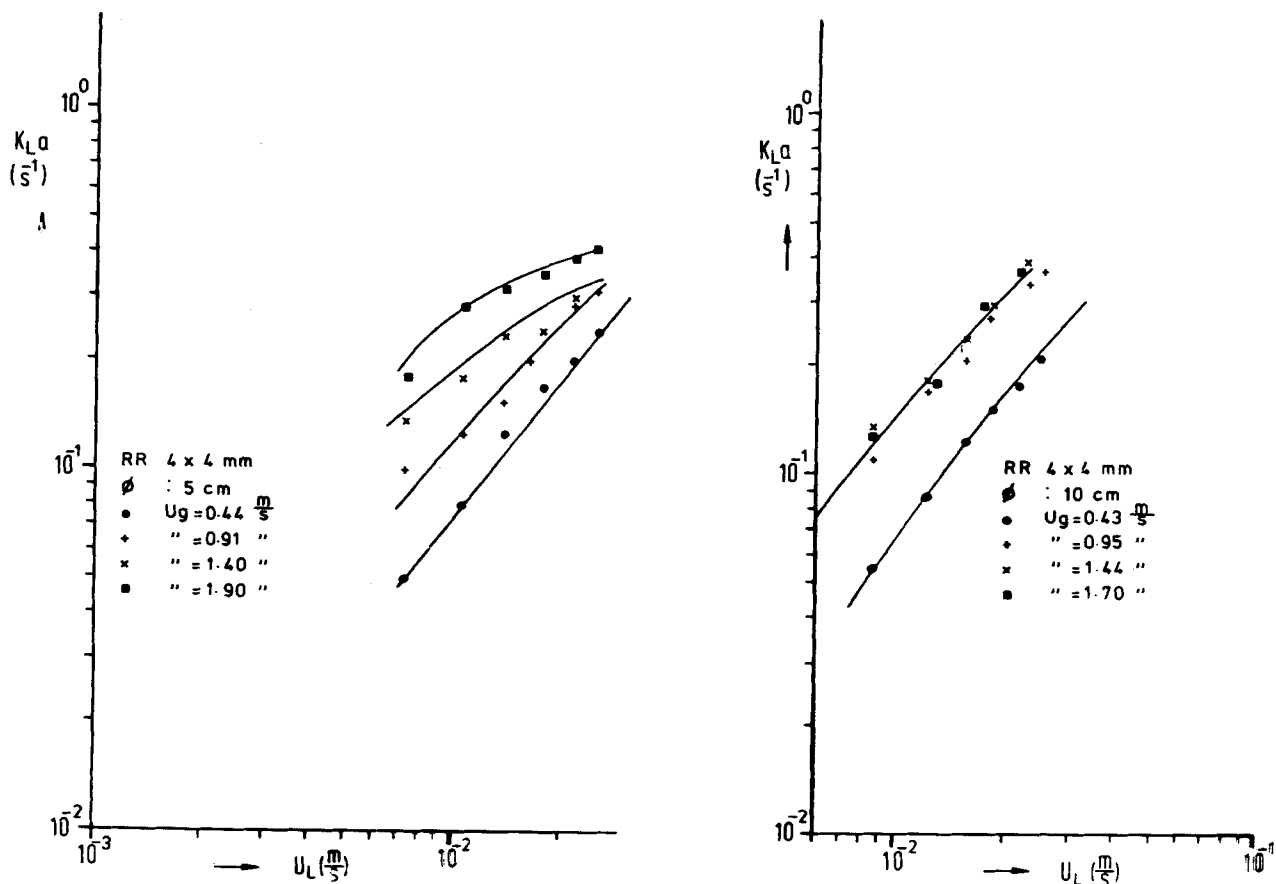


Figure 2. $k_L a$ vs. superficial liquid flow rate at various gas flow rates: column diameter 5 cm and 10 cm; RR 4 mm.

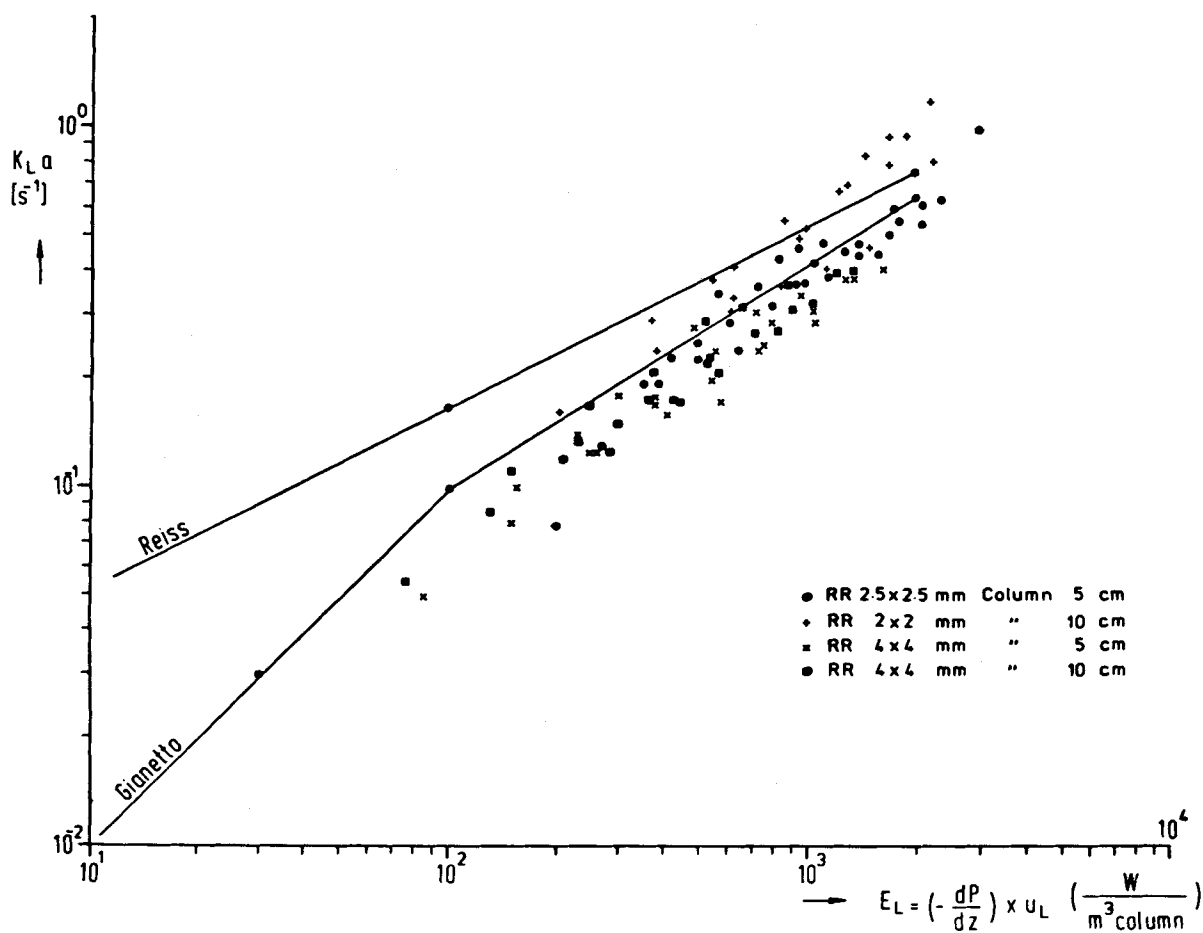


Figure 3. Influence of the energy dissipation on $k_L a$.

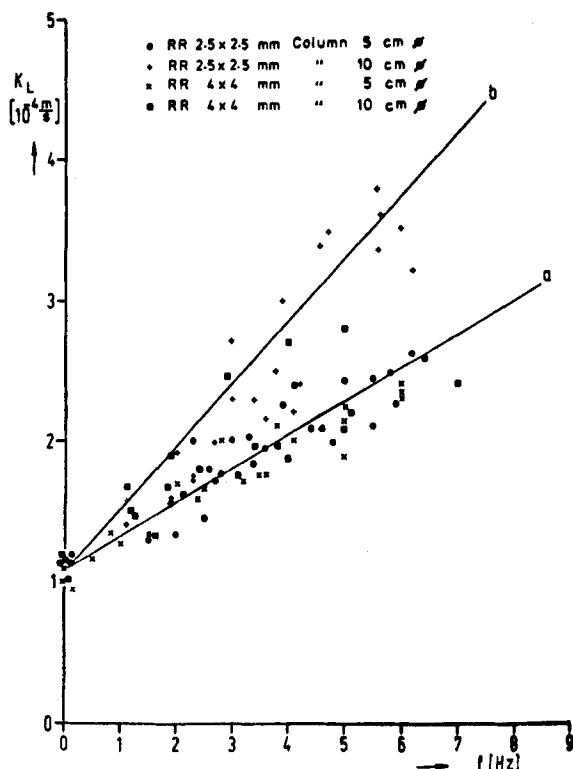


Figure 4. Relation between k_L and the pulse frequency.

increases considerably in the pulsing flow regime. Especially in the 10 cm diameter column the data points at higher gas velocities seem to aggregate around one line. The results are average values over 1 m column length, including the part where pulses are formed.

In Figure 3, $k_L a$ is plotted against the energy dissipation. Also the correlations of Reiss and Gianetto are shown. As already noted by Gianetto, the Reiss correlation seems to be too high, especially at lower energy dissipations. The modified energy dissipation definition of Hirose does not improve the correlation. The best fit is:

$$k_L a = 2.57 \cdot 10^{-3} \left\{ - \left(\frac{dp}{dz} \right) \cdot u_L \right\}^{0.72} \quad (5)$$

which is very close to the correlation of Gianetto.

As mentioned before, correlations like this have the general disadvantage of not to be based upon a fundamental approach. Nevertheless they can be very useful as an estimate for which only the pressure drop has to be known. Gianetto and Hirose tried to develop fundamental relations based on the real liquid velocity v_L ($= u_L / \beta$). It should be kept in mind, however, that this velocity does not actually exist, since there are in fact two different holdup levels in the column, independent of the liquid flow rate; when the liquid flow rate is increased the share of the higher holdup level increases through an increasing pulse frequency. Between pulses, however, the liquid velocity is constant for different liquid flow rates (Blok and Drinkenburg, 1982).

Let us therefore consider the following simple model. Between pulses the mass transfer coefficient has a certain value k_{Lc} and inside the pulses another value k_{Lp} . In this model k_{Lc} and k_{Lp} do not vary with liquid and gas flow rate since the actual liquid velocities are not affected by these parameters. In the gas-continuous part the liquid velocity is equal to that at incipient pulsing, v_{max} . The pulse velocity is practically constant. The action of the gas flow on the liquid holdup therefore influences only the mass transferring area. In this view the time average value of k_L is given by:

$$\bar{k}_L = (1 - \alpha)k_{Lc} + \alpha k_{Lp} \quad (6)$$

α is the fraction of time that, locally, a pulse is travelling past. Thus

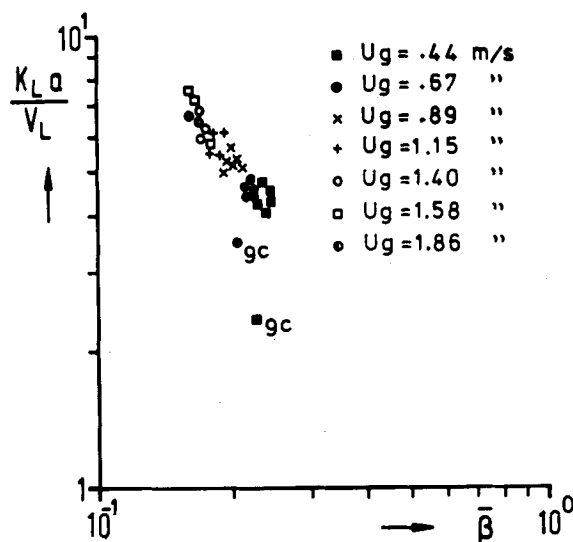


Figure 5a. Influence of liquid holdup on $k_L a / v_L$: Raschig rings 2.5 mm; column diameter 5 cm.

$$\alpha = \frac{f H_p}{v_p}$$

where f = pulse frequency, H_p = pulse height, and v_p = pulse velocity. Investigations on pulse characteristics showed that the ratio H_p / v_p does not vary significantly within the same column for varying gas and liquid flow rates. So to get a check on Eq. 6, specific areas were calculated with the relation given by Gianetto et al. (1970); i.e., k_L was determined from our $k_L a$ values.

The resulting plot of k_L vs. the pulse frequency is shown in Figure 4. Apart from some data for the 10 cm diameter column filled with 2.5 mm Raschig rings, the correlation is satisfactory. Taking for the active region of a pulse $H_p = 0.05$ m and $v_p = 1$ m/s, we can determine k_{Lc} and k_{Lp} :

$$k_{Lc} = 10^{-4} s^{-1} \quad \text{and} \quad k_{Lp} = 6 \cdot 10^{-4} s^{-1}$$

These values compare very well with reported data by Sylvester et al. (1975) in the gas-continuous and by Hirose et al. (1974) in the bubble flow regime. Following the penetration theory also an estimate of k_{Lp} and k_{Lc} can be made. Assuming the surface refreshing time to correspond with the time of the passage of a packing particle, k_{Lc} can be written as:

$$k_{Lc} = \sqrt{2 \frac{D v_{Lc}}{\pi d_p}} \quad (7)$$

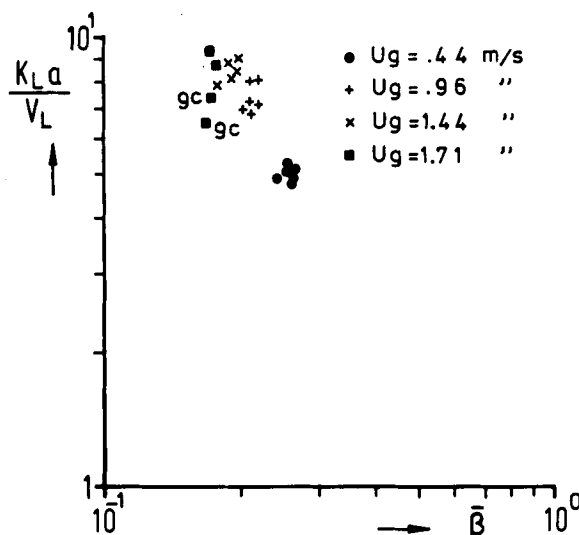


Figure 5b. Influence of liquid holdup on $k_L a / v_L$: Raschig rings 2.5 mm; column diameter 10 cm.

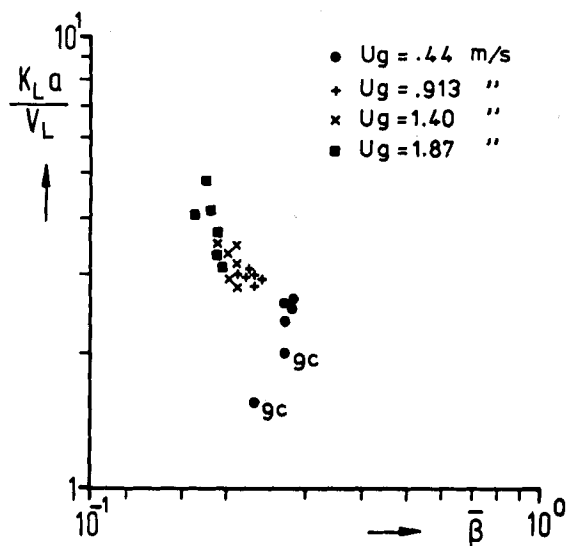


Figure 5c. Influence of liquid holdup on $k_L a / v_L$: Raschig rings 4 mm; column diameter 5 cm.

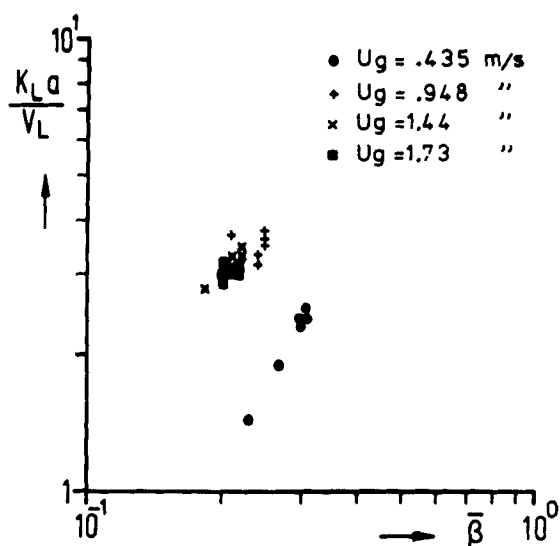


Figure 5d. Influence of liquid holdup on $k_L a / v_L$: Raschig rings 4 mm; column diameter 10 cm.

- | | | | |
|---|----------|-------------|--------------|
| ● | 4 mm RR | 5 cm column | φ |
| ■ | 4 mm RR | 10 " | " |
| ● | 25 mm RR | 5 " | " |
| ◆ | 25 mm RR | 10 " | " |
| ▲ | 6 mm RR | 8 " | " (Gianetto) |

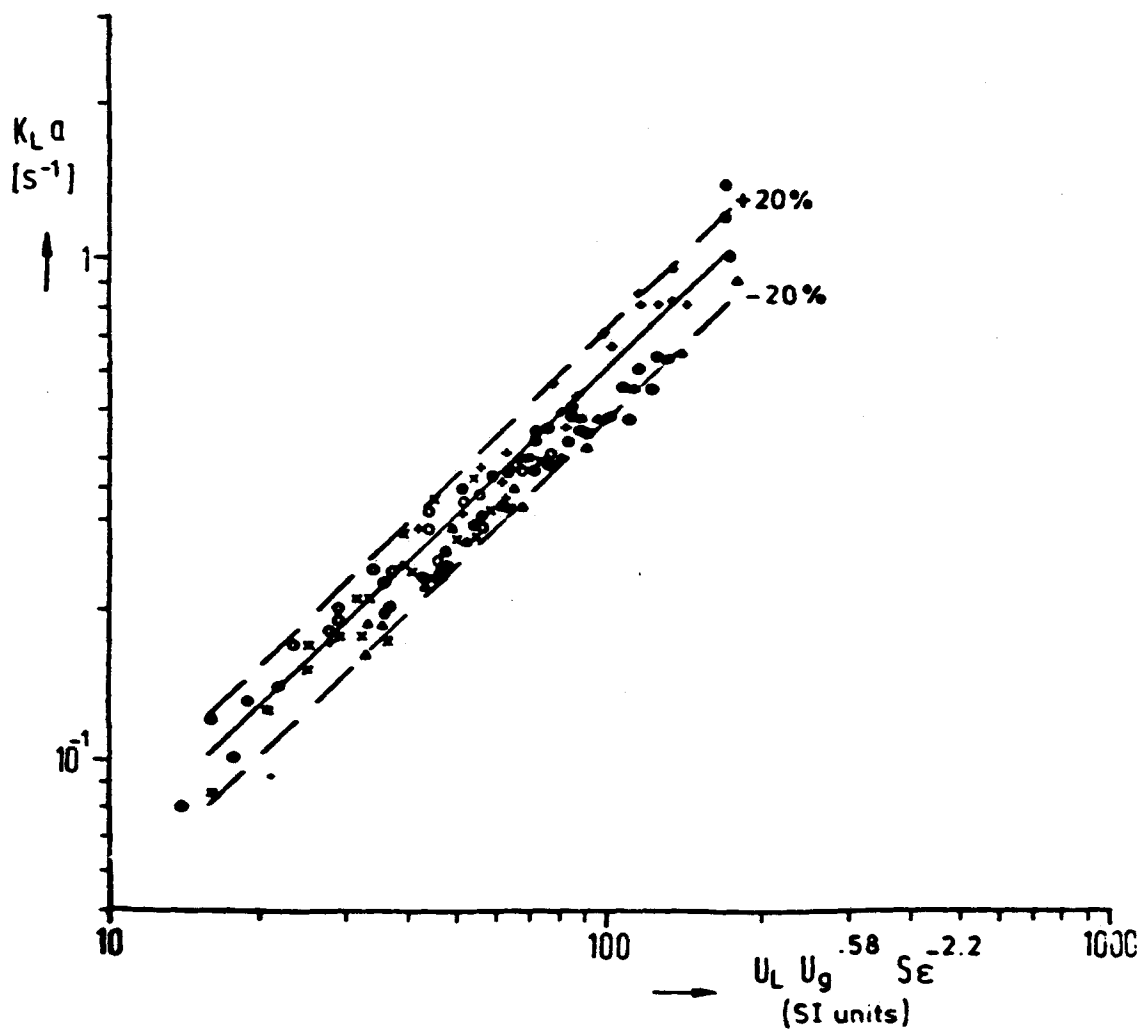


Figure 6. Final correlation for $k_L a$.

in which d_p = the particle diameter and v_{Lc} = the liquid velocity at the onset of pulsing flow. The estimation of k_{Lp} can, as a first approximation, be found with the same Eq. 7 but now with the pulse velocity substituted as the controlling velocity. We then arrive at:

2.5 mm rings	$k_{Lc} = 1.7 \cdot 10^{-4}$ m/s
	$k_{Lp} = 8.1 \cdot 10^{-4}$ m/s
4 mm rings	$k_{Lc} = 1.5 \cdot 10^{-4}$ m/s
	$k_{Lp} = 6.4 \cdot 10^{-4}$ m/s

with D taken as $1.3 \cdot 10^{-9}$ m²/s. The dependence on d_p is very weak because v_{Lc} itself is dependent on the square root of d_p (Blok et al., 1983).

In any piece of contact equipment it is the value of $k_L a$ which is important and thus the influence of the flow rates on the transferring surface must be known. In the pulsing flow regime the liquid velocities are quite high, thus complete wetting of the particles is realized. However, due to the high liquid holdup in the pulses the total mass exchange area will not be determined by the specific surface of the packing alone, but also by the liquid holdup. The influence of the liquid holdup can be estimated when the value of $k_L a/v_L$ is plotted vs. the mean relative liquid holdup β (Figure 5). For a constant gas flow rate we expect a constant holdup, thus a constant mass exchanging area. The frequency of the pulses, however, will be proportional to v_L and thus k_L can be expected to be proportional to v_L , according to Eq. 6. Figure 5 then in reality presents the influence of the liquid holdup on the mass exchanging area. It is, indeed, remarkable that for one setting of the gas flow rate, which pinpoints the liquid holdup, the value of $k_L a/v_L$ is indeed practically constant. Also some points in the gas-continuous flow regime (indicated by "g.c.") are shown and as expected they deviate from the given relation. All figures can be summarized into the relation:

$$\frac{k_L a}{v_L} = 5 \cdot 10^{-4} \cdot S \cdot \beta^{-1.2} \quad (8)$$

The dependence of the liquid holdup on the gas flow rate was determined in earlier work (Blok et al., 1982) as:

$$\frac{\beta}{\epsilon} = 0.33 \cdot u_g^{-0.26} \quad (9)$$

which is valid in the pulsing flow regime for the system water/air. The correlation is believed to hold good also for liquids with somewhat higher viscosities, as Buffham and Rathor (1978) showed that viscosities up to 10 cp do not affect the liquid holdup very much. Combining Eqs. 8 and 9 yields:

$$k_L a = 5.9 \cdot 10^{-2} \cdot S \cdot \epsilon^{-2.2} \cdot u_L \cdot u_g^{0.58} \quad (10)$$

In Figure 6 the experimental $k_L a$ values are plotted vs. the group $S \cdot \epsilon^{-2.2} \cdot u_L \cdot u_g^{0.58}$. Also data from Gianetto are shown which were directly read from his figure. The agreement is satisfactory.

NOTATION

a	= specific gas-liquid contact area, m ² /m ³ column
A	= column cross sectional area, m ²
β	= relative liquid holdup, m ³ liquid/m ³ column
c^*	= physical equilibrium concentration of CO ₂ in liquid, mol/L
c_e	= chemical equilibrium concentration of CO ₂ in liquid, mol/L
c_g	= CO ₂ concentration in gasphase, mol/L
C_i	= ion concentration, species i , g ion/L
D	= diffusion coefficient of CO ₂ in liquid, m ² /s
d_p	= particle diameter, m
ϵ	= packing porosity, m ³ void/m ³ column

η	= viscosity of liquid, N · s/m ²
f	= pulse frequency, Hz
φ_{vg}	= volumetric gas flow rate, m ³ /s
φ_{eL}	= volumetric liquid flow rate, m ³ /s
H	= column height, m
H_p	= pulse height, m
I	= ionic strength, $\sum c_i z_i^2$, g ion/L
k_r	= pseudo first order reaction rate constant, s ⁻¹
k_L	= liquid side mass transfer coefficient, m/s
k_g	= gas side mass transfer coefficient, m/s
k_{oL}	= total mass transfer coefficient based on liquid phase, m/s
k_{Lg}	= liquid side mass transfer coefficient in gas-continuous flow, m/s
k_{Lp}	= liquid side mass transfer coefficient in pulse, m/s
m	= distribution coefficient
P_o	= absolute pressure at column exit, N/m ²
ΔP	= pressure drop across the column, N/m ²
$-(dP/dz)$	= pressure drop per unit length, N/m ³
q	= ratio $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$
ρ	= density of liquid, kg/m ³
R_a	= apparent $k_L a$, s ⁻¹
R	= gas constant, N · m/kmol K
S	= specific packing area, m ² /m ³ column
u_L	= superficial liquid flow rate, m/s
u_g	= superficial gas flow rate, m/s
V	= column volume, m ³
v_L	= "real" liquid velocity, m/s
v_{Lc}	= "real" liquid velocity at pulsing flow onset, m/s
v_p	= pulse velocity, m/s
y	= CO ₂ partial pressure at column bottom, N/m ²
y_H	= CO ₂ partial pressure at column top, N/m ²
z_i	= ion valence

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Low-Density Polyethylene Vessel Reactors

Part I: Steady State and Dynamic Modelling

By the use of a perfectly mixed model and an imperfectly mixed one for low-density polyethylene vessel reactors, we show that increases in the initiator consumption with polymerization temperature are due to mixing limitations at the initiator feed. With all its parameters independently estimated, the imperfectly mixed model provides an excellent agreement with experimental data for several initiators, feed flow rates and polymerization pressures. In the temperature region of industrial interest for each type of initiator, the open-loop reactor dynamics drastically change from open-loop unstable, at low temperatures, to open-loop stable at high polymerization temperatures.

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SCOPE

The free radical polymerization of ethylene at high pressure is a reaction of broad commercial and engineering interest. In industrial practice, this process is undertaken either in autoclaves or in tubular reactors. Many engineering problems are involved in the design and operation of the vessel reactor, caused by the high values of operating pressure and temperature and by the necessity of removing the heat of polymerization. An accurate choice of conditions is essential to the economic operation of the process. Therefore, it is of practical importance to develop a mathematical model which predicts the dependence of reactor performance on the operating conditions. Furthermore, the dynamic behavior of the reactor might deviate from the desired one, leading to reactor extinction or sometimes to an explosion. For this reason it is also important to study the dynamic characteristics of the reactor.

Earlier efforts in analyzing the steady-state behavior of this high-pressure polyethylene process have been directed either to the tubular reactor (Agrawal and Dae Han, 1975; Chen et al., 1976) or to the ideal case of perfectly stirred continuous tank

reactor (Goldstein and Hwa, 1966). Recently (van der Molen et al., 1981), a large number of experimental results has been published. They provide a comprehensive picture about the influence of the most important parameters on reactor performance. In particular, they clearly demonstrate the large increases in initiator consumption that characterize this process at relatively high temperatures for each type of initiator. The same data also provide a basis for the discussion of the stability characteristics of the reactor that lead to reaction extinction.

In the present paper we introduce two transient reactor models, the second of which accurately predicts all steady state and dynamic characteristics of the reactor experimentally observed. The model parameters are independently estimated and the excellent match between model predictions and experimental data is obtained without any parameter fit.

The first model (model A) considers the reactor perfectly mixed. The second model (model B) accounts in detail about the mixing phenomena near the initiator feed point.

CONCLUSIONS AND SIGNIFICANCE

The perfectly mixed model (model A) is in agreement with the

experimental data at the region of low polymerization temperatures, but fails to account for the increases in initiator consumption observed at high temperatures. This phenomenon is accounted very accurately by the imperfectly mixed model (model B). With all its parameters independently estimated, model B shows an excellent agreement with experimental data

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